

Interfaces in Fluid-Dynamic Simulations of Single Droplets in Liquid-Liquid Systems

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Evangelos Bertakis

Berichter: Univ.-Prof. Dr.-Ing. Andreas Pfennig
Univ.-Prof. Dr.-Ing. André Bardow

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Foreword

The present work was conducted during my employment as a scientific associate at the Chair of Thermal Process Engineering of the RWTH Aachen University within the framework of the Collaborative Research Center CRC-540, funded by the Deutsche Forschungsgemeinschaft (DFG).

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Chapter 1

Introduction

In this chapter, the basic concepts and challenges involved in liquid-liquid extraction that constitute the grounds and the motivation of the present work are examined (Sec. 1.1). The targets thus set to accomplish and the organization behind the current work are presented in Sec. 1.2. Finally, an overview of the following chapters is given in Sec. 1.3.

1.1 Motivation

Liquid-liquid extraction is a method for removing a waste substance or a valuable product (transfer component) out of a liquid phase (donor phase) by adding a second liquid phase (receptor phase). This process is presented in Fig. 1.1 (left) where by mixing the two phases the transfer component (B) is extracted from the donor phase (A) into the receptor phase (C) until equilibrium is reached. A large interfacial area and a high concentration difference between the two liquid phases enhance mass transfer. The large interfacial area is realized by dispersing one of the two phases into the other in the form of small droplets (dispersed phase). Inside the extraction column the droplets are sedimenting upwards or downwards depending on the density difference between the two phases. The other phase (continuous phase) flows in counter current to the dispersed phase as depicted in Fig. 1.1 (right). The extraction process, therefore, can be modeled by focusing on its most fundamental element, i.e. a single droplet. Thus, the properties and the behavior of single droplets are elementary for the design of liquid-liquid-extraction apparatuses (Henschke, 2003).

1.1.1 Liquid-liquid extraction and single droplets

The study of single droplets involves the investigation of various phenomena and processes that can be performed in various levels of complexity, including:

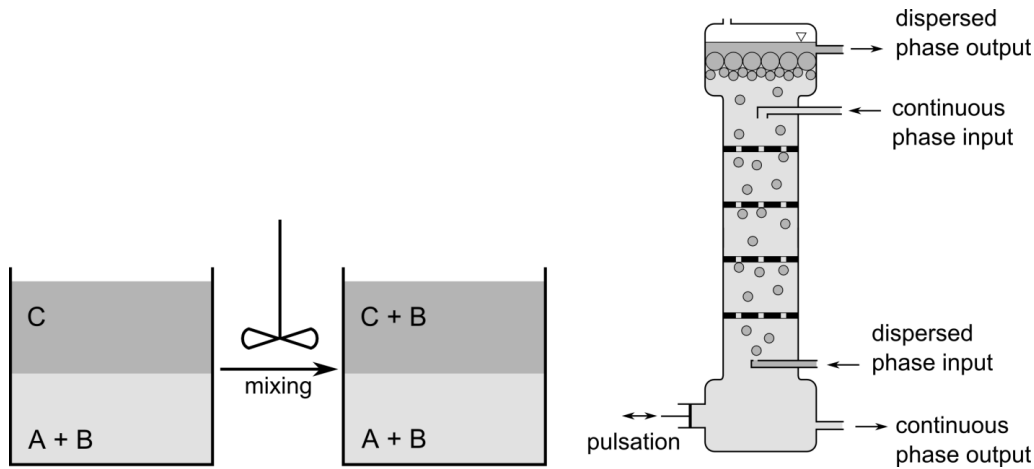


Figure 1.1: Principle of liquid-liquid extraction (left) and schematic representation of an extraction column (right).

- the transfer of a component through the droplet interface,
- the transfer of a surfactant component on the droplet interface,
- the sedimentation of droplets, single or in swarm,
- the effects of surface active agents,
- interfacial instabilities,
- the fluid flow inside and outside the droplet,
- droplet formation through an orifice or nozzle,
- droplet deformation, oscillation and breakup,
- droplet coalescence with another droplet or with a flat interface,
- droplet interaction with a vessel wall, sieve trays or packings.

The list above refers to issues regarding liquid-liquid extraction, although the same issues emerge if bubbles instead of droplets are considered. In other applications additional phenomena may be of interest like droplet precipitation and dissolution in a continuum, heat transfer, interfacial reactions and so on. A more in-depth presentation of liquid-liquid extraction issues can be found in the work of Thornton (1992).

These phenomena can be studied either isolated from each other or combined, with the utmost purpose to accurately describe the extraction process, and more specifically the mass transfer between the dispersed and the continuous phase. The key properties concerning mass transfer are:

- the concentration of the transfer component inside the droplet,
- the sedimentation velocity,
- the droplet population statistics.

These can be modeled either with semi-empirical algebraic equations, or with the help of numerical techniques as functions of time, droplet size and other factors. In addition, respective experimental investigations must be performed in order to support the development and the evaluation of the theoretical models. Such models and experimental data are provided as input for the software ReDrop, that was developed at the AVT-Thermal Process Engineering of the RWTH Aachen University and describes the complete extraction process based on the properties of single droplets (Henschke, 2003). This is achieved by theoretically dividing the extraction column in vertical sections in which droplets that represent the dispersed phase are distributed. For every droplet, the sedimentation and the mass transfer are described as functions of droplet size, droplet age, local concentration and holdup. The droplet population statistics are modeled by a stochastic process that determines whether a certain droplet will break into smaller droplets or will coalesce with a neighboring droplet. The operation time of the apparatus is discretized and in every timestep the concentration and the holdup are determined for every column section by balance equations, thus providing the conditions for the next iteration over time. Using this algorithm, a dynamic simulation of the extraction column is possible that can take various operational conditions into account.

The ultimate goal is to use ReDrop for designing industrial-scale extraction columns without the need for any pilot-plant investigations. The scale-up is thus performed directly from single-droplet laboratory experiments to the full-sized apparatus. Nevertheless, in order for trustworthy results to be obtained, robust and accurate models for the sedimentation and mass transfer are required. Furthermore, considerable experimental effort is needed for the precise measuring of the data necessary for fitting the model parameters. Therefore, focus is given on improving the reliability of the physical models that describe the properties of single droplets by better understanding the underlying phenomena and on replacing the laboratory experiments by computer simulations.

1.1.2 Challenges

Many of the phenomena that govern the behavior of single droplets are interrelated and have not yet been fully investigated in spite of their importance. This is most notably evident when considering the effects of surfactants and solute mass transfer on the fluid dynamics of the interface and, therefore, on the droplet internal circulation and sedimentation velocity.

If surfactants and mass-transfer effects are studied together, only their collective effects can be investigated, and it often becomes hard to trace the observed phenomena back to their respective causes. For example, a reduced droplet sedimentation velocity, as will be presented below, can be the effect of synergy between the presence of surfactants and interfacial instabilities induced by mass transfer. On the other hand, decoupling the surfactant and the mass transfer effects allows their separate

study and the development of theoretical models. However, this decoupling eliminates the influence that each has on the other, thus creating the assumption that the mechanisms of the individual phenomena will remain unaltered when the surfactant and the mass transfer models are combined.

In addition, due to the nature of the phenomena involved in the study of single droplets, a number of unknowns exist as parameters in the semi-empirical models that are used for designing extraction columns (Henschke, 2003). These parameters need to be fitted to data obtained in single-droplet sedimentation and mass-transfer experiments. Since conducting such experiments is not trivial, the reliable design of extraction columns remains a difficult task (Groß-Hardt, 2007).

In the coming two sections, the two main sources of complexity in the modeling of droplets and interfacial phenomena in liquid-liquid extraction systems, namely the interfacial instabilities induced by mass transfer and the effects of surfactants, are presented.

Interfacial instabilities

It has been found (Henschke, 2003; Wegener et al., 2007a) that the transfer of a component through the droplet interface during sedimentation leads to smaller droplet velocities compared to those measured in the absence of mass transfer. In a CFD simulation, the mass transfer is modeled by taking a convection and a diffusion term into account and is, therefore, dependent on the fluid flow inside and outside the droplet. In addition, the diffusion coefficient is usually so small that the mass transfer is dominated by the convection term (Nguyen, 2009). However, the mass transfer has no way of affecting the simulated flow if the physical properties of the system, i.e. the interfacial tension, the density and the viscosity, are not considered functions of concentration (Mao et al., 2001; Wang et al., 2008). Thus, the mass transfer and the fluid flow are decoupled and the effect of mass transfer on the sedimentation velocity cannot be simulated under these circumstances (Waheed, 2001).

Various authors have shown, (Wang et al., 2011; Schulze, 2007; Wegener et al., 2007b, 2009; Wegener, 2009; Burghoff, 2005; Burghoff and Kenig, 2006; Engberg and Kenig, 2012; Mao and Chen, 2004) that by introducing a local dependency of the interfacial tension on the concentration of the transfer component, the effect of the mass transfer on the system fluid dynamics can be simulated. Because the interfacial tension is lower where the solute concentration is higher, the inhomogeneous solute concentration on the droplet surface (Schombacher and Bauckhage, 1997) leads to interfacial tension gradients that induce forces which influence the fluid flow (Bird et al., 2002). The origin of the concentration inhomogeneity has been attributed to the formation of micro droplets at the vicinity of the interface based on simulations at the molecular level (Hartmann et al., 2005; Schott and Pfennig, 2004; Pfennig, 2000; Merzliak et al., 2002). The interfacial tension gradients may result to ordered flow

structures at the interface called “rolling cells” (Ruckenstein and Berbente, 1964, 1970; Ruckenstein et al., 1970; Henschke, 2001), or more random disturbances referred to as “interfacial instabilities” or “interfacial turbulence” (Fig. 1.2). These effects have been experimentally observed in the past (Hirschmann, 2007; Erkol, 2006; Sorensen, 1979; Bakker et al., 1967, 1966; Linde et al., 1967; Ellis and Biddulph, 1966; Austin et al., 1966; Maroudas and Sawistowski, 1964; Davies and Rideal, 1961) and various efforts have been made to predict and simulate their appearance (Sterling and Scriven, 1959; de Ortiz and Sawistowski, 1973a,b; Slavtchev et al., 1998; Grahn, 2006).

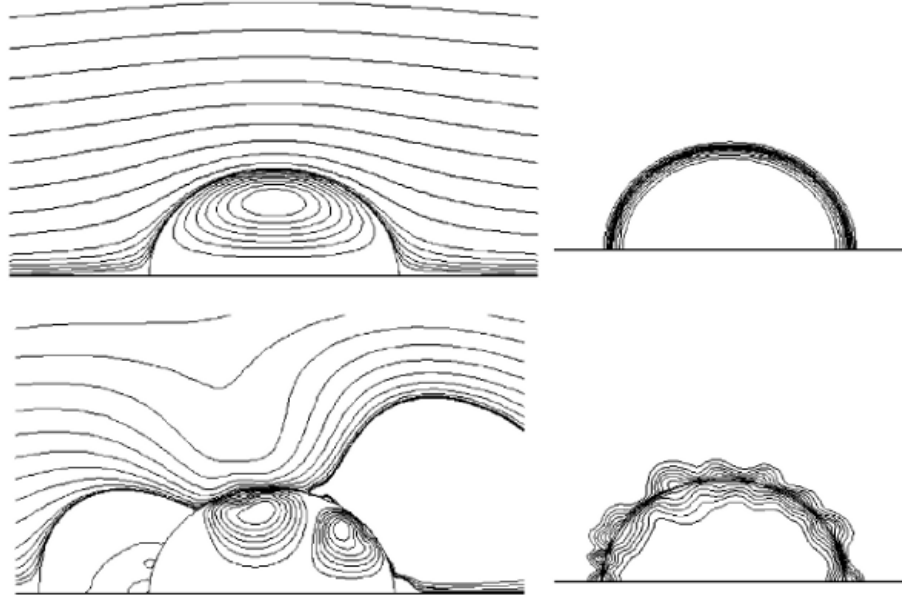


Figure 1.2: Streamlines (left) and concentration contours (right) according to Mao and Chen (2004) at the beginning of the droplet simulation (top) and when interfacial instabilities were noted (bottom).

As a result of the interfacial instabilities, the internal circulation of the droplet is distorted, which leads to a lower sedimentation velocity than in the ideal case because of the increased drag. In spite of the slower droplet movement, the interfacial instabilities also cause an acceleration of the mass transfer because of the enhanced mixing (Clift et al., 1978; Sawistowski, 1973) and interface renewal phenomena (Thornton and Anderson, 1981; Thornton et al., 1985; Javed et al., 1989) that are not being taken into account in many simulations (Altunok, 2009; Groß-Hardt et al., 2003). This is another source of discrepancy between numerical simulations and experimental investigations (Skelland and Wellek, 1964) that causes particular concern: if the drag is increased in a simulation by assuming a rigid interface so that the sedimentation velocity is realistically calculated, the resulting decrease of convection makes the mass transfer even slower (Groß-Hardt et al., 2006). Therefore, the preferred workaround in this case has been to parametrically incorporate the ef-

fect of interfacial instabilities into algebraic mass-transfer models (Henschke, 2003; Wegener and Paschedag, 2011) and to assume an artificially enhanced mixing inside the droplet (Handlos and Baron, 1957; Wellek and Skelland, 1965).

Surfactant effects

Another factor that can influence the interfacial tension, and thus the general behavior of droplets, is the existence of surface active components (surfactants) that are either used as additives or are found as impurities in liquid-liquid systems. Most notably, they hinder the mass transfer of a solute through the interface (Hashem, 2005; von Reden, 1998), they prevent droplet coalescence (Giribabu and Ghosh, 2007; Skelland and Caenepeel, 1972; Janssen and Anderson, 2011), and decrease the sedimentation velocity by making the interface more rigid (Alves et al., 2005; Harper, 2004; Farley and Schechter, 1966; Skelland et al., 1987; Zhang and Finch, 2001).

Since surfactant molecules decrease the interfacial tension of the system, their transport on a liquid-liquid interface results to similar instabilities as in the case of solute transfer (Kovalchuk and Vollhardt, 2006). However, in the case of droplet extraction the presence of surfactants hinders the mass transfer by damping both the interfacial turbulence (Nitsch and Hoffmann, 1981) and the convective transport at the interface (Lode and Heideger, 1970). In Fig. 1.3 an example is given of the solute mass transfer obstruction due to surfactants according to the findings of Beitel and Heideger (1971). Nevertheless, for systems known to exhibit interfacial instabilities the addition of surfactant can also have the opposite effect and enhance mass transfer by further augmenting interfacial convection depending on whether the surfactant is ionic or non-ionic (Mendes-Tatsis and Agble, 2000).

Various researchers have suggested that the coverage of the droplet surface with surfactants also increases the mass-transfer resistance at that interfacial region due to supposed physicochemical interactions between the solute molecules and the surfactants (Hutchinson, 1948; Garner and Hale, 1953; Garner and Skelland, 1956; Mudge and Heideger, 1970). In the limiting case, the part of the droplet interface that is covered with surfactants would be rendered totally inaccessible to the solute, thus decreasing the interfacial area that is “available” for mass transfer (Huang and Kintner, 1969). The existence and the role of the interfacial barrier has been a topic of debate in the past, (Boye-Christensen and Terjesen, 1958, 1959; Holm and Terjesen, 1954; Lindland and Terjesen, 1956; Melhus and Terjesen, 1957; Thorsen and Terjesen, 1962; Cullen and Davidson, 1956) but early studies did not take into account the effect of the surfactants on the interfacial tension and their subsequent impact on the fluid dynamics (Davies and Mayers, 1961). On the other hand, one can not dismiss the possibility that molecular interactions at the interface between the surfactant and the solute molecules may have an effect on the mass transfer (Mudge and Heideger, 1970; Borwankar and Wasan, 1986; Quintana, 1990). There-

fore, a more complete simulation approach would need to take both the hydrodynamic and the molecular effects of surfactants into account, but the simultaneous modeling of phenomena at the mesoscopic (droplet fluid dynamics) and the microscopic scale (molecular interactions) is a very challenging task.

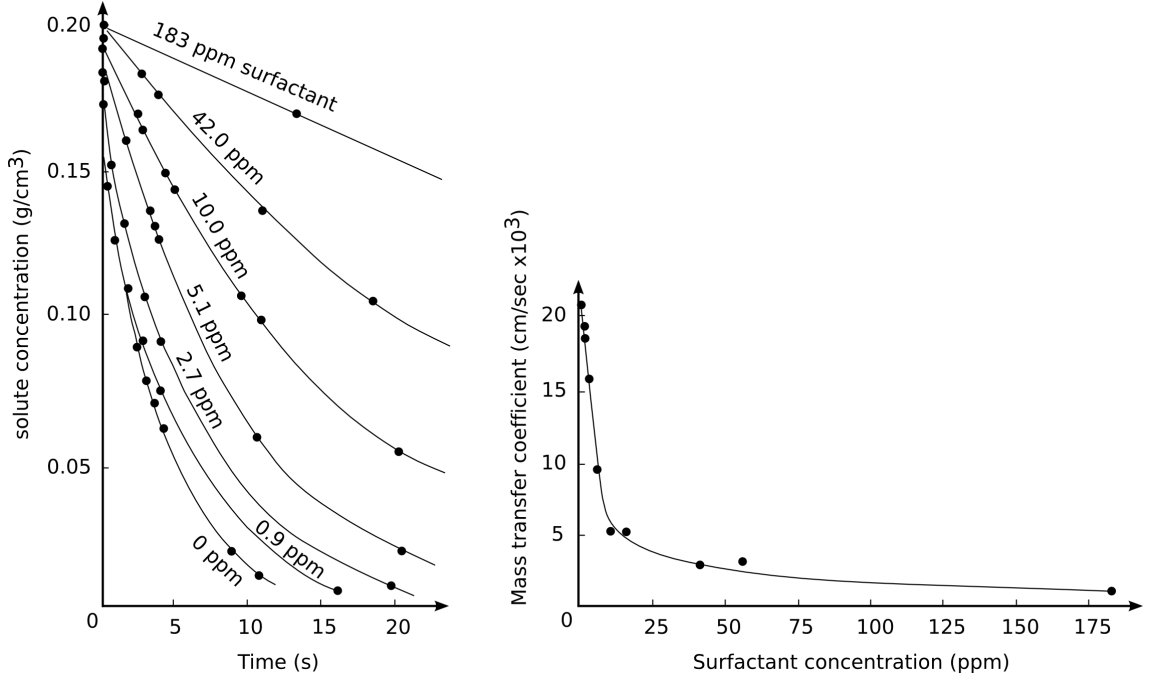


Figure 1.3: Solute extraction (left) and mass-transfer coefficient (right) at different surfactant concentrations according to Beitel and Heideger (1971). The dispersed phase was a mixture of benzene, carbon tetrachloride and Primol 355. The continuous phase was water, the transferred component was methyl carbitol and the non-ionic surfactant was Triton X-100.

Regardless on whether mass transfer is hindered by an interfacial barrier obstruction or by dampened interfacial convection, the effective droplet surface appears smaller. Thus, although the hydrodynamic approach is considered more appropriate (Lee et al., 1998), the surfactant influence may be handled by subtracting the interfacial area covered by surfactants from the total droplet surface (Li et al., 2003). In another approach, an additional mass-transfer resistance can be simply introduced in the mass-transfer model (Dehkordi et al., 2007), or a contamination factor can be fitted to experimental data in order to take the reduced mobility of the interface into account (Slater, 1995; Ghalehchian and Slater, 1999; Cauwenberg et al., 1997; Amokrane et al., 1994). A predictive model of the same mentality has also been suggested by Ashrafizadeh et al. (2008). Finally, the convective mass transfer can be omitted altogether and an effective diffusion coefficient can be fitted to experimental data (Slater et al., 1988; Liang and Slater, 1990).

1.2 Objectives

Since the mass transfer in liquid-liquid dispersions is dominated by convection and surfactant molecules have a significant impact on the hydrodynamics of the system, an important step towards a reliable modeling would be to correctly describe the fluid flow inside and outside the droplet. In addition, in order for a physical model to be usable in industrial applications, it should provide trustworthy results for a wide range of droplet diameters and surface-tension values. Furthermore, its accuracy should be validated with the help of experimental data.

