

Atomistic Simulations of Grain Boundary Migration in Face-Centred Cubic Metals

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Symbols and Abbreviations

Abbreviations

BC	: Boundary Conditions
CNA	: Common Neighbour Analysis
CSL	: Coincident Site Lattice
DSC	: Discrete Shift Complete
DF	: Driving Force
DoF	: Degree of Freedom
DQS	: Direct Quantification Scheme of elastic DF
EAM	: Embedded-Atom Method
FCC	: Face-Centred Cubic
GB	: Grain Boundary
GBD	: Grain Boundary Diffusion
GBM	: Grain Boundary Migration
IPS	: Interphase-Plane Scheme
IQS	: Indirect Quantification Scheme of elastic DF
LJ	: Lennard-Jones
LS	: Lattice Statics
MD	: Molecular Dynamics
MSD	: Mean Square Displacement
NN	: Nearest Neighbour
RDF	: Radial Pair Distribution Function
RS	: Read Shockley

Physical Properties

CoM	: Center of Mass
E^{GB}	: Grain Boundary Energy
m_{GB}	: Grain Boundary Mobility
p_{ela}	: Elastic Driving Force
p_{corr}	: Orientation-correlated Driving Force

Materials Properties

c_A	: Elastic anisotropy
G	: Shear modulus
ν	: Poisson ratio
$\Omega(T)$	: FCC atomic volume at temperature T

Physical Constants and Units of Key Properties

k_B	:	Boltzmann Constant = $8.6137 \cdot 10^{-5} \frac{eV}{K}$
a_0	:	0K Lattice Parameter = 3.616 Å for Cu
Θ_D	:	Debye Temperature = 343 K for Cu
	$\Rightarrow$	Debye Frequency $\nu_D = 7,14 \cdot 10^{12}$ Hz for Cu
Unit of GB Energy	:	$1 \frac{J}{m^2} = 1 \text{ Erg}$
Unit of Elastic Constants	:	$1 \text{ Pa} = 10 \frac{dyne}{cm^2}$
Unit of Stress	:	$1 \frac{eV}{a_o^3} = 3.38 \text{ GPa for Cu}$
Unit of elastic DF	:	$1 \frac{eV}{\Omega(0K)} = 4 \frac{eV}{a_o^3} = 13.5 \text{ GPa for Cu}$
Unit of orientation-correlated DF	:	$1 \frac{eV}{atom} = 1 \frac{eV}{\Omega(T)}$

Chapter 1

Introduction

Crystalline materials do have distinct materials properties not only due to their crystalline nature but as well due to the existence of lattice defects like vacancies, dislocations and internal interfaces. Internal interfaces like grain boundaries (GBs) play an important role in the physical behaviour of polycrystalline materials. This is often directly seen when dealing with processes of plastic deformation at elevated temperatures or thermal treatment of polycrystalline materials. Since GBs like lattice dislocations and vacancies can be highly mobile, GBs do migrate within polycrystals when experiencing a driving force. Here the rate of GB migration is thermally activated. Due to this ability, grain-boundary migration (GBM) is the fundamental process occurring during grain growth and recrystallization in solid state materials.

In spite of the importance of GB migration for microstructural evolution and although heavy research activities devoted to GB migration are conducted little is known about its atomic-level mechanism. During the 20th century a lot of experiments were conducted to investigate the basic properties of GBs, namely for instance the misorientation dependence of the GB energy or GB mobility. A lot of GB data was obtained by either polycrystalline or bicrystalline studies and general concepts like the Read-Shockley model [18] or the compensation effect [25, 26] evolved from these results. Regardless of these important and needed results detailed information and theories on GB migration on the atomic level do not exist at all or only scarcely even up to date.

Simulations in the field of GB migration on the atomic level were only conducted during the last twenty years, and only recently new concepts and approaches were introduced to obtain key parameters of GB migration successfully. The importance to understand the underlying mechanism of GB migration on the atomic level relates to experimental findings that for instance GB crystallography and GB chemistry, here one usually deals with impurity levels on the ppm scale, highly affect the mobility of GBs. Especially in the field of retarding effects of impurities on GB migration a lot of theories were put forward to explain various experimental results [24]. Although the macroscopic kinetic theory of GB migration is well described and investigated, on the atomic level only few models and ideas exist on how GBs actually migrate through crystals.

At this point one might wonder if atomic-level insight into GB migration is at all useful and whether one really gains fundamental knowledge and understanding by knowing details of the atomic-level migration mechanisms. It is difficult to answer such a question without

knowing all facts and main influences on GB migration in detail, nevertheless different issues in materials science have demonstrated impressively that indeed atomic-level processes do determine the macroscopic behaviour of materials through their direct influence on defects on the atomic-level scale. For instance in the field of dislocation dynamics it is known that i.e. impurities can pin lattice dislocations leading to different kinetics of dislocation glide and climb which are the key processes of crystal plasticity.

This work exclusively focusses on the finite temperature behaviour of planar GBs in face-centred cubic materials. Planar GBs were chosen in order to study GBs with well-defined geometries. The simulation technique of choice is molecular dynamics to allow one to study the temporal evolution of an atomic-level GB system. One major part of this work concentrated on establishing driving force schemes within atomistic simulations to be able to drive planar GBs continuously. By establishing two novel simulation methods to drive planar GBs, indeed GB migration simulations can be performed to address key problems of GB migration, namely their kinetics and the underlying GB mechanisms.

In the past decades atomistic simulations have proven to be useful tools to study issues in materials science. Throughout the 1970s and 1980s a lot of research activities were devoted to investigate GB structures of various materials. These structural analyses of GB structure are nowadays linked with high-resolution transmission electron microscopy studies to make precise statements on the atomic situation met at GBs. In the 1990s, a lot of effort was given to simulate not only the structure of GBs but as well physical processes in systems that are dominated by the presence of GBs. These are no longer only bicrystal simulations but with the onset of the nanotechnology atomistic simulations nowadays deal with nanosystems consisting of several nano-grains. Actually these systems are well suited for atomistic simulations since here the dimensions met in experiments and computer simulations are eventually the same.

Another new aspect of finite temperature behaviour of GBs are possible structural transitions of GBs below the melting point. Recent results by Keglinski [72] stress the idea that certain GBs do change their structure with temperature. His results suggest that low and high temperature regimes exist where at low temperature the GB resembles a crystalline-like GB and at high temperature the crystalline structure is lost and the GB transforms into a highly disordered structure. Such structural transitions should have impact on GB related thermally activated processes like GB self-diffusion and GB migration. Indeed such behaviour was found by Keglinski [72] as well as by this work.

Next a brief listing of molecular dynamics simulations dedicated to atomistic simulations of GB migration is given. In early studies on the finite temperature behaviour of planar GBs [13, 14, 15, 16] it was observed that even without any explicit driving forces, GB migration was found. Usually in these cases an attractive force was exerted on the GBs due to periodicity effects of the simulation box. The coupling of GB sliding with GB migration or vice versa was for instance found by Bishop [14, 15, 16] for different high-angle GBs. Here the coupled GB migration and sliding of these GBs was rationalized in terms of the DSC lattice.

In follow-up work, explicit driving forces for GB migration were introduced by utilizing curved GB systems. The first work on a curved GB system was done by Jhan and Bristowe [32] who studied GB migration of a half-sphere GB geometry. The GB geometry of Jhan and Bristowe consisted of a planar twist GB that included a GB sphere on top of it.

This sphere was constructed by stacking at maximum four ledges on top of the twist GB to form a pyramid. The main finding of Jhan and Bristowe was the confirmation of the cooperative shuffle mechanism of GB migration which was observed by Majid and Bristowe [29] in atomistic simulations and which is supported by experiments of Babcock and Balluffi [30]. Work by Sutton [31] who studied the finite temperature behaviour of a cylindrical GB system failed due to periodicity effects of the simulation box setup.

A constant driving force concept on curved GB systems was presented by Upmanyu [33] utilizing an U-shaped GB in a 2d atomistic simulation box. Various aspects of GB migration were studied by this approach like the misorientation dependence of GB mobility [27] and the compensation effect [27] as well as the vacancy emission of curved GBs during GB migration [34]. Constant driving force concepts on planar GBs are given by this work where GB migration of planar GBs was studied in the presence of different sources of driving force. A first example was published in 1997 [64] where GB migration of a planar $\Sigma 29$ [001] twist GB in the presence of an elastic driving force was studied.

Outline of this work - Finally a brief outline of this work is given. In chapter 2, the fundamentals of GBs including GB structure, GB migration and a review of atomistic GB migration simulations are given. Here the reader should get familiarized with the basic ideas and concepts related to these topics.

In chapter 3, all relevant issues related to computational aspects in order to perform atomistic simulations utilizing the molecular dynamics (MD) method are discussed. The discussion includes a presentation of atomistic interatomic interaction potentials, the basics of the used MD methods (i.e. MD method itself, time integration schemes and boundary conditions), driving force (DF) concepts to drive planar GBs within MD simulations and finally data analyses to describe and analyse atomistic systems. Additionally the underlying theory of lattice and GB self-diffusion is discussed from an atomistic point of view which forms the basis to analyse the computational data obtained by this work.

Chapter 4 presents the results of lattice mono-vacancies in face-centred cubic materials when being studied with the LJ and EAM potential as utilized in this work. This data serves as reference data when discussing the computed activation enthalpies of GB migration and GB self-diffusion of this work.

Finally this work does concentrate on atomistic computational simulation results of GB migration of planar [001] twist GBs as well as GB migration of selected tilt GBs. Chapter 5 presents extended results on GB structure, GB migration as well as GB self-diffusion of planar [001] twist GBs. In detail results of the elastic DF concept as well as of the orientation-correlated DF concept are presented. Results on GB migration and GB self-diffusion activation parameters, the compensation effect as well as the found GB migration mechanisms are discussed. Next in chapter 6, results on symmetrical and asymmetrical tilt GBs are presented. Here extended results on GB structure, GB migration as well as GB self-diffusion of the studied tilt GBs are discussed. One main highlight concerns the successful implementation of a DF to drive planar tilt GBs continuously. Here it is shown that the DF of choice which is able to drive any planar tilt GB is the orientation-correlated DF.

Chapter 2

Fundamentals

2.1 Structural Models of Grain Boundaries

Before discussing structural models of GBs at first a brief general introduction into the field of two-dimensional defects in solid state materials shall be given. Generally one speaks of an interface being present in a system if the physical properties discontinuously change across that interface. Phase boundaries i.e. exist between phases of different state of order. For example this is true for liquid-solid or liquid-gaseous interfaces. Limiting the discussion to internal interfaces in solid state materials one differentiates between either phase or grain boundaries. Phase boundaries separate grains of different phases. This i.e. could be grains having different lattice structure. Grain boundaries (GBs) separate almost stress free grains having the same lattice structure but different orientation. Throughout history the structure of GBs was seen quite differently. First models by Rosenhain [6] understood a GB as being an amorphous disordered region separating grains. A succeeding model by Mott [23] assumed that GBs are two-dimensional defects where zones of good lattice match and zones of bad lattice match exist. Following the idea of islands in the sea they put forward the idea that within GBs zones of good lattice match form islands of ordered structure in an surrounding environment of highly disordered state. This rather illustrative model makes no statement on the size and distribution of such islands and therefore lends itself only as a qualitative GB model.

A different approach is to discuss GBs in the framework of dislocations. The Read-Shockley model [18] tried to explain GBs on the basis of dislocations. Such an approach is well suited for low-angle GBs. Here it is well known that low-angle GBs can form by arrays of lattice dislocations. Although discrete lattice dislocations are having long-range stress fields, dislocation theory is able to show that by linear superposition of GB dislocation stress fields, GBs can be formed that only exhibit a short range stress field. For instance Fig. 2.2 (c) demonstrates how stabile almost stress free GBs can be formed. The spacing of GB dislocations as well as the stress field of the GB are determined by the so-called GB dislocation spacing, D , of the geometrically necessary GB dislocations that form the GB. Here the geometrically necessary number of GB dislocations is determined by a summation and cancellation of all existing dislocations at a GB. Here a dislocation is defined as a crystallographic plane ending at the GB. According to the Read-Shockley model the GB stress field decreases exponentially and the decay distance is basically governed by the GB

dislocation spacing, D , of the geometrically necessary GB dislocations. The stress field of single lattice dislocations is long-range since their stress field decreases with one over r where r is the distance from the dislocation core. This demonstrates that GBs in the framework of dislocations separate grains of different orientation almost stress free.

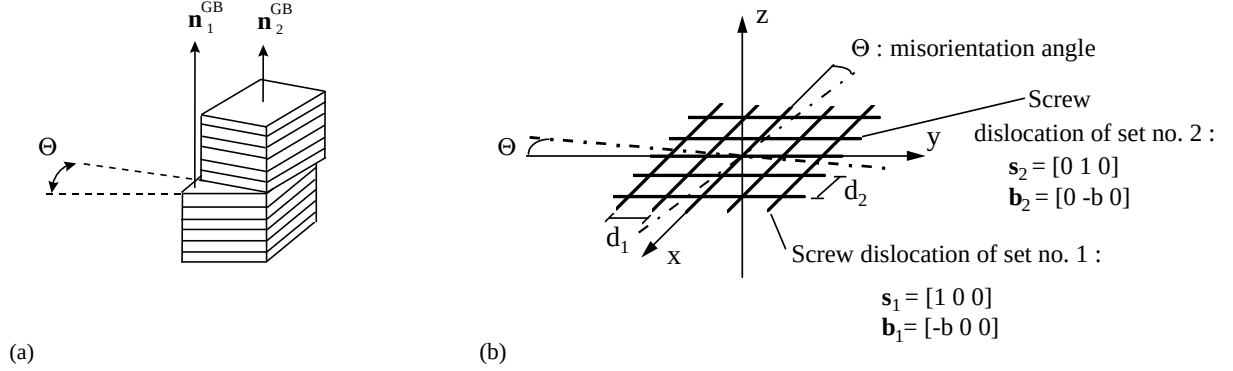


Figure 2.1: Schematic of twist GB geometry. (a) illustrates the generation scheme of symmetrical twist GBs while (b) shows the description of twist GBs in the framework of perpendicular screw dislocations.

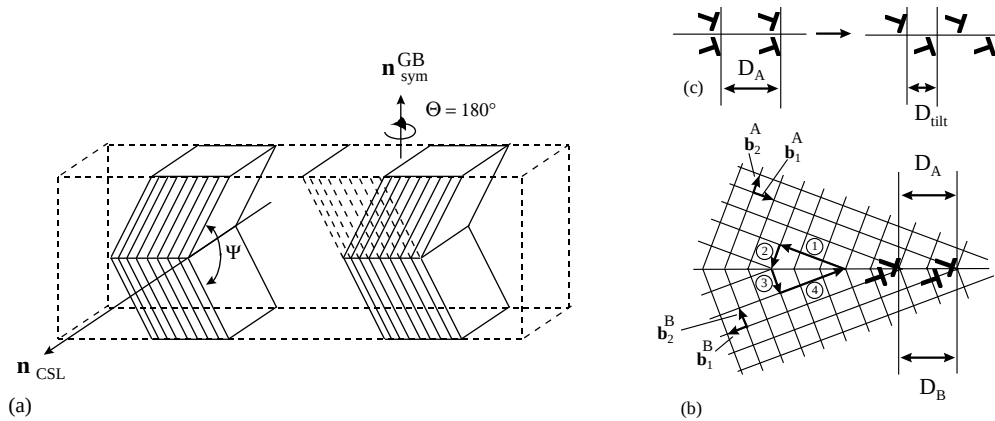


Figure 2.2: Schematic of tilt GB geometry. (a) illustrates the generation scheme of symmetrical tilt GBs while (b) and (c) show the description of tilt GBs in the framework of edge dislocations. Here it is assumed that the line element of the dislocations point out of the sheet of the paper. The circuit 1 to 4 can be used to determine the dislocation content of the GB which is shown in the right part of Fig.(b). In (c) the metastable dislocation configuration according to the CSL geometry is sketched on the left-hand side, while on the right-hand side the final relaxed low-angle GB structure is given.

GBs are distinguished into two classes of GBs. Similar to the classification of dislocations, where pure screw and edge dislocations as well as mixed dislocations are known, GBs are classified into classes of pure twist, pure tilt and general GBs. Here the general GBs consist of twist and tilt components. Fig. 2.1(a) as well as 2.2(a) present examples that demonstrate the rules for classification, namely for pure twist GBs the misorientation axis is normal to GB (see 2.1 (a)) while for pure tilt GBs the misorientation axis is found to be within the GB plane itself (see 2.2 (a) left-hand side). This classification scheme makes sense with respect

to the underlying GB dislocation content of such GBs meaning that pure twist GBs consist of a network of screw dislocations as well as pure tilt GBs are formed by pure edge dislocations. Therefore such a scheme is directly linked to the principles of the Read-Shockley model. For a chosen planar GB geometry several misorientation paths exist to form such a GB by grain rotations (see 2.2 (a) left- and right-hand side). Hence the classification scheme of GBs is not unambiguously formulated. This is best exemplified by pure symmetrical tilt GBs. Such GBs can be obtained by a twist rotation of 180° about the GB normal (see Fig. 2.2(a) and i.e. Wolf and Yip [69]).

With respect to the misorientation relationship between grains one can distinguish between special and general GBs. Special GBs are formed if the misorientation relationship between the grains leads to the formation of a crystal lattice which is continuous across the GB. This means that atoms in either of the two grains share sites on one common lattice. This common lattice is called coincident-site lattice (CSL) and corresponding misorientation relationship are called CSL misorientations. Further details on the generation principles and the CSL lattice are given in section 2.1.2.

The geometrical description of GBs is rather complex since it takes eight parameters to geometrically unambiguously define GBs [69]. Five out of the eight parameters are called macroscopic parameters since they define the misorientation relationship between the adjacent grains. The remaining three parameters are called microscopic parameters since they describe the translation state between the two grains at the GB. All eight parameters are called as well degrees of freedom (DoF) of a GB. The five macroscopic DoFs characterize the misorientation relationship and can either be described by the CSL or interface-plane scheme. The microscopic DoFs are defined by the character of each GB meaning their atomic-level forces across the GB. Consequently GBs are rather complex objects even on a purely geometric basis since it requires already eight parameters to define them unambiguously. According to this it is rather difficult to find analytical expressions that characterize the GB structure and GB properties. A first attempt in this direction was put forward by the step model of Gleiter [7]. This model is not fully incorporating the GB structure according to their eight crystallographic parameters but rather uses the density of (111) planes entering into a GB as a measure to distinguish between GBs having high and low GB mobilities.

Another important classification of GBs is the distinction between low-angle and high-angle GBs. Low-angle GBs can be well understood from the point of view of dislocation theory which is able to explain basic properties of low-angle GBs on the basis of discrete GB dislocations. It is well-known that dislocations have a rather disturbed core region and outside of the core a long-range stress field. With respect to high-angle GBs it is usually agreed that a GB loses its discrete GB dislocation character when the misorientation angle is larger than 15° . For high-angle GBs it is thought that the GB dislocations have come so close to each other that the GB is only formed by the overlapping dislocation cores. Hence the discrete GB character is lost and even the long-range stress field of the GB. Recent work on GB character [19, 62] show that the transition from low-angle to high-angle GBs might be a smooth function rather than a discontinuous one in the range of 15° . For GB properties like GB migration activation enthalpy [62], the discontinuous behaviour is still observed. Nevertheless related to the surrounding stress field of GBs it seems possible that even intermediate-angle GBs can couple in with external stress fields following the idea of a Peach-Koehler DF that can provide a sufficient driving force for GB migration [62].

In section 2.1.2 GBs are described and characterized by the coincident-site lattice (CSL) scheme which is solely connected to the misorientation relationship between two crystals. The CSL scheme is often utilized when bicrystals for experiments or simulations are generated. Concerning the generation procedure it is not connected to lattice dislocations and the way these dislocations might generate GBs. This is important to realize since during or at the early stages of recrystallization it is commonly observed that high-angle GBs do form and that their appearance may be linked to prior plastic deformation partly carried by dislocations (GB glide leading to plastic deformation is possible too) or the build-up of misorientation gradients in the material by some means which in a lot of cases is hard to attribute. Usually it is believed that GBs having the same macroscopic and microscopic GB parameters are indeed equivalent no matter on what microscopic path they were generated. Still it is interesting to realize that this indeed should be.

Turning the discussion now to low-angle GBs it is well-known that for instance low-angle tilt GBs do form by rearrangements and reactions of lattice edge dislocations in order to obtain a stable dislocation configuration [5, 3]. Considering the generation of high-angle GBs for instance prior to or during the early stages of recrystallization, these GBs must be generated by deformation mechanisms within the material and can in no way be understood by either of the mentioned generation concepts in the framework of bicrystal preparation. Since the question of the generation of high-angle GBs for polycrystal materials for instance during recrystallization is far from being well-understood nor trivial, the concept of dislocations in conjunction with GBs should be discussed in more detail in section 2.1.1.

Finalizing the discussion of GB structure and character the following recent views are presented next. Recent atomistic studies suggest that the GB structure is very much dependent on the GB character itself and the temperature range studied [72]. According to this idea the structure of a GB can be ranging from crystalline order to a disordered amorphous structure. According to Keglinski [80], the ratio of the GB energy to the energy of an amorphous metallic solid state crystal determines whether or not a GB can become amorphous. Narrowing down the discussion simply to the GB energy it is suggested and shown that high-energy GBs can be structurally disordered while low-energy GBs remain structurally ordered up to the melting temperature [72]. An important variable in this context is temperature. It was shown that some GBs, usually high-energy GBs, can undergo a transition in structural order with increasing temperature even well below the melting point. This structural transition is characterized by a disordering effect of the GB with increasing temperature. The same observation was made in this work for high-angle [001] twist GBs.

Why is the knowledge of the exact GB structure so important for this work ? The prime goal of this work is to study the physical behaviour of GBs at finite temperature. Here it is meant to study GB self-diffusion and GB migration in some detail in order to obtain activation parameter of the processes and to understand the atomic-level nature of the processes. Therefore it is essentially important that the input GB structure of these simulations agrees fairly well with the known experimental structure of GBs. Of course one has to remember that the used atomistic systems only mimic the real situation to some extent, since in the GB simulations only absolute pure system can be represented. This fact is related to the shortcoming of the used molecular dynamics approach that the accessible time range is rather limited. Hence no impurity effect can be introduced in the systems. Nevertheless HRTEM studies show that the overall atomic-level structure of highly purified GBs agrees fairly well with the structure determined by atomic-level simulations [8].

2.1.1 Read-Shockley Model

Within the Read Shockley model [18], dislocations are considered as the basic structural elements generating grain boundaries. This is known to be true for low-angle GBs. By a linear superposition of the properties of the geometrical necessary discrete dislocations of a GB one can show on purely mathematical grounds that for instance the found dislocation arrangement within low-angle GBs (see i.e Fig. 2.2 (c)) is a stabile equilibrium structure. Furthermore the range of stress field around such a GB depends on the dislocation spacing, D , of the geometrical necessary GB dislocations. These stress fields decay exponentially where D determines their decay. Furthermore the mathematical descriptions yields that for very small misorientation angles the dislocation spacing becomes so large that each dislocation behaves as a discrete lattice dislocation.

Fig. 2.1 (b) shows the dislocation content of a symmetrical twist GB while Fig. 2.2 (b), (c) demonstrates the dislocation content of a symmetrical tilt GB. It is important to mention that any atomic plane which ends at a GB is to consider as a dislocation. The effective dislocation content of for instance the sketched GB in Fig. 2.2 (b) can be determined by circumventing the defect following the path 1, 2, 3 and 4 and applying the right-hand rule. Transferring the found path to an ideal crystal region, the closing vector of the circuit is then associated with the dislocation content of the GB. Here that vector would be the effective Burgers vector of the GB. In the sketched case of Fig. 2.2 (b) the reader should note that the line vector of the dislocations, $\mathbf{s}$, is coming out of the paper's plane. Once the effective dislocation content of a GB is known, in case of twist and tilt GBs the dislocation spacing, D , can be linked to the misorientation relationship of the GB. According to Fig. 2.1 (b) and Fig. 2.2 (b) for each class of GB the dislocation spacing is found to be $D_1 = \frac{b_1}{\sin(\theta)} = D_2 = \frac{b_2}{\sin(\theta)}$ for symmetrical twist GBs and $D_A = \frac{b_2^A}{\sin(\frac{\theta}{2})} = D_B = \frac{b_2^B}{\sin(\frac{\theta}{2})}$ and $D_{tilt} = \frac{b_2^B}{2 \cdot \sin(\frac{\theta}{2})}$ for symmetrical tilt GBs.

Utilizing the results for the line energy of a single lattice dislocation and assuming a linear superposition of the properties of all dislocations forming the GB and thus summing over the number of dislocations in a certain segment of the GB we find the generic equation for the GB energy of low-angle GBs, E^{LAGB} , versus the misorientation angle θ according to Read and Shockley [5] to be

$$\begin{aligned}
 E^{LAGB} &= \theta \cdot (A_K - B_K \cdot \ln(\theta)) \\
 \text{with } A_K &= \frac{E_{core}}{b} - B_K \cdot \ln(\alpha) \\
 \text{and } B_K &= B_K^{Tilt GB} = \frac{G \cdot b}{4\pi(1-\nu)} = \frac{B_K^{Twist GB}}{1-\nu}
 \end{aligned} \tag{2.1}$$

Experimentally this equation is well represented and results of computer simulations confirm it as well. According to the original approach by Read and Shockley the range of existence was meant to be exclusively for a misorientation range up to about 15° . The 15° limit is associated with the Brandon criterion [9] saying that the nature of CSL GBs deviating from the exact CSL relationship is preserved through the build-in of DSC dislocations up to an

deviation of $\frac{15^\circ}{\sqrt{\Sigma}}$ ¹.

An extension of the Read Shockley low-angle GB model was introduced by Wolf [19] in order to investigate the misorientation dependence of the GB energy even for high-angle GBs obtained by atomistic simulations. For the analytical GB energy equation 2.1 to hold for high-angle GBs as well as for low-angle GBs, the approximation $\sin(\theta) = \theta$ made within the RS-model is dropped and the sin term itself enters in the equations through the parameter D. Conceptually speaking the nature of the GBs remains dislocation-like and for [001] twist GBs the adapted RS model according to Wolf reads

$$E_{[001]}^{GB} = \sin\left(\pi \frac{\theta}{90^\circ}\right) \cdot \left(A_K - B_K^{Twist GB} \cdot \ln\left(\sin\left(\pi \frac{\theta}{90^\circ}\right)\right) \right) \quad (2.2)$$

where A_K and B_K are given by the same relations as stated in the original RS-model of Eq. 2.1. There are several key results obtained by Wolf's study namely that the range of validity of the RS-model is clearly beyond the 15° limit. Furthermore it was found that qualitatively the GB energy as a function of the misorientation angle, θ , is well represented by the adapted RS equation 2.2 by Wolf. Within the data analysis it is even possible to assess the contribution to the overall GB energy by the core and the strain field of the GB dislocations. It is interesting to note is that indeed the dislocation strain field exists even for misorientation angles far beyond 15° . For the studied [001] twist GBs the obtained GB energies as well as the volume expansion obtained within this work are plotted in Fig. 2.3 and Fig. 2.4, respectively. Fitting the GB energy according to Eq. 2.2 the fit parameters

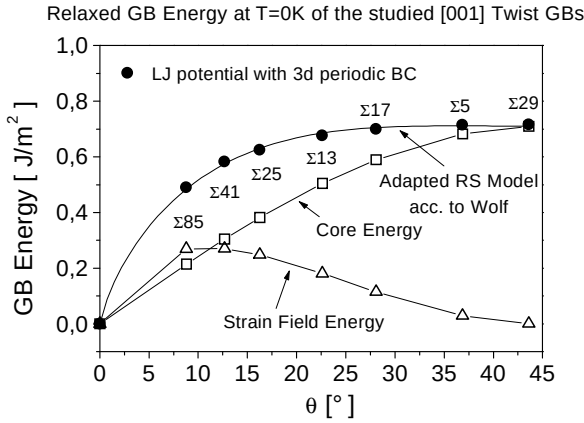


Figure 2.3: Plot of the GB energy versus the misorientation angle, θ , at 0K for the studied [001] twist GBs for the 3d LJ potential. The adapted RS model is used to fit the energy profile and to assess the contribution of the dislocation cores and strain fields to the total energy.

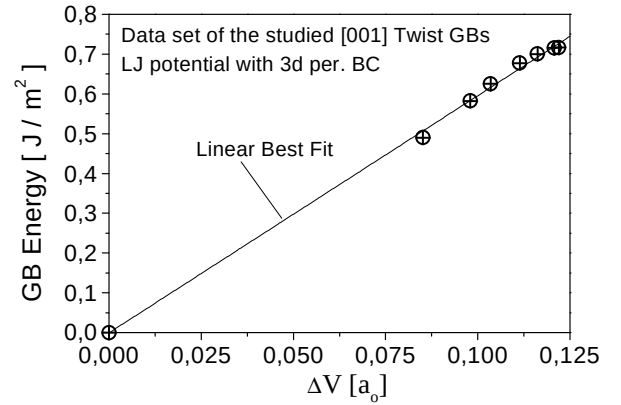


Figure 2.4: GB volume expansion of the studied [001] twist GBs at 0K for the 3d LJ potential. The linear best data fit underlines the linear dependence between the GB energy and the GB volume expansion and vice versa.

A_K and B_K are found to be $A_K = 0.71066 \pm 0.0047 \text{ J/m}^2$ and $B_K = 0.7450 \pm 0.01331 \text{ J/m}^2$. Since according to Eq. 2.1 B_K depends only on two materials properties, namely the shear

¹According to Pumphrey [10], the Brandon criterion should read $\frac{15^\circ}{\Sigma^{2/3}}$.

modulus, $G=C_{44}$, and the magnitude of the Burgers vector, b , of the geometrically necessary screw dislocations, and since B_K and $C_{44}^{3dLJPot.}$ are known, b can be determined. One gets $b \approx 0.25 a_o$. Although this value is too small by a factor of about three it still demonstrates that the adapted RS model can explain the GB energy profile. At this point it is essential to realize that the used 3d LJ potential only mimics the fcc material Cu roughly. For instance the used value of $C_{44}^{3dLJPot.}$ is about 30 percent higher than the experimentally known one. Even with respect to the differences in materials properties of the real and the model material the agreement between computed data and adapted RS model underlines its application to investigate the GB energy data. Fig. 2.3 clearly demonstrates the good agreement between the plotted computed GB data and the adapted RS model. Furthermore the contribution of the core and strain fields of the GB dislocations to the total GB energy is well illustrated and allows one to assess much better the range of validity to describe these [001] twist GBs by discrete screw dislocations.

2.1.2 Coincident-Site Lattice

This work exclusively focusses on structural and kinetic properties of coincident-site lattice (CSL) grain boundaries. Thus it seems necessary to explain in more detail the basic idea of the coincident-site lattice (CSL). In general the CSL represents lattice points of two discrete lattices that coincide if one imagines that the two lattices interpenetrate each other. If both crystals have the same crystal structure and are aligned without any misorientation or translation then the CSL would be the underlying lattice of the material. Introducing a misorientation between the two lattices described by a rotation matrix $\underline{R}$ will only give CSLs for certain misorientation angles and axes. For a better understanding of the underlying mathematics let us recall here that the position of an atom i can only be found in real space if its coordinates (x_i, y_i, z_i) as well as the unit vectors, $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$, spanning out the actual coordinate system are known. Here $\mathbf{r}_i = (x_i, y_i, z_i)$ only gives the coordinates of atom i with respect to a certain coordinate system and its real space vector would be given by $\mathbf{r}_i = x_i \cdot \mathbf{e}_x + y_i \cdot \mathbf{e}_y + z_i \cdot \mathbf{e}_z$. The same is true for two misoriented crystals that do interpenetrate each other. Here this means that for either of the two crystals the internal coordinates (x_i, y_i, z_i) of any atom i are exactly the same when bearing in mind that they are defined with respect to each coordinate system. This now offers a simple way of mathematically expressing the basic equation for coincidence, namely writing

$$\mathbf{r}^{L2} = \underline{\underline{R}} \cdot \mathbf{r}^{L1} = \mathbf{r}^{L1} + \mathbf{t}^{L1} \quad (2.3)$$

where $\mathbf{r}^{L1}$ represents the internal coordinates of a certain lattice point with respect to coordinate system no.1, $\mathbf{r}^{L2}$ the internal coordinates of that lattice point with respect to coordinate system no.2 and finally $\mathbf{t}^{L1}$ the coordinates of a translation vector of lattice no.1 with respect to coordinate system no.1. Thus any lattice point $\mathbf{r}^{L1}$ of lattice no.1 that satisfies Eq. 2.3 is a lattice point of lattice no.1 and no.2 and therefore represents a coincident point. Here one should note that the CSL is confined to describe lattice points. In order to find the vectors that span out the CSL, Eq. 2.3 needs to be rewritten and thus one obtains Eq. 2.4. Inserting the translation vectors of lattice no.1 in Eq. 2.4 would then give the CSL vectors.

$$\underline{\underline{R}} \cdot \mathbf{r}^{L1} - \mathbf{r}^{L1} = (\underline{\underline{R}} - \underline{\underline{1}}) \mathbf{r}^{L1} = \mathbf{t}^{L1} \quad \Leftrightarrow \quad \mathbf{r}^{L1} = (\underline{\underline{R}}^{-1} - \underline{\underline{1}}) \mathbf{t}^{L1} \quad (2.4)$$

Extending the discussion to any point $\mathbf{r}^{L1}$ and $\mathbf{r}^{L2}$ within the lattices leads to the concept of the O-lattice [2]. It is a more general concept than the CSL and the CSL is a sub-lattice of the O-lattice.

There are several different approaches to describe a misorientation relationship between two coordinate system. In this work the misorientation relationship is expressed by a rotation axis $[H,K,L]$ and a rotation angle θ . For certain misorientation relationships between two crystals depending on the rotation axis and angle well-defined CSL lattices exist that are characterized by a single parameter namely their Σ values. Since this work only deals with cubic materials, the further discussion is restricted to cubic materials. Well-defined misorientations between both crystals can for instance be expressed by a rational Rodrigues vector $\rho = \frac{m}{n}[H,K,L]$, where m, n, H, K and L are integers [2]. Here the misorientation angle is not explicitly set but rather defined through the distinct set of m, n, H, K and L. In terms of rotation axis and angle the Rodrigues vector represents a rotation about an axis $[H,K,L]$ by θ where θ is given by

$$\tan\left(\frac{\theta}{2}\right) = \frac{m}{n}\sqrt{H^2 + K^2 + L^2} \quad . \quad (2.5)$$

Furthermore the ratio of the volume of the primitive CSL with respect to the atomic volume of the material is characterized by Σ and formally given by

$$\Sigma = n^2 + m^2 \cdot (H^2 + K^2 + L^2) \quad . \quad (2.6)$$

Eq. 2.5 and 2.6 can be used as master equations to calculate the misorientation angle θ and Σ for a chosen rotation axis $[H,K,L]$ and m and n. If Σ as given by Eq. 2.6 is an even number, Σ is then to be divided by 2^β with β being the smallest integer to find the largest odd Σ number. The CSL scheme itself is not unique concerning the misorientation path. Theoretically a given CSL can be generated by 24 different misorientation paths for cubic materials due to the symmetry operations possible for cubic materials [5]. For instance one obtains a $\Sigma 5$ CSL by a 36.87° $[001]$ rotation as well as by a 53.13° $[001]$ rotation. These two representations are linked by the 270° $[001]$ symmetry operation of the cubic lattice. So far a GB has yet not appeared in the discussion of the CSL scheme and thus the plain CSL scheme is therefore only associated with misorienting two crystals. Utilizing the CSL concept to misorient two crystals, the final step to geometrically generate symmetrical CSL twist GBs, symmetrical CSL tilt GBs as well as asymmetrical CSL tilt GBs is to define the GB plane that will separate the two crystals from each other. This means that either one of the crystals only exists on one side of the GB, thus here the discussion of interpenetrating crystals comes to an end. Obviously the scheme itself is rather theoretical since for instance in sample preparation of experiments such a working sequence of misorienting interpenetrating crystals can only be regarded as imaginary. Concerning the nature of GBs some general statements can be made with respect to the CSL procedure if one restricts the discussion to one distinct CSL misorientation representation out of the 24 possible. Generally it can then be stated that a pure twist GB follows the rule that its GB normal and the misorientation axis are parallel. For pure tilt GBs a similar rule exists, namely that the GB normal and the tilt axis are perpendicular to each other. These rules are rather simple and once again illustrated by Fig. 2.1 (a) and 2.2 (a) and for any pure twist or tilt GB the rule will apply for at least one of the 24 misorientation representations. Unfortunately due to the high number of different representations of a given CSL the mentioned rules can be questioned for their uniqueness

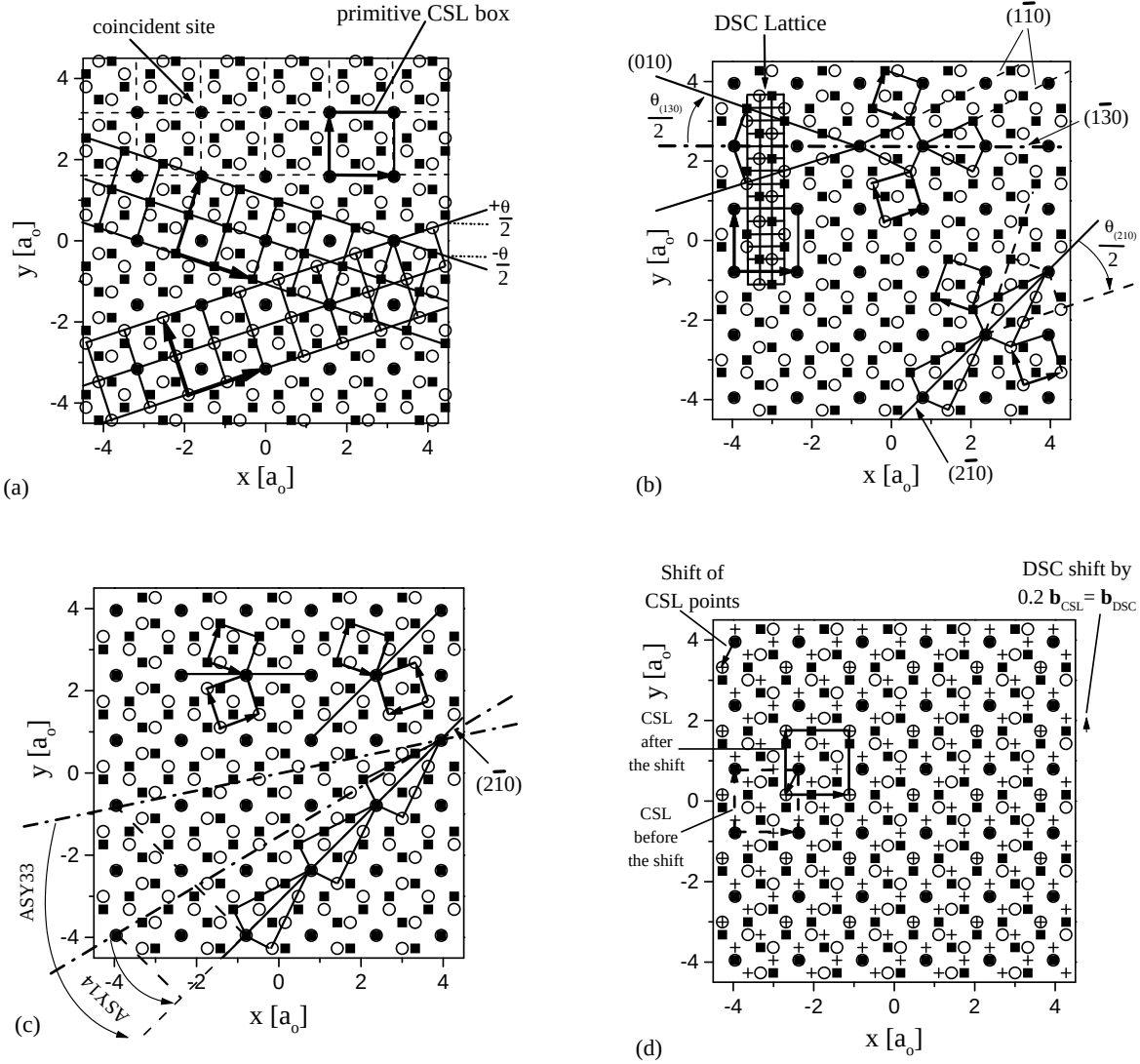


Figure 2.5: CSL scheme for $\Sigma 5$ 36.87° [001] misorientation of two fcc lattices : (a) shows plane A (full squares) and plane A' (open circles). Here full circles represent coincident sites. Plane A is misoriented by $\frac{+\theta}{2}$ with respect to the box reference system (x,y,z) and plane A' is misoriented by $\frac{-\theta}{2}$ respectively. Finally the primitive CSL cell is sketched in the upper quarter of the figure. (b) DSC lattice and different selections of tilt GB planes (see text). (c) demonstrates the scheme to generate asymmetrical tilt GBs. Here two distinct GBs are given, namely ASY14 having an inclination angle of 14.04° and ASY33 having an inclination angle of 33.69° with respect to the symmetrical $\Sigma 5$ 180.00° [210] tilt GB. Finally (d) demonstrates that a rigid lattice shift of one grain with respect to the other one by a DSC lattice vector (here $\mathbf{b}_{DSC} = \frac{1}{5}\mathbf{b}_{CSL} = \frac{1}{10}[\bar{1}30]$) still preserves the CSL. Note that only the CSL points shift to different lattice sites.

and do not withstand a thorough analysis. For instance in the case of symmetrical tilt GBs the discussion becomes slightly complicated since these GBs can be considered as special twist GBs too. More details on this will be presented in the sect. 2.1.3. To summarize at this point it should be stated that the whole discussion of GB nature and generation scheme should really focus on the GB plane and the GB type rather than the CSL scheme accompanied by a selection rule for the GB type. Nevertheless one important aspect can be drawn from the CSL scheme, namely that CSL GBs do show the periodicity of the CSL which clearly distinguishes them from general random GBs.

To illustrate the beforementioned discussion by a simple key example and to underline a few more aspects of the CSL concept, now the CSL scheme of the $\Sigma 5$ 36.87° [001] case for a fcc material will be discussed. It is well-known that this CSL can be obtained too by the following three different representations, namely 53.13° [001], 180° $[2\bar{1}0]$ and 180° $[\bar{1}30]$. Fig. 2.5 (a) illustrates the CSL for this case and presents the size of the primitive CSL cell. Here the length of the primitive square CSL within (002) planes is given by $\sqrt{\frac{\Sigma}{2}} \cdot a_o$. Note that the CSL is a three-dimensional lattice and that further lattice points are found in any (002) plane of the system since the 3d system is being formed by stacks of (002) planes having a stacking sequence of ABABAB.

A further important aspect in the discussion of the CSL is the so-called displacement shift complete (DSC) lattice which is shown in Fig. 2.5 (b). The DSC lattice is simply formed when considering lattice sites of crystal no.1 and no.2 being part of a common crystal lattice. This fine-meshed lattice shows two interesting aspects. The first is that if lattice no.1 is shifted by a DSC lattice vector with respect to lattice no.2 the CSL is preserved and only the CSL sites are shifted. Fig. 2.5 (d) demonstrates this point quite nicely for the $\Sigma 5$ 36.87° [001] CSL. The second important aspect is that since the DSC lattice is associated with lattice no.1 and no.2 and since it is continuous across the GB as seen in Fig. 2.5 (b), it is the reference lattice for GB defects like secondary GB dislocations. Therefore any secondary GB dislocations properties are given in the framework of the DSC lattice. The CSL of course is continuous across the GB too, nevertheless since it does not include all lattice sites of crystal no.1 and no.2 it does not lend itself to discuss secondary GB defects.

Fig. 2.5 (b) presents two symmetrical CSL tilt GBs for the $\Sigma 5$ 36.87° [001] CSL, namely the $\Sigma 5$ 36.87° [001] if selecting the GB plane to be a plane parallel to the x-z plane while the $\Sigma 5$ 53.13° [001] would be found if selecting the GB plane to be a plane parallel to the (y=x)-z plane. It is important to realize here that the GB planes are distinctly different, namely a (310) plane for the first case and a (210) for the second case as demonstrated in Fig. 2.5 (b) explicitly. This means that although the CSL scheme is the same the GB character is not. Finally Fig. 2.5 (c) presents two distinct asymmetrical CSL tilt GB configurations which were studied in this work. Here ASY14 is inclined by 14.04° with respect to the $(2\bar{1}0)$ plane while GB ASY33 is inclined by 33.69° . These inclination angles were picked since the asymmetrical GBs were to run through CSL points in order to obtain periodic GBs. Fig. 2.5 (a) to (d) include a lot of details on the $\Sigma 5$ 36.87° [001] tilt GBs since this tilt GB as well as the two asymmetrical tilt GBs given in Fig. 2.5 (c) were studied intensively in this work. Furthermore the $\Sigma 5$ 36.87° [001] example lends itself very nicely to demonstrate the basic aspects of the underlying CSL theory. Since the CSL concept is not exclusively associated with GBs and since several representations for a given CSL superlattice exist, another important scheme, namely the interface-plane scheme, is commonly used to geometrically generate GBs. The scheme is discussed in detail by Wolf [20, 69] and in this work it was

Σ	H,K,L $\Rightarrow \mathbf{n}_{CSL}$	m	n	Ψ	GB plane $\Rightarrow \mathbf{n}^{GB}$
5	0,0,1	1	3	36.87°	(130)
5	0,0,1	1	2	53.13°	(2 $\bar{1}$ 0)

Table 2.1: CSL scheme for $\Sigma 5$ [001] tilt GBs.

utilized to characterize and generate GBs. Its relevance in the context of GBs is due to the fact that it emphasizes the importance of the GB plane rather than the CSL misorientation scheme as given above.

2.1.3 Interface-Plane Scheme

Following the discussion in the preceding section, now the interface-plane scheme (IPS) is presented which was put forward by Wolf and Lutsko [20] to characterize the geometry of planar GBs. To characterize distinct planar GBs, this approach utilizes the information concerning the crystallographic planes of crystal number 1 and number 2 that meet at a GB. For each crystal, the plane normal of these planes is given in the principal coordinate reference system of each crystal as is sketched in Fig. 2.6(a). If $\mathbf{n}_1^{GB}$ and $\mathbf{n}_2^{GB}$ are not identical, it implies that both crystals are misoriented by a tilt rotation about the tilt axis, $\mathbf{n}_{tilt}^{GB}$, by the tilt angle, Ψ . In order to determine the tilt component of a GB, both GB plane normal vectors, $\mathbf{n}_1^{GB}$ and $\mathbf{n}_2^{GB}$, determined in each principal coordinate system, are then plotted in the coordinate system of only either one of the two principal coordinate systems. This point is illustrated in Fig. 2.6(b) where $\mathbf{n}_1^{GB}$ and $\mathbf{n}_2^{GB}$ are given in the coordinate reference system of crystal number 1. In the shown case of Fig. 2.6(b), indeed $\mathbf{n}_1^{GB}$ and $\mathbf{n}_2^{GB}$ are not identical. Hence a tilt component of this GB exists. Performing the tilt operation by rotating $\mathbf{n}_2^{GB}$ about $\mathbf{n}_{tilt}^{GB}$ by the tilt angle, Ψ , will then align both vectors, $\mathbf{n}_1^{GB}$ and $\mathbf{n}_2^{GB}$. This tilt rotation represents therefore the tilt component of this specific GB. The tilt rotation vector is formally given by $\mathbf{n}_{tilt}^{GB} = \frac{\mathbf{n}_2^{GB} \times \mathbf{n}_1^{GB}}{\sin(\Psi)}$ with $\sin(\Psi) = |\mathbf{n}_2^{GB} \times \mathbf{n}_1^{GB}|$ and Ψ being the tilt angle.

Now the complete underlying idea of the IPS misorientation scheme can be explained. Any general GB can be thought of having a tilt and a twist component. As described above, specifying the plane normals of the planes parallel to the GB within each crystal defines the tilt component of the GB. Following the tilt procedure to align the vectors $\mathbf{n}_1^{GB}$ and $\mathbf{n}_2^{GB}$, a further twist rotation about the common GB normal by θ might be necessary to align now the in-plane crystallographic vectors of crystal number one and two. This twist rotation therefore defines the twist component of the GB. Note here that the sequence of misorienting the crystals is fixed. First the tilt component needs to be defined, then the twist component can be determined.

Thus the IPS focuses in detail on the crystallography met at a GB rather than getting into the details of some misorientation scheme explicitly as it is done in the CSL scheme. Of course by defining crystallographically the planes that meet at a GB, already some misorientation information of the two crystals is supplied, namely its tilt component. Finally in the IPS,

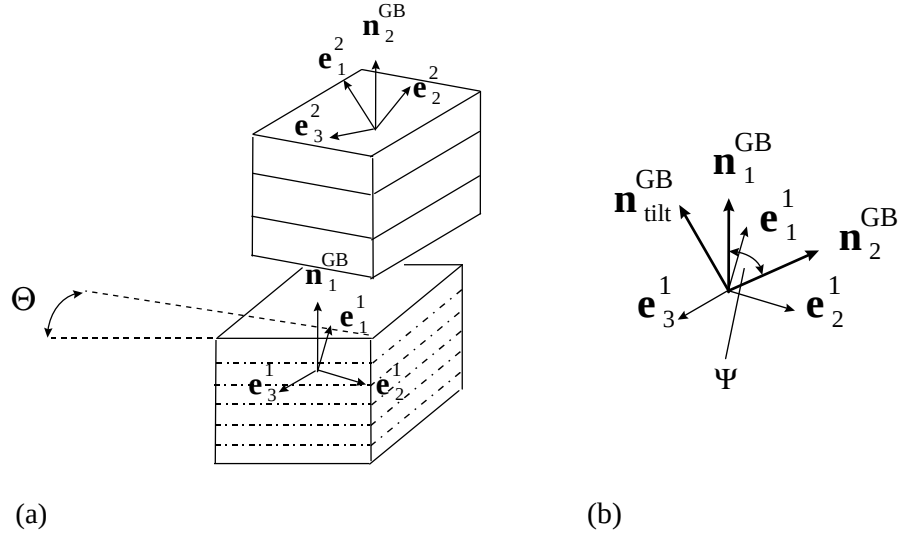


Figure 2.6: Interface-Plane Scheme. Fig.(a) presents the basic properties within the IPS for a general planar GB and introduces the twist component of a general GB. Fig.(b) illustrates the origin of the tilt component of a general GB which is solely connected to crystallography of the planes meeting at the GB. Note here that in (a) each set of planes meeting at the GB is given crystallographically according to its crystal reference coordinate system and that in (b) these coordinates are presented in the reference coordinate system of crystal number 1.

the five macroscopic and three microscopic DoFs are given by

$$\{DoFs\} = \{\mathbf{n}_1^{GB}, \mathbf{n}_2^{GB}, \theta, \mathbf{T}\} \quad (2.7)$$

while in the CSL scheme they are given by

$$\{DoFs\} = \{\mathbf{n}_{CSL}, \psi, \mathbf{n}^{GB}, \mathbf{T}\}. \quad (2.8)$$

A remark concerning the usage of the terms symmetrical and asymmetrical GBs in this context is given next. Namely, symmetrical means that the nature of the planes parallel to the GB plane on either side of the two crystals are crystallographically equivalent. Hence an asymmetrical GB is formed by two crystals were non-crystallographically equivalent planes meet at the GB. Symmetrical GBs can either be symmetrical twist or tilt GBs. Symmetrical tilt GBs identified by the IPS are always characterized by $\{\mathbf{n}_1^{GB}, \mathbf{n}_1^{GB}, 180^\circ, \mathbf{T}\}$. Hence at maximum one symmetrical tilt GB exists for one chosen crystallographic plane. No symmetrical tilt GBs exist if the stacking sequence of the $\mathbf{n}_2^{GB} = \mathbf{n}_1^{GB}$ planes is less than three [20, 69]. For instance for $\mathbf{n}_1^{GB} = [001]$ or $\mathbf{n}_1^{GB} = \frac{1}{\sqrt{2}}[110]$ GB planes, a A,B stacking sequence exists in cubic materials meaning that on (001) and (110) planes no symmetrical tilt GBs can be formed by 180° twist rotations.

For experimental bicrystal sample preparation as well as for generating bicrystalline GB simulation boxes, the IPS lends itself very nicely to generate GBs. The reason for this is rather simple since the task is to misorient two crystals in such a manner that an ideal crystal needs to be cut into two halves, then the two crystals have to misoriented with respect to the cutting plane and thus after joining the two crystals again a well-defined bicrystal has been generated. Conceptually speaking this means that prior to misorienting any crystal the GB normal needs to be known in order to cut an ideal crystal into two halves. Hence

the cutting plane or to be more precise the GB plane plays the key role in these schemes rather than the misorientation procedure.

Following the IPS, any symmetrical tilt GB can be generated by a $\theta = 180^\circ$ twist operation about the GB plane normal. This result itself is rather important to be noted since from a conceptual point of view it demonstrates the simplicity of the generation scheme of symmetrical tilt GBs. Furthermore it proves that symmetrical tilt GBs have to be considered as special twist GBs rather than tilt GBs as has been discussed by Wolf [69] in detail. Since in this work, the focus is on cubic materials and since $\Sigma 5$ twist and tilt GBs were investigated in detail, now a few more aspects of the IPS of $\Sigma 5$ GBs are presented. According to Eq. 2.5 if θ equals 180° , it follows that $m=1$ and $n=0$ and hence Σ becomes $\Sigma = N = H^2 + K^2 + L^2$. Thus for $\Sigma 5$ 36.87° [001] and 53.13° [001] symmetrical tilt GB one finds that the GB planes are respectively a (310) and a (210) plane and Eq. 2.6 yields $\Sigma 5$ in both cases as has been expected. It is important to stress here that the $\Sigma 5$ 36.87° [001] GB are obtained according to the IPS by a 180° [310] twist rotation while the $\Sigma 5$ 53.13° [001] GB by a 180° [210] twist rotation.

2.1.4 Asymmetrical CSL Tilt GBs

In this work apart from symmetrical CSL tilt GBs asymmetrical CSL tilt GBs were studied as well. With respect to the $\Sigma 5$ 53.13° [001] symmetrical tilt GB, two asymmetrical tilt GBs were already presented in Fig. 2.5(c) and their derivation is closely connected to the CSL scheme of the symmetrical tilt GB. In order to fully understand the geometrical generation scheme and characterizing properties of asymmetrical tilt GBs, next the underlying definitions are explained briefly. Conceptually speaking one can think of their generation in a two step process. Step number one is to misorient two adjacent crystals in such a manner that a symmetrical tilt GB forms. This is simply achieved by rotating one of the crystals following the interface-plane scheme by 180° about the common symmetrical GB normal $\mathbf{n}_{sym}^{GB}$. The second step is then to select a plane to form the GB which differs from the symmetrical one. The deviation from the symmetrical plane is measured by the inclination angle, ϕ , as is shown in Fig. 2.7.

The whole generation procedure is illustrated by Fig. 2.7 especially concerning the position of the asymmetrical tilt GB with respect to the symmetrical tilt GB plane. Furthermore Fig. 2.5(c) demonstrates the exact geometries for the two studied asymmetrical tilts in this work, namely ASY14 and ASY33 having inclination angles of 14.04° and 33.69° , respectively with respect to the (210) plane. Due to this generation scheme, the planes meeting at an asymmetrical GB are no longer crystallographically equivalent. Conceptually speaking any inclination angle would be possible, nevertheless since the asymmetrical GBs studied in this work are restricted to CSL asymmetrical GBs, only a limited number of CSL boundaries can be created. These are already determined by the CSL lattice connected to the CSL misorientation scheme, since within the asymmetrical CSL GB plane a subset of CSL points will be present which is the basis to geometrically construct these GBs.

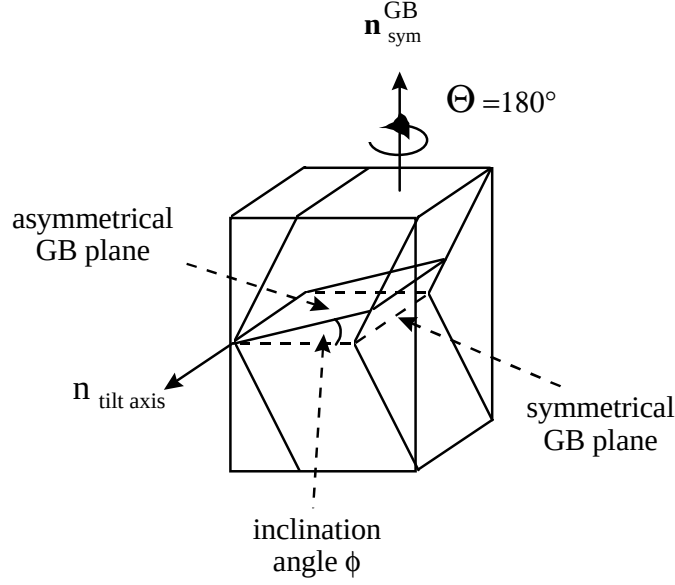


Figure 2.7: Generation scheme of asymmetrical tilt GBs. The figure illustrates that the misorientation scheme of the two crystals is connected to that for a symmetrical tilt GB while the selected GB plane differs from the symmetrical one and is inclined with respect to that plane by the inclination angle, ϕ .

2.2 Grain Boundary Migration

In crystalline materials, a lot of physical processes are thermally activated. This is true for bulk material processes like self-diffusion or different lattice dislocation processes like for instance dislocation climb. GB processes are thermally activated as well and include processes like GB self-diffusion and GB migration. The activation parameters that describe for instance the rate of diffusion or movement of either dislocations or GBs are fundamental properties. They differ between materials and can depend on for instance the character of a GB when studied in a specific material.

In this work, the focus is on GB self-diffusion and primarily on GB migration in typical fcc metals. To date no fundamental theory exists that can fully describe all aspects of GB migration in metals [24]. Several theories that describe aspects of GB migration do exist. In this section, the necessary theory to discuss the GB migration results found in this work by atomistic simulations is presented. The reader should note that the studied GB systems did not contain any impurities, lattice dislocations or i.e. second phase particles. Hence the studied atomistic systems represent the case of ideally pure systems which in GB migration experiments can never be met. In literature, there are plenty of publications on impurity effects on GB migration (for a summary see i.e. [24]). These theories will not be discussed in any detail here, since their relevance is very limited for the conclusions made in this work. Therefore the presentation of the theory of GB migration is limited to the general relationships that have been established over the years in the field of GB migration in metals and focus on two aspects :

- (1) rate theory to derive the fundamental equations of GB migration
- (2) the compensation effect.

Rate theory - The key in deriving the fundamental analytic relations describing GB migration or to be more precise the rate of GB migration goes back to fundamental concepts of Mott [23] and Turnbull [21, 22]. Both put forward basic models utilizing rate theory to describe analytically the kinetics of GB sliding and grain growth, respectively. Focussing on possible atomic-level processes at GBs taken place while GBs migrate, it is common sense that on the atomic-level atoms of the shrinking grain need somehow to align with the crystal structure of the growing grain. Two basic scenarios are imaginable. The first one, usually put forward when discussing GB migration on the atomic scale, assumes that a GB is a disordered, a few atomic distances wide, object which atoms can either enter or leave when detaching from or attaching to one crystal structure of the adjacent grains at the GB. According to simple reasoning this model is usually linked to diffusion processes within the GB and therefore can be expressed by simple rate theory relationships. Next

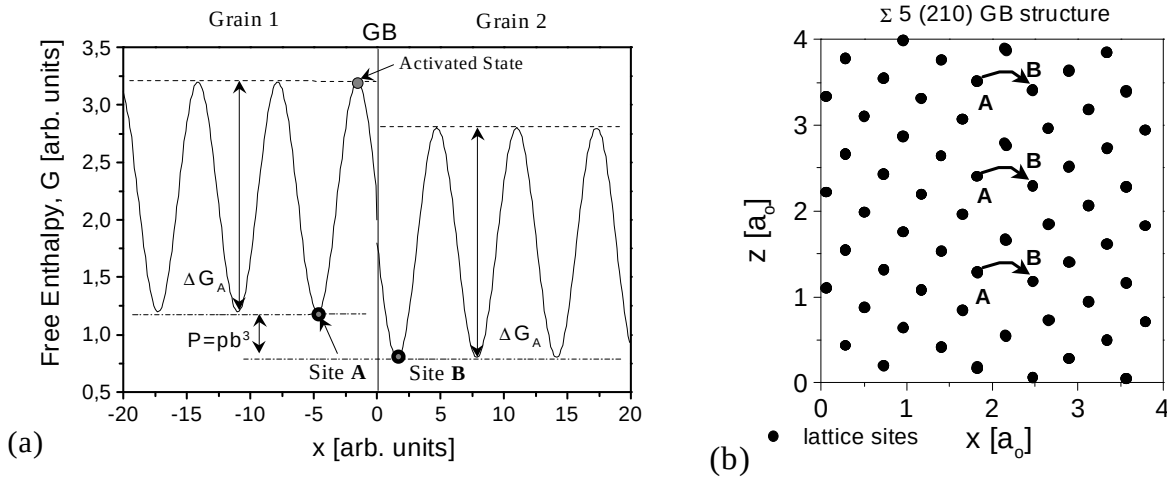


Figure 2.8: In Fig.(a) the free enthalpy, G , profile in the vicinity of a GB for a moving atom is shown. An atom crossing from site A of grain 1 to site B of grain 2 has to overcome the energy barrier, ΔG_A , while an atom crossing from site B of grain 2 to site A of grain 1 needs to overcome the energy barrier $\Delta G_A + P$. In Fig.(b) an example of the underlying atomistics at the GB is shown identifying site A in grain 1 and site B in grain 2. Here the solid circles identify lattice sites rather than positions occupied by atoms in a real GB structure.

the rate theory first introduced by Turnbull [21] is presented. Still today it is a standard approach to envision the process of GB migration by a simple single atom jump mechanism across the GB. Good introductions to rate theory can be found by Burke and Turnbull [22] on pp. 244 and Gottstein and Shvindlerman [24] on pp. 126.

Fig. 2.8(a) shows the energetical situation of a jumping atom close to a GB on either side of the GB. Here the free enthalpy of grain 1 is raised with respect to grain 2 by an excess energy, P . This energy gradient might be related to i.e. different stored energy of strain in each of the two grains due to external stress states or i.e. a difference in dislocation content. Other sources that lead to energy gradients are thinkable too. Now the rate of atoms crossing the GB from site A of grain 1 to site B of grain 2 and in the opposite direction can be calculated according to rate theory. The net rate, Γ , is $\Gamma = \Gamma_{12} - \Gamma_{21}$, where Γ_{21} is the jump rate from grain 2 to 1 and Γ_{12} the jump rate in opposite direction. In this framework, the jump events are considered diffusive requiring to overcome a free enthalpy barrier of

ΔG_A . Here ΔG_A represents the migration activation free enthalpy for vacancy migration in the bulk lattice. Since an atom detaching from grain 1 and attaching to grain 2 can only perform the jump if at site B a GB vacancy exists, hence the vacancy concentration, c_{GB} , at the GB has to be included in Eq. 2.9. c_{GB} itself is thermally activated and given by $c_{GB} = c_0 \cdot \exp(-Q_{Form}/k_B T)$ where Q_{Form} represents the vacancy formation enthalpy within the GB. Assuming a jump distance, b , for the diffusive jump of an atom across the GB, finally gives the net GB velocity which reads

$$\begin{aligned} v &= b \cdot c_{GB} \cdot \Gamma = b \cdot c_{GB} \cdot (\Gamma_{12} - \Gamma_{21}) \\ &= b \cdot c_{GB} \cdot \left(\nu_{12} e^{-\frac{\Delta G_A}{k_B T}} - \nu_{21} e^{-\frac{\Delta G_A + P}{k_B T}} \right) \end{aligned} \quad (2.9)$$

The jump distance is usually a fraction of the lattice parameter and b^3 is usually approximated by the atomic volume. The difference in free enthalpy, P , between grain 2 and 1 is related to the driving force, p , by $P = pb^3$. The driving force, p , which determines the net jump rate across the GB is given by $p = -\frac{\Delta G}{\Delta V}$. This means that when an atom is being transferred from grain 1 to 2, the system's energy is lowered by $P = pb^3$. When an atom moves into the opposite direction across the GB, the system's free enthalpy will increase by P . Here ν_{21} and ν_{12} are the attack frequencies to overcome the potential barrier and it is usually assumed that both frequencies are the same and can be approximated by the Debye frequency, ν_D .

Utilizing the above-mentioned explanations on the input properties, Eq. 2.9 now reads

$$v = b \cdot c_0 \cdot e^{-\frac{Q_{Form}}{k_B T}} \cdot \nu_D e^{-\frac{\Delta G_A}{k_B T}} \cdot \left(1 - e^{-\frac{pb^3}{k_B T}} \right) \quad (2.10)$$

Finally the ratio of the excess energy, P , and the thermal energy, $k_B T$, is usually assumed to be $\frac{pb^3}{k_B T} \ll 1$. In the conducted molecular dynamics (MD) simulations of this work, the highest driving forces, p , were about 0.01 eV/ Ω where Ω represents the atomic volume of the fcc lattice. The covered temperature range in the GB migration MD simulations extended from 600K up to 1100K. At 600K one finds $\frac{pb^3}{k_B T} = 0.19$ while at 1100K it is 0.11. Even for these highest driving forces applied in the MD simulations, the term $1 - \exp(-\frac{pb^3}{k_B T})$ can be fairly well approximated by $1 - \frac{pb^3}{k_B T}$. The encountered error is still small and about two percent for the 600K case. Here the whole discussion was based on a single atom transfer mechanism where it was assumed that b^3 equals the atomic volume. If instead of a single transfer mechanism, the volume of the activated state is several times the atomic volume, the above approximation is at question and would need to be replaced by the full $1 - \exp(-\frac{pb^3}{k_B T})$ term.

Finally the GB velocity, v , is given by Eq. 2.11

$$v = \frac{b^4 \cdot c_0 \cdot \nu_D}{k_B T} \cdot e^{-\frac{Q_{Form} + \Delta G_A}{k_B T}} \cdot p = m \cdot p \quad (2.11)$$

Eq. 2.11 represents the generic equation of GB migration which relates the GB velocity with the driving force, p , by a linear relationship. Here m is the GB mobility which holds the information of the activation mechanism of GB migration of specific GBs. For the single atom diffusion mechanism m reads

$$m = \frac{b^4 \cdot c_0 \cdot \nu_D}{k_B T} \cdot e^{-\frac{Q_{Form} + \Delta G_A}{k_B T}} \quad (2.12)$$

$$= m_0 \cdot e^{-\frac{Q_{Form} + \Delta H_A}{k_B T}} \quad (2.13)$$

where $Q_{Form} + \Delta H_A$ is now the activation enthalpy. The preexponential factor, m_0 , is then given by

$$m_0 = \frac{b^4 \cdot c_0 \cdot \nu_D}{k_B T} \cdot e^{\frac{\Delta S_A}{k_B}} \quad (2.14)$$

Eq. 2.11 to 2.14 are considered as the generic equations of GB migration in metals for the following reasons. The results of numerous experiments [25] as well as atomistic simulations [64, 33] show that the relationship between GB velocity and driving force is indeed linear. The GB mobility, m , is found to be thermally activated where the activation enthalpy ranges from GB self-diffusion to vacancy lattice diffusion and even in a lot of cases exceeds the vacancy lattice diffusion value by a factor of two to three for curved GB migration in Al [25]. The exact value of the GB migration enthalpy depends on the GB character, the chemical composition of the studied system and the exact situation met at the GB. Finally the preexponential factor, m_0 , follows the so-called compensation effect [26] and is discussed in more detail below. Hence due to the results of experiments dedicated to GB migration, it follows that the above-stated equations described the GB properties as well as the kinetics correctly.

In the theory of GB migration presented above, the underlying mechanism was the diffusion of single atoms across a GB. Within the outlined model the process was described by vacancy volume diffusion and the activation enthalpy, ΔH , was given by $\Delta H = Q_{Form} + \Delta H_A$. In Al experiments of GB migration of planar and curved low-angle $\langle 111 \rangle$ tilt GBs [62], it was found that ΔH equaled the enthalpy of vacancy lattice diffusion. In the case of high-angle GBs, the results depend on the curvature, κ , of the GB. For planar $\langle 111 \rangle$ high-angle GBs, it was found that the activation enthalpy is in the range of GB self-diffusion [62] while for curved $\langle 111 \rangle$ tilt GBs having the same misorientation relationship as the planar ones, the activation enthalpy exceeds the activation enthalpy of vacancy lattice diffusion in some cases even by a factor of two to three [25, 62]. According to these results, the generic equation for GB mobility, m , reads

$$m = m_0(c, \theta, \kappa) \cdot \exp\left(-\frac{\Delta H(c, \theta, \kappa)}{k_B T}\right). \quad (2.15)$$

This means that m_0 and ΔH are functions of the purity of the system, c , the misorientation relationship of the two grains adjacent to the GB, θ , and the curvature of the GB, κ .

A second intriguing class of atomic-level processes that could carry the atomic displacement fields of atoms during GB migration is briefly discussed now. During GB migration, the elementary step of any atom in the vicinity of a GB is to align itself to the crystal structure of

the growing grain. Assuming that one deals with a mono-atomic system and no impurities reside at the GB, it seems possible that GB migration could in principle occur by displacement fields of atoms solely within crystallographic planes parallel to the GB plane. This idea is interesting to think about especially when considering that most GBs have a finite width of about the lattice parameter and therefore usually do not present themselves as broad disordered regions. If so, the fundamental idea that atoms need to migrate a finite distance larger than the lattice parameter in order to detach from one crystal structure and later on to realign with the new crystal structure may in impurity free crystals not necessarily be a basic requirement for GB migration. Even the assumption that GB migration needs atomic displacement in the direction of the GB normal would in such a scenario not be required. Such processes were identified by atomistic simulations [32] as well as by experiments.

Compensation Effect - Next an interesting effect commonly observed when dealing with thermally activated processes like GB migration and GB diffusion is discussed. The so-called compensation effect was first observed on experimental GB mobility and GB diffusion data [25] and states for the GB migration activation parameters that the preexponential factor, m_0 , of the GB mobility, m , depends on the activation enthalpy, ΔH , according to

$$\Delta H = k_B T_C \ln(m_0) - k_B T_C \ln(m(T_C)) . \quad (2.16)$$

where T_C is the so-called compensation temperature.

Eq. 2.16 can be derived directly from Eq. 2.14 by simple algebra according to

$$\Delta S_A = \frac{\Delta H}{T_C} = k_B \ln(m_0) - k_B \ln\left(\frac{b^4 \cdot c_0 \cdot \nu_D}{k_B T_C}\right) \quad (2.17)$$

where it was assumed that the activation entropy is given by $T_C \Delta S_A = \Delta H$. This relationship between ΔS_A and ΔH can be derived theoretically applying variation principles when assuming a reference GB ground state [26]. The physical interpretation of the compensation temperature, T_C , is that it is the equilibrium temperature between ground state and activated state. This suggests that ground and activated states are structurally closely related.

A historical example that is in line with the idea of the compensation effect is the work by Mott [23] who introduced a GB model assuming islands of good and bad fit within the GB structure. His model tried to explain slip in GBs assuming that the elementary act during slip is the disordering of atoms around each island of good fit. In his model, Mott linked the activation enthalpy with the latent heat of melting and it was found that in his model the compensation temperature equals the melting temperature [26].

Usually it is assumed [26] and supported by experimental data [25] that the compensation temperature is related to phase transitions observed for a specific material either being a solid state transition or a solid-liquid transition as in the case of Mott.

2.3 Review of Atomistic GB Migration Simulations

The molecular dynamics literature dedicated to atomistic simulations of GB migration can be divided into three different classes. Class one relates to early studies which usually

focussed on finite temperature behaviour of planar GBs [13, 14, 15, 16]. The prime aim usually was to study the GB structure. During such simulations, it was then observed that a GB interacted usually with its periodic image due to applying periodic boundary conditions which led to spontaneous GB migration and GB annihilation. In these simulations no explicit driving forces were imposed on the GBs. These kind of simulations did not hold any information on GB mobility due to a lack of knowledge of driving force data as well as GB velocity data. Usually it was still possible to study the GB migration mechanism observed in the simulations. For instance the aspect of GB sliding coupled with GB migration or vice versa was intensively studied by Bishop et al. [14, 15, 16] on different high-angle GBs. The coupled GB migration and sliding of these GBs was rationalized in terms of the DSC lattice.

Within the second class of simulations, curved GB systems were utilized to indeed study GB migration itself. The first work on a curved GB system was done by Jhan and Bristowe [32] who studied GB migration of a half-sphere GB geometry. The GB setup was designed to

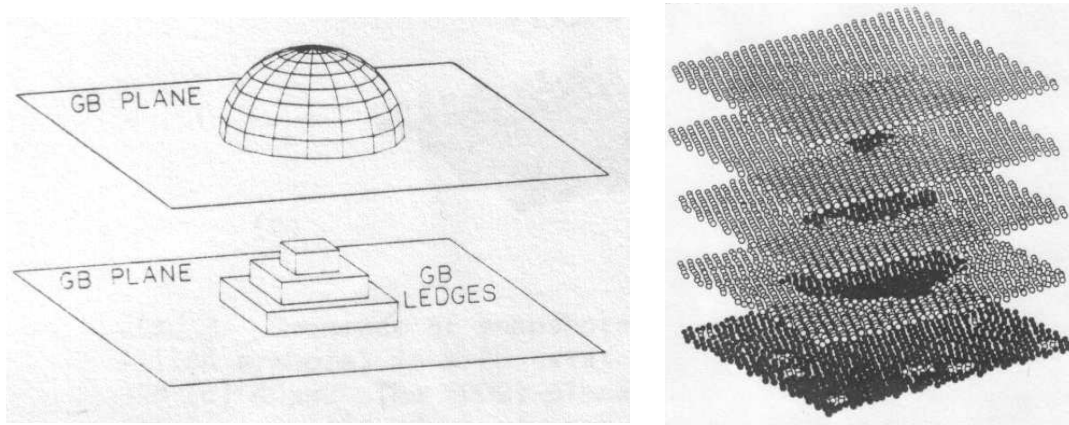


Figure 2.9: Atomistic GB migration simulations by Jhan and Bristowe [32] utilizing a spherical GB geometry. The left figure shows a schematic of the arrangement of (002) planes of the lower grain. These planes were misoriented by a [001] twist rotation with respect to the upper grain. By this procedure a ledged GB is formed. The right figure shows an example of the atomistic simulation box of the $\Sigma 29$ GB system.

avoid the generation of GB dislocations in order to study the migration behaviour of high-angle GBs comparable to those found in experiments by Babcock and Balluffi [30]. Babcock and Balluffi had observed GB migration of vicinal $\Sigma 5$ GBs and explained their experimental results by a shuffle GB migration mechanism. The GB geometry of Jhan and Bristowe consisted of a planar twist GB that included a GB sphere on top of it. This sphere was constructed by stacking at maximum four ledges on top of the twist GB to form a pyramid. A schematic of the utilized GB system as well as an atomistic example for the $\Sigma 29$ GB system is given in Fig. 2.9.

Four high-angle GBs were studied, namely the $\Sigma 5$, 29, 13 and 17. The simulation temperatures were 300K for the $\Sigma 5$ while 500K for the $\Sigma 29$, 13 and 17. An embedded-atom method potential for Gold was utilized in a constant pressure molecular-dynamics code. The whole system setup and the temperatures were chosen to be similar to the conditions met in the experiments by Babcock and Balluffi. The findings of Jhan and Bristowe were :

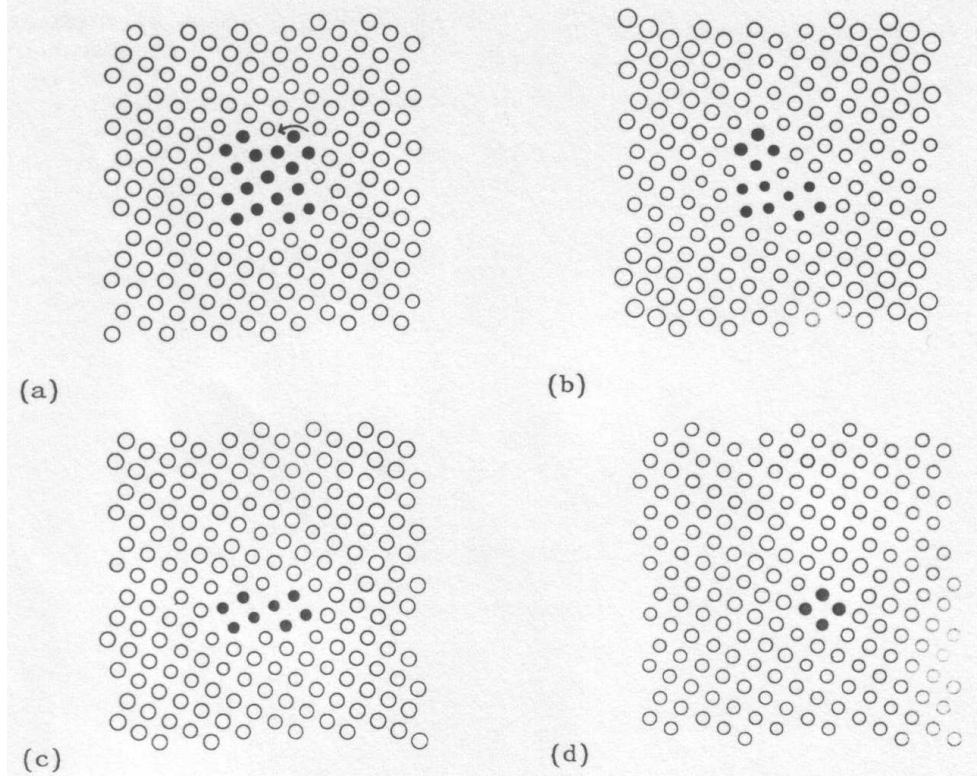


Figure 2.10: Atomistic migration mechanism of the $\Sigma 5$ twist GB system observed during GB migration simulations by Jhan and Bristowe [32]. The authors observed and the figures (a) to (d) show that atoms at the outer region of the legdes can align themselves with the growing grain by collective rotations of four atoms.

- (1) GB migration was observed for all four studied GBs.
- (2) For all GBs, a local shuffling mechanism was observed at the ledges. These shuffles generally proceeded from the periphery of the ledge to its center. An example of the $\Sigma 5$ GB is shown in Fig. 2.10. In sequence (a) to (d) it is observed that the shrinking of a ledge is achieved by the alignment of four atoms with the growing grain by a collective rotation. The four-atom shuffle appears more frequently for GBs close to the $\Sigma 5$ GB. For instance for the $\Sigma 29$ GB, it is often found too and can be seen in Fig. 2.9 on the right hand side in the (002) plane at the bottom. Islands/ledges of four atoms of the growing orientation show up in the bottom plane. They can be understood as a kind of seed of the growing grain and can be considered as the elementary act to establish the growing orientation in the (002) plane of the shrinking orientation.

The occurrence of ledges of four atoms was earlier observed by Majid and Bristowe [29] in atomistic simulations of a planar $\Sigma 5$ [001] twist GB. These ledges formed due to thermal fluctuations of the GB. The theory of shuffling motion of pure steps is discussed in detail by Sutton and Balluffi [35] on pp. 550.

Another example of the second class is an atomistic simulation dedicated to GB migration by Sutton [31] who studied the finite temperature behaviour of a cylindrical GB. The GB represented a general GB being a 45° [001] tilt GB in a fcc system. The interatomic interaction was modelled by a many body potential. Fig. 2.13 shows two schematics of the simulation box system viewed along the [001] direction. On the left, the initial situation is

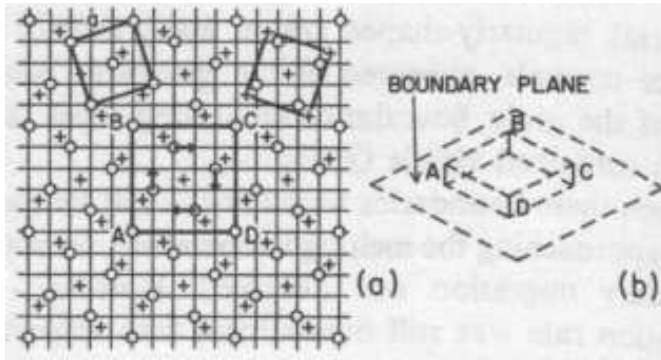


Figure 2.11: Proposed shuffling mechanism of a $\Sigma 5$ [001] twist GB according to Majid and Bristowe [29] (The figure was taken from Babcock and Balluffi [30]). In Fig.(a) the GB structure viewed along the [001] direction is shown. Here (002) planes of either grain facing each other at the GB are shown. The arrows indicate the collective four atom rotation to align these atoms with the new orientation. In Fig.(b) the formed ledge in the upper crystal due to the four atom rotation is shown.

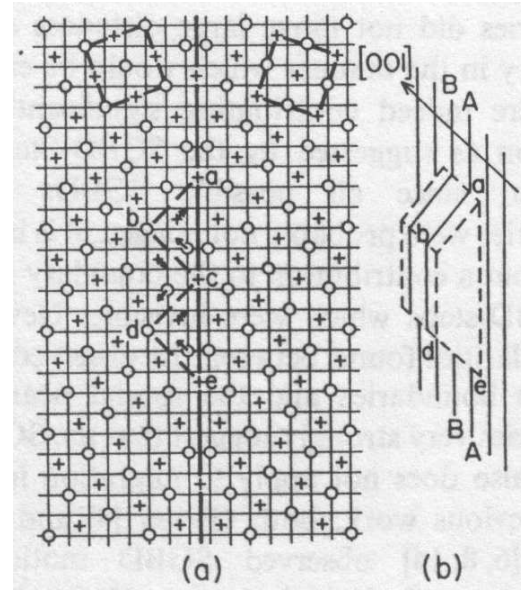


Figure 2.12: Proposed shuffling mechanism of a $\Sigma 5$ [001] tilt GB according to Babcock and Balluffi [30]. Here GB migration is achieved by a collective movement of two atoms indicated by the arrows in Fig.(a). In Fig.(b), the obtained GB ledge is shown which looks slightly different than in the twist GB case.

shown in a 2d sketch. In the center of the figure, the original simulation box is shown which is surrounded by its periodic images. On the right, a schematic of the final GB system is shown. Due to the short distance between the center cylindrical GB and its periodic image GBs, GB interaction led to an attractive force which yielded into an annihilation of the GB at some places. Sutton tried to estimate the GB mobility for the studied case but came up with a questionable result. After all such an approach does not seem to be well suited to study the steady-state migration of GBs.

Finally the third class of atomistic simulations started to utilize constant driving force concepts to study the steady-state migration of GBs. Two distinct different approaches were used. One was put forward by Upmanyu [33] utilizing an U-shaped GB in a 2d atomistic simulation box. The main advantage of this concept is that the driving force due to GB curvature remains constant during the whole processes of migration. Fig. 2.14 shows a 3d schematic of the bicrystalline GB system with a U-shaped GB. The second approach is given by this work where GB migration of planar GBs is studied in the presence of different sources of driving forces. A first example was published in 1997 [64] where GB migration of a planar $\Sigma 29$ [001] twist GB in the presence of an elastic driving force was studied. The main benefit of these simulations is that now the steady-state migration of a GB can be studied in the presence of a constant driving force. This means that the GB mobility can easily be extracted from such simulations which means that the activation parameters of GB migration become easily accessible.

An example of an atomistic GB simulation box studied by Upmanyu is shown in Fig. 2.15.

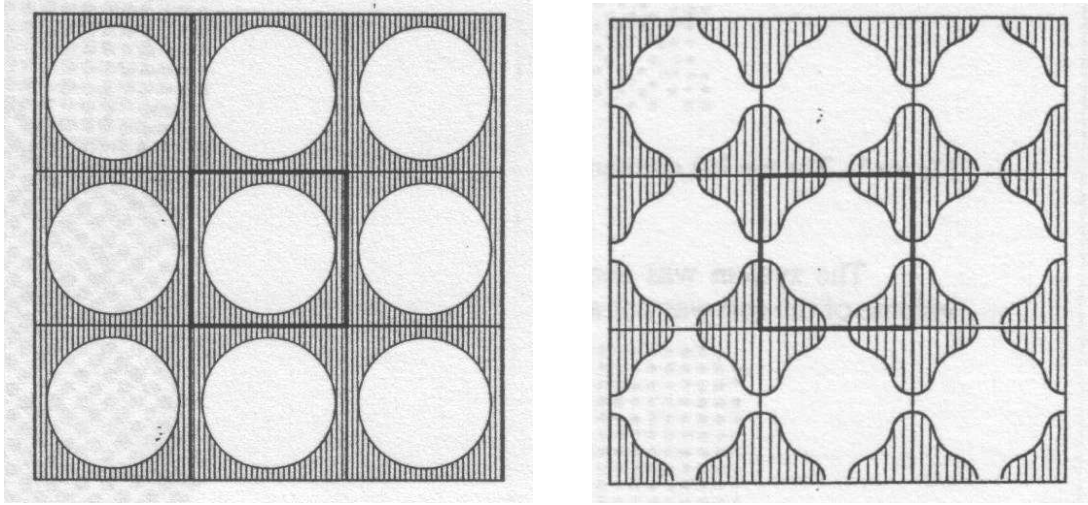


Figure 2.13: Atomistic GB migration simulations by Sutton [31] utilizing a cylindrical GB geometry. The left figure shows a schematic of the initial configuration of the system. In the center the original simulation box is shown which is surrounded by its periodic images. On the right a schematic of the final GB system is shown. Due to the short distance between the center cylindrical GB and its periodic image GBs, GB interaction led to an attractive force which yielded into an annihilation of the GB at some places.

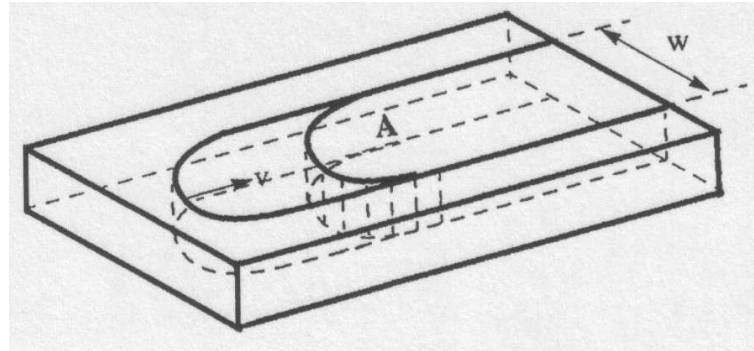


Figure 2.14: U-shape geometry utilized by Upmanyu [33] to study GB migration driven by GB curvature. For the U-shape GB geometry, a constant DF exists during the whole simulation. Here the GB moves with a GB velocity, v , in the direction indicated by the arrow. Hence the area, A , of the U-shaped grain is continuously shrinking. The driving force, p , is given for this geometry by $p = \frac{2\gamma}{w}$ where γ is the GB energy and w the width of the U-shaped grain.

Here in Fig.(a), the initial situation is shown while in Fig.(b) the GB configuration after some distance of GB migration is presented. During the migration the GB remains self-similar which leads to a constant driving force.

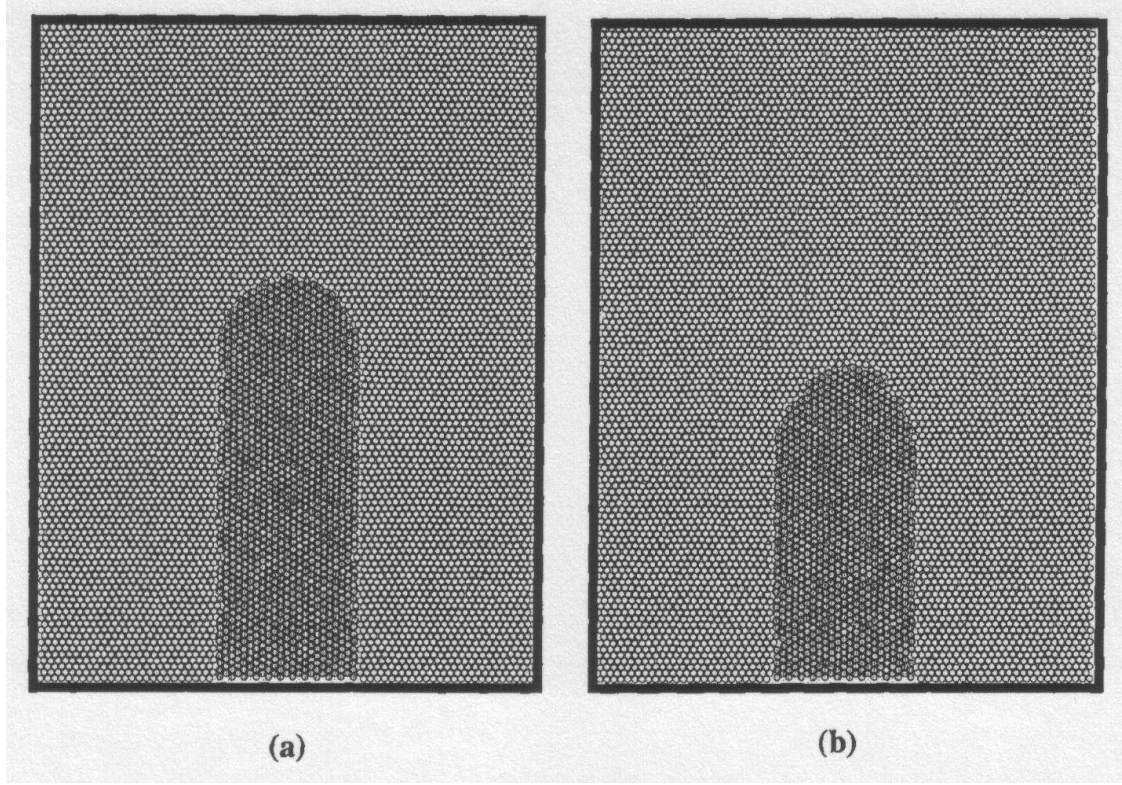


Figure 2.15: Atomistics of U-shape geometry for GB migration [33] at the initial situation shown in (a) and after some finite distance GB migration shown in (b). The GB remains self-similar during the migration which leads to a constant driving force.

Key results of the atomistic simulations by Upmanyu and Srolovitz on GB migration utilizing the U-shape GB geometry in 2d atomistic systems are :

- (1) Establish the U-shaped half-loop geometry in atomistic simulations [33].

Here the GB mobility, m , is determined by $\frac{dA}{dt} = vw = mp \cdot w = m \frac{2\gamma}{w} w = 2m\gamma$ where $\frac{dA}{dt}$ is the first time derivative of the U-shaped half-loop grain area, A , and γ the GB energy. It was shown that $\dot{A}$ is a functions of the width, w , and only asymptotes to a constant value if w is larger than 20 times the NN distance. Hence the GB mobility, m , and the activation parameters of GB migration are available by this simulation approach for the steady state motion of curved GBs.

(2) Vacancy emission for U-shaped half-loop grain geometry.

Simulating GB migration with a U-shaped GB geometry revealed that during the migration events at some point vacancies were emitted from the GB into the growing grain [33, 34]. This generation of vacancies at the GB is associated with the decrease in GB area during GB migration. The excess volume released at the GB leads to the formation of vacancies that are emitted into the growing grain.

(3) Misorientation dependence of GB mobility.

Due to the 2d approach used within the U-shaped GB migration simulations only [111] tilt GBs can be studied since in two dimensions the (111) plane in fcc materials is the only stable crystallographic plane for the used LJ potential. In [27] GB migration of [111] GBs close to the $\Sigma 7$ and $\Sigma 13$ misorientation were studied. Very good data agreement was found for the $\Sigma 7$ profiles of the misorientation dependence of the activation enthalpy and the pre-exponential factor of the reduced GB mobility, $m_0\gamma$, between the simulation data and experimental data of high-purity Al. Since no experimental data on the $\Sigma 13$ was available, only the $\Sigma 7$ data could be compared to experimental data. Large differences were found between the absolute values of the activation enthalpy between the simulation and experimental results. Here the experimental data was about seven times larger than the predicted simulation data. These differences could not be easily explained and could only be attributed to the difference in purity of the systems studied in the simulations and experiments. This is supported by experimental evidence that shows that the higher the purity of a GB system the lower the activation enthalpy of GB migration (see i.e. [24] on page 139 and [35] on page 564).

(4) Compensation effect of GB mobility data.

In [27] it was found that the vicinal $\Sigma 7$ GBs all fall on one distinct line that follows the compensation effect while the vicinal $\Sigma 13$ GBs fall on another line also obeying the compensation effect. Hence the GB migration simulation results show that the compensation effect is obeyed for U-shape GB systems as well as is found for experimental data [25].

A disadvantage of the work by Upmanyu is the restriction to only 2d GB systems. From a computational point of view this restriction is not necessary since the computer power available today and in the late 1990's should have been able to handle comparable 3d U-shape GB systems in a reasonable time. From a physical point of view it is recommended to use 3d systems since in this work it was observed that along the tilt axis which is left out in the 2d simulations, GB self-diffusion as well as GB sliding will occur during finite temperature molecular dynamics simulations. These might have some impact on the migration mechanism or at least on the GB structure. If the GB structure is affected by this i.e. at rather elevated temperatures, so will the GB migration mechanism.

Chapter 3

Computational Procedures

3.1 Introduction to atomistic simulations

Over more than 40 years, computer simulation methods have been used to study atomistic systems [1]. Two methods, namely the Monte Carlo (MC) method as well as the molecular dynamics (MD) method have become established in the field of atomic-level simulations and nowadays a vast field of materials applications are studied by these methods. The underlying methods and theory have been quite largely extended for both method over the years that their physical description of atomic-level systems and interactions as well as taking into account different boundary conditions has become more realistic. The MC method is a stochastic method while the MD method is deterministic. The MD method is well suited to study the temporal evolution of atomistic systems although the accessible time range is quite restricted and only expands to the range of nanoseconds with nowadays computer power [41]. Typical MD system sizes consist of 10^4 to 10^7 atoms [41].

In this work, exclusively MD simulations have been performed to study the finite temperature behaviour of planar GBs in bicrystalline systems. As a model material copper (Cu) was chosen and its interatomic interaction was modelled either by a Lennard-Jones (LJ) or embedded-atom method (EAM) potential. The quality of the physical description of such GB systems highly relies on the physical quality of the assumed interatomic interaction. Although the LJ as well as the EAM potential are relative simple empirical potentials, they are still suited to study GB systems. Since the physical nature of the potentials used within this work is important to know in order to assess the physical relevance of the found results for GB related thermal processes, in section 3.2 the potentials used in this work are presented and discussed.

In section 3.3 the underlying theory and the fundamental equations of motion of the MD method to study the temporal evolution of an atomic-level system are presented. The important concept of Parrinello-Rahman, time integration schemes to solve the temporal evolution of the MD equations of motion, boundary concepts used on GB systems, remarks on how finite temperature simulations were realized as well as the used MD simulation box geometry to study planar GBs are as well presented in this chapter.

In section 3.4, the utilized driving force (DF) concepts to drive planar GBs are introduced and discussed. Due to the planar geometry of the GBs, no explicit DF due to GB curvature

exists for the studied bicrystalline GB box systems. The underlying concepts of the elastic, Peach-Koehler as well as orientation-correlated DF utilized in this work are explained in detail. The commonly used basic concept of GB curvature driven GBs was presented to some extent in sect. 2.3, since it has been utilized in several atomistic simulations to study GB migration [32, 31, 33].

Finally in section 3.5, different concepts and tools to perform atomic-level data analysis are discussed. Here the fundamentals of structural data analysis are presented related to structural properties like the planar structure factor, the radial pair distribution function as well as the common neighbour analysis (CNA). A second important aspect is the data analysis related to GB self-diffusion. The underlying theory to determine the GB self-diffusion coefficient of ideal crystal as well as GB systems is presented. The chapter ends with describing how lattice vacancies can be traced and tracked utilizing the CNA method.