The present project work was conducted at the AVT-Thermal Process Engineering of the RWTH Aachen University as a follow-up of the work performed by Groß-Hardt (2007) and Waheed (2001) and was part of the interdisciplinary Collaborative Research Center CRC-540 funded by the Deutsche Forschungsgemeinschaft (DFG). The objective was to develop and test an interfacial tension model for simulating the effect of surface-active impurities on the internal flow of single droplets. For this purpose, three other institutes of the RWTH Aachen University also contributed their know-how. The projects of the Collaborative Research Center CRC-540 that performed research in the field of single droplets were:

- Project B1, Institute for Macromolecular Chemistry:
 - developed NMR sequences for measuring the fluid flow in liquid-liquid systems,
 - measured vector plots of the fluid velocities inside a levitated liquid droplet.
- Project B3, AVT-Thermal Process Engineering (this work):
 - designed the experimental setup for stably levitating an organic droplet in an aqueous counter-current (performed by Groß-Hardt (2007)),
 - developed an interfacial-tension model for simulating the effects of surfactant impurities on the fluid flow,
 - provided a framework for the comparison of the model to the experimental data.
 - evaluated the model results by comparing them to experimental data and engineering models.
- Project B4, Chair of Numerical Mathematics:
 - authored the CFD program “DROPS” for the dynamic simulation of single droplets with a deformable interface and a high interfacial tension,
 - implemented the interfacial tension model in the simulation code.
- Project C5, Chair for Scientific Computing:
 - provided a platform for solving the inverse problem, i.e. the fitting of the model parameters to the experimental data.

An overview of this collaboration is given in Fig. 1.4, where the information flowing between the projects is also being specified.

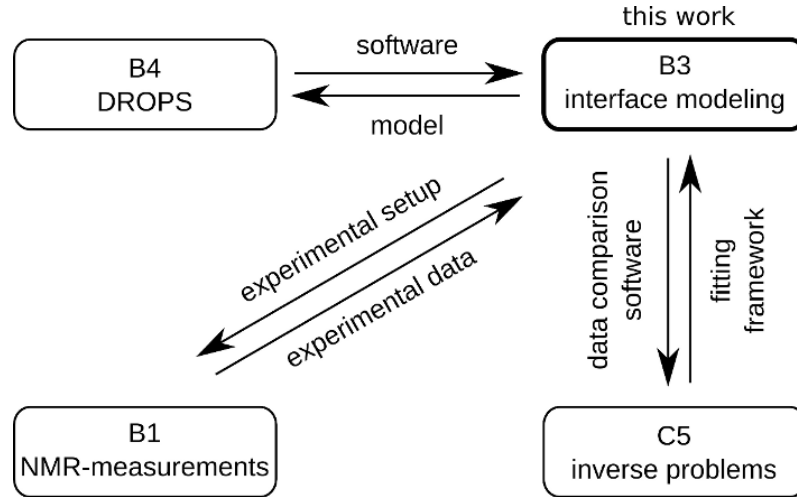


Figure 1.4: Collaborations between the projects of CRC-540 that focused on the study of single droplets.

1.3 Overview

In chapter 2, the modeling and experimentation techniques on single droplets in liquid-liquid systems is presented. In chapters 3 and 4 the experimental data and the simulation software that were provided by third parties for the needs of this work are analyzed respectively. The proposed model as well as the technique for comparing its results to the experimental data are presented in chapter 5. The obtained intermediate and final results are discussed in chapter 6, where a critical evaluation of the model and a comparison to the experimental data takes place. Finally, a summary and the conclusions of the present work are given in chapter 7.

Chapter 2

Single droplets: state of the art

In this chapter, the modeling (Sec. 2.1) and the experimental (Sec. 2.2) techniques currently available for the study of single droplets are presented. Since the literature covering single droplets is vast, a selection of issues relevant to this work is made. The topics considered include the sedimentation of single droplets (Sec. 2.1.1), droplet deformation (Sec. 2.1.2) and interfacial stagnation (Sec. 2.1.3). Focus is given on the experimental technique for quantifying the internal flow of single droplets by means of Nuclear Magnetic Resonance (Sec. 2.2.1). In Sec. 2.2.2 other methods for flow visualization are discussed.

2.1 Theory and modeling

The mobility of the interface, i.e. the extent by which the motion of the droplet with respect to the continuous phase induces a toroidal circulation inside the droplet, is directly coupled to the sedimentation velocity of the droplet (Clift et al., 1978). In addition, the interfacial tension influences the droplet shape, which is also coupled to the sedimentation velocity. Since the presence of surface-active components in the system influences the interfacial tension and may even induce interfacial stagnation, the sedimentation velocity and the droplet shape will also be affected. It is, therefore, appropriate to examine how these issues, namely droplet sedimentation and deformation as well as internal circulation and interfacial stagnation due to surfactants, have been investigated in the past.

2.1.1 Droplet sedimentation

By using the dimensionless Morton (Mo), Eötvös (EO) and Reynolds (Re) numbers, Clift et al. (1978) correlated sedimentation data and empirical information concerning the shape of sedimenting fluid particles to provide a generalizing refer-

ence chart on droplet and bubble behavior that is presented in Fig. 2.1. This graph was found valid in various publications (Smolianski et al., 2004; Smolianski, 2005; Darmana et al., 2006), and is also used in this work for evaluating the output of the simulation software.

For a given liquid-liquid system, the sedimentation velocity of a droplet can be correlated to its diameter, thus producing a curve like the one in Fig. 2.2. In the figure, the different regions of rigid, circulating, oscillating and deformed droplets can be seen. As the steady-state sedimentation velocity increases with droplet size because of the higher buoyancy, a critical diameter is reached where the flattened droplet shape leads to a higher hydrodynamic resistance. Beyond that diameter, the sedimenting droplet starts to oscillate and its terminal velocity decreases (Hu and Kintner, 1955; Schroeder and Kintner, 1965).

However, if the droplet is under the influence of surfactants or solute mass transfer, the interface will not be ideally mobile, and the curve shape will change (Henschke and Pfennig, 1999; Thorsen et al., 1968; Mekasut et al., 1979b,a). As the interface becomes partially mobile, the curve will shift downwards, thus depicting the lower sedimentation velocities that result. The sedimentation curve will reach its lowest limit when the interface becomes fully rigid (Henschke, 2003).

The shape of the curve in Fig. 2.2 has been experimentally confirmed by many authors in the past, not only for the case of liquid-liquid systems (Licht and Narasimhamurthy, 1955; Hu and Kintner, 1955; Klee and Treybal, 1956), but for gas-liquid systems as well (Koebe, 2004; Stuke, 1952). Experimental data of the instantaneous droplet velocity as a function of time obtained using a high speed camera can be found in Wegener et al. (2007a) and Wegener et al. (2010). Data of the droplet vertical position as a function of time were published by Henschke (2003).

Mack (2001) presented a criterion for categorizing the droplets according to their diameter and material properties in rigid, circulating, or oscillating droplets. The categorization is performed according to the following semi-empirical relations:

$$\text{rigid droplets:} \quad Ar \leq \frac{1.83}{Mo^{0.275}} \quad (2.1)$$

$$\text{circulating droplets:} \quad \frac{1.83}{Mo^{0.275}} \leq Ar \leq \frac{391}{Mo^{0.275}} \quad (2.2)$$

$$\text{oscillating droplets:} \quad \frac{391}{Mo^{0.275}} \leq Ar \leq \frac{1.31 \times 10^4}{Mo^{0.275}} \quad (2.3)$$

where Ar is the Archimedes number and Mo is the Morton number. From these relations, the droplet state can be estimated depending on the droplet diameter. Such categorizations can be used for defining the range of applicability for various equations for calculating the sedimentation velocity of fluid particles as presented by Peebles and Garber (1953).

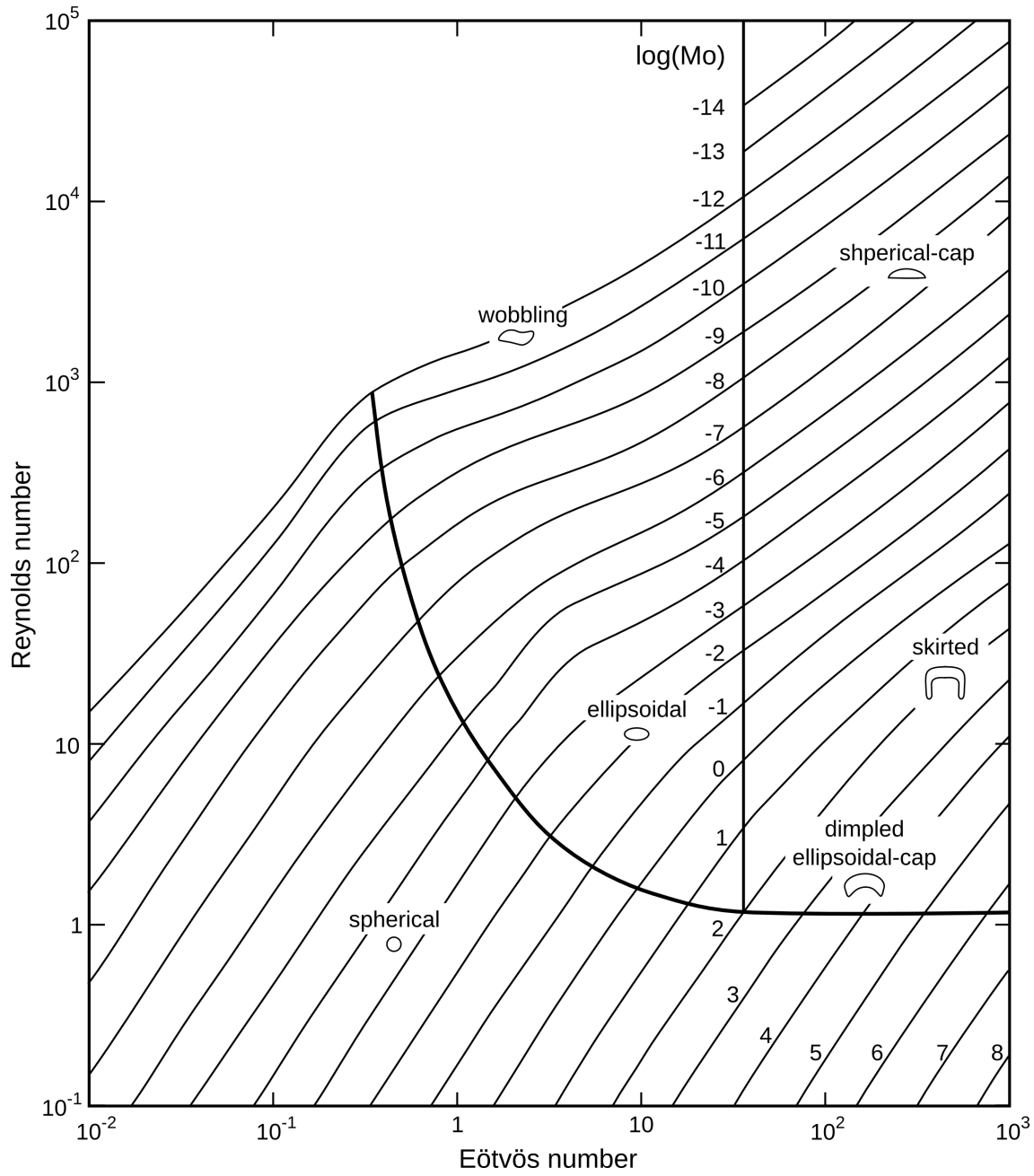


Figure 2.1: Shape regimes for bubbles and drops in unhindered gravitational motion through liquids (Clift et al., 1978).

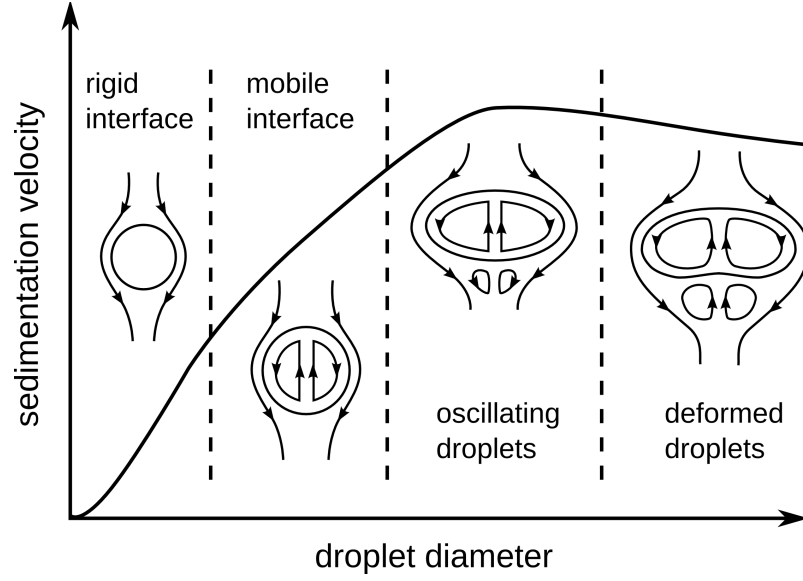


Figure 2.2: Hydrodynamic regions of droplet sedimentation (Henschke, 2003).

Henschke (2003) derived a model that allows the droplet sedimentation velocity to be described as a function of droplet diameter and that is continuous over the whole diameter range. The model is based on the physicochemical properties of the system and contains three adjustable parameters that can be fitted to experimental data. In the derivation of this model, existing equations, like those found e.g. in Brauer (1973) and Modigell (1981), were compared to experimental data and improved with the help of two-dimensional CFD simulations (Haas et al., 1972; Henschke et al., 2000; Waheed, 2001). The new correlated equations are valid for spherical droplets with either a rigid or an ideally mobile interface. The sedimentation velocity of deformed and oscillating droplets was calculated according to Clift et al. (1978) and Maneri (1995) respectively. Additional equations and parameters are used to describe the transitions between the regions of rigid, circulating, indented, and oscillating droplets, as well as to combine all the equations in a continuous function. The Reynolds number of spherical droplets with a rigid interface that do not exhibit an internal circulation is calculated (Henschke et al., 2000):

$$Re_{rigid} = \sqrt{\frac{4Ar}{3C_{D,rigid}}}, \quad (2.4)$$

$$C_{D,rigid} = \frac{432}{Ar} + \frac{20}{Ar^{1/3}} + 0.51 \frac{Ar^{1/3}}{Ar^{1/3} + 140}, \quad (2.5)$$

where $C_{D,rigid}$ is the drag coefficient of the droplet. The Reynolds number of spherical droplets with an ideally mobile interface, and, therefore, an ideal internal circulation, is calculated from:

$$Re_{circ} = \frac{Ar}{12(0.065Ar + 1)^{1/6}}. \quad (2.6)$$

The Reynolds number for spherical droplets between the two boundary states of rigid and ideally circulating interface is given by

$$Re_{shpere} = (1 - f'_{circ}) Re_{rigid} + f'_{circ} Re_{circ}, \quad (2.7)$$

$$f'_{circ} = 2(K'_{HR} - 1), \quad (2.8)$$

where the corrected Hadamard-Rybczynski factor K'_{HR} is used, that includes model parameter d_{sw} to represent the switch from rigid to ideally circulating spherical droplets:

$$K'_{HR} = \frac{3(\mu_c + \mu_d/f_{circ})}{2\mu_c + 3\mu_d/f_{circ}}, \quad (2.9)$$

$$f_{circ} = 1 - \frac{1}{1 + (d/d_{sw})^{10}}. \quad (2.10)$$

Thus, the terminal velocity of spherical droplets, that is corrected according to the extent of their interfacial mobility, is given by

$$v_{sphere} = \frac{\mu_c Re_{sphere}}{d\rho_c}. \quad (2.11)$$

The velocity of deformed droplets is calculated by the empirical equation

$$v_{def} = \sqrt{\frac{dg\Delta\rho}{2\rho_c}}. \quad (2.12)$$

Likewise, for oscillating droplets,

$$v_{os} = \sqrt{\frac{2\alpha_{sc}\sigma}{d\rho_c}} \quad (2.13)$$

where parameter α_{sc} of the model is used to scale the velocity of droplets in that region. The transition from oscillating to deformed droplets is expressed through the combination of the two respective velocities:

$$v_{def,os} = (v_{def}^\alpha + v_{os}^\alpha)^{1/\alpha} \quad (2.14)$$

where $\alpha = 8$ is set empirically. Finally, the sedimentation velocity of the droplet is calculated by combining the velocities of spherical, deformed, and oscillating droplets as:

$$v_{sed} = \frac{v_{def,os} v_{sphere}}{(v_{def,os}^{\alpha_{tr}} + v_{sphere}^{\alpha_{tr}})^{1/\alpha_{tr}}}, \quad (2.15)$$

where model parameter α_{tr} is included that represents the transition from the viscous-force dominated region to the surface-force dominated region with increasing droplet diameter.

Using this model, sedimentation curves like the one pictured in Fig. 2.2 can be reproduced. Model parameter d_{sw} influences the initial slope of the curve for small diameters, representing the change from rigid to circulating droplets. The shape of the peak is influenced by parameter α_{tr} , that represents the change from circulating to oscillating droplets. The vertical position of the plateau after the peak is influenced by parameter α_{sc} . As an alternative to fitting parameter d_{sw} to experimental data, it can be set to a value tending either to zero or to infinity. The curves that are obtained for these two values represent the behavior of droplets with either an ideally mobile or a rigid interface, respectively. The peak of the sedimentation curve corresponds to the diameter value for which the hydrodynamic resistance due to droplet deformation becomes more significant than the buoyancy force, thus leading to a decay of sedimentation velocity with increasing droplet size.

It is evident from the above that the assumption of a spherical droplet shape can severely limit the validity of any further considerations. Therefore, a method is needed to take the deformation of the droplet interface into account in CFD simulations. An overview of the available tools for this task will be the subject of the next section.

2.1.2 Droplet deformation

In general, free interfacial movement can be simulated by either “front-tracking” or “front-capturing” methods (Paschedag, 2004). Noteworthy alternative approaches for interface treatment are the “diffuse interface” method (Anderson et al., 1998; Yue et al., 2004, 2005, 2006) and the lattice-Boltzmann technique (Wolf-Glädrow, 2000; Xing et al., 2007; Lee and Fischer, 2006).

Front-capturing

In the front-capturing approach the position of the interface is represented implicitly using some indicator function. The two most popular front-capturing methods are the “volume of fluid” (VOF) and the “level-set” techniques. In the VOF method a function is used to indicate the volume fraction of a certain phase in each grid cell. The main difficulty involved in the implementation of the VOF method is that the exact location of the interface is not unique and extra care must be taken in reconstructing the interface in every time step (Delnoij et al., 1997; Delnoij, 1999; Paschedag, 2004).

For capturing the interface in the level-set method a continuous function is used that is e.g. equal to zero where the interface is located, positive in one phase and

negative in the other. This concept is demonstrated in Fig. 2.3 (left) where the level-set function is mapped on a 2D plane of a computational domain. The zero-level set of the interface capturing function is indicated by the white ellipse, which represents the surface of a slightly deformed liquid droplet, originally 4 mm in diameter. The values of the level-set function along the horizontal x-axis can be seen in the diagram of Fig. 2.3 (right), where it is evident that the level-set function is negative inside the droplet and positive in the continuous phase. In contrast to the VOF approach, the interface in the case of the level-set method is uniquely described, but an additional advection equation needs to be solved for this purpose. The major disadvantage of the level-set approach, however, is that the conservation of mass must be ensured explicitly by frequently reparametrizing the level-set function, something which is not necessary in the VOF method (Atmakidis and Kenig, 2008).

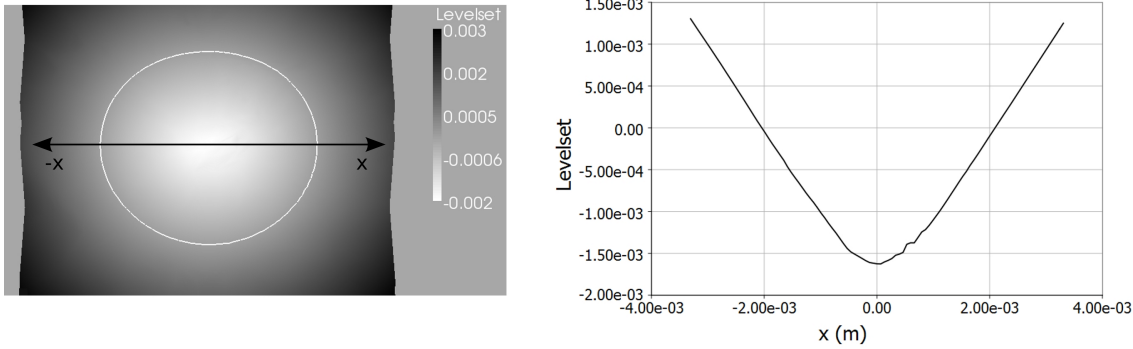


Figure 2.3: The level-set function mapped on a 2D plane (left) and along the x-axis (right).

The level-set function, proposed by Osher and Sethian (1988), was implemented by Sussman et al. (1994) for two-dimensional droplet simulations with a finite interface thickness. Although they report interesting results they do not compare their findings to experimental data. The level-set function was also used by Deshpande and Zimmerman (2006b,a) for two-dimensional simulations of mass transfer between sedimenting droplets and the continuous phase for low Reynolds numbers. Pillapakam and Singh (2001) also performed simulations with the level-set technique for droplets subjected to shear flows and sedimenting bubbles. The interaction of a droplet with an initially flat liquid interface has been simulated using the level-set approach and compared to experimental results by Zheng et al. (2005).