3.2 Interatomic Potentials

In this section several simple ways to model empirically the interatomic interaction of interacting atoms in face-centred cubic (fcc) solids are presented. The main goal of this section is to present those potentials used in this study and to give an overall impression on the key issues connected to interatomic potentials, their key parameters and the basis on which they are founded. A detailed overview on the wide range of applicable potentials to interfaces in crystalline materials is given in the monography by Sutton and Balluffi [35] in chapter 3. Copper was chosen as the model fcc material since a lot of computer simulation based information as well as experimental data exist on this well-known fcc material. Therefore all mentioned parameters associated with the different used potentials are related to Cu.

Before discussing different potentials, the reader should note that any used interatomic potential is in principle having its own materials properties. How well these materials properties agree with the real materials properties determines the quality of the potential. Generally for empirical potentials only a limited number of experimentally known physical properties of the model material are used to determine the fit parameters of the interatomic potential. Since the potential fit parameters are usually only a few, it is intrinsically evident that the potential will not be able to mimic all properties of the real material well. Hence the choice of potential depends highly on the issue to be studied.

Even if the data agreement between model and real material is poor, still the model system in itself is a physical system of its own. Results obtained by such model systems are consistent and true within the models, whether they have any relevance for the true physical behaviour of a real material depends on the correctness of the model and how well the potential can mimic the behaviour of the interatomic interaction of the material concerning the studied application of the material.

3.2.1 Pair Potentials for fcc materials

The simplest way to model the interatomic interaction of atoms is achieved by using a harmonic potential. The general form of a harmonic potential is

$$V^{harm.}(r_{ij}) = \epsilon \cdot \left(36 \cdot \left(\frac{r_{ij}}{r_0} - 1 \right)^2 - 1 \right), \quad (3.1)$$

where r_{ij} is the distance between atoms i and j , r_0 is the equilibrium distance between two atoms and ϵ determines the energy scale of the potential. From analytical theory in various fields of physics like mechanics or solid state physics it is known that already this rather simple potential can explain basic features of mechanics or solid state physics [12]. Nevertheless the harmonic potential is for a lot of physical phenomena not sophisticated enough to represent those processes. For instance the harmonic potential does not allow for thermal expansion of a crystal nor does it allow for heat transfer or conduction due to no phonon interaction [12]¹ in a crystal to occur. Due to those problems connected to the harmonicity of the potential it does not lend itself to be used in atomistic simulations. For instance an atomic system simulated in a microcanonical ensemble away from thermodynamical equilibrium could never reach its thermodynamical equilibrium due to no coupling of the phonon modes.

3.2.1.1 3d Lennard-Jones Potential

An improved approach to model the interatomic interaction of atoms is for instance achieved by using a purely pairwise potential like the Lennard-Jones (LJ) potential. It should be mentioned that different pair potentials apart from the LJ potential exist like for instance the Morse potential or the Born-Mayer potential. The choice of the used potential depends for instance on the crystal structure to be investigated since for instance the LJ potential favours the fcc over the bcc structure. Although the analytical form of the LJ potential as given in Eq. 3.2 is rather simple it overcomes those problems connected to the harmonicity of the harmonic potential as stated before due to its anharmonic form. For the used 3d LJ Cu potential the specific input parameters are $\sigma=2.3151\text{\AA}=0.905433 \cdot r_o$ and $\epsilon=0.167\text{eV}$. It should be noted here that a shifted-force procedure as given by Eq. 3.3 has been applied with a cut-off radius of $r_C=1.49a_o$, where $a_o=3.616\text{\AA}$ is the zero Kelvin lattice parameter of Cu. Under these conditions the melting temperature T_m for this potential is $T_m \approx 1250\text{K}$ and the cohesive energy per atom e_{coh} is $e_{coh} = -1.037824 \text{ eV/atom}$ obtained by 3d periodic ideal crystal simulations.

It should be mentioned at this point that the experimentally determined cohesive energy per atom for Cu is $e_{coh} = -3.50 \text{ eV/atom}$ and that the melting temperature is $T_m=1356\text{K}$. Again it should be stressed that the prime aim of utilizing this potential is only to represent a typical fcc material rather than Cu in each and every detail. One has to bear in mind here that the LJ potential contains only two adjustable parameters, namely σ and ϵ , and that those were fitted in such a way that the potential represents the correct lattice parameter of Cu, namely a_o , and that the melting temperature, T_m , is as close as possible with respect

¹for an introduction see [12] on pages 162 to 173

to available experimental data for Cu. The analytical expression for the Lennard-Jones potential is given by Eq. 3.2

$$V^{LJ}(r_{ij}) = 4\epsilon \cdot \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right), \quad (3.2)$$

and the utilized shifted force-procedure in this work is given by Eq. 3.3

$$V^{SF}(r_{ij}) = V^{LJ}(r_{ij}) - V^{LJ}(r_C) - (r_{ij} - r_C) \cdot \frac{dV^{LJ}(r_C)}{dr_{ij}}. \quad (3.3)$$

Different forms of shifted force-procedures are known in the literature (see i.e. pp. 145 to 146 in Allen and Tildesley [1] or Chen [42]) and the common feature of any of those is to truncate the potential and its first derivative smoothly at the cut-off radius. For instance within molecular dynamics simulations it is required to apply such a scheme in order to avoid discontinuities of the potential and the forces for atoms leaving and entering into the cut-off sphere of interatomic interaction. Furthermore the shifted-force scheme helps to avoid numerical instabilities during the temporal evolution of the system and facilitates to perform standard tests on the simulation data like energy conservation of the system in order to trace programming errors. For the 3d LJ potential the cohesive energy E_{coh} then reads

$$E_{coh}(\{r_{ij}\}) = \frac{1}{2} \cdot \sum_{i=1}^N \sum_{j=1}^N V^{SF}(r_{ij}) = N \cdot e_{coh} \quad (3.4)$$

where $i \neq j$ is assumed.

After introducing the specifics of the used 3d LJ potential, now the LJ potential is discussed from a more general point of view to illustrate its physical basis. In a general mathematical form the LJ potential is defined by the Eq. 3.5

$$V(r_{ij}) = \alpha \cdot r_{ij}^{-n} - \beta \cdot r_{ij}^{-p} \quad (3.5)$$

To represent an overall attractive interaction between two atoms, i and j , and to have a stable configuration at $r_{ij} = r_0$, $V(r_{ij})$ needs to have a minimum at $r_{ij} = r_0$. Mathematically this means

$$\frac{dV(r_{ij})}{dr_{ij}} \Big|_{r_0} = 0 \quad \Rightarrow \quad r_0 = \left(\frac{\alpha \cdot n}{\beta \cdot p} \right)^{\frac{1}{n-p}} \quad (3.6)$$

$$\frac{d^2V(r_{ij})}{dr_{ij}^2} \Big|_{r_0} > 0 \quad \Rightarrow \quad n > p \quad (3.7)$$

In the most simplest case, the interaction is only between two atoms. The energy minimum is given for a separation of r_0 between the two atoms and according to this boundary condition σ can be calculated. Using the terms for α , β , n and p according to Eq. 3.2, σ is given by

$$\sigma = \frac{r_0}{2^{\frac{1}{6}}} = 0.8908987 \cdot r_0 \Leftrightarrow r_0 = 1.122462 \cdot \sigma \quad (3.8)$$

Extending the discussion to 3d crystals with a range of interaction up to higher order neighbours leads to a different relationship between σ and the NN distance r_0 . Part of the calculation scheme is illustrated by standard textbooks on solid state physics like Ashcroft

and Mermin [11] on pages 398 to 401 or Kittel [12] on pages 101 to 103. In principle the calculation scheme is the same as was given above. The total potential energy of the system is calculated for a fixed rigid 3d crystal lattice having an equilibrium distance between atoms either given by the NN distance, r_0 , or the lattice parameter, a_0 . The minimum of the potential energy is to be determined for this equilibrium situation. The calculation is as follows. First the LJ potential given in Eq. 3.2 is rewritten to a form where the distance between two atoms is expressed by the NN distance, r_0 . Since for an ideal rigid 3d lattice all atoms are energetically equivalent, the whole discussion can be reduced to consider the interaction between one atom, i , and its neighbours. The cohesive energy, e_i of atom, i , is then given by

$$\begin{aligned}
 e_i &= \frac{1}{2} \sum_{j=1}^N V^{LJ}(r_{ij}) = 2\epsilon \cdot \left(\sum_{j=1}^N \left(\frac{\sigma}{r_{ij}} \right)^{12} - \sum_{j=1}^N \left(\frac{\sigma}{r_{ij}} \right)^6 \right) \\
 &= 2\epsilon \cdot \left(\left(\frac{\sigma}{r_o} \right)^{12} \sum_{j=1}^N \left(\frac{1}{r_{ij}[r_o]} \right)^{12} - \left(\frac{\sigma}{r_o} \right)^6 \cdot \sum_{j=1}^N \left(\frac{1}{r_{ij}[r_o]} \right)^6 \right) \\
 &= 2\epsilon \cdot \left(\left(\frac{\sigma}{r_o} \right)^{12} \cdot T_{12} - \left(\frac{\sigma}{r_o} \right)^6 \cdot T_6 \right) \tag{3.9}
 \end{aligned}$$

Calculating the first derivative of Eq. 3.9 with respect to r_o and putting it to zero yields a relation for σ as a function of r_o or vice versa which reads

$$\begin{aligned}
 \frac{de_i}{dr_o} &= 0 = 2\epsilon \left(-12 \cdot \left(\frac{\sigma}{r_o} \right)^{12} \cdot \frac{T_{12}}{r_o} + 6 \left(\frac{\sigma}{r_o} \right)^6 \cdot \frac{T_6}{r_o} \right) = -2 \cdot \left(\frac{\sigma}{r_o} \right)^6 \cdot T_{12} + T_6 \\
 \Leftrightarrow 2 \cdot \left(\frac{\sigma}{r_o} \right)^6 \cdot T_{12} &= T_6 \\
 \Leftrightarrow \sigma &= \left(\frac{1}{2} \cdot \frac{T_6}{T_{12}} \right)^{\frac{1}{6}} \cdot r_o \tag{3.10}
 \end{aligned}$$

If only NN enter into the calculation, the already known result given in Eq. 3.8 is again found, namely $\sigma = \left(\frac{1}{2} \right)^{\frac{1}{6}} \cdot r_o$, since T_6 and T_{12} are given by $T_6=T_{12}=12$. If the interaction range includes NN and second NN, the relation between σ and r_o is getting a little bit more complex, since now T_6 and T_{12} are given by $T_6 = 12 + 6 \left(\frac{1}{\sqrt{2}} \right)^6 = 12.75$ and $T_{12} = 12 + 6 \left(\frac{1}{\sqrt{2}} \right)^{12} = 12.094$. Here σ is given by $\sigma = 0.89878 r_o$. For an interaction range including up to the third NN, T_6 and T_{12} are given by $T_6 = 12 + 6 \left(\frac{1}{\sqrt{2}} \right)^6 + 24 \left(\frac{1}{\sqrt{3}} \right)^6 = 13.64$ and $T_{12} = 12 + 6 \left(\frac{1}{\sqrt{2}} \right)^{12} + 24 \left(\frac{1}{\sqrt{3}} \right)^{12} = 12.127$. This yields for σ , $\sigma = 0.9085 r_o$. The above calculus shows that for a given LJ potential and the range of interaction, the correct σ/r_o ratio can easily be calculated. Hence σ is fitted in such a way that the correct 0K lattice parameter of a 3d ideal crystal structure of the selected material, here Cu, is obtained.

To illustrate the anharmonicity of the LJ potential, the 3d LJ potential and an appropriate harmonic potential are plotted in Fig. 3.1. Comparing these two potentials clearly demonstrates that the LJ potential shows a strong anharmonicity which is a basis requirement to be applicable in dynamic atomistic simulations. Actually a LJ type potential seems more

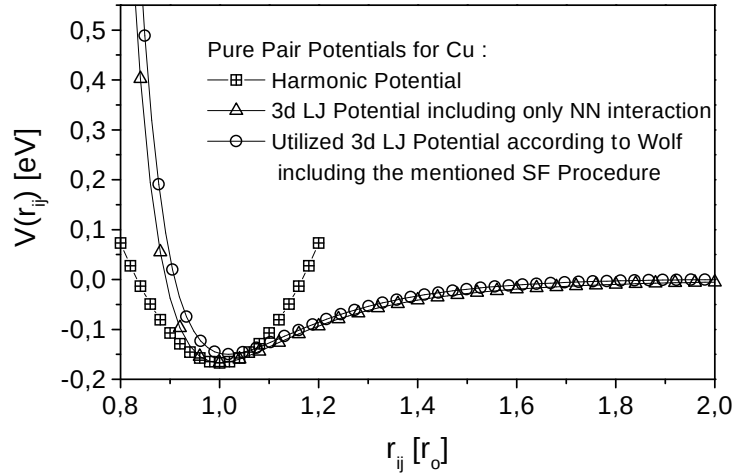


Figure 3.1: Comparison of the 3d LJ potential including only NN interactions, the utilized 3d LJ potential with applied SF procedure at the cut-off radius, $r_C=1.49a_o$, and the harmonic potential for Cu as a function of the interatomic distance, r_{ij} , of two atom i and j given in units of the NN distance, r_o . The anharmonicity of the LJ potential is clearly evident as well as the effect of the correct σ s for a specific interaction sphere of a certain cut-off radius and the application of the SF procedure.

suitable for noble gas materials like Ar since its bonding can be understood from a van der Waals interaction which is really the reason why the attractive (...) term enters into Eq. 3.2. The parameter set for Ar is $\epsilon=1.653 \cdot 10^{-21}$ J = 0.01032 eV and $\sigma=3.405$. Again the 0K lattice parameter can be determined for Ar from the $r_{0,Ar} = 3.822$ value and one finds $a_0 = \sqrt{2} \cdot r_{0,Ar} = 5.405$. Comparing the depth of the Cu and Ar LJ potential one intuitively gets a feeling why the melting temperature of these two materials are so different namely about 85K for Ar and about 1250K for Cu. Physical properties connected to the utilized

	$C_{\alpha\beta}(0K)$ [TPa]	$(\frac{dC_{\alpha\beta}}{dT})_{0K}$ [$\frac{10^{-5}TPa}{K}$]
C_{1111}	0.1815	-10.90
C_{1122}	0.1018	-6.20
C_{4444}	0.1018	-5.65
c_A	0.1239	-6.60

Table 3.1: Temperature dependence of the elastic constants of the 3d LJ Cu potential according to [37].

3d LJ potential obtained by ideal fcc crystal simulations are for instance the temperature dependence of the lattice parameter [36], the temperature dependence of the elastic constants [37] or for instance vacancy properties. Tab. 3.2 lists the temperature dependence of the lattice parameter for the 3d LJ Cu potential as well as for other Cu potentials that are discussed in sect. 3.2.2.1 and 3.2.2.2. For the utilized 3d LJ potential, the temperature dependence of the elastic constants was obtained by Jaszczak [37] for an ideal fcc crystal. The corresponding data is listed in Tab. 3.1. With respect to GB migration due to an elastic driving force it is very important to know the elastic constants since they allow one to

T [K]	LJ 3d a(T) [a ₀]	FS a(T) [a ₀]	EAM a(T) [a ₀]
200	1.00613	1.00485	1.00398
400	1.01243	1.01010	1.00818
600	1.01957	1.01580	1.01272
700	1.02375	1.01900	1.01515
800	1.02850	1.02220	1.01767
900	1.03394	1.02600	1.02034
1000	1.04017	1.03000	1.02311
1100	1.04733	1.03450	1.02605
1200			1.02911
1300			1.03249

Table 3.2: Temperature dependence of the lattice parameter, $a(T)$, for the used 3d LJ [36], the FS according to Sutton and Chen [43] and finally the EAM Cu potential according to Doyama and Kogure [44].

quantify and verify an elastic driving force analytically as is illustrated in detail in sect. 3.4. In this context the elastic anisotropy factor, $c_A = 2C_{4444} - C_{1111} + C_{1122}$, is introduced which equals zero for an elastic isotropic material.

3.2.2 Many Body Potentials for fcc materials

After dealing with simple pair potentials in the preceding paragraph and focussing on the LJ potential in more detail, now the attention is turned to more sophisticated potentials which focus on the importance of incorporating the local environment of each atom into the energy calculation scheme. Bearing in mind the complexity to model interatomic interaction, still the presented interaction potentials remain rather simple although conceptually speaking they are better physically based than simple pair potentials. Although conceptually different from simple pair potentials, this class of potentials remains simple in the sense that their generation and fitting procedures are simple and that the increase in computational resources and most important in the overall computational time only increases by a factor of two with regard to simple pair potentials.

The Finnis-Sinclair potential [38] as well as the embedded-atom method [40] belong to this new class of potentials. Here for each type of potential a Cu potential is presented which has been used within this study. Considered from a conceptual and physical point of view the Finnis-Sinclair (FS) potential and the embedded-atom method (EAM) are rather similar in their underlying physics and their capabilities. It seems almost fair to say that there exists hardly any reason to differentiate between these potentials other than their historic origin.

The main important physical aspect of this class of potentials is that they introduce the local environment of an atom in the energy calculation. Here the general idea is that an atom, i , experiences the electron density of its neighbours at its center of mass position which should act attractive on atom i . The electron density experienced by atom, i , is then used to calculate an attractive energy contribution to atom, i . In order to do so, an embedding function needs to be defined which can be given on different physical grounds. One very often

used approach is by utilizing the Rose relation [39] which couples the change of the cohesive energy of an ideal fcc crystal atom with the change of the lattice parameter. The functional form for expanding or compressing an ideal crystal is well described by the Rose relation and is therefore used to fit the embedding function after calculating the repulsive pair potential contribution and the electron density for atom, i , for a given strain state. According to this the embedding functions are usually fitted by some form of spline fit functions to the computed data which makes them easily accessible within atomistic simulations. There is a large number of papers dedicated to many body potentials for very different materials. Among these papers there is a second class of approaches that express the embedding function by an analytic expression. When utilizing analytic embedding functions, these are usually physically based on results of density functional theory or ab-initio calculations [35].

Within the last ten years new schemes have evolved to link the results obtained from ab-initio calculations to generation procedures to construct many-body potentials. Such many-body potentials will then be physically based on ab-initio results of atomistic model systems. One scheme presented by Ercolessi [41] is the force-matching method that utilizes such a concept. Such schemes are interesting from the point of view that due to these attempts, simple many-body potentials will be available that are physically well grounded and furthermore not too demanding concerning their computational resources.

3.2.2.1 Long-Range Finnis-Sinclair Potential

In this section, the basics of the Finnis-Sinclair potential [38] are illustrated and the specific case of the long-range Finnis-Sinclair potential according to Sutton and Chen [43] is discussed. For this type of Finnis-Sinclair potential, the cohesive energy U_{coh} reads

$$\begin{aligned}
 U_{coh}(\{r_{ij}\}) &= \frac{\epsilon}{2} \cdot \sum_{i=1}^N \sum_{j=1}^N \left(\frac{a_f}{r_{ij}} \right)^n - c \cdot \epsilon \cdot \sum_{i=1}^N \overbrace{\sqrt{\sum_{j=1}^N \left(\frac{a_f}{r_{ij}} \right)^m}}^{=\sqrt{\rho_i}} \\
 &= \frac{\epsilon}{2} \cdot \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}) - c \cdot \epsilon \cdot \sum_{i=1}^N \sqrt{\sum_{j=1}^N \rho(r_{ij})} = \sum_{i=1}^N e_{coh,i} \quad (3.11)
 \end{aligned}$$

where $i \neq j$ is assumed and a_f is the lattice parameter. In case of an ideal crystal at zero Kelvin, the cohesive energy is given by $U_{coh}(\{r_{ij}\}) = \sum_{i=1}^N e_{coh,i} = N \cdot e_{coh}$ with $e_{coh,i} = e_{coh}$.

ϵ , c , n and m are fit parameters for this potential and are determined from ideal crystal simulations at zero Kelvin temperature. For a given fcc material they are adjusted and fitted to the experimental values of the cohesive energy and the bulk modulus of the material. Furthermore the lattice parameter a_f is set to the experimental one as well. For numerous fcc materials these fit parameters are listed in the original paper although in the original paper no shifted-force procedure was applied. Applying a shifted-force procedure to $V(r_{ij})$ and $\rho(r_{ij})$ the fit equations for ϵ , c , n and m need to be recalculated and the used fitting procedure applied in this work was performed as follows :

- i) Choose n and m according to Sutton and Chen for a given material where $n > m$.

ii) Calculate c according to

$$c = \frac{n}{m} \cdot \sqrt{\rho_i^{SF}} \cdot \frac{\sum_{j \neq i}^N V(r_{ij}) - \frac{r_{ij}}{r_c} \cdot V(r_c)}{\sum_{j \neq i}^N \rho(r_{ij}) - \frac{r_{ij}}{r_c} \cdot \rho(r_c)} \quad (3.12)$$

iii) Insert c and e_{coh} in eq. 3.13 and calculate ϵ

$$\begin{aligned} e_{coh} &= \frac{\epsilon}{2} \cdot \sum_{j \neq i}^N V^{SF}(r_{ij}) - c \cdot \epsilon \cdot \sqrt{\sum_{j \neq i}^N \rho^{SF}(r_{ij})} \\ e_{coh} &= \epsilon \cdot \left(\frac{1}{2} \cdot \sum_{j \neq i}^N V^{SF}(r_{ij}) - c \cdot \sqrt{\rho_i^{SF}} \right) \\ \Leftrightarrow \quad \epsilon &= \frac{e_{coh}}{\frac{1}{2} \cdot \sum_{j \neq i}^N V^{SF}(r_{ij}) - c \cdot \sqrt{\rho_i^{SF}}} \end{aligned} \quad (3.13)$$

That Eq. 3.12 is indeed the valid equation to calculate c can be seen from the fact that when cancelling the terms introduced by the shifted-force procedure, the original equation by Sutton and Chen to calculate c is obtained. The terms, ρ_i^{SF} and $V^{SF}(r_{ij})$, are appropriate shifted-force terms according to the generic equation, Eq. 3.3, introducing the shifted-force procedure used in this work. For ρ_i^{SF} please note that the summation over all neighbouring atoms of atom, i , needs to be included in the correct shifted force expression of ρ_i^{SF} .

In this study, the model fcc material is Cu. The required fit parameters for the Cu FS potential without and with a shifted-force procedure are listed in Tab. 3.3 and 3.4, respectively. Here it is worth mentioning that for both procedures, the cut-off radius determines the magnitudes of the fit parameters since it intrinsically enters into the sums needed to evaluate the fit parameters. The fit parameters for Cu according to the original paper by Sutton and Chen are

m	n	ϵ [eV]	c
6	9	$1.2382 \cdot 10^{-2}$	39.432

Table 3.3: Fit parameters of the Cu FS-potential according to Sutton and Chen [43] without shifted-force procedure.

Applying a shifted-force procedure with a cut-off radius of $r_C=1.49a_o$, according to Eq. 3.12 and 3.13 the four potential fit parameters for a Cu material are assuming a cohesive energy of $e_{coh}=-3.50$ [eV/atom] as given in Tab. 3.4. Physical properties connected to this Cu FS-

m	n	ϵ [eV]	c
6	9	$1.40314 \cdot 10^{-2}$	39.1043

Table 3.4: Fit parameters of the Cu FS-potential with shifted-force procedure.

potential obtained by ideal crystal simulations are for instance the temperature dependence of the lattice parameter as listed in Tab. 3.2.

3.2.2.2 Embedded-Atom-Method Potential

In 1999 a paper by Doyama and Kogure [44] was published on embedded-atom potentials in fcc and bcc metals. Data sets for some specific materials were published which included a parameter set for Cu as well. Since the FS potential by Sutton and Chen was only fitted to four different physical parameters and even more since it was constructed rather closely to the LJ potential form, it seemed rather interesting to utilize the EAM Cu potential by Doyama and Kogure too. Our strong interest in utilizing the EAM potential was based on the circumstance that it seems physically well grounded even in respect to the FS potential by Sutton and Chen and even more in respect to the LJ potential. The number of physical parameters used to fit the EAM potential were a few more than for the FS potential, namely these were the cohesive energy, Born stability, elastic constants C_{11} , C_{12} and C_{44} , the formation energy of a vacancy, E_{vac}^F , and in case of fcc materials the stacking fault energy, E_{STF} , as well. Since for tilt GBs, 3d periodic boundary conditions can be rather restrictive, the main interest of application for this specific EAM potential had been to investigate in more detail GB systems having free surfaces.

The specific form of the potential is as follows. The total energy, E , of an atomistic system consisting of N atoms reads

$$E = \sum_{i=1}^N E_i = \sum_{i=1}^N \sum_{j=1}^N \frac{1}{2} \Phi(r_{ij}) + \sum_{i=1}^N F(\rho_i) = \sum_{i=1}^N \sum_{j=1}^N \frac{1}{2} \Phi(r_{ij}) + \sum_{i=1}^N D \cdot \rho_i \cdot \ln(\rho_i) \quad (3.14)$$

where $\rho_i = \sum_{j=1}^N f(r_{ij})$ mimics the electron density seen by atom i and $F(\rho_i)$ is the embedding function for ρ_i . Here $\sum_{j=1}^N$ represents the sum over all j neighbours of atom i for a certain interaction range. The embedding function is given analytically which facilitates its implementation. It should be mentioned here that some authors utilize the Rose relation to determine the embedding function. Such an approach usually requires that the embedding function is then fitted by some form of spline functions since an exact analytical description fails here. Finally $\Phi(r_{ij})$ and $f(r_{ij})$ need to be specified and these read

$$\Phi(r_{ij}) = A_1 \cdot (r_{C1} - r_{ij})^2 \cdot \exp(-C_1 \cdot r_{ij}) \quad (3.15)$$

$$f(r_{ij}) = A_2 \cdot (r_{C2} - r_{ij})^2 \cdot \exp(-C_2 \cdot r_{ij}) \quad (3.16)$$

where r_{C1} and r_{C2} are cut-off radii to allow for a smooth truncation of these functions. The exact values of r_{C1} and r_{C2} are $1.65 \cdot r_{NN}$ and $1.95 \cdot r_{NN}$, respectively, where r_{NN} is the nearest-neighbour distance.

At this point it should be mentioned that in the original paper Doyama and Kogure used the nearest-neighbour distance as their basic length scale. Since within this work the fcc lattice parameter is used as the basic length scale, it implies that the published data by Doyama and Kogure that have dimension of length have to be multiplied by a factor $\frac{1}{\sqrt{2}}$ to be converted to the length scale used in our simulations. Finally the fit parameters of this Cu EAM potential are listed in Tab. 3.5 with respect to the length scale used by Doyama and Kogure.

The physical properties obtained by fitting of the potential as well as the reference experimental data are listed in Tab. 3.6. They are characteristic properties of the potential and therefore of essential importance.²

²The listed experimental elastic constants agree exactly with the data given by Reid in "Deformation

$A_1 \left[\frac{eV}{r_{NN}^2} \right]$	8269.4599770489921
$A_2 \left[\frac{1}{r_{NN}^2} \right]$	0.01832510350693439
$C_1 \left[\frac{1}{r_{NN}} \right]$	10.7272912864108215
$C_2 \left[\frac{1}{r_{NN}} \right]$	0.319759369823463370
$D [eV]$	13.0792125162800630

Table 3.5: Fit parameter of the Cu EAM Potential according to Doyama and Kogure.

	$C_{11}[TPa]$	$C_{12}[TPa]$	$C_{44}[TPa]$	$E_{vac}^F[eV]$	$E_{coh}[eV]$	$E_{STF}[J/m^2]$
computed	0.18062	0.12009	0.07103	1.303	3.54	0.00876778
experiment	0.1684	0.1214	0.0754	1.30	3.54	

Table 3.6: Physical properties of the Cu EAM potential by Doyama and Kogure.

3.2.3 Summary

How can the differences and capabilities of these three different atomistic potentials in the framework of GBs and GB migration be assessed ? Concerning the zero Kelvin GB properties like the GB energy and the GB volume expansion, Wolf [47] conducted extensive atomistic simulations which demonstrated clearly that the basic physical parameters and behaviour of twist as well as tilt GBs are well represented by simple pair potentials as well as by more sophisticated many body potentials. According to Sutton and Balluffi [35] as well as Wolf [48], the weakness of simple pair potentials comes into play when the local environment of an atom deviates strongly from the ideal crystal situation. This is especially true for free surfaces. GBs where the number of broken bonds is small and which resemble to some extent almost the ideal crystal situation should have similar GB properties if studied by simple pair potentials or many body potentials. This is especially true for symmetrical tilt GBs. Concluding this thought it seems that the three mentioned potentials should yield similar GB properties even when focussing on GB migration and GB self-diffusion.

Since this work is unique concerning the application of new driving force concepts to study GB migration of either planar twist and tilt GBs, the main emphasis of this work is to establish new simulation schemes and to yield first data on GB migration regardless whether the interatomic potentials describes the model material in every physical aspect.

One simple example to assess the different behaviour of the three potentials is to compare the temperature dependence of the lattice parameter of an ideal crystal system for the

Geometry For Materials Scientists" on pages 68 to 69 as well as by Leibfried [46] on page 128. The Reid and Leibfried data refer to 300K while the computed to 0K. In the Doyama paper, the elastic constants are given in units of 10^{12} dyne/cm² with 1dyne/cm²=0.1Pa.

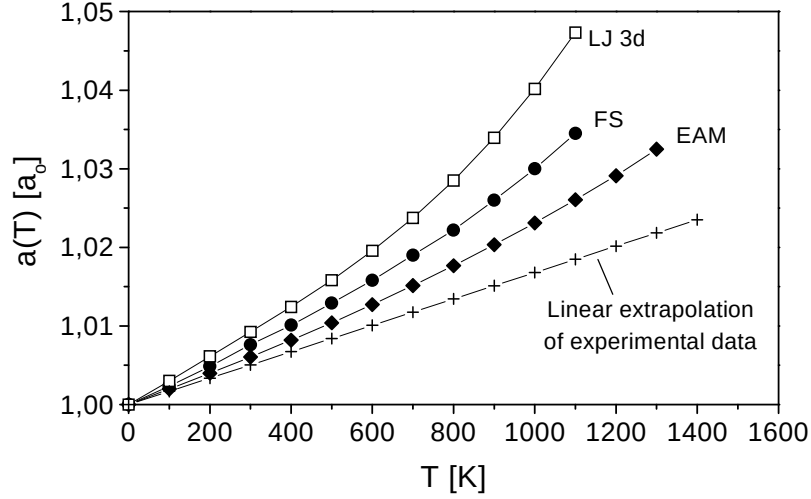


Figure 3.2: Temperature dependence of the lattice parameter of Cu for the LJ, the FS and the EAM potentials (The exact data is listed in Tab. 3.2).

three potentials. It is found from such simulations that the EAM potential comes closest to the experimental determined data (see Fig. 3.2). With respect to the shown experimental data, the reader should note that the strictly linear dependence of the shown experimental data is extrapolated from the linear thermal expansion coefficient given at about room temperature. For higher temperatures a non-linear behaviour even of the experimental data should exist. Still this simple comparison already demonstrates that all potentials show thermal expansion of the system but that the simple pairwise LJ potential overestimates the expansion the most. This demonstration underlines the above-given statement that all three potentials are suitable to study an atomistic ideal crystal or GB system but that of course details of the behaviour of the system can be different. This is as well true for activation parameters like for instance mono-vacancy properties which are discussed in detail for the LJ and EAM potential in section 4.2 and 4.1, respectively. The same applies for GB activation parameters. Still any of the discussed potentials can yield information on GB activation parameters that can be understood and reasoned within the limits of each potential and especially by comparing different activation processes for that potential.

3.3 Molecular-Dynamics Method

In this work molecular-dynamics (MD) simulations are used to study the atomic-level behaviour of GBs at finite temperatures. The method itself is nowadays well established in the field of atomistic simulations. As early as in the late 1950s [50] and early 1960s first MD simulations were performed and the basis of this method was established [1]. During the following decades, refinements of the MD method by introducing finite temperature thermostats [52, 53, 55, 54], progress in deriving sophisticated interatomic potentials [38, 40, 41] and extending the MD method by introducing the simulation box vectors as variables [56, 57] steadily increased the potential of the method.

The MD method itself is not exclusively restricted to atomistic systems. It can be utilized in different fields of application [51]. The only basic requirement is that the interaction between interacting objects can be described by a potential function. The covered range of length scale extends from microscopic systems where different atomistic phenomena are studied up to the cosmic length scale where i.e. the orbits of planets or the interaction between asteroids and space objects are modelled [51].

3.3.1 Classical Molecular Dynamics

The classical MD method originates from classical mechanics and utilizes concepts of classical mechanics. The aim of this method is to describe deterministically the time evolution of a particle system consisting of either N atoms or molecules. Since in classical mechanics a particle system can be described by a Lagrangian or Hamiltonian, for a studied atomistic system an equivalent approach can be utilized. Considering the simplest case of an interatomic interaction that purely depends only on the distance r_{ij} between two atoms, i and j , and not on their orientation nor the local environment, the Lagrangian, L , reads

$$L(\{\mathbf{r}_i\}, \{\dot{\mathbf{r}}_i\}) = K(\{\dot{\mathbf{r}}_i\}) - V(\{\mathbf{r}_i\}) = \sum_{i=1}^N \frac{m_i}{2} \dot{\mathbf{r}}_i^T \cdot \dot{\mathbf{r}}_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}), \quad (3.17)$$

where $K(\{\dot{\mathbf{r}}_i\})$ represents the overall kinetic energy and $V(\{\mathbf{r}_i\})$ the overall potential energy of the system. At this point it should be noted that throughout this work the transpose of a quantity A is labelled by A^T where A will either be a tensor of first or second rank or a (3×3) matrix. The equations of motion of each atom, i , are then derived by utilizing the Lagrangian equation of motion which finally yields

$$m_i \cdot \frac{d^2 \mathbf{r}_i}{dt^2} = - \sum_{j=1}^N \frac{dV(r_{ij})}{d\mathbf{r}_i} = - \sum_{j \neq i}^N \frac{1}{r_{ij}} \cdot \frac{dV(r_{ij})}{dr_{ij}} \cdot \mathbf{r}_{ij}, \quad (3.18)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $r_{ij} = |\mathbf{r}_{ij}|$. In this case the Hamiltonian, $H(\{\mathbf{r}_i\}, \{\mathbf{p}_i = m_i \cdot \dot{\mathbf{r}}_i\})$, reads

$$H(\{\mathbf{r}_i\}, \{\mathbf{p}_i\}) = E = \sum_{i=1}^N \frac{1}{2m_i} \mathbf{p}_i^T \cdot \mathbf{p}_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}), \quad (3.19)$$

which represents the total energy of the system and is conserved during motion. Time integration of Eq. 3.18 gives the time evolution or the trajectories of each particle, i , under

the constraints that $E=\text{const}$, $V=\text{const}$ and $N=\text{const}$. Due to these chosen constraints, such an atomistic system would be studied in the microcanonical ensemble [1].

For most MD simulations it is desired to set the macroscopic temperature, T , constant. Then the constraints are $T=\text{const}$, $V=\text{const}$ and $N=\text{const}$ which represents the canonical ensemble. Then Eq. 3.18 as well as the Lagrangian need to be altered. How finite temperature simulations can be performed and were performed in this work is discussed in more detail in sect. 3.3.5.

3.3.2 Parrinello-Rahman Method

The simulation code used within this work is based on the Parrinello-Rahman scheme [57], which allows the simulation box to vary in shape and size. This feature is rather important when dealing with GBs due to the 2d nature of the defect. For instance it is well known that GBs do have an excess volume [69, 47] which can only be modelled correctly if the box dimensions are allowed to adjust to internal and/or external stresses. In this particular case the dimension parallel to the GB normal is allowed to expand or contract according to the internal stress whereas the in-plane dimensions within the GB plane are kept fixed. This is done since it is assumed that the in-plane dimensions are determined by the bulk properties far away from the GB region.

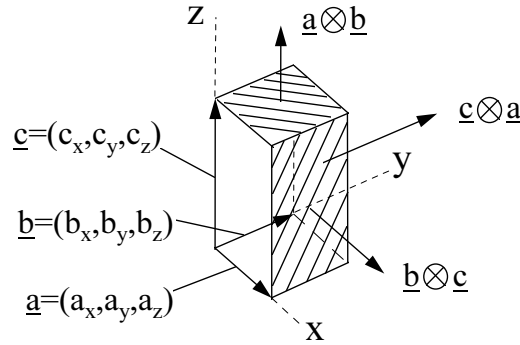


Figure 3.3: Simulation box notation according to Parrinello-Rahman scheme: The vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$ span the edges of the simulation box and its orientation is described by the vectors $\underline{b} \otimes \underline{c}$, $\underline{c} \otimes \underline{a}$ and $\underline{a} \otimes \underline{b}$. It should be noted here that these vectors do not necessarily need to be parallel to the (x,y,z) coordinate system.

Andersen [56] introduced the first concept of this kind for the hydrostatic situation of a cubic simulation box of length L . This idea of having a variable simulation box was then extended by Parrinello and Rahman [57] to the general case of a fully adjustable simulation box. Throughout this work, the matrix convention introduced by Parrinello-Rahman is used, namely that the simulation box is described by a matrix $\underline{\underline{h}}$ where its columns are given by the simulation box vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$, hence $\underline{\underline{h}}$ reads $\underline{\underline{h}}=(\underline{a},\underline{b},\underline{c})$. A schematic of a simulation box is shown in Fig. 3.3. The Parrinello-Rahman scheme now adds nine new degrees of freedom associated with the simulation box vector components to the already $3N$ degrees of freedom of a N atom atomistic system. The prime task now is to derive a new set of equations of motion for each atom and the simulation box matrix $\underline{\underline{h}}$. To do so, the

scaling of the real space coordinates of each atom by the simulation box matrix, $\underline{h}$, needs to be introduced into the Lagrangian which is expressed by $\mathbf{r}_i = \underline{h} \cdot \mathbf{s}_i$ or $\mathbf{s}_i = \underline{h}^{-1} \cdot \mathbf{r}_i$, where $\mathbf{r}_i$ and $\mathbf{s}_i$ are the coordinates in real and reduced space, respectively. The new Lagrangian is then given by

$$\begin{aligned} L & (\{\mathbf{s}_i\}, \{\dot{\mathbf{s}}_i\}, \{\underline{h}\}, \{\dot{\underline{h}}\}) \\ &= K(\{\dot{\mathbf{s}}_i\}, \{\underline{h}\}) - V(\{\mathbf{s}_i\}, \{\underline{h}\}) + K_{box}(\{\dot{\underline{h}}\}) - V_{elastic}(\{\underline{h}\}) \\ &= \sum_{i=1}^N \frac{m_i}{2} \dot{\mathbf{s}}_i^T \cdot \underline{G} \cdot \dot{\mathbf{s}}_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}) + \frac{1}{2} W \cdot TR(\dot{\underline{h}}^T \cdot \dot{\underline{h}}) - V_{elastic}(\{\underline{h}\}) \quad (3.20) \end{aligned}$$

where W is constant and has the dimension of mass and TR stands for the trace of a (3×3) matrix or second-rank tensor. Furthermore $\underline{G}$ equals $\underline{G} = \underline{h}^T \cdot \underline{h}$ and in the derivation of Eq. 3.20 it was assumed that $\dot{\mathbf{r}}_i$ can be approximated by $\dot{\mathbf{r}}_i = \dot{\underline{h}} \cdot \mathbf{s}_i + \underline{h} \cdot \dot{\mathbf{s}}_i \approx \underline{h} \cdot \dot{\mathbf{s}}_i$.

In the original paper by Parrinello and Rahman, two cases were distinguished to derive the appropriate elastic energy term $V_{elastic}(\{\underline{h}\})$ entering into Eq. 3.20. One was the hydrostatic stress state while the second one was based on applying a general stress state, $\underline{\sigma}$, to the simulation box. In the following presentation only the situation for the general stress state is mentioned and discussed, since it includes the hydrostatic situation as well. For a general stress state, $V_{elastic}(\{\underline{h}\})$ reads

$$V_{elastic}(\{\underline{h}\}) = p \cdot (\Omega - \Omega_0) + \Omega_0 \cdot TR((\underline{\sigma} - p \cdot \underline{1}) \underline{\epsilon}) \quad (3.21)$$

with Ω being the volume of the simulation box.

Next the derivation of the equations of motion for each atom in reduced space follows. These equations do not depend on the specific form of $V_{elastic}(\{\underline{h}\})$ or the kinetic energy of the box $K_{box}(\{\dot{\underline{h}}\})$, because the reduced coordinates $\mathbf{s}_i$ do not appear in these terms as can be seen from Eq. 3.20 and 3.21. Utilizing the Lagrangian equation of motion for the coordinates $s_{i,x}$, $s_{i,y}$ and $s_{i,z}$ yields

$$m_i \cdot \frac{d^2 \mathbf{s}_i}{dt^2} = m_i \cdot \ddot{\mathbf{s}}_i = - \sum_{j \neq i}^N \frac{1}{r_{ij}} \cdot \frac{dV(r_{ij})}{dr_{ij}} \cdot \mathbf{s}_{ij} - m_i \cdot \underline{G}^{-1} \cdot \dot{\underline{G}} \cdot \dot{\mathbf{s}}_i \quad (3.22)$$

The next step is to derive the equations of motion for the simulation box represented by the matrix, $\underline{h}$. In order to perform the standard calculus, first the strain tensor, $\underline{\epsilon}$, showing up in Eq. 3.21 needs to be expressed by the components of the simulation box vectors. In a linear approximation, the strain tensor, $\underline{\epsilon}$, is given by

$$\underline{\epsilon} = \frac{1}{2} \cdot \left(\left(\underline{h} \underline{h}_0^{-1} - \underline{1} \right) + \left(\underline{h} \underline{h}_0^{-1} - \underline{1} \right)^T \right) \quad (3.23)$$

and the rotation tensor, $\underline{\omega}$, by

$$\underline{\omega} = \frac{1}{2} \cdot \left(\left(\underline{h} \underline{h}_0^{-1} - \underline{1} \right) - \left(\underline{h} \underline{h}_0^{-1} - \underline{1} \right)^T \right). \quad (3.24)$$

Eq. 3.23 and 3.24 can be derived following the analysis given by Parrinello and Rahman performing the following calculus. Here it is assumed that the atomistic system deforms

homogeneously meaning that the displacement, $\mathbf{u}_j$, of an atom, j , is solely given by the deformation of the simulation box $\underline{h}$ changing from state $\underline{h}_0$ to $\underline{h}$ according to the stress state balance between an external and internal stress state. At this point a more detailed introduction to these equations seems reasonable to illustrate to the reader in more detail the background of the final equations of motion of the simulation box. The displacement, $\mathbf{u}^j$, of an atom, j , is given by

$$\begin{aligned}\mathbf{u}^j &= \mathbf{r}^j - \mathbf{r}_0^j = \underline{h} \cdot \mathbf{s}_0^j - \underline{h}_0 \cdot \mathbf{s}_0^j = \left(\underline{h} \cdot \underline{h}_0^{-1} - \underline{1} \right) \cdot \mathbf{r}_0^j \\ &= \left(\underline{h} \cdot \underline{h}_0^{-1} - \underline{1} \right) \cdot \begin{pmatrix} x_{0,1}^j \\ x_{0,2}^j \\ x_{0,3}^j \end{pmatrix} = \begin{pmatrix} u_1^j \\ u_2^j \\ u_3^j \end{pmatrix}\end{aligned}\quad (3.25)$$

Utilizing the displacement vector given by Eq. 3.25 and applying the standard linear definition to calculate the strain tensor components, $\epsilon_{\mu,\nu}$, and the rotation tensor components, $\omega_{\mu,\nu}$, as given by Eq. 3.27 and 3.27, respectively, finally leads to Eq. 3.23 and 3.24.

$$\epsilon_{\mu,\nu} = \frac{1}{2} \left(\frac{\partial u_\mu^j}{\partial x_{0,\nu}^j} + \frac{\partial u_\nu^j}{\partial x_{0,\mu}^j} \right) \quad (3.26)$$

$$\omega_{\mu,\nu} = \frac{1}{2} \left(\frac{\partial u_\mu^j}{\partial x_{0,\nu}^j} - \frac{\partial u_\nu^j}{\partial x_{0,\mu}^j} \right) \quad (3.27)$$

Finally the equations of motion of the simulation box given by Eq. 3.29 have been derived under the assumption that the strain tensor, $\underline{\epsilon}$, is given by a non-linear expression as shown in Eq. 3.28.

$$\underline{\epsilon} = \frac{1}{2} \cdot \left(\underline{h}_0^{T-1} \cdot \underline{G} \cdot \underline{h}_0^{-1} - \underline{1} \right) \quad (3.28)$$

$$\begin{aligned}W\ddot{\underline{h}} &= (\underline{P} - p \cdot \underline{1}) \cdot \underline{h}^{T-1} \Omega - \underline{h} \cdot \underline{\Sigma} \\ &= \underline{h} \cdot \underline{h}^{-1} \cdot (\underline{P} - p \cdot \underline{1}) \cdot \underline{h}^{T-1} \Omega - \underline{h} \cdot \underline{\Sigma} = \underline{h} \cdot \underbrace{\underline{DP}}_{\text{symmetric}}\end{aligned}\quad (3.29)$$

During a MD simulation with an adjustable simulation box, the time evolution of Eq. 3.29 will be numerically integrated and the time evolution of $\underline{h}$ and $\underline{\epsilon}$ can therefore be calculated. Since $\underline{h}$ and $\underline{\epsilon}$ are known, it is possible to check for consistency with respect to the temporal evolution of the matrix $\underline{h}$ by performing the following analysis

$$\underline{h} = \underline{h}_0 + \underline{u} = \underline{h}_0 + \left(\underline{h} \cdot \underline{h}_0^{-1} - \underline{1} \right) \underline{h}_0, \quad (3.30)$$

$$\underline{h} = \underline{h}_0 + \underline{\epsilon} \cdot \underline{h}_0 + \underline{\omega} \cdot \underline{h}_0, \quad (3.31)$$

where $\underline{u}$ is the displacement matrix that can be obtained in this summarized form from the displacement vectors as given by Parrinello and Rahman and $\underline{\omega}$ is the rotation tensor. It is worth mentioning at this point that these equations explicitly contain a rotation $\underline{\omega}$ and only under the assumption that such rigid body rotations are not present in the system the total displacement field is calculated solely by applying the strain tensor to the reference state $\underline{h}_0$.

The incorporation of the simulation box vectors as dynamical quantities of the system is far from being trivial. Hence in a detailed follow-up paper [58], Ray and Rahman once again discussed the issue of incorporation the simulation box vectors into the dynamical scheme of the MD method. Their basic ideas are as follows. The Hamiltonian, H , of an unstressed system as a function of the conventional real space coordinates, $\mathbf{r}_i$, and momenta, $\mathbf{p}_i$, reads

$$H(\{\mathbf{r}_i\},\{\mathbf{p}_i\}) = \sum_{i=1}^N \frac{1}{2m_i} \mathbf{p}_i^T \cdot \mathbf{p}_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}) \quad (3.32)$$

where $\mathbf{p}_i = m_i \frac{d}{dt} \mathbf{r}_i$. Scaling the real space coordinates by the simulation box matrix $\underline{h}$ then gives $\mathbf{r}_i = \underline{h} \cdot \mathbf{s}_i$ or $\mathbf{s}_i = \underline{h}^{-1} \cdot \mathbf{r}_i$, where $\mathbf{r}_i$ and $\mathbf{s}_i$ are the coordinates in real and reduced space, respectively. Since the momentum $\mathbf{p}_i$ is affected by this tranformation as well one needs to identify the new momentum that gives a canonical transformation. Utilizing the Lagrangian concept one can calculate the new momentum $\boldsymbol{\pi}_i$ by $\boldsymbol{\pi}_i = \frac{\delta L}{\delta \dot{\mathbf{s}}_i} = \underline{h}^T \mathbf{p}_i$. Since this transformation should be canonical, a new function, K , exists that is the new Hamiltonian and which should be a conserved quantity. K is a function of the new general coordinates $\mathbf{s}_i, \boldsymbol{\pi}_i$ and $\underline{h}$ and can be calculated from conventional canonical transformation theory as for instance is discussed by Goldstein [59]. One finds

$$\begin{aligned} K(\{\mathbf{s}_i\},\{\boldsymbol{\pi}_i\},\{h\}) &= H(\{\mathbf{r}_i\},\{\mathbf{p}_i\}) - \sum_{i=1}^N \mathbf{p}_i^T \underline{h} \mathbf{s}_i \\ &= H(\{\mathbf{s}_i\},\{\boldsymbol{\pi}_i\},h) - \sum_{i=1}^N \boldsymbol{\pi}_i^T \underline{h}^{-1} \underline{h} \mathbf{s}_i \\ K &= \sum_{i=1}^N \frac{1}{2m_i} \boldsymbol{\pi}_i^T \underline{G}^{-1} \boldsymbol{\pi}_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(\{\mathbf{s}_{ij}\},\underline{h}) - \sum_{i=1}^N \boldsymbol{\pi}_i^T \underline{h}^{-1} \dot{\underline{h}} \mathbf{s}_i \end{aligned} \quad (3.33)$$

The next step is then to calculate the new equations of motion of each atom by standard Hamiltonian theory, namely by calculating

$$\dot{\boldsymbol{\pi}}_i = - \frac{dK(\{\mathbf{s}_i\},\{\boldsymbol{\pi}_i\},\{h\})}{d\mathbf{s}_i} = \frac{d\underline{h}^T \mathbf{p}_i}{dt} = \dot{\underline{h}}^T \mathbf{p}_i + \underline{h}^T \dot{\mathbf{p}}_i \quad (3.34)$$

This finally leads to new equations of motion for each atom, i.

$$m_i \cdot \ddot{\mathbf{s}}_i = - \sum_{j \neq i}^N \frac{1}{r_{ij}} \cdot \frac{dV(r_{ij})}{dr_{ij}} \cdot \mathbf{s}_{ij} - m_i \cdot \underline{h}^{-1} \cdot \ddot{\underline{h}} \cdot \mathbf{s}_i - 2 \cdot m_i \cdot \underline{h}^{-1} \cdot \dot{\underline{h}} \cdot \dot{\mathbf{s}}_i \quad (3.35)$$

Comparing Eq. 3.22 and 3.35, a slight difference is observed. This difference arises from the fact that in the second calculation scheme, the term $\dot{\underline{h}} \cdot \mathbf{s}_i$ was not dropped from the equation $\dot{\mathbf{r}}_i = \dot{\underline{h}} \cdot \mathbf{s}_i + \underline{h} \cdot \dot{\mathbf{s}}_i$ as was done during the original calculation scheme of Parrinello and Rahman [58].

Concerning the equations of motion of the simulation box vectors, Ray and Rahman [58] suggest to use the thermodynamic tension, $\underline{t}$, rather than the externally applied stress tensor, $\underline{\sigma}$. Due to this, some minor changes enter into the equations of motion of the simulation box vectors, still the generic form remains the same as given in Eq. 3.29. It is as well mentioned

by Ray and Rahman [58] that the system is so insensitive concerning what equations of motion for $\underline{h}$ is used with respect to conserving properties of the system that it is difficult to tell right from wrong. For instance even when explicit errors are introduced while solving Eq. 3.29 numerically the enthalpy and the momentum remain conserved quantities. This illustrates that more attention needs to be addressed to the physical behaviour of the system rather than the mathematical procedures. Furthermore it is stated by Ray and Rahman [58] that it somehow does not even matter what detailed form Eq. 3.29 has as long as it does not violate a general form given in their paper. Our simulation experience and results support this conclusion as well.

Finally in this work, the equations of motion in reduced space of an atom, i , were integrated according to Eq. 3.22 and the equations of motion of the components of the simulation box vectors according to Eq. 3.29. Hence the original results of Parrinello and Rahman were utilized.

3.3.3 Time Integration Schemes

The main goal when performing MD simulations is to determine the temporal evolution of a many particle system in phase space and to determine structural and thermodynamic properties of the system. This can be achieved by time integration schemes based on finite difference approaches to integrate the equations of motion of the particle system for instance according to Eq. 3.18 or 3.22. Several schemes to integrate the equations of motion do exist and only briefly some general features of those shall be mentioned here. Usually these schemes are derived from Taylor series expansions for the position, velocity, acceleration and higher time derivatives of each atom at times $t+\delta t$ or $t+\delta t$ and $t-\delta t$. Here δt is the time step used to integrate the equations of motion. Even by using simple algebra one is able to rewrite the basic Taylor expansions in such a way that for instance for the later case one is able to derive the Verlet time integration scheme [1] which reads for an atom i as follows

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \frac{d\mathbf{r}_i(t)}{dt} \cdot \delta t + \frac{d^2\mathbf{r}_i(t)}{dt^2} \frac{\delta t^2}{2} + \dots \quad (3.36)$$

$$\mathbf{r}_i(t - \delta t) = \mathbf{r}_i(t) - \frac{d\mathbf{r}_i(t)}{dt} \cdot \delta t + \frac{d^2\mathbf{r}_i(t)}{dt^2} \frac{\delta t^2}{2} \pm \dots \quad (3.37)$$

A second equation for the position of atom i , $\mathbf{r}_i(t + \delta t)$, is found when adding Eq. 3.36 and 3.37 and considering each of the Taylor expansions up to third order terms. This equation does not explicitly depend on the velocity of atom i , $\frac{d\mathbf{r}_i(t)}{dt}$, at time t and reads

$$\Rightarrow \mathbf{r}_i(t + \delta t) = 2 \cdot \mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t) + \frac{d^2\mathbf{r}_i(t)}{dt^2} \cdot \delta t^2 . \quad (3.38)$$

Eq. 3.38 can now be utilized to study the temporal evolution of the real space positions of each atom. Real space positions and velocity information of an ensemble of atoms are the most basic quantities determined and needed within MD simulations since they feed the Taylor expansions³ and since they determine the system's state in phase space. The

³According to the presented Verlet algorithm, information on the velocity of each atom is not needed to determine the temporal evolution of the position of each atom. This is only true for equations of motion according to classical MD since here the velocity does not explicitly contribute to the term $\frac{d^2\mathbf{r}_i(t)}{dt^2}$ within

velocity of atom, i , at time t , $\frac{d\mathbf{r}_i(t)}{dt}$, is found when subtracting Eq. 3.36 from 3.37 and the final result equals the slope of a linear interpolation of the positions of atom, i , at times $t+\delta t$ and $t-\delta t$ and hence reads

$$\frac{d\mathbf{r}_i(t)}{dt} = \frac{\mathbf{r}_i(t + \delta t) - \mathbf{r}_i(t - \delta t)}{2 \cdot \delta t} . \quad (3.39)$$

There exist more sophisticated adapted Verlet algorithms to integrate the equations of motion but already the simple Verlet algorithm demonstrates the key elements of these kinds of integration schemes.

A different class of integration schemes only uses the t information of the atoms's position, velocity and higher time derivatives to predict the $t+\delta t$ situation according to extended Taylor series expansions. The predicted $t+\delta t$ results of the atoms's position, velocity and higher time derivatives are then refined by a corrector procedure. This class of integration schemes is called predictor-corrector scheme. A standard scheme is the Gear-predictor-corrector algorithm [1] which can be used in different forms with respect to the order of time derivatives used. In this work a fifth order Gear-predictor-corrector algorithm was used to integrate the equations of motion of each atom and if necessary of the MD simulation box too. A detailed discussion of the Gear-predictor-corrector algorithm is not given here since most textbooks on MD simulations deal in detail with the issue of integration scheme as i.e. the textbook by Allen and Tildesley [1] does.

For an atomistic system how does one define the unit of the time step and what is a typical time step to be used ? Basically one obtains the answer by analysing the Taylor series expansion and by reasoning of the various units used for instance for the energy scale, length scale or the atomic mass. For instance the x component of force, F_x , has the SI unit $[F_x] = N = \frac{J}{m}$. The units of J and m are not the natural units when dealing with atomic-level systems. These are rather the units eV and a_0 . Hence for the unit of the x component of force one gets $[F_x] = \frac{eV}{a_0}$. If one now considers the contribution of a force, $F_x(t)$, exerting on atom i to the position x at time $t+\delta t$ within a Taylor series expansion, one is able to write down an equation of all the entering units which finally defines the unit of the simulation time step, dt . One yields

$$\begin{aligned} [x] &= a_0^{Cu} = \frac{[F_x]}{[m_{Cu}]} \cdot [dt]^2 = \frac{eV}{a_0^{Cu} \cdot u} \cdot [dt]^2 \\ \Leftrightarrow [dt] &= t_{unit} = a_0^{Cu} \cdot \sqrt{\frac{u}{eV}} = 3.68 \cdot 10^{-14} s \end{aligned} \quad (3.40)$$

where u is the atomic mass unit which is equal to $1.66055 \cdot 10^{-27}$ kg and a_0^{Cu} the zero Kelvin lattice parameter of Cu. According to Eq. 3.40 the reader should note that the unit of the time step depends on the studied material since it is proportional to the zero Kelvin lattice parameter of the studied material. A commonly used time step within this work was for instance a time step of $dt=0.05 \cdot t_{unit} = 1.84$ fs for the different utilized Cu potentials. A proper choice of the used time step can be verified by checking conservation laws within the

the equations of motion of each atom. Any MD simulation at a distinct selected finite temperature or utilizing the Parrinello-Rahman concept would rely on velocity information of each atom either for fixing the temperature or explicitly as a force contribution within the equations of motion. Hence when utilizing more sophisticated equations of motion the simple Verlet algorithm is not suited best to determine the temporal evolution of the system.

utilized MD method like energy conservation and/or conservation of the linear momentum of the overall system. From a physical point of view the time step should be at least only some fraction of the minimal period related to the highest vibrational frequencies observed for the system. The Debye frequency, ν_D , can be regarded as a good first reference to assess this aspect demonstrating that a time step of a few fs is clearly much less than $\frac{1}{\nu_D}$.

3.3.4 Boundary Concepts

Different boundary concepts are utilized in atomistic systems depending on the physical properties to be studied. Commonly periodic boundary concepts are applied to simulation boxes to suppress finite size effects of the atomistic systems due to the limited number of atoms that can be considered in atomistic simulations. 3d periodic boundary conditions are quite often applied in atomistic simulations of crystalline material. They are highly suited in the situation of ideal crystal simulations and when dealing with bicrystal simulation boxes where a strong interaction of the two GBs which are only present in the system due to the applied 3d periodicity can be ruled out. Known from the literature and our own experience are that when dealing with pure twist GBs 3d periodic boundary conditions can successfully be applied when the distance between the two GBs is sufficiently large and no massive GB sliding occurs within the system. For low-angle twist GBs GB sliding becomes more and more important that even here a 3d periodic border concept might not be the best choice to study the true behaviour of these GBs. The situation changes slightly once one is dealing with tilt GBs. From the literature it is known that low as well as high-angle tilt GBs have a strong tendency for GB sliding to occur at the GB which is expressed in well-defined non-zero microscopic GB DOFs. A reason why this tendency is so pronounced could be that even high-angle tilt GBs do not completely loose their dislocation character.

If sliding at a GB becomes indeed an important issue for either twist or tilt GBs, applying 3d periodic boundary conditions might give rise to artificial, unphysical interactions of the two GBs only due to the applied 3d periodic borders. To avoid such a situation 2d simulation concepts were developed in the past by several authors to study single three-dimensional GBs. The most simple approach would be to allow free surfaces in the normal direction of the GB. Such a strategy implies that the used interatomic potential is able to present the free surfaces realistically and the an interaction of the free surfaces and the GB can be neglected. A different concept introducing ideal crystal blocks as borders in the GB normal direction is the regionI/regionII frozen block approach by Lutsko et.al. [66]. A 2d schematic of it is given in Fig. 3.4 where the used simulation box border situation is shown. Another interesting bicrystalline border concept is the Möbius concept [68]. It utilizes the circumstance that a well-defined misorientation between a crystal A and B in the GB normal direction can be inverted while calculating the interaction of crystal A with the image of crystal B or vice versa. Here a different 2d concept was used which is an adapted form of free surfaces. This 2d concept differs in two main aspects from the Lutsko concept. Here the atoms located in region II are moving according to 2d equations of motion in reduced coordinate space as introduced by the Parrinello-Rahman scheme. Namely these are the s_x and s_y components of region II atoms since for the used MD box geometry the s_z component is strongly connected to the presence of the GB. In the Lutsko concept to ensure a proper ideal crystal behaviour of region II those atoms are held fixed in reduced coordinate space and the region II atoms are always scaled with ideal crystal box parameters. Since the region

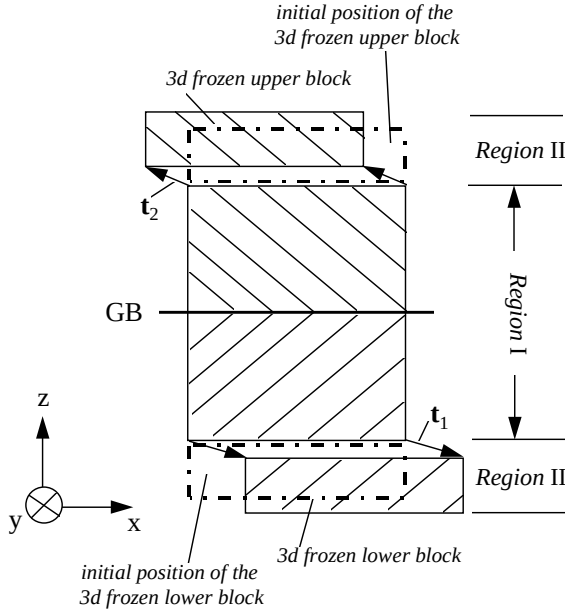


Figure 3.4: Region I/II 3d frozen block border concept according to Lutsko and Wolf. Here the blocks of region II are rigid frozen atomistic blocks which are shifted about the translations vectors, $\mathbf{t}_1$ and $\mathbf{t}_2$ respectively, according to the net force exerted by region I on either of the region II blocks.

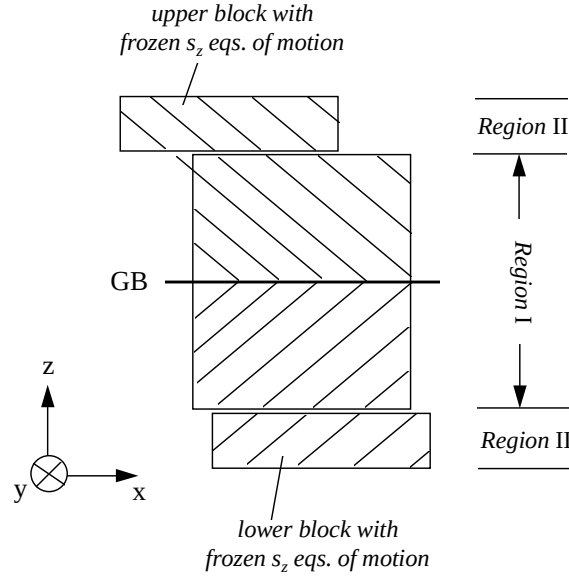


Figure 3.5: Restricted free surface border concept. Here the free surfaces are stabilized in the normal direction of the surfaces since during performed MD simulations the s_z component of region II atoms is held fixed. According to this procedure even for simple pair potentials stable surfaces can be obtained even in the presence of a DF.

II atoms are frozen due to the coupling of the region I/region II atoms the linear momentum of the total system is no longer a conserved quantity. This may become a severe disturbance of the physical behaviour of the GB system but its real effect on the system is hard to assess. Nevertheless it should have at least some effect on the evolution of the trajectories of each atom. For the restricted s_z free surface border concept used here only the z component of the linear momentum is a non-conserved quantity while the x and y component remain conserved. The second main advantage of this approach over the Lutsko concept is that GB sliding is intrinsically possible and does not require explicit translation vectors as used in the Lutsko concept.

3.3.5 Finite Temperature MD Simulations

Different forms exist to perform finite temperature MD simulations. Here one distinguishes between methods where the temperature, T , is a thermodynamical variable or not. In the case of microcanonical simulations, T is not a thermodynamical variable. Still a MD system studied under these constraints will equilibrate to a certain temperature. This equilibrium temperature will depend on the initial choice of kinetic energy introduced to the system [1].

Systems that deal with temperature as a thermodynamical variable are represented by the canonical ensemble if the number of atoms, N , the volume of the simulation box, V , as well as the desired simulation temperature are thermodynamical variables and kept thermodynamically fixed during the complete course of the simulation run. Here different MD

methods exist, namely an isokinetic method [1] which does not really represent a canonical ensemble as well as finite temperature thermostats [1, 52].

The presented results of this work were exclusively obtained by finite temperature MD simulations utilizing the Nose-Hoover thermostat [55]. The only exception to this are the results of GB migration of the $\Sigma 29$ [001] twist GB where partly results were obtained utilizing isokinetic MD simulations as well as utilizing the Nose thermostat [52]. In the used MD simulation code of this work, the Nose and Nose-Hoover thermostats were fully implemented into the Parrinello-Rahman concept.

In the case of isokinetic simulations, the desired temperature, T , can be established by rescaling the atoms' velocities after each time step according to the ratio of the desired kinetic energy in the overall system to the actual kinetic energy in the overall system [1]. This rather simple procedure restricts the temperature at all times to a preset value T . It is well known that this simulation procedure does not represent the canonical ensemble [1], therefore in the early 1980's Nose introduced a new simulation scheme to allow truly canonical simulations to be performed [52, 53]. His first canonical ensemble MD method published in 1984 [52, 53] introduced a scaling variable, s , that entered into the Lagrangian via the velocities of each atom given by $\mathbf{v}_i(t) = s(t) \cdot \dot{\mathbf{r}}_i(t)$, a kinetic term of $\dot{s}$ and a logarithmic potential function of variable, s . In this new Lagrangian, the variable s represents a heat bath. The new Lagrangian [52] reads in the framework of classical MD

$$L(\{\mathbf{r}_i\}, \{\dot{\mathbf{r}}_i\}, s, \dot{s}) = \sum_{i=1}^N \frac{m_i}{2} s^2 \dot{\mathbf{r}}_i^T \cdot \dot{\mathbf{r}}_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V(r_{ij}) + \frac{Q}{2} \dot{s}^2 - (f+1) \cdot k_B T_{eq} \ln(s) \quad (3.41)$$

where Q determines the temperature fluctuation and f the number of degrees of freedom of the physical system which for a 3d system would usually be $3N$. Applying the Lagrangian formalism to this new type of Lagrangian, the basic equations of motion of each atom as well as for the heat bath variable, s , are derived. Only one minor shortcoming is connected to the above-mentioned Nose MD simulation method [52], namely that the real time and the MD simulation time are no longer equivalent quantities since s acts as a scaling parameter for the simulation time. Since in thermal equilibrium, s only fluctuates about a mean value the average of s over the entire simulation run can be used to scale the MD simulation time to finally obtain the real time that has elapsed during the simulation run.

Due to this time scaling behaviour, Hoover [54] as well as Nose [53, 55] introduced a different approach which utilizes frictional forces, a kinetic term for the variable being associated with the heat bath and a logarithmic potential function to introduce the heat bath. Nose [55] pointed out that from the found Hamiltonian associated with the frictional force thermostat, the equations of motion of each atom and of the heat bath can no longer be directly derived, still the usually conserved system properties in MD simulations remain conserved.

3.3.6 Geometry of MD Simulation Box

The general features concerning the geometry of the used MD simulation boxes are introduced and explained in this section. The underlying geometrical concepts related to GB systems were presented when introducing GB characterization concepts like the CSL and IPS scheme (see sect. 2.1.2 and 2.1.3) and when dealing with the basic geometry of asymmetrical tilt GBs. For the studied symmetrical twist and tilt GBs as well as for the asymmetrical

tilt GBs, the construction of the used MD simulation boxes in this work followed a certain well-defined scheme. As has been discussed in the framework of the Parrinello-Rahman concept any 3d simulation box is spanned out by three distinct box vectors $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ which can be written in a matrix notation by $\underline{h}=(\mathbf{a},\mathbf{b},\mathbf{c})$. Fig. 3.6 (a) presents a MD simulation box of a perfect ideal crystal while (b) shows schematically the situation for a bicrystalline GB system. Fig. 3.6 (a) shows as an example a schematic of the MD simulation box for a simple cubic material where the $\langle 100 \rangle$ directions of the crystal are aligned with the MD simulation box coordinate system (x,y,z). Such a box could for instance be used when studying the elastic constants of a cubic material or for the determination of the temperature dependence of the lattice parameter. Since for simulating the behaviour and properties of an ideal crystal system, 3d periodic border conditions have to be applied to the MD box to avoid boundary effects due to free surfaces, the MD box vectors are important parameters since they define the size and shape of the MD cell which needs to be periodically repeated.

Turning the discussion now to GB systems, the used MD simulation box of all studied GB systems in this work is schematically sketched and given by Fig. 3.6 (b). As can be seen in the figure the GB plane normal is always parallel to the z direction of the MD simulation box coordinate system (x,y,z). The reader should note that all conducted GB simulations in this work were performed on planar GBs. Furthermore the figure illustrates that grain

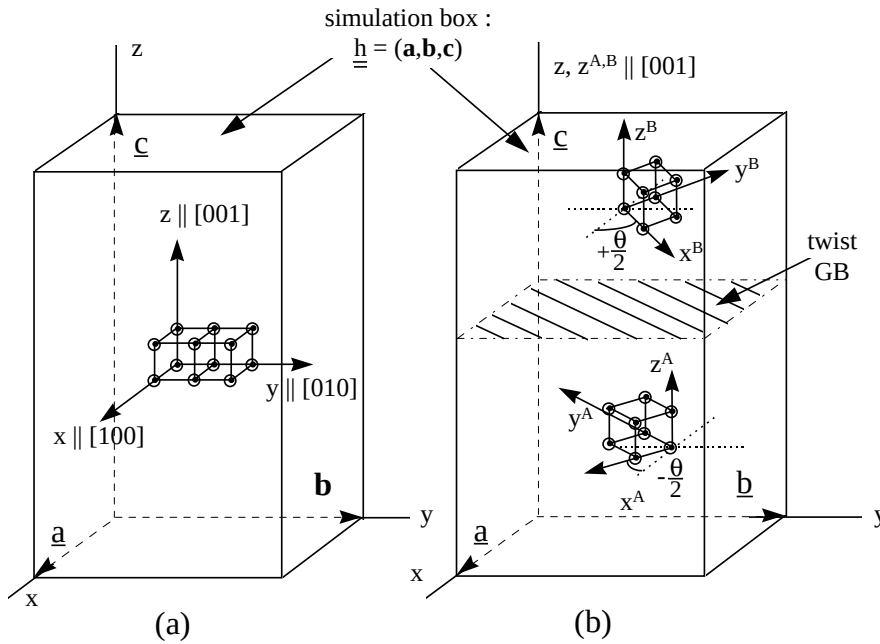


Figure 3.6: Geometry of MD simulation box : (a) shows a schematic of a MD simulation box of a perfect crystal while (b) presents a bicrystalline MD simulation box containing two grains labelled A and B for the case of an arbitrary $[001]$ twist GB. The direction of grain rotation and the primitive cells for a simple cubic material are illustrated in the figure as well. Note that both grains are symmetrically misoriented with respect to the MD simulation box coordinate system (x,y,z). The box vectors $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ that span out the simulation box and which are essential to apply any form of periodic border conditions are given in the figures as well. More details on the general aspects of the generation scheme and the geometry of the box are given in the text.

A, which is underneath the sketched GB, is misoriented by $-\frac{\theta}{2}$ about the z direction of the

MD box while grain B, which is above the GB, is misoriented by $+\frac{\theta}{2}$ about the z direction of the MD box. In this case the z-direction of the GB MD box coincides with the $\langle 001 \rangle$ direction of the cubic crystal lattice. Assuming periodicity along the z-direction of the box it is obvious that a second GB is present in the simulation box system, namely at $z=0$ or which is equivalent at $z=c_z$. Both GBs are identical and only in the case of tilt GBs differ concerning their rotational sense. Overall the two grains have a misorientation relationship which can be described by a rotation of θ about the GB plane normal given i.e. by its Miller indices $[hkl]/|[hkl]|$.

In this work only true CSL GBs were studied. This is important to note since due to the CSL concept it is ensured that periodic GB simulation boxes can be generated. The dimensions of the simulation boxes are intrinsically connected to the CSL lattice. In order to generate a CSL GB simulation box, after the misorientation procedure of both grains as described above, the CSL lattice points were looked up on the x-, y- and z-axis. These were then used to construct the simulation boxes. Usually the x-y-plane dimensions included more than one primitive CSL cell in order to suppress periodicity effects. In order to determine for instance the GB energy of a GB, an equivalent ideal crystal having the same number of atoms is necessary. Usually this reference system was given by a simulation box where the ideal crystal grain was misoriented by $-\frac{\theta}{2}$ about the z-direction of the simulation box. Here the crystallographic plane normal being parallel to the z-direction of the MD simulation box coordinate system of the GB and ideal crystal was identically the same. The lateral dimensions of the GB and ideal crystal simulation boxes were the same too. In section 5.1.2 the underlying CSL situation of the studied $[001]$ twist GBs is presented to give further insight into the atomistics of these GBs. As well further remarks are made related to the size of the primitive CSL box dimensions.

3.4 Driving Force Concepts

3.4.1 Introduction

When GB migration occurs, an important question is what is the driving force driving the GB and how can it be quantified. The topic of introducing and quantifying driving forces for GB migration plays a key role in this work since the main objective of this work is to study GB migration of planar GBs. The reason to study planar GBs rather than curved ones is that from a crystallographic point of view, the behaviour of well-defined individual GBs is to be studied rather than well-defined misorientation relationships. Due to the planar nature of the GBs to be studied, at finite temperature these planar GBs do not experience any driving force since GB curvature is zero. Curvature driven GB migration is very often studied in experiments of either polycrystalline or bicrystalline samples as well has been recently studied by computer simulations by different authors.

For planar GBs, in order to provide a sufficient driving force (DF) for GB migration an energy gradient has to be introduced into the system that in a bicrystalline setup one of the two grains is energetically favoured over the other one. In this work, three different forms of DFs were used to drive planar GBs continuously. Exclusively bicrystal simulation boxes were used in our simulations containing the planar GBs. The first approach discussed in section 3.4.2 utilizes an elastic deformation of the bicrystal leading to an elastic energy gradient in the system which forms the elastic DF. The fundamental concept of the elastic DF was analytically worked out by Furtkamp [45] during his stay at Argonne National Laboratory. His report served as the basis to implement this approach into the used MD computer code and was the starting point to further elaborate this DF concept. Here the elastic DF is associated with the bulk of the two grains. A second approach presented in section 3.4.3 utilizes a Peach-Koehler interaction. Here the interaction leading to a DF is based on the coupling of an external stress state with the GB structure itself. With respect to the elastic DF this approach is associated with the GB structure itself rather than the bulk. Finally a third DF scheme is presented in section 3.4.4 which is purely connected to the idea of coupling excess energy terms to the orientation dependence of atoms. This approach is as well a bulk phenomenon and represents an alternative to the elastic DF in various ways which is discussed in 3.4.4.

3.4.2 Elastic Driving Force

In the case of an elastic driving force one applies appropriate strain or stress to a bicrystal simulation box in order to install different amounts of elastic energy in either of the two grains. At this point one already realizes that such an approach will only work if the material under consideration behaves elastically anisotropic since then the grain's orientation will determine its elastic energy with respect to an external strain or stress state. Furthermore only certain strain or stress states will give rise to an elastic driving force for a chosen GB due to the distinct nature of the orientation relationship between the two grains. For individual planar GBs, this state needs to be identified. For instance this can be achieved by analytical linear-elastic energy calculations for distinct GB geometries. Finally due to the energy gradient of stored elastic energy within a bicrystal, the GB will then migrate into the direction of the grain having the higher elastic energy stored. The elastic driving force

itself is then simply given by the difference in elastic energy stored in the two grains. Using the data on the orientation of each grain with respect to the coordinate system (x,y,z) of the simulation box for each grain, a rotation matrix can readily be written down that relates each grain's orientation to the principal coordinate system of the crystal structure studied. These rotation matrices then can be used to transform either the applied strain or stress tensor into the principal cubic coordinate system of grain A and B in order to calculate the elastic energy stored in each grain. Here the reference state of a cubic material in its principal cubic coordinate system is defined by the situation where the $\langle 100 \rangle$ directions of the crystal are aligned with the coordinate system defining the atoms' coordinates within the grain and where the primitive cell of the system is given by a cube as illustrated by Fig. 3.6(a). The misorientation relationship between the MD simulation box coordinate system (x,y,z) and those of either grain, A and B, are illustrated in Fig. 3.6(b) for the case of a [001] planar twist GB.

This work is restricted to cubic materials. Hence the next step is to derive analytically the important relationships concerning an elastic driving force for a cubic crystal structure. The elastic energy for a cubic crystal in the principal cubic coordinate system reads (see i.e. [60] on pp. 136 to 137)

$$\begin{aligned}
 E_{elast} &= \frac{1}{2} C_{ijkl} \epsilon_{ij} \epsilon_{kl} = \frac{1}{2} C_{1111} (\epsilon_{11}^2 + \epsilon_{22}^2 + \epsilon_{33}^2) + 2 C_{4444} (\epsilon_{12}^2 + \epsilon_{13}^2 + \epsilon_{23}^2) + \\
 &\quad C_{1122} (\epsilon_{11} \cdot \epsilon_{22} + \epsilon_{11} \cdot \epsilon_{33} + \epsilon_{22} \cdot \epsilon_{33}) \\
 &= \frac{1}{2} S_{ijkl} \sigma_{ij} \sigma_{kl} = \frac{1}{2} S_{1111} (\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2) + 2 S_{4444} (\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{23}^2) + \\
 &\quad S_{1122} (\sigma_{11} \cdot \sigma_{22} + \sigma_{11} \cdot \sigma_{33} + \sigma_{22} \cdot \sigma_{33}), \tag{3.42}
 \end{aligned}$$

where the Einstein summation convention ⁴(see i.e. [60] on page 7) is implied. Transforming the strain or stress tensor into the principal cubic coordinate system of grain, A and B, and calculating the difference between the elastic energy stored in grain, A and B, finally yields the elastic driving force, p_{elast} .

$$\begin{aligned}
 p_{elast} &= E_{elast}^B - E_{elast}^A \tag{3.43} \\
 &= \frac{1}{2} C_{ijkl} (\epsilon_{ij}^B \epsilon_{kl}^B - \epsilon_{ij}^A \epsilon_{kl}^A) = \frac{1}{2} S_{ijkl} (\sigma_{ij}^B \sigma_{kl}^B - \sigma_{ij}^A \sigma_{kl}^A)
 \end{aligned}$$

The result for [001] twist or tilt GBs reads,

$$\begin{aligned}
 p_{elast} &= E_{elast}^B \left([001], +\frac{\theta}{2} \right) - E_{elast}^A \left([001], -\frac{\theta}{2} \right) \tag{3.44} \\
 &= \frac{1}{2} C_{ijkl} (\epsilon_{ij}^B \epsilon_{kl}^B - \epsilon_{ij}^A \epsilon_{kl}^A) = \sin(2\theta) \overbrace{(2C_{4444} - C_{1111} + C_{1122})}^{=c_A} \epsilon_{12} (\epsilon_{22} - \epsilon_{11}) \\
 &= \frac{1}{2} S_{ijkl} (\sigma_{ij}^B \sigma_{kl}^B - \sigma_{ij}^A \sigma_{kl}^A) = \sin(2\theta) \underbrace{(2S_{4444} - S_{1111} + S_{1122})}_{=s_A} \sigma_{12} (\sigma_{22} - \sigma_{11})
 \end{aligned}$$

if the [001] cubic axis is aligned with the z-direction of the simulation box coordinate system and where θ represents the misorientation angle for a rotation about the [001] axis. This

⁴When a letter suffix occurs twice in the same term, summation with respect to that suffix is to be automatically understood.

result implies to choose the strain tensor applied to the simulation box as follows

$$\underline{\underline{\epsilon}} = \begin{pmatrix} \epsilon_{11} & \epsilon_{12} & 0 \\ \epsilon_{12} & \epsilon_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad p = (2C_{4444} - C_{1111} + C_{1122}) \cdot \epsilon_{12} \cdot (\epsilon_{22} - \epsilon_{11}) \cdot \sin(2\theta) \quad (3.45)$$

where C_{ijkl} are the cubic elastic constants. To apply a coupled xy shear state seems reasonable since no further components of the strain tensor do appear in the elastic driving force equation 3.45. Hence any additional strain tensor component would not result in a change of the magnitude of the elastic driving force. To further simplify the situation and to avoid deformations that are accompanied by intrinsic volume changes of the simulation box, the following strain tensor, $\underline{\underline{\epsilon}}$, was chosen to be used within the [001] twist GB migration simulations $\underline{\underline{\epsilon}}$

$$\underline{\underline{\epsilon}} = \begin{pmatrix} \frac{\epsilon}{2} & \epsilon & 0 \\ \epsilon & -\frac{\epsilon}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \text{leading to} \quad p = -(2C_{4444} - C_{1111} + C_{1122}) \cdot \epsilon^2 \cdot \sin(2\theta). \quad (3.46)$$

For the performed GB migration simulations in this work on [001] twist and tilt GBs in the presence of an elastic driving force, the strain tensor and the elastic DF equation given by Eq. 3.46 form the basis of the utilized elastic driving force concept. They define the form of applicable strain tensor to the MD simulation box as well as already quantify the magnitude of elastic DF to be expected in these simulations.

At this point it is important to realize that the simulations can be performed either strain or stress controlled. As will be discussed when dealing with the GB migration results of the studied symmetrical tilt GBs, in some cases it is crucial choosing appropriate boundary conditions to observe continuous GB migration. From a practical point of view, the strain controlled MD simulations are easily to set up and are robust simulations, since the MD simulation box remains fixed and does not need to be adapted to an imposed external stress state. From a physical point of view, the stress controlled simulations should be favourable since the simulation box can adjust its size and shape to the applied external stress tensor. This is a very important feature for finite temperature GB simulations if one pays attention to the fact that GBs can change their structure and character with temperature. Recent simulation results on GB self-diffusion and the results on GB migration as well as results found in this work show clear evidence for such behaviour of GBs and demonstrate the importance of this issue.

Within this work, the strain controlled approach was used. As explained above, this was done due to the simplicity of installing a strain tensor onto a MD simulation box rather than imposing a stress state. Imposing a stress state would have required to utilize the Parrinello-Rahman concept which means more computational efforts to be taken and the risk of stability problems of the overall MD system. Even there is one important further aspect to be pointed out here with regards to the stress controlled simulations. Namely this is that usually the presence of a GB should only lead to a volume expansion normal to the GB plane and that the in-plane dimensions of the simulation box are given by the appropriate ideal crystal dimensions for a given temperature. The underlying idea is of course that bulk regions far away from the GB should have ideal crystal properties and therefore the appropriate simulation box dimensions should have ideal crystal character.

For the above given example, in any case the generic form of either a stress or strain tensor will need to be exactly the same to generate a non-zero elastic driving force. This means that a coupled xy shear stress state would be necessary to install an elastic driving force in [001] twist GB systems. Therefore the in-plane dimensions of the GB are now adjusting to the balance of internal and external stresses although from a conceptual point of view one would be eager to fix them to the strained ideal crystal situation. Evidently this can become a major problem if one assumes that for some MD GB system sizes, the in-plane stresses due to the presence of the GB have a major effect on the equilibrium size of the simulation box. Thus it would need to be shown that both approaches either fixing the in-plane dimensions or adjustable in-plane dimensions lead to the same GB structure and would give the correct in-plane ideal crystal lattice parameter in the bulk of the grains at finite temperatures. Only if the GB system is capable of satisfying these conditions, the stress and strain controlled approach should yield similar results for GB migration when installing an additional elastic driving force into the system. In conclusion according to this reasoning, it seems convincing to apply strain rather than stress to a MD simulation box in order to install an elastic DF into the system.

3.4.3 Peach-Koehler Driving Force

The well-established Peach-Koehler description on forces exerted on single lattice dislocations due to internal or external stress states (see i.e. [3] on page 203 and pp. 221) can as well be used to study the behaviour of external stress states on GBs. This implies that such GBs still have discrete GB dislocation character. It is well known that discrete GB dislocations exist for low-angle GBs and that their spacing is wide. Of course, the spacing of the GB dislocations is a function of misorientation angle and gets lesser and less for increasing misorientation. Usually for high-angle GBs it is assumed that they have lost their GB dislocation character due to the short spacing of the ideally assumed GB dislocations. Here only an overlapping of the GB cores exists which forms the GB structure.

It is known from the literature for more than 50 years [61] that low-angle GBs can be driven by Peach-Koehler forces due to the discrete nature of the GB dislocations. Within the Peach-Koehler framework, the force, $\mathbf{F}_{Disl.}$, exerted on a single dislocation of length L , Burgers vector $\mathbf{b}_{Disl.}$ and line vector $\mathbf{s}_{Disl.}$ by an either internal or external stress state, $\underline{\underline{\sigma}}$, is given by Eq. 3.47

$$\frac{\mathbf{F}_{Disl.}}{L} = (\underline{\underline{\sigma}} \cdot \mathbf{b}_{Disl.}) \otimes \mathbf{s}_{Disl.} \quad (3.47)$$

Recently it was shown experimentally that apart from low-angle GBs even intermediate to high-angle $\langle 111 \rangle$ tilt GBs can be driven by external stress states [62].

Utilizing the Peach-Koehler concept one finds that appropriately chosen pure shear stress states will result in Peach-Koehler forces on pure edge GB dislocations at least in the case of low-angle tilt GB. In this work, the Peach-Koehler DF analysis is presented and discussed in those sections where the GB migration results of the studied tilt GBs are presented. In this work, one typical low-angle $\langle 111 \rangle$ tilt GB as well as one typical $\langle 001 \rangle$ high-angle tilt GB were investigated in detail in the framework of imposing external shear stresses on the MD simulation boxes in order to install a Peach-Koehler DF.

3.4.4 Orientation-correlated Driving Force

In this section, a new scheme of introducing an artificial driving force for GB migration is presented. The driving force itself is only artificial in the sense that it does not rely on or can be directly associated with any source of DF known from experiments or simulations. This novel driving force is solely connected to the idea that an atom being in an environment of a certain crystal orientation suffers an anisotropic excess energy contribution due to an externally applied field. Utilizing this idea one can apriori construct an excess energy term for each atom, j , as a function of the structure factors $|S(\mathbf{k}_\alpha)|^2$ associated with those orientations present in the system and which are calculated in the vicinity of each atom, j . In this context the vicinity of atom, j , shall be a sphere of a certain cut-off radius centered around atom, j . Normally this cut-off radius should be the same as the one being used to evaluate the interatomic forces exerted on any atom, j , or i.e. its potential energy. Thus for each atom, j , an excess energy term, e_j^{corr} , can be obtained by a simple analytic expression as is explained in detail below. The overall sum over all atoms, j , can then simply be added to the potential energy of the overall system. By doing this the orientation-correlated DF term will enter into the Lagrangian or Hamiltonian and hence new equations of motions for each atom can be obtained readily by applying i.e. the Lagrangian equation of motion to this new Lagrangian. The exact excess energy calculation and the new equations of motion for each atom, j , are given for a bicrystal situation in the following paragraph. Of course this approach lends itself as well for nanocrystalline simulations where several orientations could be present. Since this DF is closely related to information of the crystal structure or orientation in the vicinity of each atom, the DF was named orientation-correlated DF and shall be identified within this work by the label, p_{corr} .

The structure factor of an orientation α represented by an appropriate reciprocal lattice vector $\mathbf{k}_\alpha$ is

$$\begin{aligned} |S(\mathbf{k}_\alpha)|^2 &= \frac{1}{N^2} \sum_{m=1}^N \sum_{l=1}^N \exp(i \cdot \mathbf{k}_\alpha \cdot (\mathbf{r}_m - \mathbf{r}_l)) \\ &= \frac{1}{N^2} \left(\left(\sum_{m=1}^N \cos(\mathbf{k}_\alpha \cdot \mathbf{r}_m) \right)^2 + \left(\sum_{m=1}^N \sin(\mathbf{k}_\alpha \cdot \mathbf{r}_m) \right)^2 \right). \end{aligned} \quad (3.48)$$

The overall excess energy contribution to the system, $E_{corr.DF}$, as well as the excess energy e_j^{corr} for each atom, j , within a bicrystal simulation consisting of an orientation, 1 and 2, is therefore given by

$$E_{corr.DF} = \sum_{j=1}^N e_j^{corr} = \sum_{j=1}^N \sum_{\alpha=1}^2 a_\alpha \cdot |S(\mathbf{k}_\alpha)|_j^2 = \sum_{j=1}^N a_1 \cdot |S(\mathbf{k}_1)|_j^2 + a_2 \cdot |S(\mathbf{k}_2)|_j^2, \quad (3.49)$$

where a_1 and a_2 are coefficients which determine the strength of the excess energy due to an externally applied field. In some of the conducted simulations, a_1 and a_2 were chosen to be $8.0 \cdot 10^{-3}$ eV/atom and $2.0 \cdot 10^{-3}$ eV/atom, respectively. To select reasonable values for a_1 and a_2 , results of the magnitude of the elastic driving force were used as a reference. The reader should note that in order to evaluate Eq. 3.49, in Eq. 3.48 N has to be replaced by N_j which is the number of neighbours within the cut-off sphere around atom, j , as has been discussed above.

The concept of an orientation-correlated DF was introduced into the utilized Parrinello-Rahman method as follows. Here the equations of motion for a purely pairwise potential like the LJ and within the description of classical MD are given to be able to focus on the new terms related to the orientation-correlated DF especially with respect to the beforementioned equations of motion in Eq. 3.22. Of course the concept of an orientation-correlated DF can and was easily incorporated within the MD code for the used many body potentials as well as within the framework of finite temperature thermostats.

The adapted Lagrangian now reads

$$\begin{aligned} L(\{\mathbf{s}_i\}, \{\dot{\mathbf{s}}_i\}, \{\underline{\underline{h}}\}, \{\dot{\underline{\underline{h}}}\}) &= K(\{\dot{\mathbf{s}}_i\}, \{\underline{\underline{h}}\}) - V(\{\mathbf{s}_i\}, \{\underline{\underline{h}}\}) - E_{corr.DF}(\{\mathbf{s}_i\}, \{\underline{\underline{h}}\}) \\ &+ K_{box}(\{\dot{\underline{\underline{h}}}\}) - V_{elastic}(\{\underline{\underline{h}}\}) \end{aligned} \quad (3.50)$$

Utilizing the Lagrangian equation of motion for the coordinate $s_{i,x}$, $s_{i,y}$ and $s_{i,z}$ one obtains new equations of motion with the incorporated concept of an orientation-correlated DF, namely

$$m_i \cdot \ddot{\mathbf{s}}_i = - \sum_{j \neq i}^N \frac{1}{r_{ij}} \cdot \frac{dV(r_{ij})}{dr_{ij}} \cdot \mathbf{s}_{ij} - \underline{\underline{G}}^{-1} \cdot \frac{dE_{corr.DF}(\{\mathbf{s}_i\}, \{\underline{\underline{h}}\})}{d\mathbf{s}_i} - m_i \cdot \underline{\underline{G}}^{-1} \cdot \dot{\underline{\underline{G}}} \cdot \dot{\mathbf{s}}_i \quad (3.51)$$

Here the term $\frac{dE_{corr.DF}(\{\mathbf{s}_i\}, \{\underline{\underline{h}}\})}{d\mathbf{s}_i}$ is not explicitly written out since the full analytic term is too long-winded and therefore does not lend itself for a simple easily digestible presentation. Since its final form can be obtained by simple math it is not given explicitly within this presentation. Rather at this point the highlights of an orientation-correlated DF are presented and discussed especially with respect to the elastic DF. Before this is done, a few further comments are made on the equations of motion of the simulation box.

Although from a mathematical point of view the formulation of the orientation-correlated DF would need to be incorporated into the derivation of the equations of motion of the simulation box an adaption of Eq. 3.29 was not done. Why it was not done is explained by the following assessment of the situation. Usually the orientation-correlated DF is utilized on fully relaxed GB systems at some finite temperature at a stage of thermal equilibrium. Usually in such a situation the MD simulation box should already have the correct box vectors which could be obtained by utilizing Eq. 3.29. If so, the GB migration simulations in the presence of the orientation-correlated DF could and were conducted in a lot of cases with a fixed MD box, meaning that the equations of motion of any atom were fully statisfied. Even when allowing the box to alter its size and shape, it was found that even the original equations of motion of the simulation box in the presence of the orientation-correlated DF were stable and yielded results which were in agreement with results obtained by simulations under totally different simulation conditions. According to this finding and the commonly used simulation strategy, an adaption of Eq. 3.29 was not realized.

What are characteristics and advantages of the orientation-correlated DF over i.e. the elastic DF ? One feature that both DFs share is their temperature dependence. The temperature dependence of the orientation-correlated DF for fixed coefficients, a_1 and a_2 , is equivalent to the one found for the elastic DF for fixed strain, namely it decreases with increasing temperature. This behaviour is well understood since due to the increasing thermal vibrations of each atom at higher temperatures, the structure factors decrease. According to this even the temperature dependence of the orientation-correlated DF is realistic. The

main advantage of the orientation-correlated DF over the elastic DF is that now elasticity and/or processes that lead to plasticity can be separated from the issue of introducing a DF. This is meant in such a way that GBs themselves are complex structures that introduce inhomogeneous stress and strain fields and even are associated with processes like GB glide that can lead to plastic deformation of the system. Elasticity and plasticity are manageable within the Parrinello-Rahman scheme. Therefore it seems reasonable to separate the issue of a DF from GB related issues and to utilize a DF concept that does not rely on elasticity. By doing so the Parrinello-Rahman scheme can be fully used to take care of GB processes in connection with GB migration while the needed DF to drive the GBs is supplied by the orientation-correlated DF concept.

Concerning computational time consumption the orientation-correlated DF method is almost twice as slow as a comparable simulation in the presence of an elastic DF of the same magnitude. The reason for this is simply that the calculation of the additional force contributions due to Eq. 3.51 are more demanding and complex compared to a standard pair potential procedure since here the embedding square function of the sum over the cos and sin terms have to be calculated prior to the final determination of the atomic forces which consequently cause this increase in computational time. This procedure is comparable to the computer time increase when using many body potentials instead of simple pair potentials like the LJ potential. Concerning the implementation of Eq. 3.51 it should be noted that the cos and sin function are evaluated by tables to speed up the calculation process.

Even that the computational routines are more complicated and require more computational time, nevertheless this approach has even more advantages over the elastic DF approach. Simply this is connected to the limited time regimes accessible in MD simulations which are of the order of ns. Due to this constraint large strain has to be applied to the simulation box when introducing an elastic DF, since numerous GB migration events have to occur to determine a GB drift velocity and to study the migration behaviour. The applied strain is at the upper limit applicable to these potentials and can only be justified by the time restrictions met in MD simulations. Since in the case of the orientation-correlated DF method, the driving force can easily be set to any desirable value by choosing appropriate coefficients, a_1 and a_2 , this is a nice way to overcome those unphysical elastic strain magnitudes. Furthermore fixed strain states for some tilt GBs hinder GB migration to occur at all since those states are sometimes incompatible with GB migration that is accompanied with GB glide events. This is illustrated in detail for the case of the $\Sigma 5$ [210] symmetrical tilt GB in section 6.3.1.2. Especially relating to such problems, the orientation-correlated DF approach allows any box deformation to occur which in some cases are even plastic deformations when dealing with symmetrical tilt GBs where GB migration is coupled with GB glide events. At this point it is important to mention as well that the bottle neck of this approach is a proper calculation of appropriate reciprocal lattice vectors, $\mathbf{k}_\alpha$, since those are key parameters when calculating the driving force or respectively the excess energy per atom or the force contribution according to Eq. 3.51. Since for some planar tilt GBs studied in this work, plastic deformations as well as inner grain rotations sometimes play a central role during GB migration events, it is difficult to take those processes correctly into account for a proper reciprocal lattice vector calculation. Finally the driving force can accurately be calculated in-situ which therefore allows one to make definite statements about its magnitude and temporal evolution. The discussed general features of the orientation-correlated DF are illustrated by simulation results of [001] twist GBs in section 5.2.3.1.

3.5 Data Analysis

3.5.1 Structural Analysis

An important task throughout atomistic simulations is to identify the crystal structure of the studied system or to determine the state of the material for instance being in the solid or liquid state. For a bicrystalline simulation box this could for instance mean to identify either the two grains and/or the GB. It is often quite useful to determine planar system properties as well which yield information about for instance the order in specific crystallographic planes. Planar properties are obtained from the box properties by a slicing procedure which means that the simulation box is sliced into slices of equivalent volume and for these slices static and dynamic properties can be calculated.

Order within the studied systems will be identified and quantified as follows. It will be related to the density of particles, $\rho(\mathbf{r})$, within the crystals which can be written down as

$$\rho(\mathbf{r}) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) \quad (3.52)$$

For an ideal crystal in the solid state the density of particles should be a periodic function in real space. In this context and especially in the case of liquids the state of order in the investigated system can be further determined by the radial pair distribution function (RDF), $g(\mathbf{r})$, with

$$g(\mathbf{r}) = \frac{V}{N^2} \sum_{l=1}^N \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_{lj}) \quad (3.53)$$

In the case of an ideal crystal in the solid state the radial pair distribution function should show the same periodicity as the density of particles. Therefore for the purpose of determining long-range order in the system an analysis of the Fourier transform of the density of particles will be utilized. The Fourier transform of the density of particles can readily be written down as

$$\rho(\mathbf{k}) = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \cdot \rho(\mathbf{r}) \cdot d\mathbf{r} = \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_j} \quad (3.54)$$

Since the Fourier transform does not lend itself directly for evaluation purposes, the structure factor $S(\mathbf{k})$ will be presented instead which is defined as the magnitude of the Fourier transform $\rho(\mathbf{k})$ and reads

$$\begin{aligned} S(\mathbf{k})^2 &= \frac{1}{N} \cdot \rho(\mathbf{k}) \cdot \rho(-\mathbf{k}) = \frac{1}{N} \left| \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_j} \right|^2 = \frac{1}{N} \left| \sum_{j=1}^N \cos(\mathbf{k} \cdot \mathbf{r}_j) - i \cdot \sin(\mathbf{k} \cdot \mathbf{r}_j) \right|^2 \\ &= \frac{1}{N} \left(\left(\sum_{j=1}^N \cos(\mathbf{k} \cdot \mathbf{r}_j) \right)^2 + \left(\sum_{j=1}^N \sin(\mathbf{k} \cdot \mathbf{r}_j) \right)^2 \right) \end{aligned} \quad (3.55)$$

To evaluate the structure factor a reciprocal vector has to be defined which represents the crystal structure of the real space lattice of the crystal. This can easily be done by applying

the standard procedure for the calculation of a reciprocal vector $\mathbf{k}_i$, with $i=1,2,3$, which is

$$\mathbf{k}_1 = \frac{2 \cdot \pi}{V} \cdot \mathbf{b}_{fcc} \otimes \mathbf{c}_{fcc} \quad (3.56)$$

$$\mathbf{k}_2 = \frac{2 \cdot \pi}{V} \cdot \mathbf{c}_{fcc} \otimes \mathbf{a}_{fcc} \quad (3.57)$$

$$\mathbf{k}_3 = \frac{2 \cdot \pi}{V} \cdot \mathbf{a}_{fcc} \otimes \mathbf{b}_{fcc} \quad (3.58)$$

where $\mathbf{a}_{fcc}$, $\mathbf{b}_{fcc}$, and $\mathbf{c}_{fcc}$ are the primitive lattice vectors of for instance a fcc ideal crystal structure and V is the volume spanned by these vectors, namely $V = \mathbf{a}_{fcc} \cdot (\mathbf{b}_{fcc} \otimes \mathbf{c}_{fcc})$. For a perfect ideal crystal Eq. 3.55 gives $S(\mathbf{k})^2 = N$. Usually it is more convenient to normalize $S(\mathbf{k})^2$ to 1 for a perfect ideal crystal which means for Eq. 3.55 that the right-hand side needs to be divided by $\frac{1}{N^2}$ instead of $\frac{1}{N}$.

In the case of liquids the structure is better described by a correlation function (density-density-function) instead of the particle density function. This is because in liquids there exists no long-range order far beyond the nearest neighbour distance which can better be demonstrated by the radial pair distribution function. In crystals the radial pair distribution function can be replaced by the particle density function because the periodicity of the crystal structure can be found in both functions and in ideal crystals they should have the same periodicity. The link between the structure factor and the radial pair distribution function is that the structure factor determines order within a finite volume of the system by integrating over lattice order concerning the alignment of each atom while the radial pair distribution function represents the same state of order but only by quantifying the relationship between nearest and higher order neighbours. In this sense the radial pair distribution function represents the decomposition of the structure factor according to neighbours of different order.

3.5.1.1 Slicing Procedure and Detection Scheme of Planar GBs

Some system properties of the overall system like the kinetic energy, the structure factor or the stress tensor can be determined by some means of summation from individual atom properties of the total number of atoms within the system. Since bicrystalline simulation boxes are inhomogenous objects due to the presence of the GB, for planar GB systems it seems reasonable to introduce a slicing procedure to determine system properties for finite slabs or planes parallel to the GB plane [66, 67]. According to the interface plane scheme for symmetrical GBs these slabs represent crystallographic planes equivalent to the GB planes and are thus suitable to represent the inhomogeneity of the system concerning distinct crystallographic planes. This is for instance well-seen by monitoring the potential energy of planes at the GB region and within the bulk of the grains. The structure factor as well as the planar structure factor are long-range order parameters that can be used to identify the long-range order of either 3d crystal structures or respectively the order within certain crystallographic planes. Within this work the structure factor is calculated by

$$|S(\mathbf{k}_\alpha)|^2 = \frac{1}{N^2} \left(\left(\sum_{i=1}^N \cos(\mathbf{k}_\alpha \cdot \mathbf{r}_i) \right)^2 + \left(\sum_{i=1}^N \sin(\mathbf{k}_\alpha \cdot \mathbf{r}_i) \right)^2 \right) \quad (3.59)$$

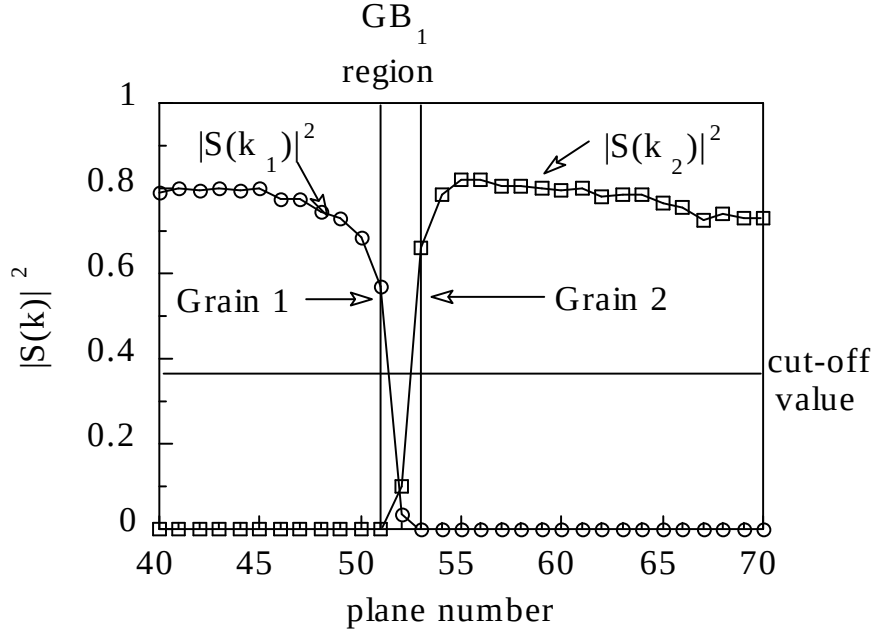


Figure 3.7: GB position according to the planar structure factor at 800K for the 3d LJ Cu potential. Here the planar structure factor profiles are plotted versus the plane number in the vicinity of GB₁ to detect the GB position according to the following classification scheme of planes parallel to the GB plane. Ideally at T=0K planes having values of $|S(\mathbf{k}_1)|^2 = 1$ and $|S(\mathbf{k}_2)|^2 = 0$ are associated with grain 1 while planes having values of $|S(\mathbf{k}_1)|^2 = 0$ and $|S(\mathbf{k}_2)|^2 = 1$ are associated with grain 2. If planes are represented by $|S(\mathbf{k}_1)|^2 < 0.5$ and $|S(\mathbf{k}_2)|^2 < 0.5$ they may be associated with the GB. Due to the thermal vibrations of the atoms the ideal value of one is not found rather than a value of 0.8 at 800K for the 3d LJ potential.

where $\mathbf{k}_\alpha$ represents a reciprocal lattice vector. This is exactly the same procedure as given by Eq. 3.55 only that we normalize it to $\frac{1}{N^2}$. The distinction between the ordinary 3d and planar structure factor is only connected to the atoms being summed over in eq. 3.59. If those atoms represented in those sums are only chosen from certain individual crystallographic planes selected prior to the analysis a planar structure factor analysis of distinct crystallographic planes can be performed. This approach can be understood as a slicing procedure of the 3d system concerning certain crystallographic planes. This slicing procedure is rather useful when dealing with GB systems to identify certain grain orientations as well as to locate the GB itself. Fig. 3.7 demonstrates this scheme for a GB system at finite temperature of 800K for the 3d LJ potential. For any plane (here (002) planes) within a bicrystalline simulation box two planar structure factors can be calculated, namely $|S(\mathbf{k}_1)|^2$ and $|S(\mathbf{k}_2)|^2$, where $\mathbf{k}_1$ represents the crystal lattice of grain 1 and $\mathbf{k}_2$ the lattice of grain 2. Keeping this in mind ideally at T=0K planes having values of $|S(\mathbf{k}_1)|^2 = 1$ and $|S(\mathbf{k}_2)|^2 = 0$ are associated with grain 1 while planes having values of $|S(\mathbf{k}_1)|^2 = 0$ and $|S(\mathbf{k}_2)|^2 = 1$ are associated with grain 2. If planes are represented by $|S(\mathbf{k}_1)|^2 < 0.5$ and $|S(\mathbf{k}_2)|^2 < 0.5$ they may be associated with the GB. Due to the thermal vibrations of the atoms the ideal value of one is not found rather than a value of 0.8 for a temperature of 800K for the 3d LJ potential as can be seen in Fig. 3.7. If thermal effects can be suppressed by an appropriate averaging procedure of the data entering into Eq. 3.59 it is possible to find at finite temper-

atures up to the melting point maximum planar structure factor values of about one. This averaging technique has been utilized in this work quite often to be able to identify either the grains and the GB region as is demonstrated by Fig. 3.7.

3.5.1.2 Radial Pair Distribution Function

The radial pair distribution function (RDF) is a measure to define long-range order in atomic-level systems. The definition of the RDF is given by Eq. 3.53. From the simulation data the RDF can be obtained as given by Allen and Tildesley [1].

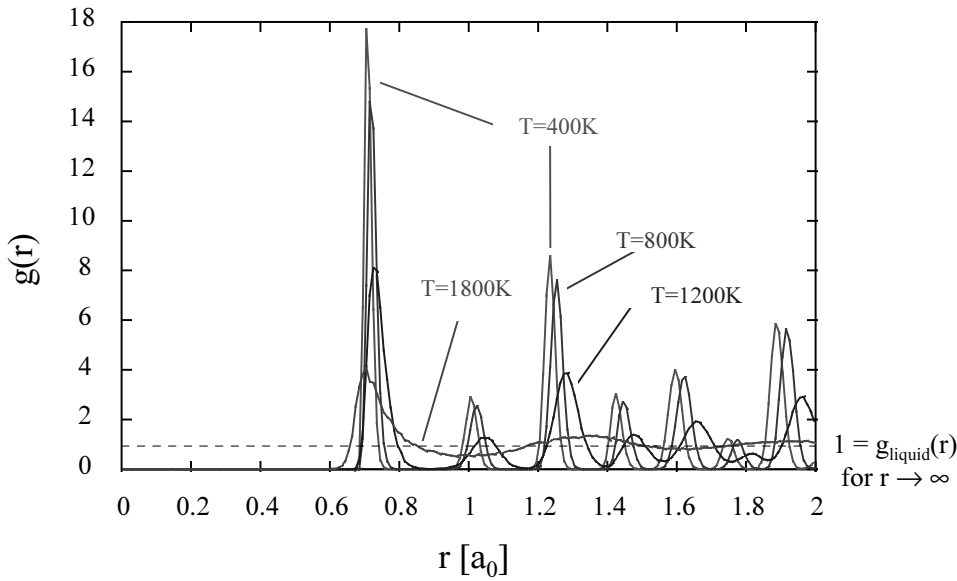


Figure 3.8: Radial pair distribution function for an ideal crystal of 512 atoms at various temperatures (400K, 800K, 1200K, and 1800K) for the Cu-LJ potential.

The RDF remarkably allows us to distinguish between the crystalline and liquid state of a material which shows in fact that the long-range order in the system breaks down nevertheless short-range order prevails. Fig. 3.8 shows a typical example of this behaviour for an ideal crystal studied at various temperatures for the Cu-LJ potential. At temperatures 400K, 800K and even 1200K the ideal crystal remains crystalline although at 1200K it is at the verge of becoming a liquid. The crystalline state can be identified by the distinct nearest and higher order neighbour peaks. A further effect of the increasing temperature is the decay of the magnitude of the peaks and their broadening. This can simply be understood by the increased vibrational distance of each atom with increasing temperature. The shift of those peaks to higher r values with increasing temperature demonstrates the lattice expansion of the crystal. Finally at a temperature of 1800K where the system is in the liquid state we observe the characteristic behaviour of a liquid still showing a strong nearest neighbour peak but higher order peaks being washed out.

In the context of GB simulations the RDF analysis can play a further important role in identifying the GB structure of GBs. In order to perform a standard RDF analysis on a GB region the GB core has to be defined and atoms have to be assigned either belonging to the GB core or the bulk. In order to do so one could think of various selection rules. Here we like

to apply an analysis of the local atomic-level structure near the GB by utilizing the common neighbour analysis. The details concerning this aspect shall be explained and discussed later on when GB structures are discussed. Of course by utilizing such a RDF analysis no exact details of the GB structure can be revealed, nevertheless one should be able to distinguish between a crystalline GB structure and a liquid-like or amorphous structure. Concerning this issue, namely whether GBs resemble crystalline or amorphous structures, this approach has been utilized by several authors [17, 72] and in this work it shall be applied too.

3.5.1.3 Common Neighbour Analysis

Here a brief description of the so-called common-neighbour structural analysis is given [73, 74]. The common neighbour analysis (CNA) is a scheme to investigate local structural order in atomic-level systems. It is well suited to identify defect structures like stacking faults, partial dislocations, vacancies and GBs. The first step in performing a CNA is to define bonds between atoms. Here the name bond is not necessarily meant chemically but rather to identify atom pairs that for instance show a nearest neighbour relationship. To obtain a list for each atom containing for instance its nearest neighbours one performs a radial distribution analysis of the overall system to generate such lists for each atom. In this context one refers to bonded pairs of atoms if they fall within the NN cut-off radius which is set here to be at the first minimum after the NN radial distribution function (RDF) peak. Now to each bonded pair three indices (jkl) can be assigned having the following meaning :

- Index j gives the number of neighbours bonded to both atoms in the pair.
- Index k gives the number of bonds between the shared neighbours in j.
- Index l gives the number of bonds in the longest continuous chain formed by the bonds in k.

Note that the bonding cut-off can be dependent on the types of atoms in the pair. To illustrate this scheme and to present characteristic (jkl) triples, first of all the derivation of the (421) triple for a fcc mono-atomic crystal structure is outlined.

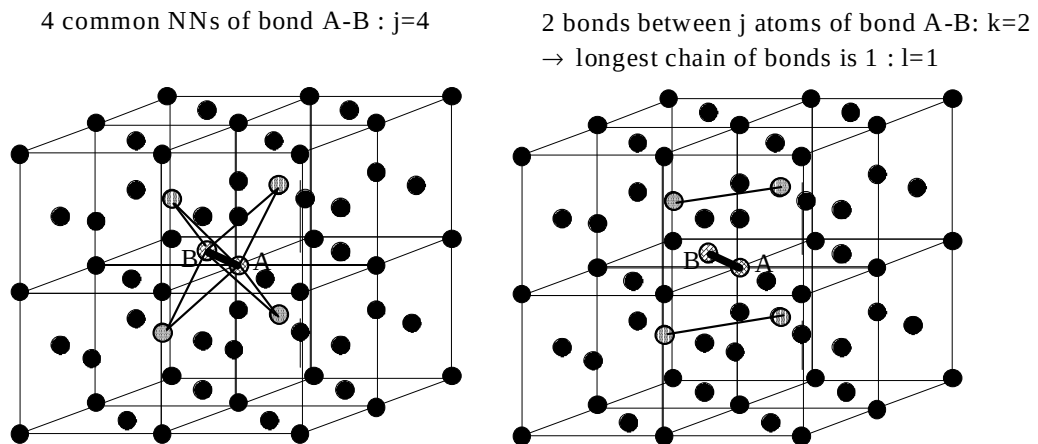


Figure 3.9: Derivation of the (421) triple for a fcc ideal crystal structure

Fig. 3.9 presents two illustrations to characterize the (421) triple. Here the bond A-B is considered and it is found that atom A and B share four common nearest neighbours

indicated in the figures by gray filled circles. The schematic on the right of Fig. 3.9 shows that two bonds exist between these shared atoms which are indicated by the straight lines connecting the gray filled circles. Finally the longest continuous chain of these bonds is one. Translating this into (jkl) terminology one obtains the triple (421) for the sketched A-B bond of Fig. 3.9. For a fcc system a few more distinct triples exist like the (422) and the (555). Ideally in a fcc system each atom has 12 nearest neighbours (NN bonds), hence investigating the local environment of an atom through a CNA can for instance tell whether or not an atom is located in an ideal fcc environment. Three simple local environments are given by the original papers [73, 74], namely :

- A fcc center forms by 12 (421) pairs.
- A hcp center forms by 6 (421) and 6 (422) pairs.
- An icosohedral center forms by 13 (555) pairs.

According to the original paper the (jkl)-indexed pairs can be differentiated by length relative to the cut-off radius, and the (jkl) will then be prefixed with either α or β where α would identify those bonds belonging to the true NN bonds. Therefore those pairs are labeled as follows : (α jkl) if the pair distance falls within the cut-off radius and (β jkl) if the pair distance is beyond the cut-off. This type of statistic gives a rough decomposition of the RDF in terms of (jkl) triples.

After describing the basic principles of the CNA method now the main application fields within this work are listed as follows. The method was used to

- detect the position of GBs.
- analyse the structure of GBs.
- detect and analyse dislocations and their structure as well as their temporal evolution.
- detect lattice vacancies and follow their temporal evolution.

These examples of application show that indeed the CNA method is a powerful tool to study atomic-level configurations and to obtain information on defects like vacancies, dislocations as well as GBs.

3.5.2 Analysis of Diffusive Processes

The temporal evolution of the mean-square displacement (MSD) of atoms within an atomic-level system can be used to determine the diffusion coefficient, D , of various diffusive processes in such systems. For an ideal bulk crystal this could for instance be the self-diffusion coefficient of lattice vacancy diffusion while for systems containing GBs the GB self-diffusion coefficient can be determined additionally. The underlying theory to extract the diffusion coefficients from atomic-level data and the applied schemes used in this work are presented next.

Analysis of Lattice Vacancy Diffusion - It is well known that if diffusive processes take place in a system, the MSD of the overall system will increase linearly with time. In order to study lattice vacancy diffusion, an ideal crystal model is usually used where one atom has been removed from the crystal. By such an approach first the vacancy formation energy can be determined through a system relaxation procedure at 0K (see section 4.1 and 4.2). Secondly the mono-vacancy migration enthalpy can be obtained by finite temperature MD simulations.

According to analytical theory (see i.e [3], chapter 5) the diffusion coefficient of vacancy migration can be determined in a microscopic atomic-level approach by either monitoring the discrete diffusive vacancy jumps or simply by determining the initial and final position of the vacancy in real space. If the jumps occur statistically which means that any jump direction is as likely as another one, then $\mathbf{R}^2 = n \cdot \lambda^2$ where $\mathbf{R} = \mathbf{r}_{vac}(t) - \mathbf{r}_{vac}(0)$ is a vector pointing from the initial position of the vacancy, $\mathbf{r}_{vac}(0)$, to its final position, $\mathbf{r}_{vac}(t)$, at time t and n is the number of vacancy jumps of average distance λ . Here for a fcc material ideally λ equals the nearest-neighbour distance $r_{NN} = \lambda = \frac{a(T)}{\sqrt{2}}$ where $a(T)$ is the temperature dependent lattice parameter of the material.

According to the CNA method and the detection scheme of vacancies as explained in section 3.5.3 distinct diffusive vacancy jumps can be identified in the atomic systems and hence the lattice vacancy diffusion coefficient according to

$$D = \frac{\mathbf{R}^2}{6 \cdot t} = \frac{n \cdot \lambda^2}{6 \cdot t} \quad (3.60)$$

can be calculated [3]. The carried out MD simulations were done with an ideal crystal of lateral dimension of $8a_o$ in x-, y- and z-direction and applying 3d periodic boundary conditions. Due to the finite size of the simulation box, the vacancy quickly leaves it and is found in image boxes of the original one during later times. To utilize the CNA scheme and to detect the spatial position of the vacancy, all atoms were moved back into the original box by exploiting the 3d periodic boundary conditions. According to this procedure the vacancy position can only be determined in the limits of the original simulation box. Therefore the true vacancy position in real space is not known due to the used re-inserting scheme into the elementary simulation box. Still the vacancy migration diffusion coefficient, D , according to

$$D = \frac{n \cdot \lambda^2}{6 \cdot t} = \frac{\sum_{i=1}^n \lambda_i^2}{6 \cdot t} \quad (3.61)$$

can be calculated. Only the possible calculation on the basis of the initial and final position of the vacancy can not be utilized. In principle one could avoid the re-inserting scheme but then the calculation scheme would get rather complicated.

The abovementioned approach is rather powerful since it is based on the true tracking of the migration of a vacancy by exploiting the CNA scheme. In this work this approach is called direct approach. It even lends itself to study correlation effects of vacancy jumps which is discussed in detail in section 4.1.

Another way to determine the vacancy properties is to analyse the displacement field of all atoms present in the system. Since each vacancy jump corresponds to an atomic jump, one can as well use the MSD information of the overall system's atoms to determine the displacement of the vacancy. Hence the displacement of a single mono-vacancy is given as well by the MSD of all atoms. This analysis scheme is called indirect approach in this work and is utilized when assessing the question of occurring correlation effects. Here it is important to note that in order to calculate the correct MSD data due to atomic jumps during the evolution of the system, no re-inserting of atoms into the original box must be done while calculating the MSD data.

Finally since according to Eq. 3.61, the linear slope of MSD data versus time is proportional to the diffusion coefficient for a given temperature, it can be used within an Arrhenius plot to determine the migration activation enthalpy of a mono-vacancy.

Analysis of GB Diffusion - In this work GB properties are of fundamental interest. Therefore to study GB self-diffusion is of prime interest to get insight into the activation parameters of GB self-diffusion. The chosen calculation scheme within this work relies on the basis of determining only the MSD contribution of GB atoms arising from GB self-diffusion. Usually in literature rather restricted atomic systems are used to study GB self-diffusion [78, 79, 72] usually to suppress GB sliding. It is a common experience that GB sliding usually occurs when utilizing 3d periodic boundary conditions. For the studied GBs this was found very often. Nevertheless all studied GBs were simulated in such a way that GB sliding was still possible. The main driving force to do so is the belief that in real material GB sliding, GB migration and GB self-diffusion always exist simultaneously. Hence in order to study real material behaviour GB sliding was not a-priori suppressed like usually done in literature.

Since GB sliding occurred during almost every conducted GB simulation, a smart analysis procedure of atomic displacements was utilized to determine only the diffusive GB MSD. Usually in the conducted MD simulations every 1000 time steps the position of each atom within the system was stored to be later on analysed. According to this, data analysis on configurations of atoms were possible to be done in time steps usually of 2.76ps. The analysis procedure itself worked in two steps. In step one at time, t , the CNA method was used to classify atoms either being true fcc atoms or not. Any true fcc atom was left out from the GB MSD analysis at time, t , and its instantaneous position was kept to be available as the reference position for the following analysis time step, $t+\delta t$. Non-fcc atoms were now focussed on to calculate the diffusive GB MSD. In order to separate GB sliding displacements from the true GB self-diffusion data, a threshold displacement of $0.35a_0$ was used. Any GB atom having a displacement less than $0.35a_0$ from time $t-\delta t$ to t was considered non-diffusive and did not enter into the calculation of the diffusive GB MSD at time t . Its position at time t was kept to be available as the reference position for the following analysis time step, $t+\delta t$. Only displacements beyond the nearest-neighbour distance were counted diffusive and used to calculate the GB diffusive MSD at time t . If considered diffusive the displacement of that atom was counted to the GB MSD and the position at time t was kept as well to be available as the new reference position for the following analysis time step, $t+\delta t$. According to this scheme only the diffusive MSD of GB atoms was determined. Apart from GB sliding, GB migration events occurred during such simulations as well although no explicit DF had been introduced. Nevertheless the presented analysis scheme was able to separate atomic displacements due to GB migration and GB sliding from the diffusive GB displacement data too.

Once the GB diffusive MSD data is determined, it is possible to determine the GB self-diffusion coefficient, D_{GB} , by exploiting Eq. 3.62 and 3.63

$$MSD(t, t_0) = \frac{SSD(t, t_0)}{N_{GB}} = \frac{1}{N_{GB}} \sum_{j=1}^{N_{GB}} (\mathbf{r}_j(t + t_0) - \mathbf{r}_j(t_0))^2 \quad (3.62)$$

$$D_{GB} = \lim_{t \rightarrow \infty} \left\langle \frac{MSD}{2 \cdot dim \cdot t} \right\rangle_{t_0} \quad (3.63)$$

where SSD represents the summed-square displacement of all true GB atoms. Here dim defines the dimension of the problem or system which is generally either two-dimensional or three-dimensional. $\langle \dots \rangle_{t_0}$ denotes that an average over different time origins t_0 has to

be performed in order to obtain the correct diffusion coefficient. In this work $\dim$ was set to three. The reason for doing so is that at high temperatures the diffusive jumps clearly become three-dimensional and no longer exclusively remain in-plane as is usually assumed in literature [65, 72].

Eq. 3.62 implies that the diffusive GB MSD is normalized to the number of GB atoms, N_{GB} . Unfortunately the definition of the GB region and its width as well as the number of GB atoms is not a simple unambiguous task. Therefore through the following discussion it will be shown that it is not necessary to normalize the GB MSD data directly to the number of GB atoms but rather to the GB area. Hence Eq. 3.62 serves as the starting point to derive the final equation to determine the GB self-diffusion coefficient.

N_{GB} needs to be quantified which can be achieved by approximating N_{GB} through the GB area, A_{GB} , the GB width, δ , and Ω_{fcc} which is the atomic volume of a single atom. The number of GB atoms is given by

$$N_{GB} \approx \frac{A_{GB} \cdot \delta}{\Omega_{fcc}}. \quad (3.64)$$

Furthermore the temporal evolution of the diffusive GB MSD data is expected to be linear in time and so in Eq. 3.63 the average over $\langle \dots \rangle_{t_0}$ becomes irrelevant for the calculation. The final equation for the GB self-diffusion coefficient, D_{GB} , which shall be utilized in this work is then given by

$$\frac{\delta \cdot D_{GB}}{\Omega_{fcc}} = \lim_{t \rightarrow \infty} \frac{\sum_{j=1}^{N^{DGB}} (\mathbf{r}_j(t) - \mathbf{r}_j(t_0 = 0))^2}{A_{GB} \cdot 2 \cdot \dim \cdot t} = \lim_{t \rightarrow \infty} \frac{SSD}{A_{GB} \cdot 2 \cdot \dim \cdot t}. \quad (3.65)$$

Here N^{DGB} represent only the diffusive GB atoms according to the abovementioned selection scheme. As is evident D_{GB} can not be obtained alone rather data on $\frac{\delta \cdot D_{GB}}{\Omega_{fcc}}$ is available. Finally $\frac{\delta \cdot D_{GB}}{\Omega_{fcc}}$ can be obtained by a simple SSD versus time plot where the linear slope or simply the slope multiplied by the factor $\frac{1}{2 \cdot \dim \cdot A_{GB}}$ gives $\frac{\delta \cdot D_{GB}}{\Omega_{fcc}}$.

3.5.3 How to detect vacancies in fcc systems ?

In this section the used detection scheme to identify lattice vacancies in 2d and 3d fcc systems will be presented. The detection scheme can be easily illustrated and understood for a 2d system by utilizing figures of atomic-level configurations. Therefore the 2d detection scheme will be discussed first. Figure 3.10 shows a 2d fcc system containing a GB and two lattice vacancies in the vicinity of the GB⁵. The shown atomic configurations lends itself to explain the detection scheme in more detail.

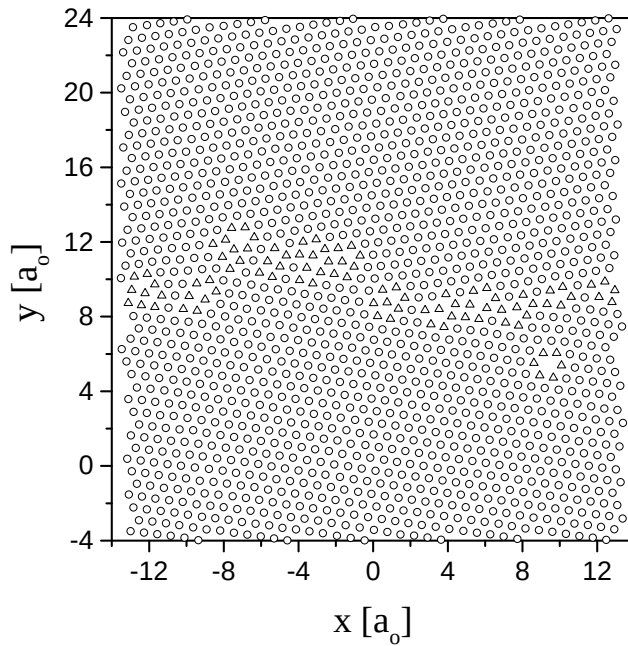


Figure 3.10: Detection scheme for vacancies in planar 2d systems : Snapshot is taken from a Σ 49 (385) tilt GB simulation⁵ at 1100K and a orien.-corr. DF of about 0.0025 eV/atom. Two species of atoms are plotted, namely species one which is identified by a circle and which represents true (111) atoms characterized by having six (200) triplets. All non true (111) atoms are related to the second species of atoms and identified by the uptriangle. The figure contains two vacancies in the vicinity of the GB. The vacancy above the GB is in the process of being emitted from the GB while the one below the GB has been emitted already some time ago.

A lattice vacancy is found as follows. The detection scheme is based on the principles and ideas of the CNA method which only need to be adapted for the 2d hexagonal situation. In analogy to the 3d fcc situation, an atom located in an ideal 2d hexagonal environment is surrounded by six nearest neighbours. With each of these six neighbours the center atom shares (200) triplets according to CN terminology. Thus any atom having six nearest neighbours with only (200) triplets is located in an ideal hexagonal site. All atoms having

⁵This example of a GB in a 2d system was taken from studies by the author on GBs in 2d systems. Non of the data will be presented in this work or has been published. Here it should only illustrate the detection scheme to identify vacancies in GB or ideal fcc crystal systems.

such relations with their nearest neighbours are associated with the class of ideal fcc (111) plane atoms. All remaining atoms that do not satisfy this selection rule are attributed to a second class of non ideal fcc atom. This classification into only two species of atoms is rather simple, nevertheless it is rather efficient for our purposes. Figure 3.10 shows a rather typical situation found quite often in the vicinity of planar 2d GB systems. As described before two different classes of atoms are marked, namely ideal fcc (111) atoms marked by a circle and all others by uptriangles. The figure shows that lattice defects like GBs and vacancies are surrounded by atoms of species two of non ideal fcc atoms. Lattice vacancies have a rather characteristic configuration of class two atoms surrounding them. This in turn can be used to detect them by a detection algorithm. As figure 3.10 demonstrates a lattice vacancy is surrounded by six nearest neighbours of class two. The position of the vacancy is determined by the center of mass of the surrounding six non ideal fcc atoms. The used detection scheme to find 2d lattice vacancies relies on the fact that six non ideal fcc atoms surround the vacancy in such a way that the center of mass of the six atoms defines the position of the vacancy and all six surrounding atoms have a nearest neighbour relationship with the position of the vacancy. According to this scheme the upper vacancy in figure 3.10 was detected which represents the situation where a vacancy is being emitted from the GB. In the presented simulations of this work, GBs are the only sources and sinks for vacancy generation and annihilation. The working procedure to find vacancies within the systems is first to classify all atoms within the system either belonging to class one or two and then to study the configurations of all class two atoms.

One should note here that the described detection scheme is only capable of detecting vacancies in their ideal equilibrium configuration of rest. Within the performed simulations one usually observes metastable configurations of vacancies that are associated with vacancy migration and which can not be identified by the discussed scheme. Of course it would make sense even to check for such metastable vacancy states, but since only certain configurations could then be detected again it would make much more sense to implement a detection scheme for free volume within the atomic-level system. Nevertheless the described scheme is good enough to identify lattice vacancies within the studied simulations, since vacancy migration is on the atomic-level scale a discontinuous process where vacancies rest at their equilibrium site for some time before a jump to a neighbouring lattice site occurs.

The presented detection scheme can be easily adapted for the 3d fcc lattice. Here one only has to consider that a lattice vacancy in a 3d system is surrounded by 12 nearest neighbours of non ideal fcc type of atoms. Other than that the same principles and restrictions of the 2d case apply to the 3d case as well.

Chapter 4

Properties of Lattice Mono-Vacancies

In this section the vacancy properties of the used potentials shall be presented and discussed in some detail. According to the literature vacancies may be considered as very important defects in the framework of GB migration. This is especially true for migration of curved GBs, hence here the decrease of GB volume during migration should result in the emission of freed volume at the GB and hence should result in vacancy formation during GB migration [34]. Additionally in present atomistic modelling of GB migration, vacancies are the only real defects that can simply be included in GB systems. Even more important GBs act as sources and sinks for vacancies which implies that vacancies can in principle be introduced into the systems through the GBs. This idea applies to static GBs at very high temperatures as well as for GBs during GB migration. Since this implies that vacancies indeed may play an important part in GB migration and atomic-level simulation of GB migration it seems important to study the behaviour and properties of mono-vacancies in some detail to understand and know their intrinsic key parameters. Furthermore when discussing the activation enthalpy of GB migration and GB self-diffusion it is worth while knowing the reference data on lattice self-diffusion as well.

The following results will prove that mono-vacancy migration can be well studied by atomic-level simulations and that vacancy jump events and migration parameters can be extracted from the raw simulation data utilizing the CNA method as described in section 3.5.3. The underlying theory and analysis schemes are laid out in the following sections and have been briefly discussed in section 3.5.2.

4.1 Cu EAM Potential

Physical interesting and important properties of the Cu EAM potential as well as in the framework of GB migration are the vacancy formation and vacancy migration enthalpy. Note that the vacancy formation energy was used to fit the potential and that its value was determined by a $T=0\text{K}$ simulation. Its value is 1.30335 eV as given in the original paper [44]. This energy equals the excess energy of an ideal crystal missing one atom with respect to a perfect ideal crystal system having the same number of atoms as the vacancy system. For the quoted value of 1.30335 eV no relaxation of the system was included which usually will occur and which should be taken into account. Allowing for individual atoms

to relax the vacancy formation enthalpy is slightly smaller than for the unrelaxed situation and was determined here to be 1.24694 eV. Thus it is found that the relaxation of the system does not dramatically lower the formation energy. In this context one should note that in order to fit the potential a rigid lattice description of an ideal crystal lattice is used. Including individual atom relaxations within the fitting procedure of the overall potential seems possible but will most likely be much more complicated than the rigid perfect lattice case.

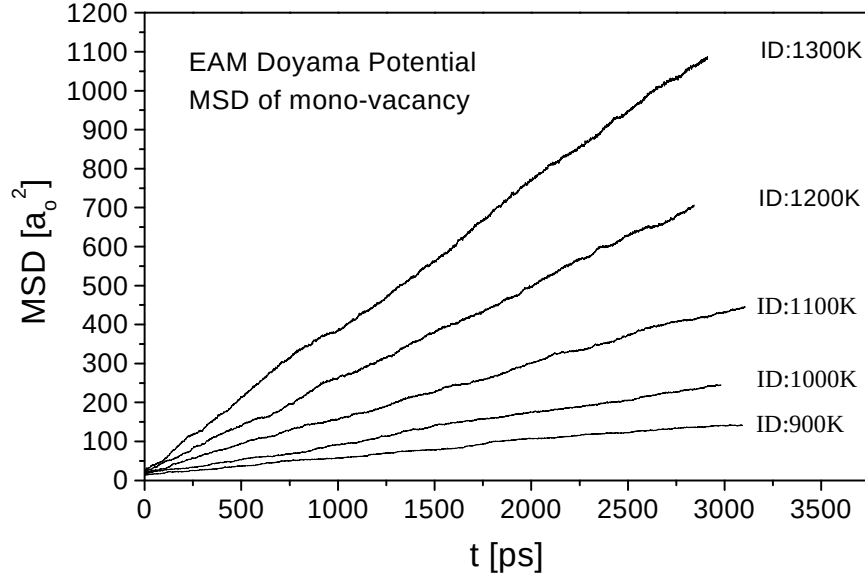


Figure 4.1: Temperature dependence of the MSD of a mono-vacancy system versus time. Here the data determined by the indirect approach is shown for 900, 1000, 1100, 1200 and 1300 K.

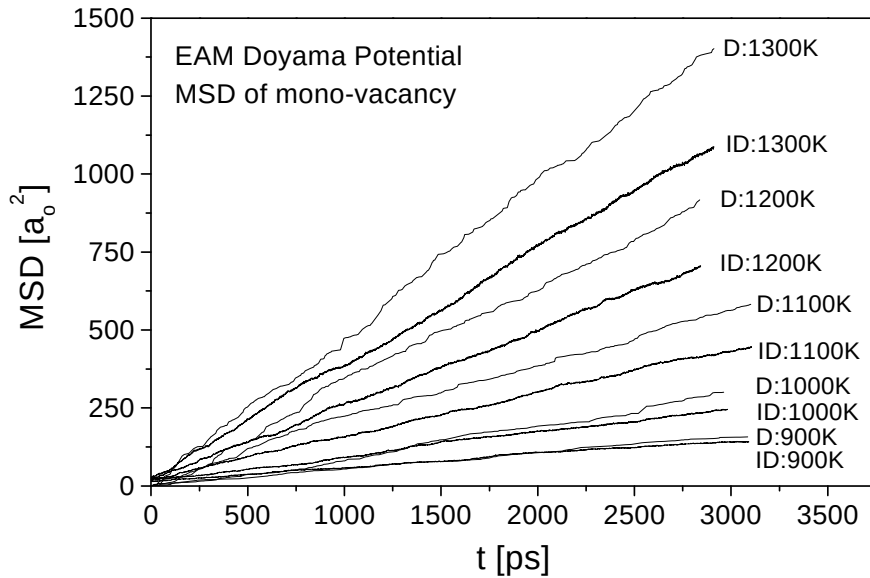
Of further interest is the vacancy migration enthalpy. It was determined by MD simulations at different temperatures of an ideal crystal containing a single mono-vacancy. According to diffusion theory the vacancy migration enthalpy can be obtained by the analysis of the mean-square-displacement (MSD) of the total system (see i.e [3], chapter 5). It is well-known that if diffusive processes take place in a system, the MSD of the overall system will increase linearly with time. In the mono-vacancy case the linear increase of the MSD of the overall system is simply caused by the individual jumps of the mono-vacancy. These discrete jumps can be monitored and by determining $n \cdot \lambda^2$ where n is the number of vacancy jumps and λ is the average jump distance at a given temperature one should be able to calculate the diffusion coefficient of vacancy migration from a microscopic point of view. Here for a fcc material ideally λ would be equal to the nearest-neighbour distance $r_{NN} = \lambda = \frac{a(T)}{\sqrt{2}}$ where $a(T)$ is the temperature dependent lattice parameter of the material. Furthermore the relation $n \cdot \lambda^2 = \sum_{i=1}^n \lambda_i^2$ only holds if indeed each individual vacancy jump can really be monitored throughout the MD simulations. Since in long-term MD simulations only a fraction of the accessible data can be stored or analysed during the runs, for runs at higher temperatures there is a high chance that no longer each individual vacancy jump can really be observed and that therefore only the occurrence of several consecutive jumps events can be identified. In this case $\sum_{i=1}^n \lambda_i^2$ would slightly differ from $n \cdot \lambda^2$. Indeed this behaviour is found in our data and is illustrated by the presented data in Tab. 4.1 as well as by

Fig. 4.3. If the jumps occur statistically which means that any jump direction is as likely as

T [K]	$r = \frac{A_D}{A_{ID}}$	total no. of jumps	correlated jumps	total no. of stored boxes
900	1.235	304	9	1120
1000	1.228	579	13	1080
1100	1.397	1126	11	1125
1200	1.326	1800	1	1030
1300	1.313	2770	5	1055

Table 4.1: Results of the MSD jump analysis for mono-vacancy jumps

another one, then $n \cdot \lambda^2$ should equal the well-known term $\mathbf{R}^2$ where $\mathbf{R} = \mathbf{r}_{vac}(t) - \mathbf{r}_{vac}(0)$ is a vector pointing from the initial position of the vacancy, $\mathbf{r}_{vac}(0)$, to its final position, $\mathbf{r}_{vac}(t)$, at time t . Therefore under ideal conditions the MSD of a single mono-vacancy is given by $MSD = n \cdot \lambda^2 = (\mathbf{r}_{vac}(t) - \mathbf{r}_{vac}(0))^2$. The slope of a MSD versus time plot is then proportional to the diffusion coefficient for a given temperature and it can be used within an Arrhenius plot to determine the migration activation enthalpy of a mono-vacancy. Fig. 4.1 presents the simulated MSD versus time plots at various temperatures for the Cu EAM potential. The MSD data of Fig. 4.1 intersects the vertical axis at a positive finite value since each of these runs was slowly taken to the desired temperature by several equilibration runs at lower temperatures. These prior runs caused this offset and for simplicity these offsets were not subtracted from the actual curves since for the linear curve fit a general linear fit equation was utilized in order to determine the exact slope of the curves. It is

**Figure 4.2:** Temperature dependence of the MSD of a mono-vacancy system versus time. Here the data determined by the indirect method (see label ID) and the direct data (see label D) are shown.

noteworthy that indeed the MSD increases linearly with time. This is true for the MSD data obtained by the analysis of the initial and final positions of atoms within the overall

system (this approach is called indirect approach and identified by the label ID) as well as by identifying individual vacancy jumps utilizing the CNA method and summing over all individual vacancy events occurring within the system over time (this approach is called direct approach and identified by the label D)¹. As can be seen from Fig. 4.2 the MSD data obtained by these two different approaches exhibits some difference which shall be illustrated now. It appears that the data obtained by the direct method is always higher than that of the indirect one. One possible explanation for this occurrence could in principle be connected to the correlation effect of individual vacancy jumps. Therefore while analysing the raw data it was checked for correlation events and their number of occurrence was counted. Indeed correlation events were observed and for low temperatures the number of correlation events increased with temperature while for the highest temperatures it decreased again. The results of this analysis are listed in Tab. 4.1. Here r represents the ratio of the MSD slope of the direct method, A_D to the MSD slope of the indirect method, A_{ID} . Taking into account the correlation effect for mono-vacancy jumps the ratio of the slope of the raw direct MSD data to the slope of the indirect MSD data should ideally equal $1.2 = (1 - \frac{2}{z})^{-1}$, where z is the coordination number which is equal to 12 for a fcc system (see i.e. [3], pp. 165). Checking the listed data in Tab. 4.1 for r one finds that r simulated is in very good agreement with theory for the lower temperatures while for the higher temperatures a higher value of 10 to 15 percent than theoretically expected one is found. This remaining discrepancy can only be understood in terms of a poor statistics of the simulated data. Referring to Tab. 4.1 two conclusions can be drawn from the listed data that are able to underline this point. The first one concerns the frequency of storing box data. Here one has to remember that only a fraction of the accessible data can be stored or analysed while running the MD code. Thus it seems that the used storing rate of a box per 1000 time steps is too small to identify accurately correlated individual vacancy jump events. This is even more true for the high temperatures. Indeed Tab. 4.1 demonstrates that the number of vacancy jumps within the

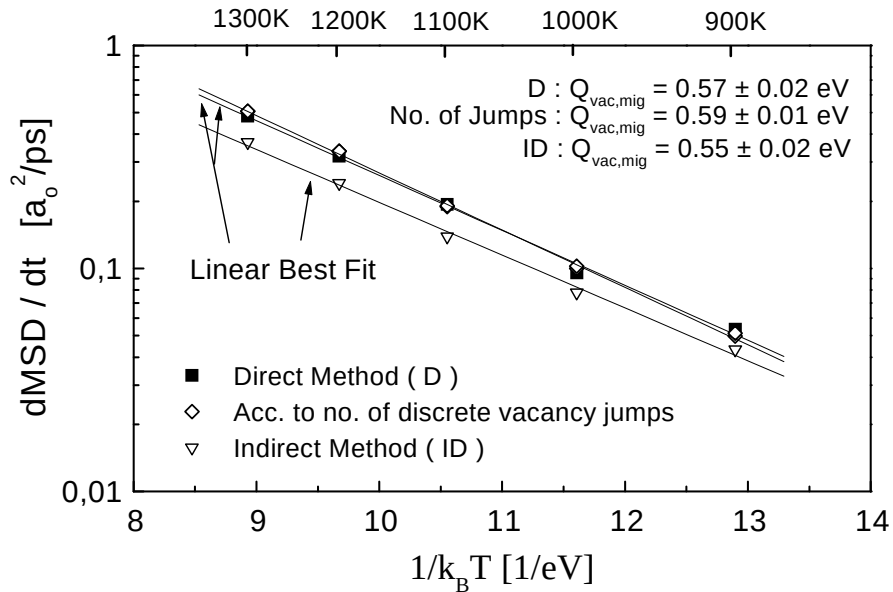


Figure 4.3: Arrhenius Plot to determine the migration activation enthalpy of a mono-vacancy for the Cu EAM potential

¹The underlying concepts of the indirect and direct method are explained in section 3.5.2.

time window of a 1000 time steps on average is more than one for the high temperature runs. Even for the 900K run a comparison of the total number of vacancy jumps to the correlated jumps shows that only three percent are correlated although according to the theory they should be about nine percent. Therefore extracting correlation events from the stored data does not work reliably under the mentioned conditions which can for instance be associated with the fixed time interval used for storing the box data. To avoid errors in the data analysis it even seems reasonable to use the overall data for the direct approach since the ratio of correlation events to true vacancy jumps should be temperature independent. Thus it should not affect the determination of the migration activation enthalpy since in an Arrhenius plot this effect should then only lead to a higher pre-exponential factor. Finally an Arrhenius plot of the MSD data obtained by the indirect approach, direct approach and by calculation $n \cdot \lambda^2$ is shown in Fig. 4.3. All three data sets are well represented by linear curve fits. According to the linear data fit one finds an activation enthalpy for mono-vacancy migration of $Q_{mig,vac}=0.55 \pm 0.02$ eV for the indirect data, $Q_{mig,vac}=0.57 \pm 0.02$ eV for the direct data and $Q_{mig,vac}=0.59 \pm 0.01$ eV for the $n \cdot \lambda^2$ data. Furthermore as has been discussed above the correlation effect does not affect the magnitude of the activation enthalpy for mono-vacancy migration and only shifts the data points to higher values with respect to the indirect approach.

4.2 Cu 3d LJ Potential

Here the mono-vacancy properties of the Cu 3d LJ potential shall be presented and discussed in detail. First let us focus on the vacancy formation energy for this potential. For the unrelaxed situation its value is simply equal to the cohesive energy per atom since for simple pair potentials $V(r_{ij})$ like the LJ potential one can show that removing an atom from a rigid perfect ideal crystal system results in a reduction of the total potential energy of that system by twice the cohesive energy per atom. Mathematically expressed it means that an energy decrease equal to $\sum_{i=1}^N V(r_{ij})$ occurs where j is the label of the later on removed atom from the system and i runs through all the neighbours of atom j . Furthermore we know that the relation $\sum_{i=1}^N V(r_{ij}) = 2 \cdot e_{coh}$ holds. Therefore if one removes one atom from a N atom perfect ideal crystal and calculates the energy of this mono-vacancy system assuming a rigid lattice, the mono-vacancy system's energy would be given by $E_{mono-vac} = (N - 2) \cdot e_{coh}$. To determine the vacancy formation energy one then has to calculate the energy of a perfect ideal crystal containing $(N-1)$ atoms which is $(N - 1) \cdot e_{coh}$. Finally this yields $(N - 1) \cdot e_{coh} - (N - 2) \cdot e_{coh} = e_{coh}$ as being the vacancy formation energy for a perfect rigid ideal crystal system. Thus for the Cu 3d LJ potential the mono-vacancy formation energy is equal to 1.037824 eV in the case of an unrelaxed system. As stated already in sect. 4.1 individual atom relaxation occurs always which leads to a reduction of the vacancy formation energy. Performing a zero Kelvin relaxation simulation for a mono-vacancy system one finds that the vacancy formation energy is 1.031688 eV which is 0.9941 times the cohesive energy for the used 3d LJ potential. Again by analysing the temporal evolution of the MSD of the total system the migration activation enthalpy can be determined. Fig. 4.4 shows the results for four different temperatures. Since in sect. 4.1 a very detailed discussion and presentation was given here only the key parameters shall be presented. Thus Fig. 4.4 only contains the direct MSD data which was calculated directly by observing individual vacancy jumps and without considering correlation effects. Performing

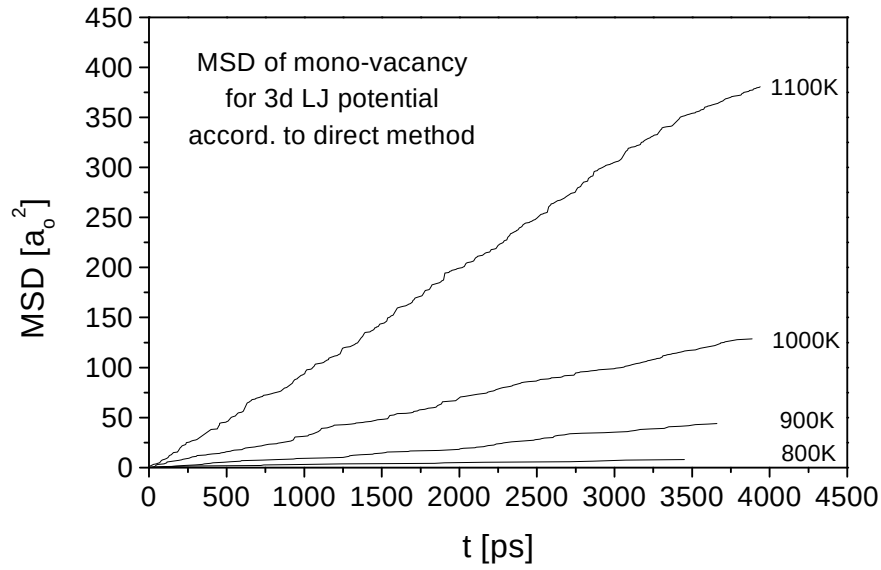


Figure 4.4: Temperature dependence of the MSD of a mono-vacancy system versus time. Here the data determined by the direct approach is shown for 800, 900, 1000, and 1100 K.

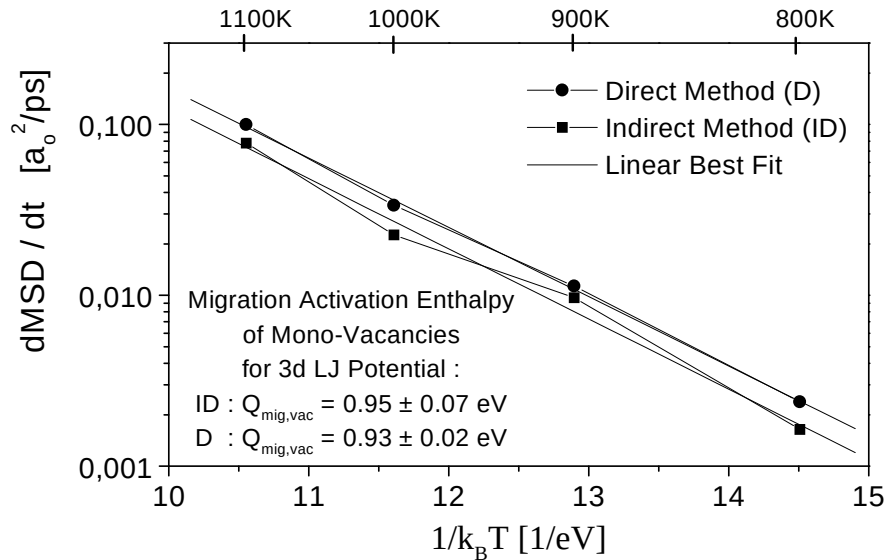


Figure 4.5: Arrhenius Plot to determine the migration activation enthalpy of a mono-vacancy for the Cu 3d LJ potential.

standard linear least square fits of these curves we yield the temperature dependence of the linear increase of the MSD with time. This data is presented in Fig. 4.5 by an Arrhenius plot. Here the results for the indirect (ID) and direct (D) approach of MSD data analysis are plotted which again demonstrates that the direct data is only shifted by a fixed amount to higher MSD values. A linear least square fit of the Arrhenius plot yields an activation enthalpy for mono-vacancy migration for the Cu 3d LJ potential of about 0.94 ± 0.02 eV. This result is in good agreement with data obtained from zero-temperature lattice-statics relaxations for vacancy migration as determined by Wolf (see [64]) where the migration activation enthalpy of a mono-vacancy for the same Cu 3d LJ potential was found to be 0.88 eV.

4.3 Summary

Finally the obtained results for the mono-vacancy formation enthalpy, $Q^{Form.}$, as well as for the mono-vacancy migration enthalpy, $Q^{Mig.}$, in the fcc bulk are summarized here for the applied interatomic potentials. As well the experimental data for Cu according to Balluffi [75] is included. Tab. 4.2 lists the data. For the formation enthalpy, $Q^{Form.}$, it was distinguished between relaxed and unrelaxed formation data. The details of this aspect can be found in the preceding section on the EAM and LJ potential. Overall there is good data

	$Q^{Form.}$ [eV]	$Q^{Mig.}$ [eV]	$Q=Q^{Form.}+Q^{Mig.}$ [eV]
LJ 3d	$1.037824^{unrelaxed}$	0.94	1.977824
	$1.031688^{relaxed}$		1.971688
EAM	$1.30335^{unrelaxed}$	0.57	1.87335
	$1.24694^{relaxed}$		1.81694
Wolf	$1.037824^{unrelaxed}$	0.88	1.917824
	$1.031688^{relaxed}$		1.911688
Experiment [75]	1.26	0.72	2.01

Table 4.2: Summary of activation parameters of lattice mono-vacancies.

agreement between the simulation data and the experimental data. The data of the EAM potential matches the experimental data better than the data of the LJ potential, still the LJ data is not too far off from the experimental one. This is especially true for the sum of the activation enthalpies, Q , where the LJ and the experimental data almost coincide.

Chapter 5

Results of three-dimensional [001] Twist GBs

5.1 Relaxed GB Structure of the studied [001] Twist GBs

5.1.1 General Remarks on the GB Relaxation Procedure

General aspects and quantities of the studied [001] twist GBs and the performed simulations are presented and discussed in this section. Almost all results on GB migration and GB self-diffusion of planar [001] twist GBs presented in this work were obtained by utilizing the 3d LJ potential and applying a 3d periodic boundary concept. For the GB migration simulations due to an orientation-correlated DF different boundary concepts and different atomistic potentials were applied. This is especially true for the GB migration and GB self-diffusion simulations of the $\Sigma 5$ [001] twist GB. Here in addition to the performed 3d LJ simulations, further simulations were done by utilizing the Cu EAM potential of Doyama and Kogure and by applying two different free (002) surface boundary concepts. The exact details on the simulation conditions are given in the appropriate sections dealing with these topics. Here only GB properties connected to the 3d LJ potential are reported since these represent the GB properties very well even with respect to more sophisticated interatomic potentials [71]. The following statements on the relaxation procedures are more general and apply therefore to any utilized interatomic potential.

The GB properties and atomic-level structures of fully relaxed GB systems were obtained by performing lattice-statics (LS) simulations according to the steepest gradient method. These zero Kelvin relaxation simulations are necessary for most GBs due to their strictly geometric CSL generation scheme. The must to perform such simulations is simply explained by the fact that most GBs differ in their equilibrium structure to quite some extent from the strictly geometrical CSL GB structure. A simple but important feature of equilibrated GBs is the so-called volume expansion, ΔV^{GB} . Wolf [71, 69] found that the volume expansion is proportional to the GB energy and therefore a key parameter of any GB. The volume expansion represents the tendency of a GB to expand or shrink in the direction of the GB normal. This is the case since for all performed simulations the in-plane dimensions of the CSL GBs were held fixed. A straightforward explanation for this procedure is simply that the lattice parameter of the bulk regions within the system need to have ideal crystal

properties. If the in-plane dimensions of the GB box would be allowed to adjust to the GB normal stresses, the lattice parameter of the bulk regions would deviate from the ideal crystal value and hence no true bulk regions would be present in the system. That a strictly geometric CSL GB structure can be the equilibrium structure is best exemplified by the Σ 3 coherent twin GB since for this case the strictly geometric CSL GB structure represents almost perfectly the equilibrium structure of this GB. Generally this is not the case, which therefore requires static relaxation simulations to be performed on the strictly geometric CSL initial structures. If MD simulations were performed on unrelaxed high energy GBs with a fixed finite time steps of i.e. 1.84fs¹, the time integration scheme would fail to yield the true atomistic trajectories of each atom which would lead to a crash of the MD simulation run and destruction of the crystalline GB system. Thus initially performing LS simulations when dealing with GB systems is very important in order to yield fully or partially relaxed GB systems that can be used as input structures for MD simulations. Furthermore key parameters of the GBs like the GB energy and the volume expansion can be obtained from these runs.

In the case of [001] twist GBs a sequence of LS simulations was sufficient to yield fully relaxed GB properties. This is remarkable because for any of the studied tilt GBs a combined LS/MD strategy had to be used to finally yield relaxed GBs. When performing only a sequence of LS simulations for the tilt GBs, the GBs were not able to reach their equilibrium structures and remained in metastable GB states. The reason for this behaviour is most likely connected to the fact that in contrast to the usual procedure in the literature to apply explicit rigid block translations to the adjacent crystals of the bicrystal to identify the microscopic translation vector, no explicit rigid block translation simulations were carried out on the GB systems within this work to find the appropriate microscopic in-plane components of the translation state of the GBs. The underlying philosophy within this work was that if necessary these translation states components would be identified and achieved by a combined LS/MD relaxation strategy. The main idea behind this concept is that at finite temperatures the GB should be able to find its equilibrium state if a sufficient temperature is applied to the system. This mentioned aspect plays an important role for the relaxation procedure of tilt GBs since for all studied tilt GBs within this work it was necessary to perform finite temperature simulations that allowed the GBs to select their appropriate microscopic translation state at the GB even without performing rigid block translation simulations. This was achieved by combining LS and MD simulations at intermediate temperatures. Such a relaxation procedure of course implies that the equilibrium GB structure at intermediate or high temperatures even represents the fully relaxed GB structure at 0K. Of course the same applies to the zero Kelvin relaxation procedures of GBs. If so the GBs should obtain their equilibrium structure if equilibrated at finite temperature even when starting off with only a partially relaxed GB structure. Of course the reader should note that all simulations to obtain fully relaxed GBs were done in several simulation steps with either gradually changing coefficients within the LS relaxation and slowly increasing as well as decreasing annealing steps with the sequence of applied MD simulations.

In the following section 5.1.2, the atomistics of the studied [001] twist GBs is presented to illustrate the relaxation occurring at the GBs as well as to suggest possible in-plane mechanisms of GB migration for the different GBs. Tab. 5.1 presents data on the volume expansion of the studied [001] twist GBs which demonstrate that the equilibrium GB structure indeed

¹This time step and 2.76fs were used throughout most of the GB migration simulations.

GB plane	θ	Σ	$E^{GB} [\frac{J}{m^2}]$	No. of CSL cells	$\Delta V^{GB} [a_o]$
(001)	43.60°	29	0.716	1;4	0.12204
(001)	36.87°	5	0.715	9	0.12080
(001)	28.07°	17	0.700	4	0.11623
(001)	22.62°	13	0.677	4	0.11144
(001)	16.26°	25	0.625	2	0.10350
(001)	12.68°	41	0.582	1	0.09801
(001)	8.80°	85	0.490	1	0.08517
(001)	6.03°	181	0.404	1	0.07324

Table 5.1: General information on the [001] twist GBs. The table includes the misorientation angle, θ , the GB energy, E^{GB} , the x-y planar dimensions of the studied GB systems, namely the number of CSL cells within each (002) plane and finally the volume expansion of the GBs, ΔV^{GB} .

differs from the strictly geometric CSL structure even for twist angles as low as 6.03° . Furthermore in section 5.1.2 the GB screw dislocation network is presented and discussed for a few of the GBs.

5.1.2 Atomistic Structure of the Relaxed [001] Twist GBs

Here the atomistic structure of the studied [001] twist GBs is presented. Since the atomistics of twist GBs is difficult to visualize the situation within (002) planes facing each other at the GB is used to gain insight into the atomic-level situation. In this work this type of data presentation is referred to as in-plane data plots. It is accomplished by showing the closest A-type (002) planes of either of the two grains in one plot. This is done to illustrate two aspects. The first one is to show to what extent atomic-level relaxation had occurred in the vicinity of the GBs. This can for instance be estimated by the coherency of the CSL points of the relaxed GB structures of either A-type or B-type planes of either of the two grains in the vicinity of the GBs. The second aspect is connected to GB migration itself and its atomic-level mechanism. Already these simple plots of the in-plane situation of A-type (002) planes right at the GB can give a hint on what could be the atomic-level mechanism of these GBs. The exact atomistic situation of the $\Sigma 29$, $\Sigma 5$, $\Sigma 17$, $\Sigma 13$, $\Sigma 25$, $\Sigma 41$, $\Sigma 85$ and $\Sigma 181$ twist GB is given by the figures 5.1 up to 5.8 respectively. An interesting aspect when inspecting these plots is that if intuitively one would connect each atom of orientation A with its closest neighbour of orientation A' one would get a displacement plot that suggests atomic displacements to change from orientation A to A' or vice versa. This of course implies that each plane could in principle change its orientation solely by in-plane displacements of the atoms. Interestingly even the largest displacement vectors of these displacement fields are in all cases much less than the NN-distance. Since the planar spacing of the (002) planes is $d_{(001)} = 0.5a_o$, diffusive jump events through the GB should range at least from $0.5a_o$ up to the NN-distance. This view might suggest that the actual atomic-level displacement during GB migration should proceed within the (002) planes rather than by jumps events from neighbouring planes due to the much shorter displacement vectors. This rather geometric viewpoint is unfortunately a little bit too simplified since actually the energy barrier an

atom is experiencing on its path will decide whether or not certain displacements actually occur. Furthermore the atoms' displacement field within i.e. an A-type plane at the GB is a three-dimensional problem which is strongly connected to the neighbouring B-type and B'-type plane that surround the A-type plane in a sandwich-like situation. Only if the displacement vectors comply with these neighbours their actual realization within the actual simulations is conceivable. Nevertheless even the mentioned rather geometric view on GB migration can give some guidance to identify the actual GB migration mechanism within the finite temperature MD simulations. Furthermore suggesting such an approach the main underlying idea is founded on two basic assumptions, namely that the GBs have a strong crystalline nature as shown by the figures of the 0K situation even at very elevated temperatures and furthermore that any atomic displacement due to GB migration would only occur within (002) planes. It is obvious that both assumptions will be violated at high temperatures, but these rather geometric consideration can already pinpoint at processes taking place within the GBs at low and intermediate temperatures.

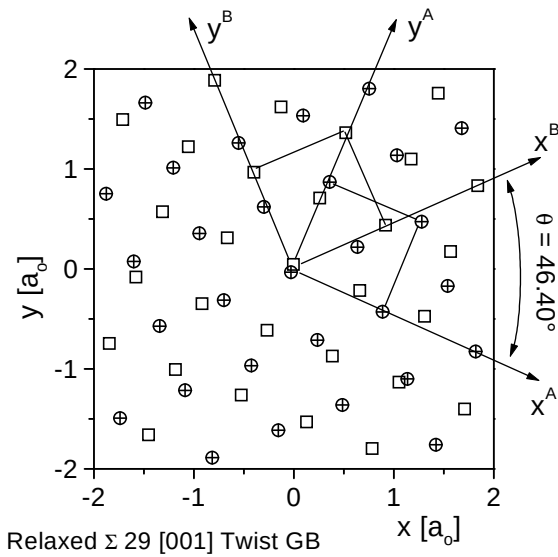


Figure 5.1: Atomistics of the $\Sigma 29$ [001] 43.60° twist GB. Here the closest A-type (002) planes facing each other at GB₂ are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

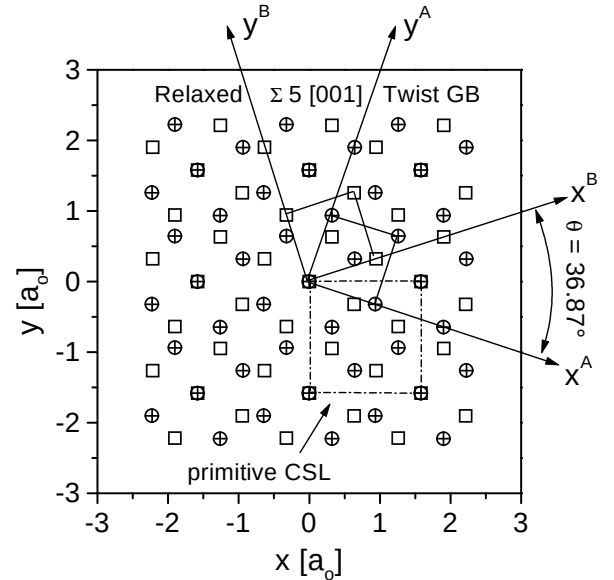


Figure 5.2: Atomistics of the $\Sigma 5$ [001] 36.87° twist GB. Here the closest A-type (002) planes facing each other at GB₂ are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

Next a short discussion on the primitive in-plane CSL cell dimensions follows. For [001] fcc twist GBs one finds theoretically that the following relation holds for the volume of the primitive CSL cell, V_{CSL} , namely

$$\Sigma \cdot \Omega = V_{CSL} = d_{(001)} \cdot A_{CSL} = \frac{1}{2} a_o \cdot A_{CSL} = \Sigma \cdot \frac{a_o^3}{4} \Leftrightarrow A_{CSL} = \Sigma \cdot \frac{a_o^2}{2}$$

In general this means that the in-plane CSL area, A_{CSL} , is given by $A_{CSL} = \mathbf{a}_{CSL} \cdot \mathbf{b}_{CSL}$ where $\mathbf{a}_{CSL}$ and $\mathbf{b}_{CSL}$ are the in-plane CSL vectors. Assuming a square for the in-plane

CSL cell, the in-plane area A_{CSL} is related in a simple manner to the magnitudes of the in-plane CSL vectors, a_{CSL} and b_{CSL} , and one finally finds

$$A_{CSL} = \sqrt{\frac{\Sigma}{2}} \cdot a_o \cdot \sqrt{\frac{\Sigma}{2}} \cdot a_o \Leftrightarrow a_{CSL} = b_{CSL} = \sqrt{\frac{\Sigma}{2}} \cdot a_o$$

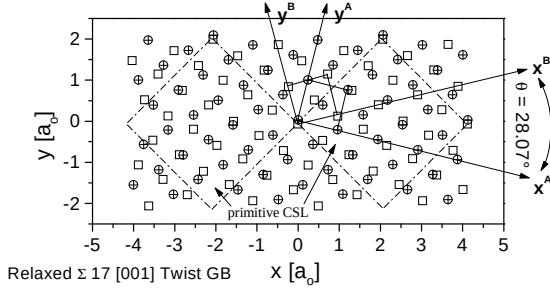


Figure 5.3: Atomistics of the $\Sigma 17$ [001] 28.07° twist GB. Here the closest A-type (002) planes facing each other at GB_2 are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

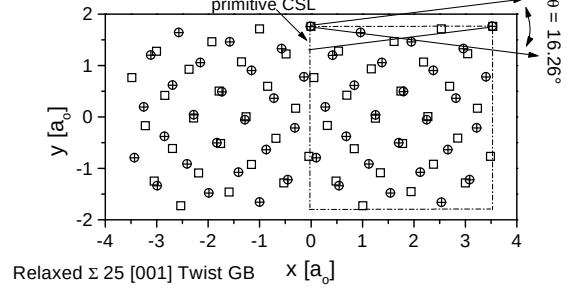


Figure 5.4: Atomistics of the $\Sigma 25$ [001] 16.26° twist GB. Here the closest A-type (002) planes facing each other at GB_2 are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

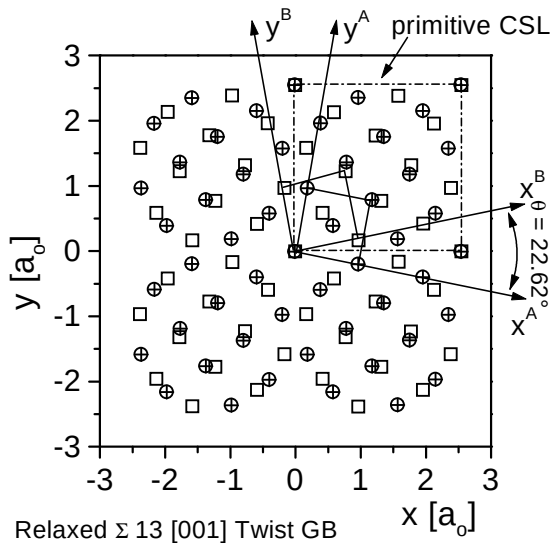


Figure 5.5: Atomistics of the $\Sigma 13$ [001] 22.62° twist GB. Here the closest A-type (002) planes facing each other at GB_2 are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

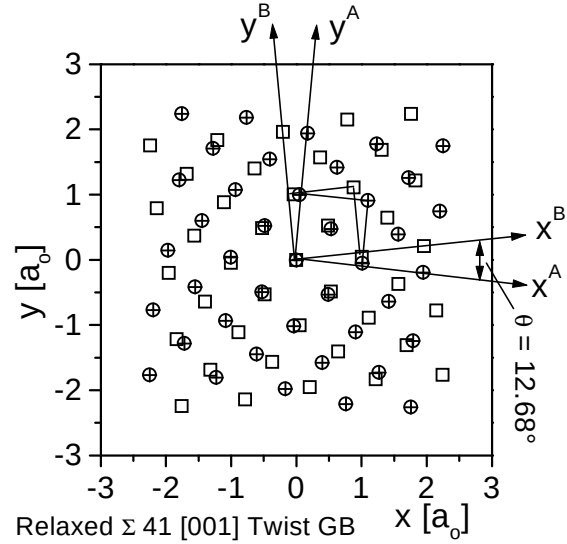


Figure 5.6: Atomistics of the $\Sigma 41$ [001] 12.68° twist GB. Here the closest A-type (002) planes facing each other at GB_2 are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

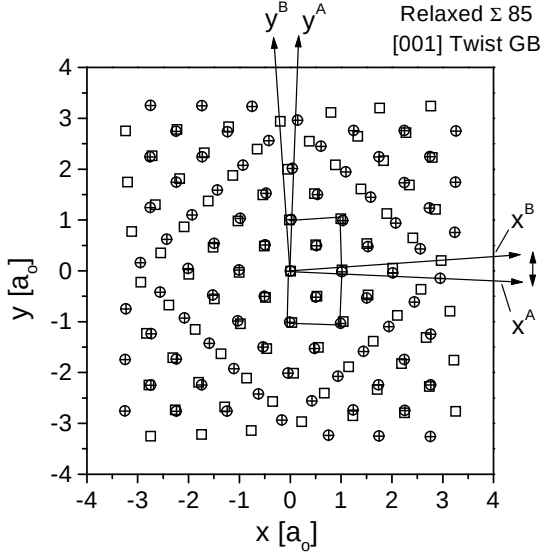


Figure 5.7: Atomistics of the $\Sigma 85$ [001] 8.80° twist GB. Here the closest A-type (002) planes facing each other at GB_2 are plotted. Atoms within plane A of grain A are given by filled circles while the atoms within plane A' of grain B are given by squares.

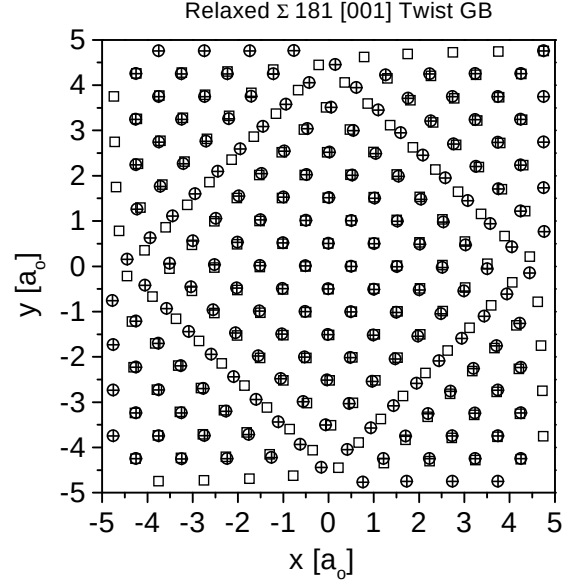


Figure 5.8: Atomistics of the $\Sigma 181$ [001] 6.03° twist GB. Here the closest B-type (002) planes facing each other at GB_2 are plotted. Atoms within plane B of grain A are given by filled circles while the atoms within plane B' of grain B are given by squares.

Next the screw dislocation content of the twist GBs is discussed. First of all symmetry aspects of the (002) plane are presented which concern the CSL pattern and the alignment of the screw dislocation network with respect to the simulation box coordinate system. As has been explained in section 3.3.6, a bicrystalline simulation box is generated in such a way that the GB normal is parallel to the z-direction of the simulation box and that the lower grain is misoriented by $-\theta/2$ and the upper grain by $+\theta/2$. Due to the symmetry of the (002) plane, the same Σ [001] twist GB is represented by two different twist angles. One is θ , the second one is $90^\circ - \theta$. Both twist angles will generate the same [001] twist GB. The only difference between these two GBs is their alignment with the chosen simulation box coordinate system. This is demonstrated by figures 5.9 and 5.10 for the $\Sigma 85$ twist GB. In the figures only non-ideal fcc atoms according to the CNA method are plotted for the LJ 3d periodic BC system. These atoms that were identified by the CNA method as non-ideal fcc atoms represent the GB screw dislocations forming the two GBs present in the system. The empty space between the GB screw dislocations is filled with atoms being ideal fcc atoms. Hence in those regions the lattice continues across the GB and is only slightly elastically distorted. The CSL points of the GB are in the center of the fcc regions. The reader should note that the figures show the GB screw dislocation networks of both GBs.

Two main aspects are different for the two $\Sigma 85$ twist GB simulation boxes. The first one is that the CSL pattern looks different. Of course the CSL pattern is unique and its pattern of GB box one can be transformed into that one of GB box two by a 45° [001] rotation. The second aspect is that the alignment of the screw dislocation network is different with respect to the x-y simulation box coordinate system. In the 8.797° case they are aligned under about 45° with respect to the x-y-z box coordinate system. For the 81.203° case they

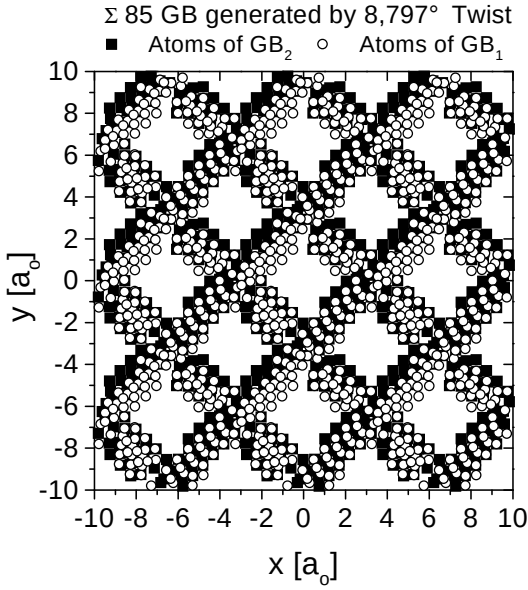


Figure 5.9: Screw dislocation network of the $\Sigma 85$ $[001]$ 8.797° twist GB

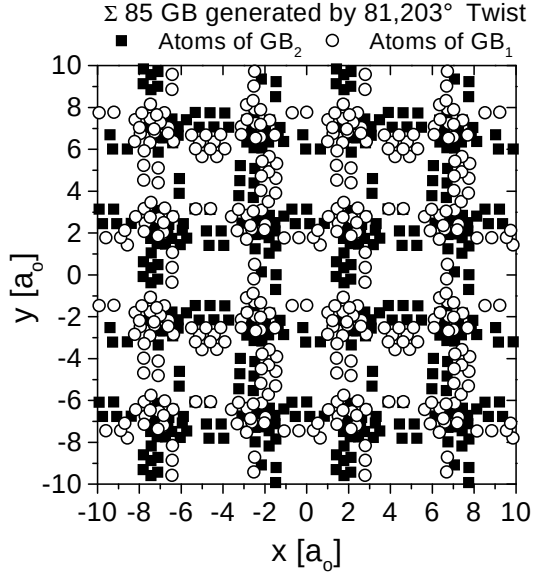


Figure 5.10: Screw dislocation network of the $\Sigma 85$ $[001]$ 81.203° twist GB

are almost parallel to the x-y-z box coordinate system.

Therefore two $[001]$ twist rotations exist to form a certain $[001]$ twist GB in fcc material. The difference in appearance is only their alignment with respect to the x-y-z simulation box coordinate system.

Apart from the $\Sigma 85$ twist, three more of the studied $[001]$ twist GBs exhibit discrete GB screw dislocation character. These are the $\Sigma 181$, $\Sigma 41$ and $\Sigma 25$ $[001]$ twist GB. The $\Sigma 25$ twist GB is at the verge of being a low-angle or intermediate-angle twist GB. The regions within the GB consisting of ideal fcc islands is reduced to four atoms per primitive CSL cell which is rather small. At intermediate and high temperatures the GB will cover the whole x-y plane leaving behind no longer any more ideal fcc atoms within the GB. For the remaining four $[001]$ GBs, the GB plane is filled throughout with GB atoms and no discrete GB screw dislocations can be identified. The analysis of the content of discrete GB screw dislocations of the studied $[001]$ twist GBs demonstrates that the CNA method is well suited to reveal the either dislocation or non-dislocation character of the studied twist GBs. The same is true for the studied tilt GBs in this work which will be discussed in more detail when dealing with tilt GB geometry.

5.2 Studies on Planar [001] Twist GBs

5.2.1 Overview on performed GB Migration Simulations

Here an overview over all conducted GB migration simulations of [001] twist GBs presented in this work is given. Eight [001] twist GBs were studied ranging from high-angle to low-angle twist GBs. Two different driving force concepts were used, namely an elastic DF and the so-called orientation-correlated DF as described in sections 3.4.2 and 3.4.4. All studied GBs were simulated in three-dimensional atomistic systems. Hence the GBs were truly two-dimensional defects. For the LJ potential, simulations with 3d periodic boundary conditions (BC) as well as with 2d periodic border conditions within the GB plane and stabilized free (002) surfaces were performed. Apart from the LJ potential, simulations with the EAM potential by Doyama and Adams and the Finnis-Sinclair potential according to Sutton and Chen were conducted as well. An overview on the conducted GB migration simulations is given in table 5.2.

Σ	θ	elastic DF	orientation-correlated DF
29	43.60°	LJ 3d periodic BC	—
5	36.87°	LJ 3d periodic BC	Doyama 2d periodic BC and free (002) surfaces LJ 2d periodic BC and stab. free (002) surfaces
17	28.07°	LJ 3d periodic BC [76]	LJ 3d periodic BC LJ 2d periodic BC and stab. free (002) surfaces
13	22.62°	LJ 3d periodic BC [76]	LJ 3d periodic LJ 2d periodic BC and stab. free (002) surfaces
25	16.26°	LJ 3d periodic BC [76]	—
41	12.68°	LJ 3d periodic BC	—
85	8.80°	LJ 3d periodic BC	LJ 3d periodic BC
181	6.03°	—	LJ 3d periodic BC

Table 5.2: Overview of conducted GB migration simulations on the studied [001] twist GBs.

The following chapters dealing with GB migration of twist GBs are divided into two main areas. First, GB migration in the framework of an elastic DF is discussed, second GB migration due to the orientation-correlated DF. In detail the used verification schemes to determine the DFs as well as the results of GB migration are presented. Following the GB migration discussion, GB self-diffusion of the eight [001] twist GBs is focussed on to gain insight into the activation parameters and possible GB structural transitions. Finally issues on the GB migration mechanism of the studied [001] twist GBs are presented.

5.2.2 GB Migration due to an Elastic Driving Force

5.2.2.1 DF Verification : Indirect Quantification Scheme

The verification and quantification of any form of driving force plays an important role when studying GBM. In this work two schemes to determine the elastic driving force are utilized. The first scheme relies on two separate ideal crystal simulations of either one of the grain's orientations of a given bicrystal to obtain the internal energy of the total MD system for the strained and unstrained case. The energy difference of the unstrained and strained system can then be used to determine the driving force at different strain and temperature. This approach shall be called indirect quantification scheme (IQS). For the $\Sigma 29$ [001] twist GB, the IQS is used to determine the elastic driving force from the simulation data. Additionally a comparison with the linear elastic model is presented as well. The second scheme utilizes an in-situ calculation scheme, named here direct quantification scheme (DQS), where the internal stress tensor and the external strain tensor are calculated for finite slabs of the system within each MD GBM simulation in order to calculate in-situ an elastic energy profile within the system by a linear elastic energy approach. This approach thus allows one to calculate the temporal and spatial evolution of the elastic driving force during each MD simulation. This scheme is exemplified by the $\Sigma 5$ [001] twist GB results.

Fig. 5.11(b) demonstrates the general idea of an elastic driving force to initiate GBM. According to sect. 3.4.2 a coupled x-y shear state should result in an elastic driving force for any [001] twist or tilt ² GB for the chosen MD box geometry. For a strain of $\epsilon=0.03$ at 0K it is found that indeed an energy gradient can be introduced in a bicrystal of the $\Sigma 29$ [001] 43.60° twist GB having a box geometry as indicated by Fig. 5.11(a). The figure illustrates the stacking sequence of (002) planes in grain A as being ABABAB like while in grain B it is A'B'A'B'A'B' like. Fig. 5.11(b) presents a plane by plane plot of the average potential energy per (002) plane versus the (002) plane position in the system for the unstrained and a strained simulation box. The unstrained profile is easily identified by the fact that the potential energy per atom at 0K of the bulk regions of either grain A or B have a value of $E_{pot}=E_{coh}$. According to the applied strain tensor given in Fig. 5.11(b) and following the analytical theory presented in sect. 3.4.2 we find that indeed grain A is having a higher elastic energy stored than grain B. At finite temperatures this energy gradient should lead to GBM in the directions as indicated by the arrows at the top of the figure. Another important aspect stressed by Fig. 5.11(b) is that an elastic driving force is a bulk phenomenon which is very well illustrated by a shift of the bulk energies that have plateau-like character. According to this it is acceptable to use ideal crystal MD boxes of the same orientation of either of the bicrystalline grains in order to assess the elastic energy stored within the bulk of the GB system's grains.

According to Fig. 5.11(b) the elastic energy stored within each grain can be determined by subtracting the energy profiles of the strained and unstrained system. The obtained energy profile thus represents the elastic energy variation along the [001] direction within the GB system which can be compared with the analytical linear elastic model as discussed in sect. 3.4.2. Fig. 5.12 shows such a plane by plane elastic energy profile for the $\Sigma 29$

²Note for a coupled x-y shear state to drive a [001] tilt GB, the GB plane normal would need to point in either the x or y direction of the MD box which differs from the usually assumed GB box geometry according to sect. 3.3.6.

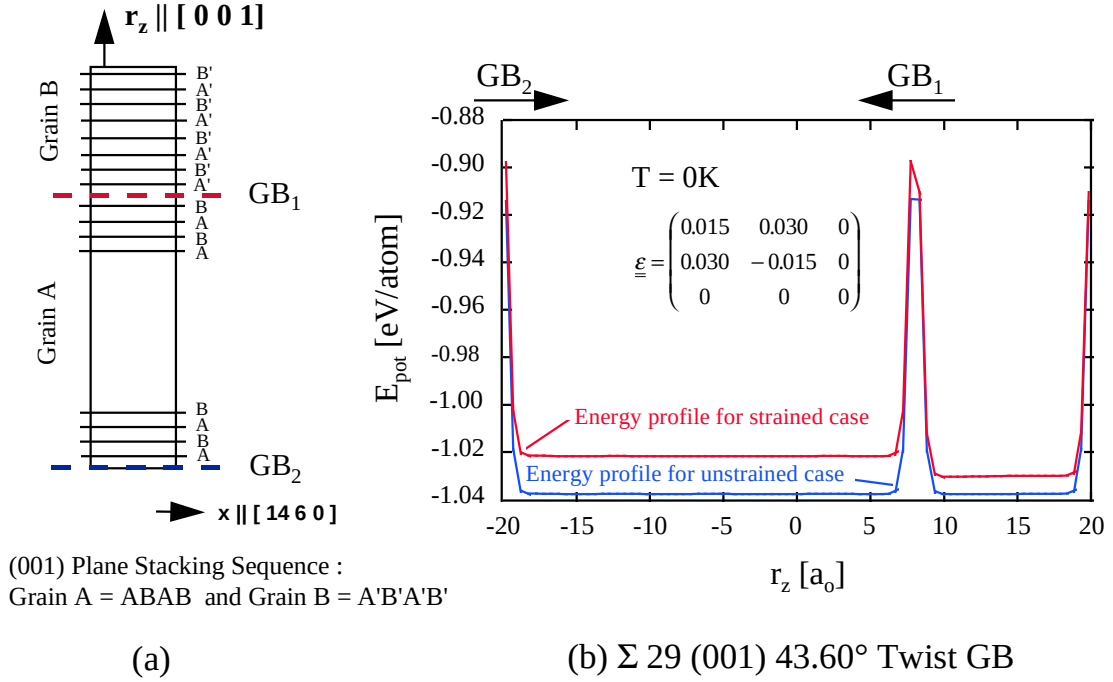


Figure 5.11: $\Sigma 29$ [001] 43.60° twist GB, $\gamma=0.708 \frac{J}{m^2}$: (a) shows a schematic of the GB system showing the stacking sequence of (002) planes in the GB system. GB₁ and GB₂ identify the GB positions. (b) presents the verification of an elastic driving force for $\epsilon=0.03$ at 0K for a 3d LJ system. Here the bulk regions of either grain for the unstrained case can be identified by having a potential energy equal to the cohesive energy of the ideal crystal of $E_{coh}=-1.037824$ eV/atom. Applying the strain homogeneously to the MD box leads to a shift of the unstrained energy profile by the amount of stored elastic energy within each grain. Thus this allows one to obtain the magnitude of stored elastic energy by subtracting the energy profiles of the strained and unstrained system. Here the two GBs, GB₁ and GB₂, are associated with the energy peaks in the profiles of (b).

twist GB at a strain of $\epsilon=0.001$ and 0K. Additionally to the computed simulation data the analytical linear elastic model data is given as well by the broken lines which demonstrates that for strain in the range of the classical elastic range the computed and model data agree very well. At finite temperatures a strain of about $\epsilon=0.001$ is not sufficient to drive the GBs over a distance of a few nm within a time range of at maximum ns. According to these underlying units within MD simulations it is easy to assess that the GB velocity must be at least in the range of one m/s in order to be detected within these simulations. This situation implies that either the applied temperatures or the driving force need to be extremely high in order to observe GB migration. Hence in the reported simulations the applied strain ranged from 0.01 up to 0.035 which is much higher than what is classically considered to be the elastic range for real materials. Since our model materials or GB systems do not include any line defects like lattice dislocations that play an important part in crystal plasticity, the used model materials still behave solely elastically even up to a strain of 0.035. Of course a deviation from the linear elastic behaviour seems reasonable and this aspect shall be dealt with next. In order to quantify the stored elastic energy for a strain of 0.01 up to 0.04 further simulations were performed for the $\Sigma 29$ twist GB system on appropriate ideal crystals. The obtained results of the elastic driving force, p_{ela} , versus

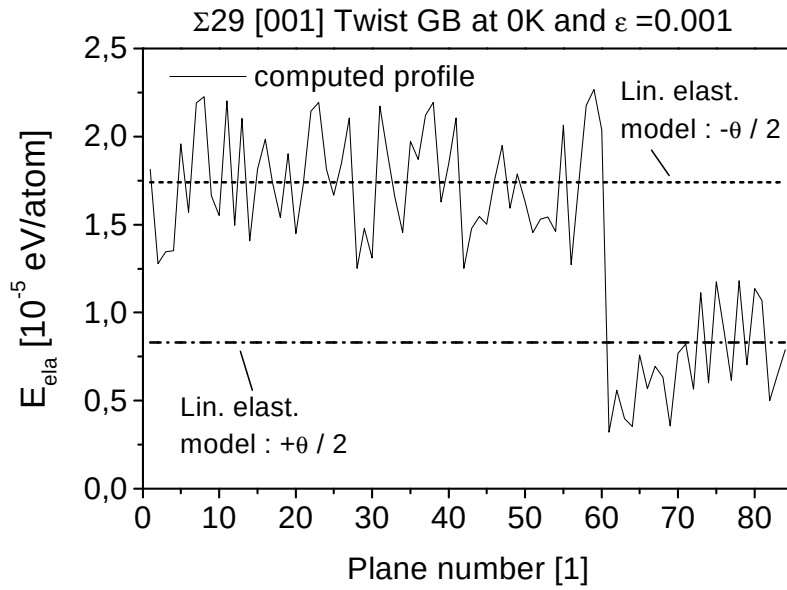


Figure 5.12: Plane by plane elastic energy profile of the $\Sigma 29$ twist GB at 0K for $\epsilon=0.001$. The zick-zack energy profile in the bulk of the two grains is due to the fact that in this example a not fully relaxed $\Sigma 29$ GB system was used.

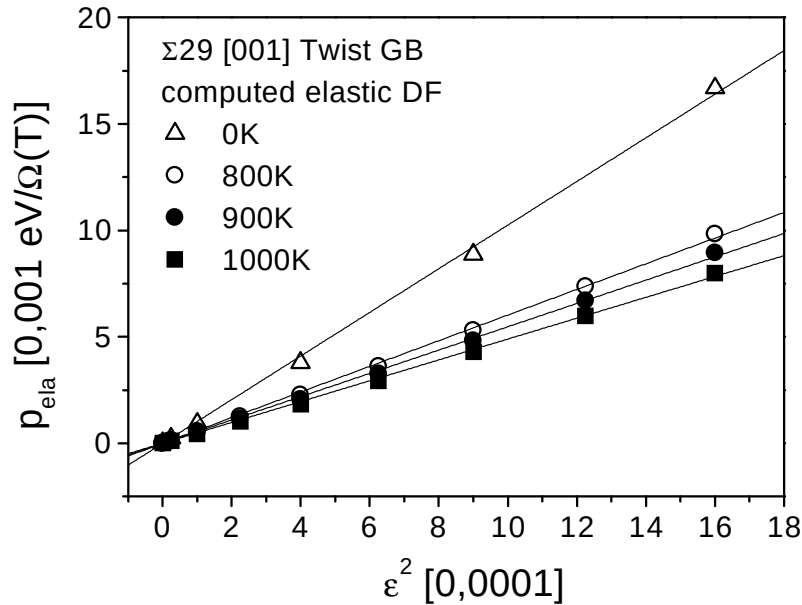


Figure 5.13: Elastic DF, p_{ela} , versus ϵ^2 at various temperatures for the $\Sigma 29$ twist GB. Here $\Omega(T)$ is the fcc atomic volume at temperature T . To assess the magnitude of the DF in conventional units the reader should note that $1 \text{ eV}/\Omega(0\text{K})$ equals 13.5 GPa for the model material of Cu. Additional to the computed elastic DF data, linear best data fits are included in the figure as well.

ϵ^2 are plotted in Fig. 5.13 for 0K, 800K, 900K and 1000K. It was found that the computed data can still be fitted very well by a linear fit if the DF data is plotted versus ϵ^2 . The slope of those fits determines $c_A \cdot \sin(2\theta)$. Hence the fitted $c_{A,Fit}$ values are available and can be compared with those accessible from the temperature dependence of the elastic constants for the 3d LJ potential as given by Tab. 3.1 in sect. 3.2.1.1. Tab. 5.3 presents the results

T [K]	$c_{A,Fit}(T)$ [$\frac{eV}{\Omega(T)}$]	$c_{A,Theo}(T)$ [$\frac{eV}{\Omega(T)}$]	$\frac{c_{A,Fit}(T)}{c_{A,Theo}(T)}$
0	10.259	9.1400	1.1225
700	6.5508	6.1157	1.0711
800	6.0293	5.6653	1.0642
900	5.4792	5.2111	1.0513
1000	4.9015	4.7517	1.0315

Table 5.3: Temperature dependence of the elastic anisotropy, c_A , of the 3d LJ Cu potential. The $c_{A,Fit}(T)$ values were determined by a linear fit of the computed driving force data p versus ϵ^2 of Fig. 5.13 and $c_{A,Theo}(T)$ was calculated from the data given in Tab. 3.1.

which show that the fitted $c_{A,Fit}$ is always larger than the linear elastic model data $c_{A,Theo}$. The difference decreases with temperature. Referring to the linear regression coefficients of all fits it was found that all of them have a value of about 0.9994 which clearly underlines the linear dependence between the DF, p , and ϵ^2 . Nevertheless Fig. 5.13 indicates that a non-linear data fit would represent the data even better which suggests nonlinearities for higher strain. Nevertheless the linear best fit of the plotted data of Fig. 5.13 was used for the Σ 29 twist GB to quantify the elastic DF for any given ϵ .

5.2.2.2 Σ 29 [001] 43.60°

The first major task was to demonstrate that by utilizing an elastic driving force concept on a planar twist GB within MD simulations indeed GBM occurs and key parameters of the migration process can be determined. The Σ 29 [001] 43.60° twist GB was the first GB to test and verify the simulation methodology of an elastic driving force and the GB migration results are given in this section. That indeed GBM occurs is clearly demonstrated by Fig. 5.14 (c) for a strain of $\epsilon=0.035$ at 800K. According to Fig. 5.13 and Fig. 5.15 the elastic DF in this case is approximately 0.0075 eV/ $\Omega(T)$ ($\approx$ 93MPa) which is in the range of DFs found in recrystallization experiments. According to Fig. 5.14 (c) the two key results demonstrated by the figure are that indeed GB migration occurs for the imposed strain of $\epsilon=0.035$ at 800K and that the distance-time behaviour of either GB is linear. Therefore the GB velocity can simply be determined by a linear best fit of the distance-time data which yields in this case an average GB velocity of 9.2 m/s. As expected the GB velocity is well above one m/s and therefore very well obtainable from the simulation data.