Yang and Mao (2005) and subsequently Wang et al. (2008) simulated the mass transfer between droplet and continuous phase in two dimensions using the level-set method. Mass-transfer experiments were also performed using sedimenting droplets that were collected and analyzed in order to calculate the overall mass-transfer coefficient. The sedimentation height was adjustable, so that the mass-transfer coefficient would be obtained for different contact times that ranged between 2–10 s. The simulation results show good agreement with the experiments, but were limited to droplets with diameter smaller than 2 mm.

The VOF method, first presented by Hirt and Nichols (1981), was used by Koebe et al. (2002, 2003); Koebe (2004) as well as by Bothe et al. (2006, 2009) to study the behavior of air bubbles sedimenting in water. In these publications the presented sedimenting-bubble shapes were very realistic, but the agreement of the terminal velocity data to the experimental values was rather qualitative. The results of van Wachem and Schouten (2002) on the other hand, also obtained using the VOF method for the same materials, were in good agreement to experimental values, but only large bubbles were investigated. Gueyffier et al. (1999) compared results obtained with the VOF method to experimental data and algebraic correlations for sedimenting bubbles and droplets showing good agreement. In addition, their shape contours of a pendant droplet overlapped nicely to pictures obtained experimentally. Renardy and Cristini (2001a,b) and Renardy et al. (2001) used the VOF method to simulate droplet deformation and breakup under shear stress. Investigations under these conditions using the VOF method were also performed by James and Lownegrub (2004), but in this case the effect of surfactants was examined as well. Other implementations of the VOF technique include the work of Lunkad et al. (2007) who simulated the spreading of liquid droplets on horizontal and inclined surfaces and the thesis of Hase (2005) on the heat and mass transfer of liquid droplets evaporating in a gaseous medium.

In order to combine the advantages and eliminate the weaknesses of the VOF and the level-set methods, it is possible to couple them as shown by Sussman and Puckett (2000); Sussman (2003); Yang et al. (2006); Coyajee et al. (2006) and Nichita et al. (2011). In Sussman et al. (2007) there is also a comparison of the simulated bubble shapes with the experimental data of Hnat and Buckmaster (1976) for rising bubbles exhibiting good accuracy. Likewise, Buwa et al. (2007) used the same method to investigate the deformation of droplets upon their generation through submerged orifices showing good agreement with the experimental data of Null and Johnson (1958).

Front-tracking

In the front-tracking methods, the interface is explicitly represented by computational elements that follow its movement through time. These elements belong either to the grid discretizing the whole computational domain (Lagrangian approach), or to a separate mesh that is used for the interface alone while the main grid remains stationary (Eulerian approach). The Lagrangian approach is mostly used for simulations where the computational domain covers only one phase and the moving interface is part of its boundary. Such is the case of bubbles rising in a liquid continuum that due to their small density and viscosity are often simulated as cavities. The Eulerian approach uses interconnected “marker-points” that represent the interface and move according to the velocity field. In another approach, namely in the “marker and cell” method proposed by Harlow and Welch (1965), marker-particles are used to follow the complete movement of one phase. The interface is thus de-

defined as lying at the boundary between the regions with and without marker particles (Hyman, 1984). Since the marker-points are scattered everywhere in the phase and are not restricted on the interface, this method is usually cited as a front-capturing technique (Jakobsen, 2008). The main disadvantage of the Lagrangian approach is that the grid quality may deteriorate as it gets deformed over time. Similarly, interfacial deformation may also make a proper update of the marker-point mesh hard to realize in the Eulerian approach (Groß, 2008).

Li and Mao (2001) and Li et al. (2003) as well as Mao et al. (2001) and McLaughlin (1996) investigated the effect of surfactants on droplets and bubbles based on the Lagrangian front-tracking method introduced originally by Ryskin and Leal (1983). Unverdi and Tryggvason (1992) presented a front-tracking method where the interface was given a thickness of the order of the mesh size to provide stability and smoothness. A front-tracking method avoiding this drawback was proposed by Ye et al. (2001). Petera and Weatherley (2001) used a Lagrangian front-tracking method for the two-dimensional axis-symmetrical simulation of a droplet falling in a quiescent liquid and their results for the sedimentation velocities were in good agreement with experimental data. Similar calculations were performed by Bozzi et al. (1997) where the authors present an extensive discussion and a literature overview on simulation and experimental issues. In Quan and Schmidt (2006) a liquid droplet accelerated by a gaseous current was simulated using a front-tracking technique coupled with adaptive-mesh methods that were used to achieve good mesh quality and to deal with large deformation. An implementation of an Eulerian marker-point front-tracking method by Cristini et al. (1998, 2001) was compared to experimental results for droplet breakup by Patel et al. (2003). Their results show intensely deformed droplets of shapes similar to those found in their experiments.

A hybrid between the front-capturing and the front-tracking methods was proposed by Tryggvason et al. (2001) and implemented by Muradoglu and Tryggvason (2008) for rising bubbles. In that approach, although the fluid flow and the interface movement are represented by two separate grids, a single set of governing equations is used for the whole flow field instead of treating each phase separately.

Other simulation techniques

The lattice-Boltzmann technique (Inamuro et al., 2004; Theodoropoulos et al., 2004; Sankaranarayanan et al., 1999; van der Sman and van der Graaf, 2008) is a mesoscopic approach based on the assumption that a fluid consists of many particles whose repeated collision and translation converge to a state of local equilibrium but always remain in motion. The “diffuse interface” or “phase field” method (Badalassi et al., 2003; Barosan et al., 2006; Kim, 2005) is similar to a front-capturing technique in that the position of the interface is located by using the chemical-potential function that varies between the phases (Zimmerman, 2006).

2.1.3 Internal circulation and interfacial stagnation

The model of Hadamard and Rybczynski for droplet circulation predicts a toroidal circulation in the droplet that extends in the whole droplet volume regardless of its size (Kronig and Brink, 1951). However, bubbles and droplets are closely approximated by solid spheres if viscous forces dominate over inertia forces (Clift et al., 1978). The interfacial rigidity of small droplets can also be attributed to the accumulation of surface-active components in the system (Edge and Grant, 1971, 1972), that are also present in materials of high purity (Harper, 2007; Holm and Terjesen, 1954; Brodkorb et al., 2003; Steiner, 1986; Andrews et al., 1988). Surfactants, however, can influence the circulation of larger droplets as well.

The basic model for taking the effect of surfactant impurities into account suggests that the surfactant molecules are being transported from the bulk phases (usually the continuous phase) to the droplet interface where they accumulate due to their surface-active nature. Due to the relative motion between the droplet and the continuous phase, they are swept towards the rear of the droplet, thus resulting to an inhomogeneous interfacial composition (Fig. 2.4, middle). Since the surfactant concentration strongly influences the interfacial tension, a similar inhomogeneity of the interfacial tension is also present. The interfacial tension is lower at the rear end of the droplet where the surfactant concentration is higher, and higher at the upper part where the surfactant concentration is lower. This interfacial-tension gradient results to a force that opposes the counter-current flow and a stagnation of the rear droplet part appears as the two forces cancel each other out (Rehage, 2000; Griffith, 1960; Newman, 1967).

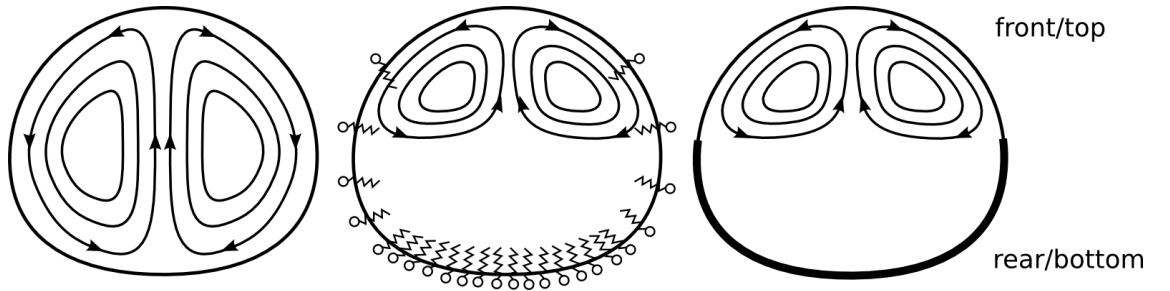


Figure 2.4: Organic droplet rising in an aqueous continuum; fully circulating droplet (left), droplet with accumulated surfactants (middle) and droplet featuring a stagnant interface at the lower part (right).

The droplet is thus separated into a circulating upper part and a lower stagnant part (Savic, 1953; Sadhal and Johnson, 1983; Kim and Subramanian, 1989a,b). The rear stagnant part of the droplet is often referred to as the “rigid cap”. The droplet internal circulation is initially toroidal as seen in Fig. 2.4 (left), but since the surfactant molecules accumulate on the interface as time passes, the circulation torus gets smaller (Fig. 2.4, middle). This dynamic behavior has been experimentally

confirmed in the past, most notably by Garner and Skelland (1955), Horton et al. (1965) and Amar et al. (2005b). Garner and Skelland (1955) described the diminishing internal circulation of droplets made of impure materials with the help of suspended aluminium particles. Horton et al. (1965) provided photographic evidence of this phenomenon, also using aluminium particles. Amar et al. (2005b), using high-resolution NMR-velocimetry techniques, provided dynamic data that quantify the damping of the liquid velocities during torus migration inside a contaminated droplet.

In the following descriptions, the droplet pole that faces against the downflow of the continuous phase current is referred to as the “top” pole, whereas the opposite pole that faces in the same direction as the counter-current flow is referred to as the “bottom” pole. Likewise, as shown in Fig. 2.5, the droplet part in the vicinity of the top pole is referred to as the “upper” part, or the droplet “front”, and the droplet part in the vicinity of the bottom pole is referred to as the “lower” part, or the droplet “rear”.

In Fig. 2.5 the torus circulation centers in a droplet for different points in time are presented according to Horton et al. (1965) (left) and Amar et al. (2005b) (right). The picture on the left is a faithful reproduction of a graph from the publication of Horton et al. (1965) that displays the migration of the circulation centers during the experiment. Since the droplets in the work of Horton et al. (1965) were sedimenting downwards, the picture was flipped vertically in order to make it comparable to the data of Amar et al. (2005b), in which the droplet was sedimenting upwards. For obtaining the graph on the right, the 2D vector-fields of fluid velocities published by Amar et al. (2005b) were used for visually locating the circulation centers. In Fig. 2.5 it can be seen that as the stagnation evolves, the circulation centers migrate from the droplet equator towards the top of the droplet as shown by the curved dashed arrows. In addition, the internal circulation velocity also gets smaller with time. Eventually, the fluid velocities in the droplet become very small and no toroidal circulation is visible.

One debatable aspect of the rigid-cap model is the form of the inhomogeneity of the surfactant concentration on the interface, and thus also the shape of the interfacial tension profile. The most widely implemented mechanism of stagnation suggests that the surfactant concentration, and thus also the interfacial tension, are smooth functions and feature a gradient along the droplet. On the other hand, Huang and Kintner (1969) proposed a mechanism according to which no surfactant-concentration gradient, and therefore no surface-tension gradient, exists on the droplet surface. According to this mechanism as the surfactant reaches the surface of the drop, it is swept to the rear by the tangential velocity on the surface. The first molecule of surfactant stays at the rear pole where the tangential velocity is zero. The molecules of surfactant that come later are positioned adjacent to the previous molecule and they are forced to stay in this position by the constant drive of the tangential velocity. The surfactant layer that grows in this manner is thought to be uniform and homogeneous because, according to Huang and Kintner (1969),

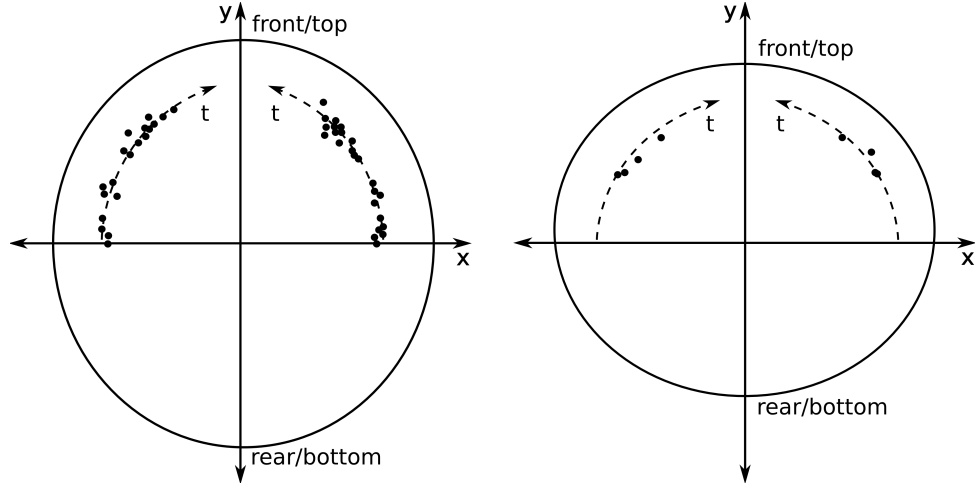


Figure 2.5: Upwards migration of the circulation centers with time inside a contaminated droplet according to the experimental data of Horton et al. (1965) (left), and Amar et al. (2005b) (right).

the only possibility that could cause a concentration gradient on the surface is molecular diffusion of the surfactant molecules themselves in the direction against the tangential velocity. Since the diffusivity of surfactant molecules is small compared to the convection imposed by the counter-current, such a concentration gradient of surfactant can not be maintained along the interface. As the surfactant layer builds up, the surface covered by the surfactant is immobile (Fig. 2.4, right). The tangential velocity drops to zero abruptly at the circumference of the surfactant, thereby causing the velocity vector to change in direction. This change in direction causes an abrupt boundary layer separation on the circumference of the surfactant layer. The experimental data of Horton et al. (1965) were cited by Huang and Kintner (1969) as supporting this behavior.

This model thus suggests that the surfactant-concentration profile, and also the interfacial-tension profile along the droplet interface is a step function rather than a smooth function that shows a continuous gradient. However, interfacial tension forces are not being considered at all by Huang and Kintner (1969) since the build-up and the shape of the surfactant layer is exclusively attributed to the force of the counter-current. The boundary layer separation that was first observed by Horton et al. (1965) may indeed be attributed to the accumulation of surfactants, since Liao and McLaughlin (2000); Cuenot et al. (1997), and Li and Mao (2001) showed that the continuous-phase flow around a contaminated fluid particle featured a recirculation zone in the rear of the particle, whereas the counter-current flow of an uncontaminated particle was viscous. This, however, does not constitute a proof of the concept of Huang and Kintner (1969) since the boundary-layer separation in the aforementioned publications was noted while an interfacial tension gradient was considered. In addition, Andrews et al. (1988) showed that at surfactant concentrations higher than those required to make the fluid particle behave like a solid sphere,

the liquid-liquid interface becomes mobile again, which cannot be explained if it is accepted that the surfactants build an immobile “wall” on the droplet surface.

Moreover, the model of Huang and Kintner (1969) does not allow the surfactant molecules to desorb from the droplet interface back into the continuous phase. The absence of desorption is unnatural, since diffusion and partition between phases are general phenomena. In addition, the rate of desorption can vary for various material systems and is decisive for the interfacial phenomena (Stebe et al., 1991). The generally accepted concept today is that in the case where the surfactants are initially present in the continuous phase, they are continuously adsorbed onto the interface at the upper part of the droplet and desorbed from the interface back into the continuous phase at the rear part of the droplet. Thus, the droplet state is actually dynamic, also when the droplet is equilibrated.

The work of Savic (1953) was the first to try to model the rigid cap and to fit the model parameters to experimental data. The modeling approach included dividing the droplet into two distinctive parts: a front mobile part and a rear rigid cap. Then through the boundary conditions of the equations of motion it was demanded that the fluid velocity at the surface of the stagnant droplet part is zero. An additional assumption of the analysis was that the viscosity of the continuous phase is much greater than the viscosity of the droplet. The parameter defining the extent of the rigid region was fitted qualitatively to the experimental data picturing the internal circulation of droplets. The model of Savic (1953) predicts a shear-stress gradient on the interface, which was coupled to the surface tension by Griffith (1962) and thus an interfacial-tension gradient occurs. However, analytical solutions of certain interfacial-tension profiles coupled to the equations of motion have not provided promising results (Schechter and Farley, 1963), as also noted by Huang and Kintner (1969).

Groß-Hardt (2007) implemented a model for simulating the rigid-cap behavior of single droplets levitated in a continuous counter-current in a two-dimensional CFD simulation. The droplet surface was divided into two parts: one ideally mobile at the top, and one stagnant at the rear. Because of the explicit no-slip condition on the droplet surface, the droplet thus exhibited a circulation in the upper part and a stagnant cap at the bottom, where the interfacial velocity is zero. The model was compared qualitatively to the vector plot of the velocities inside a toluene droplet hovering in an aqueous counter-current that was obtained experimentally using NMR velocimetry (Amar et al., 2005a,b). The model exhibited good qualitative agreement to the experimentally obtained circulation pattern (Fig. 2.6) while the overall concept was kept simple. In addition, the velocity magnitudes along the droplet interface were in good quantitative agreement to the experimental data. However, the droplet shape was spherical and non-deformable and no interfacial-tension phenomena were taken into account. Thus, the model of Groß-Hardt (2007) resembles in concept more the one of Huang and Kintner (1969) than that of Savic (1953).

Other researchers, like Ponoth and McLaughlin (2000) and consequently Zhang et al. (2001) based on the work of McLaughlin (1996) followed an approach similar to Groß-Hardt (2007) for simulating contaminated rising bubbles. However, the bubbles were treated as cavities and no internal circulation was calculated. This simplification is not valid for simulating liquid-liquid systems because of the smaller density and viscosity differences between the two phases. In all of the above publications, a recirculation in the droplet wake and a boundary layer separation is reported as shown in Fig. 2.6.

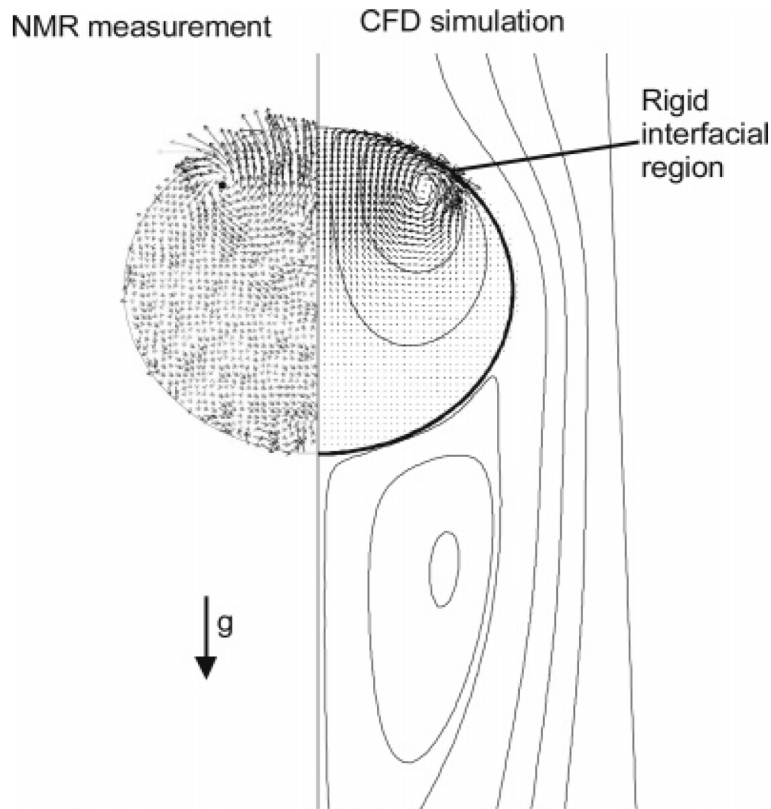


Figure 2.6: Comparison of the model by Groß-Hardt et al. (2006) (right) to a measured vector plot of the velocities inside a toluene droplet (left).

If it is assumed that the transport of surfactants on the droplet surface is instantaneous and that they do not desorb back into the bulk liquid, the stagnant-cap concept can be simplified significantly, so that it can be implemented in algebraic mass-transfer models without taking the fluid dynamic aspects of the problem into account (Vasconcelos et al., 2003; Sardeing et al., 2006). Modeling the entire procedure of surfactant transport in the system is a more challenging task, since both the physical and mathematical aspects of the problem become more complicated.