A very important aspect studied here is whether the x-y MD box dimensions play a significant role for the magnitude of the GB velocity obtained from the simulations. In principle it could very well be that there exists some effect of the planar x-y box dimensions if one considers that the activated state of atoms during GB migration includes plenty of atoms rather than being single atomic. Here one has to bear in mind that only a restricted number of atoms can be included in the MD simulation box to ensure that the temporal evolution

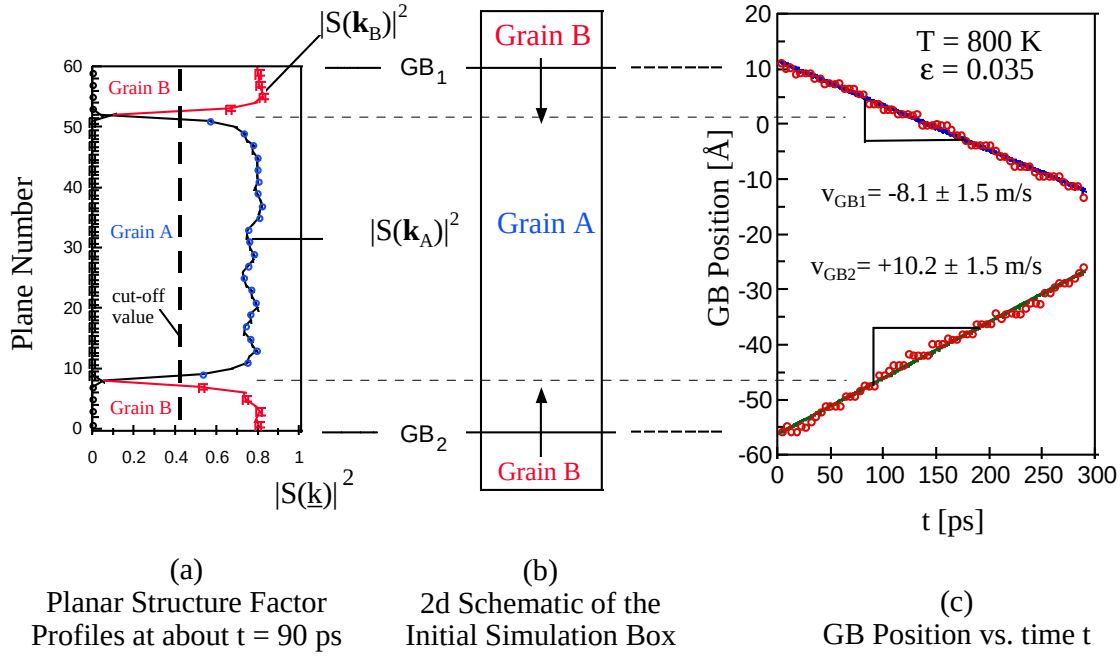


Figure 5.14: Schematic of GB migration for the $\Sigma 29$ [001] 43.60° twist GB : (a) shows the detection scheme of the GBs according to the planar structure factor profiles as has been discussed in detail in sect. 3.5.1.1. Note that here both GBs have already migrated over 8 (002) planes since at $t=0$ ps GB_1 would be located between plane 84-1 and GB_2 between 60-61. Part (b) presents a 2d schematic of the MD simulation box showing the initial GB positions at $t=0$ ps. Finally (c) shows the temporal evolution of the GB positions for a strain of $\epsilon=0.035$ at 800K. Note that the distance-time behaviour of either GB is linear which allows us to determine the GB velocity from the slope of the lines. According to the imposed DF of about 93 MPa the average GB velocity is about 9.2 m/s.

of the system can be computed within a reasonable frame of CPU time. Reasonable in this context means a few days up to one or two weeks of CPU time for a MD run of a certain GB at a certain temperature and under a certain DF. Of course an important basic requirement is that the GB system is believed to mimic the true physical behaviour of the GB system. Otherwise any undertaken simulation effort would a-priori be in vain to yield information on the principle physical processes taking place during GB migration. Therefore due to the applied periodic boundary conditions in all three spatial dimensions it should be ruled out that periodicity effects govern the physical behaviour of the system. Hence an one CSL planar GB system labeled (1x1) and a four CSL planar system labeled (2x2) were studied at 800K and various DFs in order to study periodicity effects within the system. The (1x1) system consisted of a stack of 84 (002) planes having 29 atoms per plane while the (2x2) system had 116 atoms per plane. The found GBM results for the two system sizes are shown by Fig. 5.15 and illustrate that the planar MD box dimensions have no effect on the rate of GBM for a given DF. According to the later on presented results on the temperature dependence of the GB mobility and the GB mechanism for temperatures even larger than 800K, the results for the two planar system sizes should agree even better because at the highest temperatures studied the GB migration mechanism becomes single atomic. A further very important result is that the GB velocity indeed depends linearly on the DF as stated by Eq. 2.11. This of course means that the GB mobility can be extracted from the

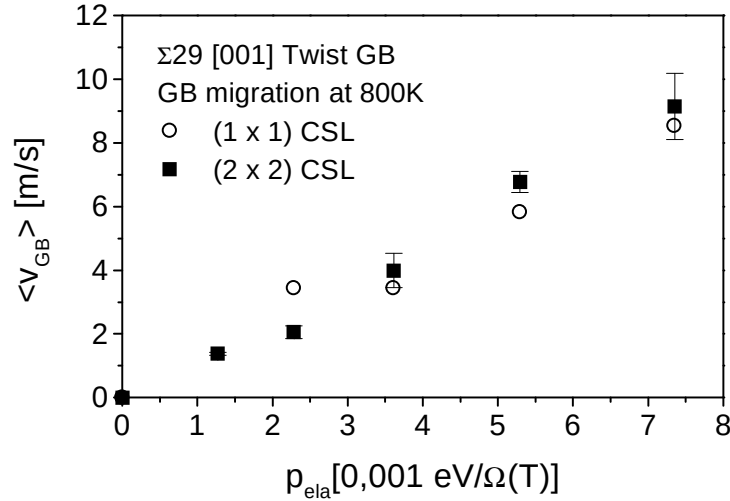


Figure 5.15: Average GB velocity versus elastic DF at 800K for different planar CSL sizes for the $\Sigma 29$ twist GB. The label (1x1) identifies simulations having primitive CSL x-y dimensions of the GB simulation box while the label (2x2) identifies a non-primitive x-y system size consisting of four CSL cells within the x-y plane of the MD box.

plotted data being the slope of the linear best data fit. Performing numerous simulations at different DFs and temperatures can therefore yield the temperature dependence of the GB mobility. For the $\Sigma 29$ twist GB the GBM results at 600K up to 1000K are summarized by Fig. 5.16. The data points show that for any temperature studied the linear relationship

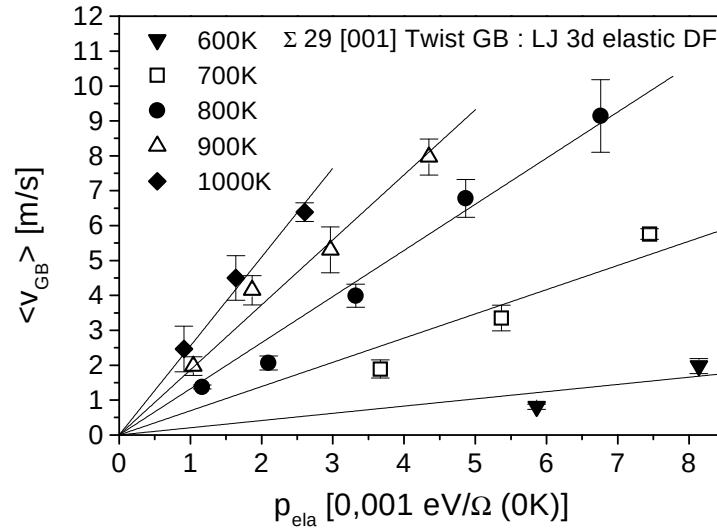


Figure 5.16: Average GB velocity versus DF of the $\Sigma 29$ twist GB. All plotted data points were obtained by non-primitive (2x2) CSL GB migration simulations. At all temperatures a linear best data fit represents the data well.

between the GB velocity versus the DF holds. This indeed is a remarkable result since it underlines the relevance of the analytical phenomenological theory of GB migration even for the computational GB model systems.

The temperature dependence of the GB mobility is presented in Fig. 5.17 by an Arrhenius

plot. In this presentation of the data the activation enthalpy is easily obtained by the slope of a linear best fit of the data. According to the figure a low and a high temperature regime exist, having distinctly different activation parameters. The crossover point from the low temperature regime to the high temperature regime is at about 760K. That indeed

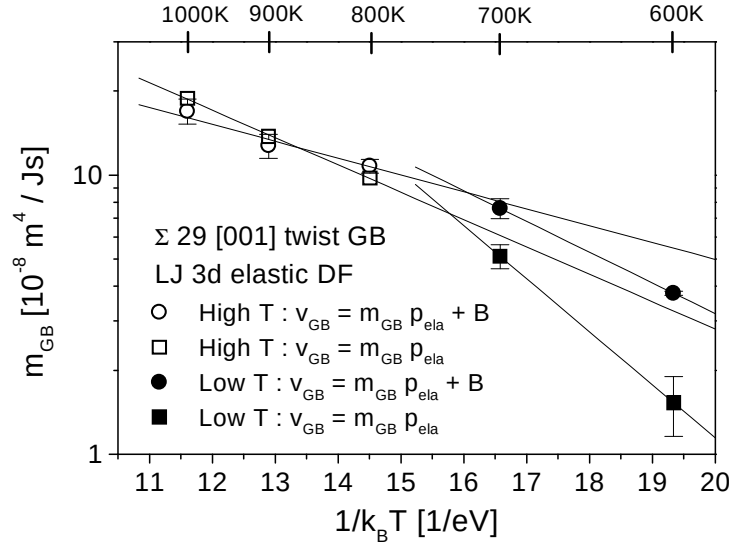


Figure 5.17: Arrhenius plot of GB mobility of the $\Sigma 29$ twist GB. According to the data two temperature regimes exist. For the low temperature regime the activation enthalpy is 0.40 eV/atom while for the high temperature regime one gets an activation enthalpy of 0.22 eV/atom.

two temperature regimes exist is not only drawn from the presented GB mobility but rather supported by further findings. Namely it was found for this GB that the GB diffusion data exhibits the same two regime behaviour [65] like the GB migration data does. Fig. 5.18 presents the GB self-diffusion data determined by MD GB simulations without any DF in the temperature of 600K up to 1000K. Clearly the figure demonstrates the two regime behaviour. Further details on the angular distribution of the diffusional jump vectors can be found in section 5.2.4. For various high-angle twist and tilt GBs in fcc material it was demonstrated by the GB self-diffusion data by Koblinski [72] that the change of the activation parameters is closely connected to the change of the GB structure. Indeed it was shown that the GB self-diffusion behaviour changes at low temperatures from crystalline lattice jumps to isotropic jump events at high temperatures. A similar behaviour is found in this work and is discussed in detail in section 5.2.4.

Looking into the atomic-level mechanism of GB migration for both regimes one finds that at low temperatures a cooperative reshuffling mechanism of several atoms occurs while for the high temperature regime a uncorrelated single atom mechanism prevails. Remarkably the transition occurs almost exactly at the same temperature found for the GB mobility and GB diffusion data. According to these findings one can draw the conclusion that indeed two temperature regimes exist for this high-angle twist GB having distinctly different activation parameter and activation mechanisms.

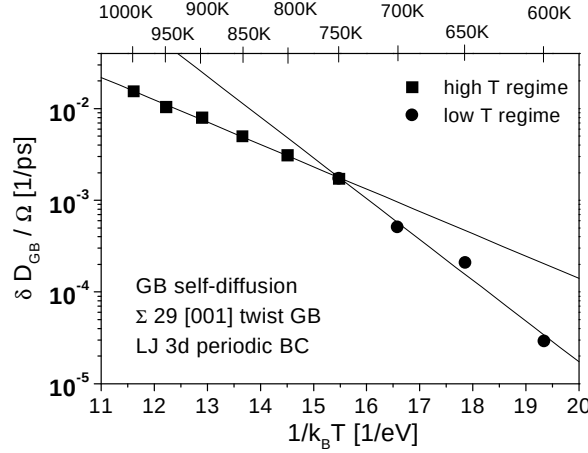


Figure 5.18: Arrhenius plot of the GB self-diffusion data of the $\Sigma 29$ [001] twist GB. Here the results of the temperature range from 600K to 1000K are given. The GB self-diffusion data exhibits the same behaviour as the GB mobility data, namely a transition of the GB self-diffusion mechanism at about 750K. This transition can be understood in terms of a GB structural transition.

5.2.2.3 DF Verification : Direct Quantification Scheme

Here a direct calculation scheme is presented to calculate the elastic DF in-situ during MD GB migration simulations. In detail this scheme utilizes a calculation scheme, named here direct quantification scheme (DQS), where the internal stress tensor and the external strain tensor are calculated for finite slabs of the overall MD system at certain time intervals within each of the MD GBM simulations itself in order to calculate in-situ elastic energy profiles within the system by a linear elastic energy approach. For [001] twist GBs these slabs are (002) crystallographic planes and thus for each (002) plane, k , the elastic energy E_{ela}^k is calculated according to

$$E_{ela}^k = -\frac{1}{2} \sum_{\alpha\beta} \sigma_{\alpha\beta}^{k(002)} \cdot \epsilon_{\alpha\beta}^{box} . \quad (5.1)$$

Here $\sigma_{\alpha\beta}^{k(002)}$ represents the components of the internal stress tensor of plane, k , which are easily accessible within the performed MD calculations and $\epsilon_{\alpha\beta}^{box}$ represents the components of externally applied strain tensor to the MD simulation box. This approach thus allows one to calculate the temporal and spatial evolution of the elastic energy within distinct (002) planes and thus is the fundamental tool to determine the elastic driving force during each MD simulation in-situ. The elastic DF itself is calculated from the energy difference between the average elastic energy stored in either of the two grains. The scheme is now exemplified here for the $\Sigma 5$ [001] twist GB and one characteristic example of the temporal and spatial evolution of the elastic energy profile within the MD simulation box is given by Fig. 5.19. Fig. 5.19 demonstrates very well that the temporal and spatial evolution of the elastic energy profile of the (002) planes can be tracked and determined by the applied calculation scheme and that the in-situ approach is able to determine the elastic DF directly from the GB migration runs itself. The main advantage of the DQS over the IQS (see sect. 5.2.2.1) is that one no longer has to rely on ideal crystal simulations to quantify the elastic DF but rather that the elastic DF can directly be determined and tracked within the actual GB migration simulations. For the studied twist GBs the results of the elastic DF data for

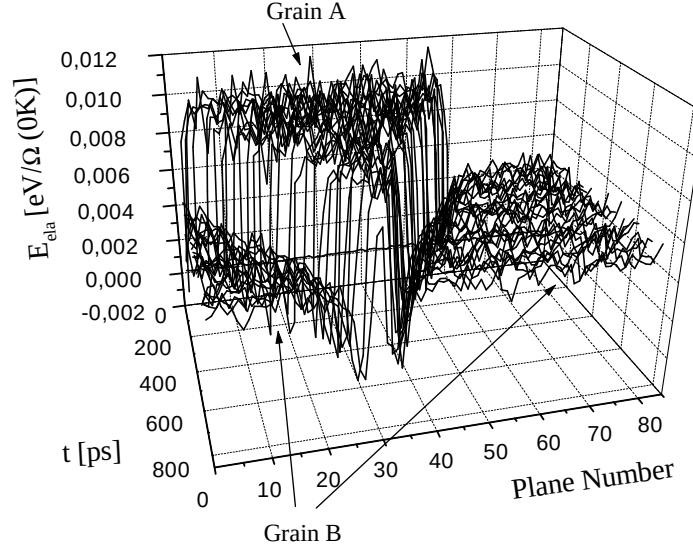


Figure 5.19: $\Sigma 5$ twist GB : Illustration of the DQS to determine and track the temporal and spatial evolution of elastic DF in-situ during GB migration simulations. Here the elastic energy, E_{ela} , for each of the 84 (002) planes present in the simulation box is plotted versus the time, t , and the plane number. This plotted data has been taken from the $\Sigma 5$ twist GB run at 800K and $\epsilon_{xy}=0.030$. The figure illustrates that indeed grain A is having a higher elastic energy stored than grain B and that due to GB migration grain A eventually is removed from the system. Within each grain the variance of the elastic energy is only little, therefore it is reasonable to utilize the average elastic energy for each grain to determine the elastic DF.

both schemes agree well. This is underlined by Tab. 5.4 which presents the temperature dependence of elastic anisotropy factor determined from the IQS data of the $\Sigma 29$ twist GB and from the DQS data of the $\Sigma 5$, $\Sigma 41$ and $\Sigma 85$ twist GB. Comparing the results it is amazing how well the data agree. This and a few other facts indeed strongly suggest to apply the DQS scheme within GB migration simulations to track the elastic DF behaviour. For instance it is typical for GB simulations with 3d periodic boundary conditions that during the final stage of GB migration when the two GBs present in the system have come very close to one another the elastic DF steadily decreases. This behaviour of the DF (see Fig. 5.20) only becomes visible when utilizing an in-situ calculation scheme during the MD simulations. Furthermore especially in the framework of tilt GBs it was helpful to utilize an in-situ analysis tool to determine the elastic DF since for those GBs the elastic DF concept failed due to GB glide events that led to a conversion of elastic shear strain into plastic shear strain. The details on this are given in sect. 6.3.1.2.

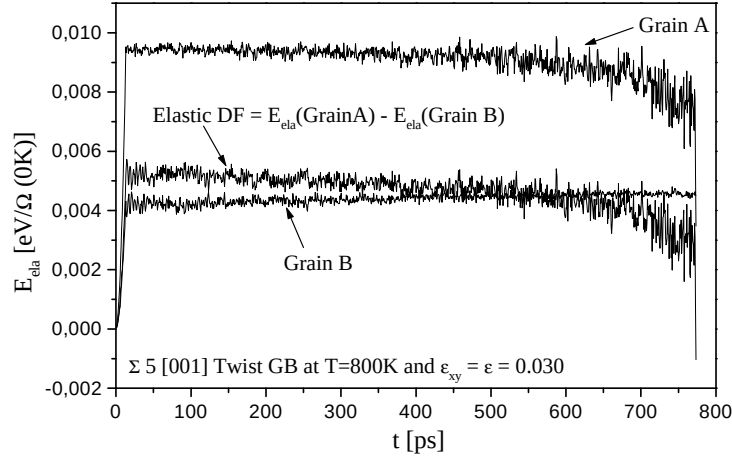


Figure 5.20: $\Sigma 5$ twist GB at $T=800\text{K}$ and $\epsilon=0.030$: Here the temporal evolution of the elastic energy stored in grain A and grain B as well as the elastic DF are plotted. The figure shows that the elastic energy of grain A steadily decreases while the one of grain B steadily increases which leads to a steady decrease of the elastic DF as well. This behaviour is neglectable with respect to the final stage of GB migration in the system where a much more dramatic effect occurs for the elastic energy of grain A after about 600ps. Now rapidly the elastic energy of grain A decreases about 10 percent within the following 200ps until finally grain A is removed from the system. This dramatic decrease is most likely connected to crystallographic destabilization of grain A during the final moments of the removal process.

T [K]	IQS $c_{A,Fit}^{\Sigma 29}(T)$ $[\frac{eV}{\Omega(0K)}]$	DQS $c_{A,Fit}^{\Sigma 5}(T)$ $[\frac{eV}{\Omega(0K)}]$	DQS $c_{A,Fit}^{\Sigma 41}(T)$ $[\frac{eV}{\Omega(0K)}]$	DQS $c_{A,Fit}^{\Sigma 85}(T)$ $[\frac{eV}{\Omega(0K)}]$	Liner elastic model $c_{A,theo}(T)$ $[\frac{eV}{\Omega(0K)}]$
700	6.11	6.09	6.36	5.93	5.70
800	5.54	5.48	5.84	5.73	5.21
900	4.96	4.85	5.02	4.67	4.71
1000	4.36	4.31	4.57	4.27	4.22

Table 5.4: Comparison of the temperature dependence of the elastic anisotropy, c_A , of the 3d LJ Cu potential for the IQS and DQS. The $c_{A,Fit}(T)$ values were determined by a linear best fit of the computed driving force data p versus ϵ^2 of Fig. 5.13, Fig. 5.21 and Fig. 5.33, respectively. Concerning the $\Sigma 29$ c_A data the reader should note that the data presented in Tab. 5.3 is given in units of $\frac{eV}{\Omega(T)}$ while here it is given in units of $\frac{eV}{\Omega(0K)}$. The use of these different units is closely connected to the different quantification schemes, namely the IQS and DQS.

5.2.2.4 Σ 5 [001] 36.87°

Here the results of GB migration of the $\Sigma 5$ [001] 36.87° twist GB due to an elastic DF are presented. The elastic DF was successfully applied to the $\Sigma 5$ GB in a temperature range from 700K up to 1100K. Utilizing the DQS scheme it was possible to calculate the elastic DF in-situ during the MD GB migration simulations. Fig. 5.21 shows the DF dependence from the strain magnitude, ϵ . The elastic DF data, p_{ela} , when plotted versus ϵ^2 is at fixed temperature well-represented by a linear best data fit. The slope equals the elastic anisotropy factor, c_A , times the $\sin(2 \cdot \theta)$ term and is in good agreement with linear elastic theory. It only differs by about 10 percent from the theoretical value due to non-linear effects. To

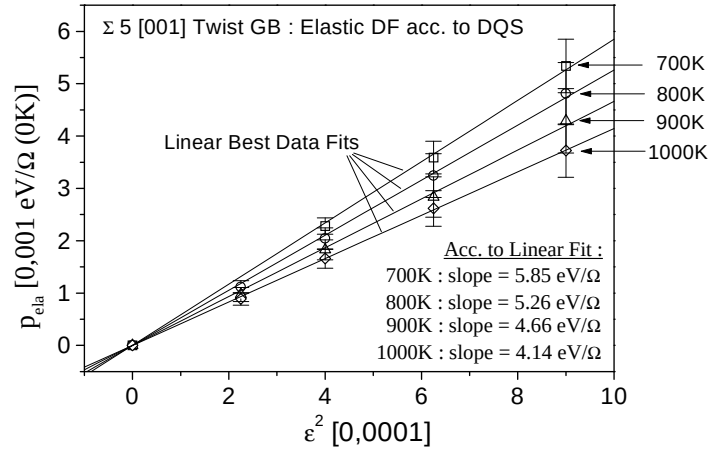


Figure 5.21: $\Sigma 5$ [001] twist GB. Elastic DF according to DQS scheme for temperatures ranging from 700K up to 1000K and different strain magnitudes. The figure demonstrates that the elastic DF data is well-represented by a linear best data fit. The slope are in good agreement with linear elastic theory and only differ due to non-linear effects.

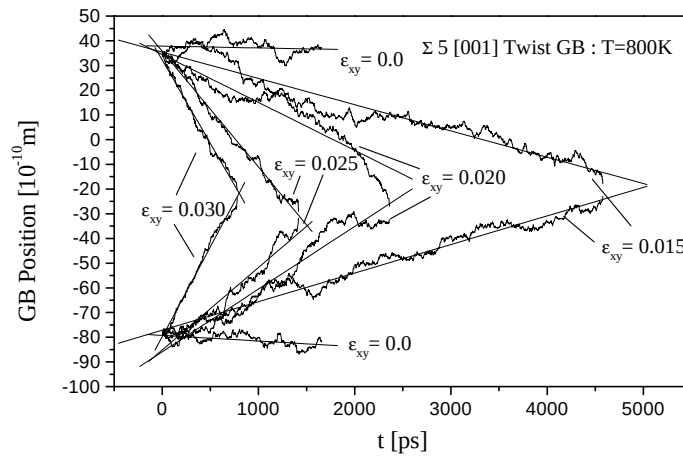


Figure 5.22: $\Sigma 5$ [001] twist GB. GB position versus time at 800K for different elastic DFs.

exemplify the GB position versus time behaviour, Fig. 5.22 shows the temporal evolution of the GB position versus time at 800K for different elastic DFs. The presented data illustrates that by best linear data fits the GB velocity can be determined. The reader should note

that some of the conducted GB migration simulations at low elastic DFs ran up to a few nano-seconds before both GBs annihilated. This indicates the required time range to be studied when dealing with GB migration of high-angle twist GBs at lower elastic DFs. This stresses the point that such extended simulations can only be conducted with time efficient atomistic potentials due to restriction of overall computer time available for each single simulation run. This is even more true if one keeps in mind that plenty of GB migration simulations are needed to yield reliable data of GB mobility at various temperatures.

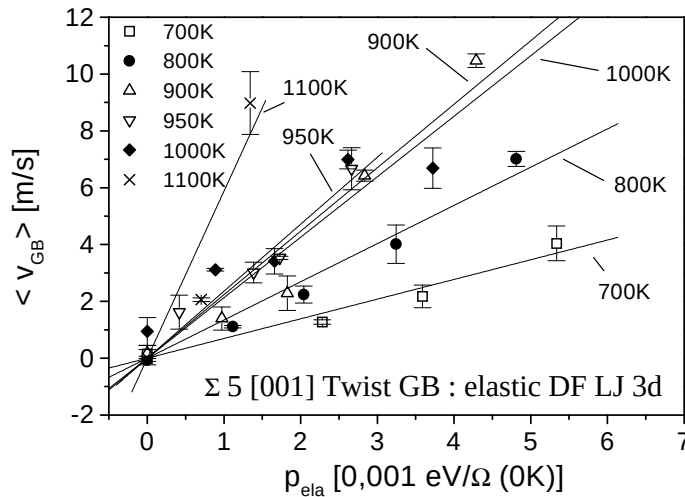


Figure 5.23: $\Sigma 5$ [001] twist GB. GB velocity versus elastic DF at 700K up to 1100K.

Next Fig. 5.23 presents the average GB velocities extracted from the GB migration simulations versus the elastic DF at temperatures ranging from 700K to 1100K. Here a few remarks are necessary with respect to the 1100K data. Reliable GB migration simulations were only possible for strain magnitudes being equal or less than 0.020. For higher strains, the system was destabilized and no useful GB migration simulations could be performed. This again points out the upper range of applicable strain at high or ultra-high temperatures with respect to the melting point of the model LJ potential.

Performing linear best data fits for each temperature yields the temperature dependence of the elastic DF as shown in Fig. 5.24. Already Fig. 5.23 as well as Fig. 5.24 reveal that the GB mobility of the $\Sigma 5$ twist GB decreases in the temperature range from 900K to 1000K. Up to 900K it was rising with increasing temperature as normally expected assuming an underlying thermally activated process. Then at 1100K the GB mobility seems to rise again.

The decrease of GB mobility between 900 and 1000K can only be understood by a structural change of GB order. Still one would ideally expect that the GB mobility should increase with increasing temperature even when a structural order transition of a GB occurs. One plausible explanation for this behaviour might be the shortcoming of the LJ potential to mimic these structural transitions well enough. As is presented in section 5.2.3.2, simulations with the Doyama EAM potential show a similar GB structural transition of the $\Sigma 5$ twist GB in this temperature range. The only clear difference to the LJ results are that the GB mobility related to the EAM results steadily increases over the whole studied temperature range. This observation supports the idea that the LJ potential might not be fully suited to identify the GB mobility dependence correctly during that temperature range. Of course within

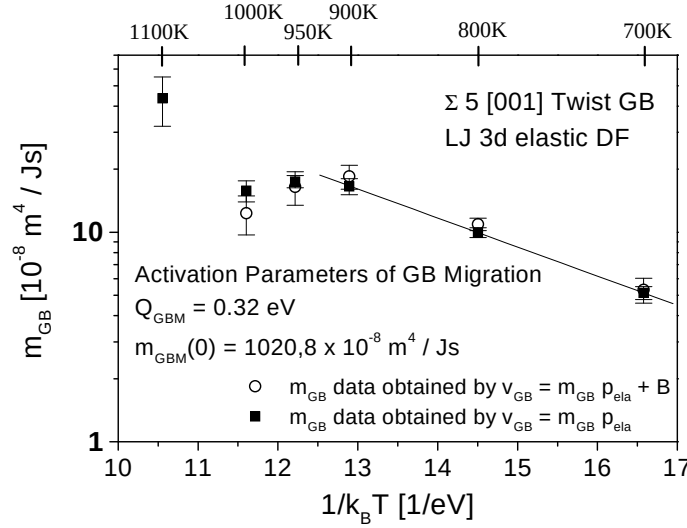


Figure 5.24: $\Sigma 5$ [001] twist GB. Arrhenius plot of the computed GB mobility data.

the LJ model the results are correct. Their correctness and meaningfulness might only be questioned with respect to experimental results or results from physically more fundamental atomistic potentials.

Finally the activation parameters of GB migration of the $\Sigma 5$ twist GB for the LJ potential and the elastic DF are given in Fig. 5.24. Here two data sets are shown. One is associated with a linear best data fit through zero of the GB velocity versus elastic DF data while the second one is associated with a general linear data fit of the same data. To distinguish between these two linear fits is driven by the fact that in some cases for some of the studied [001] twist GBs it was observed that even without an explicit DF GB migration was observed. This GB migration can only be linked to GB interaction of the two present GBs in systems utilizing 3d periodic boundary conditions. The GB mobility data of both data sets agree fine which shows that GB interaction during the $\Sigma 5$ twist GB simulations were rather small.

5.2.2.5 $\Sigma 17$, $\Sigma 13$ and $\Sigma 25$ [001] twist GBs

Here the results of Ralf Goßmann's diploma thesis [76] are presented who studied GB migration of three [001] twist GBs in the presence of an elastic DF. His diploma thesis is part of this work and was initiated after first studies and results of GB migration on the $\Sigma 29$ and $\Sigma 5$ [001] twist GBs had successfully proven that an elastic DF can be utilized to study continuous GB migration. The prime aim of his study was to obtain additional data on GB migration of [001] twist GBs having smaller misorientation angles than the $\Sigma 29$ and $\Sigma 5$ twist GB. The obtained results are given in detail in Goßmann's diploma thesis, therefore only the key results of his work are given here with respect to their relevance for this work. The three GBs were studied with a 3d periodic boundary concept and by utilizing the LJ potential. The GB MD simulation boxes consisted of 84 (002) planes. Following the outline in section 3.4.2, coupled x-y shear strain states were applied to the MD simulation box to drive the GBs continuously.

Fig. 5.25, 5.26 and 5.27 present the average GB velocity versus elastic DF obtained by his simulations. One thing that the figures indicate is that in some cases even without an

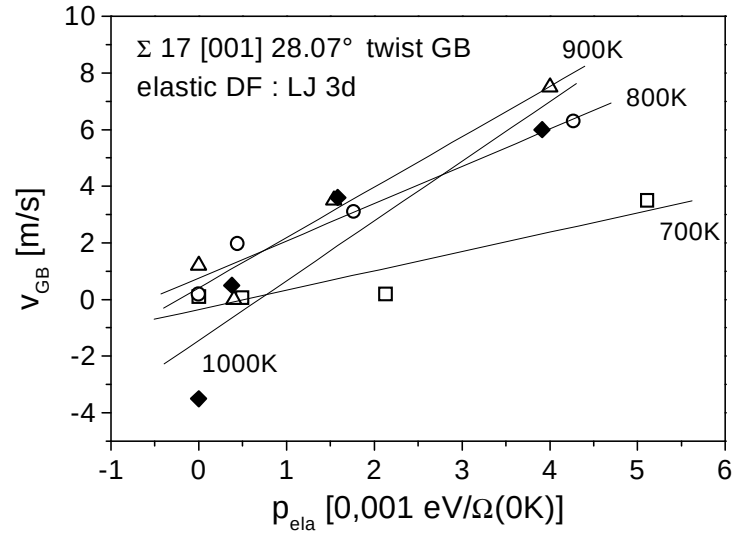


Figure 5.25: $\Sigma 17$ 28.07° [001] twist GB. The plot shows the average GB velocity versus elastic DF at different temperatures.

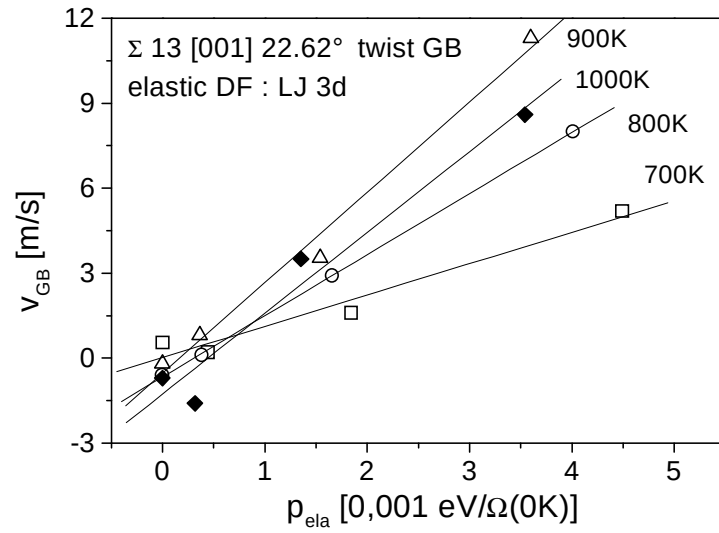


Figure 5.26: $\Sigma 13$ 22.62° [001] twist GB. The plot shows the average GB velocity versus elastic DF at different temperatures.

explicit DF, the GBs were moving. Usually this GB velocity was rather small and can be understood in terms of GB fluctuations. Still an attractive interaction between the two present GBs can neither be fully ruled out. Especially this is true in the case when negative GB velocities were obtained at zero elastic DF. A second aspect seen from the plots is the

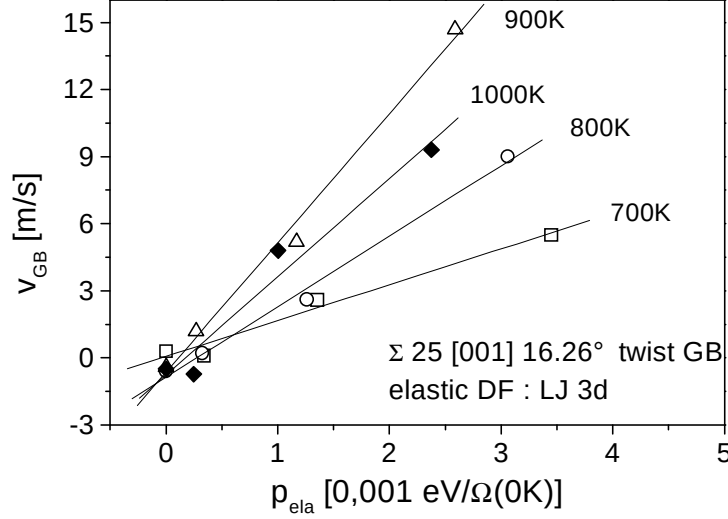


Figure 5.27: $\Sigma 25$ 16.26° [001] twist GB. The plot shows the average GB velocity versus elastic DF at different temperatures.

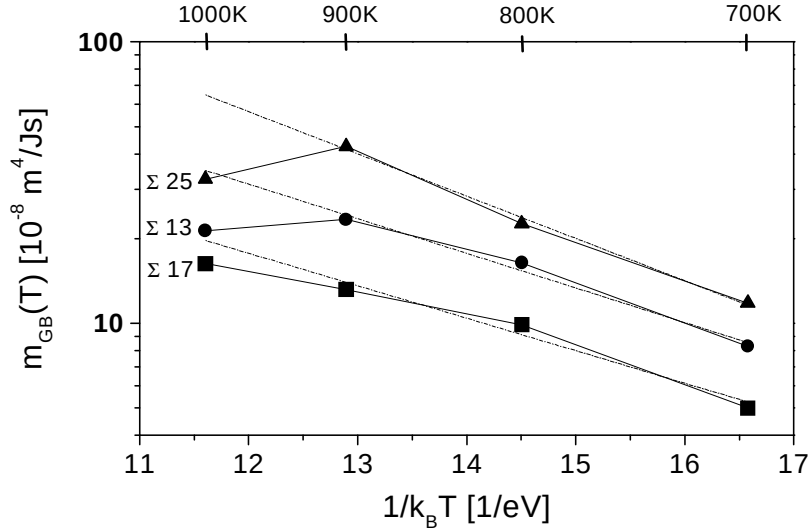


Figure 5.28: Arrhenius plot of GB mobility of the $\Sigma 17$, $\Sigma 13$ and the $\Sigma 25$ twist GB. The linear best data fit for all three GBs was performed only on the basis of the 700K to 900K GB mobility data and is shown by the dashed lines.

observation that the GB mobility for all three GBs steadily increases in the temperature range from 700K to 900K. Then at 1000K the GB mobility decreases and only for the $\Sigma 17$ twist GB it appears to have still increased. Looking at the GB velocity versus elastic DF data at 1000K of the $\Sigma 17$ GB, the zero DF GB velocity is rather high with respect to the other two twist GBs. Especially this data point leads to the rather high GB mobility value

of the $\Sigma 17$ GB at 1000K. Hence it can be imagined that even for the $\Sigma 17$ GB, the 1000K GB mobility would rather be at level with the 900K data or even be slightly smaller.

The decrease of GB mobility at 1000K can only be understood by an occurring GB structural transition or GB structure weakening. As was discussed for the $\Sigma 5$ twist GB it seems plausible that the LJ potential might not be fully capable to mimic these structural transitions well enough.

Finally in Fig. 5.28 the GB mobility of the $\Sigma 17$, $\Sigma 13$ and the $\Sigma 25$ twist GBs are presented in an Arrhenius plot. Utilizing of only the 700K to 900K GB mobility data yields for each GB the GB migration activation parameters. Tab. 5.5 summarizes the results.

GB plane	θ	Σ	Q_{GBM} [eV]	m_o [$10^{-6} \frac{m^4}{Js}$]
(001)	28.07°	17	0.267 ± 0.040	4.32
(001)	22.62°	13	0.284 ± 0.030	9.39
(001)	16.26°	25	0.346 ± 0.020	35.94

Table 5.5: GB migration activation parameters of of the $\Sigma 17$, $\Sigma 13$ and $\Sigma 25$ [001] twist GBs. The results where obtained for the LJ potential, 3d periodic BC and the elastic DF.

5.2.2.6 $\Sigma 41$ [001] 12.68°

Here the GB migration results of the $\Sigma 41$ [001] 12.68° twist GB are presented. The $\Sigma 41$ twist GB is with respect to its misorientation angle of 12.68° truly a low-angle GB. Indeed the screw dislocation network generating the GB can be identified utilizing the CNA method. In section 5.1.2, the screw dislocation network of all studied [001] low-angle GBs was discussed.

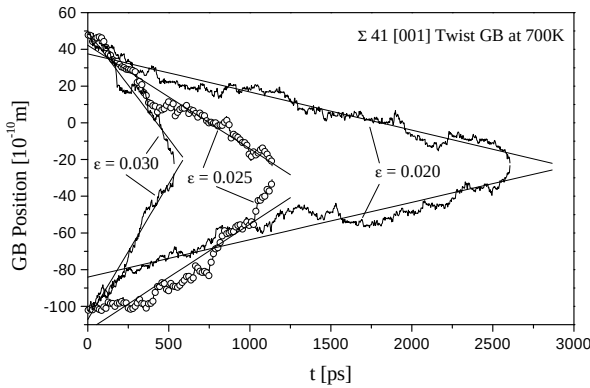


Figure 5.29: GB position versus time plots of the $\Sigma 41$ twist GB at 700K.

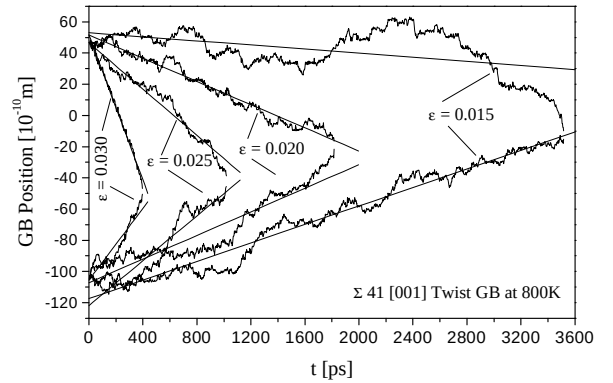


Figure 5.30: GB position versus time plots of the $\Sigma 41$ twist GB at 800K.

In the conducted GB migration simulations of the $\Sigma 41$ twist GB, the LJ potential and 3d periodic BC were used. The temperature range from 700K up to 1000K was studied utilizing an elastic DF. In order to illustrate the GB position versus time behaviour, Fig. 5.29 and 5.30 show the situation at 700K and 800K respectively. Indeed for all applied strain

levels continuous GB migration occurred which allowed us to extract the GB velocities by linear best data fits. Only in some cases at strain of 0.015, GB fluctuations and attractive GB interaction became quite strong which led to rather non-linear behaviour of the GB position versus time profiles.

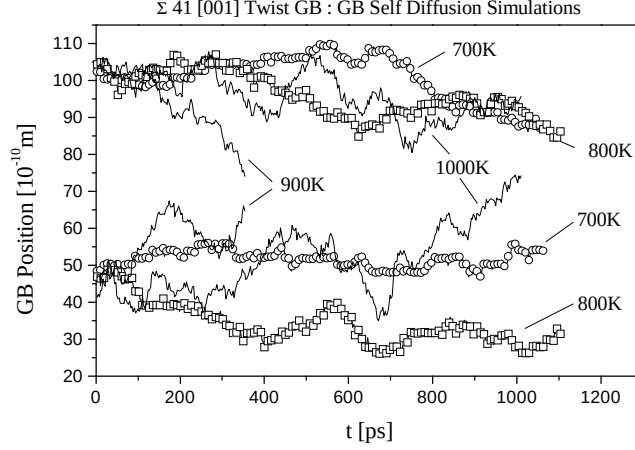


Figure 5.31: Behaviour of the $\Sigma 41$ twist GB in the presence of no elastic DF. Plotted are the GB position versus time profiles at 700K up to 1000K. Strong GB interaction appears to be present in the system since in all cases the GBs move towards each other and even in the case at 900K they annihilate.

That an attractive interaction between the two present GBs indeed exists in the studied box system is best exemplified by the simulation results with no explicit DF. Fig. 5.31 shows these results. These simulations were used to extract the GB self-diffusion activation parameters as presented in section 5.2.4. Strong GB interaction appears to be present in the system since in all cases the GBs move towards each other and even in the case at 900K they annihilate after about 350ps. Since the simulation box setup is asymmetrical meaning that 60 (002) planes form the lower grain while 24 (002) planes form the upper one, the GBs moved in the direction of shorter separation. This supports the idea that strong GB interaction must have existed in the system. This interaction is solely connected to the

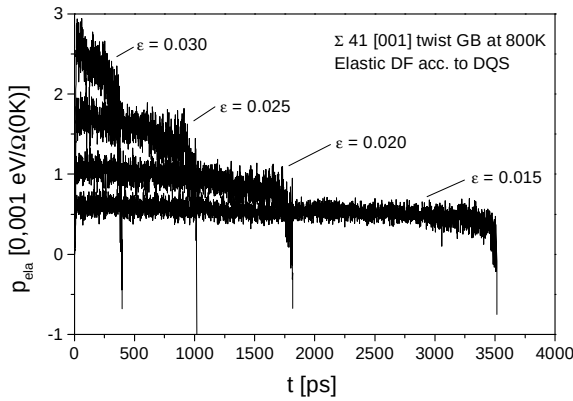


Figure 5.32: Elastic DF at 800K of the $\Sigma 41$ [001] GB determined from the simulations according to the DQS.

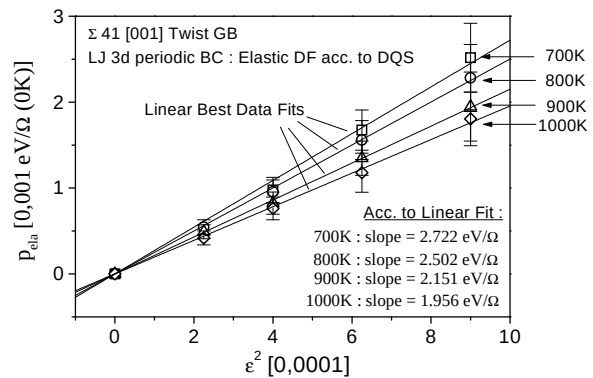


Figure 5.33: Elastic DFs determined from the GBM simulations according to the DQS for 700K up to 1000K.

spatial dimensions between the two GBs and could have been avoided if more (002) planes had been used to build up the simulation box.

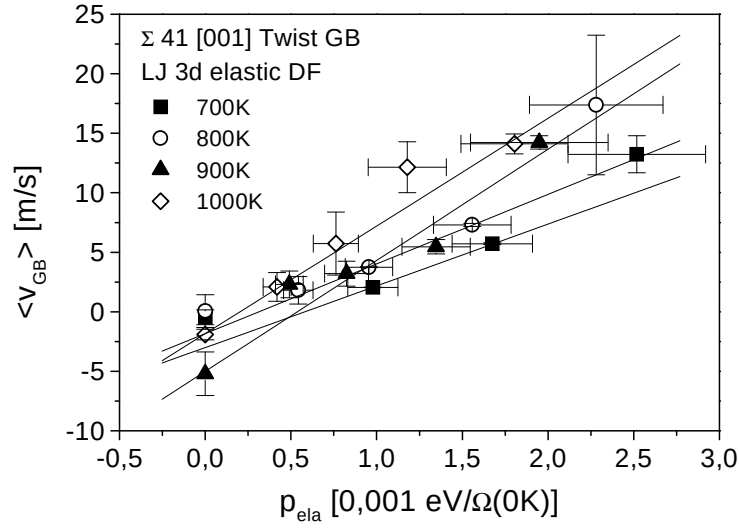


Figure 5.34: GB velocity versus elastic DF plot of the $\Sigma 41$ [001] twist GB. Simulation results utilizing 3d periodic BC as well as 2d periodic BC are plotted. The 2d periodic BC data is identified by the data points having no error bar for the GB velocity.

Next the elastic DF determined by the DQS scheme is given in Fig. 5.32 and 5.33. Fig. 5.32 shows the temporal evolution of the elastic DF at 800K for different strain, ϵ . The 3d periodic BC effect on the elastic DF is well observed for the high strain levels. Hence the error bar of the elastic DF for the high strain cases are much larger than for the low strain cases. Fig. 5.33 illustrates this point as well as that the determined elastic DF still agrees fine with what is expected from linear elastic theory.

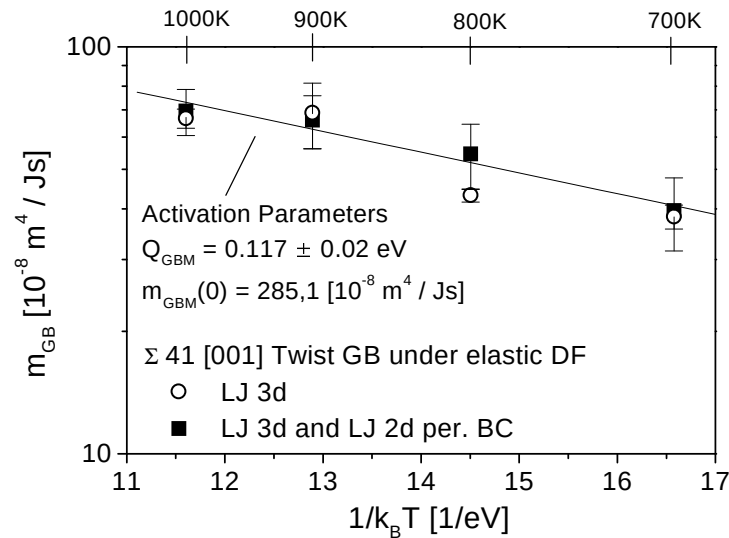


Figure 5.35: $\Sigma 41$ twist GB : Arrhenius plot of GB mobility data obtained from simulations with the LJ potential and 3d periodic BC.

Turning now the discussion to the GB velocity versus elastic DF situation, Fig. 5.34 presents

those plots for the determined data from 700K to 1000K. According to the figure the temperature dependence of the GB mobility is rather small compared with the dependence known from the high-angle twist GBs. This is directly visible in an Arrhenius plot of the GB mobility versus $1/k_B T$ as shown in Fig. 5.35. Interestingly the GB mobility data seems to increase steadily with increasing temperature although again the 1000K data seems to make the exception to the overall behaviour. At least it seems that the 1000K is at level with the 900K data or slightly higher. The shown data points relate to simulation results of simulations utilizing 3d periodic BC as well as 2d periodic BC.

Finally a linear best data fit of the plotted data of Fig. 5.35 yields the activation parameters of GB migration of the $\Sigma 41$ twist GB. Here the 700K to 1000K data were fitted resulting in an activation enthalpy of about 0.12eV. In comparison to the high-angle and intermediate-angle twist GBs, 0.12 eV is distinctly smaller activation enthalpy. As supported by the other low-angle GB results it seems that low-angle and high-angle twist GB results form two separate sets of activation parameter data. This can be understood in terms of difference in GB character and hence migration mechanism which is discussed in section 5.2.2.8 and 5.2.6.

5.2.2.7 $\Sigma 85$ [001] 8.80°

The low-angle twist GB with the smallest twist angle studied in the presence of an elastic DF was the $\Sigma 85$ [001] 8.80° twist GB. The elastic DF concept can be successfully applied to study GB migration even for this low-angle twist GB. As expected from linear-elastic theory, the achievable elastic DFs are smallest with respect to all studied [001] twist GBs within this work. This is well explained by the $\sin(2\theta)$ term in Eq. 3.46. One interesting feature related to the elastic DF concept was found for this GB.

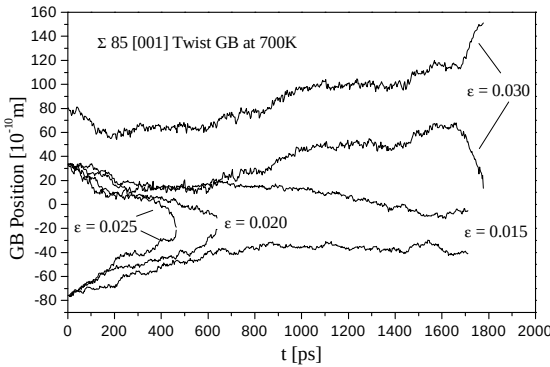


Figure 5.36: Plots of the GB position versus time of the $\Sigma 85$ twist GB at 700K.

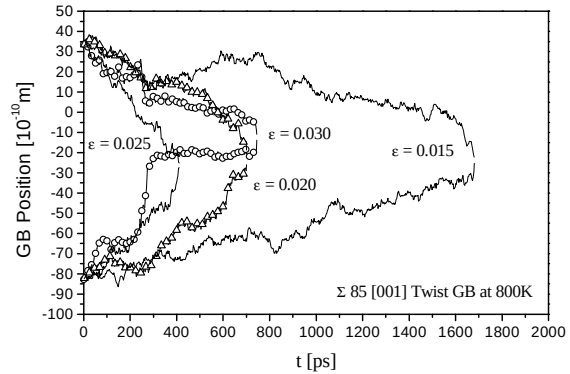


Figure 5.37: Plots of the GB position versus time of the $\Sigma 85$ twist GB at 800K.

Usually it was observed that at high temperatures, strain of 0.035 or 0.030 could not be successfully applied to the simulation boxes due to destabilization effects on the crystal structure. At low temperatures like 700K and 800K, usually a strain of 0.030 never caused any problems. For instance even for the $\Sigma 41$ twist GB, strain of 0.030 was successfully applied and drove the GBs continuously towards each other. For the $\Sigma 85$ twist GB as Fig. 5.36 and 5.37 demonstrate, strain of 0.030 does not only lead to continuous GB migration that drives the GBs towards each other but even seems to initiate long periods of time where the GBs basically move in the same direction. This is best exemplified by the 700K data. Due

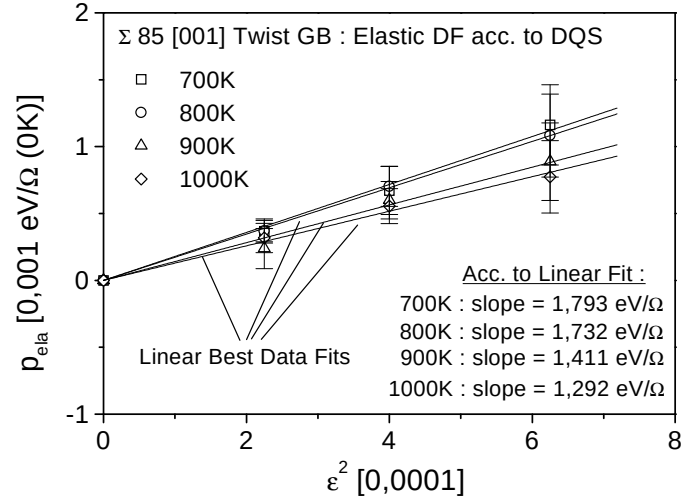


Figure 5.38: Elastic DFs determined from the GBM simulations according to the DQS for 700K up to 1000K.

to this behaviour no simulation runs with strain of 0.030 were considered when evaluating the GB velocity versus elastic DF behaviour. Fig. 5.39 presents the GB velocity versus elastic DF plots for temperatures from 700K to 1000K. Again like for the $\Sigma 41$ twist GB, the temperature dependence of the GB mobility is only a weak function of temperature. Additionally as Fig. 5.38 reveals, the elastic DF was smeared out by the 3d periodic BC effect as well as its temperature dependence no longer was as well distinguished as in the cases of the other studied twist GBs. This underlines the fact that the range of applicability of the elastic DF has almost come to its limits. Twist GBs with even smaller misorientation angles will probably move continuously in the presence of an elastic DF, still the data analysis will become more difficult. This is especially true when applying 3d periodic BC. It is thought that 2d periodic BC with pseudo free (002) surfaces would be a better choice when performing such simulations.

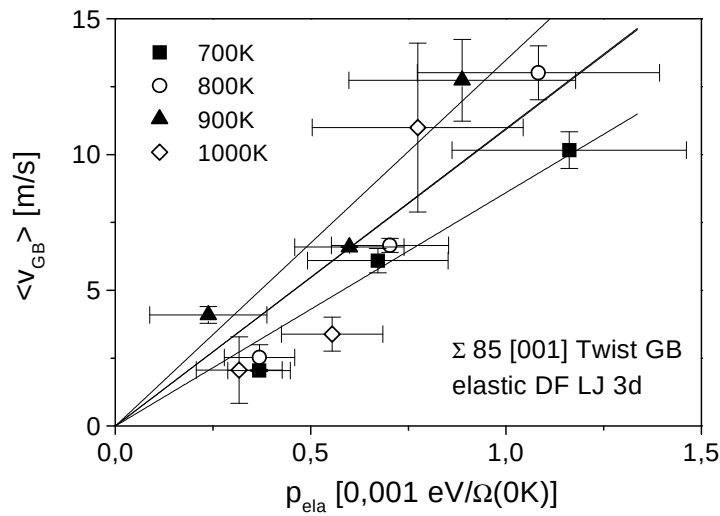


Figure 5.39: Average GB velocity versus elastic DF of the $\Sigma 85$ [001] twist GB at 700K to 1000K.

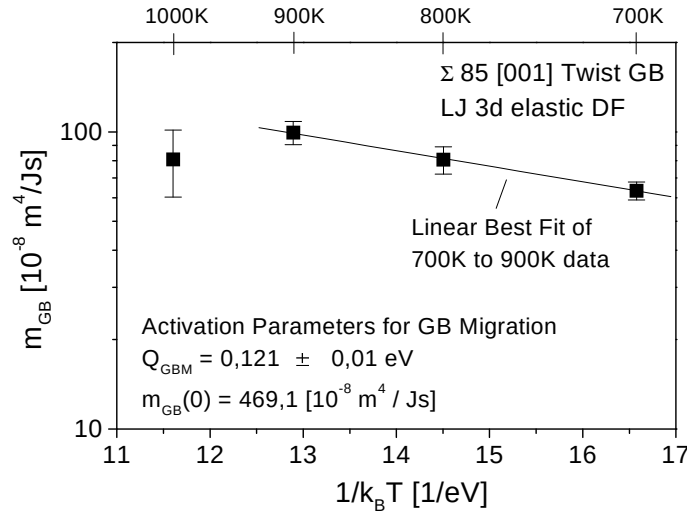


Figure 5.40: Arrhenius plot of the $\Sigma 85$ GB mobility results in the presence of an elastic DF. Again the 1000K GB mobility data point does not comply with the general expected temperature dependence.

Finally the temperature dependence of the GB mobility is plotted by an Arrhenius plot in Fig. 5.40. Again like for the $\Sigma 41$ twist GB, the 1000K GB mobility data point does not comply with the general expected temperature dependence. Hence in order to determine the GB migration activation parameters only the 700K to 900K data points were fitted according to a linear best data fit. For the activation enthalpy 0.12eV was found. With respect to the obtained error bars, the activation enthalpy of the $\Sigma 41$ and $\Sigma 85$ twist GB are the same and distinctly different from the data found for the high-angle and intermediate-angle GBs.

5.2.2.8 Discussion of the GB migration results due to an elastic DF

The GB migration results of high-angle as well as low-angle [001] twist GBs in the presence of an elastic DF were presented in the preceding sections. The results demonstrate that [001] twist GBs in a fcc material move continuously in the presence of an elastic DF. Strain magnitudes of 0.01 to 0.03 provide sufficient DFs to move these GBs continuously over distances of a few hundred angstrom in a time range of a few nanoseconds. The presented theoretical linear elastic model is capable of predicting the observed DFs correctly and only a correction of about 10 percent is found between the simulation DF data and the theoretical one. This difference can be well understood in terms of non-linear elasticity effects predominantly present at higher strain states. An in-situ calculation scheme (DQS) of the elastic energy for each (002) plane was established to reveal the temporal evolution of the elastic DF during the MD simulations. The misorientation dependence of the elastic DF expressed by the $\sin(2\cdot\theta)$ term (see Eq. 3.46) is confirmed by the simulation results. This confirms that the elastic DF becomes smaller and smaller when changing from high-angle GBs to low-angle GBs assuming a fixed strain state.

The computed elastic DF data demonstrate that for simulations with 3d periodic boundary conditions, the elastic DF decays rapidly when the two GBs present in the system have approached each other quite closely. Since from a practical point of view, any form of DF during GB migration experiments or simulations should remain as constant as possible, it seems better to utilize boundary conditions like the 2d periodic BC with stabilized free (002) surface planes to ensure such behaviour over a wider range of time. Advantages and disadvantages of 3d periodic or 2d periodic BC with stabilized free (002) surface planes are as follows. With a 3d periodic BC approach, GB velocity data of two GBs is available from one simulation run which helps to assess the error of GB velocity much easier. Nevertheless some interaction between the two present GBs in the simulation box can not be ruled out and such interaction becomes more prominent if the GBs are very close to one another. Furthermore if GB glide events play a leading role during the migration mechanism, disturbances from the presence of a second GB should be very likely.

One prime goal of the investigation was to determine the misorientation dependence for GB migration of [001] twist GBs. Tab. 5.6 summarizes the found results. In order to

GB plane	θ	Σ	Q_{GBM} [eV]	m_o [$10^{-6} \frac{m^4}{Js}$]
(001)	43.60°	29	0.438	73.06
	43.60°	29	0.226 ± 0.008	2.57
(001)	36.87°	5	0.319 ± 0.001	10.21
(001)	28.07°	17	0.267 ± 0.040	4.32
(001)	22.62°	13	0.284 ± 0.030	9.39
(001)	16.26°	25	0.346 ± 0.020	35.94
(001)	12.68°	41	0.109 ± 0.030	2.19
(001)	8.80°	85	0.121 ± 0.010	4.69

Table 5.6: GB migration activation parameters of the studied [001] twist GBs. The results were obtained for the LJ potential with 3d periodic BC and an elastic DF.

visualize the results, the activation enthalpy of GB migration, Q_{GBM} , is plotted versus the

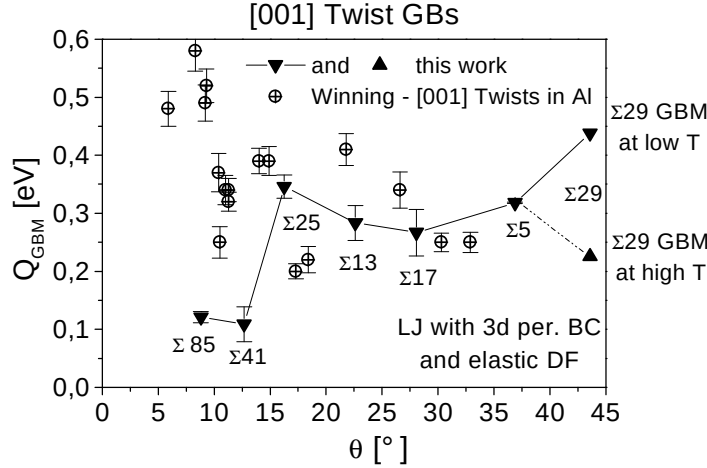


Figure 5.41: Misorientation dependence of the activation enthalpy of GB migration of the studied [001] twist GBs. The shown data represent the results of the LJ 3d periodic BC simulations in the presence of an elastic DF. Additionally experimental data of planar [001] twist GBs in Al according to Winning [63] are plotted as well.

misorientation angle, θ , as shown in Fig. 5.41. Special attention needs to be paid to the $\Sigma 29$ GB results. Here a low temperature and a high temperature regime were found. Both found data are plotted in the figure. For the other six twist GBs only the activation parameters that can be associated with the low temperature regime were obtained by the data analysis. This usually meant that only the 700K to 900K GB mobility data could be considered for the analysis. Usually the GB mobility data at 1000K suggested that some form of GB structural transition occurs since usually the 1000K mobility does not fit into the general trend of the low temperature dependence of the GB mobility. One key example is the $\Sigma 5$ twist GB where the deviation from the expected behaviour occurred again at about 900K. Since the temperature range could not easily be extended to much higher temperatures, it was difficult to answer how the GB mobility would continue. EAM results of the $\Sigma 5$ twist GB discussed in context with the orientation-correlated DF suggest that the drop in GB mobility at 1000K might be linked to the weakness of the LJ potential to mimic the structural transition of the GBs well enough.

Furthermore the distinction between high-angle and low-angle GBs seems to be reflected by the GB migration activation parameters as well. The drop of GB migration enthalpy for the two true low-angle twist GBs, namely the $\Sigma 41$ and $\Sigma 85$, to about 0.12 eV seems to reflect the difference in nature of low-angle and high-angle GBs. As found in the simulations, the low-angle twist GBs consist of screw dislocation networks that remain stable throughout the studied temperature range. Hence their migration mechanism is linked to a movement of the screw dislocation network itself. The high-angle twist GBs move in the low temperature regime by collective shuffle mechanisms which are usually in-plane mechanisms. At elevated temperatures, an out-of-plane component enters into the migration mechanism which might be the cause for the change of GB migration mechanism. This might be reflected by the drop of GB mobility above 900K.

A data comparison with recent experimental data of Winning [63] is next. Winning studied planar [001] low- and high-angle twist GBs in Al where the GBs were driven by a Peach-Koehler driving force. The studied GBs were non-CSL GBs, still overall Winning's data

lends itself for a first data comparison. In order to rationalize the computed GB migration enthalpies, it is observed experimentally that high-angle curved tilt GBs have a rather high GB migration enthalpy while the same planar tilt GBs have a much lower enthalpy. Furthermore it is observed that planar [001] tilt GBs have a higher activation enthalpy than [001] twist GBs. Finally the level of purity of a studied GB system determines to some extent how large the GB migration activation enthalpy becomes. Comparing now the data by Wining and the computed data of this work, at least one gets the impression that the GB migration enthalpies of the high-angle GBs are in a comparable range. Knowing that in Al the vacancy lattice self-diffusion enthalpy is 1.29eV and in Cu 2.01eV, the expected experimental activation data of a Cu material would be by about 35 percent larger than the Al data assuming a simple scaling behaviour. Looking at the low-angle data, the data agreement is poor. Here it seems that the difference is highly attributed to purity effects. The screw dislocation network of the studied low-angle GBs in this work could follow the ideal behaviour of screw dislocations without being pinned or dragging along impurities. So the low-angle results represent the ideal nature of a screw dislocation network moving through the system which can explain the extremely low activation enthalpies.

The obtained activation parameters lend itself to be analysed with respect to the compensation effect. The compensation effect highlights the question of structural transitions occurring within the GB structure. Doing the standard compensation effect analysis to the twist GB data, the following discussion is initiated. Fig. 5.42 shows the compensation plot of the computed GB migration activation parameters of the studied [001] twist GBs. The

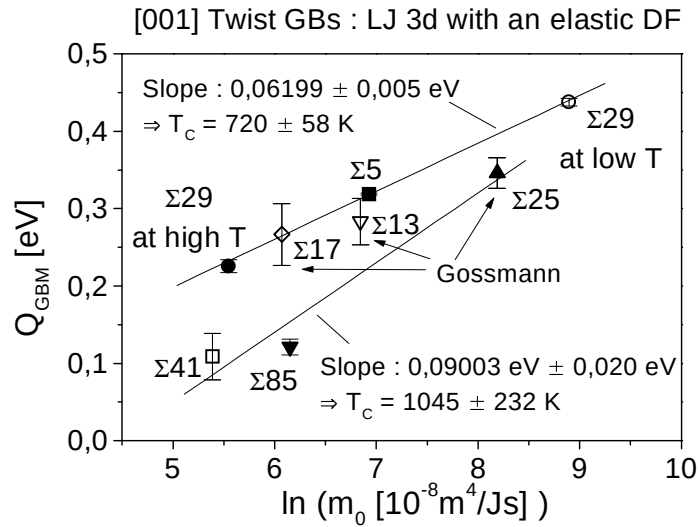


Figure 5.42: Compensation plot of the GB migration activation parameters of the studied [001] twist GBs.

plotted data seems to suggest the following. Two data sets seem to exist that are associated with either low-angle and high-angle [001] twist GBs. The found compensation temperatures seem realistic. Especially it is interesting that the low-angle twist GBs have a rather high T_C with respect to the high-angle GBs. Due to the nature of low-angle twist GBs one might associate here T_C with the melting temperature. The lower T_C for the high-angle twist GBs could be associated with a possible change of the activation enthalpy as was observed for the $\Sigma 29$ twist GB.

Concluding the analysis of the compensation effect of the studied [001] twist GBs, the following conclusions can be drawn from the data :

- (1) The found T_C for the low-angle and high-angle [001] twist GBs seem realistic.
- (2) Since the compensation temperatures seem reasonable compared to known experimental data and according to the basic concept of the compensation effect, the following conclusions can be drawn. The results indirectly support the reasoning that the found GB migration activation enthalpies and the pre-exponential factors of the found [001] GB mobility really represent the behaviour of [001] twist GBs in absolute pure GB systems. Otherwise one could have expected that even if the computed GB migration activation parameters did follow the compensation effect, still the compensation temperature itself could have been totally unphysical. For instance if it was found that T_C was 10000K then this would pinpoint that the model system does not really represent any real material.

Finally an overall reasoning is given with respect to experimental observations. Due to the relative high elastic DFs, the found GB velocities are rather high compared to velocities known from experimental work. The need for high DFs is related to the fact that within the MD simulations only a time range of a few nanoseconds is accessible with standard modern computer power. The found GB velocities ranged from a few m/s up to almost 100 m/s. From a theoretical point of view one could expect for the [001] twist GBs that the maximum possible GB velocity should be about 1300 m/s assuming a mechanism that relies on phonons. Here it was assumed that the minimum time interval for one (002) plane to change its orientation is determined by the Debye frequency ν_D due to $\tau_D = 1/\nu_D$. v_{GB}^{max} would then be given by $v_{GB}^{max} = 0.5a_0/\tau_D = 1291$ m/s. Here a Debye temperature of 343K was assumed. Clearly the Debye temperature demonstrates that the studied temperature range of 600K up to 1000K is within the regime of classical physics which supports the choice of MD as the simulation method.

5.2.3 GB Migration due to an orientation-correlated Driving Force

In this section GB migration results of five [001] twist GBs driven by the orientation-correlated DF concept are presented. These simulations can be regarded as fundamental simulations to demonstrate that indeed the orientation-correlated DF concept can drive [001] twist GBs and allows one to study continuous GB migration. Another important aim and emphasis to perform these simulations was to investigate the effect of different DF sources on the rate of GB migration. As will be demonstrated in section 5.2.3.1, the nature of the elastic DF and the orientation-correlated DF are rather similar. Both DFs are associated with the bulk grains and are therefore rather different than i.e. a Peach-Koehler DF concept which directly couples in with the GB structure.

Out of the five [001] twist GBs, the $\Sigma 5$ [001] 36.87° twist GB was chosen to be studied carefully under different boundary conditions and applying different interatomic potentials. Because of its unique nature, the $\Sigma 5$ GB was chosen to highlight different aspects of GB migration. One feature of the $\Sigma 5$ GB is its rather unique GB structure. As known from the literature and as has been found in this work as well, at low temperatures during GB migration the non-CSL GB atoms can change their crystal orientation by a simple cooperative rotation of four atoms. Since for the $\Sigma 5$ GB this is one possible GB migration mechanism and since it can be easily identified, the GB lends itself for a detailed study. Furthermore the $\Sigma 5$ GB is truly a high-energy GB as for instance the $\Sigma 29$ GB. Hence the occurrence of structural GB transition in the studied temperature seems rather likely and was observed for the GB migration and GB self-diffusion data.

5.2.3.1 General aspects of the orientation-correlated DF concept

Within GB migration studies it is very important to know the temporal evolution of the DF and to be able to quantify it. This is rather simple for the orientation-correlated DF, p_{corr} , since it has been analytically introduced into the equations of motion of each atom and hence it is readily available (see Eq. 3.49 to 3.50). Fig. 5.43 shows the temporal evolution of the orien.-corr. DF for some of the conducted EAM $\Sigma 5$ GB migration simulations. It shows the temperature dependence of the orien.-corr. DF as well as the temporal evolution of the DF for the $\Sigma 5$ [001] 36.87° twist GB for different DF coefficients. The DF coefficients were i.e. $a_1=0.008$ eV/atom and $a_2=0.002$ eV/atom which yielded an orien.-corr. DF ranging from 0.005 eV/atom down to 0.00406 eV/atom depending on the simulation temperature. As well coefficients $a_1=0.006$ eV/atom and $a_2=0.002$ eV/atom were used yielding orien.-corr. DFs ranging from 0.00335 eV/atom down to 0.00300 eV/atom. The shown data was obtained by EAM simulations utilizing 2d periodic BC within the GB plane and free surfaces in the direction of the GB normal. The figure should stress two things. The first one is that due to the chosen boundary conditions the DF remains constant throughout the whole simulation. This is because the single GB present in the system can move twice the distance than in a comparable system with 3d periodic BC before reaching the free surface. Usually in conducted simulations where 3d periodic BC were applied, the GBs usually annihilated at the end of the simulation runs. Due to this the DF decreased already quite noticeably even before the GBs annihilated (see Fig. 5.60). This decline of DF and the enhancement of GB interaction is unwanted and acts as a disturbance with respect to the GB migration data. Of course for the single GB simulations when the GB comes very close to the free surface a similar decrease of DF would be observed. Therefore all simulations with non 3d

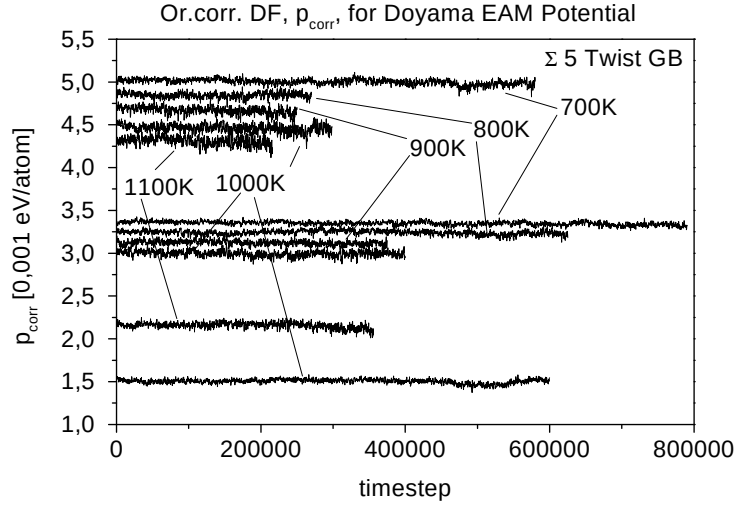


Figure 5.43: Orientation-correlated DF of the $\Sigma 5$ [001] 36.87° twist GB at different T and different DF coefficients. Here the temperature dependence of the orien.-corr. DF as well as the temporal evolution of the DF can be seen. For the EAM simulations 2d periodic BC within the GB plane and free surfaces in the GB normal direction were applied.

periodic BC were only run to the point where the GB was still 10 to 30 (002) planes away from the free surface.

The second point to stress is that the orien.-corr. DF behaves in the same way as the elastic DF with respect to temperature. Fig. 5.44 presents the temperature dependence of the orien.-corr. DF of the $\Sigma 5$ [001] 36.87° twist GB for fixed DF coefficients. Two data sets are presented : (1) GB migration simulations with LJ 2d periodic BC and DF coefficients $a_1=0.010$ eV/atom and $a_2=0.002$ eV/atom and (2) GB migration simulations with EAM 2d periodic BC and DF coefficients $a_1=0.008$ eV/atom and $a_2=0.002$ eV/atom. Therefore with

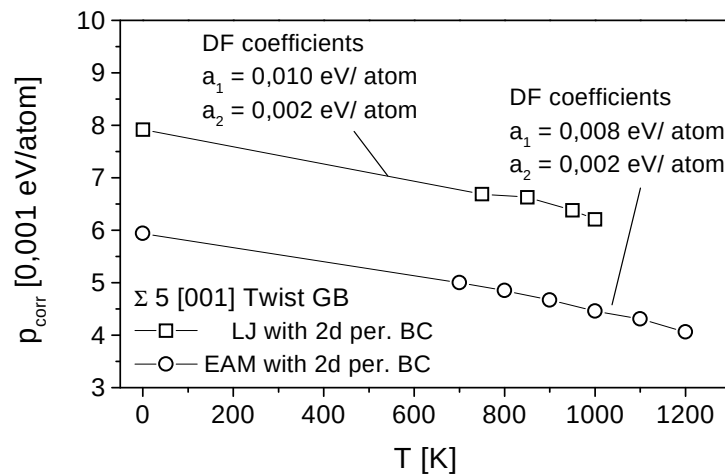


Figure 5.44: Orientation-correlated DF for the $\Sigma 5$ [001] 36.87° twist GB at different T . Here the temperature dependence of the orien.-corr. DF is plotted for fixed DF coefficients. Two data sets are presented : (1) GB migration simulations with LJ 2d periodic BC and (2) GB migration simulations with EAM 2d periodic BC.

increasing temperature for fixed DF coefficients, the orien.-corr. DF decreases. Due to the nature of the DF, this decrease is well-explained by the thermal vibrations of the system's atoms which is well-known and expressed by the Debye-Waller factor. Therefore although the nature of the orien.-corr. DF is solely connected to the structural order in the vicinity of an atom, it still follows general behaviour of known DFs, namely for fixed DF parameters a decrease of DF with increasing temperature. This is best seen in comparison with the elastic DF as presented within this work.

For the elastic DF it was shown analytically that the DF does decrease with decreasing twist angle (see i.e. Eq. 3.46). The same behaviour can be found for the orien.-corr. DF. To underline this, for seven [001] twist GBs presented in this work the orien.-corr. DF was calculated at 10K with DF coefficients $a_1=0.008$ eV/atom and $a_2=0.002$ eV/atom. Figure 5.45 shows the results. Here the average excess energy installed in grain 1, E_{Grain1} , and in grain 2, E_{Grain2} , as well as the orien.-corr. DF are plotted. The figure shows that

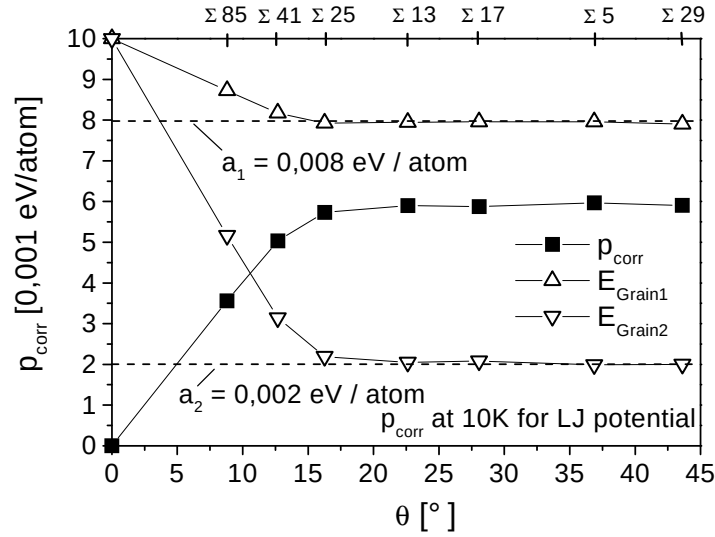


Figure 5.45: Misorientation dependence of the orientation-correlated DF for the [001] twist GBs at 10K.

in the low-angle GB regime the orien.-corr. DF steadily decreases to zero with decreasing twist angle. At zero twist angle, thus for an ideal crystal situation, the DF has to be zero due to its mathematical construction and following common sense. Still in the ideal crystal situation as well, an excess energy will be stored in the crystal which underlines the physical correctness of the DF.

According to the presented facts and data, it was shown that the orien.-corr. DF is comparable in its physical behaviour to other experimental or simulation-based DFs. Only related to its physical origin the orien.-corr. DF can be thought of being artificial since it can not directly be associated i.e. to elasticity, magnetic moments of atoms or similar physical properties that can interact with external fields. The basic idea of utilizing this DF is based on such phenomena. Therefore the orien.-corr. DF can be regarded as an alternative DF that in some cases can be advantageous for GB migration simulations. This is best exemplified when dealing with certain tilt GBs since there the elastic DF is not able to drive the GBs continuously (see sections 6.3.1.2 and 6.3.1.3). Therefore the orien.-corr. DF offers a choice to study continuous GB migration for such GBs.

5.2.3.2 $\Sigma 5$ [001] 36.87°

The performed studies in this work on the $\Sigma 5$ [001] 36.87° twist GB were rather extended to cover different aspects of this GB. As shown in section 5.2.2.4, GB migration of the $\Sigma 5$ twist GB was studied in the presence of an elastic DF and for the LJ potential. To extend these simulations and to study the effect of boundary conditions as well as source of DF for GB migration, further simulations applying different concepts were performed. Additionally GB self-diffusion was studied for non-driven GBs as well as for driven GBs in order to assess the question what role GB self-diffusion plays in the overall picture of GB migration.

One focus point of the performed simulations was to utilize different boundary concepts as well as to employ the Cu EAM potential by Doyama and Kogure. The exact simulation conditions were the following. For the Cu EAM potential, 2d periodic boundary conditions within the (002) planes and free (002) surfaces were realized. For the LJ potential, 2d periodic boundary conditions within the (002) planes were applied while in the [001] direction pseudo (002) free surfaces were used as described in section 3.3.4. As an example of the

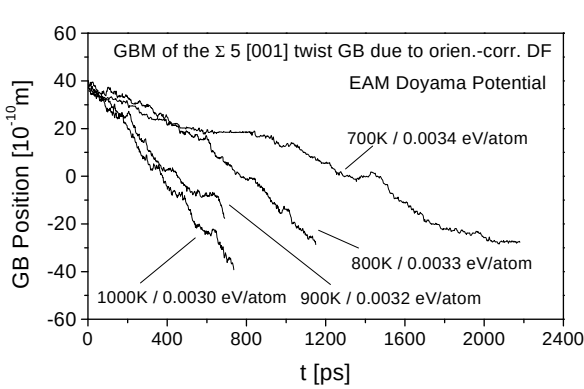


Figure 5.46: GB position versus time plots of a few $\Sigma 5$ [001] 36.87° twist GB migration simulations for the Cu EAM potential at 700K, 800K, 900K and 1000K.

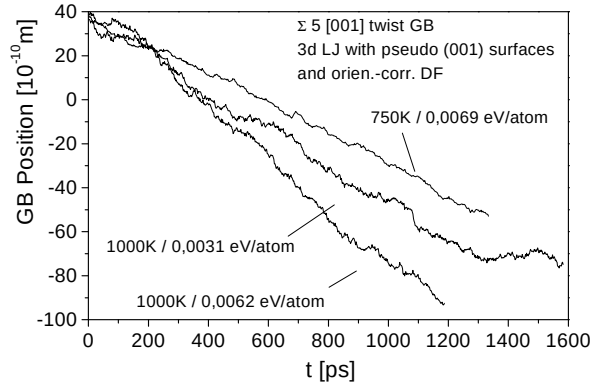


Figure 5.47: GB position versus time plots of GB migration simulations of the $\Sigma 5$ [001] 36.87° twist GB for the LJ potential and 2d periodic BC with stabilized (002) surfaces at various temperatures.

performed simulations, Fig. 5.46 and 5.47 show plots of the GB position versus time of part of the performed simulations. These figures exemplify that due to the non-periodicity in [001] direction, the GBs can travel a larger distance than in simulations where periodicity along the [001] direction was applied and assuming the same box dimensions. There are at least two reasons in favour of utilizing free (002) surface boundary concepts. One is that due to this the distance the GBs can travel increases and hence the confidence in the GB velocities extracted from these data increases as well. Furthermore possible interaction between the two GBs present in 3d periodic systems is avoided although to some extent some form of interaction between a single GB and free surfaces can in principle be possible too once the GB will have come very close to one of the (002) surfaces. Next Fig. 5.48 and 5.49 present the obtained GB velocity versus orien.-corr. DF, p_{corr} , for the performed LJ and the EAM simulations. The reader should note that due to the wider temperature range of the EAM potential, GBM simulations for the EAM potential were done for temperatures ranging from 700K up to 1200K. Furthermore the EAM simulations were utilizing boundary

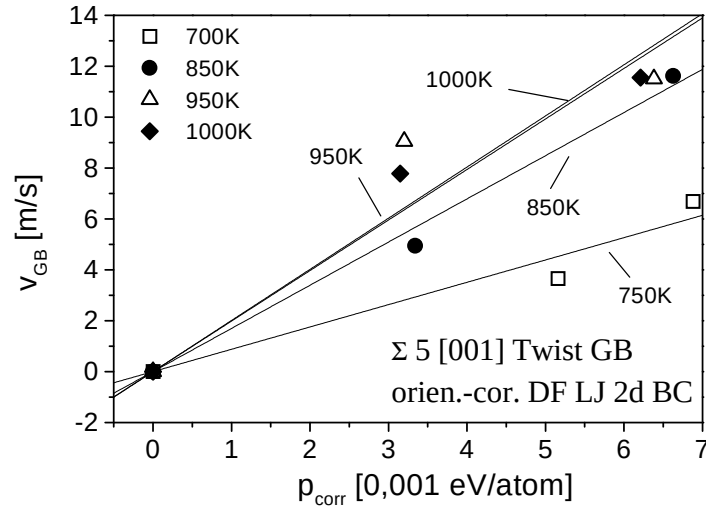


Figure 5.48: Plot of the GB velocity versus orien.-corr. DF at different temperatures of the $\Sigma 5$ [001] 36.87° twist GB for the LJ 2d periodic BC simulations with pseudo (002) free surfaces.

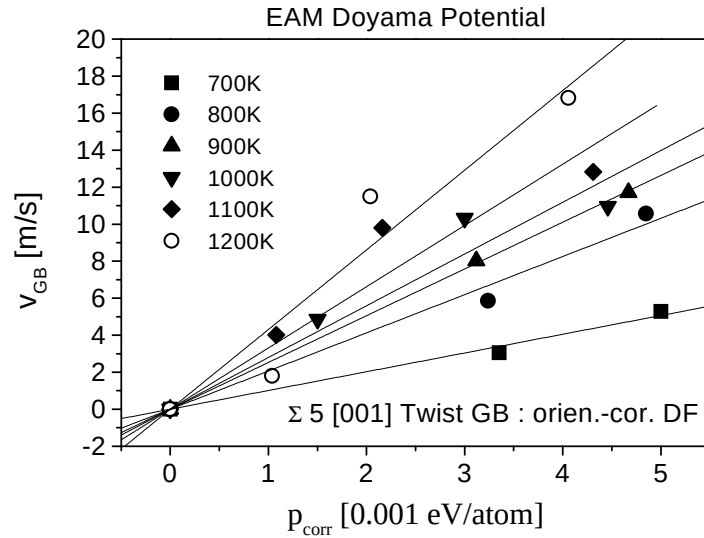


Figure 5.49: Plot of the GB velocity versus orien.-corr. DF at different temperatures of the $\Sigma 5$ [001] 36.87° twist GB for the EAM Doyama potential and 2d periodic BC simulations with free (002) surfaces.

conditions with free (002) surfaces and even up to 1200K these surfaces remained stable. This is important to note and reflects the superiority of the EAM potential over the LJ one. A true free (002) boundary concept does not work for the LJ potential over the whole desired temperature range and hence pseudo (002) free surface boundary conditions were required to study the behaviour of a single GB. It is further interesting that the extracted GB velocities for both potentials are rather similar. Hence Fig. 5.50 confirms that the temperature dependence of the GB mobility for both potentials is rather similar. Fig. 5.50

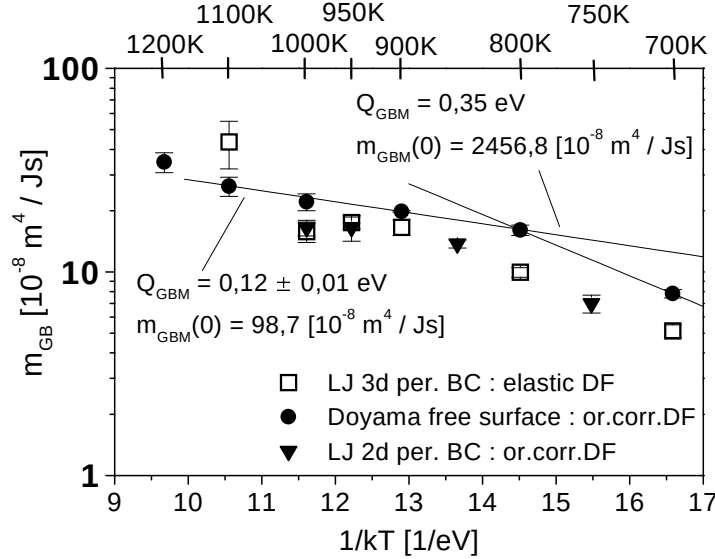


Figure 5.50: Arrhenius plot of the GB mobility of the $\Sigma 5$ [001] 36.87° twist GB for the orien.-corr. and elastic DF. Here the overall data of all conducted GBM simulations on the $\Sigma 5$ twist GB are presented. The data comparison shows that the LJ results for either of the used DFs agree very well and that the difference between the EAM and LJ results is rather small.

reveals several things about the $\Sigma 5$ twist GB and the used DF concepts. The GB mobility results of the LJ elastic DF and the LJ orien.-corr. DF demonstrate that the obtained GB mobility data agrees perfectly fine. In consequence this means that the simulations with 3d periodic BC and the ones with the 2d periodic BC and pseudo (002) free surfaces result in the same GB mobility. Additionally the elastic DF and the orien.-corr. DF give the same GB mobility data. As was discussed in section 5.2.3.1, the nature and physical behaviour of both DFs is the same, hence it does not surprise at all that the GB migration properties are identical. Hence one important conclusion can be drawn, namely that the orien.-corr. DF is indeed capable to study GB migration and to yield GB migration properties of physical relevance. Therefore the found GB migration activation parameters are identically the same as found from the LJ elastic DF simulations presented in section 5.2.2.4.

Extending the discussion to the EAM GBM results, several aspects become visible. First of all the EAM data reveals that the $\Sigma 5$ twist GB undergoes a structural transition at about 800K. Interestingly the LJ mobility in the temperature range up to 900K shows the same temperature dependence as the EAM data meaning the activation enthalpy is almost identical. Being aware of the EAM results for the complete studied temperature range, the LJ results appear in a different light. Without knowledge of the EAM data, the LJ data at high temperatures are difficult to interpret since they slightly decrease with increasing

temperature between 900K and 1000K. Knowing that the EAM data clearly identifies the structural transition of the $\Sigma 5$ twist GB, the LJ data can be interpreted in the same way. Hence the LJ GB mobility up to 900K represents the low temperature behaviour of the GB with an underlying ordered crystalline GB structure. At high temperatures the GB undergoes a structural disorder. Most likely due to the poor physical behaviour of the LJ potential the GB mobility data in the high temperature range is slightly decreasing. The shortcoming of the LJ potential is supported by the fact that both, the elastic DF and the orien.-corr. DF results, show exactly the same behaviour over the whole studied temperature range.

GB self-diffusion - Now the discussion is extended to GB self-diffusion of the $\Sigma 5$ twist GB. Here two main aspects were of interest to do extended studies. One is whether or not

EAM 2d per. BC and orien.-corr. DF

T [K]	p_{corr} [0,001 eV/atom]	$\delta D_{GB} / \Omega$ [1/ps]
600	0,00	0,000124
650	0,00	0,000310
700	0,00	0,000804
700	3,35	0,000898
700	5,00	0,001002
800	0,00	0,002436
800	3,24	0,002050
800	4,85	0,002663
900	0,00	0,004223
900	3,12	0,004384
900	4,67	0,004654
1000	0,00	0,007207
1000	1,50	0,007469
1000	3,00	0,007042
1000	4,46	0,007852
1100	0,00	0,012796
1100	1,10	0,012712
1100	2,16	0,011722
1100	4,31	0,013161
1200	0,00	0,021940
1200	1,00	0,025606
1200	2,04	0,026495
1200	4,06	0,030623

LJ 2d per. BC and orien.-corr. DF

T [K]	p_{corr} [0,001 eV/atom]	$\delta D_{GB} / \Omega$ [1/ps]
750	5,16	0,0010136
750	6,69	0,0012010
850	3,34	0,0042041
850	6,63	0,0042148
950	3,20	0,0093457
950	6,38	0,0086679
1000	3,15	0,0137255
1000	6,21	0,0137216

Table 5.7: GB self-diffusion coefficient determined from GB migration simulations of the $\Sigma 5$ [001] twist GB. Here the results of the LJ 2d per. BC and EAM 2d per. BC simulations in the presence of an orien.-corr. DF are presented. For simulation runs at fixed temperature but different DFs, the GB diffusion coefficient remains the same. No systematic effect of the magnitude of the DF is observed on the GB diffusion coefficient.

a structural transition of the $\Sigma 5$ twist GB can be found in the GB self-diffusion data. The

second aspect of interest was whether GB self-diffusion via vacancies is the same for driven and non-driven GBs. Finally the effect of the used interatomic potential was included in the discussion as well. Fig. 5.51 presents an Arrhenius plot of the GB self-diffusion

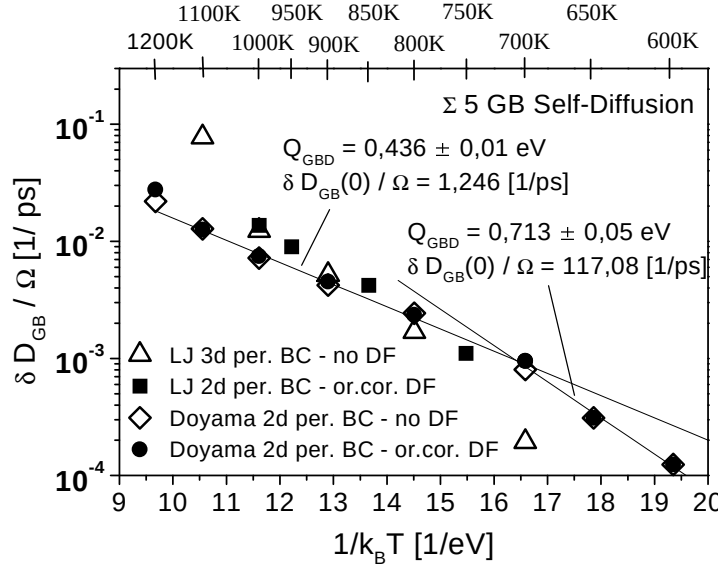


Figure 5.51: Arrhenius plot of the GB self-diffusion coefficient determined from non-driven and driven $\Sigma 5$ [001] twist GB simulations. Simulation results of the LJ and EAM potential are included in the plot.

coefficient for non-driven and driven GB simulations as well as for conducted LJ and EAM simulations. The shown data clearly shows that for both potentials a structural transition of the GB occurs. Comparing the transition temperatures of the GB self-diffusion and the GB migration data for both potentials, the LJ data again suggests a structural change of the GB at a higher temperature. Hence qualitative consistency between the LJ and EAM results is found. The absolute transition temperature obtained by the GB self-diffusion data is less than that for the GB migration data. This is true for both potentials. The LJ and EAM results qualitatively agree very well and exhibit the same physical behaviour with respect to scaling behaviour between low temperature and high temperature activation parameters. As found for the LJ potential, the EAM activation enthalpy of GB migration is about half that of GB self-diffusion. Furthermore the high temperature activation enthalpy is about half of the low temperature data.

Next the GB self-diffusion via vacancies is studied for non-driven and explicitly driven GBs. Table 5.7 and Fig. 5.51 present the determined data for LJ and EAM simulations on the $\Sigma 5$ [001] twist GB. The data reveals that GB self-diffusion via vacancies remains the same for non-driven and driven GBs. This is very interesting to note since already the activation parameters of GB self-diffusion and GB migration show that GB self-diffusion and GB migration are distinctly different GB processes. No effect of the magnitude of the used DF on the GB self-diffusion data was found. In some cases it seems that GB self-diffusion enhances with increasing DF. This behaviour is only true for some simulation results, for the overall results it can not be confirmed.

Hence the following conclusions can be drawn from the GB self-diffusion results. GB self-diffusion remains the same for non-moving and moving GBs. GB self-diffusion and GB

migration due to an elastic or orien.-corr. DF are distinctly different processes.

5.2.3.3 $\Sigma 17$ [001] 28.07°

GB migration of the $\Sigma 17$ [001] 28.07° twist GB was studied in the presence of the orientation-correlated DF with two different boundary concepts and for the LJ potential. One boundary concept was the 3d periodic BC while the second one utilized 2d periodic BC with pseudo (002) free surfaces. Fig. 5.52 and 5.53 show GB position versus time plots for some of the conducted runs. The main focus to study the $\Sigma 17$ twist in the presence of the orien.-

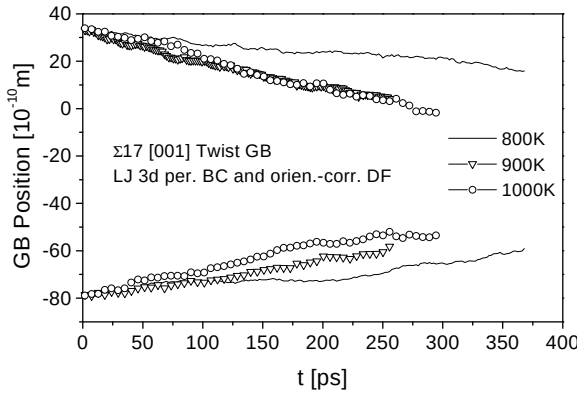


Figure 5.52: Plot of GB position versus time of the $\Sigma 17$ [001] 28.07° twist GB at 800K to 1000K for the LJ potential and 3d periodic BC.