In a more comprehensive formulation, the surfactant is considered to be contained in the bulk liquid phase and to be insoluble in the droplet. The surfactant transport between the interface and the continuous phase is defined by an adsorption-desorption

mechanism (Levich, 1962; Lochiel, 1965) and an adsorption isotherm is used to describe the dependence of the surfactant concentration on the interface from its concentration in the bulk phase. For this purpose, the Langmuir or the Frumkin adsorption isotherms have been implemented (Ferri and Stebe, 1999; Janssen et al., 1997; Eggleton and Stebe, 1998; Stebe et al., 1991; Kruijt-Stegeman et al., 2004), or other similar equations (Datwani and Stebe, 1999; Johnson and Stebe, 1996). The Gibbs adsorption equation is then used in conjunction with the adsorption isotherm to derive an “equation of state” for describing the dependence of the interfacial tension on the surfactant concentration at the interface (Johnson and Borhan, 1999; Chan and Borhan, 2005). Such equations of state are, for example, the Frumkin or the Szyszkowski equations (Fdhila and Duineveld, 1996; He et al., 1991; Lin et al., 1990; Chen and Stebe, 1996; Yang and Gu, 2004), or, by assuming that the interfacial surfactant concentration is much lower than the saturation value, a linear equation can be derived that corresponds to an “ideal gas” equation of state (Borhan and Mao, 1992; McLaughlin, 1996). Here, as an example, the Langmuir (Eq. 2.16) and the Szyszkowski (Eq. 2.17) equations are presented:

$$\frac{\Gamma_s}{\Gamma_\infty} = \frac{Kc_s}{1 + Kc_s}, \quad (2.16)$$

$$\sigma = \sigma_{pure} + RT\Gamma_\infty \ln \left(1 - \frac{\Gamma_s}{\Gamma_\infty} \right), \quad (2.17)$$

where σ is the actual interfacial tension, σ_{pure} is the interfacial tension of the uncontaminated system, Γ_s is the surfactant concentration of the interface, Γ_∞ is the surfactant concentration of the saturated interface for monolayer adsorption, R is the ideal gas constant, c_s is the surfactant concentration in the continuous phase, T is the absolute temperature and K is the Langmuir adsorption coefficient that represents the adsorption to desorption rate at the interface. Alternatively, by combining the equation of state and the adsorption equation an expression is derived for describing the interfacial tension as a function of the adsorption coefficients and the bulk-fluid surfactant concentration (Wasserman and Slattery, 1969).

This theoretical scheme introduces constants like c_s , K and Γ_∞ and thus, although this approach is well-founded, it can not be applied in cases where the surfactants are treated as impurities and their nature is, therefore, unknown. In such a case, the surfactant-dependent variables need to be fitted to experimental data (Chen and Lee, 2000; Lee, 2003). In addition, the case where the surfactants are contained in the droplet is not covered by such models, although this may as well be the case in experimental investigations. Furthermore, if the surfactants are soluble in both phases their partitioning between the droplet and its environment must be taken into account in the adsorption-desorption kinetics (Liggieri et al., 1997; Ravera et al., 2000). An advantage of this approach is that, because of its dynamic nature, the time dependency of the droplet characteristics on the surfactant accumulation can be determined, like e.g. its time-dependent sedimentation velocity (Zholkovskij et al., 2000).

An interesting point is that the actual reason of the interfacial stagnation, namely the interfacial-tension gradient, is not at the focal point of the discussions in the literature. In older publications (like e.g. in Savic (1953); Griffith (1962) and Schechter and Farley (1963)), the surface-tension gradient was thus adjusted so that the force that emerged canceled out the shear stress that was posed on the droplet surface by the flow of the counter-current. In more modern publications in which a surfactant-transfer model is implemented for obtaining the interfacial-tension profile along the droplet, the surface-tension gradient itself is no longer a directly controlled variable. Instead, the surfactant distribution along the droplet interface, represented by the the interfacial surfactant concentration, is the key variable in such studies.

Muradoglu and Tryggvason (2008) as well as Tasoglu et al. (2008) and Tasoglu (2008) present many qualitative simulations of bubbles with surfactants using the Szyszkowski equation of state (Liao et al., 2006). Although the simulations showed that a surfactant concentration gradient appears that leads to interfacial stagnation and a smaller sedimentation velocity, the simulated spherical bubbles do not feature a rigid cap. The velocity magnitudes in the bubble and on its surface decrease smoothly, so that the center of the internal circulation torus remains at the droplet equator. Moreover, no boundary-layer separation, and no recirculation are noticed in the bubble wake. In the work of Muradoglu and Tryggvason (2008) the interesting remark is made that although the Szyszkowski equation provides a good model for low interfacial surfactant concentrations, it results in an unphysical negative surface tension for high surfactant concentrations. Such a shortcoming can be easily remedied numerically, but certainly poses theoretical concerns.

Using the same methodology, Li and Mao (2001) simulated single droplets in 2D where both a rigid cap and a recirculation in the droplet wake were noticed. It was found that larger surfactant concentrations caused a size increase of the rigid cap in the rear part of the droplet and of the recirculation vortex in the continuous phase behind the droplet. However, although various degrees of contamination were tested, the rigid cap remained relatively small in comparison to the droplet size. In that work, the plots of the surface tension and its gradient along the droplet interface were provided (Fig. 2.7). It was shown that the surface tension curve that results from the adsorption equations features one maximum at the front part of the droplet, and one minimum at the rear part of the droplet. In between, the surface tension is smooth and its gradient exhibits a rather sharp peak. Interestingly, from Fig. 2.7 (left) it can be seen that surfactant is present everywhere on the droplet surface since no point exists with an interfacial tension equal to that of the pure system, where the dimensionless interfacial tension would be equal to unity.

In the same study, Li and Mao (2001) make a revisit to the stagnant cap model where they argue that the discontinuities on the interfacial mobility that emerge from the approach of Savic (1953) constitute an important physical deficiency of the model. In addition, they state that the determination of the rigid-cap size is a difficult numerical task that does not justify the usage of that model in favor against the more physical surfactant-adsorption approach. To these observations it needs to be

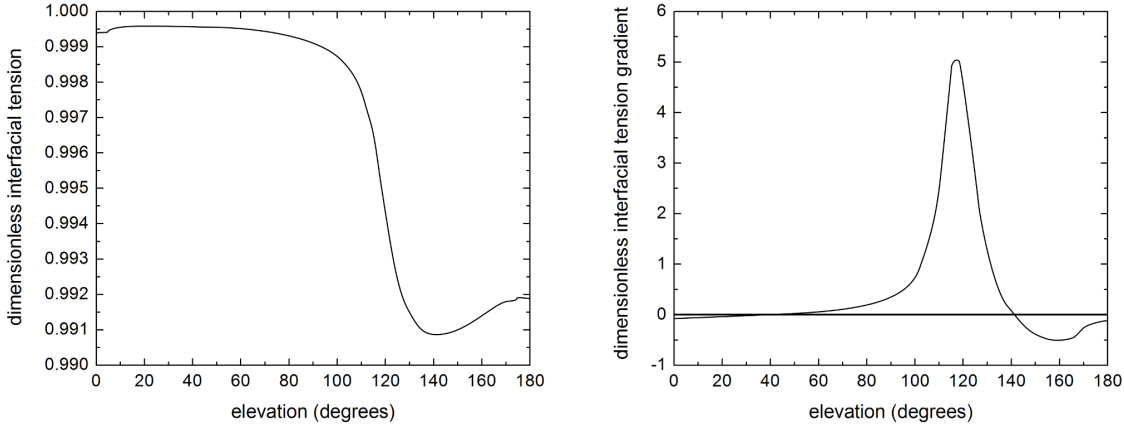


Figure 2.7: Profiles of the interfacial tension (left) and of the interfacial tension gradient (right) along the droplet according to Li and Mao (2001).

added that the applicability of the rigid-cap model, as expressed by Savic (1953) and Groß-Hardt (2007), is reduced, if the CFD simulation features a movable interface. This is because these studies implement the stagnant cap physics by treating the droplet surface as an immovable boundary of the computational domain on which the appropriate boundary conditions are applied. If the droplet surface deforms, then the boundary condition will have to be moved thus increasing the complexity of the simulation. This drawback eliminates the rigid-cap model as an option for modeling deformable droplets as well as other phenomena like droplet breakup or coalescence. The adsorption approach on the other hand has not yet delivered results showing that the simulated fluid circulation inside the droplet matches the one that is visualized experimentally.

In this work, a hybrid between the two approaches is examined. The interfacial tension profile along the droplet surface is defined explicitly, similar to the work of Schechter and Farley (1963), and no adsorption equation is implemented. On the other hand, the interfacial velocity discontinuity of the Savic (1953) model is absent in this work since no *a priori* assumption is made concerning the mobility of the interface, like in the case of an adsorption-desorption model. The parameters of the interfacial-tension profile are then adjusted so that a rigid cap appears that best fits the experimental data.

2.2 Quantification of internal droplet flow

The quantitative experimental evaluation of sedimentation and interfacial stagnation models is usually based on terminal velocity and mass-transfer data that can be obtained using standardized methods that employ ordinary laboratory glassware and cameras (Henschke, 2003; Bart et al., 2006), although other experimental techniques, such as phase-doppler anemometry or rainbow refractometry, may also be

implemented (Lohner et al., 2000). Nevertheless, these data supply information regarding only the macroscopic behavior of single droplets that is averaged over a time period and do not provide insight regarding the dynamic phenomena within the droplet and at the droplet interface. Since the fluid flow significantly influences the sedimentation and the extraction rate, a more detailed model should succeed in describing the internal droplet circulation. For validating such a model, a direct comparison of the fluid velocities between simulation and experiment is necessary. Although various techniques are available for the visualization of the fluid flow inside and around a moving droplet, the data thus obtained are only qualitative.

The quantitative measurement of the fluid velocities at the scale of a few millimeters, that is the relevant droplet diameter in liquid-liquid extraction, is not a trivial task. The applied experimental method should be non-invasive in order to avoid the perturbation of the system upon measuring. In addition, for capturing the dynamic character of the phenomena in the droplet, the measuring technique should be relatively fast. NMR Velocity Imaging fulfills these criteria and an overview of this experimental method will thus be presented in the following section. For comparison and completeness, the alternative technique of Particle Image Velocimetry, as well as other qualitative methods for flow visualization will also be presented briefly.

2.2.1 NMR Velocity Imaging

The so-called “NMR Velocity Imaging” technique is the combination of Magnetic Resonance Imaging (MRI), or alternatively “NMR-Imaging”, with velocity encoding methods for obtaining discretized vector maps of the velocities within a flowing liquid.

The principle of Velocity Imaging lies in measuring the displacement of spin-bearing molecules, that are contained in a sample inside the NMR apparatus, the position of which has been encoded by imposing a space dependence on the strength of the surrounding magnetic field. More specifically, the “Pulsed Field Gradient” PFG-NMR procedure for obtaining the velocity on one dimension in a certain volume element of a flowing liquid can be generally summarized in the following steps:

1. at the initial time-point $t_0 = 0$ impose a magnetic field gradient $\mathbf{g}(\delta)$ of strength $\mathbf{g}$ and duration δ ,
2. wait a time interval Δt ,
3. at time $t = t_0 + \Delta t$ impose a refocusing magnetic field gradient $-\mathbf{g}(\delta)$,
4. acquire the signal.

The effect of the first field gradient is to impose a spatially dependent linear magnetic field onto the sample. Each nuclear spin thus obtains a phase shift that is proportional to its position at time t_0 . Particle displacements during δ are assumed to be negligible. After the time interval Δt the refocusing gradient results in a

second phase shift which gives an overall shift of spin that is proportional to the displacement of the particle during the velocity encoding time Δt . Since the two field gradients are of opposite sign and equal in strength, they will leave no effect on the spins that remained stationary during the velocity encoding sequence. The total signal amplitude is then obtained by summing the phase shifts of all spins in the control volume. By applying a Fourier transformation on the acquired signal the average propagator is calculated that represents the probability distribution of displacements during Δt for that volume element. In addition, the average propagator stresses the integral aspect of motion, i.e. the total displacements that are accumulated in the volume element over the time interval Δt (Stapf, 2002).

The application of PFG-NMR can be extended toward a multiple encoding of positions and displacements in order to make the resulting signal sensitive only to velocity *changes* between the two encoding intervals, i.e. the acceleration (Han et al., 2000; Stapf, 2001). For a more elaborate analysis of the various NMR velocimetry and imaging techniques, the interested reader is referred to the book of Stapf and Han (2006) and the references therein. To the author's knowledge, the only research group employing NMR velocimetry for measuring the fluid flow inside liquid drops, is based at the Institute for Macromolecular Chemistry of the RWTH Aachen University. In the publications of that institute, like e.g. in Amar (2006), Amar et al. (2005a), and Amar et al. (2005b), two-dimensional velocity vector fields inside an organic liquid droplet levitating in an aqueous counter-current flow can be found, where the dependence of the rigid-cap size on time and droplet diameter are also presented. A two-dimensional vector map of the velocities inside a water droplet falling through air were published by Han et al. (2001) where the effect of surfactants on the droplet shape was also visualized in three dimensions. However, the necessary information was accumulated using data from multiple individual droplets instead of a single falling droplet.

2.2.2 Other techniques

Another experimental method that is capable of providing quantitative velocity plots of the flow inside a liquid droplet is Particle Image Velocimetry. A qualitative representation of the fluid motion can also be provided by a variety of other imaging techniques.

Particle Image Velocimetry

In Particle Image Velocimetry (PIV) small solid particles are added to the liquid that is used in the experiment in order to optically trace its flow. A high power laser is used to selectively illuminate a 2D plane of the fluid while a camera positioned perpendicular to the plane obtains multiple pairs of consecutive snapshots of the

moving particles. The captured images are discretized into a large number of smaller fields whose displacement vector can be calculated by following the movement of the tracer particles between the snapshot pairs. By knowing the time interval between the captured frames a representative velocity for each field can be estimated, thus creating a velocity vector map of the fluid flow. Using additional cameras, three-dimensional velocity vectors can be obtained as well (Lai et al., 2008; Troolin and Longmire, 2008).

A similar method to PIV called “darkfield particle trace photography” was first used by Horton et al. (1965) in order to quantitatively obtain the velocities of the circulating torus in a levitated droplet. With the help of PIV however, falling droplets may also be studied as presented by Yamauchi et al. (2000). If the concentration of the tracer particles in the fluid is too high, it may be difficult to follow the movement of the particles in space. In such a case PIV is limited to providing only qualitative representations of the fluid flow. Such studies are mostly popular in early approaches of the technique such as those of Garner and Hale (1953); Garner and Skelland (1955) and Savic (1953).

In PIV the material of the particles is chosen so that its density matches the density of the liquid that is being studied. Therefore, the buoyancy force will be zero and the particles will follow the fluid motion. Moreover, it is assumed that the tracer particles and the laser do not change the physical properties of the system, like, most importantly in the case of liquid droplets, the interfacial tension, the temperature, or the density. An unwanted phenomenon, however, that occurs during the application of the PIV method is that the tracer particles tend to adsorb at the interface and change its rheological behavior (Grün and Hampe, 2000). Therefore, a less invasive measuring technique is needed for studying interfacial effects in single-droplet systems. Groß-Hardt (2007) compared the PIV technique to NMR Velocity Imaging with the conclusion that NMR Velocity Imaging is a more appropriate method for measuring the fluid velocities inside a droplet levitated in a counter-current flow field.

Qualitative visualization

Various qualitative techniques have been developed in order to obtain information concerning the circulation inside a moving droplet, the behavior of its trailing wake, the development of the mass transfer between the droplet and the continuous phase, and of related interfacial phenomena like interfacial instabilities.

For the visualization of the mass-transfer process, a discoloration technique can be used where a titration indicator such as phenolphthalein together with sodium hydroxide can be inserted in the dispersed phase and an acid, such as acetic acid, can be used as a transfer component in the continuous phase. As the transfer component is transported into the droplet and changes the pH, the color inside the droplet will also change, thus giving a qualitative map of the solute concentration in the droplet.

The simplicity of this method has made it popular in the past, but is still being used today (Garner, 1950; Pawelski et al., 2005; Schulze, 2007).

The so-called “molecular tagging” techniques are another category of flow visualization methods that are based either on fluorescence and phosphorescence effects, or to the activation of a photochromic dye that is induced by irradiation with an ultra-violet light (Grün and Hampe, 2000). The photochromic dye can be implemented to visualize bubble wakes by diluting it into the liquid continuous phase as demonstrated by Sanada et al. (2007, 2009). However, inserting even a small quantity of dye in a liquid-liquid system may drastically alter its behavior by introducing or suppressing various interfacial phenomena (Anderson and Quinn, 1970).

For the visualization of interfacial instabilities, the “holographic interferometry” method can be used, as demonstrated by Hertel (1987) (in Hampe (2000)). This method is based on the physical dependency of the refractive index on the composition of a solution and poses the advantages that enables the real-time recording of the ongoing physical phenomena in a non-invasive way (Tourneau et al., 2000).

Chapter 3

Experimental methods and data

Experimental NMR-velocimetry data were provided for the purpose of this work by the Institute for Macromolecular Chemistry of the RWTH Aachen University. A description of the measuring apparatus and method is given in Sec. 3.1.1. A presentation of the data and a commentary on the experimental errors follows in Sec. 3.1.2. For testing the accuracy and reliability of the simulation software, single droplet sedimentation data were obtained from the work of Paesch (1998). These data as well as the experimental procedure and the properties of the materials used are presented in Sec. 3.2.

3.1 Levitated droplet

In order to obtain accurate data using the NMR Velocity Imaging technique the droplet was required to remain levitated at a stable position inside the NMR resonator for the whole duration of the measuring process. For this reason, a levitation apparatus was developed by Groß-Hardt (2007) and utilized for producing the experimental data used in this work. The NMR measuring sequence, dubbed the “spin-echo” sequence, initially implemented in the works of Amar et al. (2005a,b); Amar (2006); Groß-Hardt et al. (2006) and Groß-Hardt (2007) necessitated about 8 min in order to measure a two-dimensional vector plot of the fluid velocities inside the droplet with a resolution of 128×128 data points. In order to enhance the accuracy of the measurements and in order to enable the future investigation of mass transfer phenomena (Amar et al., 2008), a new NMR-sequence was developed at the Institute for Macromolecular Chemistry of the RWTH Aachen University called “FLIESSEN”, which stands for “Flow Imaging Employing a Single-Shot ENcoding” (Casanova et al., 2009). This sequence, next to other improvements, requires less than 1 s for the same measurement (Blümich and Casanova, 2009). In this chapter, the results obtained using the two measuring sequences will be presented and the characteristics of the respective flows will be compared. For details on the new measuring NMR-sequence see the work of Amar et al. (2010).

3.1.1 Experimental technique

Materials

The standard solvent-extraction test system proposed by the European Federation of Chemical Engineering of toluene and water was studied (Misek et al., 1985). The two materials were mutually saturated and the toluene-rich organic phase was used for producing the droplets in the aqueous continuous phase. The physicochemical properties of the mutually saturated phases are presented in Table A.1. In the experiments using the old measuring sequence, deuterated water (D_2O) was used instead of H_2O in order to suppress the measurement signal of the continuous phase below the detectability limit. In this way, only the velocities of the toluene droplet would appear in the experimental results. Deuterated water with a degree of deuteration of 99.8% and toluene of 99.8% purity were both supplied by Sigma Aldrich. The FLIESSEN measuring sequence, however, utilized a selective excitation technique that made the usage of plain distilled water possible by filtering out its signal (Blümich and Casanova, 2007).

In this work, no surface active materials were added to the system. The interfacial tension given in Table A.1 is that of the pure system. The interfacial stagnation studied in the current as well as in previous works (Amar, 2006; Groß-Hardt, 2007) resulted from impurities already present in the measuring apparatus and the materials used (Blümich and Casanova, 2009). Since it has not been possible to eliminate their existence by thoroughly cleaning the apparatus and using purified materials, their effect needed to be taken into account in computer simulations through an appropriate interface model.

Apparatus

The NMR-assembly consisted of a Bruker DSX 500 spectrometer with a superconducting magnet with a field strength of 11.7 T (500 MHz ^1H Larmor frequency), standard Bruker microimaging hardware providing a maximum magnetic gradient strength of 1.0 T/m as well as a birdcage resonator with 10 mm inner diameter. The droplet levitation device consisted of a glass cell designed for keeping the droplet at a steady position over long periods of time, a Verder VG015 gear pump and a Hamilton PS/2 precision syringe pump with a 2500 μL syringe and an injection needle with 0.7 mm inner diameter. The control of the gear pump and the syringe pump was performed with computer software implemented using Visual Designer. Additional equipment included a glass nozzle for the generation of the droplets and glass reservoirs for the aqueous and the organic phases as shown in Fig. 3.1. Due to the strong magnetic field of the NMR-apparatus, the pumps and the computer hardware were kept at a distance from the magnet and long PEEK tubes and PTFE fittings were used for connecting the individual parts.

The glass cell had a total length of 170 cm and outer diameter of 10 mm so that it would exactly fit inside the birdcage resonator. The cell was made of two glass pipes with a 7.2 mm inner diameter that were connected on each side of a third glass part that featured a double cone inner geometry. The double cone was especially fabricated with low tolerances regarding axial symmetry and had a smallest inner diameter of 5.5 mm and an inclination of 1.95° in order to guarantee a laminar flow of the continuous phase.

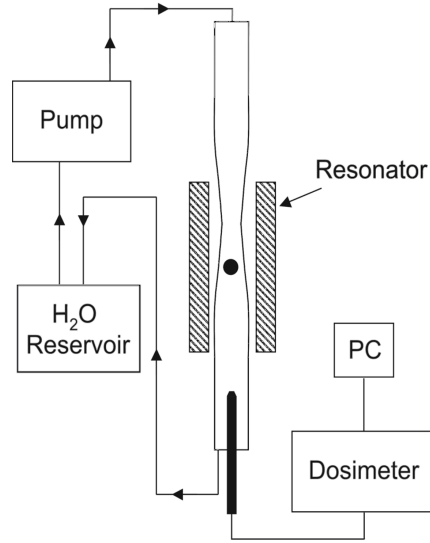


Figure 3.1: Experimental setup for NMR velocity imaging.

Procedure

The size of the droplets studied was chosen based on the experimental data presented by Henschke (2003) that suggest that droplets with a diameter of approximately 4 mm would exhibit an internal circulation without oscillating, provided that the interface is not rigid. Larger diameters would lead to unstable droplets or to collisions with the cell walls (Amar et al., 2005a). After filling the device with the continuous phase, the syringe pump was used to generate a single droplet by injecting a predefined volume of the organic phase into the continuous phase through a nozzle at the base of the glass cell. The injected volume thus defined the droplet diameter. The speed of the syringe plunger and the shape of the nozzle tip guaranteed that the droplet would detach from the nozzle without the generation of secondary droplets.

After the droplet was injected, it was let to travel upwards under the influence of the gravity until it reached the magnetic center of the NMR apparatus. At that point the gear pump was turned on to generate a counter-current of the continuous phase that would keep the droplet levitated at a stable position. Due to the varying inner geometry of the cell the droplet would equilibrate at the most favorable

vertical position according to the counter-current velocity, the droplet size and the mobility of its interface. While the droplet remained at this levitated state, the fluid velocities inside the droplet were measured using the NMR apparatus. The time interval between droplet generation and initialization of the NMR measurement was approximately 20 s. After the measurement, switching off the counter-current would let the droplet rise to the top of the cell above the continuous phase inlet.

3.1.2 Experimental data

The NMR Velocity Imaging technique measures the fluid velocities inside the droplet by encoding signal (spins) in one dimension, and tracing how that signal translates in that dimension during the velocity encoding time Δt as presented in Sec. 2.2.1. In order to reduce the measuring time, only the vertical and one horizontal dimension may be considered, thus leading to the acquisition of velocities that are averaged in the second horizontal dimension. In addition, the obtained information is discretized in space using a predefined pixel size. The experimental results, therefore, consist of two scalar matrices, one containing the horizontal and one containing the vertical velocity components. Thus, the two matrices can be used together to generate a two-dimensional vector matrix with the fluid velocities inside the levitated droplet. Each matrix element can be allocated to a physical position by knowing the pixel size that was used for the space discretization during the measurement.

The velocity encoding time and the space discretization introduce three types of errors in the measured data:

1. Since the fluid velocities are measured as signal transpositions over time, the obtained vector is unavoidably averaged over the velocity encoding time Δt . This fact becomes more important if the encoded signal follows a curved path in space, as shown in Fig. 3.2 (left) for a droplet that is levitated as in the present experiments. If a fluid element is initially positioned at point 1 with a velocity tangential to the pictured streamline and during the velocity encoding time moves to point 2, then its velocity will be measured with acceptable accuracy. However, if in the more pronounced case of a large Δt the fluid element is allowed to move to point 3, then the obtained velocity vector will be erroneous both in magnitude and direction. Nevertheless, although $\Delta t \rightarrow 0$ would be numerically ideal, making Δt too small would make diffusive displacements of signal significant, which is something that would again lead to inaccuracies.
2. Due to the fact that the measured signal amplitude is the result of the phase shifts of all spins in each control volume during signal acquisition, the spin displacement information that is obtained is averaged over the whole volume element. Therefore, a smaller pixel size would lead to velocity measurements of higher accuracy, but technical limitations pose restrictions to its size (Groß-Hardt, 2007).

3. In order to allocate the fluid velocities to their respective physical positions, an imaging module is applied in the NMR-sequence in a stage after the velocity information has been encoded in the measured signal. A displacement of the molecules that carry the signal during the time between the velocity encoding and the end of the imaging module would thus lead to an erroneous velocity spatial mapping unless the molecules move a distance of less than one pixel during that time. As shown in Fig. 3.2 (right), if the encoded signal moves from point 1 to point 2 during the measurement, then both its velocity and location will be correctly acquired. If, however, during the imaging module the signal is displaced from point 1 to point 3, then the position of the velocity vector will be designated to the wrong pixel, although its magnitude will be accurately measured.

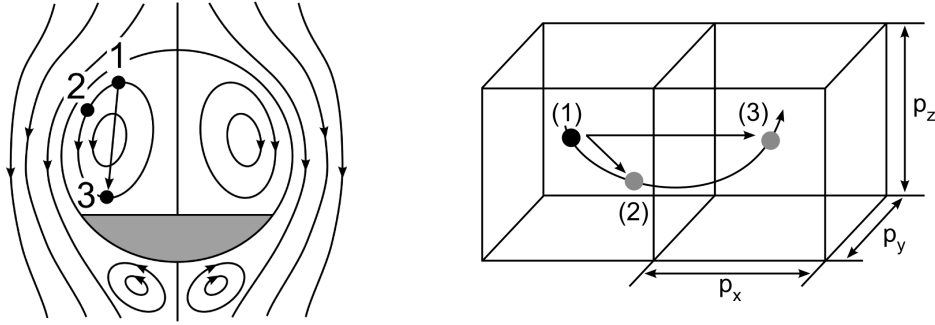


Figure 3.2: Qualitative representation of error due to the velocity encoding (left) and due to the spatial discretization (right).

The type-1 and type-2 errors are addressed in this work by the development of the NMR imaging function that is presented in Sec. 5.2.2. The type-3 errors can be avoided if the appropriate pixel size is chosen to correspond to the highest velocity magnitudes in the droplet and the duration of the imaging sequence. In this work, an imaging accuracy of 1 pixel in each direction has been ensured. However, the standard spin-echo sequence necessitates that each line of the velocity matrix is obtained using individual velocity encoding steps that may be repeated only at 200 ms intervals (Amar et al., 2005a). In the FLIESSEN sequence the need for these relatively long time intervals has been eliminated by decoding the velocity information after each imaging step, thus enabling the immediate initialization of the next velocity imaging stage. In this way, the overall duration of the measurement is an order of magnitude smaller.

For the purpose of this work, two experimental series were provided by the Institute for Macromolecular Chemistry of the RWTH Aachen University: one obtained using the spin-echo sequence (Fig. 3.3) and one using the newly developed FLIESSEN sequence (Fig. 3.4). In Table 3.1, the parameters of the two experiments are presented. Both experiments constitute of a series of two-dimensional vector maps obtained at different time points while the droplet was kept levitated inside the NMR apparatus.

In Fig. 3.3 and Fig. 3.4 the experimental data are presented using three different methods. A three-dimensional surface diagram is used (left) to plot the magnitudes of the velocity vectors (middle) inside the droplet as a function of space. In the diagrams, high peaks of dark color correspond to high velocities whereas lower areas of lighter color correspond to low velocities. In order to obtain a more expressive depiction of the flow pattern inside the droplet, the velocity maps have also been used to calculate the respective streamlines (right). In all data plots, the flow of the continuous phase is from top to bottom.

Table 3.1: Comparison of the experimental parameters of the spin-echo and the FLIESSEN NMR-sequences.

	spin-echo sequence	FLIESSEN sequence
velocity encoding time (ms)	2.5	4.3
resolution (pixels in each dimension)	128	128
pixel size (μm)	78	55
droplet volume (μL)	42	34
horizontal droplet diameter (mm)	4.5	4.1
vertical droplet diameter (mm)	3.9	3.8
water flowrate (mL/s)	1.8	1.6

In both experimental series a region at the rear of each droplet can be distinguished, in which the fluid velocities are smaller than in the upper part of the droplet. This region is usually referred to as the “stagnant cap”. In addition, as time passes the stagnant cap grows and the velocity magnitudes in the upper part of the droplet decrease. These observations are in agreement with the previous findings of Amar et al. (2005b). However, it can be seen that the velocities in the mobile part of the droplet in Fig. 3.3 are greater in magnitude than those in Fig. 3.4. In addition, if the experimental time at which each frame was obtained is considered, it is noticed that the stagnation rate in the new experimental series is much higher. These discrepancies can be attributed to different degrees of contamination in the two experiments. Nevertheless, the data can be safely used for extracting conclusions concerning the accuracy of the two NMR-sequences as well as for the development of an interfacial model for taking the interfacial stagnation into account in CFD simulations.

From the velocity patterns in Fig. 3.3 and Fig. 3.4 (left) a difference in the measured velocity distribution in the droplet between the two experimental series can be observed. The old experimental series feature a pair of spikes in the velocity magnitude diagrams, whereas a smoother velocity distribution is observable at the upper part of the droplet in the respective diagrams of the new experimental series. Furthermore, the front stagnation point at the top of the droplet is evident in the vector plots of the new series, while this is not distinguishable in the old experiments, where relatively big upwards-oriented velocity vectors are found instead.

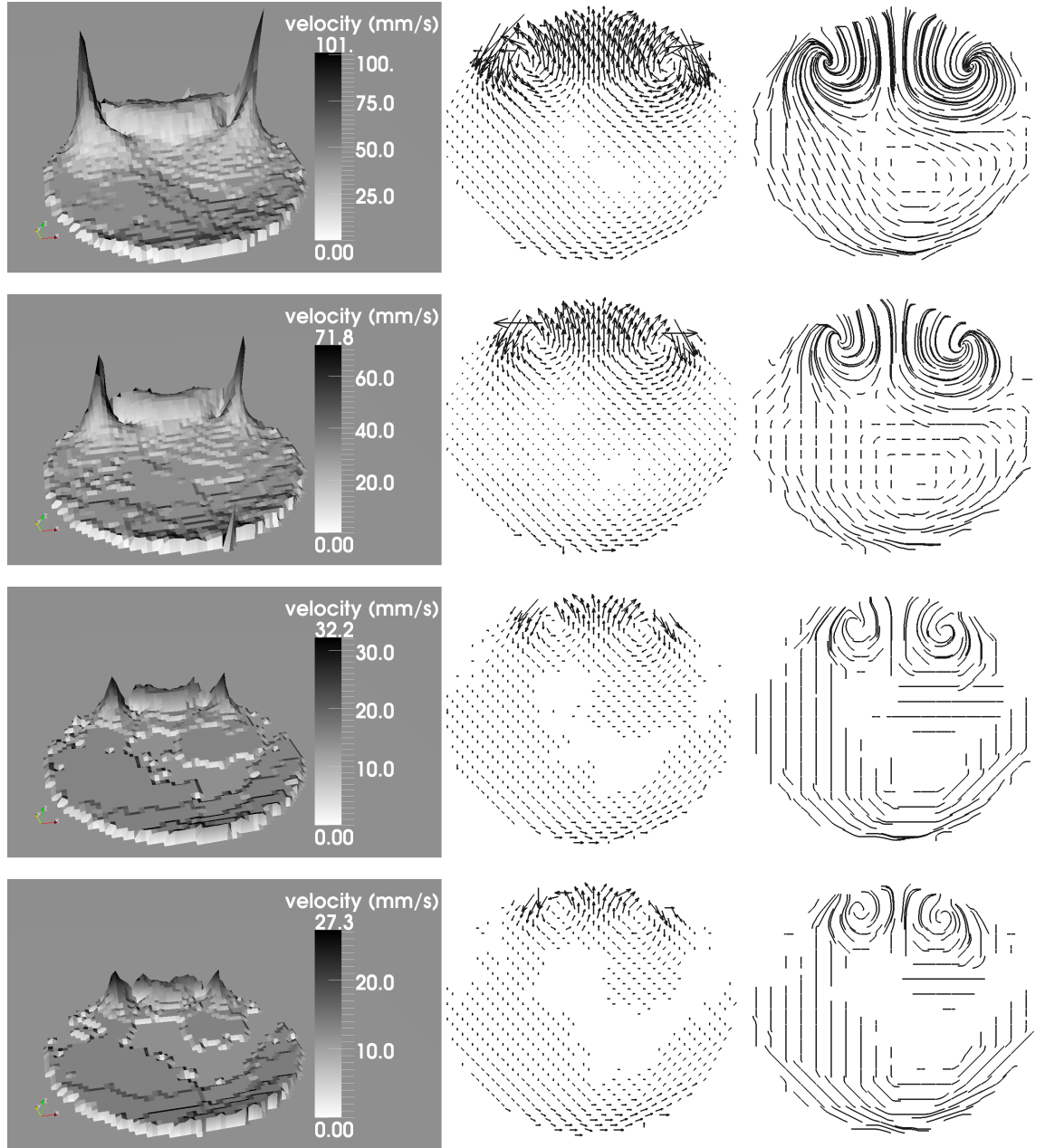


Figure 3.3: Velocities inside a levitated droplet obtained using the spin-echo sequence. Left: velocity magnitudes; middle: velocity vectors; right: streamlines. Measurement time-points since droplet generation (from top to bottom): 10 min, 6 h, 19 h and 23 h. The experimental parameters can be found in Table 3.1.

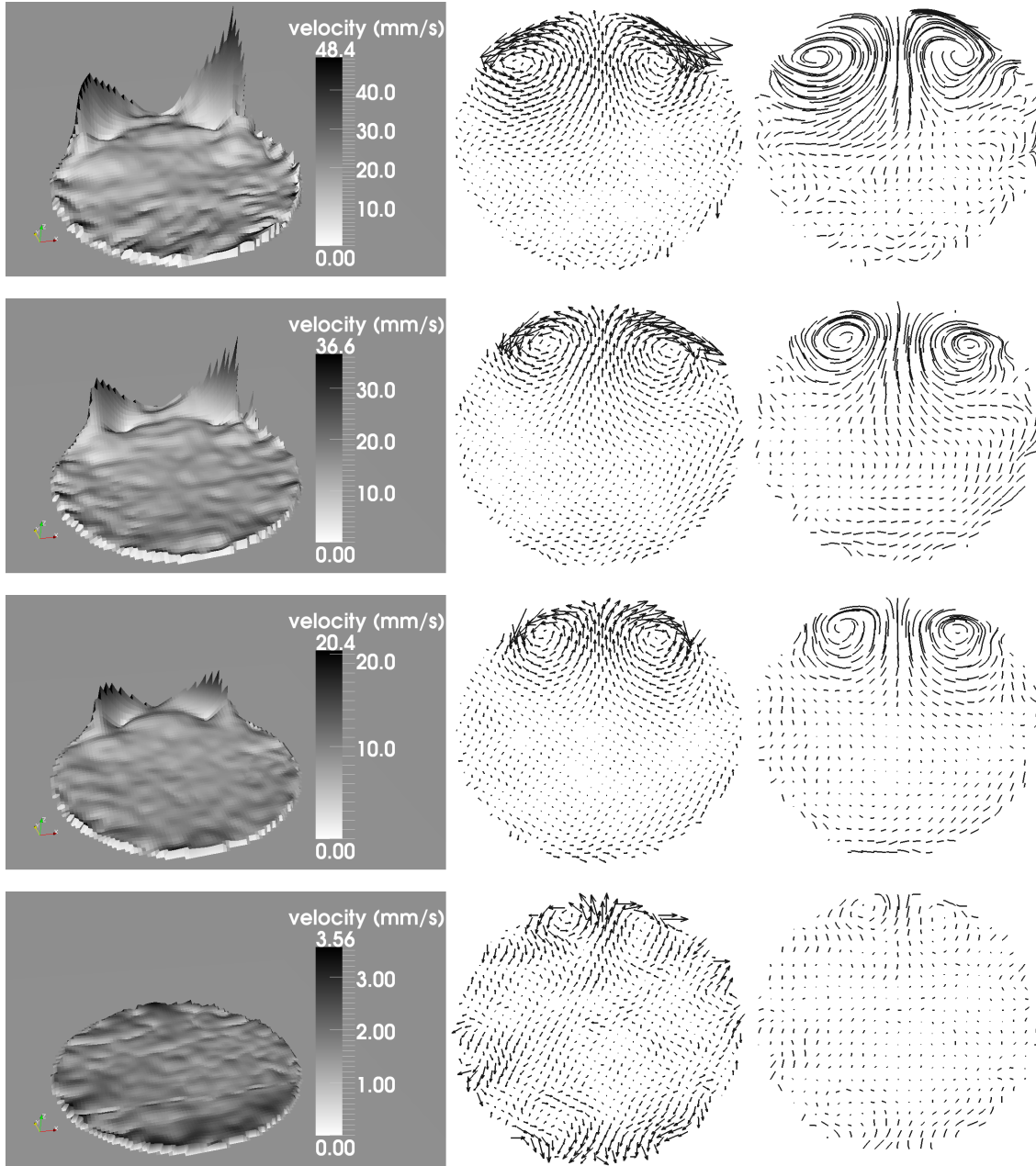


Figure 3.4: Velocities inside a levitated droplet obtained using the FLIESSEN sequence. Left: velocity magnitudes; middle: velocity vectors; right: streamlines. Measurement time-points since droplet generation (from top to bottom): 30 s, 2 min, 3.5 min and 29 min. The experimental parameters can be found in Table 3.1.

These differences can be explained if the pixel size with which the two experiments were performed is considered. As seen in Table 3.1, the matrix resolution and the droplet size in the two experiments were similar, but the pixel size was smaller in the new experimental series, thus leading to an increase of the resolution of the matrix section that contained actual velocity data. In addition, the obtained velocities are calculated by averaging the measured information over a smaller fluid volume.

From the streamlines in Fig. 3.3 and Fig. 3.4 (right) it can also be seen that the old experimental series, due to their low resolution, failed to capture the velocities around the outer rim of the droplet. Moreover, the curvature of the streamlines is better depicted in the new series. Since the interfacial region is of interest in this work, a high resolution becomes significant for obtaining velocity data as close to the interface as possible.

3.2 Sedimenting droplet

Since single-droplet sedimentation experiments have been established as a standard procedure for the investigation of liquid-liquid extraction systems (Henschke, 2003), the accuracy and the reliability of the CFD-software was also tested by comparing the calculated sedimentation velocities of single droplets to experimental data and fitted models. For the purpose of this work, measured terminal velocities of organic droplets sedimenting in a stagnant continuum were obtained from the work of Paesch (1998) that was conducted at the Chair of Thermal Process Engineering of the RWTH Aachen University.

3.2.1 Experimental technique

Materials

For the evaluation of the simulation software, the solvent extraction standard-test system of n-butanol droplets sedimenting in water was considered (Misek et al., 1985). The physicochemical data of the mutually saturated continuous and dispersed phase are given in Table A.2. The water used was deionized and bidistilled. The n-butanol was of analytical grade provided by Merck Germany.

Apparatus

For the sedimentation-velocity measurements a standard sedimentation apparatus is used (Henschke, 2003; Groß-Hardt et al., 2002). A drawing of the sedimentation apparatus is presented in Fig. 3.5. The droplets are generated through a nozzle submerged in a cylindrical cell that contains the continuous phase. The cell was

40 mm in diameter and 500 mm in height and featured a marked measuring region 100 mm in length. The droplet generation was controlled by a Hamilton “Microlab M” syringe dosimetry pump.

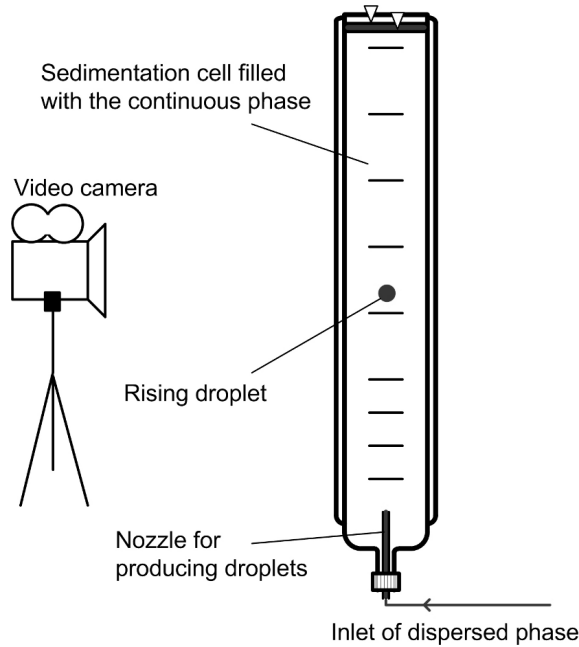


Figure 3.5: Experimental setup for measuring the droplet sedimentation velocity.