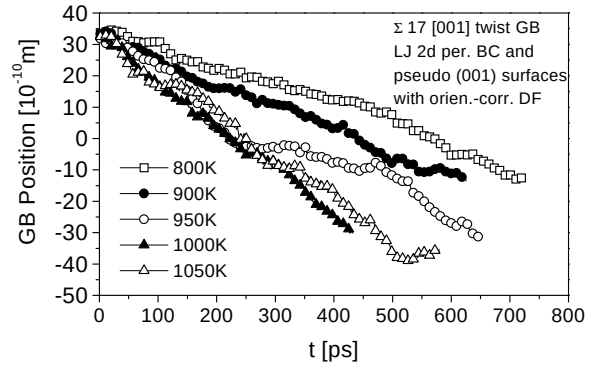


Figure 5.53: Plot of GB position versus time of the $\Sigma 17$ [001] 28.07° twist GB at 800K to 1050K for the LJ potential and 2d periodic BC with pseudo (002) free surfaces.

corr. DF was to check how well the elastic DF and the orien.-corr. DF results agree. To crosscheck that the GB velocity of 3d periodic BC and 2d periodic BC simulations agree, only a few 3d periodic BC simulations were performed. The GB velocities extracted from these simulations agreed fairly well although not exactly. As can be seen in Fig. 5.52, the time range studied in the 3d periodic BC simulations was not too extended which hence might explain the slight difference between the 3d periodic and the 2d periodic GB velocities. Overall no strong effect of the boundary conditions was found.

The overall GB velocity data mainly obtained by 2d periodic BC simulations is presented in Fig. 5.54 in a GB velocity versus orien.-corr. DF plot. Performing linear data fits of the GB velocity data yields the temperature dependence of the GB mobility. Plotting the GB mobility data in an Arrhenius plot finally gives the activation parameters of GB migration. Fig. 5.55 shows two data sets of GB mobility. One is the GB mobility data obtained by Gossmann due to an elastic DF while the second is the data presented in this section due to the orien.-corr. DF. Overall the GB mobility data agree fine and only the activation parameters differ slightly. For the elastic DF an activation enthalpy of 0.267 ± 0.04 eV was found while for the orien.-corr. DF 0.355 ± 0.05 eV. Hence the difference in activation enthalpy can be explained with respect to the found error bars.

Another interesting point is whether or not the $\Sigma 17$ twist GB undergoes a structural transition in the studied temperature range. This idea needs to be considered since due to its GB energy of 0.677J/m^2 , the $\Sigma 17$ twist GB can still be consider as an high energy with

respect to the Σ 29 and 5 twist GB. With respect to the misorientation angle of 28.07° the Σ 17 twist GB seems to be an intermediate angle twist GB. Referring to the GB mobility

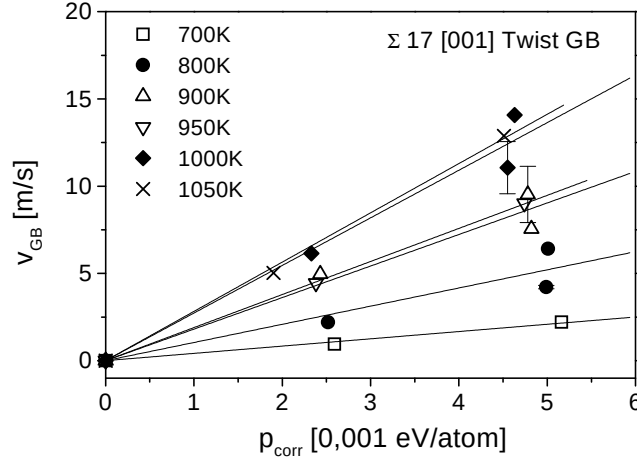


Figure 5.54: Plot of the GB velocity of the Σ 17 [001] 28.07° twist GB versus orien.-corr. DF at different temperatures. The plot contains mainly results extracted from 2d periodic BC LJ simulations. The 3d periodic results can be identified in the plot by the data points having error bars.

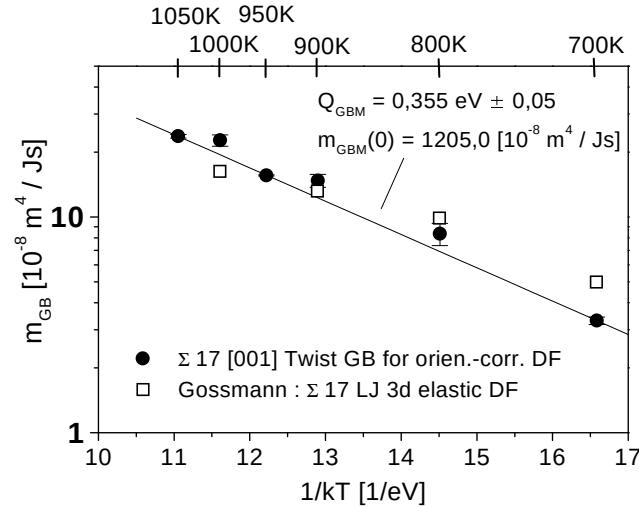


Figure 5.55: Arrhenius plot of the GB mobility of the Σ 17 [001] 28.07° twist GB. Two data sets are shown. One is the GB mobility data obtained by Gossmann due to an elastic DF while the second one is the data presented in this section due to the orien.-corr. DF. Overall the mobility data agree fine and only the activation parameters differ slightly.

data in Fig. 5.55 it seems possible that a low and a high temperature range exists even for this GB. Still the presented GB mobility data does not fully convince as in the cases of the Σ 29 and Σ 5 twist GB. Furthermore the overall mobility data is well represented by a single linear data fit, therefore no attempt was made to interpret the Σ 17 GB mobility consisting of two temperature regimes. In order to seriously address this issue more data points at different temperatures would be necessary. Furthermore according to the Σ 5 twist GB results it would make sense to utilize an EAM potential rather than the LJ potential.

5.2.3.4 $\Sigma 13$ [001] 22.62°

In this section the GB migration results of the $\Sigma 13$ [001] 22.62° twist GB utilizing the orientation-correlated DF concept are presented. Two different boundary concepts and the LJ potential were utilized in the simulations. One boundary concept was the 3d periodic BC while the second one was the 2d periodic BC with pseudo (002) free surfaces. Fig. 5.56 shows various examples of GB position versus time behaviour with and without the orien.-corr. DF as well as for the two utilized boundary conditions at 800K. Fig. 5.57 shows similar GB

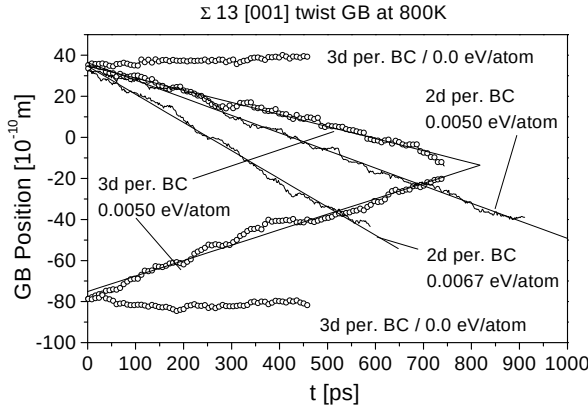


Figure 5.56: GB position versus time plot of the $\Sigma 13$ twist GB at 800K.

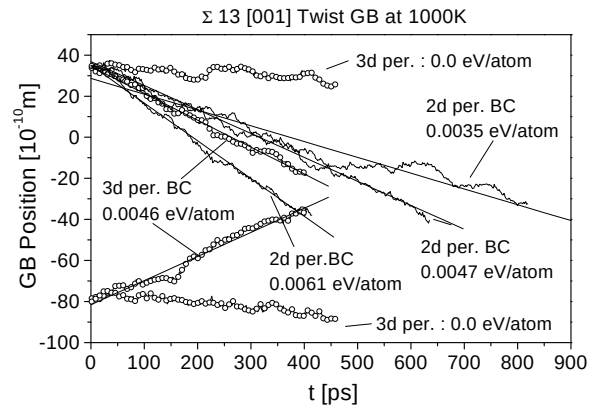


Figure 5.57: GB position versus time plot of the $\Sigma 13$ twist GB at 1000K.

simulation results as Fig. 5.56 but only for the 1000K situation. The two figures demonstrate that the GB position profiles and hence the GB velocities extracted from the 3d periodic BC and 2d periodic BC simulations agree fairly well. Additionally the non-driven GBs remain almost at their initial position and only exhibit thermal fluctuations in the studied time ranges. This covered time range is comparable with the time range of the LJ 3d periodic GB migration simulations. Hence it can be concluded that no strong GB interaction was present in the 3d periodic BC simulations that might have acted as an retarding DF.

Fig. 5.58 presents the GB velocity versus orientation-correlated DF of the $\Sigma 13$ [001] twist GB at different temperatures and for the two different boundary conditions. Most of the presented data is linked to the LJ 2d periodic simulations. A linear best data fit is well suited to represent the data and hence yields the temperature dependence of the GB mobility. Finally the temperature dependence of the GB mobility data is plotted in an Arrhenius plot as seen in Fig. 5.59. Here three data sets are shown. Two are linked to the GB mobility data obtained by Gossmann due to an elastic DF while the third one is the data presented in this section due to the orien.-corr. DF. As discussed and presented above, the difference between linear best data fits done by Gossmann yield almost identical GB mobilities which is well seen in the Arrhenius plot. Overall the mobility data of the elastic and orien.-corr. DF agree fine and only for the 700K data a difference between the elastic DF and the orien.-corr. data is observed. Again like in the case of the $\Sigma 17$ twist GB, the GB mobility data due to the orien.-corr. DF implies a low temperature and high temperature regime. Taking this into account and performing linear best data fits of the data yield the following GB migration activation parameters of the $\Sigma 13$ twist GB (see Tab. 5.8).

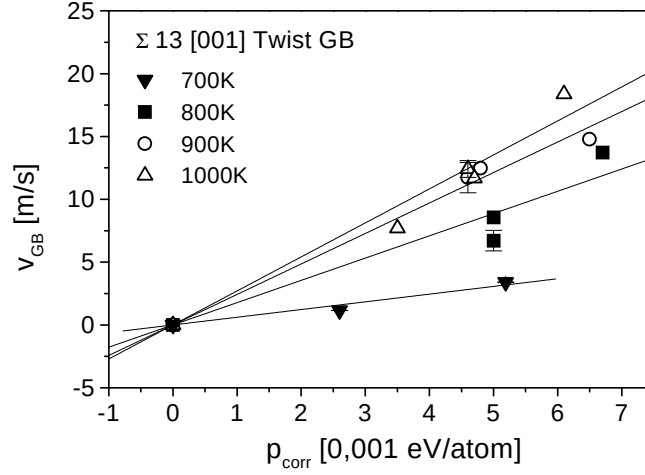


Figure 5.58: GB velocity versus orientation-correlated DF of the $\Sigma 13$ [001] twist GB at different temperatures. The plot contains mainly results extracted from 2d periodic BC LJ simulations. The 3d periodic results can be identified in the plot by the data points having error bars.

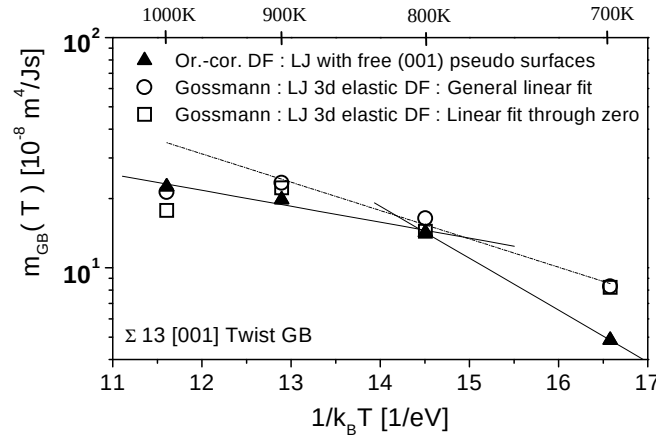


Figure 5.59: Arrhenius plot of the temperature dependence of GB mobility of the $\Sigma 13$ [001] twist GB. Three data sets are shown. Two are GB mobility data obtained by Gossmann due to an elastic DF while the third one is the data presented in this section due to the orien.-corr. DF. Overall the mobility data agree fine and only for the 700K data a difference between the elastic DF and the orien.-corr. data is observed.

	elastic DF Gossmann	orien.-corr. DF low T regime	orien.-corr. DF high T regime
Q [eV]	0.284	0.520	0.160
$m_{GBM}(0)$ [10^{-6} m ⁴ /Js]	9.39	266.77	1.47

Table 5.8: GB migration activation parameters of the $\Sigma 13$ [001] twist GB for the elastic DF (data by Gossmann) and the orien.-corr. DF.

5.2.3.5 Σ 85 [001] 8.80°

Here the GB migration results of the $\Sigma 85$ [001] 8.80° twist GB utilizing the orientation-correlated DF concept are given. For the simulations the 3d LJ potential and 3d periodic BC were used.

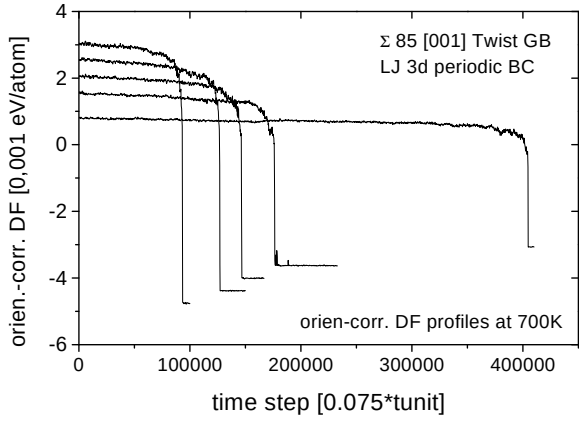


Figure 5.60: Temporal evolution of the orien.-corr. DFs for the 700K $\Sigma 85$ twist GB migration simulations.

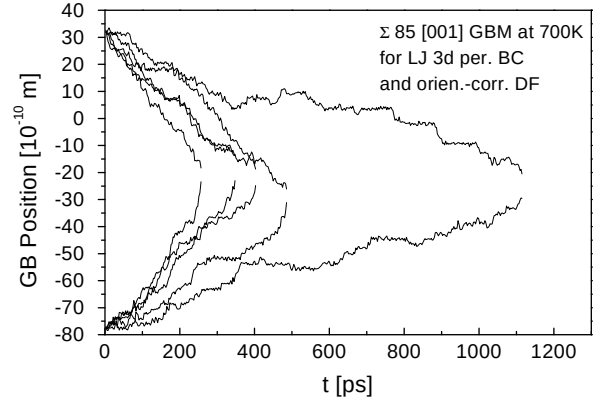


Figure 5.61: GB position versus time for LJ simulations with 3d periodic BC and the orientation-correlated DF of $\Sigma 85$ twist GB at 700K.

Fig. 5.60 shows the temporal evolution of the orien.-corr. DF for different settings of DF coefficients, a_1 and a_2 , at 700K. The temporal evolution of the DF exhibits the 3d periodic BC effect, namely that once the two GBs have come very close to each other the excess energy of the shrinking grain is becoming smaller and smaller compared to the situation when that grain was still rather extended within the system. This behaviour can only be understood in terms of crystal structure weakening of the shrinking grain due to the closeness of the two GBs. The same effect is observed with the elastic DF and is solely connected to the used 3d boundary conditions.

The figure demonstrates as well that rather high DFs can be achieved for this low-angle [001] twist GB depending only the exact choice of a_1 and a_2 . This is distinctly different from the elastic DF where only a maximum strain of 0.03 to 0.035 can be used without stabilizing the crystal structure. This is even more true for higher temperatures where the maximum applicable strain magnitude becomes less and less compared to low temperature situation. In contrast Fig. 5.62 demonstrates that even at 1000K orien.-corr. DFs of 0.00275 eV/atom can be achieved with no destabilization effects of the crystal structure. For the elastic DF only maximum DFs of 0.00125 to 0.0015 eV/Ω were achievable which correspond to a strain magnitude of 0.025. As was discussed and presented in section 5.2.2.7, a strain magnitude of 0.030 led to rather obscure GB migration phenomena which did not allow us to extract reliable data for GB migration from the simulation runs. According to this observation, the orien.-corr. DF lends itself to study GB migration at DF levels that can not be achieved by means of the elastic DF. Furthermore no explicit mechanical destabilization effects of the crystal's grain structure were observed for the orien.-corr. DF even when applying in some case DF levels as high as 0.007 eV/atom (see section 5.2.3.3). Fig. 5.61 exemplifies that the GB position versus time profiles can be fitted very nicely by linear regression fits which

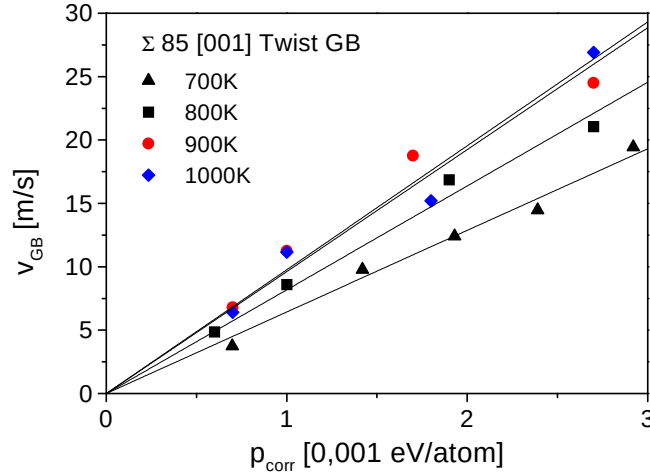


Figure 5.62: Average GB velocity versus orien.-corr. DF of the $\Sigma 85$ [001] twist GB at different temperatures.

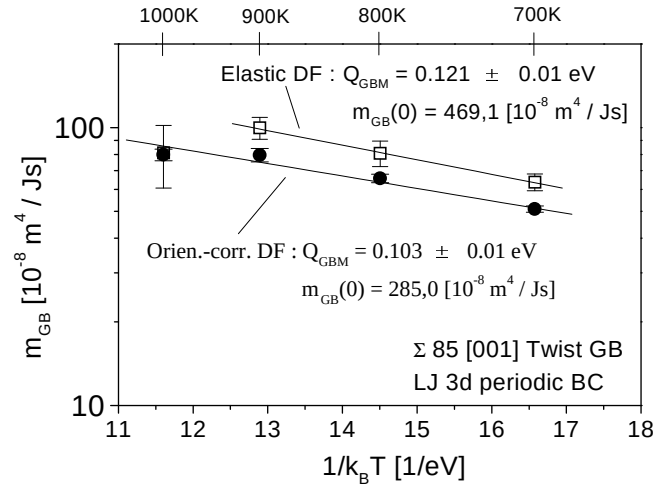


Figure 5.63: Arrhenius plot of the $\Sigma 85$ GB mobility for GB migration due to an elastic and orien.-corr. DF.

hence yield the GB velocities. No rather unusual behaviour as seen for the elastic DF was found for the case of the orien.-corr. DF.

Finally Fig. 5.63 presents the Arrhenius plot of the GB migration mobility of the $\Sigma 85$ twist GB. Two data sets are shown. One is related to the results due to an elastic DF while the other one is related to results due to an orien.-corr. DF. In both cases 3d periodic BC were utilized. The elastic DF results show a drop in GB mobility at 1000K with respect to the low temperature GB mobility data. The orien.-corr. DF results show a similar behaviour at 1000K but far less pronounced. Indeed the orien.-corr. DF results over the whole studied temperature range are well represented by a linear best data fit which does not work for the elastic DF results. The determined GB migration enthalpies for both DFs agree fine and are given in Fig. 5.63. Overall it was observed that GB mobility data obtained by the orien.-corr. DF show less pronounced drops in GB mobility at high temperatures. Key examples for this tendency are the GB mobility results of the $\Sigma 17$, 13 and 85 twist GBs.

5.2.3.6 $\Sigma 181$ [001] 6.03°

Here the GB migration results of the $\Sigma 181$ [001] 6.03° twist GB utilizing the orientation-correlated DF concept are given. For the simulations the LJ potential and 3d periodic BC were used. The simulation box consisted of 76 (002) planes, leading to a total number of 13756 atoms within the system. Initially 36 (002) planes were assigned to each grain. The fully relaxed GB energy was 0.404J/m^2 .

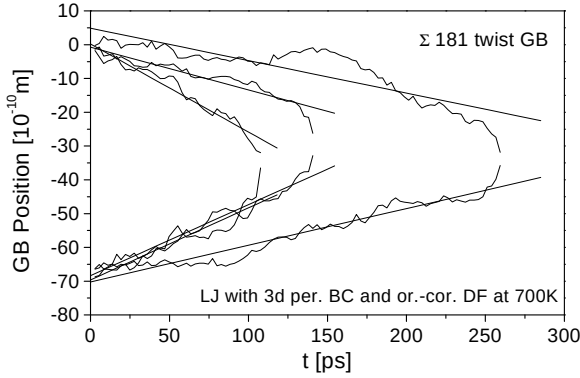


Figure 5.64: GB position versus time plots of LJ simulations with 3d periodic BC and the orientation-correlated DF of the $\Sigma 181$ twist GB at 700K.

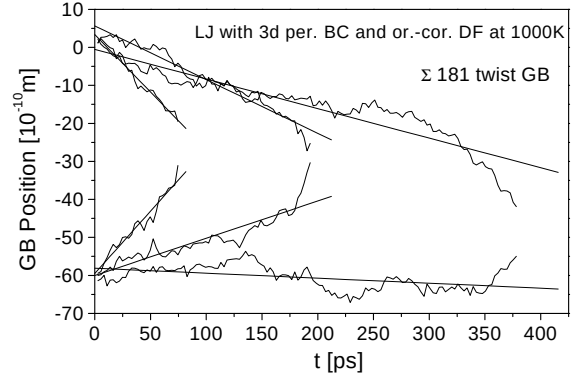


Figure 5.65: GB position versus time plots of LJ simulations with 3d periodic BC and the orientation-correlated DF of the $\Sigma 181$ twist GB at 1000K.

The studied temperature range extended from 500K up to 1000K in step of 100K. To exemplify the GB position versus time behaviour, Fig. 5.64 to 5.65 present the found GB position versus time plots at 700K and 1000K, respectively. Here the profiles for three different orientation-correlated DFs and the linear best data fit of the GB position versus time profiles are shown. Additionally Fig. 5.66 presents the GB position versus time plots

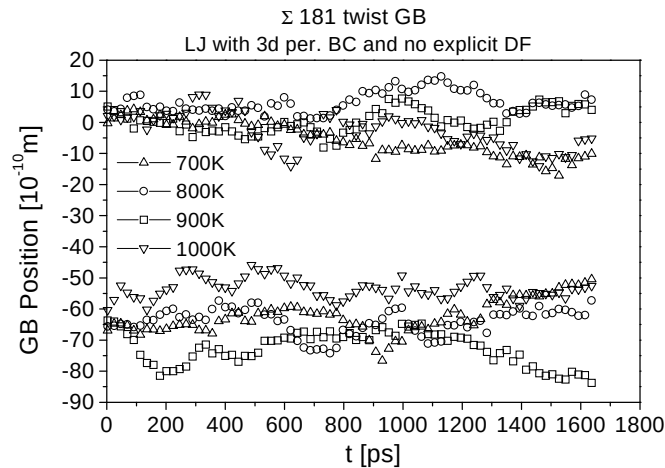


Figure 5.66: GB position versus time plots of LJ simulations with 3d periodic BC of the $\Sigma 181$ twist GB with no explicit DF. These simulations were used to study the GB self-diffusion of the $\Sigma 181$ twist GB.

from 700K to 1000K when no explicit DF was introduced into the system. The plots

demonstrate that apart from thermal fluctuations at elevated temperatures, the GBs do not interact strongly and hence no continuous GB migration is observed that would lead to the annihilation of the two GBs. Next GB velocity versus orientation-correlated DF

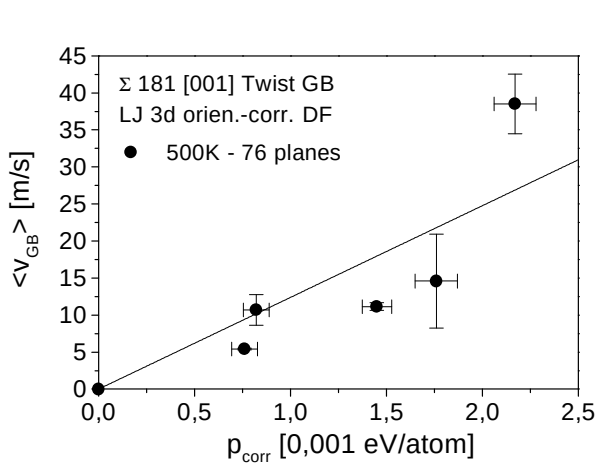


Figure 5.67: Plot of the GB velocity versus orientation-correlated DF of the $\Sigma 181$ twist GB at 500K.

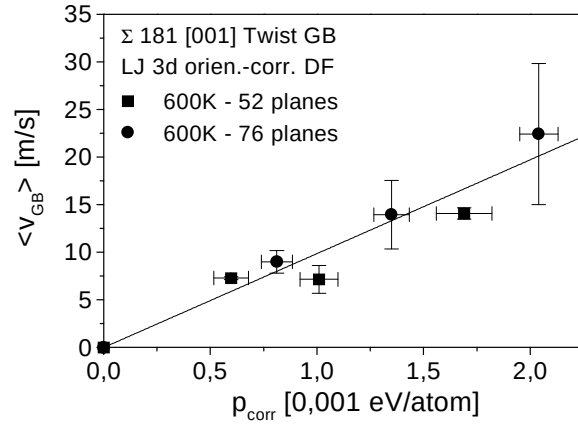


Figure 5.68: Plot of the GB velocity versus orientation-correlated DF of the $\Sigma 181$ twist GB at 600K. Here the results of the 76 (002) plane system and of a 52 (002) plane system are plotted.

plots at 500K and 600K are given in Fig. 5.67 and 5.68, respectively. For the 600K case, two GB systems were studied, namely a 72 (002) plane system as well as a 52 (002) plane system. The found GB velocities for the two system sizes agree fine and in this case the GB mobility at 600K was determined from the overall data sets. The 500K data shown

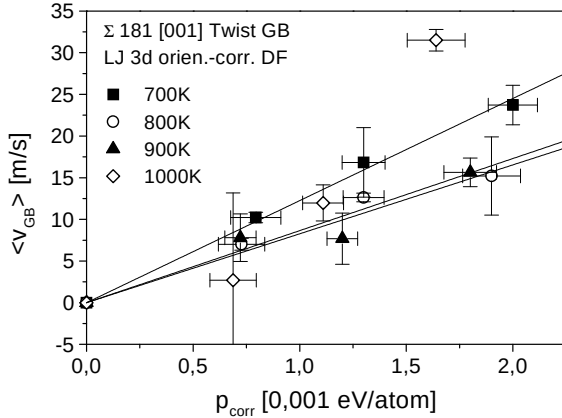


Figure 5.69: GB velocity versus orientation-correlated DF plots of the $\Sigma 181$ twist GB at 700K to 1000K.

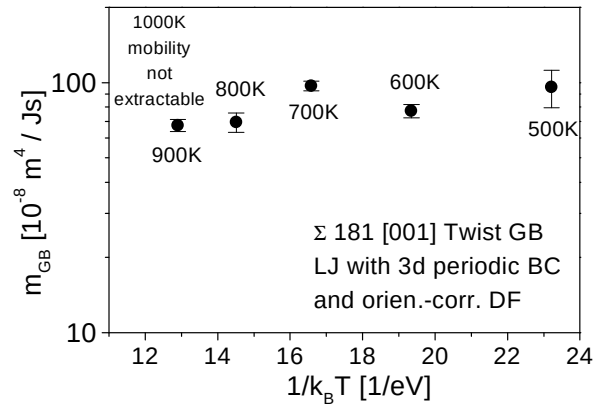


Figure 5.70: Arrhenius plot of the $\Sigma 181$ GB mobility for GB migration due to an orientation-correlated DF.

in Fig. 5.67 reveal that in some cases rather high GB velocities were found and that the overall data does not fit too well on a single linear best data fit. It seems more likely that two linear data fits would represent the data much better, namely one slow and one high velocity branch. Some rather high GB velocity error bars are shown in these plots which identify that in some case the difference in GB velocity between the two GBs can be quite

large. This reflects that at least of one the GBs is not moving in an ideal state. This could be due to a disturbance by the presence of the second GB or for instance by GB related processes at the GB. Here it is known that vacancies can be emitted from a moving GB and the emission as well as recombination of such vacancies with the GB can act as a dragging force [33, 34]. The emission and recombination of vacancies at the GB was observed usually at elevated temperatures for the studied GBs in this work.

Finally Fig. 5.69 presents the GB velocity versus orientation-correlated DF plots at 700K up to 1000K. Here it is observed that the 1000K GB mobility could not be determined by a simple linear best data fit. Therefore the 1000K GB mobility was not determined and was ignored in the Arrhenius analysis. Fig. 5.70 gives the Arrhenius plot of the GB mobility of the $\Sigma 181$ [001] twist GB. The interpretation of the data is not straightforward since no clear trends in the temperature dependence are visible. According to the low-angle nature of this GB, it is assumed that the $\Sigma 181$ [001] twist GB can move almost thermally non-activated which is reflected by the data. Still it is at question whether or not this indeed is the correct explanation of the observed GB mobility fluctuation.

The example of the $\Sigma 181$ [001] twist GB shows that even rather low-angle GBs can be driven by the orientation-correlated DF. Since the misorientation angle becomes quite small, the magnitude of DF is becoming small too compared to the situation met for high-angle GBs. The main problem is connected to the physical interpretation of some of the GB velocity results as well as for the GB mobility data. Some of the observed problems could be related to the MD simulation box size which only consisted of 72 (002) planes. It is suggested to redo the conducted simulations with bigger MD systems as well as applying an EAM potential instead of the used LJ potential.

5.2.3.7 Discussion of the GB migration results due to an orientation-correlated DF

The GB migration results of the studied [001] twist GBs in the presence of the orientation-correlated DF are summarized and discussed next. The main findings are :

- (1) The orientation-correlated DF can drive [001] twist GBs continuously and hence lends itself to study GB migration of high-angle as well as low-angle GBs.
- (2) The orientation-correlated DF can easily be obtained in-situ during the MD simulations. Hence its exact magnitude and its temporal evolution can be followed precisely.
- (3) The obtained GB migration enthalpies are listed in Tab. 5.9. They agree well with the results found for the elastic DF taking into account the found error bars.

GB	Interatomic Potential	orien.-corr. DF Q [eV] low T regime	orien.-corr. DF Q [eV] high T regime
$\Sigma 5$	LJ 2d per.BC	0,32	—
$\Sigma 5$	EAM 2d per.BC	0,35	0,12
$\Sigma 17$	LJ 3d + 2d per.BC	0,36	—
$\Sigma 13$	LJ 3d + 2d per.BC	0,52	0,16
$\Sigma 85$	LJ 3d per.BC	0,10	—

Table 5.9: GB migration activation enthalpies of the studied [001] twist GBs for the orientation-correlated DF.

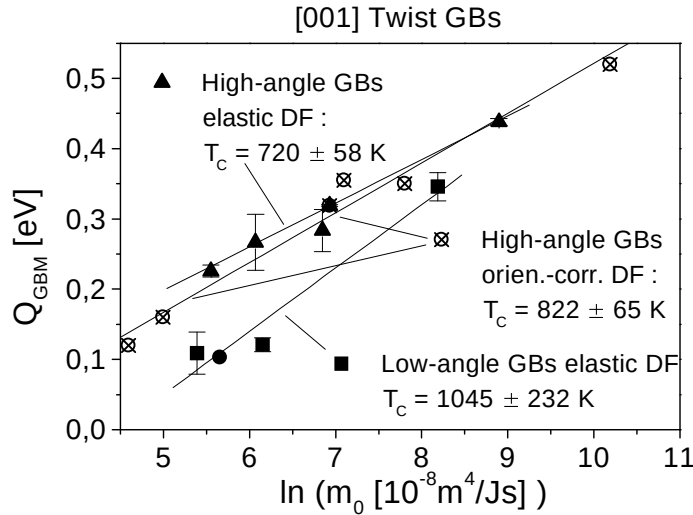


Figure 5.71: Compensation plots of the GB migration activation parameters of the studied [001] twist GBs. Here the results of the elastic and orientation-correlated DF are plotted in order to be able to make a data comparison.

The data of the pre-exponential factor, m_0 , of the GB mobility for the orientation-correlated DF is comparable to the elastic DF results. When plotting the activation parameters obtained by the orientation-correlated DF in a compensation plot, the data analysis gives a

slightly higher compensation temperature than for the elastic DF. The data comparison of the elastic DF and orientation-correlated DF results is shown in Fig. 5.71.

(4) The GB migration mechanisms found for the elastic and the orientation-correlated DF are the same.

5.2.4 GB Self-Diffusion of Planar [001] Twist GBs

Another interesting aspect of GBs is their static behaviour at finite temperatures. GB self-diffusion is a well-known process within GBs and has been studied experimentally as well as by computer simulations [77, 78, 79, 80, 72]. Within this work GB self-diffusion was studied to obtain reference data on the activation enthalpy of GB self-diffusion of various [001] twist GBs and to check the applicability of the used calculation scheme to detect and quantify GB self-diffusion. To establish reference GB self-diffusion activation data by means of MD simulations was driven by the demand to make a comparison between GB self-diffusion and GB migration activation data. Furthermore the GB self-diffusion data, especially the angular distribution of the jump vectors of GB atoms, was utilized to assess the question whether or not the studied GBs undergo structural transitions within the studied temperature range. Such an approach was already successfully used by Keblinski [80, 72] to study the GB structure of twist and tilt GBs from intermediate to high temperatures. The main suggestion of Keblinski [72] is that high-angle GBs with rather high GB energies can undergo a structural transition below the melting point from an ordered crystalline structure to a liquid-like structure. This structural transition has to be seen in the activation parameters of such GBs, namely in the GB self-diffusion, GB migration and GB sliding data.

Another important simulation work with respect to this work is the study by Nomura and Adams [79]. They studied GB self-diffusion applying lattice statics simulations (LS) to six different [001] twist GBs in Cu utilizing a Cu EAM potential according to Foiles. Their goal was to establish activation data for GB self-diffusion, namely to determine the GB vacancy formation energy and the GB vacancy migration energy. Due to this goal and for a few other reasons they chose LS simulations rather than MD simulations. The only convincing point to choose LS simulations rather than MD is the fact that it is rather difficult in MD simulations to determine separately the vacancy migration and the vacancy formation energy [77, 79, 78]. Usually in MD simulations the temporal evolution of the mean-square displacement (MSD) of the GB atoms is utilized to calculate the GB self-diffusion coefficient at a chosen temperature. Utilizing an Arrhenius concept then the activation enthalpy of GB self-diffusion can be obtained (see section 3.5.2). Here the work of Nomura serves as a reference to evaluate the results obtained by this work. Nomura and Adams established the misorientation dependence of [001] Cu twist GBs by application of computer simulations which hence lends itself for a direct comparison. The misorientation dependence of the GB activation enthalpies obtained by this work as well as by Nomura is presented in Fig. 5.82.

Due to the open structure of GBs with respect to the bulk crystal regions, the process of GB self-diffusion can be investigated by MD GB simulations and key parameters of GB self-diffusion can be obtained. Here the following simulation approach was used to study GB self-diffusion of the $\Sigma 29$, $\Sigma 5$, $\Sigma 17$, $\Sigma 13$, $\Sigma 25$, $\Sigma 41$, $\Sigma 85$ and $\Sigma 181$ [001] twist GB. 3d LJ simulations were performed applying a 3d periodic boundary concept. With regards to recent work by Keblinski [72] this approach is different since no explicit frozen block concept is utilized to a-priori suppress GB sliding events that usually occur during finite temperature GB simulations with 3d periodic boundary conditions. At least it is a common personal experience of the author that for all studied high-angle twist GBs either during GB migration simulations and for static finite temperature GB simulations, GB glide events occur quite frequently. Due to this circumstance the frozen block border concept as introduced by Lutsko [66] was initially utilized by Keblinski in order to avoid a dramatic contribution to the total MSD of the overall GB system by GB glide events. Since the

suppression of GB glide events can not be and was not utilized in any of the presented GB migration simulations, it seemed better to utilize a smart atomic displacement analysis in order to track only the diffusive displacement jumps of atoms over at least a distance of the NN-distance. These jumps events can then be considered exclusively diffusive and linked to the GB self-diffusion process occurring within each GB. The underlying analysis principle to extract only the GB diffusive MSD is presented in detail in section 3.5.2. Furthermore the reader should note that all presented simulations in this section were performed with no explicit DF other than possible interactions between the two present GBs.

Next the temporal evolution of the diffusive MSD or to be precise the diffusive SSD for the studied [001] twist GBs is presented and the exact situation for each GB can be found in Fig. 5.72 up to Fig. 5.79. Here the diffusive GB SSD data was normalized to twice the GB

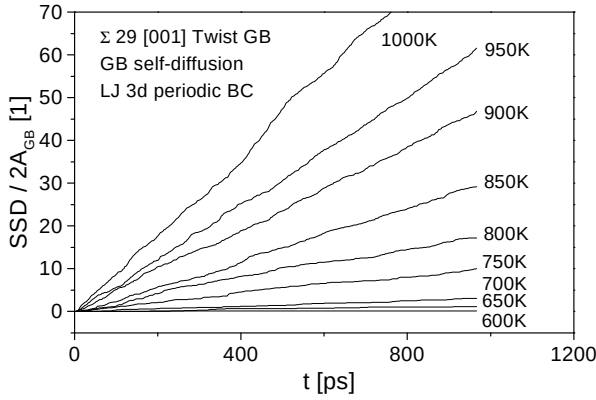


Figure 5.72: Total diffusive SSD per GB area of the $\Sigma 29$ [001] 43.60° twist GB at different temperature.

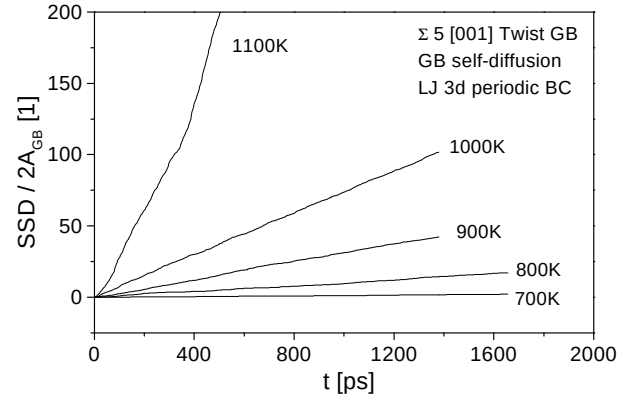


Figure 5.73: Total diffusive SSD per GB area of the $\Sigma 5$ [001] 36.87° twist GB at different temperature.

area, $2 \cdot A_{GB}$, in order to be representative for the later on to determine GB self-diffusion coefficient, D_{GB} . To use twice the GB area was necessary since two [001] twist GBs were present in the simulation box due to the applied 3d periodic boundary conditions.

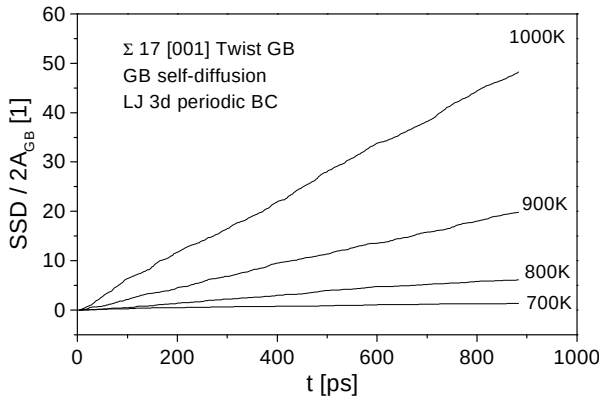


Figure 5.74: Total diffusive SSD per GB area of the $\Sigma 17$ [001] 28.07° twist GB at different temperature.

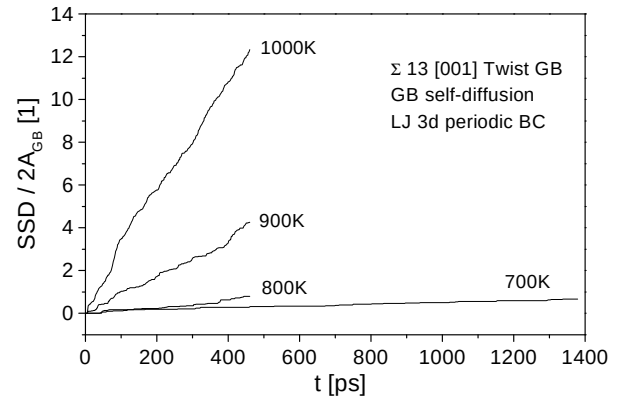


Figure 5.75: Total diffusive SSD per GB area of the $\Sigma 13$ [001] 22.62° twist GB at different temperature.

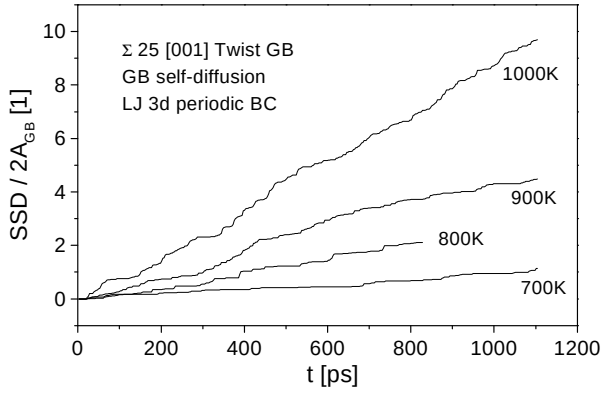


Figure 5.76: Total diffusive SSD per GB area of the $\Sigma 25$ [001] 16.26° twist GB at different temperature.

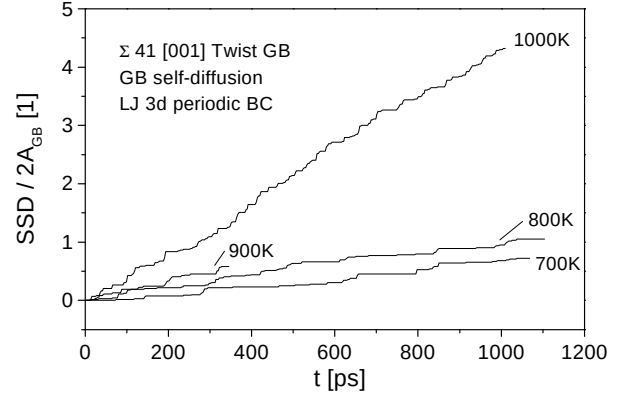


Figure 5.77: Total diffusive SSD per GB area of the $\Sigma 41$ [001] 12.68° twist GB at different temperature.

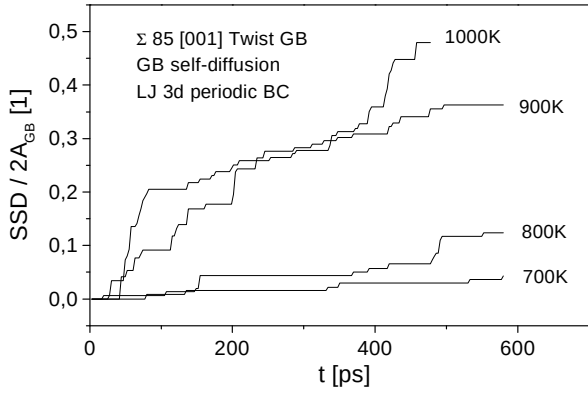


Figure 5.78: Total diffusive SSD per GB area of the $\Sigma 85$ [001] 8.80° twist GB at different temperature.

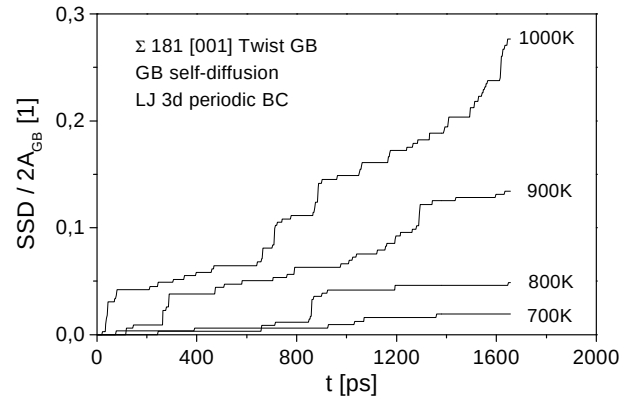


Figure 5.79: Total diffusive SSD per GB area of the $\Sigma 181$ [001] 6.03° twist GB at different temperature.

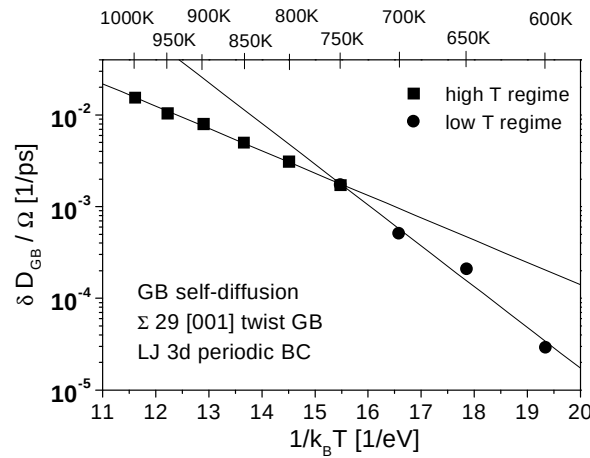


Figure 5.80: Arrhenius plot of the GB self-diffusion data of the $\Sigma 29$ [001] twist GB. Here the results of the temperature range 600 to 1000K are given.

According to Eq. 5.2 the GB self-diffusion coefficient is determined by the slope of the SSD data. Here as has been discussed in section 3.5.2 the data is normalized to twice the GB area as well as GB self-diffusion is considered to be a three-dimensional process.

$$\delta \cdot D_{GB} / \Omega = \frac{dSSD/dt}{2 \cdot A_{GB} \cdot 6} \quad (5.2)$$

Usually it was found in this work that at intermediate and high temperatures the diffusive jumps of atoms occurred no longer exclusively in-plane but very often out-of-plane. Additionally the GB self-diffusion coefficient can only be determined in an expression still containing the GB width, δ . δ itself is temperature dependent as was shown by Keglinski [72]. The change of GB width with temperature was found in this work as well. Nevertheless since in most simulations runs more or less GB migration events occurred most likely related to GB interaction of the two present GBs, no attempt was made to determine the GB diffusional width itself. It is surprising that the MSD data analysis by Keglinski [72] was solely done in-plane although their δ data itself suggests a lot of out-of-plane GB self-diffusion activities.

Fig. 5.80 presents the GB self-diffusion data of the $\Sigma 29$ twist GB. The data is representative for the studied high-angle twist GBs since it exhibits one important aspect. For the $\Sigma 29$ and $\Sigma 5$ twist GB it was found in this work that for the GB self-diffusion and GB migration temperature dependence a low temperature and high temperature regime exists. This is best exemplified for the GB self-diffusion data of the $\Sigma 29$ twist GB as presented in Fig. 5.80. This found behaviour is in agreement with work of Keglinski [72] who report such behaviour for high energy twist and tilt GBs as well. For the activation enthalpy it is found here that the high temperature activation enthalpy is about half of the low temperature one.

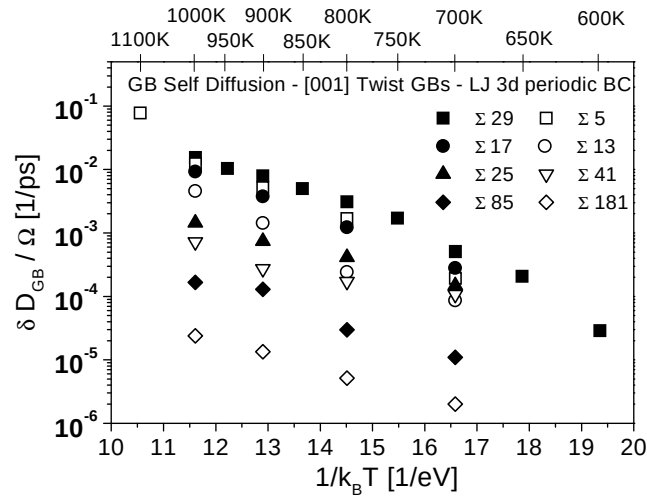


Figure 5.81: Arrhenius plot of the GB self-diffusion data of the [001] twist GBs. The simulations were done for the LJ potential with 3d periodic BC and in the presence of no DF.

To get an overview over the overall GB self-diffusion data of the eight [001] twist GBs, the determined temperature dependence of the GB diffusion coefficient, D_{GB} , is presented in an Arrhenius plot in Fig. 5.81. For most of the data a simple linear general fit of the data gives the activation parameters for GB diffusion of these [001] twist GBs, namely the GB self-diffusion enthalpy and the GB self-diffusion pre-exponential factor. The found data is

listed in Tab. 5.10. Both quantities are important in order to study the compensation effect of the diffusion data. Next the misorientation dependence of the GB self-diffusion data is

GB plane	θ	Σ	Q_{GBD} [eV]	$\ln(\frac{\delta \cdot D_{GB}^0}{\Omega} [\frac{1}{ps}])$
(001)	43.60°	29	1.023 ± 0.086	9.518
	43.60°	29	0.560 ± 0.014	2.342
(001)	36.87°	5	1.042	8.757
	36.87°	5	0.684 ± 0.007	3.560
(001)	28.07°	17	0.701 ± 0.030	3.464
(001)	22.62°	13	0.816 ± 0.097	3.949
(001)	16.26°	25	0.446 ± 0.020	-1.376
(001)	12.68°	41	0.252 ± 0.016	-4.979
(001)	8.80°	85	0.585 ± 0.081	-1.727
(001)	6.03°	181	0.507 ± 0.020	-4.735

Table 5.10: GB self-diffusion activation parameters of the studied [001] twist GBs for the LJ potential utilizing 3d periodic BC. The shown data relates to MD finite temperature simulations without any DF.

presented. Here a direct comparison with the Nomura and Adams data lends itself to assess data agreement. Here it should be repeated that the GB self-diffusion data by Nomura was determined by 0K LS simulations. Comparing the data of this work and the Nomura data, a similar orientation dependence of the activation enthalpy is observed namely that with decreasing misorientation angle the activation enthalpy decreases. This statement only reflects the general trend of both data sets. A more detailed discussion of the data of this work demonstrates that for the two lowest low-angle twist GBs, namely the $\Sigma 181$ and $\Sigma 85$, the activation enthalpies again increase with decreasing twist angle. It is believed that for even smaller twist angles the activation enthalpy should rise further or at least stay on a rather high level. Finally when converging to zero misorientation angle the volume self-diffusion activation enthalpy of 1.97 eV would need to be found for the used LJ potential of this work.

Another interesting aspect are the low and high temperature GB self-diffusion regimes of the $\Sigma 29$ and $\Sigma 5$ twist GB. The low temperature data of the $\Sigma 29$ GB coincides with the Nomura data perfectly well. Bearing in mind that the Nomura data relates to an EAM potential this fact is probably only coincidental. Still the results of the EAM Doyama and the LJ potential for the $\Sigma 5$ illustrate that the activation enthalpy of the LJ and EAM potential will not differ dramatically. Therefore the $\Sigma 29$ and $\Sigma 5$ activation enthalpies are in a comparable range with respect to the Nomura data. It is especially interesting that it is the low temperature activation enthalpy data which suggests that the Nomura approach was only able to determine GB self-diffusion data which is linked solely to highly structured GBs. Any crystal structure transition effects which are known from experiments and simulations could not be reflected in Nomura's work. Overall the agreement between the Nomura data and this data is surprising which in turn confirms the usefulness of the used GB self-diffusion analysis scheme used in this work. This is especially important to note since within the presented simulations the GBs were not restricted to show no GB glide nor GB migration events. Please note that a detailed analysis of GB self-diffusion in the presence of and without GB migration due to an explicit DF is given in section 5.2.3.2. The general

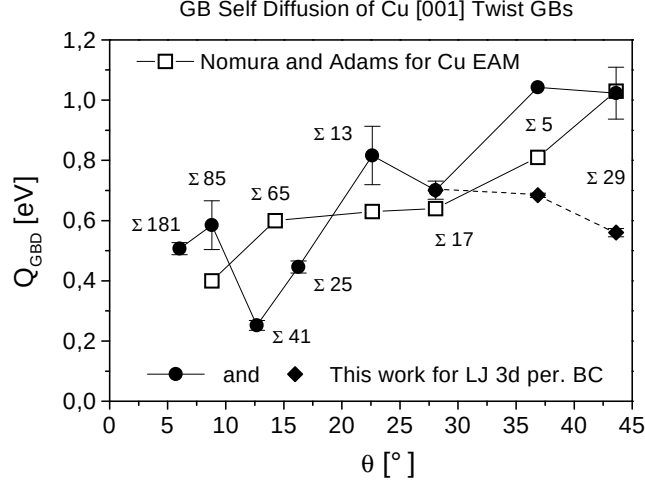


Figure 5.82: Misorientation dependence of the activation enthalpy of GB self-diffusion of the studied [001] twist GBs. The shown data represent the results of the LJ 3d periodic BC simulations of this work and as a reference the results by Nomura [79].

conclusion of that analysis is that GB self-diffusion remains almost identical for stationary and moving GBs [83, 84]. This is confirmed by recent experimental work and hence adds further confidence in the used data analysis of this work.

Finally the GB self-diffusion activation data is analysed with respect to the compensation effect. The data seems to distinguish between low-angle and high-angle GBs. What is meant

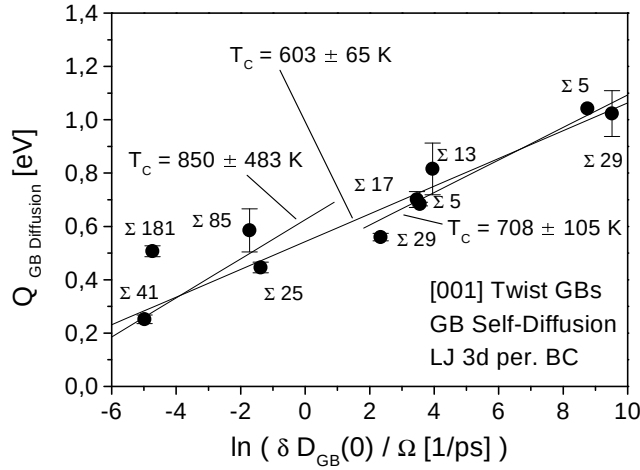


Figure 5.83: Compensation plot of the GB self-diffusion data for the studied [001] twist GBs. Three linear data fits were done. One data fit of the overall data yielding 605K for the compensation temperature, second a data fit of only the high-angle GB data yielding 708K and finally a fit of only the low-angle GB data yielding 850K.

by this is best exemplified by the $\Sigma 85$ data. What is interesting to note is that for the $\Sigma 181$, $\Sigma 85$, $\Sigma 41$ and $\Sigma 25$ twist GBs, the $\delta \cdot D_{GB}(0)/\Omega$, is much smaller than for the high-angle GBs. At first sight even the overall data can be fitted quite well by a linear best fit. What raises some doubts to do so is the fact that the $\Sigma 85$ activation enthalpy is rather high but $\delta \cdot D_{GB}(0)/\Omega$ seems rather low compared to the $\Sigma 5$ and $\Sigma 17$ data. This is especially true

if one notices the spread of the $\Sigma 29$, $\Sigma 5$, $\Sigma 17$ and $\Sigma 13$ activation enthalpy data having similar $\delta \cdot D_{GB}(0)/\Omega$ values which are distinctly different than $\delta \cdot D_{GB}(0)/\Omega$ value of the $\Sigma 85$ GB. Furthermore the overall linear best fit of the data finds 603K as the compensation temperature. This temperature should be related to a structural transition of the GBs. It is suggested by the self-diffusion data of the $\Sigma 29$ and $\Sigma 5$ that these GBs undergo a structural transition in the temperature range of 700 to 750K. Including the error bar of the linear best fit of 65K the results are not too far off. With respect to the findings of Koblinski [72] it is expected that the transition temperature of low-energy GBs and therefore low-angle twist GBs should be much higher than for high-angle GBs. For our data this suggests that the low-angle and high-angle data form two separate data sets which need to be fitted independently. Performing such separate fits of the low-angle and high-angle GB data, the compensation temperature is 850K and 708K respectively. For the low-angle GB fit one should note the relative high error bar of 483K. In general it seems that the data is in agreement with the compensation effect and that the compensation temperature roughly agrees with the structural transition temperature of low- and high-angle GBs.

Analysis of structural order of diffusive GB jumps. In order to assess how ordered or disordered the GBs remain at elevated temperatures, an analysis of the angular distribution of the GB diffusion displacement vectors of observed diffusional jumps was done. Such an analysis gives some insight into the question whether or not the GBs undergo structural transitions within the investigated temperature regimes [72]. The presented data in Fig. 5.84

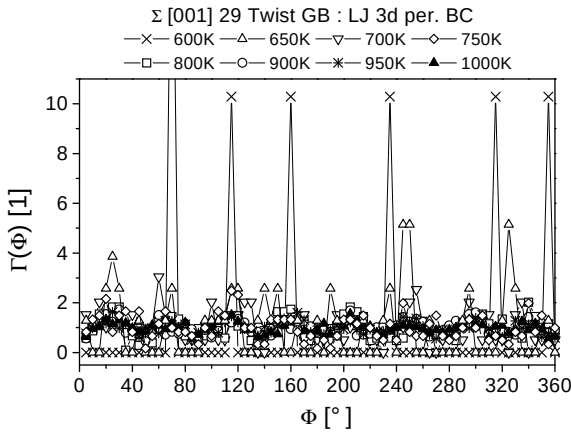


Figure 5.84: Angular distribution of the diffusion jump vectors of the $\Sigma 29$ [001] 43.60° twist GB at different temperatures.

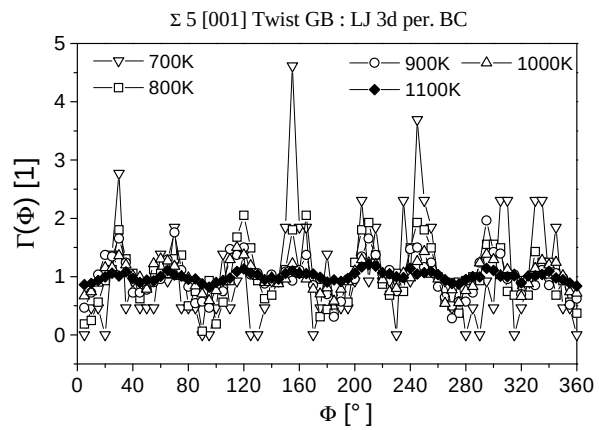


Figure 5.85: Angular distribution of the diffusion jump vectors of the $\Sigma 5$ [001] 38.87° twist GB at different temperatures.

to Fig. 5.91 represent the normalized angular distribution of diffusional GB jump events of at least the NN length. To perform such an analysis, first the CNA method was utilized to determine only the GB atoms. Then the displacement vectors had to be analysed. Since GB sliding might interfere with the analysis scheme, a well-thought updating scheme of the reference position of each GB atom was worked out to ensure that only diffusive GB jump events are analysed for their angular distribution. Once these jumps were identified, all such jump events within a conducted MD GB diffusion simulation were analysed regarding their angular distribution within (002) planes. Therefore the jump vectors were projected into a (002) plane and then analysed with respect to their jump angle. The reference coordinate system for this analysis has been the x-y simulation box coordinate system. For a complete

MD run, the overall jump events and their angular distributions were accumulated and a histogram containing 72 classes of 5° , $\gamma(i)$, was made. In order to normalize the angular histogram, the data of each class, $\gamma(i)$, was normalized by calculating $\Gamma(i) = \frac{\gamma(i)}{\sum_{i=1}^{72} \gamma(i)}$. According to this normalization, an isotropic uniform angular distribution would have the value 1 for all 72 angular classes. Usually at low temperatures the GBs will have some

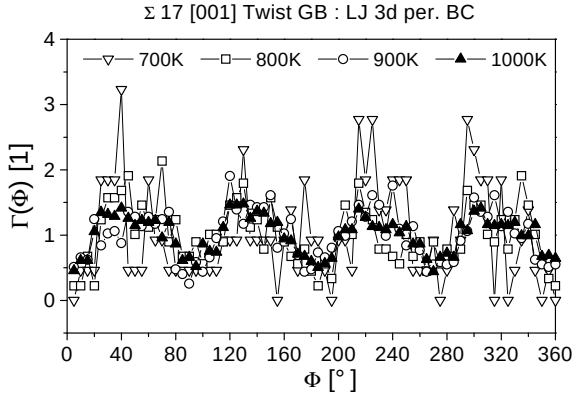


Figure 5.86: Angular distribution of the diffusion jump vectors of the $\Sigma 17$ [001] 28.07° twist GB at different temperatures.

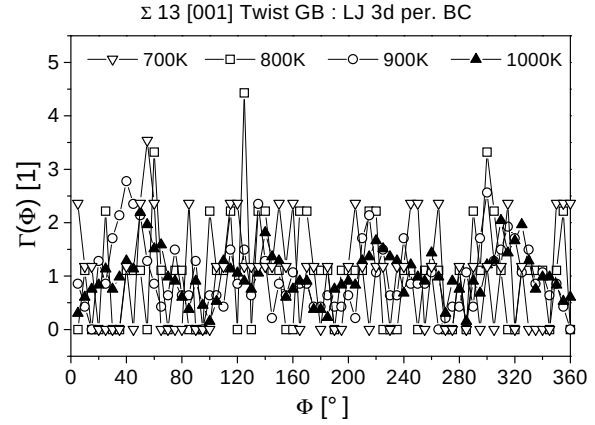


Figure 5.87: Angular distribution of the diffusion jump vectors of the $\Sigma 13$ [001] 22.62° twist GB at different temperatures.

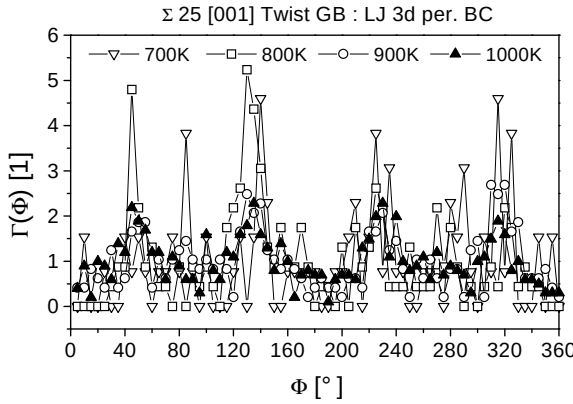


Figure 5.88: Angular distribution of the diffusion jump vectors of the $\Sigma 25$ [001] 16.26° twist GB at different temperatures.

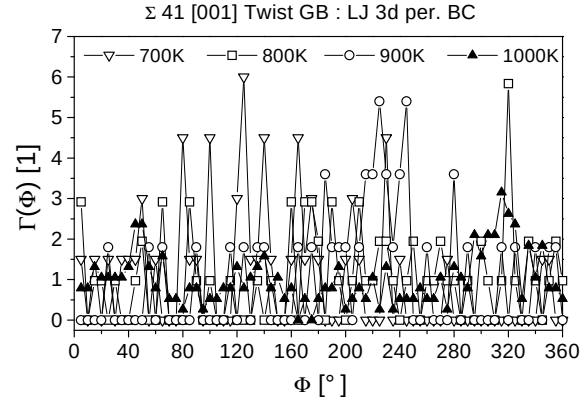


Figure 5.89: Angular distribution of the diffusion jump vectors of the $\Sigma 41$ [001] 12.68° twist GB at different temperatures.

structural order which has to be reflected in the diffusional data. Therefore such angular distributions should reflect the crystalline order of the GB structure and hence show well-defined peaks at certain diffusional jump angles. The value of those classes should be well beyond 1. Once a GB has lost its crystalline structure and becomes a highly nonstructured disordered region, the angular distribution should be uniform and ideally one for all angular classes.

The analysis relies on the fact that discrete single GB diffusional jumps can be identified within the system. In the conducted MD simulations only after every 1000 time steps a box

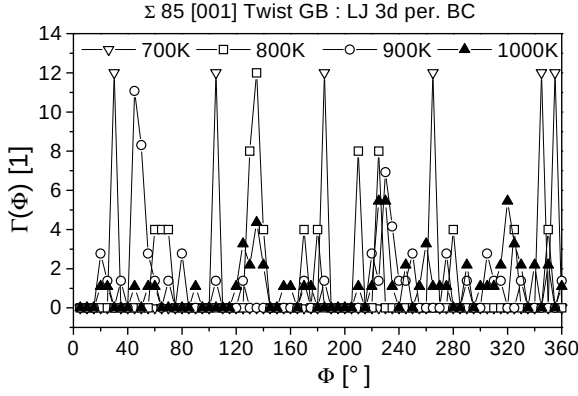


Figure 5.90: Angular distribution of the diffusion jump vectors of the $\Sigma 85$ [001] 8.80° twist GB at different temperatures.

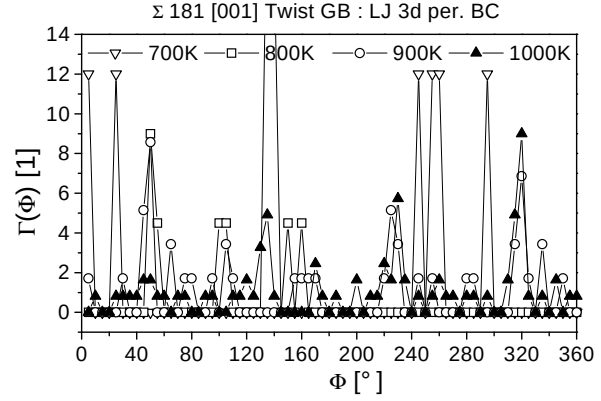


Figure 5.91: Angular distribution of the diffusion jump vectors of the $\Sigma 181$ [001] 6.03° twist GB at different temperatures.

containing the position of all atoms in the system was stored. For high temperatures this means that not every single jump event can be identified, since here numerous jump events can have occurred within the time range of a 1000 time steps. Nevertheless the approach is capable to identify diffusional GB jump events and yields solid data on their angular distribution.

How can the different plots of the angular distribution of the GB diffusion jump vectors now be interpreted? First of all it should be stressed that a conclusion from the presented data is not straightforward. This is due to the fact that none of the plots at the highest temperatures studied really exhibits the characteristics of an disordered liquid-like state. Hence it is rather difficult to distinguish between a crystalline and a crystalline disordered GB structure. Nevertheless two main conclusions are drawn :

- (1) All high-angle GBs, especially the $\Sigma 29$ and $\Sigma 5$, seem to undergo a crystalline structural transition far below the melting temperature. Although the highest temperature profiles are not ideally one and still show the characteristics of an underlying crystal structure of the GB, still they have come quite close to a uniform distribution. The strength of the GB structure weakening can not really be answered only on the basis of the angular distribution data.
- (2) The studied low-angle GBs seem to remain crystalline throughout the studied temperature range. The thermal weakening of the GB structure seems less pronounced than in the case of the high-angle [001] twist GBs.

5.2.5 GB Migration Mechanism

Here details of the GB migration mechanism of [001] twist GBs are presented. The tools to identify the GB migration mechanism are quite limited. The dilemma is that the 3d atomic-level data is rather complex to be viewed in 3d. Hence usually a reduction to 2d plots can help to reveal the GB migration mechanism. This can be done by using projections along certain crystallographic directions. For [001] twist GBs this approach is not really helpful since only the [001] direction can help to lower the complexity of the plots. Still such plots are neither really helpful due to the overlay of positional data of two bulk grains and two [001] twist GBs assuming 3d periodic BC being used.

In this work, plots of single (002) planes were used to identify the GB migration mechanism. Here the fundamental idea is that at least at low temperatures the displacement field of atoms is dominated by in-plane movement of atoms. This idea is supported by the findings of Majid and Bristowe [29] where for the $\Sigma 5$ [001] twist GBs a ledge mechanism was observed. These ledges did form by collective in-plane rotations of four atoms. According to this idea, the temporal evolution of a specific (002) plane is followed to identify the in-plane behaviour and movement of the in-plane atoms. To plot only the instantaneous position of each atom in a (002) plane is not enough to get an idea of the migration mechanism. Further information is necessary to gain more information. The following scheme was used to obtain more information :

- (1) Initially mark atoms belonging to a specific (002) plane.

Initially attribute all atoms in a selected (002) plane to this plane. During the temporal evolution of the selected plane count how many of the original atoms have remained in the plane and how many atoms have entered from neighbouring planes. In the simulations it is observed that the higher the temperature, the more atoms come from neighbouring planes.

- (2) Characterize the in-plane displacement field of atoms.

The initial position of every (002) in-plane atom is marked by a up-triangle. The instantaneous position of each atom is marked by a circle. At each time step when the atomistic configuration of the selected (002) plane is analysed, the instantaneous position of an atom is connected with its initial position by a black line. This line identifies the in-plane displacement vector of each atom. If an atom left its original plane, its initial position is no longer connected to any atoms instantaneous position. If an atom entered the selected (002) plane from a neighbouring plane, only its instantaneous position is plotted by a circle. Hence any up-triangle that is no longer linked to an instantaneous position identifies an atom that has left the selected (002) plane. Any circle that is not connected to an up-triangle identifies an atom that has entered from a neighbouring plane.

- (3) Bond order characterization.

The bond order with respect to NN atoms is analysed to identify neighbours belonging either to orientation one, orientation two or neither of the two orientations. Here each bond between atoms is analysed with respect to the expected bond angle for either of the two orientation. The detected angles were allowed to deviate from the ideal ones by a few degrees to compensate the effect of thermal vibrations of the atoms. A color code was used to label the bonds. Orientation one which refers to the lower grain is colour-coded red while bonds associated with the upper grain are colour-coded blue. If a bond did not belong to neither

of the two orientations it was colour-coded green. The number of ordered bonds is plotted as well. Here each atom can have four NN bonds where the bond is shared between two atoms. Thus the total number of bonds is number of atoms within the (002) plane times two.

(4) Evaluate the planar structure factor.

Finally the planar structure factor is calculated to identify the long-range order within the selected (002) plane. This is helpful to quantify the process of orientation change of the selected (002) plane. Still it is only of minor help to identify the GB migration mechanism.

Usually it is quite helpful to have a certain idea about the underlying GB migration mechanism before one starts the data analysis. This can help to concentrate the data analysis in a certain direction which might then reveal the mechanism. For the studied [001] twist GBs, the displacement fields of atoms within a distinct (002) plane can be guessed by analysing the positions of atoms in plots on A and A' (002) (or B and B') planes as is shown in Fig. 5.1 to 5.8. Already these plots identify a possible four atoms collective rotation for the truly high-angle [001] twist GBs. For the low-angle [001] twist GBs, the screw dislocation network can be analysed as well and its temporal evolution can be followed.

Finally the found GB mechanisms of the studied [001] twist GBs can be classified as follows.

- (1) Collective shuffle mechanism of four atoms : $\Sigma 29$, $\Sigma 5$ and $\Sigma 17$
- (2) Dislocation based mechanism : $\Sigma 41$, $\Sigma 85$ and $\Sigma 181$
- (3) Neither of the two mechanisms or hard to identify : $\Sigma 13$ and $\Sigma 25$

In the following sections, details of the found mechanisms are shown to exemplify them to the reader. As well a CD is included in this work which holds animations which can further illustrate the found mechanisms (For further information please see the appendix.).

5.2.5.1 Collective shuffle mechanism

It was found in this work that the $\Sigma 29$, $\Sigma 5$ and $\Sigma 17$ twist GBs at least at low and intermediate temperature are moving by a collective shuffle mechanism. The elementary act of the collective shuffle mechanism is a collective four atom shuffle. Majid and Bristowe [29] were the first people to report the shuffle mechanism for the $\Sigma 5$ [001] twist GBs. In atomistic GB migration simulations by Jhan and Bristowe [32] utilizing a half-shere GB geometry, the same local shuffle mechanism was observed as well. They studied four high-angle twist GBs, namely the $\Sigma 5$, $\Sigma 29$, $\Sigma 13$ and $\Sigma 17$. The simulation temperatures were 300K for the $\Sigma 5$ while 500K for the $\Sigma 29$, $\Sigma 13$ and $\Sigma 17$. These shuffles generally proceeded from the periphery of the ledge to its center.

The used temperature range by Majid and Bristowe was rather low compared to the temperatures in this work. According to the experience made in this work, it does not surprise that the four atom shuffle could be easily detected by Majid and Bristowe since in this work the data analysis at low temperatures is much more simplified than at rather elevated temperatures. Usually at higher temperatures, the grain starts to vibrate or slide which makes the data analysis more complicated.

Now representative plots of the collective shuffle process for GB migration of the $\Sigma 29$, $\Sigma 5$ and $\Sigma 17$ twist GBs are shown to demonstrate the four atom shuffle mechanism.

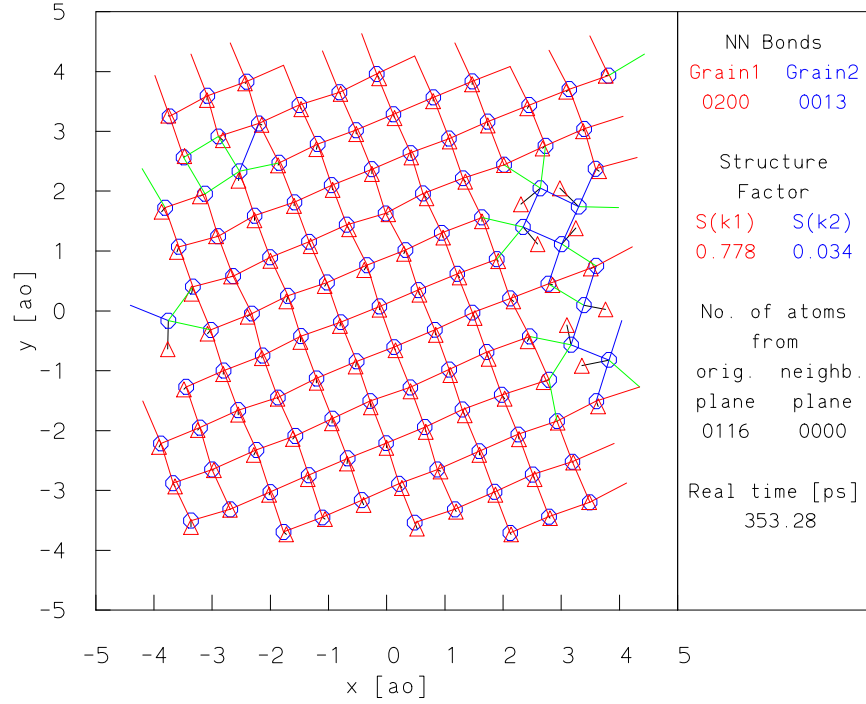


Figure 5.92: $\Sigma 29$ [001] twist GB - Plane 50 at 700K and orient.-corr. DF. Elementary step of the collective shuffle mechanism when four atoms rotate collectively in an otherwise ideal (002) plane of the other orientation and form a ledge in this (002) plane.

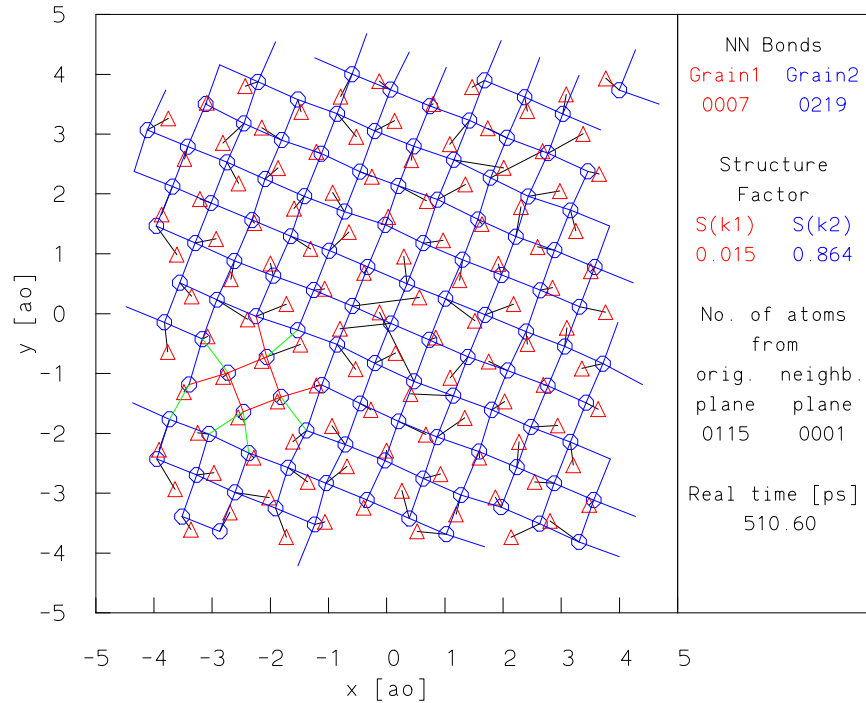


Figure 5.93: $\Sigma 29$ [001] twist GB. After the plane has aligned with the growing grain, the elementary step of the collective shuffle mechanism is observed again in this plane due to a fluctuation of the shrinking grain into this (002) plane.

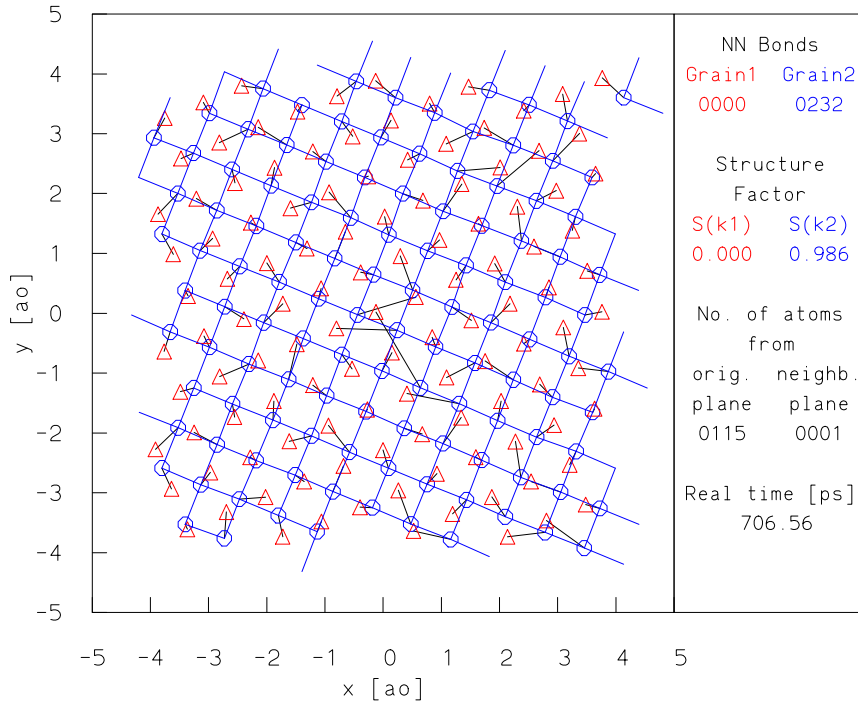


Figure 5.94: $\Sigma 29$ [001] twist GB. Final situation of the displacement field of the (002) in-plane atoms after the GB has moved further down into the shrinking grain. The displacement field shows the in-plane four atom shuffles at different sites. Here the original MD cell contains 116 atoms and hence represents a (2x2) CSL system.

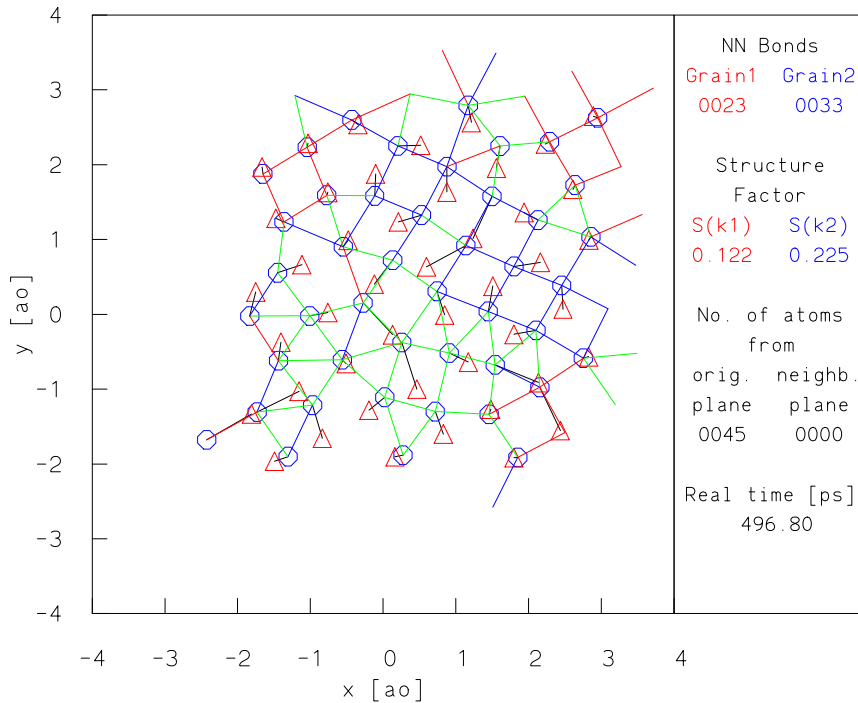


Figure 5.95: $\Sigma 5$ [001] twist GB - Plane 54 at 800K and elastic DF. Elementary step of collective shuffle mechanism when four atoms rotate collectively in an otherwise ideal (002) plane of the other orientation and form a ledge in this (002) plane.

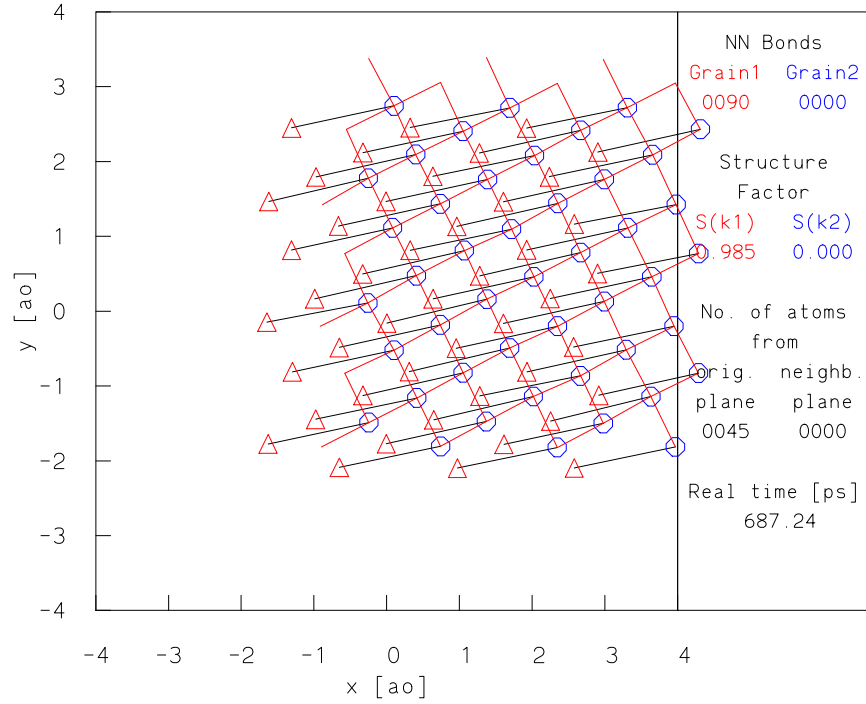


Figure 5.96: $\Sigma 5$ [001] twist GB - Plane 65 at 750K and orient.-corr. DF. This example demonstrate that even at low temperatures, GB sliding occurs. Here the (002) plane has slid a certain extent before the GB sweeps through the plane.

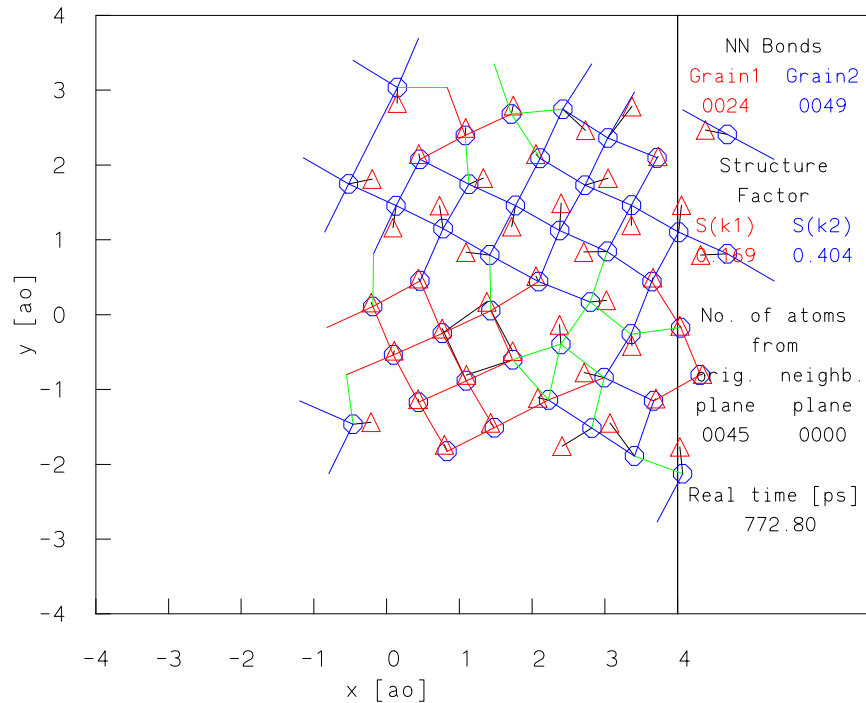


Figure 5.97: $\Sigma 5$ [001] twist GB. In order to identify the collective shuffles, the reference positions of each atom given by the up-triangles are updated just before the (002) planes becomes part of the GB. Here the plane consists of 45 atoms and hence represents a (3x3) CSL system. Again the collective shuffles can be observed.

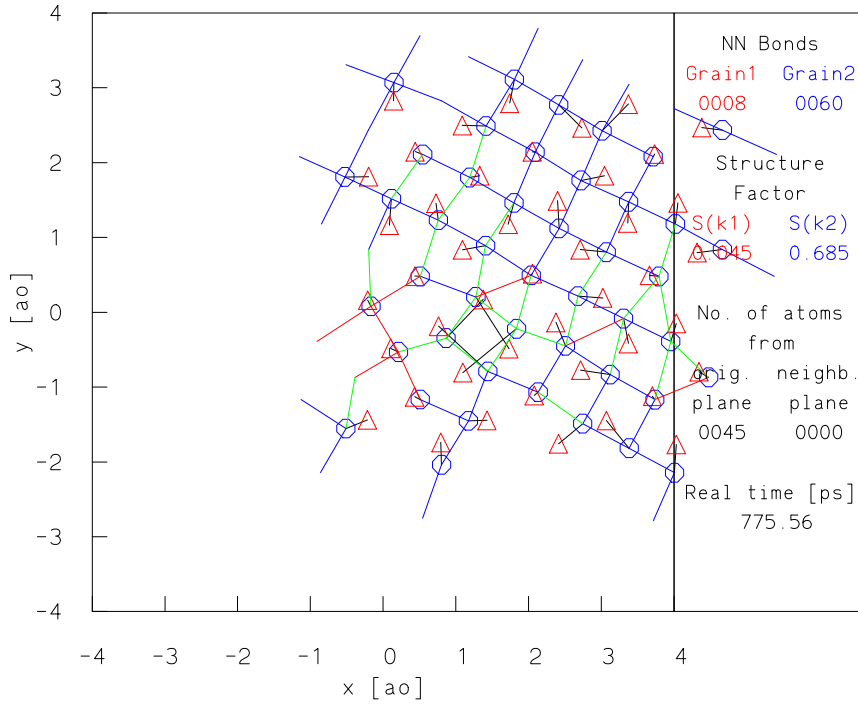


Figure 5.98: $\Sigma 5$ [001] twist GB - continuation of the sequence. Collective shuffles occur in both directions either to install the new orientation or to reinstall the old one. Consecutive shuffles can occur in different directions of rotational sense.

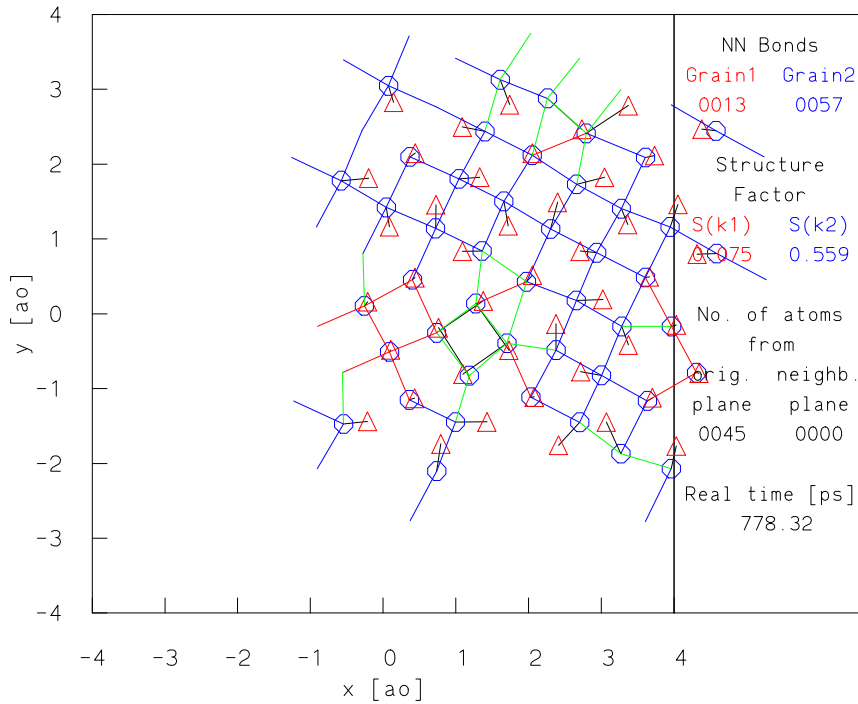


Figure 5.99: $\Sigma 5$ [001] twist GB. Continuation of the process which clear shows the shuffles. If the reference position had not been updated before the (002) plane entered into the GB, from the analysis of the displacement field of the atoms, the shuffles would hardly be noticeable.

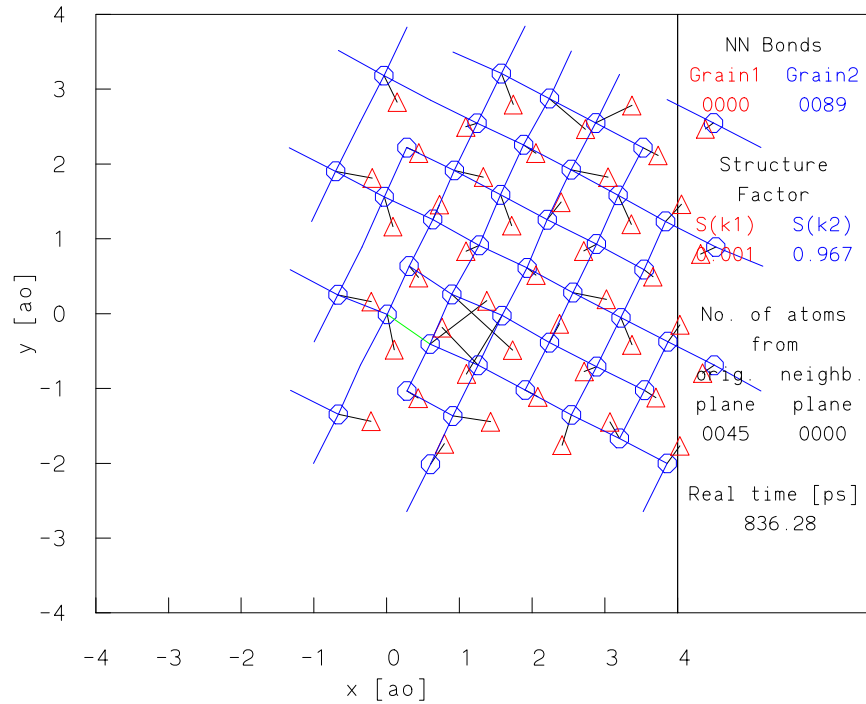


Figure 5.100: $\Sigma 5$ [001] twist GB - final situation of the displacement field of the (002) plane. In the lower left region, a displacement configuration of four atoms looking like a pound sign shows up. It is as well present in Fig. 5.98. This configuration was formed by three consecutive collective four atom shuffles with the same rotational sense.

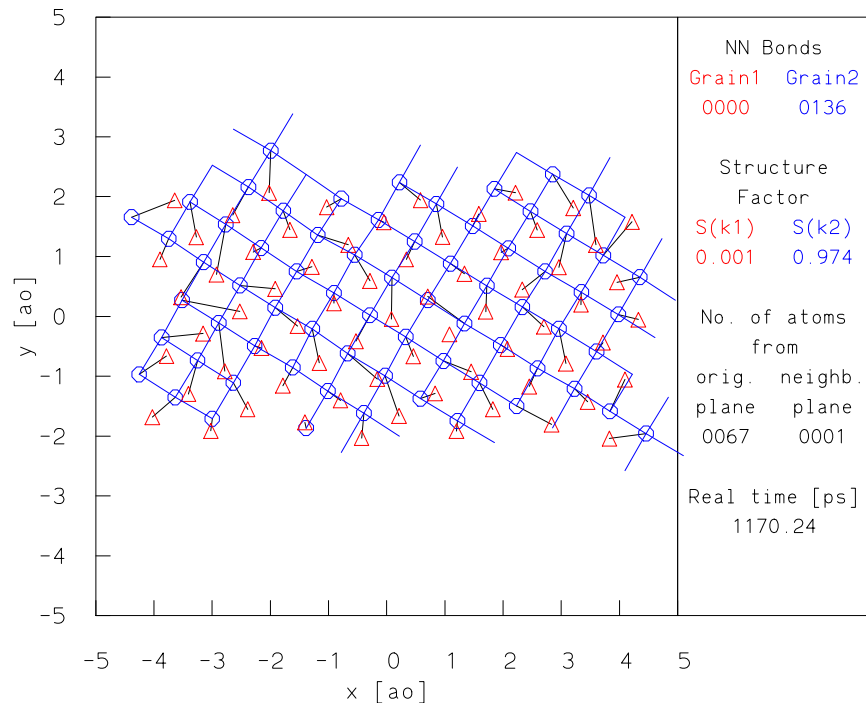


Figure 5.101: $\Sigma 17$ [001] twist GB - Plane 44 at 700K and orient.-corr. DF. Final situation of the displacement field of the (002) in-plane atoms after the GB has aligned itself with the growing grain. The displacement field shows at least one in-plane four atom shuffle which demonstrate that the shuffle mechanism is found for this GB as well.

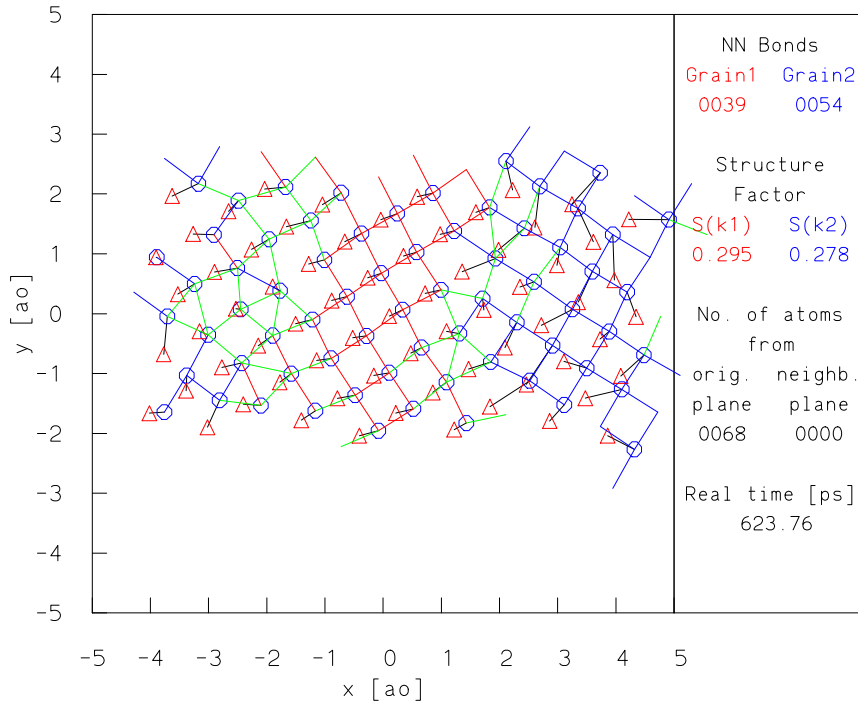


Figure 5.102: $\Sigma 17$ [001] twist GB - Plane 50 at 700K and orient.-corr. DF during the process of being swept by the GB. The ledge character of the process and the collective shuffle of four atoms can be seen in the figure. At this point both orientations are present in this (002) plane.