Procedure

The droplet size was determined as the diameter of the volume-equivalent sphere based on the liquid volume discharged by the dosimetry pump, that was set as a free variable. For each drop volume the nozzle was chosen from a set of nozzles with different inner diameters such that clean detachment of the drop from the tip of the nozzle was achieved. The experimental error in determining the droplet diameter decreases as the droplet volume increases. The droplet diameter error in this work varies from ± 0.1 mm for the smallest droplet to ± 0.05 mm for the biggest one.

Upon generation, the droplet was given about 12 cm acceleration distance in order to reach its terminal velocity and its position is monitored using a camera recording 30 frames per second. For every droplet diameter two series of measurements were performed. In each of the two series, 20 droplets were generated separated by 3 s time-intervals. The average frame amount of all droplets recorded from the time the droplet enters the measuring region to the time of exit, delivers the droplet travel time for the given distance. From these data the terminal rise velocity of the droplet is calculated. In a batch of 20 droplets, the maximum deviation of a single measurement from the average was found to be no greater than 3 frames, whereas the maximum deviation between two measurements was no greater than 4 frames.

The averages of the two series were also in good agreement, presenting a deviation of maximum 1 frame. Since the sedimentation distance was the same for all droplets, this uncertainty in the determination of the sedimentation time means that the measurement error of the droplet terminal velocity increases as the sedimentation speed rises. If the deviation of 1 frame between the two series averages is considered representative of the experimental uncertainty, then the experimental errors in terms of velocity can be calculated and are presented in Table 3.2. The relative errors in this work vary from 1.5% for the slowest droplet to 2.1% for the fastest one.

The measuring cell and the nozzle were cleaned using chromosulfuric acid, and then washed with bidistilled water and acetone. The dosimetry syringe, as well as the PTFE tubings that were used, were cleaned with acetone and then dried. An additional washing step was performed using the same organic solvent that was also used in the dispersed phase. The temperature of the measurements was 293 ± 0.5 K.

3.2.2 Experimental data

The measured sedimentation velocities are presented as a function of droplet diameter in Table 3.2 together with the respective Reynolds, Eötvös and Archimedes numbers. The Morton number is dependent only on the material properties, and is, therefore, constant for the given binary system. For the n-butanol+water system, the Morton number equals $Mo = 1.22 \times 10^{-6}$. According to Eq. 2.2 and Eq. 2.3, it is found that n-butanol droplets with $0.48 \text{ mm} \leq d \leq 2.85 \text{ mm}$ should have an internal circulation. Smaller droplets should be rigid whereas bigger droplets should exhibit an oscillating behavior. Moreover, with the help of Fig. 2.1 (Clift et al., 1978), it can be estimated that droplets with $Re < 25$, $Eo < 0.8$ and thus $d \leq 1.0 \text{ mm}$, are expected to be spherical, whereas droplets beyond this limit are expected to be ellipsoidal.

Table 3.2: Experimental sedimentation velocities and dimensionless numbers for n-butanol droplets in continuous water phase.

d (mm)	v_{sed} (mm/s)	$\pm$ (mm/s)	Re	Eo	Ar	shape
1.56	45	0.67	49.9	2.07	2690	ellipsoidal
1.79	52	0.9	66.2	2.72	4064	ellipsoidal
2.12	59	1.16	88.9	3.82	6752	ellipsoidal
2.26	61	1.24	98.0	4.34	8180	ellipsoidal
2.48	63	1.32	111.0	5.22	10808	ellipsoidal
3.06	62	1.28	134.8	7.95	20303	oscillating
3.48	58	1.12	143.5	10.3	29864	oscillating

The model suggested by Henschke (2003), that was presented in Sec. 2.1.1, was fitted to the experimental data of Table 3.2 and the results are shown in Fig. 3.6 together with the model lines representing the ideally mobile and the rigid droplet interface. For a system free of surface-active impurities, the CFD-implementation of a free surface model, like the level-set function that was used in this work, should provide results that come close to the model curve representing the ideally mobile droplet interface. This is because the free surface modeling in a CFD simulation can not take interfacial stagnation phenomena into account unless they are considered explicitly in the mathematical formulation. In this work, such a model is implemented only in the case of the levitated droplet. As seen in Fig. 3.6, the model of Henschke (2003) presents a good fit to the experimental data and the values of the fitted parameters were: $d_{sw} = 1.63$ mm, $\alpha_{sc} = 3.76$ and $\alpha_{tr} = 2.98$.

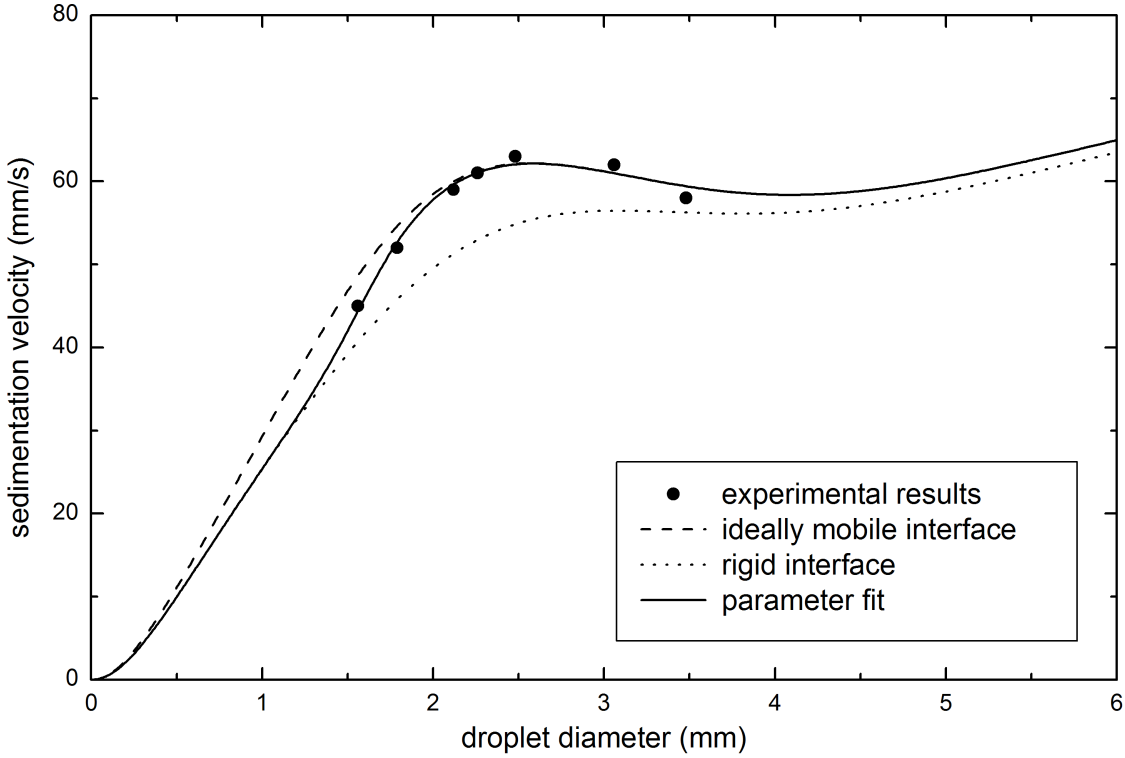


Figure 3.6: Experimental data and sedimentation curves of the Henschke (2003) model.

Chapter 4

The simulation tool DROPS

For the numerical simulation of the sedimenting and the levitated droplets the custom-made 3D finite element package DROPS (Groß et al., 2002) is used. This software was developed at the Chair of Numerical Mathematics of RWTH Aachen. The code is written in C++ and is also used in other applications such as heat transfer and flow problems in falling films (Groß et al., 2005). In Sec. 4.1 some of the numerical methods and modules implemented in DROPS are briefly discussed. In Sec. 4.2 the geometrical setups of the simulations are presented for the case of the sedimenting droplet as well as for the case of the levitated droplet. For a more detailed description the reader is referred to the work of Groß et al. (2006) as well as the DROPS manual (Reusken, 2009) and the citations therein. Since the simulation of three-dimensional two-phase flow problems has a very high numerical complexity, most parts of the code have been parallelized. For the parallelization aspects of the DROPS code see the work of Terboven et al. (2005) and Fortmeier and Bucker (2011a,b).

4.1 Governing methods

4.1.1 Fluid dynamics and interface capture

For the modeling of the two-phase droplet problem the two phases Ω_1 (droplet) and Ω_2 (continuous phase) are assumed to behave like incompressible immiscible Newtonian fluids. Conservation of mass and momentum yields the incompressible Navier-Stokes equations in each phase with a free boundary condition at the interface $\Gamma = \Gamma(t) = \partial\Omega_1$, where the standard assumption is made that the interfacial tension balances the jump of the normal stress on the interface (Eq. 4.1) and that the normal and tangential velocities at the interface are continuous (Eq. 4.2), i. e.:

$$[\mathbf{T} \cdot \mathbf{n}]_\Gamma = \sigma \kappa \mathbf{n} - \nabla_\Gamma \sigma, \quad (4.1)$$

$$[\mathbf{u}]_\Gamma = 0. \quad (4.2)$$

Here, $\mathbf{n} = \mathbf{n}_\Gamma$ is the unit normal at the interface (pointing from Ω_1 in Ω_2), σ is the interfacial tension, $\kappa = -\nabla \cdot \mathbf{n}$ is the curvature of the interface Γ , where the negative sign implies that the curvature center is in the droplet, $\mathbf{u} = \mathbf{u}(x, t)$ is the velocity vector and $\mathbf{T}$ the stress tensor that can be expressed as:

$$\mathbf{T} = -p\mathbf{I} + \mu\mathbf{D}(\mathbf{u}), \quad (4.3)$$

where, $\mathbf{I}$ is the identity matrix, $p = p(x, t)$ is the pressure, μ is the dynamic viscosity, and $\mathbf{D}(\mathbf{u})$ is the deformation tensor:

$$\mathbf{D}(\mathbf{u}) = \nabla \mathbf{u} + (\nabla \mathbf{u})^T. \quad (4.4)$$

In Eq. 4.1, the term $\sigma \kappa \mathbf{n}$ represents the capillary force, which is the interfacial tension component that is normal to the interface. The tangential component, which is represented by the term $\nabla_\Gamma \sigma$, is the so-called Marangoni force (James and Lowengrub, 2007; Xu et al., 2006; Teigen et al., 2010), in which ∇_Γ denotes the tangential gradient along the interface and is defined as:

$$\nabla_\Gamma = (\mathbf{I} - \mathbf{n} \otimes \mathbf{n})\nabla. \quad (4.5)$$

The Marangoni force appears, therefore, only when a gradient of the interfacial tension exists (Chung, 2010; Ferziger and Peric, 2002; Croce et al., 2010). If the Marangoni force is not canceled out by any other forces in the system, a fluid flow along the interface will appear as a result. In addition, this flow will be directed from regions of lower interfacial tension to regions of higher interfacial tension. The Marangoni force is often referred to in the literature in connection to interfacial tension gradients that exist due to temperature inhomogeneities (Shyy, 1994; Shyy et al., 1996). Interfacial tension gradients can however exist also due to concentration inhomogeneities, either of chemical species that are being transferred from one phase into the other, or of surfactant species that accumulate on the interface, as is the case in this work.

The effect of the interfacial tension can be expressed in terms of a localized force at the interface, i. e. the so-called “continuum surface force” (CSF) model (Brackbill et al., 1992). This localized force is given by

$$f_\Gamma = \sigma \kappa \delta_\Gamma \mathbf{n}_\Gamma - \nabla_\Gamma \sigma \delta_\Gamma, \quad (4.6)$$

where δ_Γ is a function that is zero everywhere except on Γ . In the CSF model the discontinuous interfacial-tension force is replaced by a continuous formulation in order to avoid instabilities. The interface is thus represented by a continuous transition region that is not necessarily aligned with the grid and the surface force

acts everywhere within this region. The CSF method thus eliminates the need for interface reconstruction and simplifies the calculation of the interfacial tension effects (Jakobsen, 2008).

This force-localization approach can be combined with the level-set method for capturing the unknown interface as described in Chang et al. (1996). The level-set function, denoted by $\phi = \phi(x, t)$, is a scalar function with:

- $\phi(x, t) < 0$ for $x \in \Omega_1(t)$,
- $\phi(x, t) > 0$ for $x \in \Omega_2(t)$ and
- $\phi(x, t) = 0$ for $x \in \Gamma(t)$.

Hence, the interface is implicitly given by the zero-level of the level-set function. The jumps in the coefficients ρ and μ can be described using the level-set function in combination with the discontinuous Heaviside function H :

$$\rho(\phi) := \rho_1 + (\rho_2 - \rho_1)H(\phi), \quad (4.7)$$

$$\mu(\phi) := \mu_1 + (\mu_2 - \mu_1)H(\phi), \quad (4.8)$$

where

$$H(\phi) = \begin{cases} 0 & \text{for } \phi < 0 \\ 1 & \text{for } \phi > 0 \end{cases}. \quad (4.9)$$

Together with suitable initial and boundary conditions for $\mathbf{u}$ and ϕ , a combination of the CSF approach with the level-set method leads to the following continuous model for the two-phase transient problem in $\Omega \times [0, t]$ (Tornberg and Engquist, 2000; Sussman et al., 1999):

$$\rho(\phi) \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla p + \rho(\phi) \mathbf{g} + \text{div}(\mu(\phi) \mathbf{D}(\mathbf{u})) + f_\Gamma \quad (4.10)$$

$$\text{div } \mathbf{u} = 0 \quad (4.11)$$

$$\phi_t + \mathbf{u} \cdot \nabla \phi = 0 \quad (4.12)$$

where the linear hyperbolic level-set equation for the advection of the interface is introduced for $t \geq 0$ and $x \in \Omega$ (Eq. 4.12).

However, relying only on advection for the evolution of the level-set function is not enough, since it would degenerate over time. This affects the treatment of the discontinuities and the refinement of the interfacial region. To avoid this undesirable behavior a reparametrization scheme for the level-set function was implemented such that ϕ remains close to a signed distance function. Moreover, this reparametrization is used to smooth the level-set function close to the interface and thus stabilize its evolution. Another problem with the level-set function is that mass conservation is not inherently included in the formulation (Sec. 2.1.2). In general, the volume of the

droplet will shrink with time. This numerical loss of volume reduces if a finer grid is used. An interface shift is applied to compensate for the volume loss (Groß et al., 2006). An alternative approach for obtaining better mass conservation is given by Zimmerman (2006), using a suitable source term in the transport equation for ϕ .

For the discretization of the flow variables and of the level-set function a finite-element approach is used (Groß et al., 2002). For the spatial discretization of the velocity $\mathbf{u}$ and pressure p the co-called $P_2 - P_1$ (piecewise quadratic-piecewise linear) finite-element pair is used. The level-set function ϕ is discretized by continuous piecewise quadratic finite elements. For the numerical treatment of the surface force term f_Γ a modified Laplace-Beltrami technique is applied to avoid an explicit computation of the curvature which would involve the approximate evaluation of second order derivatives. More details concerning the interface approximation and discretization of the surface-force term can be found in Groß and Reusken (2007b).

4.1.2 Extended finite elements

Many liquid-liquid extraction systems of technical relevance have a high interfacial tension that leads to a respectively high pressure jump across the interface. Since the interface is implicitly given by the zero level of the level-set function, it is in general not aligned with the triangulation that is used in the discretization of the flow problem. This non-alignment causes difficulties with respect to the discretization of the localized interfacial-tension force and the discretization of the pressure variable, which is discontinuous across the interface.

In standard finite-element spaces the functions used for discretization are either continuous or discontinuous across element borders, but in general continuous across the interface due to the non-alignment. Therefore, the standard discretization functions are not very suitable for the approximation of the discontinuous pressure. In many simulations this causes strong unphysical oscillations of the velocity vector at the interface, the so-called “spurious velocities” or “spurious currents” (Scardovelli and Zaleski, 1999). These spurious velocities can be avoided to a large extent if in addition to the modified Laplace-Beltrami discretization that is used for the interfacial-tension force, an “extended finite-element” (XFEM) space is implemented for the discretization of the pressure. The XFEM approach was originally introduced and applied to fracture mechanics in Moës et al. (1999) and Hansbo and Hansbo (2004).

For the construction of the XFEM space, the standard finite element space Q_h and its piecewise linear nodal basis functions $q_1, \dots, q_n \in Q_h$ with $n := \dim Q_h$ are considered. In addition, $\mathcal{I}_\Gamma \subset \{1, \dots, n\}$ is defined as the set of indices associated to the tetrahedra intersected by Γ . For each of these indices $i \in \mathcal{I}_\Gamma$, an additional basis function q_i^Γ is introduced which is discontinuous at the interface:

$$q_i^\Gamma(\mathbf{x}) := q_i(\mathbf{x}) \cdot (H_\Gamma(\mathbf{x}) - H_\Gamma(\mathbf{x}_i)), \quad (4.13)$$

with $H_\Gamma(\mathbf{x}) = 0$ for $\mathbf{x} \in \Omega_1$ and $H_\Gamma(\mathbf{x}) = 1$ for $\mathbf{x} \in \Omega_2$. The XFEM space Q_h^Γ is thus defined by the span of $\{q_i\}_{i=1}^n \cup \{q_i^\Gamma\}_{i \in \mathcal{I}_\Gamma}$. Thus, the XFEM space consists of all functions which are piecewise linear on each of the subdomains Ω_1 and Ω_2 , but may have a jump across the interface. In this way, the pressure jump across the interface of a droplet can be estimated with a higher accuracy than with the conventional finite element space $(P_2 - P_1)$ as demonstrated by Groß and Reusken (2007a). In Fig. 4.1 (Esser et al., 2009), a toluene droplet levitated in an aqueous continuum is shown, simulated using the conventional finite element discretization (left) and the XFEM technique (right). Using the standard FEM space Q_h , the pressure jump due to the high interfacial tension is not accurately resolved and the spurious velocities that appear at the vicinity of the interface deform the droplet surface and lead to unphysical flow patterns. In the case of the XFEM space Q_h^Γ the spurious velocities are not present and a smooth representation of the liquid-liquid interface is achieved.

In this work, two versions of the DROPS CFD-package were considered: one based on the standard finite-element space $(P_2 - P_1)$ and one using the XFEM approach for the pressure variable. These two versions were compared based on the example of an n-butanol droplet rising freely in an aqueous continuum. Although this standard test-system had a relatively low interfacial tension the obtained results were suggestive of the quality of the XFEM method. More details regarding the pressure XFEM space for two-phase flow problems can be found in Reusken (2008). An alternative approach for avoiding large spurious oscillations in the velocity and pressure fields is the “ghost fluid method” described in Fedkiw and Liu (1998) and Fedkiw et al. (1999).

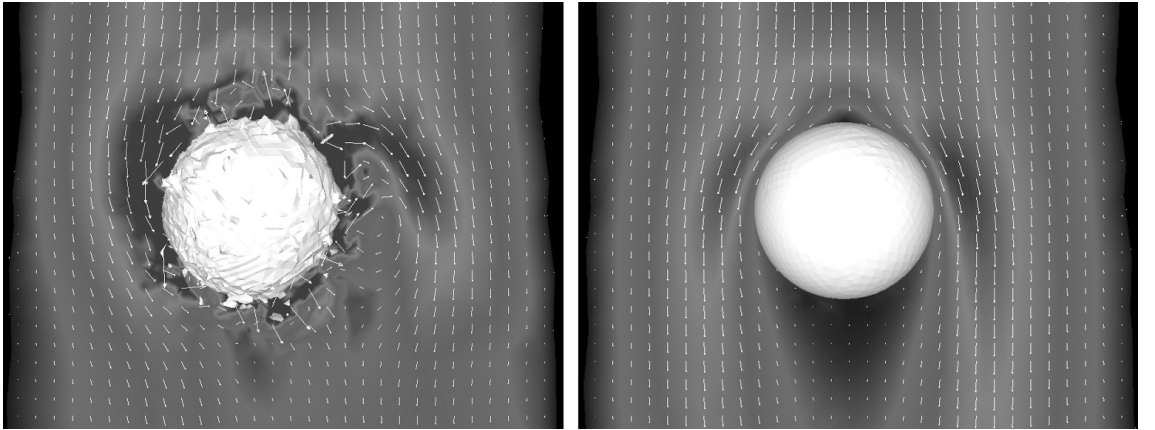


Figure 4.1: Representation of the liquid-liquid interface between a toluene droplet levitated in an aqueous counter-current simulated using the conventional finite element (left) and the XFEM methods (right) (Esser et al., 2009).