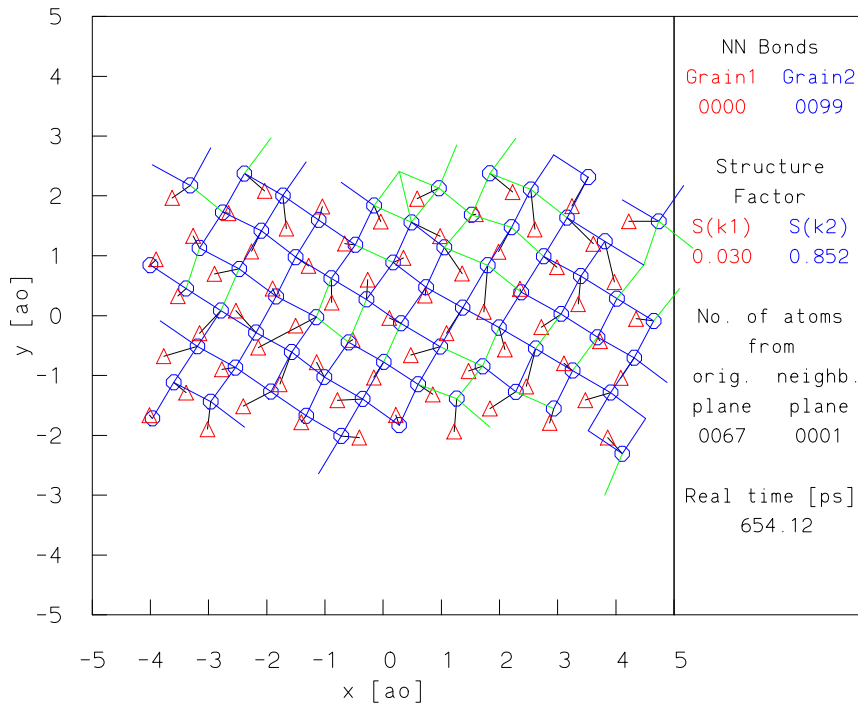


Figure 5.103: $\Sigma 17$ [001] twist GB - continuation of the above sequence. Final situation of the displacement field of the (002) in-plane atoms after the GB has aligned itself with the growing grain. The displacement field shows again in-plane four atom shuffles.

5.2.5.2 Dislocation based mechanism

Here the GB migration mechanism observed for the truly [001] low-angle twist GBs is reported. The behaviour of the $\Sigma 41$, $\Sigma 85$ and $\Sigma 181$ twist GB during GB migration was found to be connected to the screw dislocation networks forming these GBs. The found mechanism can be characterized as follows :

- (1) The GB nature in the studied temperature range of 700K to 1000K is given by a discrete network of screw dislocations. This network is even present at the highest applied temperatures.
- (2) No or hardly any jumps of atoms across the GB are observed during GB migration even at the highest studied temperatures. This shows that the GB migration mechanism is predominately occurring exclusively in each (002) plane. This is a quite different behaviour than found for the high-angle twist GBs at elevated temperatures.
- (3) GB glide and hence grain sliding is reduced with decreasing twist angle. The $\Sigma 41$ twist GB still shows some tendency for GB sliding, still its magnitude is far less than for instance compared to the behaviour of the $\Sigma 5$ twist GB. A reason for this behaviour is that for smaller twist angles, the ideal crystal regions where the lattice across the GB simply continues become more extended. Additionally no explicit driving force was imposed on the screw dislocation network that would initiate GB sliding.
- (4) The final displacement field found in each (002) plane after the GB has swept the plane is dominated by in-plane displacements that are linked to the GB screw dislocation cores. Here the atoms move in a cooperative manner. The largest displacement vectors found are less or in the range of the NN distance.

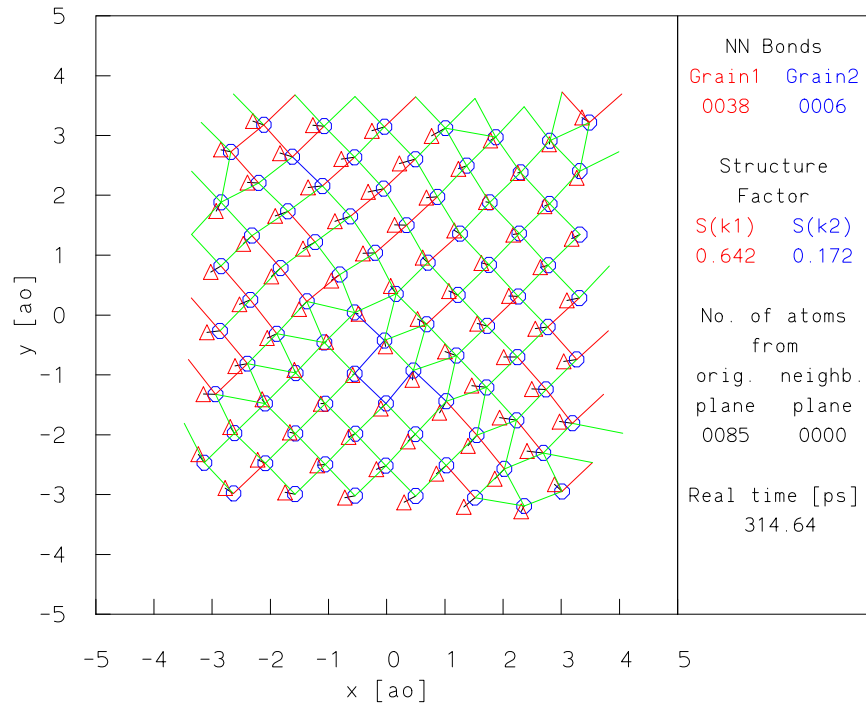


Figure 5.104: $\Sigma 85$ [001] twist GB - Plane 40 at 700K and orient.-corr. DF. A zick-zack bond situation marked by bonds belonging to neither orientation is found close to the GB dislocation cores. These are typical configurations and identify the screw dislocation cores.

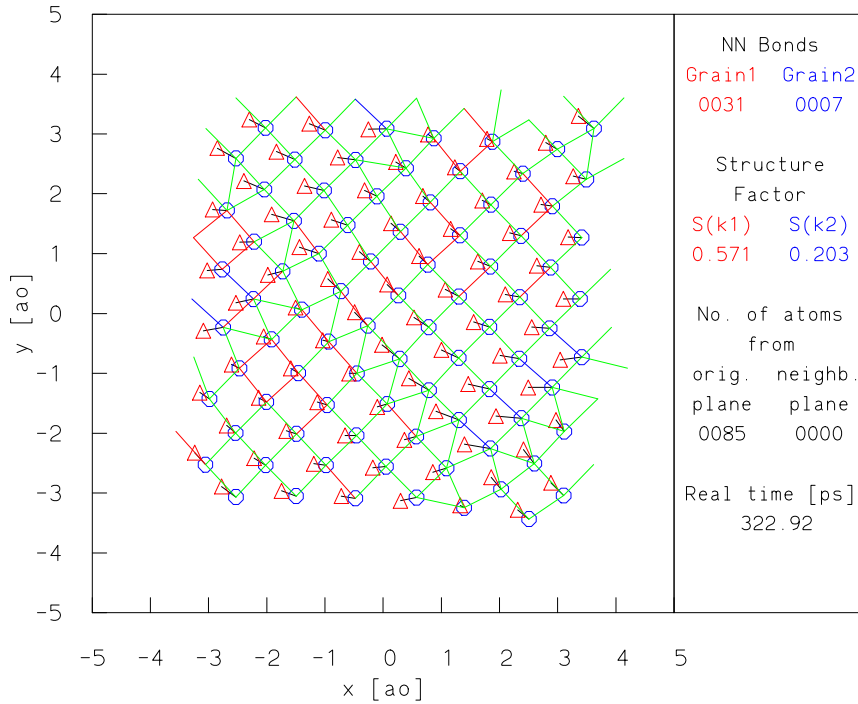


Figure 5.105: $\Sigma 85$ [001] twist GB - continuation of the above sequence. The figure identifies that the screw dislocation network slightly shifts within the (002) plane, still this shift is not continuously occurring in one pronounced direction.

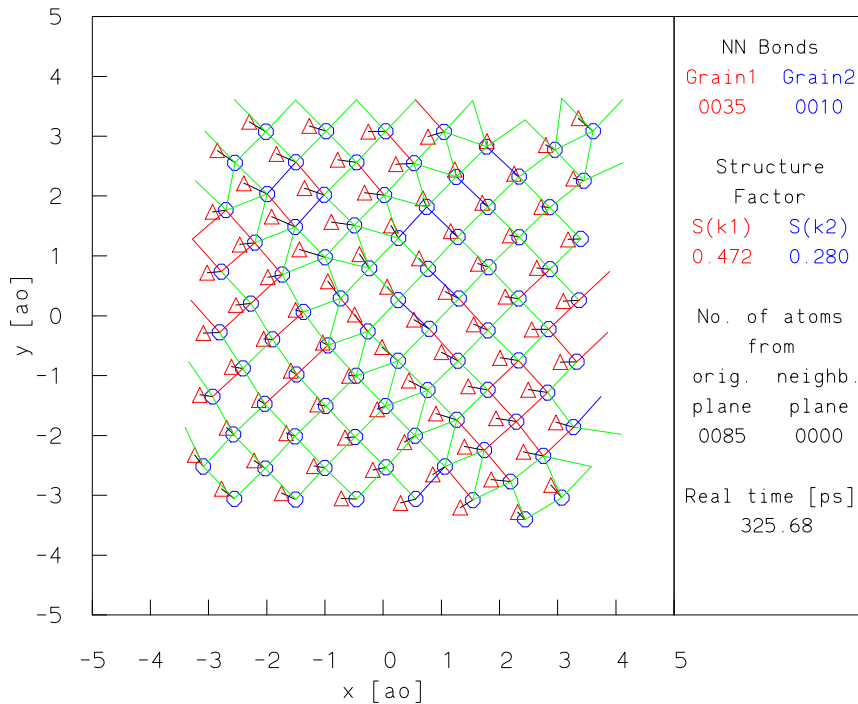


Figure 5.106: $\Sigma 85$ [001] twist GB - continuation of the sequence. When the GB reaches a (002) plane, the bond situation within that plane is highly dominated by atomistic bonds belonging to neither of the two present orientations. Still for the low-angle analysis of bonds, the used error bar of bond angle is about $\pm 2^\circ$ since the misorientation itself become quite small. Hence the likelihood of finding bonds of neither orientation is becoming more likely.

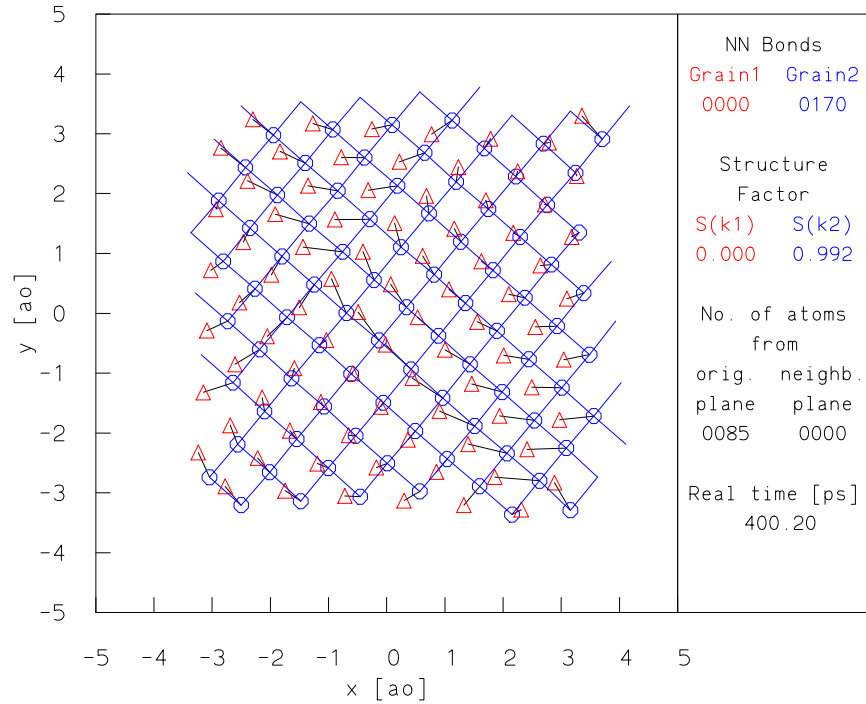


Figure 5.107: $\Sigma 85$ [001] twist GB. Final displacement field of in-plane (002) atoms after the GB has further moved into the shrinking grain. No atom has left nor entered the plane which underlines the in-plane mechanism occurring.

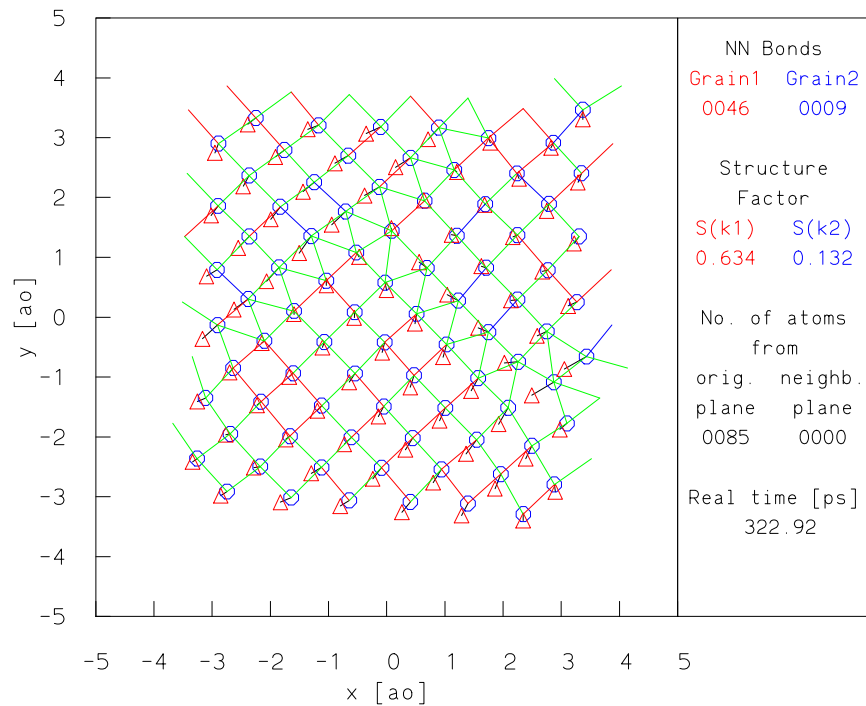


Figure 5.108: $\Sigma 85$ [001] twist GB - Plane 40 at 1000K and orient.-corr. DF. Even at 1000K the discrete screw dislocation content prevails and dominates the mechanism. Again the zick-zack bonds are found close to the cores of the screw dislocations.

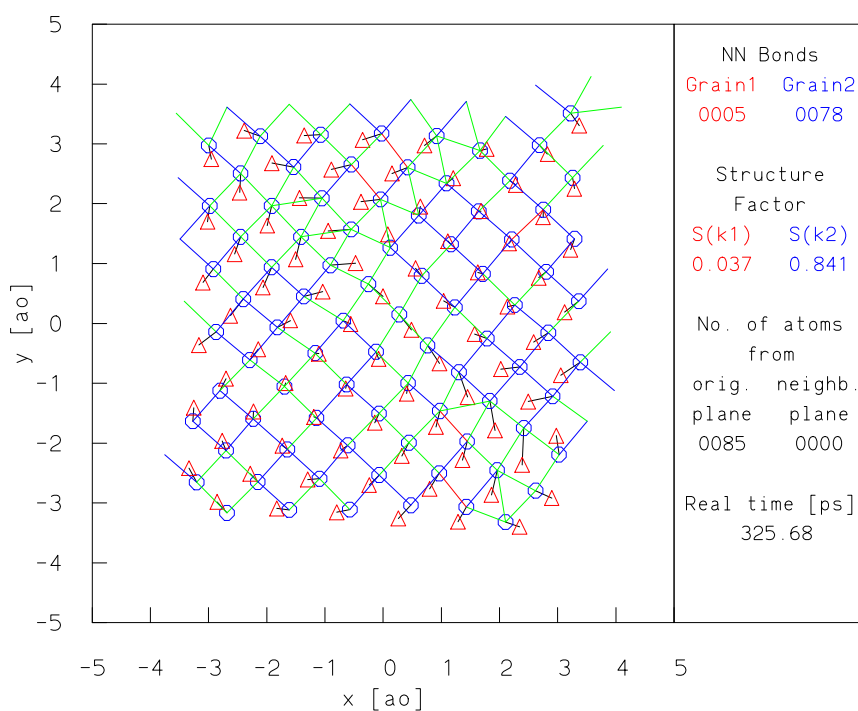


Figure 5.109: $\Sigma 85$ [001] twist GB - continuation of the above sequence.

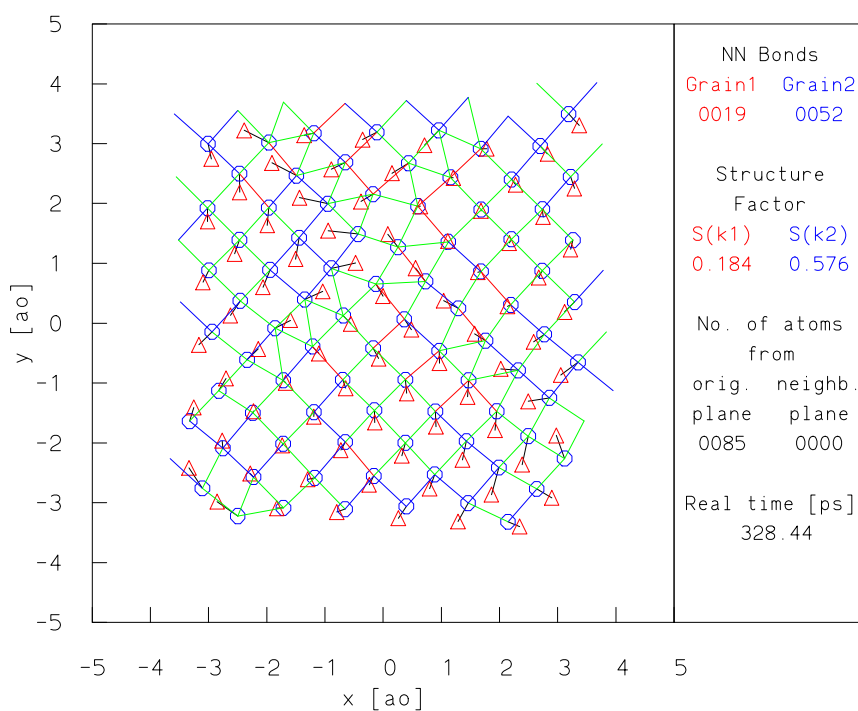


Figure 5.110: $\Sigma 85$ [001] twist GB - continuation of the above sequence.

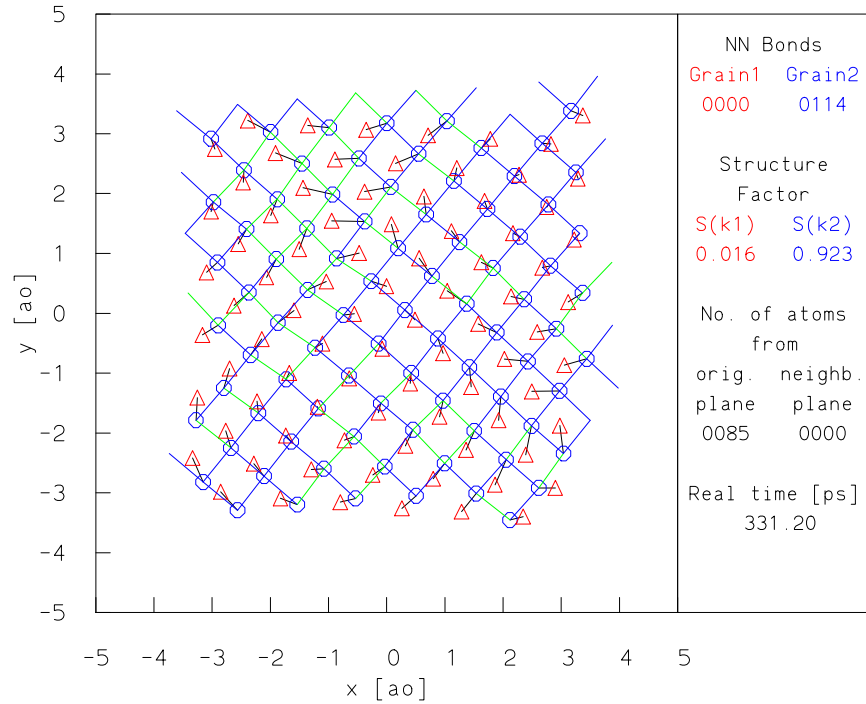


Figure 5.111: $\Sigma 85$ [001] twist GB. Final displacement field of in-plane (002) atoms after the GB has further moved into the shrinking grain.

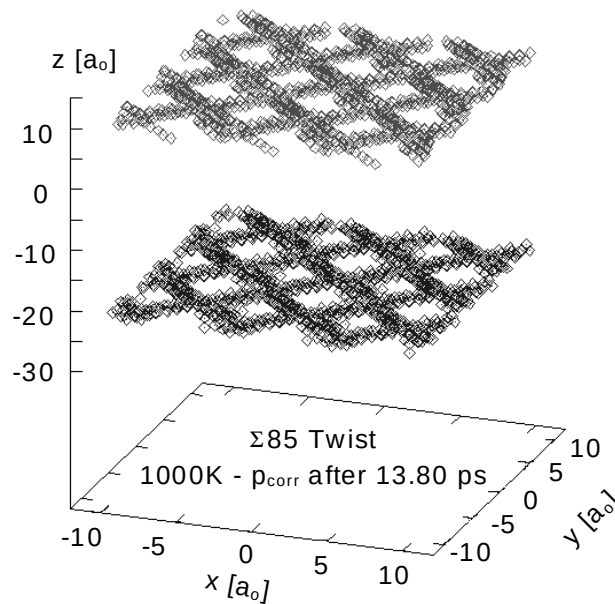


Figure 5.112: $\Sigma 85$ [001] twist GB - screw dislocation network during GB migration at 1000K and an orien.-corr. DF of 0.0018 eV/atom. Here the CNA method was utilized to identify only non-ideal fcc atoms. These atoms form the screw dislocation network of the two present GBs and can be followed with time.

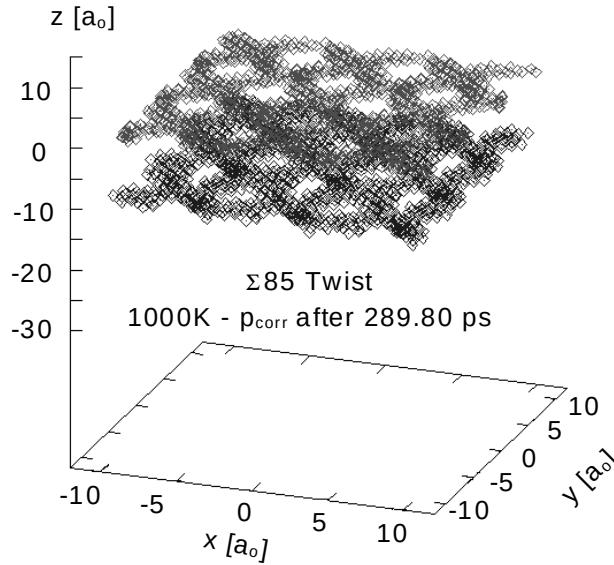


Figure 5.113: $\Sigma 85$ [001] twist GB - continuation of the simulation shown in Fig. 5.112. At the highest studied temperatures as well as when the GBs have come very close to each other, the discrete screw dislocation network character prevails.

Finally after presenting the (002) in-plane situation of the low-angle twist GBs in Fig. 5.104 to 5.111, next the direct identification of the screw dislocation network by utilizing the CNA method is presented. Examples shown in Fig. 5.112 and 5.113 show that even at a 1000K, the discrete screw dislocation network of the for instance $\Sigma 85$ twist GB prevails. In order to be able to identify the screw dislocation network much easier, the original MD cell was repeated periodically within the (002) plane. Even when the GBs have almost reached each other after successive GB migration events, the situation does not change. This demonstrates that these low-angle twist GBs behave almost ideally on the basis of discrete screw dislocation networks in a fcc system containing no impurities. This finding helps to rationalize that the found activation enthalpies of the low-angle twist GBs are very low even compared to the studied [001] high-angle twist GBs in this work. As well it explains the observed drop in activation enthalpy found in this work when changing from high-angle [001] twist GBs to low-angle twists.

5.2.6 Discussion of the overall [001] Twist GB results

Here an overall discussion is given related to all aspects of the conducted atomistic simulations of this work on [001] twist GBs.

GB migration results - Two driving force concepts were applied to planar [001] low-angle and high-angle twist GBs, namely the elastic and orientation-correlated DF. Both concepts led to continuous GB migration where the GB distance versus time profiles were linear with time. Hence GB velocities could be extracted from these simulations. These and the corresponding DF data then allowed one to determine the temperature dependence of GB mobility. The GB mobility data follows an Arrhenius relationship which reveals the activation parameters of GB migration. The found activation enthalpies for GB migration of the [001] twist GBs are slightly smaller compared to experimental reference data of [001] twist GBs in Al. Two data sets are found, namely one that is associated with the studied high-angle [001] twist GBs and a second one which is associated with the studied low-angle [001] twist GBs.

GB plane	θ	Σ	Q_{GBD}/Q_{vac} [1]	Q_{GBM}/Q_{GBD} [1]	Q_{GBM}/Q_{fus} [1]
(001)	43.60°	29	0.519	0.428	3.4
	43.60°	29	0.284	0.404	1.7
(001)	36.87°	5	0.528	0.306	2.5
	36.87°	5	0.347	0.466	—
(001)	28.07°	17	0.355	0.381	2.1
(001)	22.62°	13	0.414	0.348	2.2
(001)	16.26°	25	0.226	0.776	2.7
(001)	12.68°	41	0.128	0.433	0.8
(001)	8.80°	85	0.297	0.207	0.9
(001)	6.03°	181	0.257	—	—

Table 5.11: Scaling behaviour of the found GB activation enthalpies of the studied [001] twist GBs for the LJ potential. Here the activation enthalpy of volume self-diffusion via lattice mono-vacancies in a fcc system modelled by the used LJ potential of this work with 3d periodic BC is $Q_{vac}=1.972\text{eV}$. Further Q_{GBD} represents the GB self-diffusion enthalpy as determined in this work for each GB and Q_{GBM} is the GB migration enthalpy. Finally Q_{fus} is the latent heat of fusion as determined in [64] and reads $Q_{fus}=0.13\text{eV}$.

To rationalize the magnitude of the GB migration enthalpies found for the studied [001] twist GBs, a comparison is made with the computed activation enthalpies of GB self-diffusion of each GB and volume self-diffusion via mono-vacancies. Tab. 5.11 lists the found ratios of activation enthalpies, namely $r_{vac}^{GBD} = \frac{Q_{GBD}}{Q_{vac}}$ and $r_{GBD}^{GBM} = \frac{Q_{GBM}}{Q_{GBD}}$. According to the listed data, the following conclusions can be made :

(a) The GB self-diffusion activation enthalpy found for the $\Sigma 29$ and $\Sigma 5$ twist GBs in the low temperature regime are about half the value for volume self-diffusion via mono-vacancies. The other listed data in Tab. 5.11 of r_{vac}^{GBD} range from 0.128 to 0.414 depending on the misorientation angle of the GB. According to general belief, the general expectation was to find r_{vac}^{GBD} to be approximately 0.5.

(b) The found data of r_{GBD}^{GBM} range from 0.207 to 0.776 depending on the misorientation angle of the GB. Generally speaking the ratio is one third to one half. This clearly demonstrates that GB migration and GB self-diffusion are distinctly different processes. This is supported by the results of the GB migration mechanism of for instance the studied high-angle [001] twist GBs where a collective four atom shuffle was identified as the key element.

(c) Following the idea of Mott [23], the GB migration enthalpy, Q_{GBM} , is given by $Q_{GBM}=n \cdot Q_{fus}$ where n is the average number of atoms involved when changing the orientation from one grain to the other one and Q_{fus} represents the latent heat of fusion. The ratio of Q_{GBM} and Q_{fus} is listed in Tab. 5.11 which reveals that for the high-angle [001] twist GBs, the average number, n , of involved atoms in the shuffle process is between three and four. For the low-angle GBs, n is found to be one. This result in connection with the observed four atom shuffle for most of the studied [001] high-angle twist GBs gives a clear picture that the migration mechanism of these GBs can be understood by the collective shuffle mechanism.

Comparing the activation enthalpies of GB migration obtained by this work with data presented in the work by Upmanyu [27] leads to the following discussion. Upmanyu had studied 2d atomistics systems for a fcc model material. Only (111) planes could be modelled due to the intrinsic properties of the utilized LJ potential. To study GB migration a U-shaped GB geometry was utilized. In their work the energy unit that determined the strength of all energy terms was given by the input parameter of the LJ potential, namely ϵ . Due to the 2d atomistic system size, the GB itself becomes a line defect. GBs studied by Upmanyu were GBs in the vicinity of the $\Sigma 13$ and $\Sigma 7$ [111] tilt GB. Their found minimum and maximum GB migration enthalpies were, $Q_{min}=0.302\epsilon$ and $Q_{max}=0.456\epsilon$, respectively. To make a direct comparison to the found GB migration enthalpies in this work, the used LJ ϵ value of this work needs to be used to convert to data given in eV. In this work ϵ was $\epsilon=0.167\text{eV}$. Hence the minimum and maximum GB migration enthalpies obtained by the work of Upmanyu are, $Q_{min}=0.050\text{eV}$ and $Q_{max}=0.076\text{eV}$, respectively.

This is a rather surprising result since it shows that the Upmanyu activation enthalpies are almost one order of magnitude smaller than the data found in this work. If this drastic difference can solely be explained by the different GB geometries is hard to assess. Definitely their used approach of utilizing only 2d atomistic systems does not seem to be too helpful. This demonstrates that the found GB migration enthalpies in this work are at least much higher than the data found in the work by Upmanyu. According to the idea that curved GBs in experiments have rather high activation enthalpies, this data comparison is even more surprising. Referring to the found GB migration activation enthalpies of the studied planar tilt GBs in this work, a similar comparison with respect to the Upmanyu data can be made and the same conclusions are drawn.

Finally the computed activation parameters follow the compensation effect. Two regimes were identified, namely a low-angle and high-angle [001] twist GB regime. For the low-angle GBs, the compensation temperature is in the range of the melting temperature while for the high-angle GBs it is close to the transition temperature observed for the GB migration as well as GB self-diffusion activation enthalpy of the $\Sigma 29$ and $\Sigma 5$ twist GB.

GB migration mechanism - The found GB mechanisms of the studied [001] twist GBs can be classified as follows.

(a) Collective shuffle mechanism of four atoms. For the $\Sigma 29$, $\Sigma 5$ and $\Sigma 17$ GBs, the four

atom shuffle mechanism as reported by Majid and Bristowe [29] and Jhan and Bristowe [32] was found as well. Hence this work confirms the shuffle mechanism for driven high-angle [001] twist GBs and was able to associate this mechanism with an activation enthalpy as given above.

(b) Dislocation based mechanism. The $\Sigma 41$, $\Sigma 85$ and $\Sigma 181$ [001] twist GB are moving by a dislocation based mechanism. This mechanism is linked to the discrete screw GB dislocations where the discrete character of the dislocation network gets more and more pronounced with decreasing misorientation angle.

(c) Neither of the two mechanisms or hard to identify. For the $\Sigma 13$ and $\Sigma 25$ [001] twist GB, the GB migration mechanism was difficult to identify and no general statements could be made on the mechanism.

GB self-diffusion - All studied [001] twist GBs were investigated with respect to GB self-diffusion utilizing finite temperature molecular dynamics simulations. Good data agreement between the activation enthalpy data of this work and the data by Nomura and Adams [79] was found. Here it should be stressed again that the data by Nomura and Adams refers to the 0K situation or at least low temperature situation. The self-diffusion activation enthalpies underline this aspect, since GB self-diffusion activation enthalpies found in this work that are associated with a high temperature regime clearly deviate from the Nomura and Adams data.

Finally the computed activation parameters follow the compensation effect. Two regimes were identified, namely again a low-angle and high-angle [001] twist GB regime. For the low-angle GBs, the compensation temperature is again in the range of the melting temperature while for the high-angle GBs it is close to the transition temperature observed for both GB migration as well as GB self-diffusion activation enthalpy of the $\Sigma 29$ and $\Sigma 5$ twist GB.

Chapter 6

Results of three-dimensional Tilt GBs

6.1 Relaxed GB Structure of the studied symmetrical Tilt GBs

6.1.1 $\Sigma 5$ [001] 53.13°

Here the GB structure obtained by LJ simulations utilizing 3d periodic boundary conditions is shown. To get an idea how the simulation box geometry and the orientation of each grain with respect to the chosen simulation box coordinate system has been, Fig. 6.1 shows a schematic of the simulation box of the $\Sigma 5$ [001] 53.13° tilt GB. The tilt axis is parallel to the x-axis while the GB normal, the [210] direction, is parallel to the z-axis. It is noteworthy

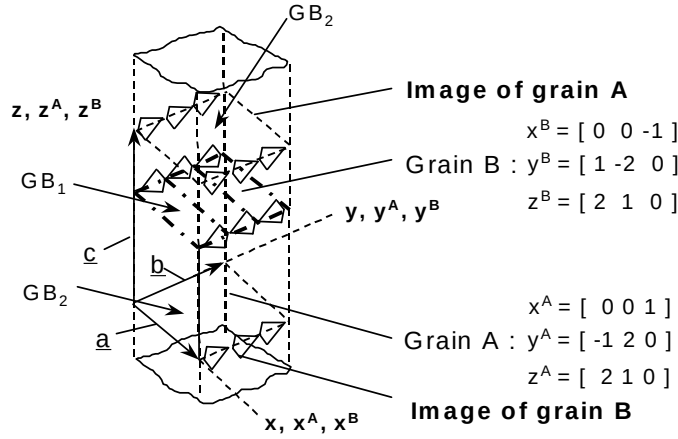


Figure 6.1: $\Sigma 5$ [001] 53.13° symmetrical tilt GB - 3d schematic of the simulation box indicating the crystallographic orientation of the two grains forming the GB. The center GB is labelled GB_1 while the second GB present due to applying 3d periodic boundary conditions is labelled GB_2 . GB_2 is having the same atomistic structure as GB_1 , only that its rotational sense and hence its dislocation pattern differs from GB_1 by a 180° rotation about the x-axis of the simulation box coordinate system. This is illustrated by the structural unit cell (kites) at either of the two GBs. These kites are associated with the structure within (002) planes. The crystallographic planes facing each other at the GB are (210) planes.

that this GB can be generated either by a tilt operation, namely by a rotation about the $[001]$ tilt axis by 53.13° , as well as by a twist rotation about the $[210]$ direction by 180° . All generated symmetrical tilt GBs in this study were generated by rotations about the GB plane normal by 180° .

Although the GB structure and GB energy slightly differ when utilizing i.e. the 2d periodic boundary concept with pseudo free surfaces with the LJ potential or applying an EAM potential, still the atomistic GB structure of the $\Sigma 5$ $[001]$ 53.13° tilt GB as shown in Fig. 6.2 is representative for the fully relaxed GB structure for the different mentioned conditions. The GB energy, γ , was found to be $\gamma = 0.975 \frac{J}{m^2}$. In Fig. 6.2 atoms within one A and one

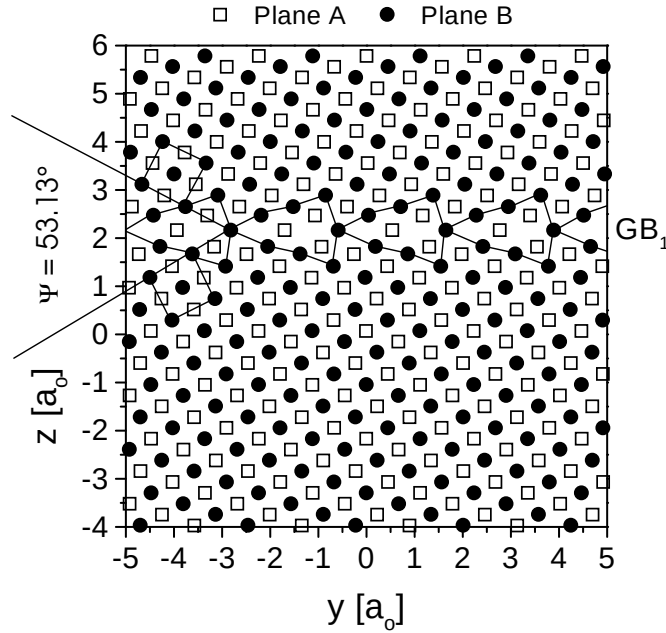


Figure 6.2: Relaxed atomistic structure of the $\Sigma 5$ $[001]$ 53.13° tilt GB viewed along the $[001]$ tilt axis. Atoms within one A and one B (002) plane at the vicinity of GB_1 are shown. Further the tilt angle $\psi = 53.13^\circ$ is indicated. Additionally the structural unit cell (kites) forming the GB is plotted. Here the reader should note that these kites are associated with the structure within distinct (002) planes.

B (002) plane at the vicinity of GB_1 are shown. The structural unit cell (kites) forming the GB is plotted. Here the reader should note that these kites are associated with the structure within distinct (002) planes.¹ In the literature usually the structural unit cell is drawn including atoms from A and B planes. This unit cell has not been indicated in this figure but can easily be found in the structure and agrees fine with the literature [28, 81]. Interestingly when analysing the 3d GB structure according to the CNA method, the 3d structural unit cells as commonly shown in the literature, just pops out as is evident from Fig. 6.3.

Finally the aspect of to what extent this truly high-angle GB can really be considered having a character of discrete GB dislocation is discussed. Formally as was laid out in section 2.1.1,

¹The reason to identify the structural unit cell of the GB within one distinct (002) refers to the fact that when in section 6.3.2.2 the GB migration mechanism is discussed, most presented data plots will focus on the situation of the in-plane behaviour of atoms within (002) planes. Hence it is good to realize already at this point how the structural unit cell of this GB looks like.

the $\Sigma 5$ [001] 53.13° tilt GB can be described by two sets of GB edge dislocations. Due to the close spacing of these GB dislocations it is common belief and common sense that an overlapping of the core regions of these dislocations occurs which smears out the discrete GB dislocation character and only leaves behind a highly disordered region called GB.

By utilizing the CNA method, in fact it can be shown that the $\Sigma 5$ [001] 53.13° tilt GB no longer shows any dislocation type character and hence does not show any long-range stress fields at the GB as is associated with GBs consisting of discrete well-separated GB dislocations. Fig. 6.3 and 6.4 present the results of the CNA analysis in the vicinity of GB₁. The shown data was taken from 10K MD simulations. In the two figures only two species

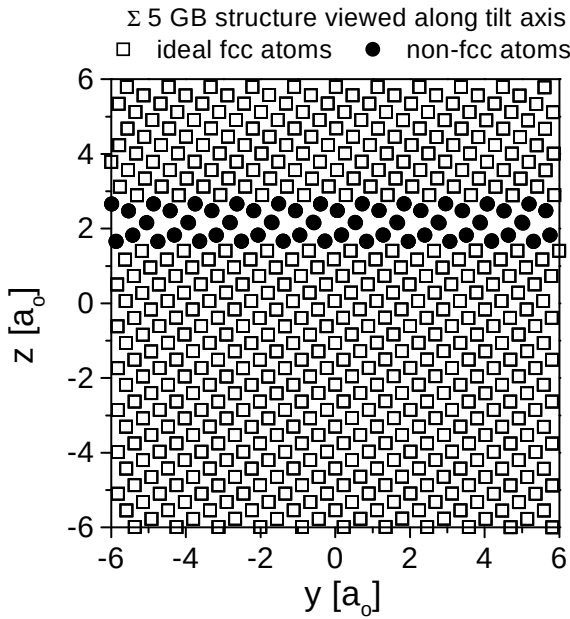


Figure 6.3: Atomistic structure of GB₁ of the $\Sigma 5$ tilt GB according to CNA method viewed along the tilt axis at 10K. Two species of atoms are shown, namely ideal fcc and non-ideal fcc atoms. Clearly the GB is a broad region consisting of five (210) planes and showing no discrete GB dislocation content.

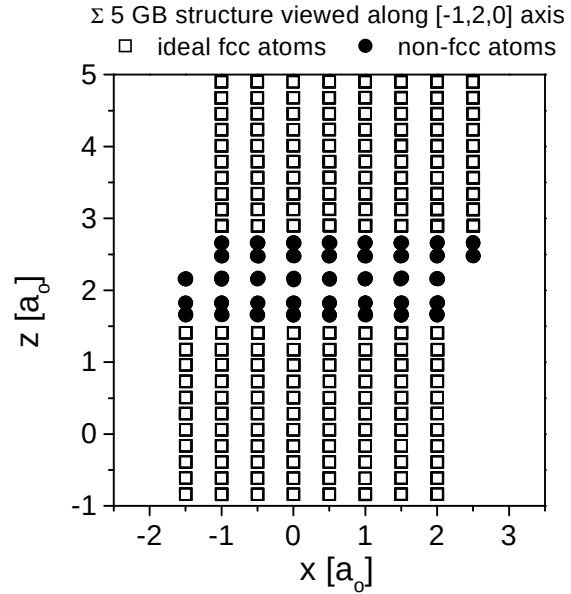


Figure 6.4: Atomistic structure of GB₁ of the $\Sigma 5$ tilt GB according to CNA method viewed along the $[\bar{1}20]$ direction at 10K. Again only two species of atoms are shown, namely ideal fcc and non-ideal fcc atoms. The fully relaxed GB has an microscopic translational state along the tilt axis of $0.5 a_o$ which corresponds to one (001) planar spacing.

of atoms are shown, namely ideal fcc and non-ideal fcc atoms. It is evident from the figures that clearly the GB is a broad region consisting of five (210) planes and showing no discrete GB dislocation content. Both figures further indicate the microstructural translation state at the GB. A slight shift occurs in y-direction, second the volume expansion is seen in z-direction and finally the translational state in x-direction is $0.5 a_o$. This found translational state at the GB is well-known from literature [28].

Finally a few remarks are made on the second existing $\Sigma 5$ [001] tilt GB. This is the $\Sigma 5$ [001] 36.87° tilt GB. In the literature it has often been studied either with respect to GB structure [28, 81], GB diffusion [77, 78, 72, 81] as well as GB sliding and migration [14, 15]. The reader should note that the $\Sigma 5$ [001] 36.87° and $\Sigma 5$ [001] 53.13° tilt GBs are indeed different GBs since the crystallographic planes facing each other at the GB are (310) and (210)

planes, respectively. Here the symmetry effects related to these two misorientation angles differs between $[001]$ twist and tilt GBs, since for the $[001]$ twist GBs both misorientation angles, 36.87° and 53.13° , form the same twist GB.

6.1.2 $\Sigma 73 [1\bar{1}1] 11.64^\circ$

Here $\Sigma 73 [1\bar{1}1] 11.64^\circ$ symmetrical tilt GBs were studied utilizing a 3d periodic border concept. To obtain the relaxed equilibrated GB structure coupled LS and intermediate finite temperature MD simulations were performed on the initially geometric CSL GB system. The obtained atomic-level situation in the vicinity of the GB and within the whole simulation box are shown in Figs. 6.5, 6.7 and 6.8. The GB energy was found to be $E^{GB}=0.726$ J/m² for the 3d LJ potential. Even that the GB energy is about 0.1 J/m² higher than the result by Wolf, this GB system is well relaxed. Wolf utilized his frozen block border concept which explains the difference in GB energy. Since the $\Sigma 73$ GB shall be studied in the presence of external stress states leading to a Peach-Koehler DF on the GB, only a 3d periodic border concept was found to be a stable border concept when utilizing the Parrinello-Rahman scheme. None of the 2d border concepts discussed in sect. 3.3.4 yielded any reliable GB migration data and usually resulted in a crash of the simulation runs. Therefore the 3d periodic GB system can be considered at least to be a good reference system with respect to a fully relaxed GB system utilizing some sort of 2d border concept. Fig. 6.5 simply shows the atomic-level situation in the vicinity of GB₁ when viewed along

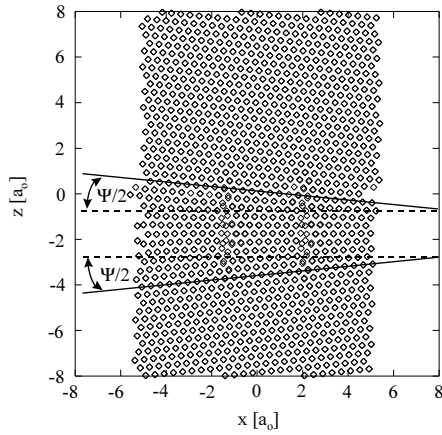


Figure 6.5: Relaxed three-dimensional atomistic structure of the $\Sigma 73 [1\bar{1}1] 11.64^\circ$ symmetrical tilt GB viewed along the $[1\bar{1}1]$ tilt axis. The reader should note that here and in the following figures the full 3d systems are shown without explicitly labeling the ABC stacking sequence of the $(1\bar{1}1)$ planes.

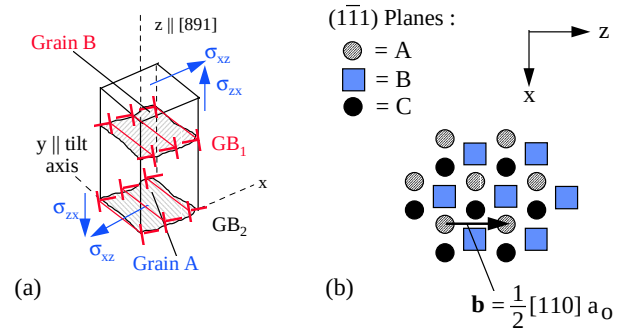


Figure 6.6: Schematic of the $\Sigma 73 [1\bar{1}1] 11.64^\circ$ symmetrical tilt GB. (a) shows the simulation box geometry and the dislocation content of GB₁ and GB₂ due to the 3d periodic border concept utilized. A pure xz external shear stress state is shown too which should lead to a Peach-Koehler DF on each GB dislocation. (b) presents the stacking sequence of the $(1\bar{1}1)$ planes and the geometry of the Burgers vector $\mathbf{b}$ of the discrete GB dislocations.

the $[1\bar{1}1]$ direction for the three-dimensional GB box. The reader should note that in any of the presented figures on the atomistics of the GB system overlapping ABC $(1\bar{1}1)$ planes are shown and that therefore the atomic-level structure needs to be interpreted in terms of

single $(1\bar{1}1)$ planes as is schematically sketched in Fig. 6.6(b). Since a simple plot of the position of each atom does not reveal any distinct details of the GB structure, each atom was analysed by the CNA scheme. Interestingly plots consisting only of the positions of true FCC atoms within the overall system selected according to the CNA reveal the dislocation content of the GB. According to the CNA results of Fig. 6.7 and 6.8 and according to the underlying RS theory (see Eq. 6.1) the shown $\Sigma 73$ GB structure consists of three discrete edge dislocations where i.e. each dislocation of GB_1 (see Fig. 6.6(a)) is having a Burgers vector of $\mathbf{b} = b \cdot [-\sin(\Psi/2), 0, \cos(\Psi/2)]$ with $b = a_o/\sqrt{2}$ and a line vector of $\mathbf{s}_{\Sigma 73} = [0\bar{1}0]$. Hence the x dimension of the simulation box is therefore given by $h_{11} = 3 \cdot D_{\Sigma 73}$ with $D_{\Sigma 73}$ being the spacing of the GB edge dislocations as given by Eq. 6.1.

$$D_{\Sigma 73} = \frac{b_{[110]}}{2 \cdot \sin(\frac{1}{2} \Psi_{\Sigma 73})} = \frac{a_o}{\sqrt{2} \cdot 2 \cdot \sin(\frac{1}{2} \Psi_{\Sigma 73})} = 3.487a_o \quad (6.1)$$

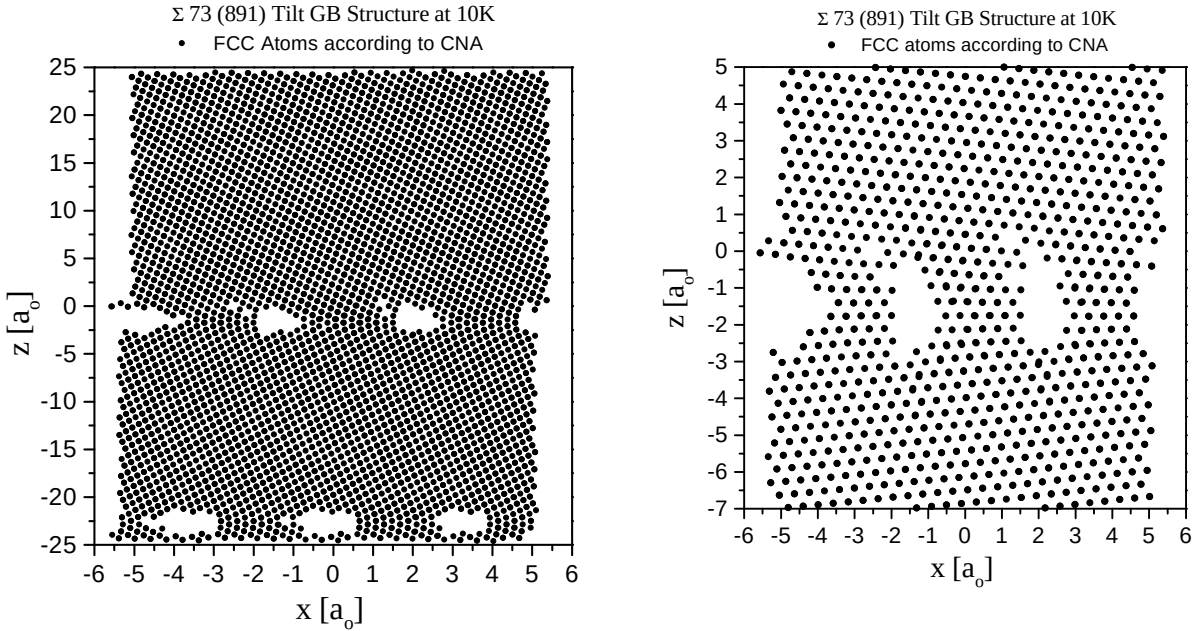


Figure 6.7: 3d system of the $\Sigma 73$ $[1\bar{1}1]$ 11.64° symmetrical tilt GB at 10K for the 3d LJ potential viewed along the $[1\bar{1}1]$ direction. Here only the FCC atoms are plotted which were determined by the CNA within the total simulation box. The plot demonstrates that discrete dislocations are generating the GB and that the core regions of the discrete GB dislocations are identified by the regions of non-FCC atoms which were left out in the figure.

Figure 6.8: 3d system of the $\Sigma 73$ $[1\bar{1}1]$ 11.64° symmetrical tilt GB at 10K viewed along the $[1\bar{1}1]$ direction. Here as in fig. 6.7 only the FCC atoms are plotted in the vicinity of GB_1 according to the CNA. The plot demonstrates that discrete dislocations are generating the GB and the dislocations core regions are identified by the applied CNA selection scheme. The spacing of the dislocations is given by the theoretical value of $D_{\Sigma 73} = 3.487a_o$ which agrees very well with the situation found in the figure.

6.2 Relaxed GB Structure of the studied asymmetrical Tilt GBs

Here the GB structure and GB generation procedures of the two studied asymmetrical tilt GBs, ASY14 and ASY33, that can be associated with the $\Sigma 5$ [001] 53.13° ($\Sigma 5$ [210] 180°) symmetrical tilt GB are presented. Before the GB structural details are presented in sections 6.2.1 and 6.2.2, now the generation procedure and the underlying crystallographic considerations of the underlying $\Sigma 5$ (210) symmetrical tilt GB and the two asymmetrical tilt GBs are discussed. It should be stressed here that the asymmetrical tilt GBs are CSL GBs in order to be able to utilize periodic boundary concepts during the atomistic finite temperature simulations. First the CSL geometry of the $\Sigma 5$ (210) symmetrical tilt

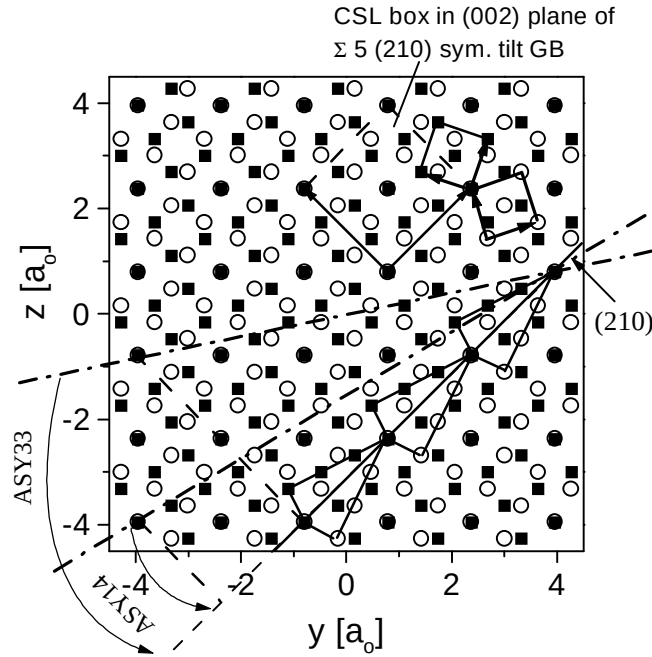


Figure 6.9: Geometrical and crystallographic relationships between the $\Sigma 5$ (210) symmetrical tilt GB and the $\Sigma 5$ [001] 53.13° $\Phi=14.04^\circ$ (ASY14) and the $\Sigma 5$ [001] 53.13° $\Phi=33.69^\circ$ (ASY33) asymmetrical tilt GBs. The figure shows the (002) in-plane CSL box of the $\Sigma 5$ (210) symmetrical tilt GB as well as the inclination of the asymmetrical tilt GBs. Tilt GB ASY14 is having an inclination angle of $\Phi=14.04^\circ$ while tilt GB ASY33 is having an inclination angle of $\Phi=33.69^\circ$ with respect to the (210) plane. Furthermore the figure should help to visualize the (002) in-plane CSL box vectors of the $\Sigma 5$ (210) symmetrical tilt GB.

GB is presented since it provides the basic CSL vectors to form the asymmetrical CSL GBs. According to Fig. 6.1 and 6.9 the CSL vectors of the $\Sigma 5$ [001] 53.13° tilt GB can be crystallographically identified for the lower grain A by

$$\begin{aligned} \mathbf{x}_{CSL}^{\Sigma 5(210)} &= [001] \\ \mathbf{y}_{CSL}^{\Sigma 5(210)} &= [\bar{1}20] \\ \mathbf{z}_{CSL}^{\Sigma 5(210)} &= [210] \end{aligned} \quad (6.2)$$

and for the upper grain B by

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5(210)} &= [00\bar{1}] \\ \mathbf{y}_{CSL}^{\Sigma 5(210)} &= [1\bar{2}0] \\ \mathbf{z}_{CSL}^{\Sigma 5(210)} &= [210].\end{aligned}\quad (6.3)$$

These CSL vectors are used as elementary vectors when constructing the CSL boxes of the asymmetrical tilt GBs. Since the asymmetrical tilt GBs are $[001]$ tilt GBs, only the $\mathbf{y}_{CSL}^{\Sigma 5ASY14}$ and the $\mathbf{z}_{CSL}^{\Sigma 5ASY14}$ CSL vectors for instance for the $\Sigma 5 [001] 53.13^\circ$ ASY14 tilt GB need to be constructed by the CSL vectors of the symmetrical $\Sigma 5 (210)$ tilt GB. These read for the $\Sigma 5 [001] 53.13^\circ$ ASY14 tilt GB

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5ASY14} &= \mathbf{x}_{CSL}^{\Sigma 5(210)} = [001] \\ \mathbf{y}_{CSL}^{\Sigma 5ASY14} &= 4 \cdot \mathbf{y}_{CSL}^{\Sigma 5(210)} - 1 \cdot \mathbf{z}_{CSL}^{\Sigma 5(210)} \\ \mathbf{z}_{CSL}^{\Sigma 5ASY14} &= 1 \cdot \mathbf{y}_{CSL}^{\Sigma 5(210)} + 4 \cdot \mathbf{z}_{CSL}^{\Sigma 5(210)}\end{aligned}\quad (6.4)$$

and

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5ASY33} &= \mathbf{y}_{CSL}^{\Sigma 5(210)} = [001] \\ \mathbf{y}_{CSL}^{\Sigma 5ASY33} &= 3 \cdot \mathbf{y}_{CSL}^{\Sigma 5(210)} - 2 \cdot \mathbf{z}_{CSL}^{\Sigma 5(210)} \\ \mathbf{z}_{CSL}^{\Sigma 5ASY33} &= 2 \cdot \mathbf{y}_{CSL}^{\Sigma 5(210)} + 3 \cdot \mathbf{z}_{CSL}^{\Sigma 5(210)}\end{aligned}\quad (6.5)$$

for the $\Sigma 5 [001] 53.13^\circ$ ASY33 tilt GB. These CSL vectors within the (002) plane of the $\Sigma 5 [001] 53.13^\circ$ ASY14 and ASY33 tilt GB are shown in Fig. 6.10 and 6.11, respectively. They demonstrate the much more extended CSL box size of the asymmetrical tilt GBs with respect to the $\Sigma 5 (210)$ symmetrical tilt GB.

Now the crystallographic planes facing each other at the GB are calculated. Here one only needs to exploit Eq. 6.2 up to 6.5. For the ASY14 tilt GB this yields for the lower grain A

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5ASY14} &= [001] \\ \mathbf{y}_{CSL}^{\Sigma 5ASY14} &= 4 \cdot [\bar{1}20] - 1 \cdot [210] = [\bar{6}70] \\ \mathbf{z}_{CSL}^{\Sigma 5ASY14} &= 1 \cdot [\bar{1}20] + 4 \cdot [210] = [760]\end{aligned}\quad (6.6)$$

and for the upper grain B

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5ASY14} &= [00\bar{1}] \\ \mathbf{y}_{CSL}^{\Sigma 5ASY14} &= 4 \cdot [1\bar{2}0] - 1 \cdot [210] = [2\bar{9}0] \\ \mathbf{z}_{CSL}^{\Sigma 5ASY14} &= 1 \cdot [1\bar{2}0] + 4 \cdot [210] = [920]\end{aligned}\quad (6.7)$$

Hence planes facing each other at the ASY14 tilt GB are (760) planes of the lower grain A and (920) planes of the upper grain B.

For the ASY33 tilt GB this yields for the lower grain A

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5ASY33} &= [001] \\ \mathbf{y}_{CSL}^{\Sigma 5ASY33} &= 3 \cdot [\bar{1}20] - 3 \cdot [210] = [\bar{7}40] \\ \mathbf{z}_{CSL}^{\Sigma 5ASY33} &= 2 \cdot [\bar{1}20] + 3 \cdot [210] = [470]\end{aligned}\quad (6.8)$$

and for the upper grain B

$$\begin{aligned}
 \mathbf{x}_{CSL}^{\Sigma 5 ASY33} &= [00\bar{1}] \\
 \mathbf{y}_{CSL}^{\Sigma 5 ASY33} &= 3 \cdot [1\bar{2}0] - 2 \cdot [210] = [\bar{1}\bar{8}0] \\
 \mathbf{z}_{CSL}^{\Sigma 5 ASY33} &= 2 \cdot [1\bar{2}0] + 3 \cdot [210] = [8\bar{1}0]
 \end{aligned} \tag{6.9}$$

Hence planes facing each other at the ASY33 tilt GB are (470) planes of the lower grain A and ($8\bar{1}0$) planes of the upper grain B.

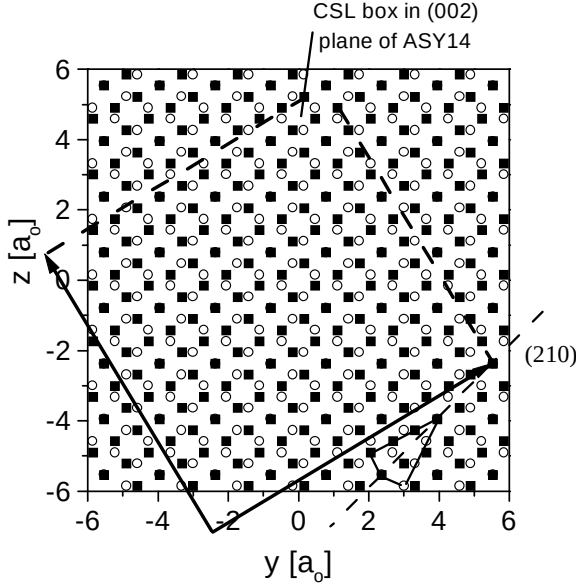


Figure 6.10: Inclination of the $\Sigma 5$ [001] 53.13° ASY14 asymmetrical tilt GB with respect to the $\Sigma 5$ (210) symmetrical tilt GB. The inclination of the GB plane of ASY14 tilt GB with respect to the $\Sigma 5$ (210) symmetrical tilt GB is shown as well as the (002) in-plane CSL box that was used to construct the GB system.

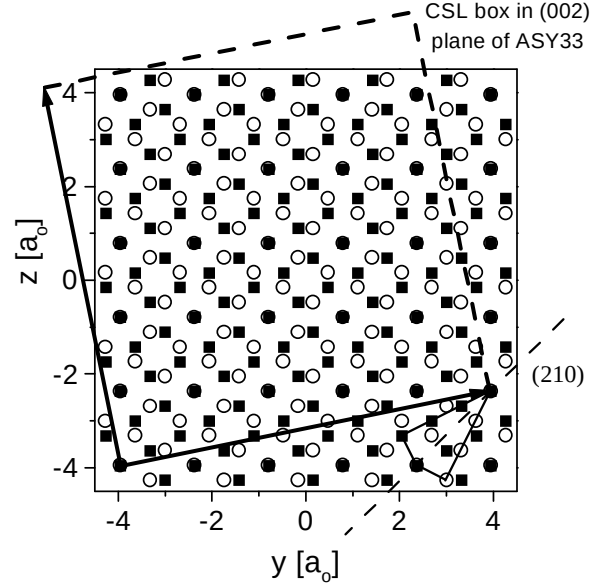


Figure 6.11: Inclination of the $\Sigma 5$ [001] 53.13° ASY33 asymmetrical tilt GB with respect to the $\Sigma 5$ (210) symmetrical tilt GB. The inclination of the GB plane of ASY33 tilt GB with respect to the $\Sigma 5$ (210) symmetrical tilt GB is shown as well as the (002) in-plane CSL box that was used to construct the GB system.

Finally it is stressed again to release the importance of the reference system of the $\Sigma 5$ [001] 53.13° symmetrical tilt GB. The two asymmetrical tilt GBs, ASY14 and ASY33, are linked to the $\Sigma 5$ [001] 53.13° symmetrical tilt GB because all three GBs share the same misorientation relationship between grain A (lower grain) and grain B (upper grain). The only difference between the three GBs is the choice of the GB plane which for the $\Sigma 5$ [001] 53.13° symmetrical tilt GB is a (210) plane while for the ASY14 asymmetrical tilt GB the GB plane is inclined by 14.04° with respect to the (210) plane and (760) / (920) planes are facing each other at the GB. For the ASY33 the GB is inclined by 33.69° with respect to the (210) plane and (470) / ($8\bar{1}0$) planes are facing each other at the GB.

Only one further symmetrical [001] tilt GB can be formed by the basic CSL vectors of the $\Sigma 5$ (210) symmetrical tilt GB which is the $\Sigma 5$ (310) symmetrical tilt GB. It is inclined by 45° with respect to the (210) plane and its CSL vectors can be determined the same way

as for the asymmetrical tilt GBs, namely by

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5(310)} &= [001] \\ \mathbf{y}_{CSL}^{\Sigma 5(310)} &= [\bar{1}20] - [210] = [\bar{3}10] \\ \mathbf{z}_{CSL}^{\Sigma 5(310)} &= [\bar{1}20] + [210] = [130]\end{aligned}\tag{6.10}$$

and for the upper grain B

$$\begin{aligned}\mathbf{x}_{CSL}^{\Sigma 5(310)} &= [00\bar{1}] \\ \mathbf{y}_{CSL}^{\Sigma 5(310)} &= [1\bar{2}0] - [210] = [\bar{1}\bar{3}0] \\ \mathbf{z}_{CSL}^{\Sigma 5(310)} &= [1\bar{2}0] + [210] = [3\bar{1}0]\end{aligned}\tag{6.11}$$

Hence the same crystallographic (310) planes are facing each other at the GB which therefore makes this GB to be a symmetrical tilt GB.

6.2.1 $\Sigma 5 [001] 53.13^\circ \Phi=14.04^\circ$

In the preceding section 6.2, the underlying geometrical considerations to generate the $\Sigma 5 [001] 53.13^\circ \Phi=14.04^\circ$ asymmetrical tilt GB were discussed in terms of the CSL and with respect to the symmetrical $\Sigma 5 (210)$ tilt GB. Here the found atomistics in the vicinity of the

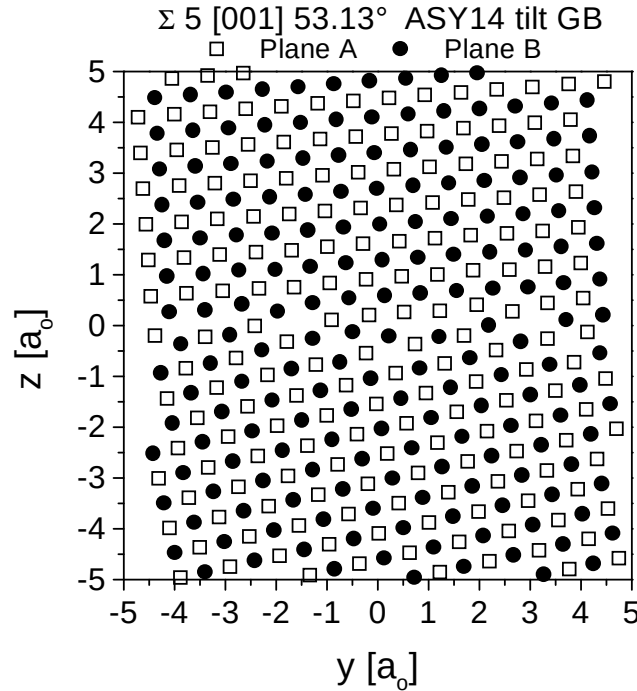


Figure 6.12: Atomistics of the $\Sigma 5 [001] 53.13^\circ \Phi=14.04^\circ$ asymmetrical tilt GB. The figure shows two (002) planes labelled A and B in the vicinity of the GB. For the ASY14 asymmetrical tilt GB, (760) planes in the lower grain and (920) planes in the upper grain are facing each other at the GB.

GB are presented for LJ MD simulations utilizing 2d periodic boundary conditions within

the GB plane (x-y plane of the simulation box coordinate system) while pseudo free surfaces in the direction normal to the GB plane (z-direction). Fig. 6.12 shows the atomistics of the $\Sigma 5$ ASY14 tilt GB where two (002) planes are shown. The crystallographic planes meeting at the GB are (760) planes in the lower grain and (920) planes in the upper grain as was explained in section 6.2.

The simulation box consisted of six (002) planes, the system in total having a number of 6210 atoms. The relaxed GB energy was 1.041 J/m^2 . In y-direction only one CSL unit cell was installed having a length of $\sqrt{85} a_o$. In order to get a clearer picture of the GB

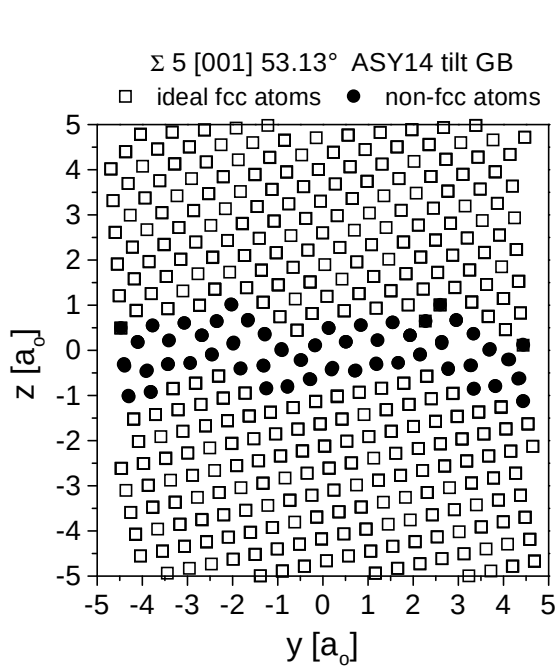


Figure 6.13: CNA analysis of the $\Sigma 5$ [001] 53.13° ASY14 asymmetrical tilt GB viewed along the tilt axis through the 3d system. Two atomic species are shown, namely ideal fcc atoms and non-fcc atoms. The non-fcc atoms reveal those atoms that are associated with the GB structure.

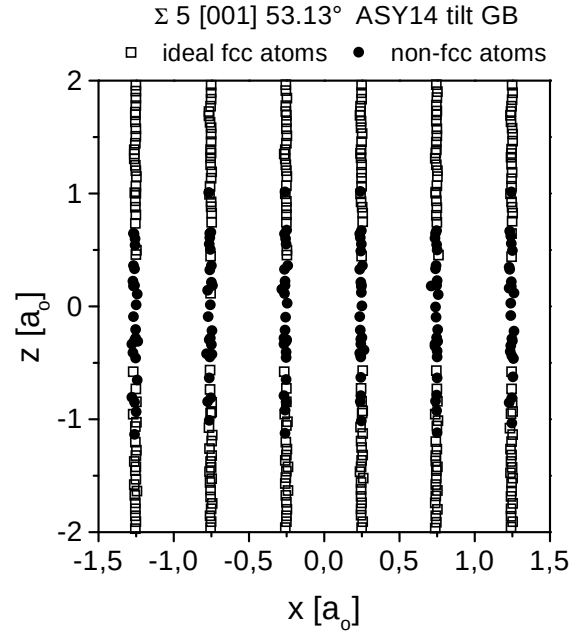


Figure 6.14: CNA analysis of the $\Sigma 5$ [001] 53.13° ASY14 asymmetrical tilt GB viewed along the y-direction through the 3d system. Two atomic species are shown, namely ideal fcc atoms and non-fcc atoms. The figure illustrates that the microscopic translational state along the x-direction is zero. This is different from the $\Sigma 5$ (210) symmetrical tilt GB where t_x is $0.5a_o$.

structure, the CNA method was used to identify ideal fcc atoms as well as non-fcc atoms. Usually the non-fcc atoms can be attributed to the GB and help to reveal the GB structure. Fig. 6.13 and 6.14 present the situation in the vicinity of the GB viewed along the tilt axis and the y-direction, respectively. Fig. 6.14 demonstrates that the microscopic translational state along the x-direction is zero. This is different from the $\Sigma 5$ (210) symmetrical tilt GB where t_x is $0.5a_o$.

6.2.2 Σ 5 [001] 53.13° $\Phi=33.69^\circ$

Here the found atomistics in the vicinity of the Σ 5 [001] 53.13° $\Phi=33.69^\circ$ asymmetrical tilt GB are presented for LJ simulations utilizing 2d periodic boundary conditions within the GB plane (x-y plane of the simulation box coordinate system) while pseudo free surfaces in the direction normal to the GB plane (z-direction). Fig. 6.15 shows the atomistics of the Σ 5 ASY33 tilt GB where two (002) planes are shown. The crystallographic planes meeting at the GB are (470) planes in the lower grain and (8 $\bar{1}$ 0) planes in the upper grain as was explained in detail in section 6.2.

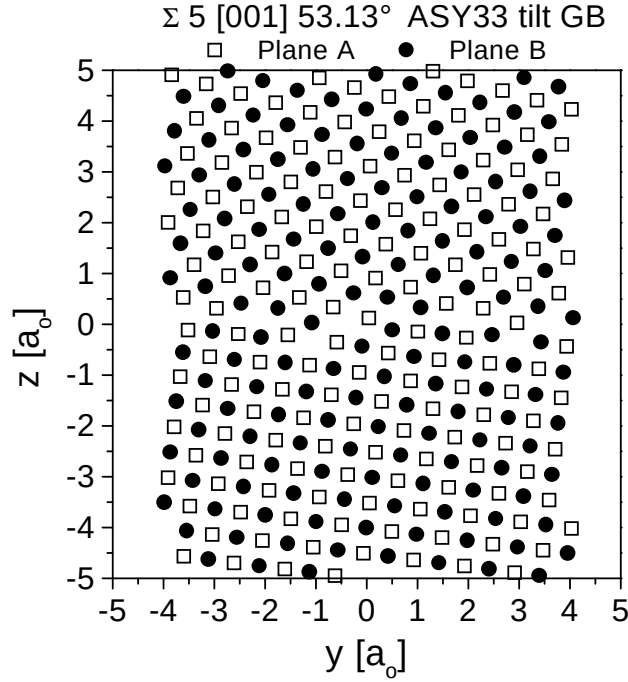


Figure 6.15: Atomistics of the Σ 5 [001] 53.13° $\Phi=33.69^\circ$ asymmetrical tilt GB. The figure shows two (002) planes labelled A and B in the vicinity of the GB. For the ASY33 asymmetrical tilt GB, (470) planes in the lower grain and (8 $\bar{1}$ 0) planes in the upper grain are facing each other at the GB.

The simulation box consisted of six (002) planes and the overall system had 6240 atoms. The relaxed GB energy was 1.164 J/m². In y-direction only one CSL unit cell was installed having a length of $\sqrt{65} a_o$. In order to get a clearer picture of the GB structure, the CNA method was used to identify ideal fcc atoms as well as non-fcc atoms. Usually the non-fcc atoms can be attributed to the GB and help to reveal the GB structure much better than for instance as Fig. 6.15. Fig. 6.16 and 6.17 present the situation in the vicinity of the GB viewed along the tilt axis and the y-direction, respectively. Fig. 6.17 demonstrates that the microscopic translational state along the x-direction is zero. This is different from the Σ 5 (210) symmetrical tilt GB where t_x is $0.5a_o$.

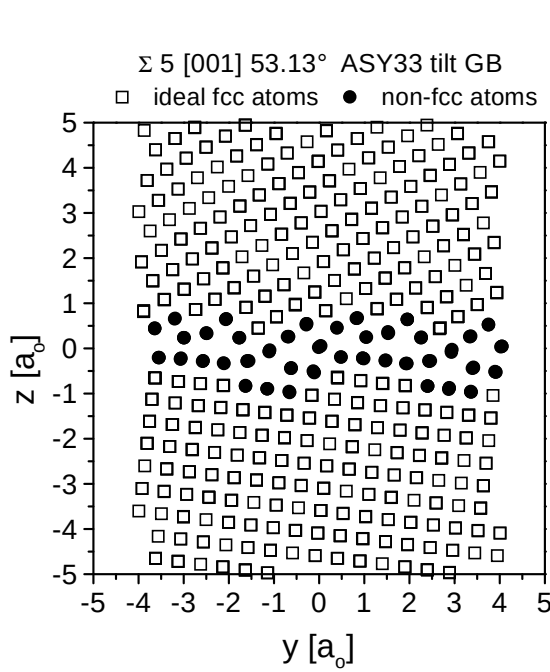


Figure 6.16: CNA analysis of the $\Sigma 5$ [001] 53.13° ASY33 asymmetrical tilt GB viewed along the tilt axis through the 3d system. Two atomic species are shown, namely ideal fcc atoms and non-fcc atoms. The non-fcc atoms reveal those atoms that are associated with the GB structure.

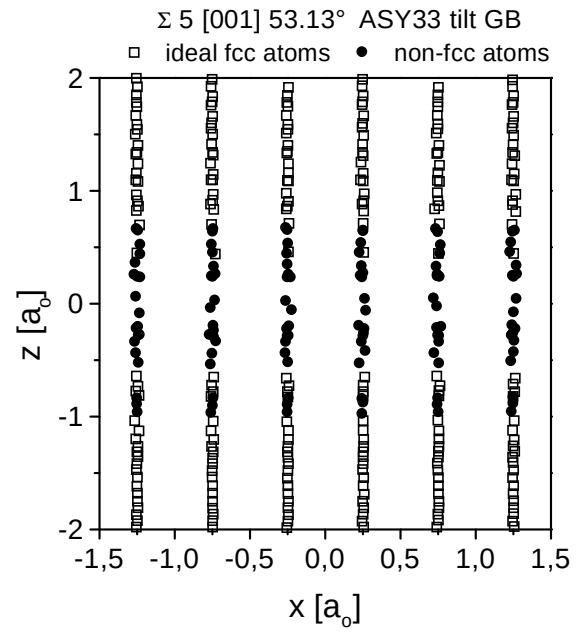


Figure 6.17: CNA analysis of the $\Sigma 5$ [001] 53.13° ASY33 asymmetrical tilt GB viewed along the y-direction through the 3d system. Two atomic species are shown, namely ideal fcc atoms and non-fcc atoms. The figure illustrates that the microscopic translational state along the x-direction is zero. This is different from the $\Sigma 5$ (210) symmetrical tilt GB where t_x is $0.5a_o$.

6.3 GB Migration of Planar Symmetrical Tilt GBs

6.3.1 Elastic Driving Force

6.3.1.1 Verification

To illustrate the elastic driving force concept with respect to tilt GBs, the $\Sigma 5$ [001] 53.13° tilt GB is one of two key examples to exemplify the details of the scheme. According to the linear elastic theory presented in sect. 3.4.2 for [001] GBs and with respect to the usually assumed MD GB box geometry, the usually applied x-y coupled shear strain tensor for [001] twist GBs needs to be transformed due to the specific box geometry of the $\Sigma 5$ [001] tilt GB. Here it should clearly be stated that this required transformation of the strain tensor is only due to the usual procedure to align the GB normal with the z direction of the MD simulation box. Otherwise if the [001] crystallographic direction would remain aligned with the z direction of the MD box, a coupled x-y shear state would work fine for [001] tilt GBs too and would give rise of an elastic DF. To visualize the specific need to transform the coupled x-y shear tensor, Fig. 6.18 shows the box geometry and the strain tensor components needed for an elastic DF for general [001] twist GBs (see part (a)) and in part (b) for the $\Sigma 5$ [001] 53.13° tilt GB. One finds that for the $\Sigma 5$ tilt GB the applied strain tensor becomes a coupled y-z shear state due to the fact that the [001] misorientation axis is now parallel to the x direction of the MD box coordinate system. The exact form of the strain tensor is given

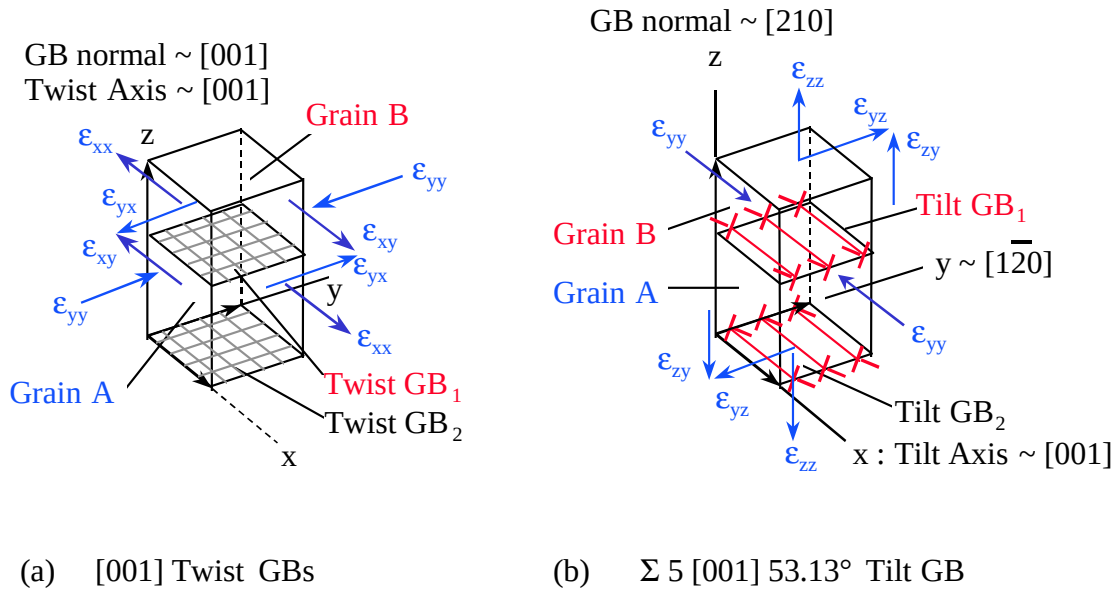


Figure 6.18: $\Sigma 5$ tilt GB : Strain tensor components applied to the MD box in case of [001] twist GBs (see (a)) and for the $\Sigma 5$ [001] 53.13° tilt GB as presented in (b) to install an elastic DF.

by $\underline{\epsilon}_{ela}$ as given below. After dealing with the exact form of the strain tensor applicable to the $\Sigma 5$ [001] 53.13° tilt GB simulation box, two examples of distinct strain states shall be given to demonstrate the existence of an elastic DF. These results were obtained at 10K by the IQS and DQS which were used to extract the elastic energy profiles from the raw

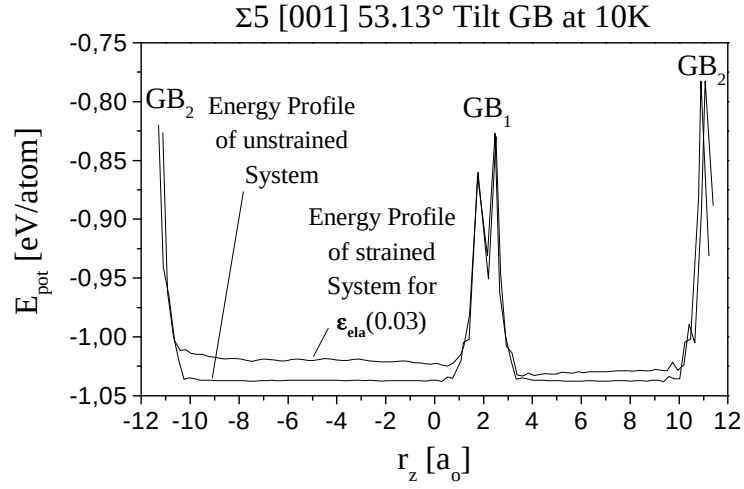


Figure 6.19: $\Sigma 5$ [001] 53.13° tilt GB : Potential energy profile at 10K for a 3d LJ system. Here the average potential energy within (210) planes is plotted versus the z position, r_z , of each (210) plane. Note for the unstrained case that the bulk regions can be identified having a potential energy almost equal to the cohesive energy of the ideal crystal, namely $E_{coh} = -1.037824$ eV/atom. For the case under strain $\epsilon_{ela}(0.03)$ was applied to the MD box. The location of the two GBs, namely GB_1 and GB_2 , is given by the corresponding potential energy peaks.

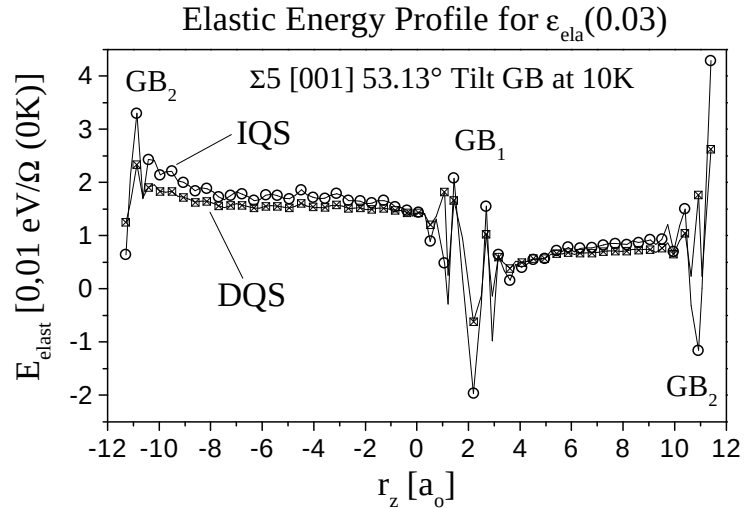


Figure 6.20: $\Sigma 5$ [001] 53.13° tilt GB : Elastic DF at $T=10K$ due to the application of $\epsilon_{ela}(0.03)$ on the MD box. Here the average elastic energy within (210) planes is plotted versus the z position, r_z , of the (210) planes for the IQS and DQS. These profiles agree very well and underline the opportunity to apply the DQS as an in-situ detection scheme of the elastic DF within finite temperature MD simulations.

simulation data. The IQS and DQS are well explained in sect. 5.2.2.1 and the reader is referred to that section for additional reading. Before the results of the system's behaviour in the presence of an elastic DF or some distinct strain states are given, the general form of strain tensors applied to the MD simulation box shall be presented next. These were

$$\underline{\epsilon}_{ela}(\epsilon) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\frac{\epsilon}{2} & \epsilon \\ 0 & \epsilon & +\frac{\epsilon}{2} \end{pmatrix}, \quad \underline{\epsilon}_{yz}(\epsilon) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & \epsilon & 0 \end{pmatrix} \quad \text{and} \quad \underline{\epsilon}_{non}(\epsilon) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \epsilon \\ 0 & 0 & 0 \end{pmatrix}.$$

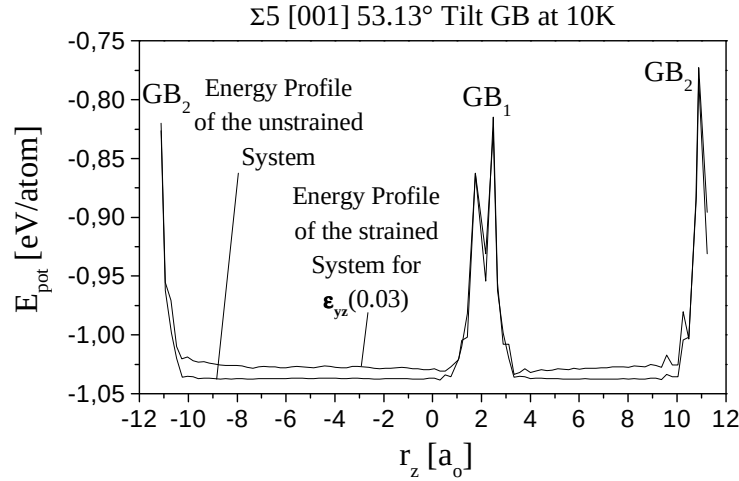


Figure 6.21: $\Sigma 5$ [001] 53.13° tilt GB : Potential energy profile at 10K for a 3d LJ system. Here the average potential energy within (210) planes is plotted versus the z position, r_z , of each (210) plane. Note for the unstrained case, the bulk regions can be identified having a potential energy almost equal to the cohesive energy of the ideal crystal. For the case under strain $\underline{\epsilon}_{yz}(0.03)$ was applied to the MD box.

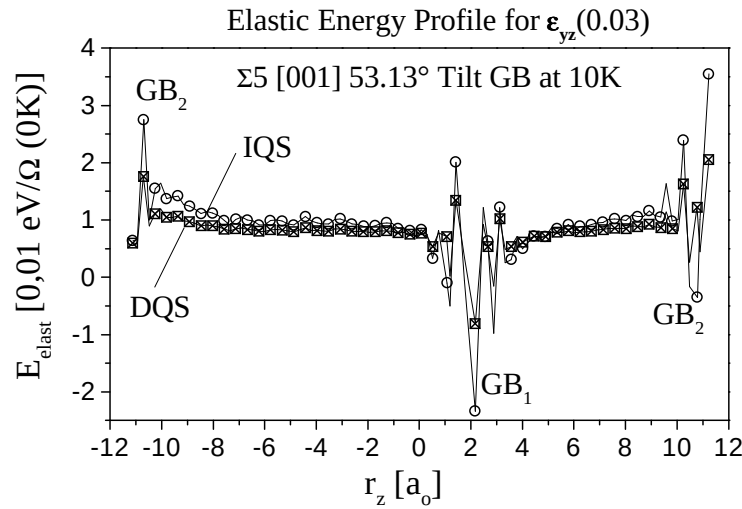


Figure 6.22: $\Sigma 5$ [001] 53.13° tilt GB : Elastic DF at $T=10K$ due to the application of $\underline{\epsilon}_{yz}(0.03)$ on the MD box. For additional information see caption of Fig. 6.20.

The reader should note here that by definition a true strain tensor is symmetric. Due to this $\underline{\underline{\epsilon}}_{non}(\epsilon)$ is not a true strain tensor, but represents a strain tensor plus an additional rotation. In the literature such a shear state is known as simple shear. The true strain tensor of $\underline{\underline{\epsilon}}_{non}(\epsilon)$ is $\underline{\underline{\epsilon}}_{yz}(\frac{\epsilon}{2})$. The relevance of simple shear states is connected to crystal plasticity by dislocations. GB glide can as well lead to such simple shear states and in this work this non-symmetric tensor was applied to the MD box to investigate GB sliding coupled with GB migration. Further details on these issues are given in sect. 6.3.1.2.

According to the analytic linear elastic model of an elastic DF and according to the presented data at 10K of Fig. 6.19, only the strain tensor $\underline{\underline{\epsilon}}_{ela}$ results in an elastic DF and hence should lead to continuous GB migration of GB₁ and GB₂. Among the listed strain tensors there is no other one that does result in an elastic DF. This is for instance demonstrated by Fig. 6.21 and 6.22 for the strain state $\underline{\underline{\epsilon}}_{yz}$. A finite temperature of 10K was chosen for this analysis in order to utilize MD simulations to compute the necessary data. All presented data were computed for the 3d LJ potential. Fig. 6.19 shows a plane by plane plot of the average potential energy within (210) planes versus the z position, r_z , of each (210) plane at 10K for the $\Sigma 5$ [001] tilt GB. Here the location of the two GBs, GB₁ and GB₂, can be associated with the potential energy peaks. The existing energy gradient between the lower and the upper grain can clearly be observed in the system since the amount of elastic energy stored in the lower grain A is larger than in grain B. To illustrate this point even better, Fig. 6.20 presents the average elastic energy profile within each (210) plane obtained by the IQS and DQS. Here the IQS was calculated from the data seen in Fig. 6.19, namely by subtracting the energy profile of the unstrained case from profile of the strained situation. The comparison of the IQS and DQS data of Fig. 6.20 impressively demonstrates the very good agreement of both schemes. Furthermore it underlines the fact that the DQS can be used as an in-situ characterization scheme to follow the temporal and spatial evolution of the elastic energy stored within each grain.

The second example given by Fig. 6.21 and 6.22 shall exemplify that indeed only the strain state $\underline{\underline{\epsilon}}_{ela}$ yields an elastic DF. Strain states lacking the components of $\underline{\underline{\epsilon}}_{ela}$ do not lead to an elastic DF. This is clearly underlined by Fig. 6.21 and 6.22. Again the good agreement of the IQS and DQS is pointed out by Fig. 6.22.

6.3.1.2 $\Sigma 5$ [001] 53.13°

The presented GB migration results in the presence of an elastic DF for [001] twist GBs and the underlying linear elastic theory suggest that for [001] tilt GBs the elastic driving force concept could be utilized as well to drive these tilt GBs. According to Fig. 6.19 and 6.20 one finds indeed that an elastic DF can be introduced into [001] tilt GB systems by applying coupled y-z shear strains to the MD simulation box. Thus it was expected that elastic DFs would drive [001] tilt GBs continuously. Here the emphasis is on continuously. The results presented in this section do show that in fact the GBs move over a finite distance until eventually the migration ceases. When it became obvious that for some reason no continuous GB migration was achieved by the elastic DF concept, the main question arose why the elastic DF concept works well for [001] twist GBs but fails for [001] tilt GBs. The key to understand these findings is connected to the specific form of the applied coupled y-z shear strain tensor to the $\Sigma 5$ tilt GB MD box. Obviously the yz strain component, ϵ_{yz} , itself can in principle initiate GB glide which could in principle be coupled with GB

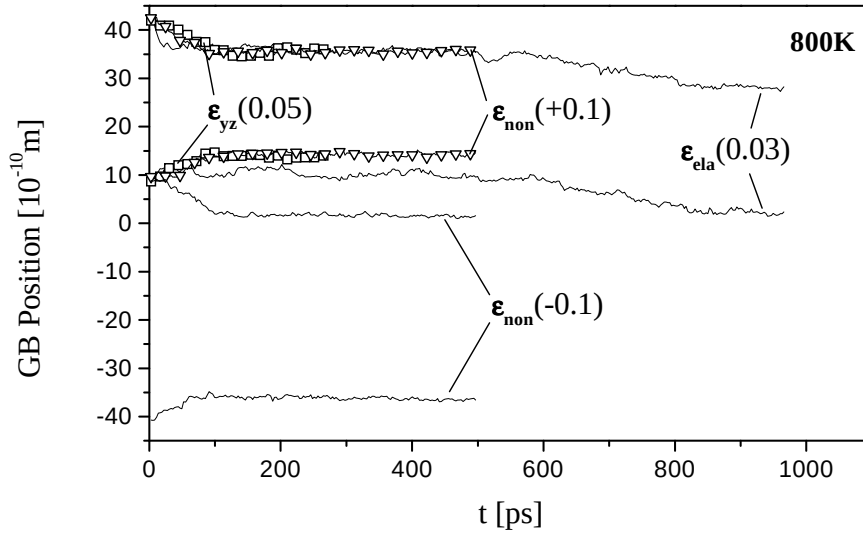


Figure 6.23: $\Sigma 5$ tilt GB : GBM simulations at 800K for different strain states.

migration. In fact Bishop et. al [14] had shown that for the $\Sigma 5$ [001] 36.87° tilt GB such a coupling indeed exists. Taking this idea and the mentioned results into account additional simulations were performed to investigate the behaviour of the tilt GBs if only pure and simple yz shear strains were applied to the MD box. Obviously for these strain states no elastic DF is introduced in the system as suggested by the theory and underlined by Fig. 6.21 and 6.22. Fig. 6.23, 6.24 and 6.25 show the GB migration results of the $\Sigma 5$ [001] 53.13°

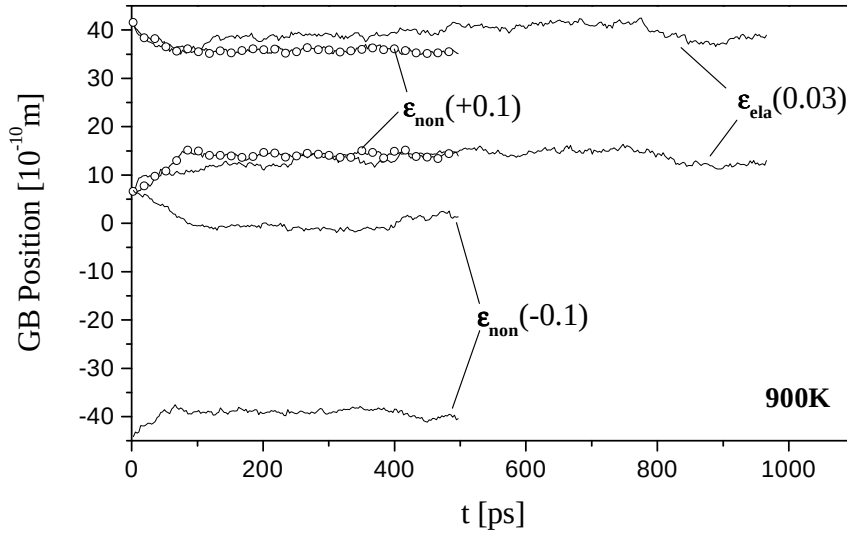


Figure 6.24: $\Sigma 5$ tilt GB : GBM simulations at 900K for different strain states.

tilt GB at 800K, 900K and 1000K respectively for the application of different strain tensors. Fig. 6.23 and 6.24 demonstrate that for the simulations in the presence of an elastic DF due to the applied strain tensor, $\underline{\epsilon}_{ela}(0.03)$, the GBs migrate about $5\text{\AA}$ until the migration ceases. A further important aspect of these simulations is that the GBs do migrate in a direction opposite to the elastic DF. This is rather surprising and these migration events

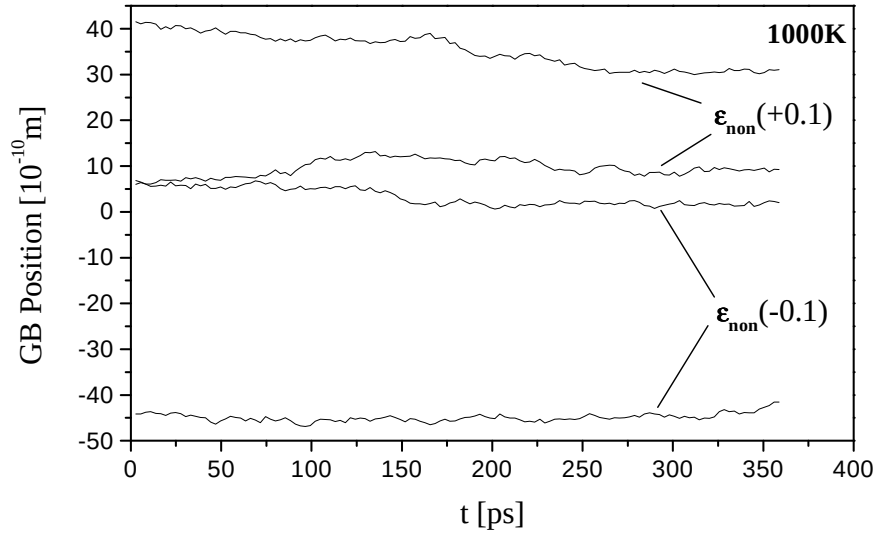


Figure 6.25: $\Sigma 5$ tilt GB : GBM simulations at 1000K for different strain states.

can therefore not be associated with the elastic DF. The only reasonable explanation of the obtained results is that even in the presence of the elastic DF the yz strain component initiated GB glide events that were coupled with GB migration. These GB glide events eventually would have converted the initial elastic strain ϵ_{yz} into plastic strain ϵ_{yz} . Of course the result of such a scenario would be that the elastic DF would eventually disappear due to the conversion of elastic strain into plastic strain. At this point a technical aspect of the simulations comes into play. The usual procedure within such simulations was that the strain tensor was not applied to the MD box at once but rather that the strain was introduced into the system over a finite period of time, t_{intro} . For the presented data at 800K and 900K in the presence of an elastic DF, t_{intro} was set to 4,500 time steps which equaled 12.42 ps in real time. In general this procedure was used in order to suppress strong system's disturbances due to the imposed strain states. The used period of time, t_{intro} , of the simulations under different strain states is given in Tab. 6.1. The results at 800K and 900K for the strain state $\underline{\epsilon}_{ela}(0.03)$ point out that after the initial glide and migration events the separation between GB_1 and GB_1 remained constant since either of the GBs did not move or both moved in one direction keeping their distance of separation fixed.

In order to verify whether GB glide events dominate the system's behaviour further simulations were performed with strain tensors $\underline{\epsilon}_{xy}(0.05)$ and $\underline{\epsilon}_{non}(\pm 0.1)$ at 800K. For those MD simulations t_{intro} was increased to 31,500 time steps which equals a real time of 86.94 ps in order to be able to follow the system's response more carefully. Two major results can be gained from these simulations. As Fig. 6.23 shows GB migration only occurred while the strain tensor was incrementally increased. Once its final magnitude had been reached GB migration ceased. The second major result is that GB migration is associated here with pure or simple yz shear states rather than the elastic DF. Indeed we find that the migration distance for the strain state $\underline{\epsilon}_{xy}(0.05)$ and $\underline{\epsilon}_{non}(0.1)$ are the same, indicating that the symmetric strain tensor determines the distance of migration. Finally a change of GB migration direction is simply achieved by changing the sign of the yz shear state as demonstrated in Fig. 6.23 by results of strain state $\underline{\epsilon}_{non}(-0.1)$. At 900K the obtained results almost perfectly match the results at 800K for the strain states $\underline{\epsilon}_{non}(\pm 0.1)$ as Fig. 6.24 indicates. The total

distance of migration of the GBs within the first 100ps for the elastic DF is less than for the simple and pure yz shear states, because the yz shear component of $\underline{\epsilon}_{ela}$ was less than the one for $\underline{\epsilon}_{yz}$ and $\underline{\epsilon}_{non}$. These results are therefore well understood in the assumed model of GB glide coupled with GB migration. Finally the results at 1000K shall be discussed.

T [K]	Applied Strain Tensor	t_{intro} [ps]
800	$\underline{\epsilon}_{ela}(0.03)$	12.42
800	$\underline{\epsilon}_{yz}(0.05)$, $\underline{\epsilon}_{non}(\pm 0.1)$	86.94
900	$\underline{\epsilon}_{ela}(0.03)$	12.42
900	$\underline{\epsilon}_{non}(\pm 0.1)$	62.10
1000	$\underline{\epsilon}_{non}(\pm 0.1)$	62.10

Table 6.1: Details on the $\Sigma 5$ tilt GB Migration Simulations under different states of external strain.

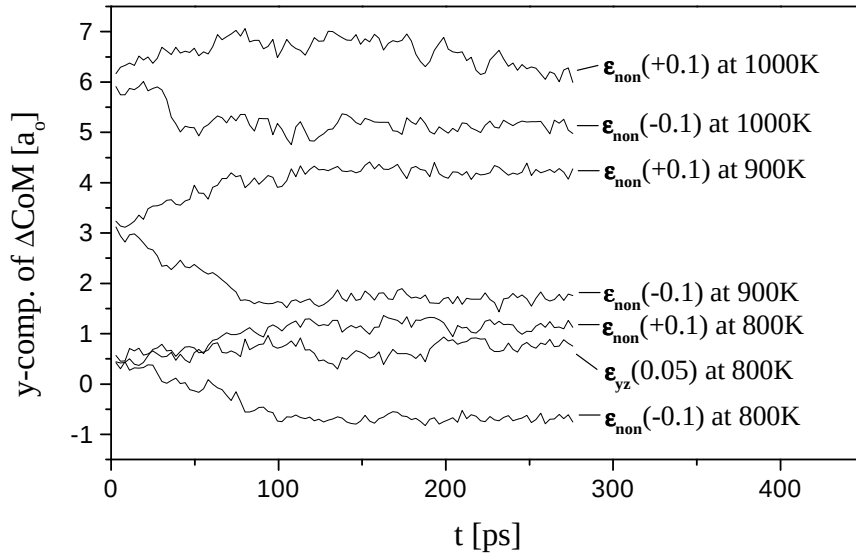


Figure 6.26: $\Sigma 5$ tilt GB : Plotted is the y component of the difference of the center of mass, ΔCoM , between the upper and lower grain versus the time, t , at 800K, 900K and 1000K for different strain states. The plotted ΔCoM data was shifted by $+3.0 a_0 \cdot \frac{(T-800K)}{100K}$ on the y-axis to be able to distinguish between the plots.

At 1000K the system's response seems to have changed slightly from the 800K and 900K situation as Fig. 6.25 suggests. At 1000K only simple yz shear strain states were applied to the MD box to study the glide behaviour of the GBs. According to Fig. 6.25 it is not obvious that GB migration occurs that is coupled to GB glide especially if we consider that here t_{intro} was 62.10ps. Within this window of time no explicit GB migration is detectable from the data which is clearly different from the findings at lower temperatures. One can suspect that still GB glide is occurring but due to the effect of temperature the GB structure had changed from a strong crystalline structure to a more disordered one. If so GB glide would still take place but rather as a glide of two crystals sharing a disordered interface. This

glide would be comparable to glide of lubricated grains. One main aspect would therefore be that a coupling of GB glide and GB migration only exists if the GB possesses a crystalline structure that can transmit the glide displacement into the lattice within a DSC description leading to GB glide accompanied by GB migration. In order to confirm the stated importance of GB glide, Fig. 6.26 presents the y component of the difference of the center of mass, ΔCoM , between the upper and lower grain versus the time, t , at 800K, 900K and 1000K for different strain states. One main conclusion drawn from the figure is that indeed the time evolution of ΔCoM proves the existence of GB glide along the y direction of the MD GB box. The coupling between GB glide events and GB migration is well illustrated when studying the system's behaviour for the strain state $\epsilon_{non} (+0.1)$ and $\epsilon_{non} (-0.1)$. The plotted data agree very well with the finding that the direction of GB migration changes if the glide direction changes too which again stresses the coupling between GB glide events and GB migration. A RDF analysis of the GB atoms was performed too to check whether structural changes occur at 1000K. No disorder effect was found in that analysis and due to the fact that no conclusion could be drawn from the analysis rather that at all studied temperatures it seems that the GB remained crystalline-like the figure of the RDF analysis has not been included here. Details on the GB mechanism are given in sect. 6.3.2.2 which underline the stated situation of the above presentation and discussion of the results that GB glide coupled with GB migration is the key characteristic of these simulations.

6.3.1.3 Remarks on GB Migration of tilt GBs due to Elastic DFs

According to the GB migration results of the $\Sigma 5$ [001] 53.13° tilt GB presented in sect. 6.3.1.2 it was demonstrated that although an elastic DF could be introduced into the MD simulation box by an appropriate coupled yz shear state, no continuous GB migration was obtained. In fact none of the observed GB migration events occurred due to the elastic DF but rather because GB glide was initiated by the yz shear state. Taking further into account the results of GB migration of [001] twist GBs in the presence of an elastic DF due to a coupled x-y shear state, one has to draw the conclusion that two requirements must be fulfilled in order to observe continuous GB migration due to an elastic DF. The first one is rather trivial namely that indeed a strain state exists that introduces an elastic DF into the GB system. Due to the anisotropy of the elastic constants for cubic materials it seems that for any GB this fundamental requirement is satisfied. The second requirement seems then more important since it determines whether really GB migration occurs continuously in the presence of an elastic DF. Namely according to the presented results and due to the gained experience on several different tilt GBs one comes to the conclusion that any tilt GB can not be driven continuously by an elastic DF concept if GB glide events are initiated by components of the elastic DF strain tensor. For the generally chosen MD box geometry in this work these components can only be the xz or yz shear strain components. Hence if it is required that the elastic DF strain tensor contains these shear components in order to yield a non-zero elastic DF, then it seems very likely that GB glide is initiated by such a strain tensor rather than GB migration. The $\Sigma 5$ [001] 53.13° tilt GB is the first example to demonstrate this point although here GB glide is accompanied by GB migration.

Now the results for the $\Sigma 7$ [1 $\bar{1}$ 1] 38.21° tilt GB shall be briefly given since it acts as the second key example in this discussion. Here the concept of an elastic DF shall be presented only briefly to demonstrate that for the $\Sigma 7$ [1 $\bar{1}$ 1] 38.21° symmetrical tilt GB the elastic DF fails as well to drive this tilt GB continuously. At first the verification of the elastic DF

within the analytical DF concept shall be illustrated. Since the algebra becomes a little bit more complicated when assuming a general form for the applied strain tensor in this case, a numeric scheme is put forward now to calculate the elastic DF. Briefly the main aspects will be illustrated for the $\Sigma 7$ $[\bar{1}\bar{1}1]$ tilt GB although the underlying idea and schemes are rather simple and straightforward. Additionally a numeric calculation scheme can easily be implemented and computed on any standard computer with only a few seconds of CPU time. The basic information for the calculus is the crystallographic orientation of the two grains with respect to the MD coordinate box system. Once this information is known it is simple math to write down the rotation matrices for each grain that allow one to transform the strain tensor applied to the simulation box into the principal coordinate system of each cubic grain. Performing the transformation for both grains, the elastic energy difference becomes easily accessible and by testing various strain states applied to the simulation box, strain states can be identified that lead to an elastic DF.

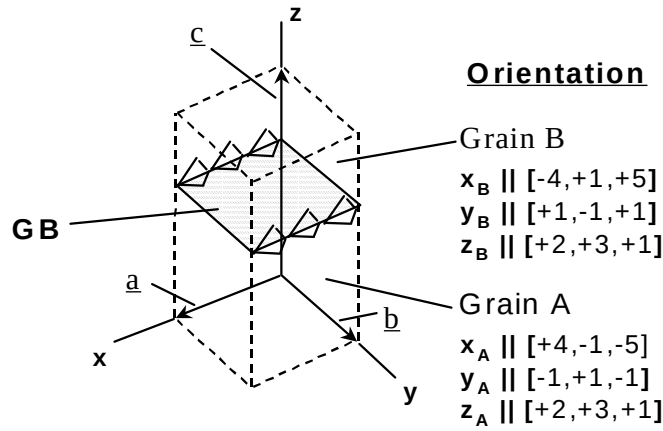


Figure 6.27: $\Sigma 7$ $[\bar{1}\bar{1}1]$ 38.21° symmetrical tilt GB. The figure shows a 3d schematic of the simulation box and supplies additional information on the crystallography of each grain with respect to the MD box coordinate system (x,y,z).

According to the above-mentioned scheme the rotation matrices of each grain for the $\Sigma 7$ $[\bar{1}\bar{1}1]$ 38.21° symmetrical tilt GB with respect to the used MD box coordinate system (x,y,z) are simply determined by the crystallographic vectors as listed in Fig. 6.27. By transforming the strain tensor or the stress tensor applied to the simulation box into the principal cubic crystal coordinate system of each grain we can now calculate the elastic energy stored in each grain by any box deformation. In the case of the symmetrical $\Sigma 7$ $[\bar{1}\bar{1}1]$ tilt GB when choosing a model strain tensor such as $\epsilon_{\Sigma 7}$ as given below the elastic DF, p_{ela} , can be calculated in the linear elastic regime by the above procedure and for the chosen $\epsilon_{\Sigma 7}$ this then reads

$$\epsilon_{\Sigma 7} = \begin{pmatrix} 0 & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & 0 & 0 \\ \epsilon_{xz} & 0 & 0 \end{pmatrix} \rightarrow p_{ela} = (2C_{4444} - C_{1111} + C_{1122}) \cdot \epsilon_{xy} \cdot \epsilon_{xz} \cdot 1.58712 \quad (6.12)$$

where C_{ijkl} are the cubic elastic constants. According to Eq. 6.12 one realizes that here the strain component ϵ_{xz} is essential in order to obtain a non-zero elastic DF. Referring to the results of the $\Sigma 5$ $[001]$ 53.13° tilt GB already this result of the elastic DF indicates that continuous GB migration can not be studied by such an elastic DF approach. Indeed numerous performed simulations on the $\Sigma 7$ $[\bar{1}\bar{1}1]$ 38.21° symmetrical tilt GB in the presence

of the given strain tensor of Eq. 6.12 for different magnitudes of strain and temperatures were not able to lead to continuous GB migration. Without the results of the $\Sigma 5$ [001] 53.13° tilt GB such findings would be rather confusing since for the $\Sigma 7$ tilt GB the elastic DF can be verified easily by the IQS at i.e. zero Kelvin or low temperatures. As has been explained already the key to understand these results is connected to the distinct form of the strain tensor, namely that ϵ_{xz} needs to be non-zero. The final conclusion therefore is again that any strain state that relies on strain components ϵ_{xz} and/or ϵ_{yz} will not be able to drive GBs continuously due to the occurrence of GB glide events that will transform the elastic strain components into plastic strain components which therefore leads to a disappearance of the initial elastic DF.

6.3.2 External Shear Stress States

In the following sections, results of atomistic simulations on the effect of external shear stress states on the finite temperature behaviour of a low-angle and a high-angle tilt GB are presented. Here the underlying concept to be utilized to initiate GB migration is the Peach-Koehler DF concept. Some aspects of the simulation results to be presented were already presented and published during the ReX99 international conference in Tsukuba Science city in Japan held in 1999 [82].

6.3.2.1 $\Sigma 73$ $[\bar{1}\bar{1}1]$ 11.64°

In sect. 6.1.2 it was shown that the $\Sigma 73$ tilt GB consists of an arrangement of discrete edge dislocations. Therefore the $\Sigma 73$ GB can act as a model system to study GB migration due to a Peach-Koehler DF. What fundamental insight on GB migration can be gained from such a study? Of course it is well known that low-angle GBs can be driven by external shear stress states, nevertheless it is interesting to verify some well-known results within atomistic simulations of planar GBs to gain further insight into several aspects. Computationalwise these are the atomic-level migration mechanism as well as the activation parameters for GB migration. Furthermore it is interesting to see how these results compare to the known experimental data on low-angle GB migration. This is especially true since low-angle GBs are well understood in terms of discrete dislocations and the obtained results might help to identify similarities and differences between GB migration of low-angle and high-angle tilt GBs. Therefore it makes sense to study the GB migration behaviour of a low-angle tilt GB in order to obtain reference data and intuition on GB migration that can even be later on used to rationalize some results found for high-angle tilt GBs. From a computational point of view these simulations can even underline the capabilities of the applied simulation method in order to study GBs in the presence of external stress states.

For the $\Sigma 73$ tilt GB a Peach-Koehler DF on GB_1 and GB_2 can be achieved as follows. According to the simulation box geometry sketched in Fig. 6.6(b) a pure xz external stress state, $\underline{\sigma}_{xz}$, will result in a Peach-Koehler force, $\mathbf{F}_{Disl.}^{GB1}$, on i.e. each GB dislocation of GB_1 according to

$$\begin{aligned}
 \frac{\mathbf{F}_{Disl.}^{GB1}}{L} &= \left(b \cdot \begin{pmatrix} 0 & 0 & \sigma_{xz} \\ 0 & 0 & 0 \\ \sigma_{xz} & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} -\sin(\frac{\Psi}{2}) \\ 0 \\ \cos(\frac{\Psi}{2}) \end{pmatrix} \right) \otimes \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix} \\
 &= b \cdot \sigma_{xz} \begin{pmatrix} \cos(\frac{\Psi}{2}) \\ 0 \\ -\sin(\frac{\Psi}{2}) \end{pmatrix} \otimes \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix} = b \cdot \sigma_{xz} \begin{pmatrix} \sin(\frac{\Psi}{2}) \\ 0 \\ -\cos(\frac{\Psi}{2}) \end{pmatrix} \\
 &= b \cdot \sigma_{xz} \begin{pmatrix} 0.1014 \\ 0 \\ -0.9948 \end{pmatrix} = -\frac{\mathbf{F}_{Disl.}^{GB2}}{L}
 \end{aligned} \tag{6.13}$$

The result for any GB dislocation of GB_2 is easily obtained from the result of GB_1 and is already given in Eq. 6.13 as well. The result is easily found since the GB dislocations of GB_2 are antiparallel to the ones of GB_1 . Thus within the calculus only a minus sign needs to be introduced either for the line vector or the Burgers vector of the GB dislocations of GB_2 with respect to the given data of the GB_1 dislocations.

To summarize the results one finds that a negative pure external xz shear stress state will drive the GB dislocations of GB_1 in the positive z direction of the simulation box while the GB dislocations of GB_2 will be driven in the negative z direction. A positive external pure external xz shear stress state will do the opposite, namely drive GB dislocations of GB_1 in the negative z direction while the GB dislocations of GB_2 will be driven in the positive z direction. A Peach-Koehler DF can now be obtained by considering Eq. 6.13 and the density of GB dislocations, $\rho_{\Sigma 73}$, within the GB structure. The density of the GB dislocations is simply given by $1/D_{\Sigma 73}$ where $D_{\Sigma 73}$ is the dislocation spacing as given by Eq. 6.1 in sect. 6.1.2. One finally gets for the Peach-Koehler DF, p_{PK}^{GB1} , on GB_1 and p_{PK}^{GB2} on GB_2

$$p_{PK}^{GB1} = \frac{b \cdot \sigma_{xz}}{D_{\Sigma 73}} \begin{pmatrix} \sin(\frac{\Psi_{\Sigma 73}}{2}) \\ 0 \\ -\cos(\frac{\Psi_{\Sigma 73}}{2}) \end{pmatrix} = -p_{PK}^{GB2} \quad (6.14)$$

After dealing with the issue of the existence of a Peach-Koehler DF for the $\Sigma 73$ low-angle tilt GB, now the results obtained when applying distinct pure xz shear stresses to the $\Sigma 73$ GB system are reported. The results were obtained for the 3d LJ potential and utilizing a 3d periodic border concept. As has been mentioned already in sect. 6.1.2 the 3d periodic border concept was the only border concept successfully utilized when dealing with external stress states applied to the simulation box since any of the mentioned 2d periodic border concepts failed to give a stable time evolution of the simulation box which usually resulted in a crash of the simulation runs after a few tenthousand time steps after introducing the full external stress states to the simulation box.

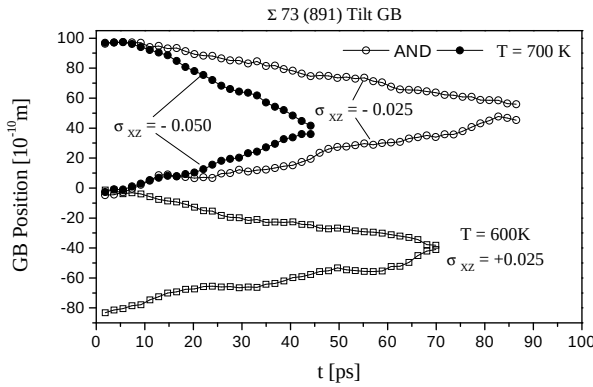


Figure 6.28: Plot of the GB position of the $\Sigma 73$ GB versus time at 600K and 700K in the presence of a Peach-Koehler DF.

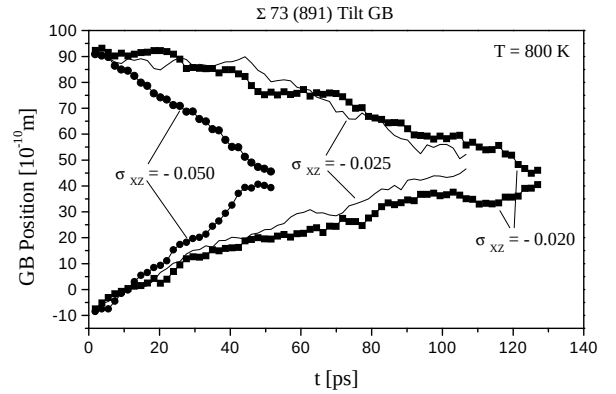


Figure 6.29: Plot of the GB position of the $\Sigma 73$ GB versus time at 800K in the presence of a Peach-Koehler DF.

Fig. 6.28 up to 6.31 show the results of the GB position versus time for different temperatures and xz shear stresses. The change of GB position with time is fitted well by a linear relationship which therefore allows the GB velocity to be determined quite easily from these plots. The 600K data are used here to demonstrate that a change in the stress direction leads to a change of GB migration as well. It should be stressed at this point that the GBs move in all cases in the direction of the Peach-Koehler DF. It can be concluded that indeed the GBs behave according to the Peach-Koehler description. To plot the GB velocity data versus the Peach-Koehler DF, the DF needs to be calculated for a given σ_{xz} . Note here that the σ_{xz} is given in units of 3.38 GPa which equals eV/a_o^3 for Cu. Here only the z component

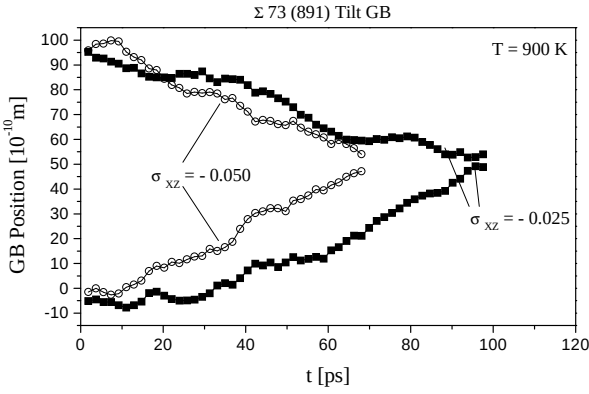


Figure 6.30: Plot of the GB position of the $\Sigma 73$ GB versus time at 900K in the presence of a Peach-Koehler DF.

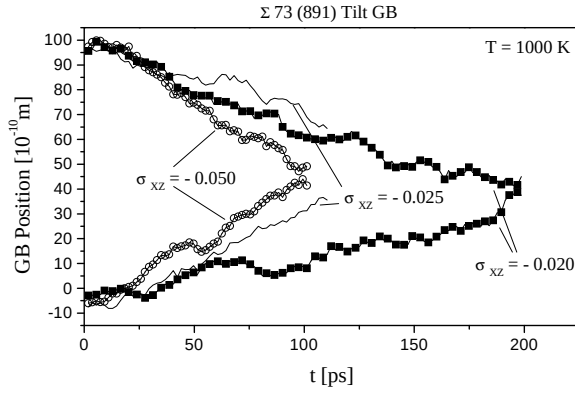


Figure 6.31: Plot of the GB position of the $\Sigma 73$ GB versus time at 1000K in the presence of a Peach-Koehler DF.

of Eq. 6.14 needs to be considered since only the z component of the Peach-Koehler DF drives the GB along its normal direction. One finds

$$p_{PK,z}^{GB1} = -2 \cdot \sigma_{xz} \cdot \sin\left(\frac{\Psi_{\Sigma 73}}{2}\right) \cdot \cos\left(\frac{\Psi_{\Sigma 73}}{2}\right) = -0.201745 \cdot \sigma_{xz} [3.38 \text{ GPa}] = -p_{PK,z}^{GB2}. \quad (6.15)$$

All conducted simulations in the presence of external pure xz shear stresses were conducted

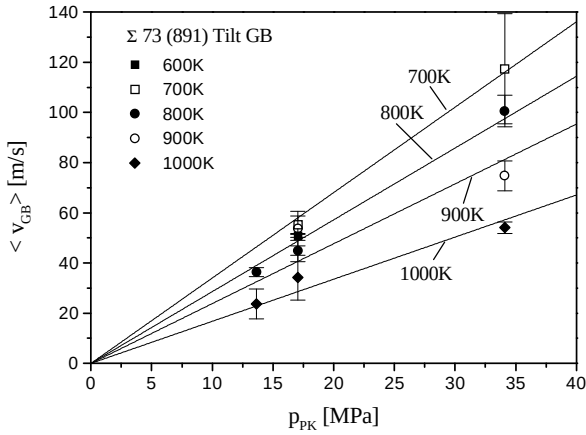


Figure 6.32: Plot of the average GB velocity, $\langle v_{GB} \rangle$, of the $\Sigma 73$ GB versus the Peach-Koehler DF for various temperatures. $\langle v_{GB} \rangle$ was averaged over the individual results of GB_1 and GB_2 . For all temperatures a linear data fit represents the results well which determines the GB mobility, m_{GB} , as being the slope of the linear best data fit.

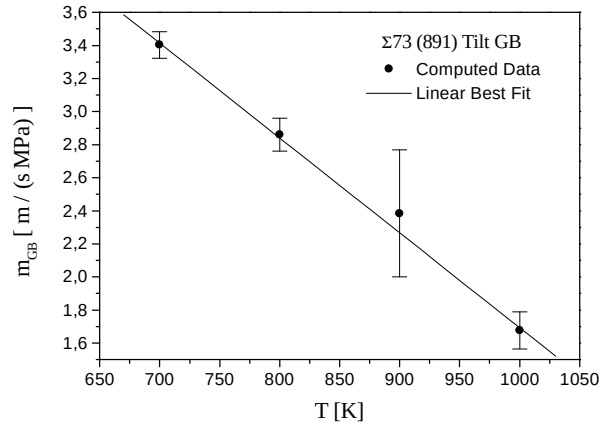


Figure 6.33: Plot of the GB mobility of the $\Sigma 73$ GB versus temperature, T . Interestingly the mobility decreases linear with T which could refer to a weakening of the coupling of the external stress state to the GB structure with increasing T .

under the condition that all nine components of the simulation box, $\underline{h}$, were allowed to adjust according to the equations of motion following the full Parrinello-Rahman scheme. Even that all nine components were allowed to vary only components related to the xz shear stress increased linearly with time while GB migration and GB glide occurred. The other

ones remained constant and only fluctuated or increased scarcely demonstrating the stability of the box evolution in the stressed situation. Fig. 6.34 presents the profiles of the temporal evolution of the xz strain tensor component at different temperatures and different stresses underlining the stated box behaviour. Here the reader should note that the simulation box was only allowed to deform according to symmetric strain tensors. This was enforced as follows. After each time step the rotation tensor was calculated in a linear approximation and its contribution to the box evolution was eliminated by subtracting the negative rotation tensor applied to the initial box geometry from the instantaneous one. According to this scheme the simulation box only deformed according to true symmetric strain tensors. This becomes an important aspect when discussing the details of the processes occurring during GB migration of the $\Sigma 73$ GB. After the two GBs had annihilated and the system became an

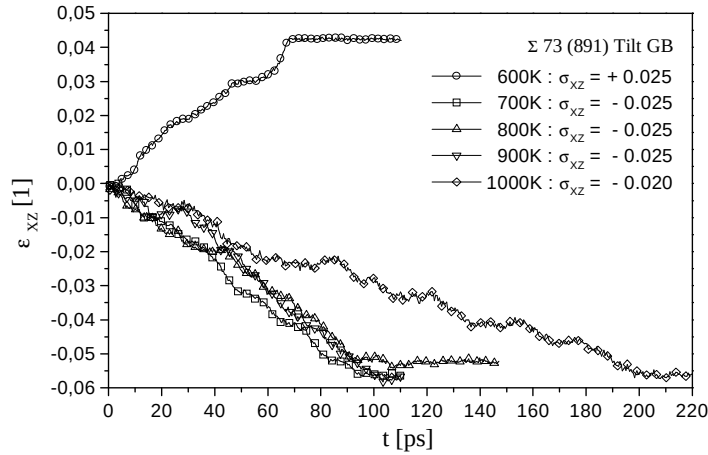


Figure 6.34: Plot of the time evolution of the strain component ϵ_{xz} at different temperatures and different external stress states for the $\Sigma 73$ tilt GB. Once GB migration ceases, so does the accumulation of the xz shear strain.

ideal crystal, the accumulation of the xz strain component ceased too. Here the accumulation of strain needs to be understood in terms of plastic deformation of the system connected to occurring GB glide which is discussed in detail on the following pages. According to Fig. 6.34 the maximum xz shear for the case that GB₁ moves up and GB₂ down is about -0.058 while for the opposite case namely that GB₁ moves down and GB₂ up it is about +0.045. The difference of these two results is explained by the fact that the separation of the two GBs is not equal for both szenarios. It is less for the second case resulting in less xz shear strain accumulation due to the shorter overall migration distance (see for instance Fig. 6.35).

If now one turns the attention to the temperature dependence of the GB mobility shown in Fig. 6.33, the figure states that the mobility is linearly decreasing with increasing temperature. This is rather unusual considering that usually the GB mobility follows an Arrhenius relationship. As is demonstrated in detail below the structure of this GB is linked to discrete edge dislocations that migrate in a cooperative manner by glide events along a $[110]$ direction on $(1\bar{1}2)$ lattice planes. This suggests that the activation enthalpy is rather small, maybe even almost zero. Therefore one expects the GB mobility to be only a weak function on temperature either increasing slightly with temperature or remaining constant. In order to obtain further insight into this unexpected result of the temperature dependence of the

GB mobility of the Σ 73 GB, a closer look at the behaviour of the discrete GB dislocations at different temperatures is necessary.

Now at first the 600K situation is discussed. To illustrate the atomic-level situation, Fig. 6.35 up to 6.38 show the atomistics during the migration process at low temperatures and positive external xz shear stresses. Here only true fcc atoms identified according to the CNA scheme by having 12 (421) bond pairs and the position of the core centers of the discrete GB dislocations are plotted. Here the center of each GB dislocation core was determined by identifying all non-fcc atoms in the vicinity of each dislocation through a sorting procedure utilizing two sets of histograms to map the x-z position of each atom. Once all non-fcc atoms were attributed to each dislocation, the center of mass (CoM) for each dislocation was calculated within the x-z plane in order to locate and track the position of each GB dislocation core within the x-z plane. Already applying such a simple selection rule to identify only two classes of atoms allows one to describe the spatial and temporal evolution of each GB dislocation within the x-z plane and even proves the existence of separate individual GB dislocations as being the main element generating the GB structure. This aspect was already pointed out when discussing the geometry of this GB, but it again shows the capabilities of the CNA scheme to study and identify the key elements within important materials science processes like GB migration. It should be stressed here that even at a 1000K discrete GB dislocations were present at the GBs showing that the Σ 73 GB maintained its dislocation character for the whole temperature range studied. Another important aspect

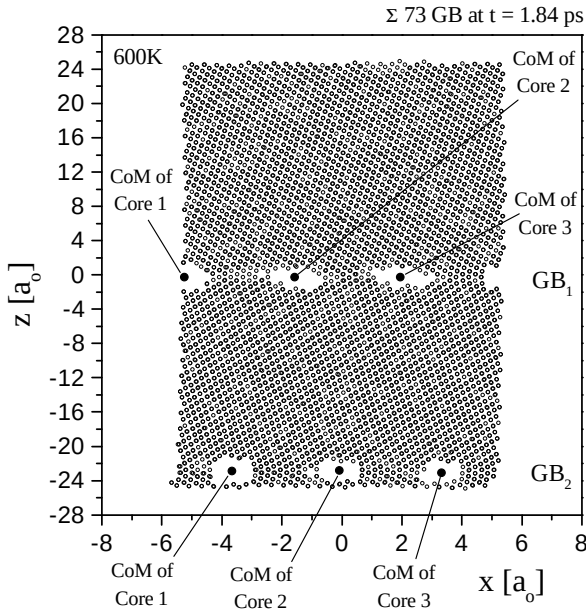


Figure 6.35: Initial situation of the Σ 73 GB system at $t=1.84\text{ps}$, 600K and an external pure shear stress of $\sigma_{XZ} = +0.025$. Each GB consists of three discrete GB dislocations where the CoM of each GB dislocation is given by the filled circle.

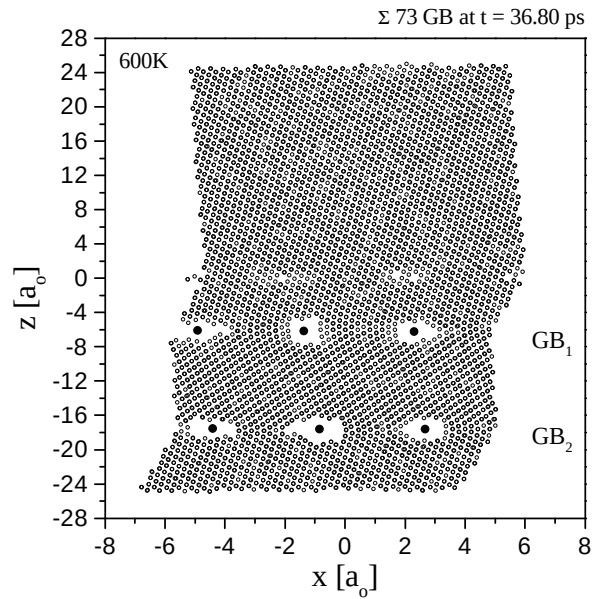


Figure 6.36: Situation at $t=36.8\text{ps}$. The discrete dislocation cores are moving in the directions given by the Peach-Koehler DF. Already the characteristic change of shape of the grains at the GBs appears indicating that GB glide events occur at the GBs.

concerning this GB is that in the regions between the dislocation cores the lattice remains continuous meaning that the change of the crystal orientation from one lattice to the other

one is achieved by a bending of the $(1\bar{1}\bar{2})$ lattice planes rather than by an abrupt change of the crystal orientation usually found for high-angle GBs.

Fig. 6.35 up to 6.38 show that indeed the GBs move as discrete GB dislocations in the direction given by the Peach-Koehler DF. The four given figures show the initial situation up to the final moments before the two GBs annihilate. This plotted data corresponds with the data shown in Fig. 6.28. Two important aspects are to be noted in the figures. The first one relates to the characteristic change of shape of the grains at the GBs resulting from glide events at the GBs. The second aspect is that the two grains do rotate in one direction by inner grain rotations. These are really inner grain rotations since according to the abovegiven description, the simulation box was only allowed to deform following a symmetric strain tensor. Here the reader should note that due to the different used scales for the x and z axis, the magnitude of GB glide as well as grain rotation is appearing to be much stronger than it actually is. Again it should be underlined here that all plotted atomistic data represents three-dimensional data meaning that the system is viewed along the $[1\bar{1}1]$ tilt axis through a fully 3d system. It is remarkable that such a simple and crude data plot shows the structure at the GB well enough, since usually 3d plots become rather difficult to interpret due to the overlapping of the atomistics of individual crystallographic planes. According to this one could suggest that the system is intrinsically two-dimensional, nevertheless a lot of findings in this work indicate that the third dimension along the tilt axis is of very importance due to diffusive jump events and translational GB states according along this direction.

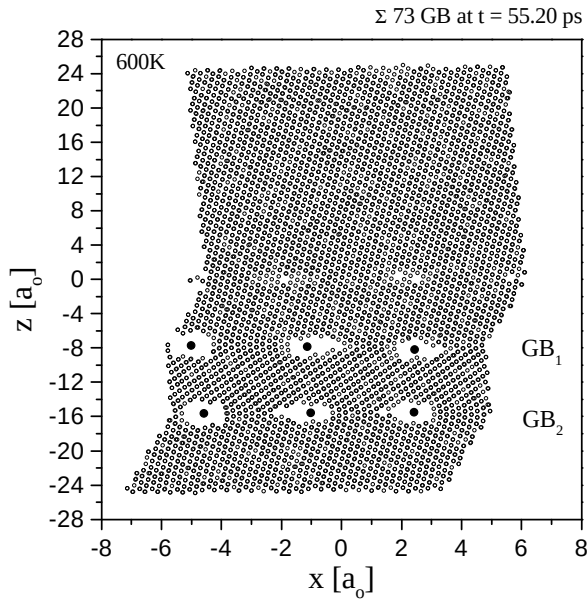


Figure 6.37: Situation at $t=55.2\text{ps}$. The discrete dislocation cores are still intact and already a slight rotation of the two grains can be detected.

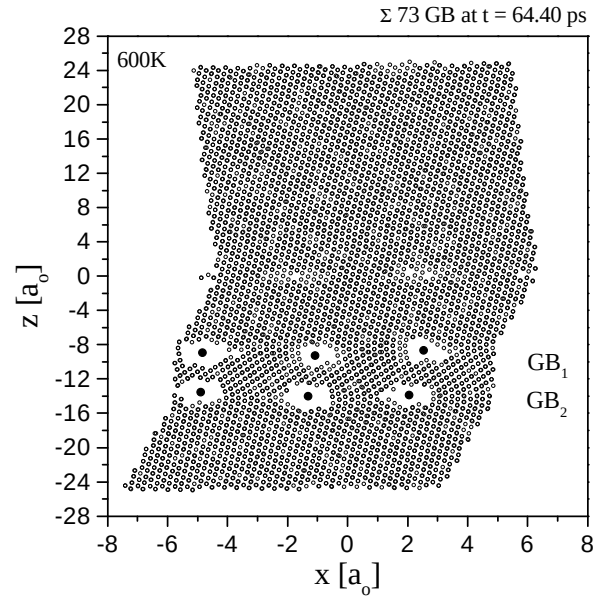


Figure 6.38: Situation at $t=64.4\text{ps}$. Final situation just before the two GBs annihilate and the shrinking grain finally disappears. Interestingly even now the six GB dislocation cores remain intact.

Since the GB dislocation cores can be located well the temporal evolution of each dislocation core as well as the trajectory of each core within the x-z plane were determined. Here Fig. 6.39 shows for the 600K simulation that the distance-time profile of each dislocation

core follows the general temporal evolution of the GB very well. Of course this result is trivial since the stacked dislocation cores generate the GB. The deviation of each core from the average position of the GB might hint at the atomistic processes occurring within the moving GB. Therefore a very interesting aspect of such an analysis is to investigate what coupling between each core during the event of GB migration exists. Since here only limited data on this issue was available and the general features of the migration process were detectable even by simple data analysis, no distinct analysis of the coupling between the cores was performed. Nevertheless the existing data already shows that each core seems to vibrate at a certain frequency and their spatial order concerning the z direction changes by some periodic function as well. The trajectories of the six dislocation cores within the x - z

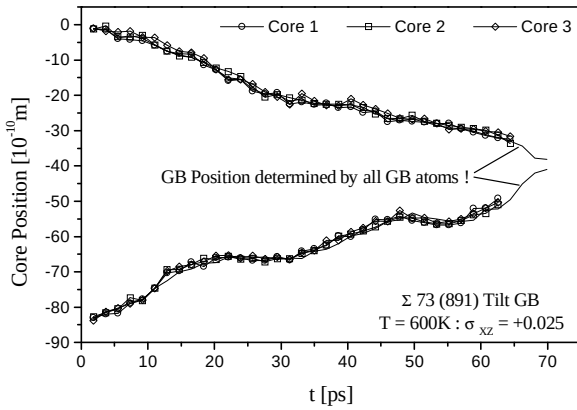


Figure 6.39: Comparison of the z position of each GB dislocation core with the temporal evolution of the two GBs. The general features of the distance-time behaviour are represented by all profiles. The plots as well indicate some form of possible coupling between the cores of each GB.

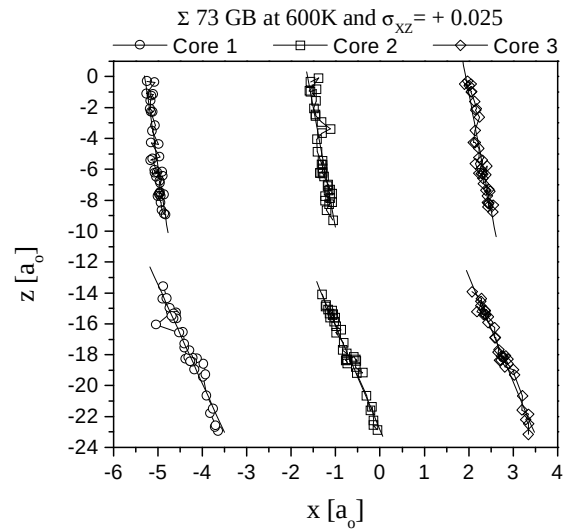


Figure 6.40: Trajectories of the six dislocations cores within the x - z plane of the $\Sigma 73$ GB system at 600K and $\sigma_{xz} = + 0.025$.

plane for the 600K simulation are given by Fig. 6.40. The plot reveals that the spacing of the dislocation cores remains constant throughout the simulation for each GB and that it agrees very well with the result of Eq. 6.1.

GB migration mechanism - To fully understand the processes occurring during GB migration the observation of GB glide events and a lattice rotation needs to be understood. Since the overall simulation box deforms according to a symmetric strain tensor, this external change of the box needs to be linked to internal processes taking place. Fig. 6.41 sums up the observations found for simulations performed in the presence of positive external xz shear stresses while Fig. 6.42 shows the key elements for simulations conducted in the presence of negative external xz shear stresses. It is once again important to state that the accumulation of xz strain is purely plastic and that it originates from GB sliding. The inner grain rotation is only a consequence of the restriction that the external strain tensor needs to be symmetric. According to this the external strain state can be explained by the internal process of GB sliding leading to simple xz shear, $\underline{\epsilon}_{sim}$, which is then accompanied by an inner grain rotation, $\underline{\omega}_{in}$. Therefore the external box strain state can be expressed by

the following equation in case of positive xz shear stresses, namely

$$\frac{1}{2} \begin{pmatrix} 0 & 0 & \epsilon_{xz} \\ 0 & 0 & 0 \\ \epsilon_{xz} & 0 & 0 \end{pmatrix}_{box} = \begin{pmatrix} 0 & 0 & \epsilon_{xz} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{sim} + \frac{1}{2} \begin{pmatrix} 0 & 0 & -\epsilon_{xz} \\ 0 & 0 & 0 \\ +\epsilon_{xz} & 0 & 0 \end{pmatrix}_{in} \quad (6.16)$$

while for negative external xz shear stresses it reads

$$\frac{1}{2} \begin{pmatrix} 0 & 0 & -\epsilon_{xz} \\ 0 & 0 & 0 \\ -\epsilon_{xz} & 0 & 0 \end{pmatrix}_{box} = \begin{pmatrix} 0 & 0 & -\epsilon_{xz} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{sim} + \frac{1}{2} \begin{pmatrix} 0 & 0 & +\epsilon_{xz} \\ 0 & 0 & 0 \\ -\epsilon_{xz} & 0 & 0 \end{pmatrix}_{in} \quad (6.17)$$

In order to demonstrate the underlying GB migration mechanism and according to the need of the simulation box to comply with the internal GB processes and the external boundary conditions, Fig. 6.41 and 6.42 summarize the fundamental processes occurring for positive and negative external xz shear stresses. An important feature found in the simulations is the occurrence of lattice rotations. Here the rotational sense is connected to the magnitude of the applied external xz shear stress. For negative xz shear stresses the rotation angles are negative while for positive xz shear stresses they are positive.

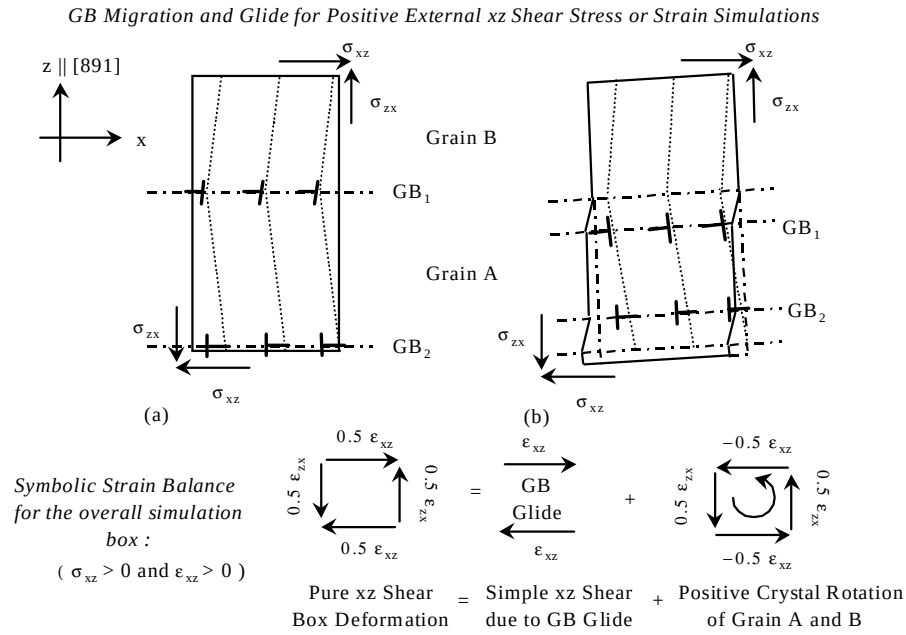


Figure 6.41: Schematic of the system's behaviour due to GB migration and GB glide events of the $\Sigma 73$ tilt GB for external positive pure xz shear stresses. (a) shows the initial situation while (b) presents the position of the GBs as well as the change of the shape of the grains at the GBs after a few consecutive migration events. A symbolic equation of the strain balance is given to show that the external found symmetric strain tensor corresponds to the internal processes of GB glide and inner grain rotation events.

Fig. 6.43 verifies and quantifies the observed rotation angle at 800K and $\sigma_{xz} = -0.020$. For this case the rotation angle was found to be about -3° . Obviously the magnitude of the rotation angle will depend on the occurring GB glide events during the GB migration simulations.

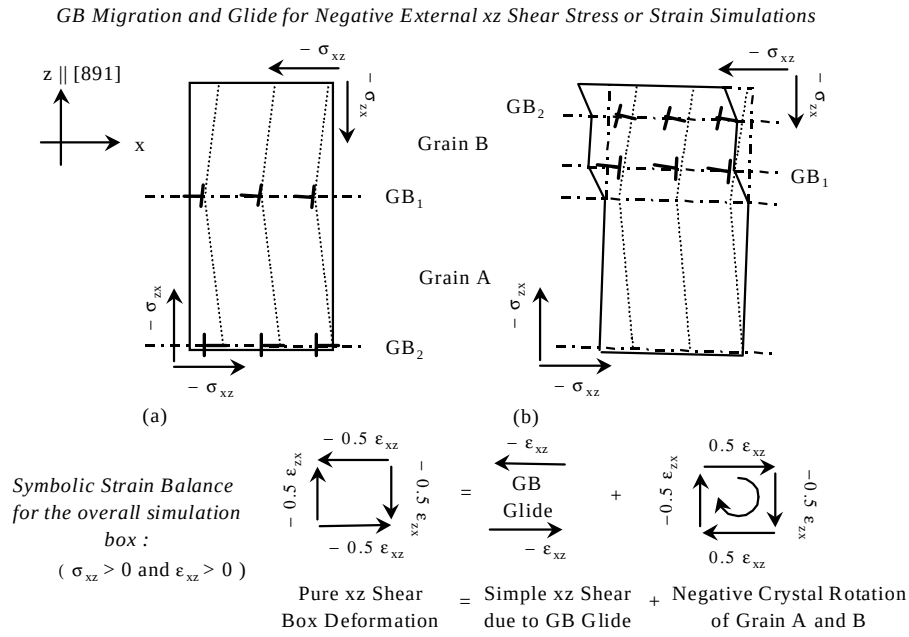


Figure 6.42: Schematic of the system's behaviour due to GB migration and GB glide events of the $\Sigma 73$ Tilt GB for external negative pure xz shear stresses. For further information on the details see caption of Fig. 6.41 and the text.

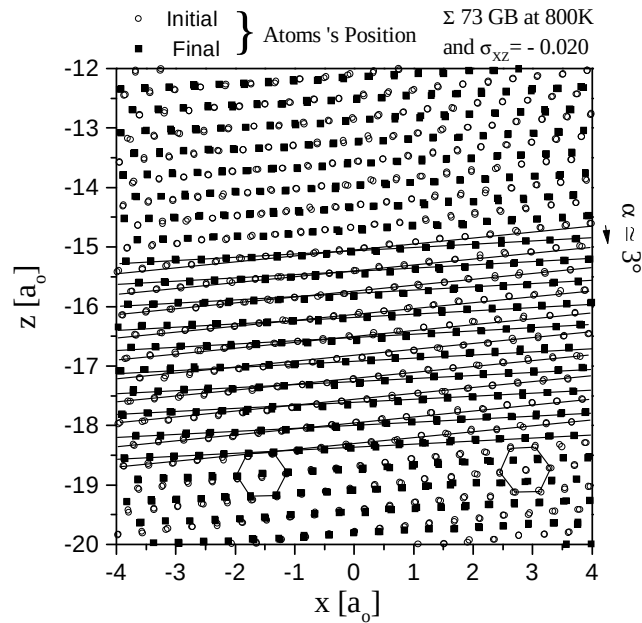


Figure 6.43: Verification and quantification of the crystal rotation after GB migration is completed.

Finally Fig. 6.44 and 6.45 demonstrate that the discrete GB dislocation character of the $\Sigma 73$ tilt GB prevails throughout the studied temperature range. Hence the spatial and temporal evolution of the GB dislocation cores can be followed throughout the simulations. This again underlines that GB migration of this low-angle tilt GB is thermally non-activated. As well the figures indicate that grain rotations occur. This is best seen from the temporal

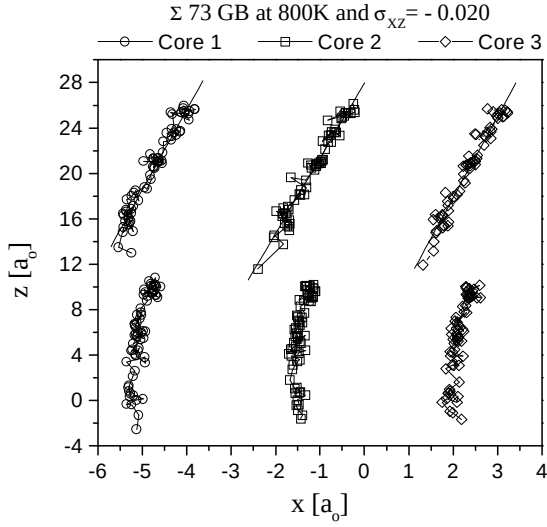


Figure 6.44: Trajectories of the six dislocations cores within the x-z plane of the $\Sigma 73$ GB system at 800K and $\sigma_{xz} = -0.020$.

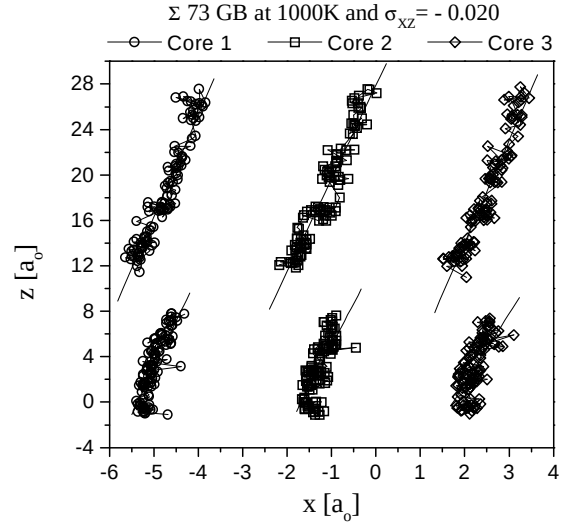


Figure 6.45: Trajectories of the six dislocations cores within the x-z plane of the $\Sigma 73$ GB system at 1000K and $\sigma_{xz} = -0.020$.

evolution of the GB dislocation core displacements of the center GB. These profiles are not simply linear but curved. These found non-linear trajectories underline that during the migration of the GB dislocation cores, grain rotations must have taken place.

6.3.2.2 Σ 5 [001] 53.13°

In sect. 6.1.1, the GB structure of the Σ 5 [001] 53.13° ([210] 180°) tilt GB was presented. One key result of the discussion was that the GB does not consist of discrete GB dislocations but rather is identified by a structure where the GB dislocation cores overlap and the GB is formed by a layer of non-ideal fcc atoms of width of five (210) planes.

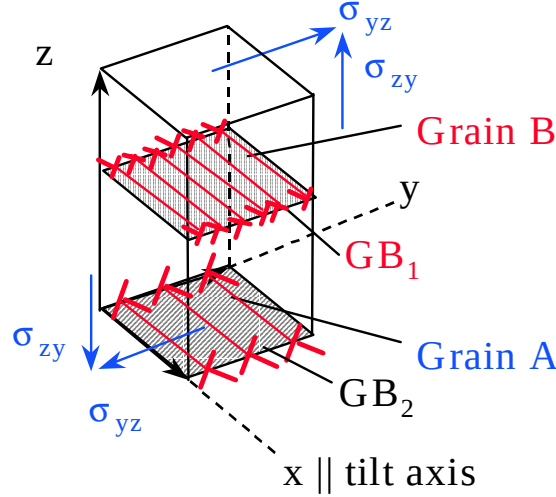


Figure 6.46: Schematic of the Σ 5 [001] 53.13° symmetrical tilt GB simulation box illustrating some GB dislocations and the externally applied pure yz shear stress state. For GB₁ both types of GB dislocations are sketched while for GB₂ only one type is shown.

Although the option to drive the Σ 5 tilt GB by a Peach-Koehler DF does not really exist due to the missing discrete GB dislocations, first the standard calculus based on an idealized GB dislocation pattern can be performed in order to derive the basic Peach-Koehler force equations. Later it will be stressed that the used yz shear stress states really initiate GB sliding which is coupled by GB migration. In this discussion it helps to know that a Peach-Koehler DF would have driven the GBs in opposite directions as found in the simulations. The direction of GB migration of the Σ 5 (210) tilt GB can only be understood in terms of GB sliding accompanied by GB migration.

According to the simulation box geometry sketched in Fig. 6.1 and 6.46, a pure yz external stress state, $\underline{\sigma}_{yz}$, will result in a Peach-Koehler force, $\mathbf{F}_{Disl.}^{GB1}$, for the two sets of GB dislocation of GB₁ according to

$$\begin{aligned}
 \frac{\mathbf{F}_{Disl.}^{GB1}}{L} &= \left(b \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sigma_{yz} \\ 0 & \sigma_{yz} & 0 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ \pm \sin(\frac{\Psi}{2}) \\ \cos(\frac{\Psi}{2}) \end{pmatrix} \right) \otimes \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\
 &= b \cdot \sigma_{yz} \begin{pmatrix} 0 \\ \cos(\frac{\Psi}{2}) \\ \pm \sin(\frac{\Psi}{2}) \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = b \cdot \sigma_{yz} \begin{pmatrix} 0 \\ \pm \sin(\frac{\Psi}{2}) \\ -\cos(\frac{\Psi}{2}) \end{pmatrix} \\
 &= b \cdot \sigma_{yz} \begin{pmatrix} 0 \\ \pm 0.4472 \\ -0.8944 \end{pmatrix} = -\frac{\mathbf{F}_{Disl.}^{GB2}}{L}
 \end{aligned} \tag{6.18}$$

Here it should be noted that the $\pm$ sign of the y component of the Peach-Koehler force relates to the two sets of GB dislocations forming one GB, i.e. GB₁. The GB dislocation originating from grain B is having the positive sign while the one originating from grain A is having the negative one. The z component of the Peach-Koehler force points for both sets of GB dislocations in the same direction.

The result for any GB dislocation of GB₂ is easily obtained from the result of GB₁ and is already given in Eq. 6.18. The result is easily found since the GB dislocations of GB₂ are antiparallel to the ones of GB₁. Thus within the calculus only a minus sign needs to be introduced either for the line vector or the Burgers vector of the GB dislocations of GB₂ with respect to the given data of the GB₁ dislocations.

At this point one important aspect has to be pointed out and underlined. According to common belief, no Peach-Koehler interaction is expected for the $\Sigma 5$ (210) tilt GB. If so, still the yz pure shear stress state can initiate GB sliding where the direction of sliding coincides with the direction of the y-component of the Peach-Koehler force. It should be stressed that GB sliding can occur without any form of Peach-Koehler DF simply on the grounds that the yz pure stress state can move grain A with respect to grain B assuming that the GB can overcome the potential barrier for GB sliding thermally. So the final conclusion drawn from the Peach-Koehler discussion is that GB sliding is expected to occur only due to the yz pure shear stresses without any interaction between GB dislocations and external stress field. As known from literature, it is expected that at low temperatures where the GB keeps a crystalline GB structure [72], GB sliding coupled with GB migration will occur [14, 15].

GB sliding and migration due to an external yz pure shear stress state - After introducing the basic concepts that can explain why for the $\Sigma 5$ (210) tilt GB, GB sliding might occur, now the found simulation results are presented. The studied GB system consisted of 100 (210) planes where initially 60 (210) planes belonged to the lower grain and 40 (210) planes to the upper grain. Eight (001) planes were stacked in x-direction and the overall number of atoms was 4800. The relaxed GB energy is 0.974 J/m² for the LJ potential and applying 3d periodic BC to the simulation box. The interatomic distance between (210) planes is 0.2236068 a_o. The simulations were performed utilizing the full Rahman-Parrinello concept allowing all nine box variables to adjust to the internal-external stress balance. Here all nine box variables were used since the box evolution is not simply given by a pure yz shear. Since inner grain rotations were observed during these simulations, at least the strain components ϵ_{yy} and ϵ_{zz} needed to be included as adjustable box variables. With respect to the Rahman-Parrinello concept it was reasonable to apply 3d periodic BC to the simulation box in order to ensure that the box variable equations of motion remain stable when external stress states were applied. For simulations with 2d periodic BC and either free surfaces or pseudo free surfaces the stability of the box variable equations of motion where quite unstable and often led to crashing of the simulation runs. Finally the Nose-Hoover thermostat was applied to perform finite temperature simulations. Fig.6.47 presents profiles of the GB positions versus time for different yz pure shear stresses. Tab. 6.2 contains information on the simulation conditions for each shown profile.

The simulation results reveal a few interesting facts. First of all, continuous GB migration of GB₁ and GB₂ in the presence of non-zero yz pure shear stress states is found. Interestingly the direction of migration is opposite to the direction associated with the Peach-Koehler analysis. For instance for negative yz pure shear stress, GB₁ moves downwards which is clearly in contradiction to Eq. 6.18. Hence the only conclusion drawn from the data

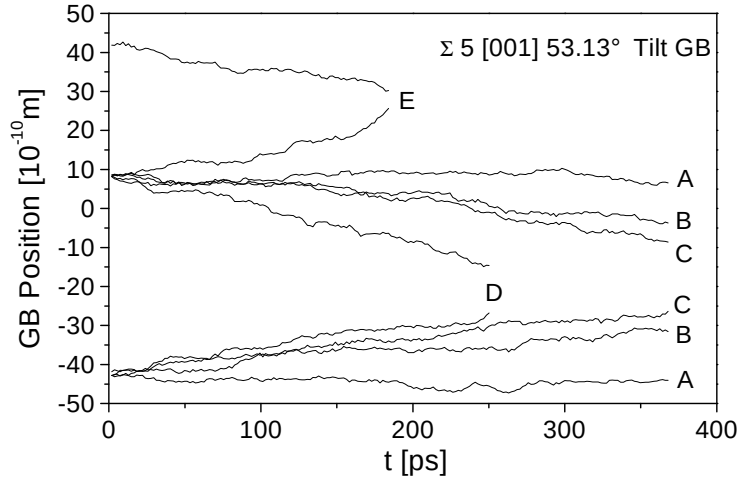


Figure 6.47: $\Sigma 5$ (210) symmetrical tilt GB. GB position versus time plots for different yz pure shear stresses. Tab. 6.2 contains information on the simulation conditions for each shown profile. For run D and E, the GBs did annihilate during the cause of the simulations and left behind an ideal crystal.

must be that the occurring GB migration is linked to a different source which is GB sliding of the $\Sigma 5$ (210) tilt GB. As Fig. 6.47 and Tab. 6.2 show that only a limited number of

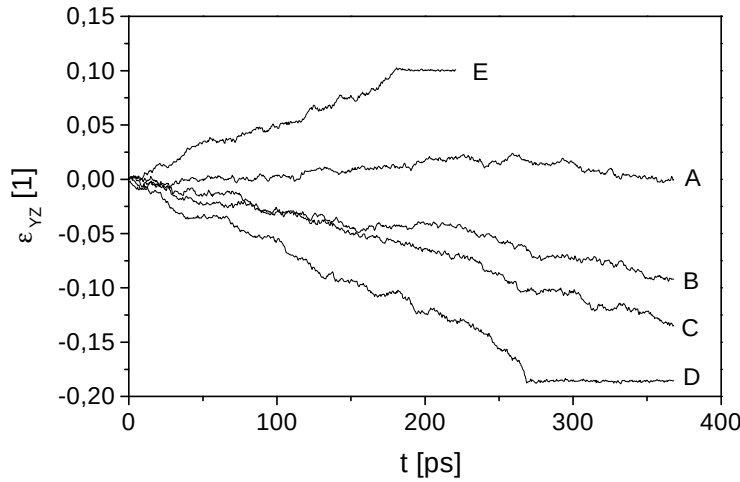


Figure 6.48: $\Sigma 5$ (210) symmetrical tilt GB - Strain build-up of the strain component ϵ_{yz} during GB sliding coupled with GB migration.

simulations in the presence of yz pure shear stress states were performed. These simulations were intended to demonstrate that indeed an application of yz shear stresses results in GB sliding accompanied by GB migration. Changing the stress sign (see run E in Fig. 6.47 and 6.48) leads to GB sliding and migration into the opposite direction. Furthermore run E and D reveal that once the GBs have annihilated and only a single ideal crystal is left behind, the accumulation of yz shear strain ceases. This identifies that the accumulation of yz shear stress is related to the occurring GB processes predominately GB sliding. Furthermore the results show that higher shear stress levels lead to faster GB migration and sliding.

No extended simulations at different yz shear stress levels and various temperatures were

T [K]	σ_{yz} [3.38GPa]	Given label	$\langle v_{GB} \rangle$ [m/s]
800	+0.00	A	0.0
800	-0.02	B	2.7
900	-0.02	C	4.6
800	-0.03	D	7.9
800	+0.02	E	5.5

Table 6.2: Information on stress level and GB velocity of performed yz pure shear stress simulations of $\Sigma 5$ (210) symmetrical tilt GB.

performed, since the DF for GB migration is difficult to assess from these simulations. Hence to perform the standard analysis to determine the GB velocity versus DF at different temperatures to yield the temperature dependence of GB mobility was not feasible. This is clearly different from the situation of the $\Sigma 73$ (891) tilt GB, where a Peach-Koehler DF can drive the discrete GB dislocations and therefore a DF was obtainable from the simulations. Still the simulations are suitable to reveal the coupling of GB sliding and migration as is discussed in the following paragraph.

GB sliding and migration mechanism - Now the details of the coupling between GB sliding and GB migration of the $\Sigma 5$ [001] 53.13° tilt GB will be presented. The analysis is following the often used approach within this work to extract only data of one specific crystallographic plane from the 3d data, here a (002) plane containing atoms of both grains. This in-plane analysis helps to understand how atoms within a single (002) plane move during GB sliding and migration. Furthermore atoms coming from neighbouring planes can be identified very easily as well. In order to gain microscopic information on the movement of each atom within a (002) plane, the following analysis scheme was used. The initial position of each atom within a (002) plane is identified by an up-triangle, the instantaneous position by a circle. The initial and instantaneous positions are connected by a line to reveal the displacement of each atom. If an atom leaves the plane only its initial position remains in the plot being now no longer connected by a line to any instantaneous position. If an atom enters the plane only its instantaneous position is plotted by a circle since its initial position is in a neighbouring (002) plane. This analysis scheme makes sure that atoms leaving and entering the plane can be identified. Furthermore the NN bond situation between atoms is analysed concerning its association with either grain A or B or non of the two grains.

Fig. 6.49 to 6.51 show one distinct example of GB sliding and migration of run B at 800K. The figures show a three stage process of GB sliding and migration in the vicinity of GB_1 . In stage I the initial situation before a GB glide and migration event occurs within a (002) plane is shown. Here the initial position of each atom is identified by an up-triangle, the instantaneous position by a circle. The kite structure at GB_1 is clearly visible. Following this in stage II the situation at GB_1 after one DSC glide and migration event is plotted. Here the upper grain B moved half a DSC vector to the left while the lower grain A shifted half a DSC vector to the right. In total the glide event is characterized by one DSC y vector. Very interesting is the change of the kite structure at GB_1 . The initial kites were not reproduced and a new kite structure has formed. At this stage no atom has left nor entered the plane from neighbouring planes, thus the whole displacement field of atoms is characterized by in-plane movements of atoms. Finally stage III shows the situation at GB_1

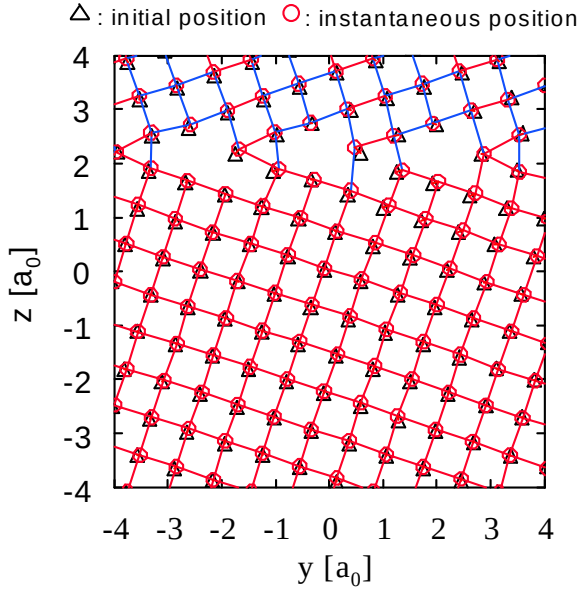


Figure 6.49: Stage I - Initial situation at GB_1 within one (002) plane. The initial position of each atom within a (002) plane is identified by an up-triangle, the instantaneous position by a circle. The kite structure at GB_1 is clearly visible and at this stage no GB sliding nor GB migration event has occurred. A more detailed explanation of the used symbols as well as lines within Fig. 6.49 to Fig. 6.51 is given in the text.

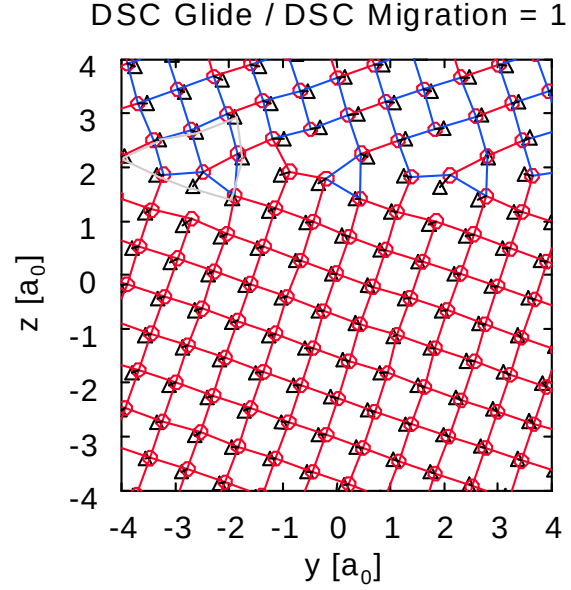


Figure 6.50: Stage II - Situation at GB_1 after one DSC glide and migration event. Here the upper grain B moved half a DSC vector to the left while the lower grain A shifted half a DSC vector to the right. In total the glide event is characterized by one DSC y vector. Very interesting is the change of the kite structure at GB_1 . The initial kites were not reproduced and a new kite structure has formed. At this stage no atom has left nor entered the plane from neighbouring planes.

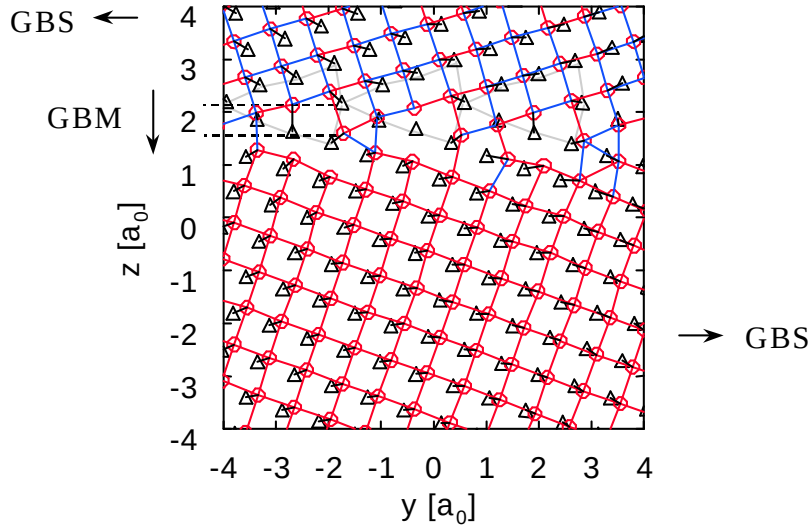


Figure 6.51: Stage III - Situation at GB_1 after two DSC glide and migration events. Here the upper grain B moved one DSC y vector to the left while the lower grain A shifted one DSC y vector to the right. It is interesting to note that the initial kite structure is now reproduced again. At least one atom has left the plane while one has come from a neighbouring plane.

after two DSC glide and migration events had occurred. Here the upper grain B moved one DSC y vector to the left while the lower grain A shifted one DSC y vector to the right. It is interesting to note that the initial kite structure is now reproduced again. At least one atom has left the plane while one has come from a neighbouring plane within the shown section of GB_1 as shown in Fig. 6.51. Analysing all simulation runs listed in Tab. 6.2 concerning the atomic-level displacement of atoms reveals that the GB sliding / migration mechanism is not solely an in-plane displacement process of atoms within each (002) plane but that jumps of atoms from and to neighbouring (002) planes are necessary to give the complete mechanism. This is an interesting observation since it raises the question whether or not the $\Sigma 5$ [001] 53.13° symmetrical tilt GB can even move continuously when GB glide events are explicitly suppressed by denying the simulation box to adjust to the internal-external stress balance. This would of course require a different sort of DF which has to be the orientation-correlated DF. In section 6.3.3.1 this aspect is studied by imposing the orientation-correlated DF to the $\Sigma 5$ [001] 53.13° GB and allowing the simulation box in different degrees of freedom to adjust to the stress state balance acting on the simulation box.

6.3.3 Orientation-correlated Driving Force

6.3.3.1 $\Sigma 5$ [001] 53.13°

Before the GB migration results due to the orientation-correlated DF are presented, first simulation results related to the finite temperature behaviour of the $\Sigma 5$ (210) symmetrical tilt GB are presented. All performed simulations presented and discussed in this section were obtained by MD simulations utilizing the Doyama EAM potential as well as applying 3d periodic boundary conditions. Guided by the experience obtained by the LJ external yz shear stress simulations, it was thought that the Doyama potential is suited better than the LJ to study the impact of different degrees of freedom of the simulation box in the presence of the orientation-correlated DF. Practically speaking the impact of different degrees of freedom of the simulation box on GB migration due to an orientation-correlated DF means that two sets of simulations were performed where different variables of the simulation box were allowed to adjust. In one set of simulations, only the h_{33} component of the simulation box matrix, $\underline{h}$, was allowed to adjust according to the internal and external stress balance. In the second set of simulations, the box components h_{22} , h_{23} , h_{32} and h_{33} were allowed to adjust. The underlying idea to differentiate between these simulations was to investigate the question whether or not the $\Sigma 5$ (210) symmetrical GB can only move continuously if GB migration is accompanied by GB sliding as was found from the yz shear stress state simulations.

The studied GB system consisted of 100 (210) planes where initially 60 (210) planes belonged to the lower grain and 40 (210) planes to the upper grain. Eight (002) planes were stacked in x -direction and the overall number of atoms was 4800. The relaxed GB energy is 0.899 J/m^2 for the Doyama EAM potential when applying 3d periodic BC to the simulation box. Finally the interatomic distance of (210) planes is $0.2236068 a_o$. Before discussing the GB migration results, first the GB self-diffusion situation of the $\Sigma 5$ (210) symmetrical GB is presented next.

GB self-diffusion - Finite temperature MD simulations were performed from 800K up to 1100K. Plots of the obtained GB position versus time profiles of the $\Sigma 5$ (210) symmetrical

tilt GB at different temperatures are shown in Fig. 6.52. The figure demonstrates that for

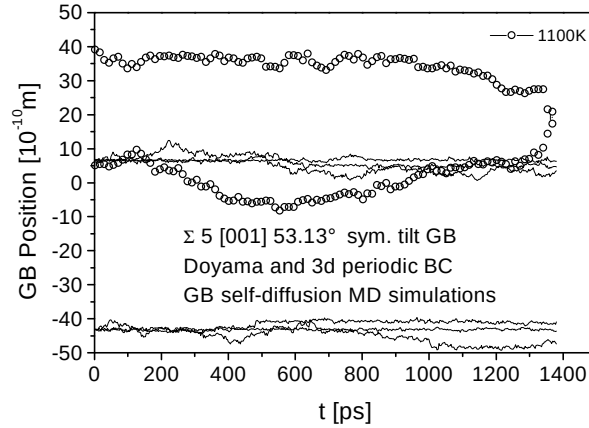


Figure 6.52: GB position versus time plots of the $\Sigma 5$ (210) symmetrical tilt GB at different temperatures. The figure demonstrates that for temperatures 800K to 1000K, the GB only fluctuates about its equilibrium position. The 1100K data reveals that the GBs attractively interact in direction of the shorter separation (+z-direction) which finally leads to GB migration and annihilation of the GBs just at the end of the simulation run.

temperatures 800K to 1000K, the GB only fluctuates about its equilibrium position. The 1100K data reveals that the GBs attractively interact in direction of the shorter separation (+z-direction) which finally leads to GB migration and annihilation of the GBs just at the end of the simulation run. Fig. 6.53 presents the normalized MSD data profiles at

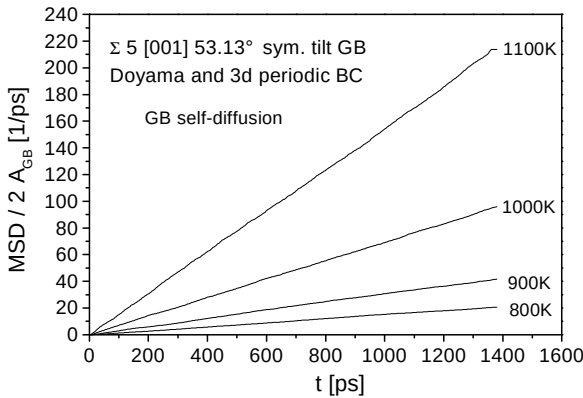


Figure 6.53: Normalized MSD of the $\Sigma 5$ (210) symmetrical tilt GB at various temperatures. Here the diffusive atomic-level jump data were extracted from the atomistic displacement data to yield the MSD versus time data. All profiles are well described by linear best data fits.

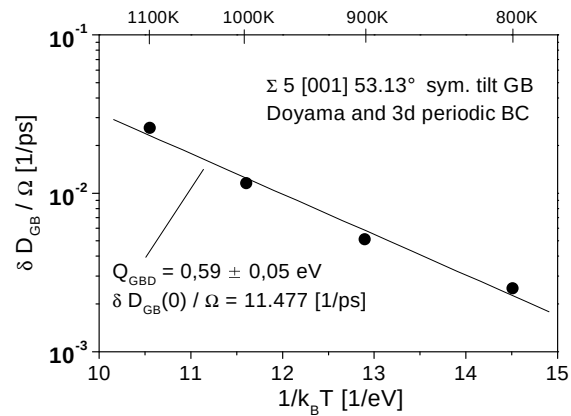


Figure 6.54: Arrhenius plot of GB self-diffusion coefficient of the $\Sigma 5$ (210) symmetrical tilt GB. The found data fairly well fits to a linear best data fit which gives 0.59 ± 0.05 eV as the activation enthalpy for GB self-diffusion of this GB.

various temperatures. Here the MSD data was obtained from the diffusive atomic-level jump data that were extracted from the overall atomistic displacement fields of all atoms associated with the GBs. To identify GB atoms the CNA method was utilized. Additionally

a complex data analysis procedure was applied to the raw displacement data to sort out MSD contributions associated with GB glide events.

Performing linear best data fits of the MSD profiles of Fig. 6.53 gives after following a normalization procedure the temperature dependence of the GB self-diffusion coefficient. The Arrhenius plot of the GB self-diffusion coefficient of the $\Sigma 5$ (210) tilt GB is given in Fig. 6.54. The activation enthalpy of GB self-diffusion is found to be 0.59 ± 0.05 eV and the pre-exponential factor being 11.477 [1/ps]. Recently Suzuki and Mishin [81] reported for the $\Sigma 5$ (210) tilt GB a GB self-diffusion enthalpy of 0.532 eV for vacancy GB self-diffusion either parallel or normal to the tilt axis. Their results were obtained by an EAM potential as well. Hence their data lends itself very much for a comparison. The very good data agreement between their and the result of this work confirm and support the MSD data analysis for the studied fully free 3d GB systems of this work. This is remarkable since Suzuki and Mishin studied a rather restricted GB system utilizing a frozen block concept as introduced by Lutsko [66].

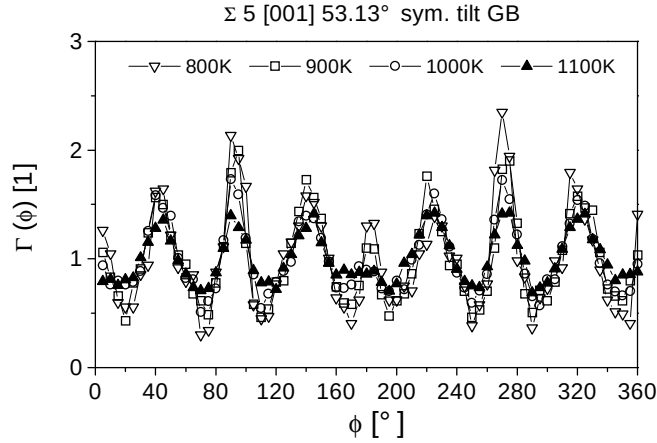


Figure 6.55: Angular distribution of the diffusion jump vectors of the $\Sigma 5$ (210) symmetrical tilt GB at different temperatures.

According to the temperature dependence of the GB self-diffusion coefficient it seems that the $\Sigma 5$ (210) tilt GB remains crystalline throughout the studied temperature range. To further assess this, the angular distribution of the diffusion jump vectors of the $\Sigma 5$ (210) GB is plotted at different temperatures in Fig. 6.55. The data profiles indicate that the GB structure remains the same in the temperature range from 800K to 1100K. Only a slight decrease in amplitude of the 1100K data is found compared to the 800K. This result supports the approach to represent the temperature dependence of the GB self-diffusion coefficient in an Arrhenius plot by a single linear best data fit.

After dealing with GB self-diffusion of the $\Sigma 5$ (210) tilt GB in the preceding paragraphs, now results of GB migration in the presence of an orientation-correlated DF are presented. Two sets of simulations were performed. In one set only the h_{33} component of the simulation box matrix, $\underline{h}$, was allowed to adjust according to the internal and external stress balance. In the second set of simulations, the box components h_{22} , h_{23} , h_{32} and h_{33} were allowed to adjust.

GB migration with adjustable h_{33} box variable - According to the results found for the yz shear stress simulations and being aware of the found GB migration mechanism

under these conditions, it seemed interesting to study whether or not the $\Sigma 5$ (210) tilt GB can even move continuously if GB sliding is either suppressed or at least hindered by choosing the appropriate conditions for the temporal evolution of the simulation box. Hence finite temperature simulations were performed where only the h_{33} box variable was allowed to adjust to the present stress state balance according to the Rahman-Parrinello scheme. Under this constriction for the simulation box it was found that indeed the $\Sigma 5$ (210) tilt GB can move continuously in the presence of the orientation-correlated DF. Two examples of GB position versus time profiles are shown in Fig. 6.56 and 6.57. At 800K and lower DF, the GBs hardly want to move still at rather high DFs they move quite rapidly through the system. Although some GB position versus time plots were not ideally linear, still they were fitted with a linear best data fit. This is especially true for the 800K profiles. The

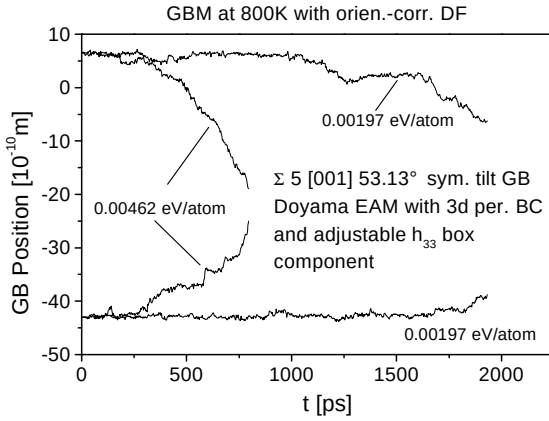


Figure 6.56: GB position profiles at 800K of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable h_{33} box variable and orien.-corr. DF.

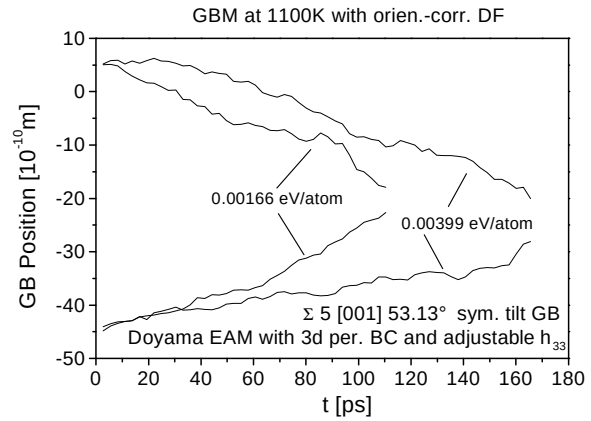


Figure 6.57: GB position profiles at 1100K of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable h_{33} box variable and orien.-corr. DF.

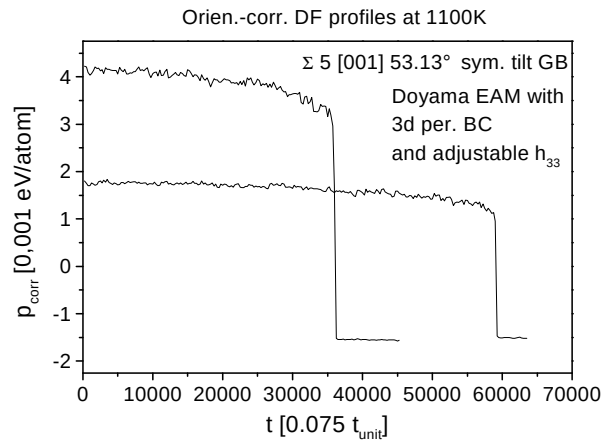


Figure 6.58: Orien.-corr. DF profiles at 1100K of the data presented in Fig.6.57. The usually observed decline of DF close to the annihilation of the two GBs in a system where 3d periodic BC are applied is observed.

obtained GB velocities of GB₁ and GB₁ were averaged and then plotted in Fig. 6.59 versus

the orientation-correlated DF, p_{corr} . For some data points the error bar became quite large which expresses the tendency of one GB to move while the other one remained more static. The orientation-correlated DFs, p_{corr} , for instance as plotted for the 1100K simulations in Fig. 6.58, can be easily extracted from the simulations and show the typical decrease of DF during the course of GB migration when applying 3d periodic BC to the simulation box. 3d periodic BC are recommended when studying the temporal evolution of the simulation box variables. This is even more true when all nine box variables are allowed to adjust. The DF was usually imposed on the system in such a way that in the lower grain A a higher excess energy was installed than for the upper grain B which led to the shrinkage and disappearance of grain A. Finally the temperature dependence of the GB mobility was determined by doing

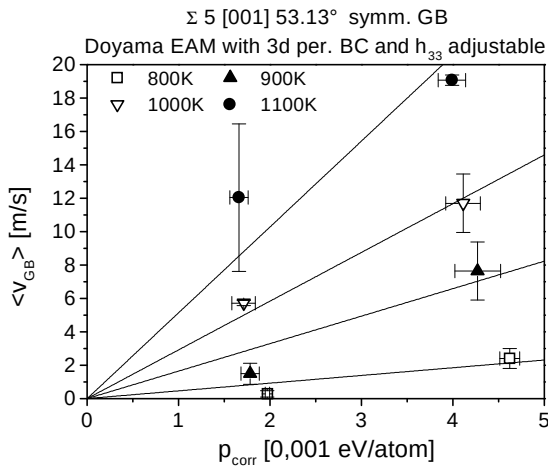


Figure 6.59: Average GB velocity versus orien.-corr. DF of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable h_{33} box variable and orien.-corr. DF. at 800K to 1100K.

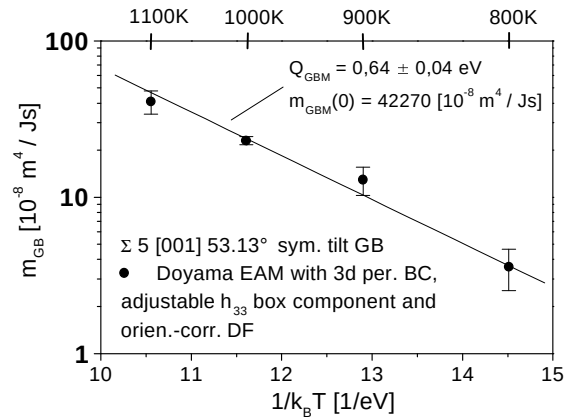


Figure 6.60: Arrhenius-Plot of GB mobility of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable h_{33} box variable and orien.-corr. DF.

linear best data fits of the GB velocity versus orientation-correlated DF plots as shown in Fig. 6.59. Next plotting the GB mobility in an Arrhenius plot giving in Fig. 6.60 yields the activation parameters of GB migration. The found activation enthalpy is $0.64 \pm 0.04 \text{ eV}$ and the pre-exponential factor $42270 [10^{-8} \text{ m}^4 / \text{Js}]$. All data points fit fairly well on a single linear best data fit.

The analysis of the displacement fields of atoms within separate (002) planes reveals that indeed no extended GB sliding events are observed during GB migration. Hence the simulation box restriction only to allow the h_{33} box variable to adjust, forced the GB to activate a different GB migration mechanism to allow the GB to move continuously through the system. Since it was already observed for the yz shear stress simulations that during GB sliding and migration GB diffusion was necessary to reconstruct the GB structure, it does not surprise that the $\Sigma 5$ (210) GB can move by a diffusive controlled or assisted mechanism that is not coupled to GB sliding.

GB migration with adjustable $h_{22}, \dots, h_{33}$ box variables - The second set of simulations included simulations where the h_{22} , h_{23} , h_{32} and h_{33} box variables were allowed to adjust according to the stress state balance while the orientation-correlated DF drove the GBs. The h_{22} , h_{23} , h_{32} and h_{33} box variables were selected to be adjustable since they are elementary to ensure GB glide events. To demonstrate that indeed under these boundary

conditions for the simulation box, GB sliding and GB migration is again coupled, Fig. 6.61 presents GB position versus time profiles at 800K and 1100K while Fig. 6.62² shows the temporal evolution of the strain component ϵ_{YZ} for all conducted simulations of this paragraph. The analysis of the ϵ_{YZ} profiles is rather interesting since it proves that under the studied boundary conditions of the simulation box GB sliding and GB migration occur again coupled. Interestingly the data shows that the higher the temperature the lower the accumulated ϵ_{YZ} strain gets.

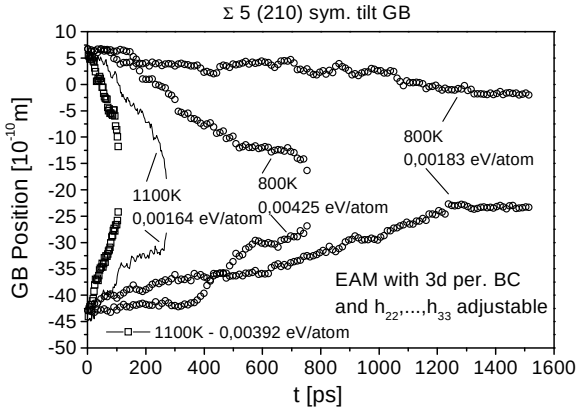


Figure 6.61: GB position versus time plots of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable $h_{22}, \dots, h_{33}$ box variables and orien.-corr. DF. at 800K to 1100K.

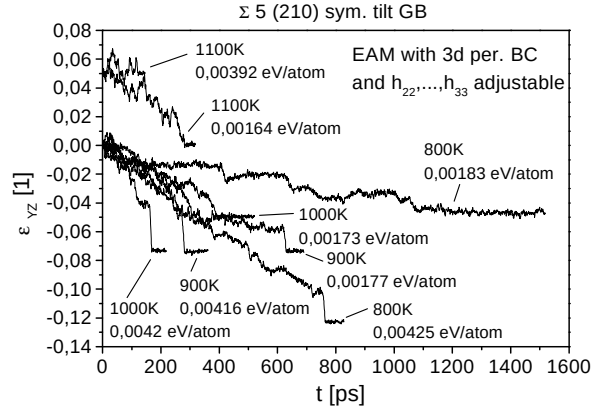


Figure 6.62: Temporal evolution of the strain component, ϵ_{YZ} , obtained by simulations of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable $h_{22}, \dots, h_{33}$ box variables and orien.-corr. DF.

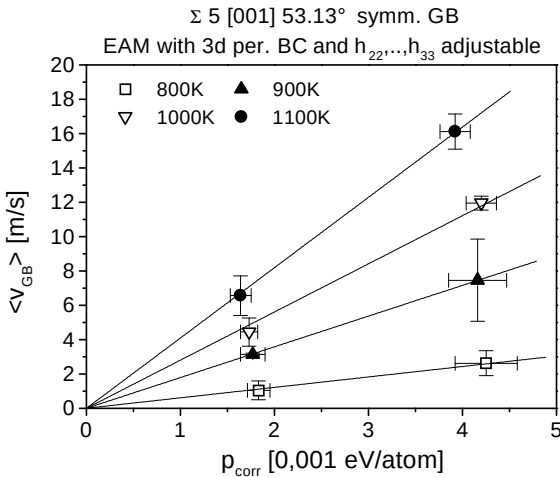


Figure 6.63: Average GB velocity versus orien.-corr. DF of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable $h_{22}, \dots, h_{33}$ box variables and orien.-corr. DF. at 800K to 1100K.

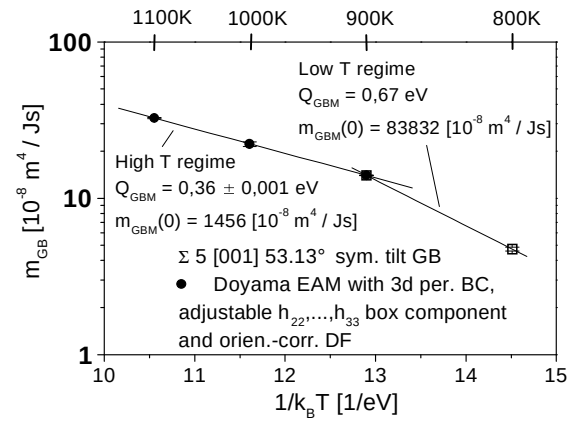


Figure 6.64: Arrhenius-Plot of GB mobility of the $\Sigma 5$ (210) symmetrical tilt GB with adjustable $h_{22}, \dots, h_{33}$ box variables and orien.-corr. DF.

²The 1100K ϵ_{YZ} profiles were shifted by 0.05 on the y axis to help to distinguish between all shown ϵ_{YZ} profiles.

The 900K data impressively shows that for different magnitudes of orientation-correlated DF at one temperature, still the same accumulated ϵ_{YZ} strain is found. This is not ideally found for all temperatures. The decrease in ϵ_{YZ} strain accumulation with increasing temperature can be understood in terms of a change in GB mechanism from a coupled GB sliding and migration mechanism to a more diffusion controlled GB mechanism. This expresses and underlines again that a change in GB character with increasing temperature occurs for this GB. Next the average GB velocity versus orientation-correlated DF at different temperatures is shown in Fig. 6.63 and an Arrhenius plot of the temperature dependence of the GB mobility is given in Fig. 6.64. These two figures again show that the results appear a little different compared to the results of the simulations with only an adjustable h_{33} box variable. First of all the obtained GB velocities of GB₁ and GB₂ of a single simulation run agree much better as is exemplified by the relative small error bars compared to Fig. 6.59. Additionally the average GB velocity versus orientation-correlated DF plots are almost perfectly linear relationships which was not observed to the same degree for the simulations with only an adjustable h_{33} box variable. This implies that the true GB migration mechanism of the Σ 5 (210) tilt GB is given by the coupled GB sliding and migration mechanism. Hence the conducted simulations with adjustable $h_{22}, \dots, h_{33}$ box variables yield rather good results that agree with theory very well. Still the data implies a change of GB mechanism with increasing temperature which is reflected by the two regime fit of the GB mobility data. Since the error bars of the GB mobility data are extremely small, it seems that the data can be trusted very much and truly a low temperature and high temperature regime for GB migration exists.