4.1.3 Parallelization

To achieve a higher accuracy using DROPS, the computational grid must be locally refined in the vicinity of the interface. For three-dimensional simulations of high-resolution a parallel version of the code is needed for computation efficiency. The standard finite-element (P_2 - P_1) discretization of the Navier-Stokes equations and of the level-set equation have an inherent data locality property and their parallelization is thus straightforward. Nevertheless, since the XFEM space depends on the location of the interface that is not constant with time, the dimension of Q_h^Γ may change because some additional basis functions may appear or disappear while the interface is moving. Therefore, this method is more difficult to parallelize since the extended finite-element space changes depending on the dynamics of the interface. In Sec. 6.1 of this work, the results of parallel simulations using the P_2 - P_1 discretization are presented, courtesy of the Chair for Scientific Computing of the RWTH Aachen University (Fortmeier and Bucker, 2011a,b). For the reasons described above, however, the XFEM simulations were performed on a serial computer.

4.2 Computational domains and grids

For the levitated droplet, the geometry of the computational domain and the initial mesh were generated using the software package GAMBIT. The dimensions of the domain were defined to match those of the experimental apparatus. Since the diameter of the experimental measuring cell is constant for most of its length, only its middle part that featured the double cone inner geometry was considered in the simulation. The geometry and the dimensions of the computational domain for the levitation apparatus are shown in Fig. 4.2.

The droplet is initially centered in the lower part of the double-cone geometry using an approximation for its position on the vertical axis. During the simulation, the droplet is free to equilibrate at its most favored location depending on its size, the inlet velocity of the continuous phase (that is defined as a boundary condition) and its interfacial tension profile. For saving computational time, the results of a previous simulation, in which the droplet has reached a steady-state condition, could be used for initializing a subsequent simulation with a different interfacial-tension profile.

For the sedimenting droplet, the geometry and the grid were generated using DROPS. The initial tetrahedral triangulation of the computational domain used in the simulations is shown in Fig. 4.3. At the initialization of the simulation, the droplet is centrally placed slightly above the bottom of an orthogonal computational domain. The domain dimensions were set depending on the droplet diameter so that the walls are at a relatively safe distance from the droplet interface (see Sec. 6.1.1 for

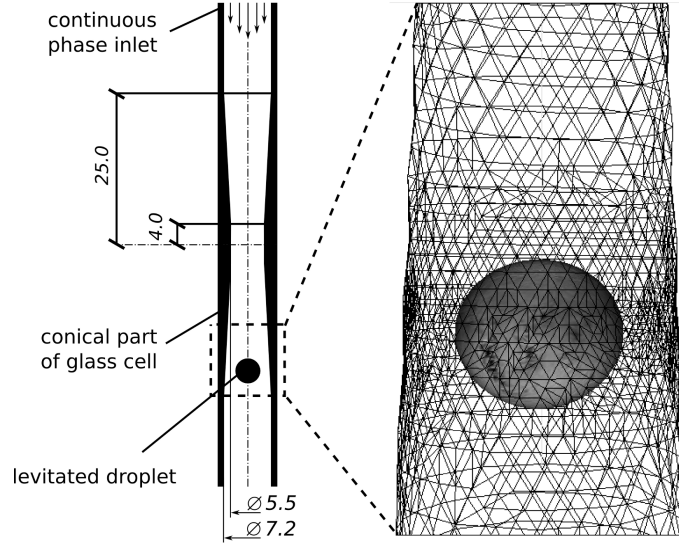


Figure 4.2: Computational domain and initial grid for a levitated droplet.

a discussion on the issue). Depending on the droplet diameter, the domain height is chosen such that during the simulation the droplet moves approximately through half the domain height. Due to this, the effect of the upper domain wall can be neglected. In both the levitated and the sedimenting droplet cases, a no-slip boundary condition was applied on the domain walls.

The spatial discretization is based on a multilevel hierarchy of tetrahedral grids. An adaptive refinement algorithm (Groß and Reusken, 2005) was implemented in order to obtain a high grid resolution close to the interface where most of the interesting phenomena occur. The mesh size in the vicinity of the interface is decreased gradually and directly related to the number of (local) refinement levels. In a refinement step a marked tetrahedron is divided into eight new elements and in a subsequent step, “hanging nodes” are eliminated. The refinement algorithm is such that strongly deteriorated tetrahedra with very small angles do not occur. As time evolves the grid is updated by refinement and coarsening to adapt it to the new position of the drop as shown in Fig. 4.4 for the case of the sedimenting droplet. The size of the region around the droplet interface where the local refinement is applied is set using a simulation parameter. In the present work, this parameter has a value of approximately the droplet radius and the grid resolution is characterized by the mesh size of the elements close to the droplet interface.

The number of refinement levels has a considerable impact on the simulation’s duration. Using an AMD Athlon 64 X2 4200+ CPU with 3 GB of memory, the time needed to perform the simulations presented in this work ranged from 2 days for simulations with relatively coarse grids and small domains, to 10 days for simulations with fine grids and large domains. Table 4.1 presents some characteristic grids

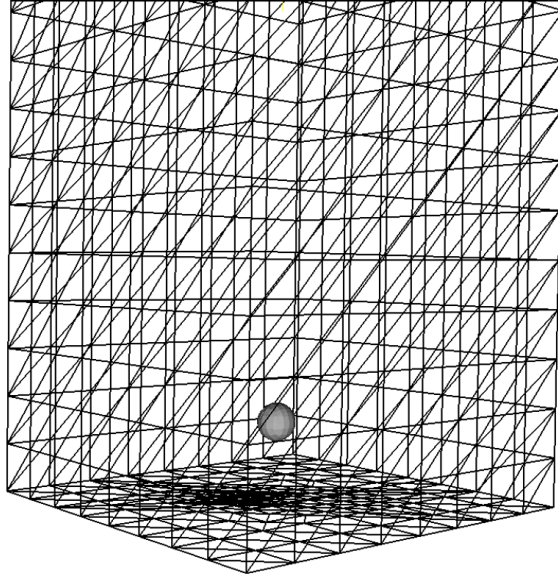


Figure 4.3: Computational domain and initial grid for a sedimenting droplet with diameter of 1.0 mm

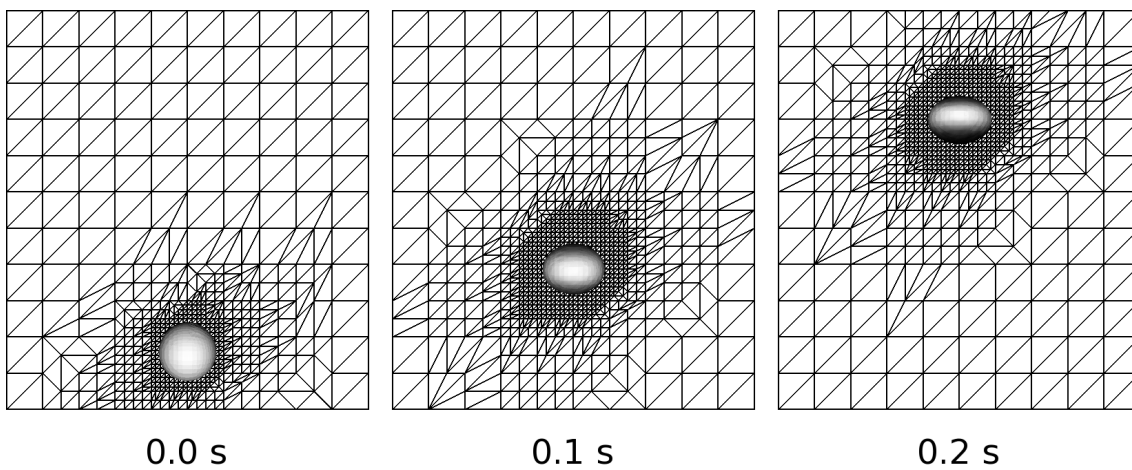


Figure 4.4: Evolution of the grid with droplet movement.

sizes and simulation times for different refinement levels of various computational domains and droplet diameters. In this work, the mesh size at the droplet interface is used to represent the resolution of the grid and is denoted by h . Additionally, the dimensionless mesh size, defined by the fraction h/d , is used to indicate the grid resolution in relation to the droplet diameter. The size of the computational domain is indicated by the the horizontal distance ξ_0 of the droplet interface to the computational-domain wall at the beginning of the simulation.

The data in Table 4.1 show that, for the same computational domain, each refinement level reduces the smallest mesh-element size h to half, but the amount of grid knots and cells, as well as the computational time, increase exponentially. However, due to the local refinement, the computational domain can be quadrupled in size and, even if the refinement level and the mesh size are kept constant, the amount of cells will only double.

Table 4.1: Characteristic grid sizes and average simulation times.

d (mm)	refinement level	h (mm)	h/d	knot amount	cell amount	ξ_0 (mm)	simulation time (min/step)
2.0	2	0.625	0.313	13025	68272	9.0	0.60
2.0	3	0.313	0.157	18456	100352	9.0	3.34
2.0	4	0.156	0.078	45893	264224	9.0	12.0
3.0	2	0.625	0.208	14987	79872	8.5	1.62
3.0	3	0.313	0.104	28875	162672	8.5	5.46
3.0	4	0.156	0.052	111100	654768	8.5	32.7
4.0	2	0.625	0.156	15260	81712	13	1.85
4.0	3	0.313	0.783	29680	167712	13	7.25
4.0	3	0.313	0.783	62480	352032	28	12.3

Chapter 5

Interface modeling of the levitated droplet

In Sec. 5.1.1 of this chapter, the model used to simulate the experimentally measured droplet internal flow and the rigid cap that were discussed in Chap. 3 will be introduced. The physical meaning of the model will be the topic of Sec. 5.1.2. In Sec. 5.2.1, the inverse problem of fitting the model parameters to the experimental data will be defined, and the methods involved in solving it will be discussed. The techniques used to compare the CFD simulations to the experimental data will be presented in Sec. 5.2.2.

5.1 The variable interfacial-tension model

As discussed in Sec. 2.1.3, earlier attempts to model the single droplet behavior under the influence of surfactants have not been focusing on the interfacial-tension profile of the droplet. Droplet stagnation was a result emerging from either surfactant transport mechanisms or boundary conditions that were explicitly set at the liquid-liquid interface. Thus, the interfacial-tension profile on the droplet has not been investigated in depth. The model implemented in this work, dubbed “VarIT” (**V**ariable **I**nterfacial **T**ension), focuses on the impact of the interfacial-tension gradient on the internal fluid dynamics of the droplet. The interfacial-tension gradient does not result from the solution of a surfactant transport equation coupled with an equation of state, but is defined with the help of three adjustable parameters (Sec. 5.1.1). In addition, the simulation of the rigid cap is not performed by dividing the droplet interface into a mobile and an immobile part with the respective boundary conditions, but by solving the inverse problem based on experimental data (Sec. 5.2). Although a model based on a surfactant transport mechanism would be physically better founded, when the surfactant species and their concentration in the liquid-liquid system are unspecified, many key variables and equations needed

for a more detailed description would consequently be unknown. Moreover, as it will be shown in Sec. 5.1.2, the VarIT-model parameters do not lack physical meaning, although this is expressed in a qualitative manner.

Surfactant-transfer models in the literature depicted rigid caps that were very small in comparison to the caps measured in the experiments used in this work (Li and Mao, 2001). On the other hand, models like the one of Groß-Hardt (2007) that take a no-slip boundary condition at the rear part of the droplet surface for granted can not be used to reach conclusions regarding the surfactant concentration gradient on the interface. In the VarIT model, the stagnation at the rear of the droplet is a consequence of the balance between the forces resulting from the imposed interfacial-tension gradient, and the shear stress induced by the continuous phase. Thus, a high degree of adjustability is achieved while it is still possible to extract conclusions regarding the system's physical state. Also in this case however, in order for any conclusions to be correct, the internal droplet flow must be validated through quantitative comparison to experimental data.

5.1.1 Model definition

The modeling concept is based on a variable interfacial tension (Fig. 5.1, left) that is caused by the inhomogeneous distribution of the surfactant molecules on the droplet surface (Fig. 5.1, right) as described in Sec. 2.1.3. The interfacial-tension gradient (Fig. 5.1, middle) is developed as a consequence of the following factors:

- the continuous phase counter-current,
- forces tangential to the interface and opposite to the continuous phase flow that are caused by the inhomogeneity of the interfacial tension,
- continuous transport of surfactant molecules to and from the interface.

The fluid dynamics at the vicinity of the interface are governed by the first two factors and the material properties of the system. Concerning the second point, it needs to be noted that although the surfactants are the reason for the tangential forces within the interface, these forces also play a role in maintaining the inhomogeneous distribution of surfactants on the droplet surface. Concerning the third point, the surfactants may originate from either or both of the two phases, but in any case the thermodynamic and the momentum-conservation principles need to be satisfied. This means that the surfactant molecules may move onto and away from the interface through convection and diffusion, while taking into account their solubilities in each phase and the fact that the interface is energetically their most favored location. The surface tension gradient is maintained by a combination of all of the factors listed above. However, the VarIT model does not discriminate between them, and the surface-tension curve is defined with the help of the following three parameters that configure its shape and position:

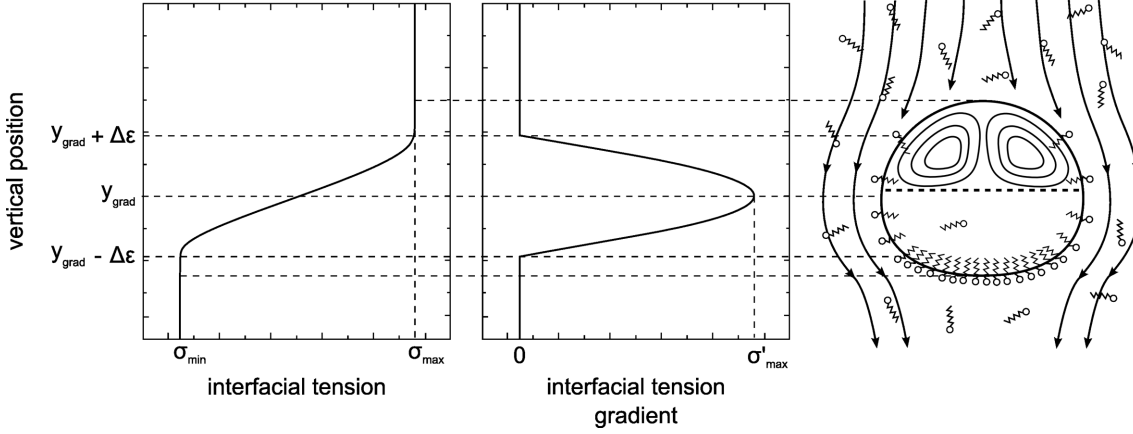


Figure 5.1: Profiles of the interfacial tension (left) and its gradient (middle) along the droplet surface, and their qualitative relation to the VarIT model concept (right).

1. $y_{grad,rel}$: defines the position of the interfacial-tension gradient center. This position is defined in relation to the droplet upper and lower edges, namely:
 - $y_{grad,rel} = 0$: upper edge
 - $y_{grad,rel} = 1$: barycenter
 - $y_{grad,rel} = 2$: lower edge

Since the droplet is allowed to move freely, defining variable $y_{grad,rel}$ relatively to the droplet upper and lower edges, couples it to droplet translatory motion, but not to rotational motion.

2. $\Delta\epsilon$: defines the width of the interfacial-tension gradient. The vertical length of the interfacial-tension gradient is equal to $2\Delta\epsilon$. Variable $\Delta\epsilon$ is used together with variable $y_{grad,rel}$ so that the interfacial-tension gradient will move with any translatory motion of the droplet, but it will not be affected by droplet deformation.
3. α : defines the difference between the minimum and the maximum surface-tension values that are used in the model. Since surfactants decrease the interfacial tension:

$$\begin{aligned} \sigma_{min} &= \alpha \cdot \sigma_{max} \\ 0 < \alpha < 1 \end{aligned} \tag{5.1}$$

From parameter $y_{grad,rel}$ the absolute position of the interfacial-tension gradient center y_{grad} is calculated using the vertical coordinates of the droplet barycenter and the upper droplet edge y_{bary} and y_{top} respectively:

$$y_{grad} = y_{grad,rel} \cdot y_{bary} + (1 - y_{grad,rel}) y_{top} \tag{5.2}$$

For every point on the interface P_y^{int} with vertical coordinate P_y^{int} , the surface tension is calculated with the help of variable y_{test} , that expresses the point's distance from the interfacial-tension gradient center, and variable θ that is used to calculate the interfacial tension at that point.

$$y_{test} = P_y^{int} - y_{grad} \quad (5.3)$$

$$\theta = \frac{\pi y_{test}}{2\Delta\epsilon} \quad (5.4)$$

For every P_y^{int} the value of y_{test} is checked and the respective interfacial tension is attributed to that point according to Eq. 5.5:

$$\sigma = \begin{cases} \sigma_{max} & \text{where } y_{test} > \Delta\epsilon, \\ \sigma_{min} & \text{where } y_{test} < -\Delta\epsilon, \\ \sigma_{min} + \frac{1}{2}(\sigma_{max} - \sigma_{min})(\sin(\theta) + 1) & \text{otherwise.} \end{cases} \quad (5.5)$$

The sine function in Eq. 5.5 is used in order to obtain a continuous interfacial-tension gradient function along y and thus simplify the numerical implementation of the model. This results in an interfacial-tension gradient curve shown in Fig. 5.1 (middle) that features a maximum at the center of the interfacial-tension slope. This peak represents the point where the gradient-induced interfacial force is strongest. The gradient of the interfacial tension with respect to y is:

$$\sigma' = \begin{cases} \frac{\pi}{4\Delta\epsilon}(\sigma_{max} - \sigma_{min})\cos(\theta) & \text{where } -\Delta\epsilon < y_{test} < \Delta\epsilon, \\ 0 & \text{otherwise.} \end{cases} \quad (5.6)$$

A similar interfacial-tension gradient profile was also suggested by Griffith (1962) based on Savic (1953). In that work, the equation for the interfacial-tension profile that would result in complete droplet stagnation was derived analytically. The Stokes stream function was used to predict the shear-stress profile on the droplet surface that was caused by the droplet's relative motion to the continuous phase. A force induced by an interfacial-tension gradient was used to counter-act the force of the continuous phase so that interfacial stagnation would appear. The result was a trigonometric function for the interfacial tension whose derivative featured a maximum similar to the one shown in Fig. 5.1 (middle). The interfacial-tension gradient was applied along the whole droplet length and its maximum was located at the droplet equator since the Stokes stream function also predicted the maximum shear stress at that point. The importance of the interfacial tension *gradient*, as opposed to the interfacial tension alone, is thus stressed.

In this work, the experimental data show droplets that are not completely stagnant. Therefore, the stagnation is limited to the rear part of the droplet and not along the entire droplet surface, as opposed to the work of Griffith (1962). Nevertheless, in both cases a suitable interfacial-tension profile along the y -axis is sought the gradient of which produces a force along the droplet surface that cancels out the

shear stress of the counter-current flow. Since this force is a result of the interfacial-tension gradient and not the interfacial tension itself, the actual values of σ_{max} and σ_{min} have no significant impact on the droplet stagnation as long as the gradient profile $\sigma'(y)$ remains unaltered. In Sec. 6.3.2 this aspect is addressed in more detail. The limiting values σ_{max} and σ_{min} are, however, of physical importance as will be discussed in the following section (Sec. 5.1.2).

5.1.2 Physical interpretation

Although the VarIT model is of empirical nature, it represents a physically founded phenomenon, i.e. the distribution of surfactants on the droplet surface. This phenomenon is described by the model parameters that define the shape and the position of the interfacial-tension gradient. Therefore, different combinations of values of the model parameters result in different conditions, each with its own physical meaning. Depending on the system's state, or on the desired shape of the interfacial-tension gradient, various cases can be identified based on the relations between σ_{pure} , σ_{top} and σ_{max} . Variable σ_{pure} is the interfacial tension of the pure system and σ_{top} is the interfacial tension at the top of the droplet. σ_{max} is the maximum interfacial tension on the model curve and can be practically set to any positive value. However, there must always be $\sigma_{top} \leq \sigma_{pure}$, since the interfacial tension on the droplet may not exceed that of the pure system. Fig. 5.2 shows the various physical states that were examined in this work, which are:

1. In a usual case that is often discussed in the literature, the interfacial tension at the upper droplet part, σ_{top} , is equal to the interfacial tension of the pure binary system without any impurities σ_{pure} . The maximum value of the model curve is set equal to that value, i.e:

$$\sigma_{top} = \sigma_{pure} = \sigma_{max}$$

This case is shown in Fig. 5.2 (left). This setting means that at least the top droplet pole is free of surfactants and that the interfacial tension gradient at that point will be zero. By adjusting the values of parameters $y_{grad,rel}$ and $\Delta\epsilon$ the size of the uncontaminated surface region on the upper part of the droplet can be defined. An example is given in Fig. 5.2 (left) where in the case of curve (i) only the top droplet pole is uncontaminated whereas curve (ii) defines an uncontaminated region in roughly the upper 1/3 of the droplet.