Comparing the GB mobility data obtained by the simulations with only the adjustable h_{33} box variable and adjustable $h_{22}, \dots, h_{33}$ box variables shown in Fig. 6.65 reveals very good data agreement between both data sets. With respect to the error bars there is excellent data agreement between both sets of data. It is interesting to note that out of all data

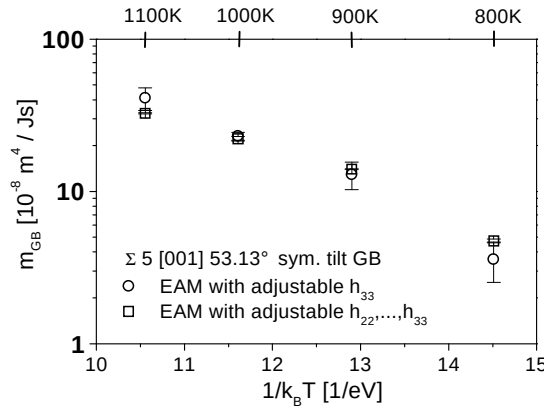


Figure 6.65: Data comparison of Arrhenius plots of GB mobility of the Σ 5 (210) symmetrical tilt GB for adjustable h_{33} box variable and adjustable $h_{22}, \dots, h_{33}$ box variables.

points, the 800K data points match the poorest. This again supports the idea that due to the different simulation box boundary conditions, ideal GB migration was hindered in the low temperature simulation runs with only an adjustable h_{33} box variable.

6.4 Studies on Planar Asymmetrical Tilt GBs

6.4.1 GB self-diffusion

Two asymmetrical tilt GBs were studied in this work. These are the $\Sigma 5$ [001] 53.13° $\Phi=14.04^\circ$ and $\Sigma 5$ [001] 53.13° $\Phi=33.69^\circ$ asymmetrical tilt GB where Φ represents the inclination angle with respect to the (210) plane. Throughout this work these two GBs are labelled ASY14 and ASY33 tilt GB, respectively.

6.4.1.1 $\Sigma 5$ [001] 53.13° $\Phi=14.04^\circ$

In this section the results of MD simulations at finite temperatures without any explicit DF are reported. The results of the simulations show that the ASY14 tilt GB remains stable at its initial position in real space throughout the whole studied temperature range. Only a fluctuation about its equilibrium position is observed. Additionally GB self-diffusion was studied in order to determine the activation parameters of the $\Sigma 5$ ASY14 tilt GB.

The simulation details are as follows. LJ MD simulations were performed from 700K to 1000K in step of 50K applying 2d periodic boundary conditions within the GB plane (this is the x-y-plane of the simulation box coordinate system) while pseudo free surfaces were realized in z-direction. The system consisted of six (002) planes containing overall 6210 atoms. The relaxed GB energy was 1.041 J/m^2 . The GB displacement plots for temperatures 700K, 800K, 900K and 1000K are shown in Fig. 6.66. In order to present several GB position

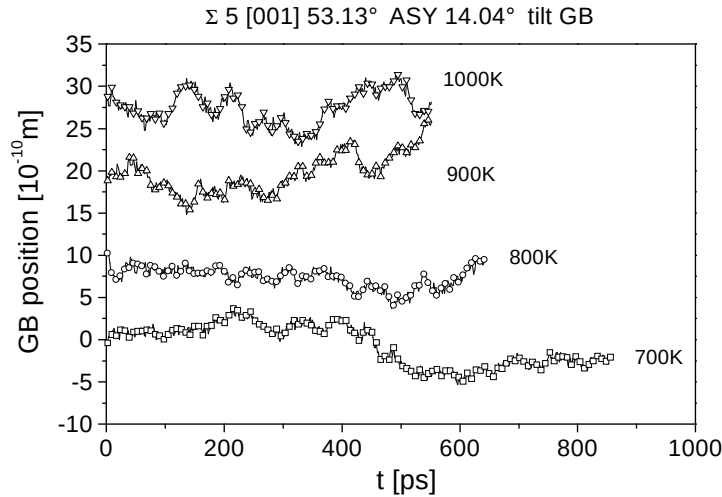


Figure 6.66: GB position of the $\Sigma 5$ [001] 53.13° ASY14 asymmetrical tilt GB versus time at different temperatures. In order to present several GB position profiles at different temperatures in one plot, the GB position data were shifted according to their temperature, T , by $10\text{\AA} \cdot \frac{T-700\text{K}}{100\text{K}}$ with respect to the y-axis. The figure demonstrates that the GB only fluctuates about its equilibrium position at all temperatures.

profiles at different temperatures in one plot, the GB position data of Fig. 6.66 were shifted according to their temperature, T , by $10\text{\AA} \cdot \frac{T-700\text{K}}{100\text{K}}$ with respect to the y-axis. The plots

demonstrate that the GB slightly moves although its movement can only be interpreted as thermal fluctuations about its equilibrium position.

Before presenting and discussing the GB self-diffusion data, an analysis of the RDF of the GB atoms as well as the center of mass (CoM) behaviour of the two grains A and B of the ASY14 tilt GB are presented. The temperature dependence of the RDF of the GB atoms as shown in Fig. 6.67 can help to reveal whether or not the GB undergoes a structural transition within the studied temperature range of 700K up to 1000K [72]. In Fig. 6.67, RDF plots of the GB atoms which were determined by the CNA method are shown. During the calculation of the RDF including all GB atoms, all GB atoms and atoms from the neighbouring planes of the adjacent crystalline grains were considered as potential neighbours. Hence the RDF is not solely connected to bonds between exclusively GB atoms but even bonds with atoms from the adjacent crystalline grains. This presented RDF calculation scheme was used in order to include all possible neighbours starting from nearest neighbours (NN) to fifth NN. According to this RDF calculation scheme, the analysis

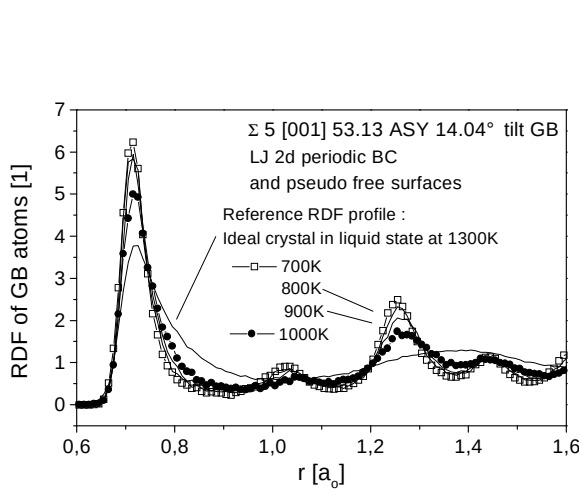


Figure 6.67: RDFs of GB atoms of the $\Sigma 5$ ASY14 tilt GB. The RDF profile of a liquid state ideal crystal at 1300K for the LJ potential is included to serve as a reference to identify a liquid GB state.

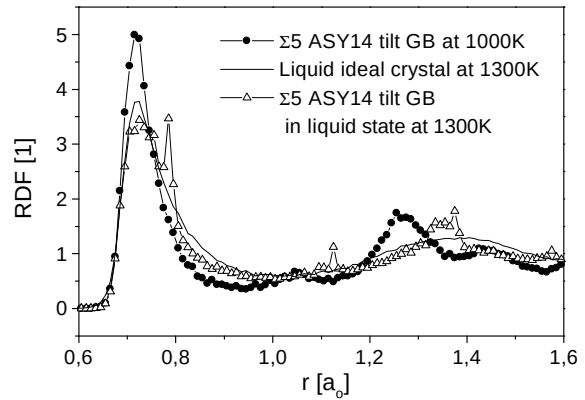


Figure 6.68: Detailed analysis of the 1000K RDF of GB atoms of the $\Sigma 5$ ASY14 tilt GB. The RDF profile of a liquid state ideal crystal at 1300K and the RDF of GB atoms of the liquefied $\Sigma 5$ ASY14 tilt GB at 1300K are included in the figure. Both reference profiles agree fairly well and point out that the $\Sigma 5$ ASY14 tilt GB at 1000K is in a disordered state which resembles the liquefied state of the GB at 1300K very much.

of the RDF profiles become difficult. As a reference to exemplify a RDF profile of a liquid state system, the RDF of an ideal crystal at 1300K being in the liquid state is included in Fig. 6.67. Clearly a difference between the RDF of the GB atoms and the liquid state situation is observed. This difference is only connected to the third NN peaks. For the NN and 2nd NN, the liquid state RDF profile and the highest temperature profiles of the $\Sigma 5$ ASY14 tilt GB agree very well. According to the RDF calculation scheme used for the case of the GB atoms, it is believed the majority of the contribution to the third NN peak is associated with neighbours from the crystalline grains adjacent to the GB that enter into the calculation. In order to clarify this point, MD simulations were performed where only eight planes on each side of the GB were allowed to move according to their MD equations

of motion. The remaining 188 planes were frozen and only their lattice parameter was set to the appropriate MD temperature. In a sequence of simulations, the temperature was raised to 1300K which is beyond the melting temperature of the used LJ potential, so that the 16 planes of the GB liquefied. Now the standard RDF analysis for the GB atoms was performed to see how the RDF profiles are affected by the contributions from the crystal regions of the adjacent grains. Fig. 6.68 presents the 1000K GB RDF, the liquid state ideal crystal RDF and finally the 1300K liquid state GB RDF of the $\Sigma 5$ ASY14 tilt GB. The figure demonstrates that a very well data agreement exists for the liquid state ideal crystal RDF and the 1300K liquid state GB RDF. It is interesting to note that the 1300K liquid state GB RDF shows a pronounced third NN peak which is the only clear difference to the liquid state ideal crystal RDF. Hence the third NN peak must be linked to the contributions of atoms from the crystal regions of the adjacent grains. The shift between the third NN peak of the 1000K and the 1300K data is explained by the thermal expansion of the system at higher temperatures. The final conclusion from this discussion is that indeed the 1000K RDF and even the highest temperature RDFs of the $\Sigma 5$ ASY14 tilt GB are associated with a liquid-like GB structure. This finding can be used to explain the results found for the center of mass and the GB self-diffusion temperature dependence which suggests that the $\Sigma 5$ ASY14 tilt GB undergoes a structural transition in the studied temperature range. This discussion is next.

An interesting aspect of the analysis of the static simulations is whether or not GB glide events are observed. One way to identify such glide events is to monitor the temporal evolution of the center of mass (CoM) of the two grains present in the system. Once

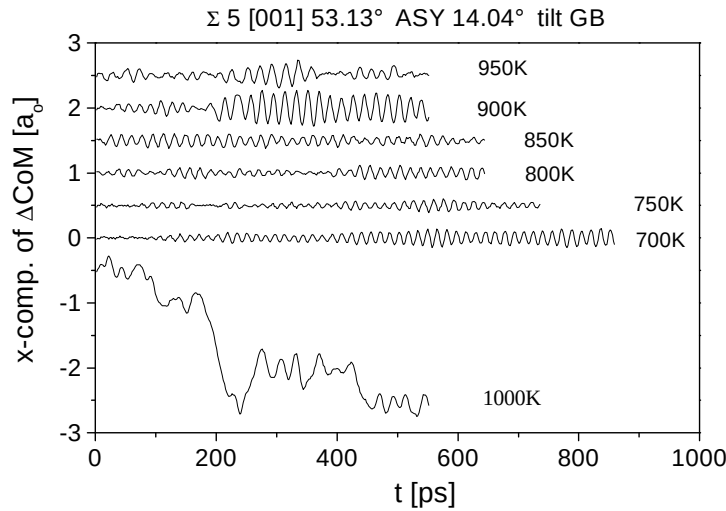


Figure 6.69: x-component of ΔCoM of $\Sigma 5$ [001] 53.13° asymmetrical tilt GB ASY14. The plotted ΔCoM data were shifted by $+0.5 a_0 \cdot \frac{(T-700K)}{50K}$ on the y-axis to be able to distinguish between each plot. Only the 1000K data was shifted by $-0.5a_0$.

the CoM data of each grain is calculated the relative displacement of both grains can be calculated by $\Delta\text{CoM} = \text{CoM}(\text{Grain B}) - \text{CoM}(\text{Grain A})$. Here the CoM data are 3d vectors in real space. For all conducted simulations from 700K up to 1000K in steps of 50K such ΔCoM profiles exist. For further analysis especially the x- and y-component of ΔCoM are interesting. The reader should note that the x-component is parallel to the tilt axis and that the spacing between (002) planes is $0.5a$. The found ΔCoM profiles of the x-component for

all studied temperatures are shown in Fig. 6.69. The analysis of the relative displacement of the center of mass, ΔCoM , of both grains shows that up to 950K the x-component as well as the y-component of ΔCoM periodically vibrate about their initial equilibrium position. The vibration amplitude of the x-component does not exceed beyond 0.25 to 0.3a which means that no glide events along the tilt axis occur. The vibrations are not simply sinusoidal vibrations with one frequency but seem to contain higher harmonics too. The frequency spectrum was determined by a Fourier analysis of the x-component of the ΔCoM data. The main frequency at low temperatures is about $7 \cdot 10^{10}$ Hz and decreases with increasing temperature to lower frequencies. A second frequency shows up in the spectrum at about $18 \cdot 10^{10}$ Hz. At 1000K the high frequency vibrations disappear and the grains begin to glide along the tilt axis. Fig. 6.69 shows that at 1000K GB glide events of distance 0.5a occur several times during the overall simulation. Still even the 1000K ΔCoM profile shows vibrations. The occurrence of such vibrations can be understood as follows. At low temperatures the two grains do vibrate but the vibration amplitude is not high enough that GB glide events can occur. This is because the temperatures are too low to overcome the energy barrier for GB glide. At elevated temperatures GB glide events do occur. They are initiated by grain vibrations for some finite time before a GB glide event occurs. Clearly the 1000K ΔCoM profile shows such vibrations. Since the 1000K ΔCoM profile is not a simple monotonic function in time and contains a large background signal due to the GB glide events, a Fourier transformation is difficult to perform. The first task would be to remove the background signal from the 1000K ΔCoM profile in order to perform a Fourier transformation that would clearly identify the vibration frequencies. Separating the background with a linear best data fit helps to perform the Fourier transformation which shows that indeed a low frequency vibration exists even at 1000K. The y-component of the

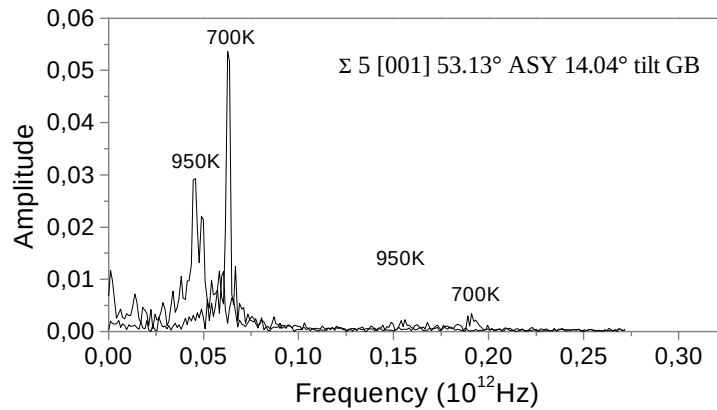


Figure 6.70: Frequency spectra of the x-component of ΔCoM for the $\Sigma 5$ ASY14 tilt GB. Two frequencies can be identified having a value of about $7 \cdot 10^{10}\text{Hz}$ and $18 \cdot 10^{10}\text{Hz}$. With increasing T the peaks shift towards smaller frequencies.

ΔCoM profiles shows the same temperature dependence as the x-component. Only here a single frequency is found in the Fourier spectrum which is far less pronounced than found for the x-component.

GB self-diffusion - The available atomic-level data of the static simulations is further used to determine the temperature dependence of the GB self-diffusion coefficient associated with a vacancy mechanism. This is achieved by an analysis of the diffusive mean-square

displacement of the GB atoms. Here the analysis follows the same way as has been discussed in section 3.5.2 and has been used for the [001] twist and the other tilt GBs. Fig. 6.71 presents the diffusive MSD profiles at various temperatures. Fitting the linear time dependence of the MSD data and including the appropriate normalization of the data yields the GB self-diffusion coefficient.

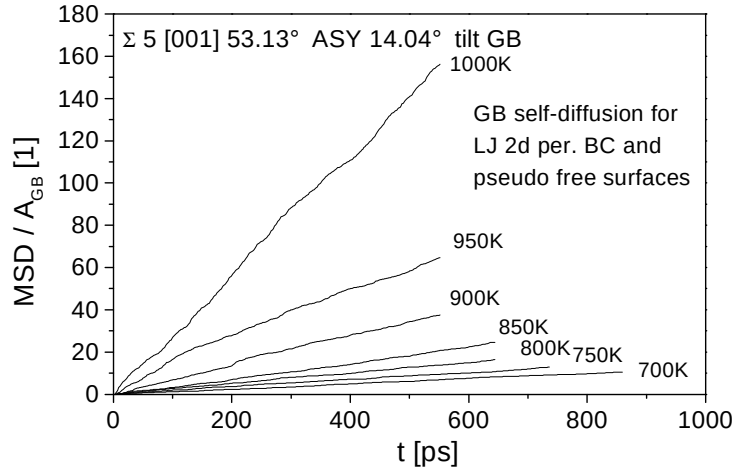


Figure 6.71: Temporal evolution of the diffusive MSD of the $\Sigma 5$ ASY14 tilt GB at various temperatures.

Finally the temperature dependence of the GB self-diffusion coefficient is presented in an Arrhenius plot which yields the activation parameters of the $\Sigma 5$ asymmetrical ASY14 GB. Fig. 6.72 shows the Arrhenius plot which reveals that a low temperature regime as well as

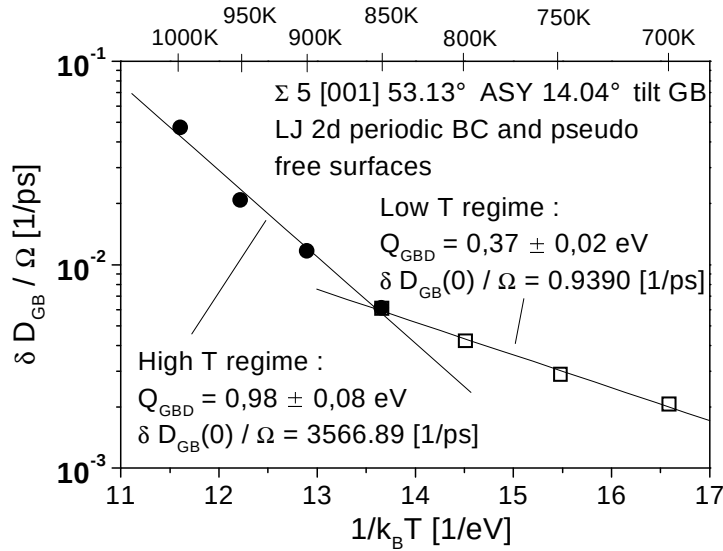


Figure 6.72: Arrhenius plot of the GB self-diffusion coefficient of the $\Sigma 5$ ASY14 tilt GB.

a high temperature regime exists for the GB self-diffusion data of the GB. In contrast to the so far found GB self-diffusion data of twist and tilt GBs, here the high temperature regime is described by larger activation parameters than the low temperature regime. The

activation parameters are listed in Fig. 6.72 and show that the high temperature activation enthalpy is about twice as large as the low temperature one.

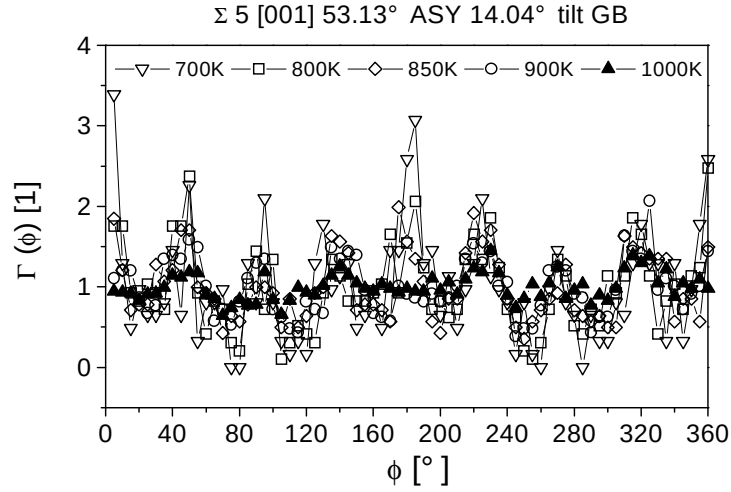


Figure 6.73: Angular distribution of the diffusion jump vectors of the $\Sigma 5$ asymmetrical tilt GB ASY14 at different temperatures. An isotropic distribution would ideally have a constant value of one throughout the whole range of angles.

The main driving question is whether a structural transition can be found in structural data describing the structural order within the GB. The RDF profiles in Fig. 6.67 and 6.68 are able to identify such the structural transition of the $\Sigma 5$ ASY14 tilt GB from a crystalline to a liquid-like GB state. A second way to describe the state of order within the GB is to utilize the diffusion jump vectors that were used to calculate the MSD profiles. Fig. 6.73 shows the angular distribution of these diffusive jump vectors of the $\Sigma 5$ ASY14 tilt GB at different temperatures. These profiles alone can not really answer the question related to a structural transition of the GB beyond any doubt. The difference between the 700K profile and the 1000K profile is not pronounced. Knowing from the GB self-diffusion data that the transition occurs at about 850K, it seems that the 850K to 1000K data remain almost at a constant level. It seems that a slight difference between the low and high temperature regime exists, still the significance of the data difference can not really be assessed.

6.4.1.2 $\Sigma 5$ [001] 53.13° $\Phi=33.69^\circ$

Following the discussion of the $\Sigma 5$ ASY14 tilt GB, here the results of MD simulations at finite temperatures of the $\Sigma 5$ ASY33 tilt GB without any explicit DF are reported. As for the $\Sigma 5$ ASY14 tilt GB, the results of the simulations show that the GB remains stable at its initial position in real space throughout the whole studied temperature range. Only a fluctuation about its equilibrium position is observed. Additionally again GB self-diffusion was studied in order to determine the activation parameters of the $\Sigma 5$ ASY33 tilt GB. The data presentation and discussion of the $\Sigma 5$ ASY33 tilt GB is kept short since a more detailed description was given for the $\Sigma 5$ ASY14 tilt GB. Overall the results of the $\Sigma 5$ ASY14 and ASY33 tilt GB are quite comparable which justifies such a procedure.

LJ MD simulations were performed from 700K to 1000K in step of 50K applying 2d periodic boundary conditions within the GB plane (x-y-plane of the simulation box coordinate

system) while pseudo free surfaces were realized in z-direction. The system consisted of six (002) planes containing overall 6240 atoms. The relaxed GB energy was 1.164 J/m². GB position versus time plots for temperatures of 700K up to 1000K in steps of 50K are shown in Fig. 6.74. In order to present several GB position profiles at different temperatures in

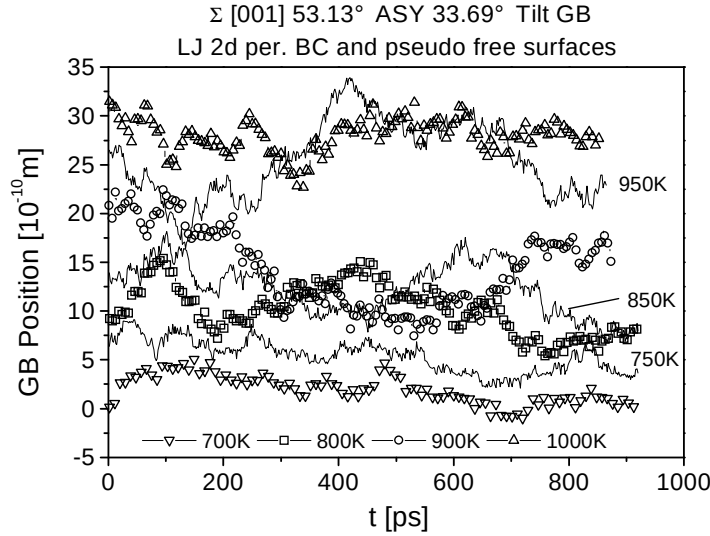


Figure 6.74: GB position of the $\Sigma 5$ [001] 53.13° ASY33 asymmetrical tilt GB versus time at different temperatures. In order to present all GB position profiles for the studied different temperatures in one plot, the GB position data were shifted according to their temperature, T , by $5\text{\AA} \cdot \frac{T-700\text{K}}{50\text{K}}$ with respect to the y-axis. The figure clearly demonstrates that the GB only fluctuates about its equilibrium position at all temperatures.

one plot, the GB position data plotted in Fig. 6.74 were shifted according to their temperature, T , by $5\text{\AA} \cdot \frac{T-700\text{K}}{50\text{K}}$ with respect to the y-axis. Although the data presentation is still a little bit difficult to follow, the plots demonstrate that the GB does not move continuously and that its movement can only be interpreted in terms of thermal fluctuations about its equilibrium position.

Next the analyses of the RDFs of the GB atoms are presented in Fig. 6.75 and 6.76. How these profiles can be interpreted and what additional simulations were necessary to obtain the final results has been discussed and presented in detail for the $\Sigma 5$ ASY14 tilt GB in section 6.4.1.1. According to the shown comparison of RDF profiles of an ideal crystal in the liquid state and the $\Sigma 5$ ASY33 tilt GB at 1000K as well as at 1300K where it is liquefied, demonstrates that the $\Sigma 5$ ASY33 tilt GB at 1000K can be understood in terms of a liquid-like GB structure which is distinctly different from the low temperature crystalline GB structure. This finding can explain the temperature dependence of the CoM data as well as of the GB self-diffusion data which are presented and discussed next.

Again a detailed presentation and discussion of the center of mass (CoM) analysis has been given in section 6.4.1.1. The available simulation results of the temporal evolution of the x-component of relative displacement, ΔCoM , of the two grains present in the system are shown in Fig. 6.77. The plotted profiles cover the temperature range from 700K up to 1000K in steps of 50K. Analysing the profiles of the x-component of the ΔCoM yields that the centers of mass and hence the grains vibrate periodically in the temperature range of

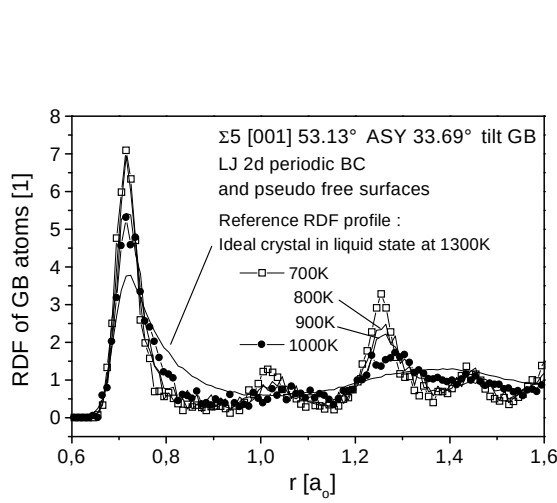


Figure 6.75: RDFs of GB atoms of the $\Sigma 5$ ASY33 tilt GB. The RDF profile of a liquid state ideal crystal at 1300K for the LJ potential is included to serve as a reference to identify a liquid-like GB state.

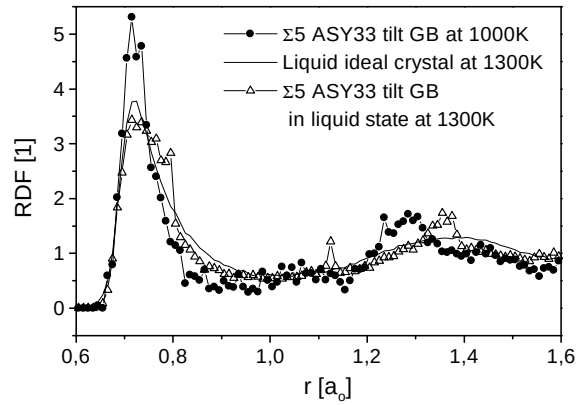


Figure 6.76: Detailed analysis of the 1000K RDF of GB atoms of the $\Sigma 5$ ASY33 tilt GB. The RDF profile of a liquid state ideal crystal at 1300K and the RDF of GB atoms of the liquefied $\Sigma 5$ ASY33 tilt GB at 1300K are included in the figure. Both reference profiles agree fairly well and point out that the $\Sigma 5$ ASY33 tilt GB at 1000K is in a disordered state which resembles the liquefied state of the GB at 1300K very much.

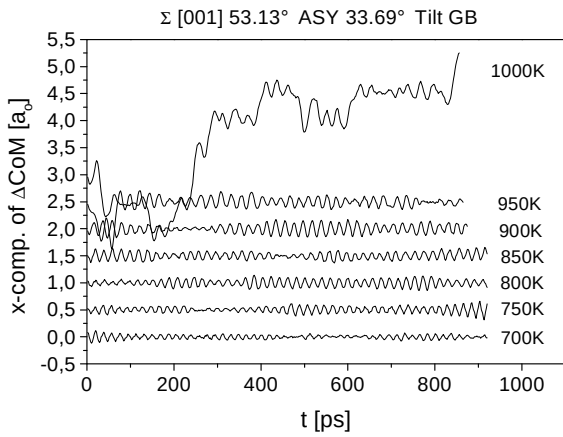


Figure 6.77: x-component of ΔCoM of $\Sigma 5$ [001] 53.13° asymmetrical tilt GB ASY33. The plotted ΔCoM data were shifted by $+0.5 a_0 \cdot \frac{(T-700K)}{50K}$ on the y-axis to be able to distinguish between each plot.

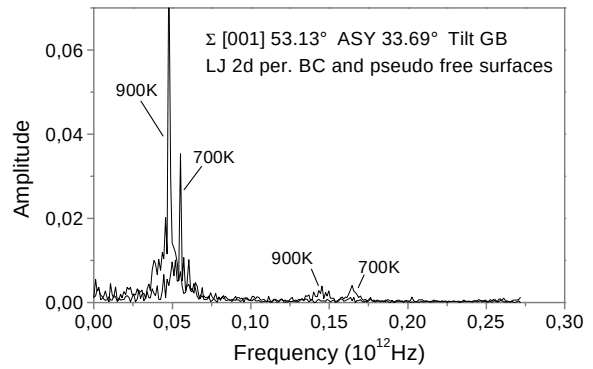


Figure 6.78: Frequency spectra of the x-component of ΔCoM of the $\Sigma 5$ ASY33 tilt GB. Two frequencies can be identified having a value of about $6 \cdot 10^{10}\text{Hz}$ and $17 \cdot 10^{10}\text{Hz}$ at 700K. With increasing temperature, the peaks shift towards smaller frequencies as demonstrated by the 900K data.

700 to 950K without showing any GB glide events along the tilt axis. At 950K only initially two GB glide events did occur. At 1000K, numerous GB glide events along the tilt axis are observed which are initiated by vibrations that finally are able to overcome the potential barrier of GB glide. At low temperatures the lowest vibration frequency was found to be at about $6 \cdot 10^{10}$ Hz while at higher temperatures it shifts to a lower frequency of about $5 \cdot 10^{10}$ Hz. The frequencies were obtained by a Fourier analysis of the ΔCoM data and its results and two spectra are given in Fig. 6.78. Overall the behaviour of the $\Sigma 5$ ASY14 and ASY33 tilt GBs with respect to the occurrence of GB glide along the tilt axis is very similar.

GB self-diffusion -The available atomic-level data of the static simulations is now used to determine the temperature dependence of the GB self-diffusion coefficient associated with a vacancy mechanism. This is achieved by an analysis of the diffusive mean-square displacement of the GB atoms. Here the analysis follows the same way as has been discussed in section 3.5.2 and has been used for the [001] twist and the other tilt GBs. Fig. 6.79 presents the diffusive MSD profiles at various temperatures. Fitting the linear time dependence of the MSD data and including the appropriate normalization of the data yields the GB self-diffusion coefficient, D_{GB} .

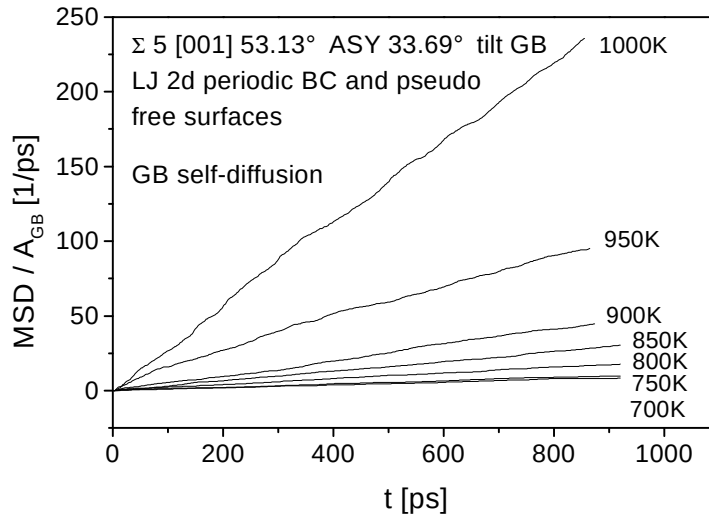


Figure 6.79: Temporal evolution of the diffusive MSD of the $\Sigma 5$ ASY33 tilt GB at various temperatures.

Finally the temperature dependence of the GB self-diffusion coefficient when being plotted in an Arrhenius plot yields the activation parameters of the $\Sigma 5$ ASY33 tilt GB. Fig. 6.80 shows this Arrhenius plot. It reveals that a low temperature regime as well as a high temperature regime exists for the GB self-diffusion data similar to the results found for the $\Sigma 5$ ASY14 tilt GB. The transition temperature is at about 900K which is 50K higher than the one found for the $\Sigma 5$ ASY14 tilt GB. The activation parameters are listed in Fig. 6.80. The low temperature activation enthalpy is 0.48 ± 0.06 eV which is about 0.1 eV higher than for the $\Sigma 5$ ASY14 tilt GB. As well the high temperature activation enthalpy is 1.31 ± 0.06 eV which is about 0.3 eV higher than for the $\Sigma 5$ ASY14 tilt GB. As found for the $\Sigma 5$ ASY14 tilt GB, the RDF profiles in Fig. 6.75 and 6.76 are able to identify a structural transition of the $\Sigma 5$ ASY33 tilt GB from a crystalline to a liquid-like GB state at elevated temperatures. Again a second way to describe the state of order within the GB is to utilize

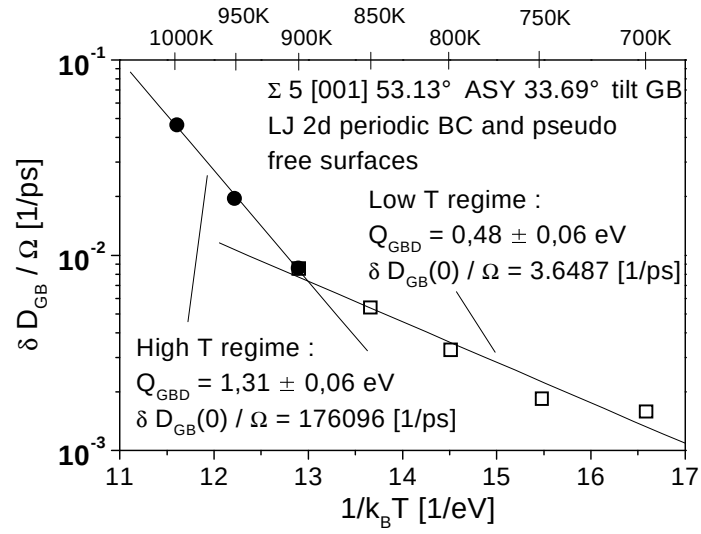


Figure 6.80: Arrhenius plot of the GB self-diffusion coefficient of the $\Sigma 5$ ASY33 tilt GB.

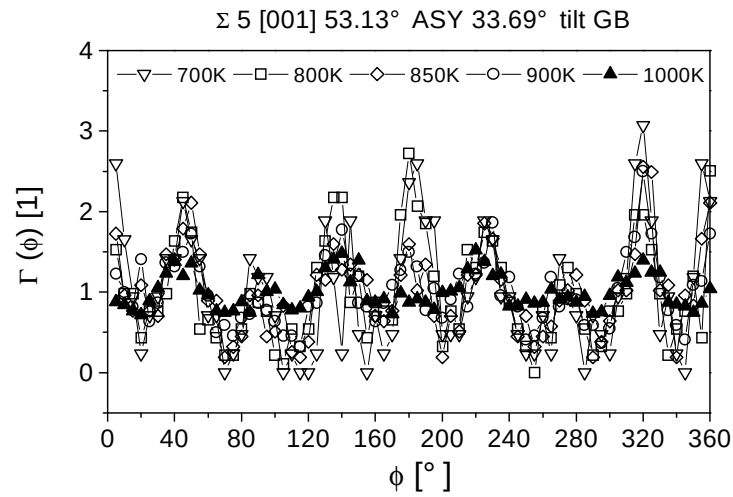


Figure 6.81: Angular distribution of the diffusion jump vectors of the $\Sigma 5$ ASY33 tilt GB at different temperatures.

the diffusion jump vectors that were used to calculate the MSD profiles. Fig. 6.81 shows the angular distribution of these diffusive jump vectors of the $\Sigma 5$ ASY33 tilt GB at different temperatures. These profiles alone do not really hint at a structural transition of the GB in the studied temperature range beyond any doubt. As for the $\Sigma 5$ ASY14 tilt GB, it seems difficult to associate these profiles with structural order transitions.

One interesting suggestion is to utilize GB diffusion data of a highly confined GB system where only a limited number of planes in the vicinity of the GB are allowed to move according to the MD equations of motion at for instance a temperature of 1300K. 1300K is higher than the melting point of the LJ potential which means that the GB must have liquefied. Performing the standard analysis to extract the diffusive MSD GB data could help to derive a reference angular distribution profile which is clearly connected to a GB in the liquid state.

Such simulations were performed for the $\Sigma 5$ ASY33 tilt GB. Examples of the physical behaviour of the confined GB system at finite temperature are presented by showing the 400K and 1300K GB structure in Fig. 6.82 and 6.83, respectively. Both figures show a view

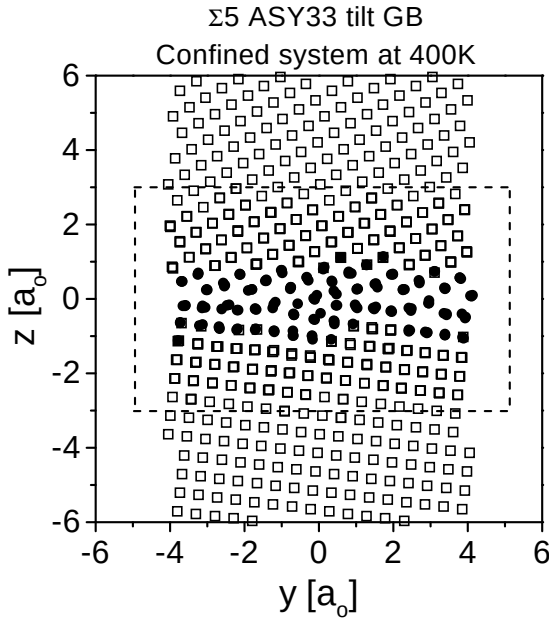


Figure 6.82: View along the tilt axis through the fully 3d system of the confined $\Sigma 5$ ASY33 tilt GB at 400K. The GB is restricted to a few planes at the GB and does not expand over all 16 MD dynamic slabs of size 0.31a. The region where the atoms are allowed to move according to the MD equations of motion is indicated by the dashed rectangle.

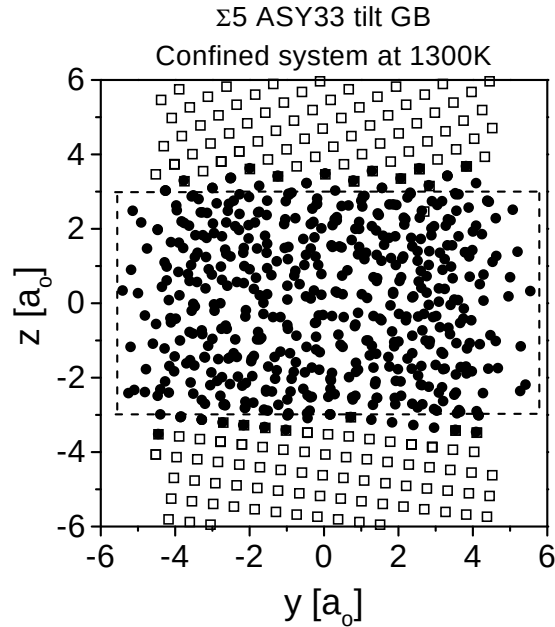


Figure 6.83: View along the tilt axis through the fully 3d system of the confined $\Sigma 5$ ASY33 tilt GB at 1300K. The GB now expands over all 16 MD dynamic slabs of size 0.31a and forms a liquid layer between the stabilized lower and upper grain. Ideal fcc atoms are identified by squares while non-ideal fcc atoms by circles.

along the tilt axis through the fully 3d system of the confined $\Sigma 5$ ASY33 tilt GB. Ideal fcc atoms are identified by squares while non-ideal fcc atoms by circles. The MD dynamic system consisted of eight slabs of size 0.31a on either side of the GB. Each slab consisted of either five (740) or (810) crystallographic planes depending whether it belonged to the lower or upper grain, respectively. The spacing between single crystallographic (740) as

well as (810) planes is $0.062a$. In order to perform the slicing procedure in z-direction of the system (see section 3.5.1.1), a spacing of $0.062a$ is too small to ensure proper slicing. Hence five crystallographic planes on either side of the GB were combined to slabs of $0.31a$ width in z-direction. Hence a total of 16 dynamic MD slabs leads to a MD system size of $4.96a$ in z-direction. In the figures, the dynamic area is marked by a dashed rectangle. At 400K, the GB is restricted to a few planes and does not expand over the complete MD dynamic region of the 16 slabs. Its low temperature GB structure is comparable to the known 0K equilibrium structure shown in Fig. 6.16. Heating the system beyond the melting temperature, the complete dynamic area becomes liquefied and hence does the GB which is exemplified by the 1300K situation.

For the ASY33 tilt GB, a simulation run over 920 ps was performed to study GB diffusion in the liquefied system. The final goal was to determine the angular distribution of diffusive jump vectors that form the MSD profile which can serve as a reference distribution that is clearly linked to a liquid phase GB structure. Here the same real simulation time was used as for the other MD simulations that led to the determination of the GB diffusion coefficient and the angular distribution. This was done to make sure that the same level of statistics enters into the underlying diffusive data. Of course one has to bear in mind that the same level of statistics can not really be reached when using the same real simulation time at all temperatures because at the lowest temperature only a few ten to a few hundred diffusive jumps will occur while at 1300K 108008 diffusive jumps were observed within the 920 ps. According to this, the best statistics is found for the highest temperature run assuming the same MD real time.

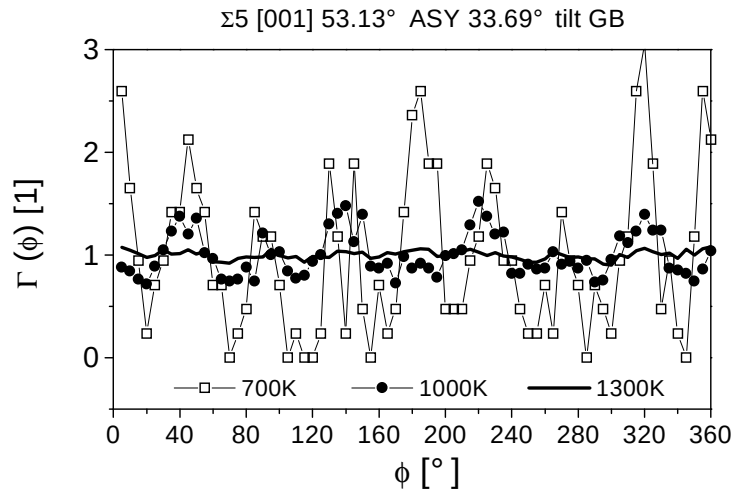


Figure 6.84: Angular distribution of the diffusive jump vectors of the $\Sigma 5$ ASY33 tilt GB at 700K and 1000K for the free GB system as well as the distribution of the confined GB system at 1300K.

Fig 6.84 shows the found 1300K angular distribution as well as the data at 700 and 1000K of the unrestricted ASY33 tilt GB system. The 1300K angular distribution is almost perfectly one over the whole angular range. This demonstrates that a truly liquid phase, either being an ideal crystal or GB system, will obtain a truly isotropic angular distribution. In conclusion this means that even the 1000K angular distribution is showing some features of an underlying crystalline structure due to the occurrence of well associated peaks. Still

it is very difficult to answer to what extent the $\Sigma 5$ ASY33 tilt GB at 1000K is ordered or disordered. Only a complete analysis of several physical properties that characterize structural order can help to give a better picture on structural transitions of GBs.

6.4.2 GB migration due to orientation-correlated Driving Force

Here the GB migration results of the $\Sigma 5$ ASY14 and ASY33 tilt GB in the presence of the orientation-correlated DF are given. In both cases a 2d periodic BC concept with pseudo free surfaces was applied to the simulation box. This was done to ensure that the GBs can travel a large distance without any interference from either a second GB or the pseudo free surface region. Thus the GBs were able to move continuously a distance of 90 to 100 Å. Additionally the orientation-correlated DF remained at a constant level and did not show the decline effect known from 3d periodic BC simulations.

Before presenting the details of the GB migration results of both GBs, next a short summary of the results is given. Both GBs moved continuously in the presence of the orientation-correlated DF where the studied temperature range was from 800K up to 1000K and even 1050K for the ASY33 tilt GB. For both GBs, the GB mobility increases up to 950K with increasing temperature while for higher temperatures it again decreases. The found GB migration activation parameters are as follows for the GB mobility data up to 950K.

Tilt GB	Φ [°]	Q_{GBM} [eV]	$m_{GBM}^{(0)}$ [$10^{-8} \text{ m}^4 / \text{Js}$]
ASY14	14.04	0.20 ± 0.03	205.1
ASY33	33.69	0.25 ± 0.03	393.7

Table 6.3: GB migration activation parameters of the studied asymmetrical [001] tilt GBs.

Compared to the found GB diffusion activation enthalpies in the low temperature regime, the corresponding GB migration activation enthalpies are about half of the GB self-diffusion activation enthalpies. Interestingly the same ratio was found for the studied [001] twist GBs. As well as for most of the studied [001] twist GBs, the sudden drop in GB mobility with increasing temperature at about 1000K was found for the asymmetrical [001] tilt GBs as well. It is further interesting to note that the symmetrical $\Sigma 5$ (210) tilt GB behaves a little differently with respect to its activation parameters of GB self-diffusion and GB migration. Here for the low temperature regime, the GB migration enthalpy and the GB self-diffusion enthalpy are the same. At higher temperatures, the GB migration mechanism changes according to the found GB migration activation parameters having a smaller activation enthalpy of about half of its low temperature activation enthalpy. Hence here again the ratio of two between the GB self-diffusion enthalpy and the GB migration enthalpy is found.

6.4.2.1 $\Sigma 5$ [001] 53.13° $\Phi=14.04^\circ$

Here only briefly the most important results and figures are shown to be able to follow the found GB migration results of the $\Sigma 5$ ASY14 tilt GB. MD GB migration simulations were

performed from 800K up to 1000K in step of 50K. Fig. 6.85 shows the GB position versus time profiles at 900K for four different orientation-correlated DFs. Each distance versus time profile can be nicely fitted by a linear best data fit which yields the GB velocity of each simulation run. The corresponding orientation-correlated DF, p_{corr} , versus time plots of the

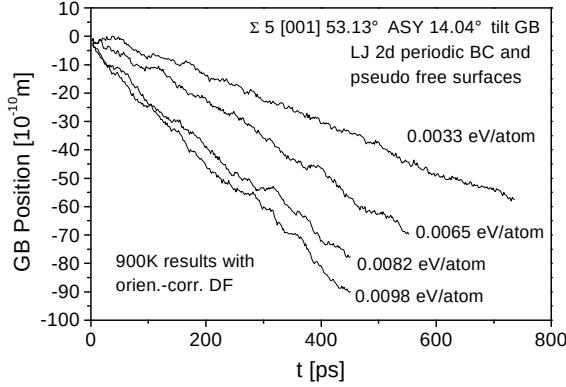


Figure 6.85: GB position versus time for GBM simulation runs at 900K of the $\Sigma 5$ [001] 53.13° ASY14 tilt GB.

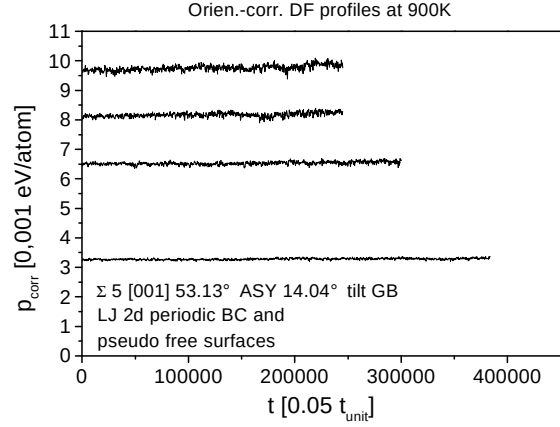


Figure 6.86: Orient.-corr. DF for GBM simulation runs at 900K of the $\Sigma 5$ [001] 53.13° ASY14 tilt GB.

900K runs are given in Fig. 6.86. They demonstrate that the DF remains very constant over the total simulation run and that the DF data can easily be extracted from this data. Finally

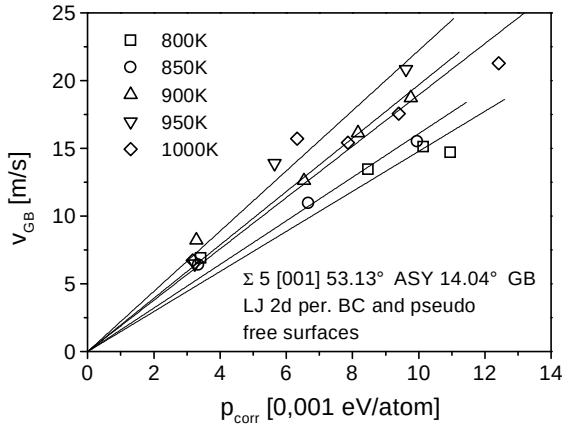


Figure 6.87: GB velocity versus orien.-corr. DF, p_{corr} , at different temperatures of the $\Sigma 5$ [001] 53.13° ASY14 tilt GB.

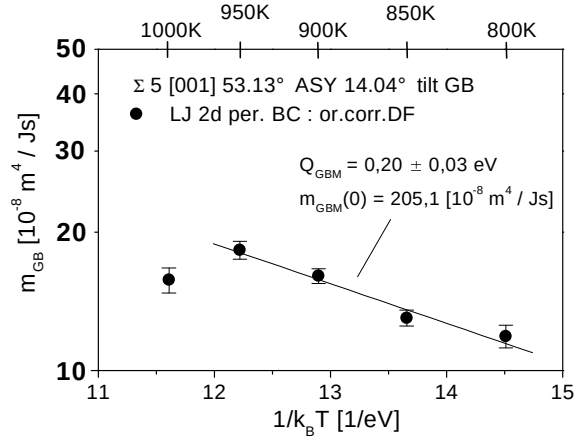


Figure 6.88: Arrhenius plot of the GB mobility for simulations with the orien.-corr. DF of the $\Sigma 5$ [001] 53.13° ASY14 tilt GB.

Fig 6.87 presents the GB velocity versus DF data for the whole studied temperature range. The figure already indicates that the GB mobility of the ASY14 tilt GB is a weak function on temperature. Performing linear best data fits of the GB velocity versus DF data yields for each temperature the GB mobility. The temperature dependence of the GB mobility is plotted in an Arrhenius plot in Fig. 6.88. The GB mobility from 800K up to 950K increases with increasing temperature and can be fitted linearly yielding an activation enthalpy of 0.20 ± 0.03 eV. The 1000K GB mobility drops with respect to the lower temperatures and

does not follow the found tendency of the low temperature regime. This implies that the GB undergoes a structural transition between 950 and 1000K which causes this decrease in GB mobility. That indeed a GB transition occurs within that temperature range is supported by the GB self-diffusion data.

6.4.2.2 Σ 5 [001] 53.13° $\Phi=33.69^\circ$

As for the ASY14 tilt GB, here only a brief presentation of the most important GB migration results of the Σ 5 ASY33 tilt GB are given. Overall the results of the ASY14 and ASY33 tilt GB are quite comparable. For the ASY33 tilt GB, MD GB migration simulations were performed from 800K up to 1050K in step of 50K. Fig. 6.89 shows the GB position versus time profiles at 950K for three different orientation-correlated DFs. Each distance versus time profile can be fitted by a linear best data fit which yields the GB velocity of each simulation run. The corresponding orientation-correlated DF, p_{corr} , versus time plots of the

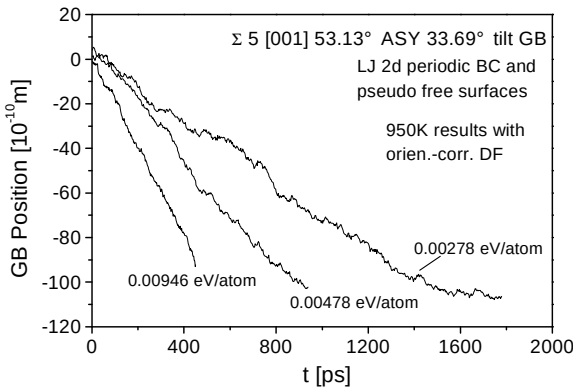


Figure 6.89: GB position versus time for GBM simulation runs at 950K of the Σ 5 [001] 53.13° ASY33 tilt GB.

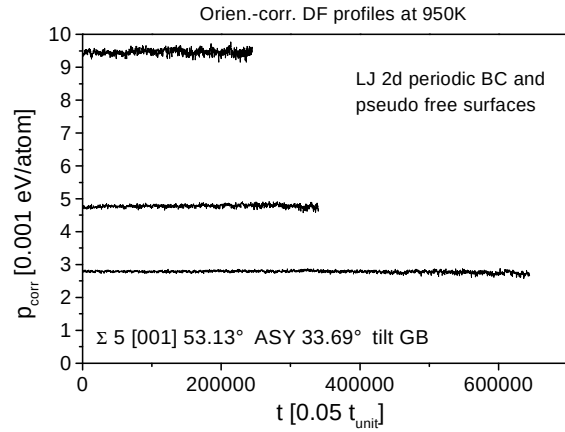


Figure 6.90: Orien.-corr. DF for GBM simulation runs at 950K of the Σ 5 [001] 53.13° ASY33 tilt GB.

950K runs are given in Fig. 6.90. They again demonstrate that the DF remains constant over the complete simulation run. Finally Fig 6.91 presents the GB velocity versus DF data for the whole studied temperature range. The figure indicates that the GB mobility of the ASY33 tilt GB is a weak function on temperature. Performing linear best data fits of the GB velocity versus DF data yields for each temperature the GB mobility. The temperature dependence of the GB mobility is plotted in an Arrhenius plot in Fig. 6.92. The GB mobility from 800K up to 950K increases with increasing temperature and can be fitted linearly yielding an activation enthalpy of 0.25 ± 0.03 eV. The 1000K GB mobility is slightly higher than the 950K data point but not really following the linear trend of the low temperature data. Finally the 1050K GB mobility is decreased with respect to the linear increasing GB mobility data of the low temperature regime. Again as for the ASY14 tilt GB this implies that the ASY33 GB undergoes a structural transition between 950 and 1000K which causes this decrease in GB mobility. That indeed a GB transition occurs within that temperature range is supported by the GB self-diffusion data.

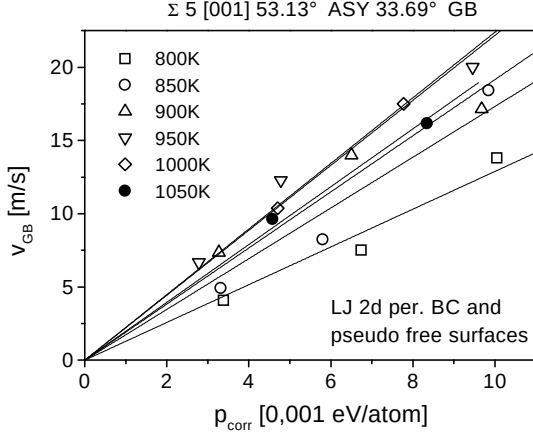


Figure 6.91: GB velocity versus orien.-corr. DF, p_{corr} , at different temperatures of the $\Sigma 5$ [001] 53.13° ASY33 tilt GB.

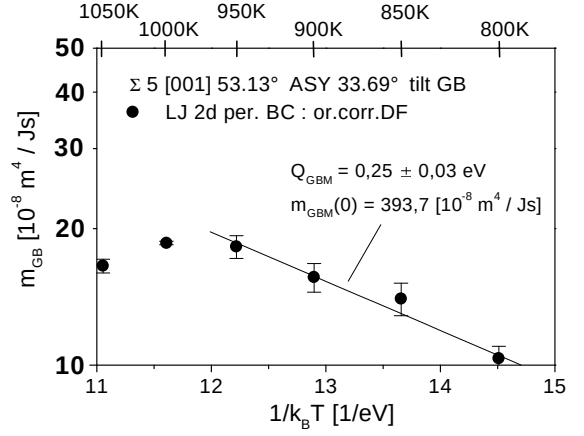


Figure 6.92: Arrhenius plot of the GB mobility for simulations with the orien.-corr. DF of the $\Sigma 5$ [001] 53.13° ASY33 tilt GB.

6.5 Discussion of the overall Planar Tilt GB Results

One main focus point of this work was to study GB migration of planar tilt GBs. An important necessary condition to do so is to find a suitable DF that can successfully drive the GB continuously. Looking back on the GB migration results of planar tilt GBs presented in the preceding chapters of this work, it becomes evident that the installation of driving force concepts that can successfully drive tilt GBs continuously is not a simple task. Following the positive results of GB migration of [001] twist GBs, it was believed that the installation of an elastic DF can successfully drive tilt GBs too. As was presented and explained in detail in section 6.3.1, an application of an elastic DF does not lead to continuous GB migration but only finite non-continuous migration distances. The main cause for this finding is that parts of the elastic installed strains are converted to plastic strain due to the initiation of GB glide events that lead to a disappearance of the initially present elastic DF. Usually due to the orientation of the bicrystalline grains of tilt GBs, strain components are needed to yield an elastic DF which as well drive GB sliding.

Hence an elastic DF approach can not be utilized when dealing with tilt GBs. The next step was to verify whether or not external stress states can be utilized to drive tilt GBs continuously. Here the underlying idea is that the GB dislocations can couple in with an external stress state which then leads to a Peach-Koehler type DF. For low-angle tilt GBs it is known from literature that such a DF concept works fine. In this work, GB migration of the low-angle $\Sigma 73$ [111] symmetrical GB was successfully studied utilizing a Peach-Koehler DF. Although the GBs were moving continuously and GB velocities could easily be extracted from the simulation runs for given external stress states, the DF issue is not as simple as expected. For the initial situation, the Peach-Koehler DF can be calculated on the basis of the underlying GB dislocation content of the studied GB. For low-angle GBs, these discrete GB dislocations can be found in the GB structure and the overall picture fits together nicely. Only one weakness of the approach is that the evolution of the system in the presence of shear stresses requires that the simulation box deforms according to a symmetric strain tensor. GB migration in the presence of external shear stresses is to different extents coupled with GB sliding. Again the applied shear stresses to the simulation

box intrinsically initiate GB sliding. According to the set external shear stress states and the boundary conditions of the simulation box evolution, inner grain rotations are observed during GB migration. According to this, during GB migration the GB becomes inclined to its initial orientation which in turn means that the Peach-Koehler DF does not remain constant during a simulation run. The temporal change of the DF depends on the level of GB sliding and hence GB rotation. For the studied $\Sigma 73$ [111] symmetrical GB, the grain rotation is small and hence does not have a big influence on the DF.

The application of the Peach-Koehler DF concept can only be utilized on tilt GBs that still show a discrete GB dislocation character. For truly high-angle GBs like the $\Sigma 5$ (210) symmetrical GB, an overlapping of the GB dislocation cores occurs wiping out the discrete nature of the discrete GB dislocations. Hence for such GBs, no Peach-Koehler DF is expected to drive these GBs continuously. The transition between the low-angle and high-angle regime is not sharply at 15° but the low-angle regime extends even to higher misorientation angles. Simulation results of the $\Sigma 13$ [001] tilt GB show that this GB can successfully be driven by the Peach-Koehler approach. Still the GB rate is rather small and at some temperatures even GB migration ceases. That the observed GB migration is truly connected to the Peach-Koehler DF is underlined by the direction of migration which was in agreement with the direction calculated by the standard Peach-Koehler analysis. This is important to note since the driving external stress states are shear stress that can initiate GB sliding too. If such shear stresses initiate GB sliding, this can be accompanied by GB migration. This was found for the $\Sigma 5$ (210) symmetrical tilt GB. Here the GB migration events occurred in directions opposed to the predicted direction of the Peach-Koehler analysis. Hence for the $\Sigma 5$ (210) symmetrical tilt GB, GB sliding was the elementary process occurring due to the external shear stresses which was just accompanied by GB migration. Such a scenario is not favourable with respect to determine GB migration mobility data. Since for such simulations, the magnitude of DF is not really known, no GB mobility can be obtained by such simulations.

According to this neither the elastic DF nor external shear stress states are either successful or convincing DF concepts to study continuous GB migration of tilt GBs. The way out of this dilemma has been the establishment of the novel DF concept of the orientation-correlated DF by this work. The idea to come up with such a concept was really driven by the failure of the other two mentioned concepts. The unique idea of the orientation-correlated DF concept is that the origin of the DF and possible occurring processes at a GB like GB sliding are uncoupled. Since the elastic DF as well as the Peach-Koehler DF concept rely on either strain or stress that will couple in with any GB, the uncoupling or the direct interaction of the DF and the GB had to be avoided in the orientation-correlated DF concept. Following the general idea of DFs where different magnitudes of excess energy are introduced into the grains depending on their orientation either i.e. by the density of dislocations, the stored elastic energy or magnetic energy, the basic idea of the orientation-correlated DF by introducing excess energy to the grains was born.

The results of the [001] twist GBs as well the results of the tilt GBs demonstrate that the orientation-correlated DF can be used successfully for planar twist as well as for symmetrical and asymmetrical planar tilt GBs. This has been a major breakthrough for studying continuous GB migration of planar tilt GBs. Although the orientation-correlated DF is not connected to a specific physical DF, its behaviour and features are those of a bulk DF. Details on the temperature and misorientation dependence were given for the [001] twist

GBs but the same results are true for tilt GBs.

The thermally activated processes of GB self-diffusion and GB migration were studied for the $\Sigma 5$ [001] symmetrical and asymmetrical tilt GBs while only GB migration due to an Peach-Koehler DF was studied for the $\Sigma 73$ [111] symmetrical tilt GB. The results of the $\Sigma 73$ [111] tilt GB demonstrate that indeed a Peach-Koehler DF can drive low-angle GBs continuously which was discussed earlier in one of the above paragraphs. It was found that the GB mobility data of the $\Sigma 73$ [111] tilt GB does not follow an Arrhenius behaviour and linearly decreases with increasing temperature. Hence no activation data could be extracted from the computed GB mobility data following the standard Arrhenius scheme. Still the GB mobility data lends itself to state that GB migration of the $\Sigma 73$ [111] tilt GB is not thermally activated which implies that the activation enthalpy must be nearly zero in case of a Peach-Koehler DF.

Due to the above-mentioned findings of the $\Sigma 73$ [111] symmetrical tilt GB, here the focus of discussion on thermally activated processes of tilt GBs relates to the results of the $\Sigma 5$ symmetrical and asymmetrical tilt GBs. Tab. 6.4 presents the obtained results of the activation parameters of GB migration and GB self-diffusion of the $\Sigma 5$ symmetrical and asymmetrical tilt GBs. The listed data of Tab. 6.4 allows one to make some general statements which

GB	Potential	Q_{GBM} [eV]	$m_{GBM}(0)$ [$10^{-8} \text{ m}^4/\text{Js}$]	Temp. regime	Q_{GBD} [eV]	$\frac{\delta \cdot D_{GB}(0)}{\Omega}$ [$\frac{1}{ps}$]
$\Sigma 5$ (210) ^a	EAM	0.64 ± 0.04	42270	One	0.59 ± 0.05	11.477
$\Sigma 5$ (210) ^b	EAM	0.67 0.36	83832 1456	Low High		
$\Sigma 5$ ASY14	LJ	0.20 ± 0.03	205.1	Low High	0.37 ± 0.02 0.98 ± 0.08	0.9390 3566.89
$\Sigma 5$ ASY33	LJ	0.25 ± 0.03	393.7	Low High	0.48 ± 0.06 1.31 ± 0.06	3.6487 176096

Table 6.4: GB migration and self-diffusion activation parameters of the studied $\Sigma 5$ [001] symmetrical and asymmetrical tilt GBs. The listed GB migration activation parameters are associated with the orientation-correlated DF.

^aGBM data obtained by simulations with adjustable h_{33} component.

^bGBM data obtained by simulations with adjustable $h_{22}, \dots, h_{33}$ components.

were in a similar way found for the activation parameters of the [001] twist GBs as well. Comparing the found GB self-diffusion and GB migration activation enthalpies of each tilt GB in the low temperature regime, the GB migration activation enthalpies are about half of the GB self-diffusion activation enthalpies. Interestingly approximately the same ratio was found for the studied [001] twist GBs. As well as for most of the studied [001] twist GBs, a sudden drop in GB mobility with increasing temperature at about 1000K was found for the asymmetrical [001] tilt GBs as well. It is further interesting to note that the symmetrical $\Sigma 5$ (210) tilt GB behaves a little different with respect to its activation parameters of GB self-diffusion and GB migration. Here for the low temperature regime, the GB migration enthalpy and the GB self-diffusion enthalpy are the same. At higher temperatures, the GB migration mechanism changes according to the found GB migration activation parameters having an activation enthalpy of about half of the low temperature activation enthalpy of GB

self-diffusion. Hence here again the ratio of approximately two between the GB self-diffusion and the GB migration enthalpy is found.

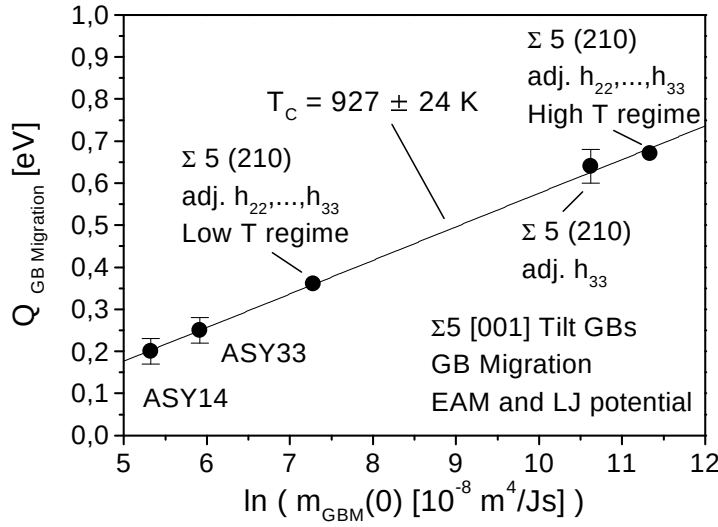


Figure 6.93: Compensation plot of the GB migration activation data of the studied $\Sigma 5$ [001] symmetrical and asymmetrical tilt GBs. LJ as well as EAM data are included in the plot. All data points lie one a single line which is associated with a compensation temperature, T_c , of 927K.

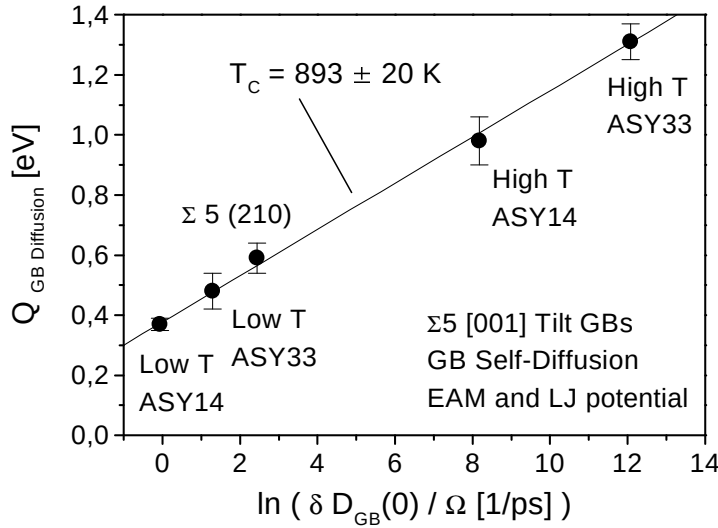


Figure 6.94: Compensation plot of the GB self-diffusion activation data of the studied $\Sigma 5$ [001] symmetrical and asymmetrical tilt GBs. LJ as well as EAM data are included in the plot. All data points lie one a single line which is associated with a compensation temperature, T_c , of 893K.

The next step is to do a compensation effect analysis of the GB migration and GB self-diffusion activation data. Here the LJ and EAM results are included in one analysis, since it was found for the $\Sigma 5$ [001] twist GB that the difference in activation enthalpy between LJ and

EAM data is quite small. Fig. 6.93 and 6.94 show the compensation plots of GB migration and GB self-diffusion, respectively. In both plots, all shown data points lie very well on a single line. Hence the determination of the corresponding compensation temperature can easily be done. For GB migration of the $\Sigma 5$ symmetrical and asymmetrical tilt GBs, a compensation temperature of 927K is found while a compensation temperature of 893K is found for the GB self-diffusion data. Both temperatures can be considered the same taking into account the found error bar of about 24K. This found compensation temperature is reflected by the Arrhenius plots of the GB mobility and the GB self-diffusion coefficient. Hence the overall found activation data of GB migration and GB self-diffusion and the data analysis with respect to the compensation effect give a consistent picture of the physical behaviour of the studied $\Sigma 5$ tilt GBs. Therefore the assumed structural transition of all studied $\Sigma 5$ tilt GBs in the range of 900K to 1000K seems convincing. The structural transition is a solid-state transition, most likely a disordering effect of the crystalline GB structure. It can not be associated with a truly liquid-state structure, since the comparison of the angular distribution of diffusive jump vectors of a truly liquid GB (see section 6.4.1.2) as well as the GB self-diffusion activation enthalpy of 0.39eV [64] of a truly bulk LJ metal liquid indicate and underline that this disordering effect must be of crystalline nature.

Chapter 7

Summary and Outlook

7.1 Summary and Outlook

In this work, atomistic GB migration and GB self-diffusion simulations of planar [001] twist GBs as well as various planar tilt GBs in face-centred cubic bicrystals have been presented. The utilized simulation method of choice was molecular dynamics. Due to the planar geometry of the studied GBs, no DF on the GB is exerted due to GB curvature. Therefore one necessary and important feature of this work was to derive DF concepts to drive planar GBs continuously within atomistic simulations. Two novel DF concepts within atomistic simulations were presented and discussed in detail in this work, namely an elastic DF concept as well as the so-called orientation-correlated DF concept. Both DFs are bulk concepts and their physical nature as well their physical behaviour are quite comparable.

[001] twist GBs - Extensive simulations were performed on planar [001] low-angle as well as high-angle GBs utilizing the elastic and orientation-correlated DF. Utilizing these concepts planar [001] twist GBs could be driven continuously. As expected according to general rate theory of GB migration, the computed GB velocity depended linearly on the installed DF in the system. The DF itself was computed in-situ during the conducted MD simulations in order to follow its temporal evolution. The GB velocity was extracted from GB position versus time plots. Performing numerous simulations at different DF magnitudes as well as temperatures, the temperature dependence of GB mobility was successfully computed. The computed activation parameters following an Arrhenius description reflected two GB regimes, namely a low-angle and a high-angle regime. The activation enthalpies of the [001] high-angle GBs as well as observed configurations of the displacement fields of atoms in distinct (002) planes of these GBs during the process of re-orientation reveal that at least some of the studied [001] high-angle twist GBs move by a collective shuffle mechanism. Here the shuffle mechanism usually involves a group of four atoms. Further analysis of the activation enthalpy following the concept of Mott [23] indicates that within the shuffle three to four atoms are involved. Additionally it was shown in this work that GB migration and GB self-diffusion are distinct different processes. For two of the studied [001] twist GBs, namely the $\Sigma 29$ and $\Sigma 5$ twist GB, a structural GB transition was observed indicated by the temperature behaviour of the activation enthalpies of GB migration and GB self-diffusion.

The physical properties of GB migration of [001] twist GBs either driven by an elastic DF

or orientation-correlated DF are equivalent. Only minor differences are observed for the found activation parameters of GB migration where usually the pre-exponential factor was slightly smaller for the orientation-correlated DF compared to the results of the elastic DF. The observed GB migration mechanism for both DF schemes is identical. Evenmore the found GB migration mechanism for the high-angle [001] twist GBs agrees perfectly fine with existing simulation literature on GB migration of curved GB systems.

The studied low-angle [001] twist GBs are characterized structually and related to GB migration properties like activation enthalpy and GB migration mechanism by their discrete screw dislocation network. Hence their GB migration properties are distinctly different from the high-angle twist GBs. Due to non-existing impurities in the studied atomistic GB bicrystals, the screw dislocation network of the studied low-angle GBs can move almost thermally non-activated. This is best exemplified by the results of the $\Sigma 181$ [001] twist GB.

Various tilt GBs - Since hardly any experimental data exists on GB migration of twist GBs and since tilt GBs are considered to dominate materials behaviour, the simulation efforts were extended to study various tilt GBs. According to the successful results of GB migration of [001] twist GBs in the presence of an elastic DF, the elastic DF concept was applied to symmetrical tilt GBs. Although finite distance GB migration could be achieved with the elastic DF, no truely continuous GB migration was achieved. Investigating this behaviour, it was found that the initially installed elastic DF was eventually decreasing to zero due to conversion effects of strain tensor components. It could be shown that strain tensor components necessary to yield an elastic DF were converted during the course of the simulations from being elastic into plastic strain components. This behaviour is connected to the finding that these strain tensor components initiate GB sliding which leads to the build-up of plastic strain. According to these findings, the elastic DF concept can not be successfully applied to symmetrical as well as asymmetrical tilt GBs to drive them continuously.

In a second approach, a Peach-Koehler DF concept was utilized. For low-angle tilt GBs this approach is suitable to drive GBs continuously which was exemplified for the $\Sigma 73$ [111] tilt GB. In case of the $\Sigma 73$ tilt GB it was found that GB migration is not thermally activated. Extending the Peach-Koehler method to the $\Sigma 5$ (210) high-angle tilt GB results in continuous GB migration as well although the migration direction is opposite as proposed by the Peach-Koehler analysis. Here it was demonstrated that the applied shear stresses lead to GB sliding which is coupled with GB migration. Since it is expected that usually high-angle GBs tend to GB sliding, the Peach-Koehler DF is not suited well to study continuous GB migration as well.

Finally utilizing the orientation-correlated DF on the $\Sigma 5$ (210) symmetrical as well as on two asymmetrical $\Sigma 5$ tilt GBs demonstrates that any tilt GB can be driven by the orientation-correlated DF concept. This result is a major highlight and breakthrough of this work since it demonstrates the successful implementation of the orientation-correlated DF concept to drive any kind of planar GB continuously. Again major aspects related to GB migration as mentioned above for the [001] twist GBs were found for the studied $\Sigma 5$ GBs as well. Again it is found that GB migration and GB self-diffusion are distinctly different processes. Again a structural GB transition is observed in the GB migration mobility data of the $\Sigma 5$ (210) symmetrical tilt GB. A similar effect is observed for the GB self-diffusion coefficient of the two studied asymmetrical tilt GBs where the activation enthalpy is increased by a factor of two to three in the high temperature range compared to the low temperature

one. Comparing the found GB self-diffusion and GB migration activation enthalpies of the asymmetrical tilt GBs in the low temperature regime, the GB migration activation enthalpies are about half of the GB self-diffusion activation enthalpies. Interestingly approximately the same ratio was found for the studied [001] twist GBs. As well as for most of the studied [001] twist GBs, a sudden drop in GB mobility with increasing temperature at about 1000K was found for the asymmetrical [001] tilt GBs as well.

It is further interesting to note that the symmetrical $\Sigma 5$ (210) tilt GB behaves a little different with respect to its activation parameters of GB self-diffusion and GB migration. Here for the low temperature regime, the GB migration enthalpy and the GB self-diffusion enthalpy are the same. At higher temperatures, the GB migration mechanism changes according to the found GB migration activation parameters having an activation enthalpy of about half of the low temperature activation enthalpy of GB self-diffusion. Hence here again the ratio of approximately two between the GB self-diffusion and the GB migration enthalpy is found.

Finally it was shown that the GB migration and GB self-diffusion activation data follow the compensation effect. For GB migration of the $\Sigma 5$ symmetrical and asymmetrical tilt GBs, a compensation temperature of 927K is found while a compensation temperature of 893K is found for the GB self-diffusion data. Both temperatures can be considered the same taking into account the found error bar of about 24K. This found compensation temperature is reflected by the Arrhenius plots of the GB mobility and the GB self-diffusion coefficient. Hence the overall found activation data of GB migration and GB self-diffusion and the data analysis with respect to the compensation effect give a consistent picture of the physical behaviour of the studied $\Sigma 5$ tilt GBs. Furthermore it was found for the asymmetrical tilt GBs that at a temperature of about 950K, GB sliding along the tilt axis occurs. This as well is an indication of structural changes within these GBs. Therefore the assumed structural transition of all studied $\Sigma 5$ tilt GBs in the range of 900K to 1000K seems convincing.

Outlook - The methods described in this work to study GB migration of planar GBs in atomistic simulations can now be used to study GB migration of any desired GB. This has become possible due to the introduction of the orientation-correlated DF concept. It is highly suggested to utilize this method to continue the study of atomistic simulations especially in the field of planar tilt GBs. The field of possible planar GBs is not restricted to face-centred cubic materials since the presented DF concepts can easily be adapted to different materials as for instance body-centred cubic materials.

Additionally it is suggested to put some effort into the introduction of additional lattice defects into the atomistic bicrystal models to study their impact on GB migration of planar GBs. Two aspects could be considered, namely segregation effects at GBs as well as to study random GBs where additional secondary GB dislocations are intrinsically introduced into the GB structure.

Due to the increasing computer power during recent and in the coming years especially in the low budget computer market, computational resources are available to do massive calculations on large scale atomistic systems. This is as well supported by the availability of the low cost computer operating system Linux which allows one even to build Linux clusters with rather limited costs (see i.e. the Beowulf clusters installed at the Interface Group in the MSD division at ANL by Phillpot and Thompson).

It is hoped and anticipated that the scientific community will continue to conduct scientific

research on planar GBs utilizing atomistic simulations. The driving force concepts are available and can be easily implemented in existing MD codes. It is expected that such simulations will reveal interesting aspects of GBs like further elucidating the field of GB structural transitions.

7.2 Zusammenfassung und Ausblick

In dieser Arbeit wurden atomistische Simulationen zur Korngrenzenbewegung und Korngrenzenselbstdiffusion von ebenen [001] Drehkorngrenzen als auch verschiedenen Kippkorngrenzen in kubisch-flächenzentrierten Bi-Kristallen präsentiert. Die Simulationsmethode der Wahl war Molekulardynamik (MD). Auf Grund der ebenen Geometrie der untersuchten Korngrenzen herrscht keine treibende Kraft auf Grund von Korngrenzenkrümmung vor. Daher war ein nötiger und wichtiger Teil dieser Arbeit treibende Kraftkonzepte zu entwickeln, um ebene Korngrenzen kontinuierlich in atomistischen Simulationen treiben zu können. Zwei neuartige treibende Kraftkonzepte innerhalb von atomistischen Simulationen wurden in dieser Arbeit aufgezeigt und im Detail diskutiert. Diese sind das elastische und das sogenannte orientierungsbezogene treibende Kraftkonzept. Beide Konzepte sind Bulk-Konzepte und ihre physikalische Natur wie auch ihr physikalisches Verhalten sind einander sehr ähnlich.

[001] Drehkorngrenzen - Ausgedehnte Simulationen wurden an ebenen [001] Kleinwinkel- als auch Großwinkelkorngrenzen unter Ausnutzung einer elastischen als auch orientierungsbezogenen treibenden Kraft durchgeführt. Unter Ausnutzung dieser Kraftkonzepte konnten die ebenen [001] Drehkorngrenzen kontinuierlich getrieben werden. Wie laut Rantentheorie erwartet, hing die berechnete Korngrenzengeschwindigkeit von der in das System eingebrachten treibenden Kraft linear ab. Die treibende Kraft selbst wurde in-situ während der durchgeführten MD Simulationen berechnet, um ihre zeitliche Entwicklung verfolgen zu können. Die Korngrenzengeschwindigkeit wurde aus Ort-Zeit-Diagrammen bestimmt. Durch Durchführung einer Vielzahl an Simulationen bei unterschiedlich großen treibenden Kräften als auch Temperaturen konnte die Temperaturabhängigkeit der Korngrenzenbeweglichkeit erfolgreich bestimmt werden. Die berechneten Aktivierungsparameter folgten einer Arrhenius Darstellung und zeigten zwei Korngrenzenbereiche auf, nämlich einen Kleinwinkel- und einen Großwinkelkorngrenzenbereich. Die Aktivierungsenthalpien der [001] Großwinkelkorngrenzen als auch die beobachteten Konfigurationen in den (002) in-plane Verschiebungsfeldern der Atome dieser Korngrenzen während des Umlagerungsprozesses während der Korngrenzenbewegung offenbarten, daß zumindest einige der untersuchten [001] Großwinkelkorngrenzen sich durch einen kollektiven Schiebemechanismus bewegen. Der kollektive Schiebevorgang beinhaltet normalerweise eine Gruppe von vier Atomen. Weitere Analysen bezüglich der gefundenen Aktivierungsenthalpien dem Konzept von Mott [23] folgend ergaben, daß innerhalb des Schiebevorganges drei bis vier Atome beteiligt sind. Weiterhin konnte in dieser Arbeit gezeigt werden, daß Korngrenzenbewegung und Korngrenzenselbstdiffusion getrennte unterschiedliche Prozesse sind. Für zwei der untersuchten [001] Drehkorngrenzen, nämlich der $\Sigma 29$ und $\Sigma 5$ Drehkorngrenze, wurde eine Strukturänderung beobachtet, die sich im Temperaturverhalten der Aktivierungsenthalpien für Korngrenzenbewegung und Korngrenzenselbstdiffusion zeigte.

Die physikalischen Eigenschaften für Korngrenzenbewegung von [001] Drehkorngrenzen getrieben durch entweder eine elastische oder die orientierungsbezogene treibende Kraft

entsprechen einander. Nur geringfügige Unterschiede wurden innerhalb der berechneten Aktivierungsparameter beobachtet, wobei häufiger gefunden wurde, daß der Präexponentialfaktor der Korngrenzenbeweglichkeit bei Vorliegen der orientierungsbezogenen treibenden Kraft kleiner ausfiel als bei Vorliegen einer elastischen treibenden Kraft. Der beobachtete Korngrenzenbewegungsmechanismus ist identisch für beide Kraftkonzepte. Weiterhin stimmt der gefundene Korngrenzenbewegungsmechanismus der [001] Großwinkeldrehkorngrenzen mit vergleichbarer Literatur ermittelt an einem gekrümmten Korngrenzensystem überein.

Die untersuchten [001] Kleinwinkeldrehkorngrenzen sind strukturell als auch bezogen auf ihre Korngrenzenbewegungseigenschaften wie z.B. ihrer Aktivierungsenthalpie oder ihrem Korngrenzenbewegungsmechanismus bestimmt durch ihr diskretes Netzwerk an Korngrenzenschraubenversetzungen. Daher sind ihre Korngrenzenbewegungseigenschaften eindeutig verschieden von denen der untersuchten Großwinkeldrehkorngrenzen. Auf Grund des nicht Vorhandenseins von jeglichen Verunreinigungen in den untersuchten atomistischen Bi-Kristallen kann sich das Netzwerk von Korngrenzenschraubenversetzungen quasi thermisch nicht aktiviert bewegen. Dieser Umstand wird am besten durch das Beispiel der $\Sigma 181$ [001] Drehkorngrenze verdeutlicht.

Verschiedene Kippkorngrenzen - Da kaum experimentelle Daten über Korngrenzenbewegung von Drehkorngrenzen existieren und da Kippkorngrenzen wesentlich das Materialverhalten dominieren, wurden die Simulationsanstrengungen auf verschiedene Kippkorngrenzen ausgeweitet. Auf Grund der erfolgreichen Ergebnisse mittels der elastischen treibenden Kraft an [001] Drehkorngrenzen wurde zuerst das Prinzip der elastischen treibenden Kraft auf symmetrische Kippkorngrenzen angewandt. Obgleich Korngrenzenbewegung über eine endliche Distanz erzielt werden konnte, konnte keine echte kontinuierliche Korngrenzenbewegung erzeugt werden. Bei näherer Untersuchung des Phänomens stellte sich heraus, daß die anfangs in das System eingebrachte elastische treibende Kraft allmählich auf Null abfiel, da Umwandlungseffekte bezüglich bestimmter Komponenten des Dehnungstensors stattfanden. Es konnte gezeigt werden, daß Dehnungstensorkomponenten, die für die elastische treibende Kraft unentbehrlich waren, während des Verlaufes der Simulationen von ihrem elastischen Zustand in plastischen umgewandelt wurden. Dieser Umstand ist mit der Tatsache verknüpft, daß exakt diese Dehnungstensorkomponenten Korngrenzen gleiten initiieren, welcher zum Aufbau von plastischer Dehnung führt. Auf Grundlage dieser Zusammenhänge zeigte sich, daß der elastische treibende Kraftansatz für symmetrische als auch asymmetrische Kippkorngrenzen nicht zu einer kontinuierlichen Korngrenzenbewegung führt.

In einem zweiten Ansatz wurde ein Peach-Koehler treibendes Kraftkonzept benutzt. Für Kleinwinkelkipkorngrenzen ist dieser Ansatz passend und führt zu einer kontinuierlichen Korngrenzenbewegung, was exemplarisch für die $\Sigma 73$ [111] Korngrenze gezeigt werden konnte. Im Falle der $\Sigma 73$ [111] Kippkorngrenze wurde thermisch nicht aktivierte Korngrenzenbewegung gefunden. Die Ausdehnung der Peach-Koehler Methode auf die $\Sigma 5$ (210) Großwinkelkorngrenze resultierte in kontinuierliche Korngrenzenbewegung, obgleich die Bewegungsrichtung entgegengesetzt zur prognostizierten Richtung laut Peach-Koehler stand. Es zeigte sich, daß die angewandten Scherspannungen zu Korngrenzengleiten führten, welches für diese Korngrenze mit Korngrenzenbewegung gekoppelt ist. Da man davon ausgehen kann, daß gerade Großwinkelkorngrenzen zu Korngrenzengleiten neigen, ist eine an die Peach-Koehler angelehnte treibende Kraft nicht geeignet, um systematisch kontinuierliche Korngrenzenbewegung zu untersuchen.

Unter Anwendung der orientierungsbezogenen treibenden Kraft konnte für die symmetrische $\Sigma 5$ (210) und für zwei asymmetrische $\Sigma 5$ Kippkorngrenzen gezeigt werden, daß jegliche ebene Kippkorngrenze durch das orientierungsbezogene Kraftkonzept kontinuierlich getrieben werden kann. Dieses Ergebnis ist ein wesentliches Highlight und ein Durchbruch innerhalb dieser Arbeit, der zeigt, daß die erfolgreiche Umsetzung des orientierungsbezogenen treibenden Kraftkonzeptes es ermöglicht eine jegliche ebene Korngrenze kontinuierlich zu treiben. Wesentliche Ergebnisse, die in ähnlicher Weise auch bei den [001] Drehkorngrenzen erzielt wurden, wurden für die untersuchten Kippkorngrenzen ebenfalls gefunden. Wiederum konnte gezeigt werden, daß Korngrenzenbewegung und Korngrenzenseibstdiffusion eindeutig unterschiedliche Prozesse darstellen. Weiterhin wurden auch hier Änderungen der Korngrenzenstruktur innerhalb der Korngrenzenbeweglichkeitsdaten der symmetrischen $\Sigma 5$ (210) Kippkorngrenze gefunden. Ein ähnliches Verhalten wurde für das Temperaturverhalten des Korngrenzenseibstdiffusionskoeffizienten der zwei untersuchten asymmetrischen Kippkorngrenzen beobachtet. In diesem Falle war die Aktivierungsenthalpie um einen Faktor zwei bis drei im Hochtemperaturbereich gegenüber dem Tieftemperaturbereich erhöht. Vergleicht man die berechneten Enthalpien für Korngrenzenbewegung und Korngrenzenseibstdiffusion der asymmetrischen Kippkorngrenzen im Tieftemperaturbereich, so ergibt sich, daß die Korngrenzenbewegungsenthalpie ungefähr die Hälfte der Enthalpie für Korngrenzenseibstdiffusion ausmacht. Erstaunlicherweise wurde ein ähnliches Verhältnis bei den untersuchten [001] Drehkorngrenzen gefunden. Vergleichbar zu den untersuchten [001] Drehkorngrenzen wurde bei den beiden asymmetrischen Kippkorngrenzen ein plötzlicher Abfall der Korngrenzenbeweglichkeit bei circa 1000K beobachtet.

Es ist weiterhin interessant, daß sich die symmetrische $\Sigma 5$ (210) Kippkorngrenze ein wenig anders bezüglich ihrer Aktivierungsparameter für Korngrenzenbewegung beziehungsweise Korngrenzenseibstdiffusion verhält. Hier findet man für den Tieftemperaturbereich, daß die Enthalpie für Korngrenzenbewegung und Korngrenzenseibstdiffusion annähernd gleich sind. Zu höheren Temperaturen hin wechselt der Korngrenzenbewegungsmechanismus laut der gefundenen entsprechenden Aktivierungsparameter für Korngrenzenbewegung. Hierbei findet man nun, daß die Aktivierungsenthalpie für Korngrenzenbewegung ungefähr der Hälfte der Aktivierungsenthalpie für Korngrenzenseibstdiffusion entspricht. Entsprechend wird hier wieder ein Verhältnis von zwei bezüglich der Aktivierungsenthalpien gefunden.

Abschließend wurde gezeigt, daß die Aktivierungsparameter für Korngrenzenbewegung als auch für Korngrenzenseibstdiffusion dem Kompensationseffekt folgen. Eine Kompensationstemperatur von 927K wurde für die Korngrenzenbewegungsdaten der symmetrischen bzw. asymmetrischen $\Sigma 5$ Kippkorngrenzen gefunden. Bezüglich der Korngrenzenseibstdiffusionsdaten ergab sich für diese Korngrenzen eine Temperatur von 893K. Beide Temperaturen entsprechen einander unter der Berücksichtigung des gefundenen Fehlerbalkens von ungefähr 24K. Die ermittelte Kompensationstemperatur wird in den entsprechenden Arrhenius-Diagrammen der Korngrenzenbewegung bzw. Korngrenzenseibstdiffusion wiedergefunden. Die gesamten gefundenen Aktivierungsdaten fügen sich zu einem konsistenten physikalischen Bild dieser Korngrenzen zusammen. Weiterhin wurde für die asymmetrischen Kippkorngrenzen beobachtet, daß bei circa 950K Korngrenzengleiten entlang der Kippachse eintritt. Dieses Verhalten wird ebenso mit der Strukturänderung dieser Korngrenzen in diesem Temperaturbereich in Zusammenhang gebracht. Alles in allem erscheint daher die Schlußfolgerung einer tatsächlichen Strukturänderung dieser Kippkorngrenzen sehr überzeugend und schlüssig.

Ausblick - Die in dieser Arbeit beschriebenen Methoden zur Untersuchung von Korngrenzenbewegung von ebenen Korngrenzen mittels atomistischer Simulationen können nun angewandt werden, um Korngrenzenbewegung einer jeglichen ebenen Korngrenze zu untersuchen. Dies ist durch die Einführung des orientierungsbezogenen treibenden Kraftkonzeptes ermöglicht worden. Es wird empfohlen, dieses Kraftkonzept weiterhin zu benutzen, um atomistische Simulationen gerade im Bereich der ebenen Kippkorngrenzen zu verwenden. Das Anwendungsgebiet ist nicht begrenzt auf flächenzentrierte kubische Systeme, sondern kann einfach an unterschiedlichste Materialien wie z.B. raumzentrierte kubische Systeme angepaßt werden.

Weiterhin wird empfohlen, Anstrengungen zu unternehmen, um die Berücksichtigung weiterer Gitterdefekte in den atomistischen Bi-Kristallsimulationen zu berücksichtigen, um ihren Einfluß auf die Korngrenzenbewegung ebener Korngrenzen zu studieren. Besonders zwei Aspekte könnten berücksichtigt werden, nämlich Segregationseffekte an Korngrenzen als auch Untersuchungen an allgemeinen Korngrenzen, die sich dadurch auszeichnen, daß sekundäre Korngrenzenversetzungen innerhalb der intrinsischen Struktur der Korngrenzen eingebracht werden.

Auf Grund der stetig ansteigenden Computerleistung innerhalb der letzten Jahre besonders im Bereich der Niedrigpreiscomputer stehen Rechenkapazitäten zur Verfügung, um massive Berechnungen an großen atomistischen Systemen durchführen zu können. Dies wird weiterhin dadurch unterstützt, daß das Niedrigpreis-Betriebssystem Linux zur Verfügung steht, welches einem unter anderem ermöglicht, Linuxcluster mit geringfügigem finanziellen Aufwand zu realisieren (siehe z.B. die Beowulf-Linuxcluster installiert in der Interface Group in der MSD Division am ANL durch Phillpot und Thompson).

Es wird gehofft, daß die wissenschaftliche Welt die hier beschriebenen Ansätze aufgreifen wird, um weitere wissenschaftliche Arbeiten zum Themenkreis der atomistischen Simulation der Korngrenzenbewegung an ebenen Korngrenzen durchzuführen. Die treibenden Kraftkonzepte stehen zur Verfügung und können einfach in existierende MD-Codes implementiert werden. Man kann von solchen Simulationen erwarten, daß weitere interessante Aspekte über Korngrenzen gefunden werden, die z.B. ein tieferes Verständnis für den Bereich der Strukturübergänge innerhalb von Korngrenzen ergeben werden.

Appendix A

Contents of the CD

Included in this work is a CD that contains examples of the observed GB migration mechanism of either twist or tilt GBs. The examples are provided by animated GIF sequences in a web browser environment. In order to view the examples, please open a standard web browser and then open the HTML file called **start.html** which is found on the CD in the directory CD. Please note that in the subdirectory structure of the CD the animated GIF files are provided and can be found. These animated GIFs were built with the Professional Gif Construction Set by Alchemy Mindworks.

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Diplomthema : "Bestimmung effektiver Elektronenmassen und longitudinal-optischer Phononenmoden in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ durch Fitangepassung von Magnetowiderstandssoszillationen"
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Berufliche Tätigkeiten

08/1986 - 10/1986 Werksstudent im VW-Werk in Salzgitter-Thiede
10/1990 - 12/1990 studentische Hilfskraft in der Praktikumsbetreuung
04/1994 - 06/2000 wissenschaftlicher Mitarbeiter am Institut für Metallkunde und Metallphysik, RWTH Aachen
01/1995 - 02/1996 : Forschungsaufenthalt am Argonne National Laboratory, Argonne, USA in der Interface Group innerhalb der Materials Science Division als Stipendiat des Deutschen Akademischen Austauschdienstes innerhalb des HSP II/AUFE Programms
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