2. In a similar case, σ_{top} is equal to σ_{pure} , but σ_{max} is set to a greater value:

$$\sigma_{top} = \sigma_{pure} < \sigma_{max}$$

This setting means that only the top droplet pole is free of surfactants and that the interfacial tension gradient at that point will be non-zero. This case is shown in Fig. 5.2 (middle) by the curve named “case 2”.

3. In the cases where the droplet is fully covered with surfactants, but there is still a gradient of surfactant concentration along the interface, the interfacial tension at the top droplet pole may be lower than σ_{pure} :

$$\begin{aligned}\sigma_{max} &= \sigma_{pure} \\ \sigma_{min} &< \sigma_{top} < \sigma_{pure}\end{aligned}$$

Also in this case, the interfacial tension gradient at the upper droplet edge will be non-zero. This case is shown in Fig. 5.2 (middle) by curve “case 3”.

It needs to be noted that Fig. 5.2 focuses on the condition on the top droplet pole for illustration purposes. The shapes of the curves can be further adjusted by variations of the surface tension σ_{min} at the bottom droplet pole where a zero or non-zero interfacial tension gradient can also be applied.

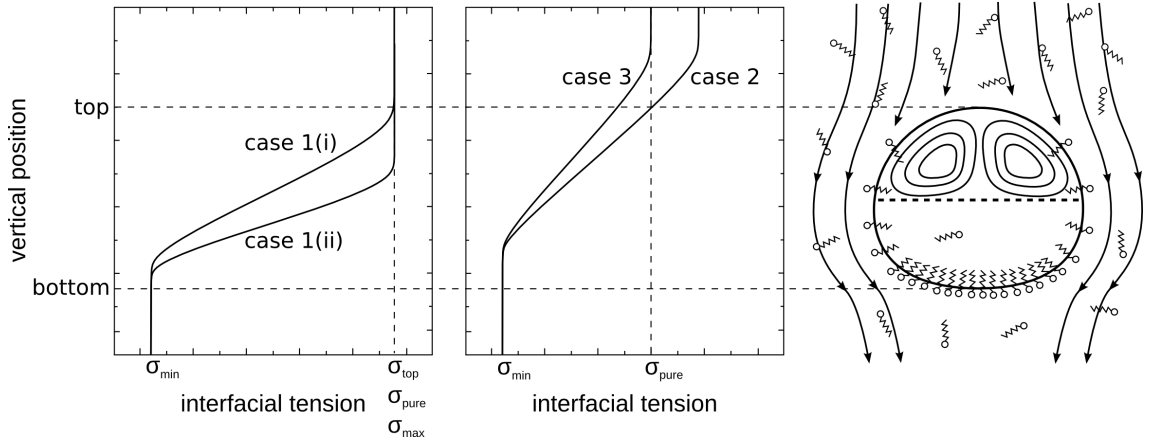


Figure 5.2: Profiles of the interfacial tension along the droplet surface for a zero (left) and a non-zero (middle) interfacial-tension gradient at droplet top, as well as their qualitative relation to the VarIT model concept (right).

Droplet contamination in a liquid-liquid system can be defined with the help of the parameters defined above. Parameter $y_{grad,rel}$ indicates the extent of the contamination by specifying how much of the droplet interface is covered with surfactants. Parameter $\Delta\epsilon$ represents the hydrodynamic conditions at the interface. These conditions are defined both by the flow of the continuous phase around the droplet and the effect of the surfactants that tend to counter-act it. Finally, parameter α represents both the concentration of the surfactants on the interface under given flow conditions, and the impact of the surfactants on the interfacial tension.

5.2 The inverse problem

The VarIT model was implemented in the CFD software DROPS at the Chair of Numerical Mathematics of the RWTH Aachen University. With the help of DROPS, the fluid flow inside the droplet is calculated and obtained in the form of velocity data distributed on a three-dimensional Cartesian grid. These data can be compared to the velocity maps that are measured using NMR-velocimetry as presented in Chap. 3. The combined package VarIT-DROPS can, therefore, be utilized for fitting the model parameters to the experimental data. By doing this, the interfacial tension profile is obtained that results to the droplet internal flow that best matches the one in the experiment. Thus, an inverse problem is defined where the physical phenomenon, i.e. the fluid velocities inside the droplet and more specifically the rigid cap, is measured experimentally and its unmeasurable driving force, i.e. the droplet interfacial-tension gradient, is fitted to the data. Therefore, insight is provided concerning the more fundamental cause of the rigid cap, which is the surfactant-concentration gradient on the droplet surface. Moreover, no study exists in the literature where such a comparison is performed and an experimentally validated interfacial-tension profile is obtained.

5.2.1 Inverse problem description

In order to fit the parameters of the VarIT model to the experimental data, the DROPS output needs to be compared to the NMR experiments. However, before the actual comparison takes place, the following processing steps are necessary:

1. Reduce the dimensionality of the simulated data from 3D to 2D by averaging in a horizontal direction. This emulates the measuring of the 2D experimental data, as will be analyzed below.
2. Define the deviation vector for use in the fitting algorithm.
3. Transform the simulated data to account for flow curvature effects.

The first two points will be discussed in this section. The third point consists of a data transformation that includes the calculation of the objective function, and will be discussed in Sec. 5.2.2.

Horizontal averaging

The NMR apparatus measures the fluid velocities inside the droplet by encoding signal (spins) in one dimension, and tracing how that signal translates in that dimension over time. Since the NMR signal can not be encoded in more than one dimension simultaneously, the velocity components U_x^{exp} , U_y^{exp} and U_z^{exp} , need to

be measured separately. Therefore, it needs to be assumed that the droplet state is stationary during the time that is needed for all three velocity components to be measured. Since previous work showed that the fluid flow in the droplet may undergo changes with time (Amar et al., 2005b), the measurement time needs to be minimized in order for this assumption to be valid. A reasonable compromise is to exclude the measurement of one of the horizontal velocity components from the NMR sequence, and measure the remaining two components as averages in that direction, as presented in Sec. 3.1.2. This reduces the dimensionality of both the data set and the measured velocities to 2D. More specifically, if U_z^{exp} is neglected, the obtained 2D velocity map consists of the U_x^{exp} and the U_y^{exp} velocity components that are averaged over the whole droplet body in the z -direction.

On the other hand, the DROPS simulations provide 3D velocity vectors distributed in a 3D cartesian grid. Therefore, the simulation data have to undergo the same dimensionality reduction in order for them to be directly comparable to the experimental data. This means ignoring the U_z^{sim} velocity components, and averaging U_x^{sim} and U_y^{sim} in the z -direction for every pixel on the $x-y$ plane. In the simulation however, it is possible to use any of the horizontal axes as the averaging direction. For convenience, it will be assumed in this chapter that the averaging is performed along the z -axis. Should the x -axis be used instead, then the x and z symbols must be exchanged in the discussion that follows. Since the NMR signal obtained from the continuous phase is not taken into account in the measurement, the velocities of the continuous phase are represented by zeros in the resulting data-set. The DROPS output function performs the same data filtering by checking the value of the levelset function for each location and setting the continuous phase velocities to zero. The horizontal averaging of the simulated data on the $x-y$ plane is thus performed by taking only the non-zero pixels in the z -direction into account. This process is shown in Fig. 5.3 where the 3D DROPS-output is shown on the left, and the averaged 2D data for the U_x^{sim} velocity component on the right.

After this transformation, both the simulated and the experimental datasets consist of two 2D matrices, one containing the horizontal velocity components, and one containing the corresponding vertical velocity components. Each element of the 2D matrices can be allocated to a specific position in space according to its position in the matrix and the pixel size. This process reallocates point (0,0,0) from its original position at the cell center to the lower left corner of the data matrix as shown in Fig. 5.3. Two matrices belonging to the same dataset must have the same horizontal resolution n_x and vertical resolution n_y and the same pixel dimensions p_x and p_y . Nevertheless, the resolution of the simulation matrix n_x^{sim} and n_y^{sim} , as well as its pixel dimensions p_x^{sim} and p_y^{sim} , need not be the same as the ones of the experimental dataset, and a higher resolution and a smaller pixel size is desirable as it will be described in Sec. 5.2.2. If the simulated and the experimental datasets are of different size, the larger matrix should be cropped to match the smaller one. This cropping should be performed so that only pixels that contain zeros are discarded,

i.e. no actual velocity information is lost.

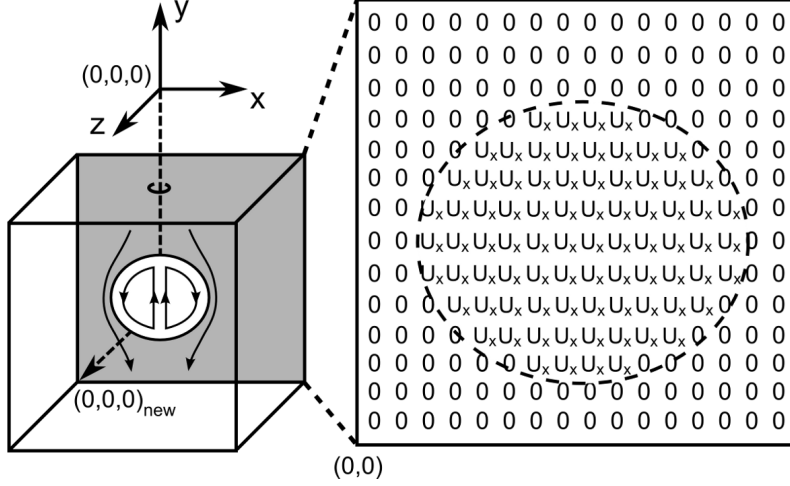


Figure 5.3: Averaging scheme of the 3D DROPS data. The dashed line in the data matrix on the left approximates the droplet interface.

The deviation vector

Before presenting the pixel-by-pixel comparison of the two data-sets in Sec. 5.2.2, it is necessary to define the vector that contains the deviations between the simulation and the experiment. With the help of this vector, the objective function is calculated that is used for fitting the parameters of the VarIT model to the experimental data. The definition of the deviation vector depends on the strategy that will be chosen concerning the comparison of the two data-sets. With regard to this strategy, the following alternatives may be considered:

1. A pixel-by-pixel comparison may be performed directly. This will produce a deviation vector of length $n_x^{exp} \cdot n_y^{exp}$.
2. The droplets may be centered in their existing matrices before the pixel-by-pixel comparison takes place. In this case the deviation vector will also have a length of $n_x^{exp} \cdot n_y^{exp}$.
3. After the droplets are centered in their existing matrices, the data-sets are subdivided into at least as many sectors as there are model parameters to be fitted. The pixel-by-pixel comparison is then performed in these sectors individually. The deviation vector has thus a length equal to the amount of sectors and each of its elements represents the summed result of each comparison.

In all of the above cases, it is assumed that the droplet is visible as a whole in the experimental data before any transformations are applied. In the first of the three

cases presented above, the droplet position within the data-set is ignored. If the two droplets do not overlap, this will essentially introduce penalties within the deviation vector, and therefore also in the objective function, since non-zero velocities in one data-set will be compared to zeros in the other. This may be a desirable outcome if the two data-sets are always obtained from the exact same location inside the levitation cell under identical counter-current velocities and only slight deviations in the behavior of the interface are being fitted. In this case, the droplet position in the simulation should also match the one in the experiment and the application of penalties for discrepancies in droplet position is reasonable. However, if during the fitting procedure the model parameters do not result to a near-optimum fit, this strategy will introduce severe penalties that will make the interpretation of the deviation vector meaningless. Since the velocities that are being compared may not necessarily come from the same location in the droplet, no insights can be gained concerning the actual fluid flow discrepancies between simulation and experiment. Thus, this method is not practical if a detailed comparison is always necessary.

This deficiency is eliminated in the second case, where the droplet velocity data are centered in their matrices. This transformation is performed individually for the experimental and the simulated data-sets, but both the U_x matrix and the U_y matrix of a data-set must be transformed in parallel to avoid causing a mismatch of the horizontal and the vertical velocity components. Although by implementing this technique there is no penalty given if the droplets of the two data sets have different positions, there are still penalties calculated if the two droplets deviate in shape. This strategy is the one applied in this work.

These first two cases produce a deviation vector that is of significant length and does not provide any tangible information concerning the goodness of fit, unless the value of the objective function, i.e. the sum of its squared elements, is calculated. The third approach offers a solution to this issue, since the choice of the sectors may be made such that the elements of the deviation vector provide qualitative information concerning how well the simulated fluid flow matches the experimental flow in different parts of the droplet. For example, since the VarIT model features three parameters, the droplet may be divided into four quarters: two quarters representing the corresponding two vortices of the upper circulation torus as viewed in the 2D experimental data, and two quarters representing the rigid cap below.

Yet another approach would be to locate the droplet in each data-set, i.e. the region of non-zero velocities, and crop the matrices around the droplet before proceeding with the pixel-by-pixel comparison. This, however, is not recommended since if the simulated droplet deforms, it is possible that the length of the deviation vector will change. This is likely to cause problems if an optimization algorithm is used for the parameter fitting, where it is required that the length of the deviation vector remains constant throughout the fitting iterations.

5.2.2 Imaging function

The simulated data consist of localized instantaneous velocities, whereas the velocities obtained experimentally are averaged in time and space. As a consequence, a functional relationship between the simulated and the measured data-sets needs to be established in order for them to be comparable. Since the experimental data are treated as target values for fitting the VarIT model parameters, such a function should obtain the simulated velocities as input and transform them into a form comparable to the experimental data. By considering the measuring principle applied in the NMR experiments, the so-called “imaging function” is developed for this transformation and comparison. The final result of the imaging function is the value of the objective function that is used to solve the inverse problem. The imaging function will be presented in this section for the case where the data-sets that are being compared are two-dimensional, but the underlying concept is also applicable in 3 dimensions.

Physical meaning

The main consideration in the derivation of the imaging function is that the NMR velocimetry sequence implemented in the experiments does not measure the fluid velocities, but transpositions of encoded signal in space over a timestep Δt . This timestep, called “velocity encoding time” is a free experimental variable, but practical reasons (see Chap. 3) set a lower limit to its value. The velocity encoding time together with the measured transpositions Δx and Δy is used to calculate the components of the velocity vector U_x^{exp} and U_y^{exp} respectively (Groß-Hardt, 2007; Amar, 2006). This technique does not consider the curvature of the fluid flow within Δt , and that information is, therefore, not included in the experimental data. However, the experimental velocity encoding time lies in the magnitude order of 10^{-3} s whereas the simulation timestep has an magnitude order of 10^{-4} s. Therefore, the simulated data represent a better approximation of the fluid flow, since they are obtained using a smaller timestep. In order to take the fluid-flow curvature into account in the comparison of the two data-sets, the simulated velocity data need to be transformed into position data, since this is the actual information measured in the NMR experiments.

In Fig. 5.4 the imaging function concept is presented in more detail. If the NMR signal is encoded at time $t = t_0$ at the point (x_{t_0}, y_{t_0}) and at a later time $t = t_0 + \Delta t$ it is detected at the point $(x_{t_0} + \Delta x, y_{t_0} + \Delta y)$, the velocity U^{exp} is obtained. This experimental velocity suggests that the signal within the time interval Δt moved a distance Δx on the horizontal axis and a distance Δy on the vertical axis, i.e. on the dashed line pictured in Fig. 5.4. However, the signal trajectory within that time-frame could coincide with the curved solid line of Fig. 5.4. Since the DROPS simulation can provide a better approximation of that trajectory, the simulated velocity in this example would be U^{sim} . If the two velocities U^{exp} and U^{sim} are

compared without taking the curvature of the path-line into account, an artificial deviation would be calculated in this case. Likewise, in another case, simulated and measured velocities may be found equal while, in fact, they are not.

The solution to this problem consists of comparing the positions $(x_{t_0}^{exp}, y_{t_0}^{exp})$ and $(x_{t_0}^{sim}, y_{t_0}^{sim})$ at $t = t_0$ from the experiment and the simulation respectively, rather than the velocities U^{exp} and U^{sim} at $t = t_0 + \Delta t$. The positions at $t = t_0 + \Delta t$ are calculated from the given pixel sizes p_x and p_y and resolutions n_x and n_y of the experimental and the simulated data-sets and are therefore known. From the experimental velocity U^{exp} , the position $(x_{t_0}^{exp}, y_{t_0}^{exp})$ is calculated using point $(x_{t_0} + \Delta x, y_{t_0} + \Delta y)$ and the velocity encoding time Δt . This calculated position corresponds to the position of the encoded signal at $t = t_0$. Based on the simulated data, the position $(x_{t_0}^{sim}, y_{t_0}^{sim})$ is obtained by calculating the streamline starting at $(x_{t_0} + \Delta x, y_{t_0} + \Delta y)$. This position corresponds to the approximated position of an encoded “pseudo-signal” that would result to velocity U^{exp} if the simulated flow exactly matched the experiment and if the simulated droplet had been “measured” using the NMR. If the simulation and the experiment do not match, the distance between $(x_{t_0}^{exp}, y_{t_0}^{exp})$ and $(x_{t_0}^{sim}, y_{t_0}^{sim})$ is the measure of their deviation.

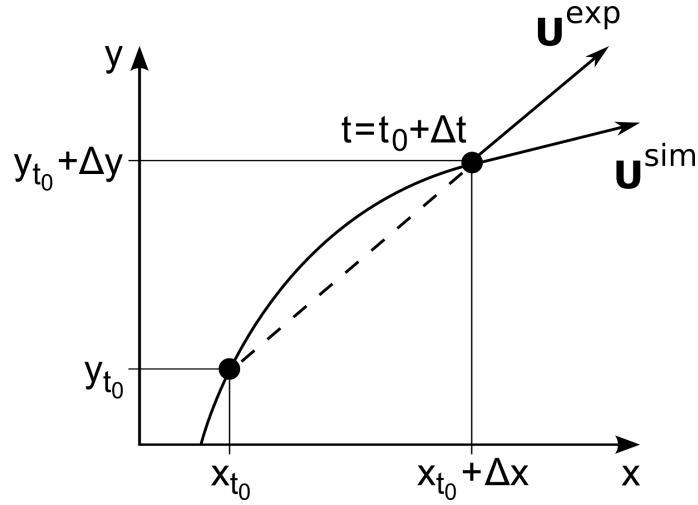


Figure 5.4: Theoretical concept of the imaging function.

In Fig. 5.4 the measured and the simulated flows result to the same translation of signal, and should therefore be regarded equivalent, although the velocities U^{exp} and U^{sim} may be of different magnitudes and may point at different directions. Using the technique described above, the two flows are indeed found to be equivalent since $x_{t_0} = x_{t_0}^{exp} = x_{t_0}^{sim}$ and $y_{t_0} = y_{t_0}^{exp} = y_{t_0}^{sim}$. In addition, using this method, the comparison between simulation and experiment not only takes the velocity magnitude into account, but also the velocity direction.

Another issue emerges from the inability of the NMR to distinguish between signals (spins) that at the time point $t = t_0 + \Delta t$ are located in the same voxel (Groß-Hardt, 2007). In the measurement, the position $x_{t_0}^{exp}$ is thus obtained based on that

spin “mixture”, and is therefore better represented as a position average. For this reason, the simulated velocity matrices that are used in the imaging function are of higher resolution than the experimental matrices. This higher resolution facilitates the calculation of an average position $x_{t_0}^{sim,av}$ from a group of simulated pixels, that is compared to the position $x_{t_0}^{exp}$ that is obtained from a single experimental pixel. This procedure will be presented in detail in the next section.

Numerical implementation

For simplicity, only the equations for the horizontal velocity component will be presented in the discussion that follows. These equations are also applicable for the vertical velocity component if x is replaced by y .

Based on the previous description of the imaging function, the following equations can be written for the experimental data:

$$x_{t_0+\Delta t}^{exp} = x_{t_0}^{exp} + \Delta x \quad (5.7)$$

$$U_x^{exp} = \frac{\Delta x}{\Delta t} \Leftrightarrow x_{t_0}^{exp} = x_{t_0+\Delta t}^{exp} - \Delta t U_x^{exp}. \quad (5.8)$$

Using these equations, the matrices of the experimental data-set will no longer contain the velocity components U_x^{exp} and U_y^{exp} , but the respective positions $x_{t_0}^{exp}$ and $y_{t_0}^{exp}$.

From the simulated data matrices, the signal path lines are approximated by supposing steady state during Δt and calculating the respective streamlines of the fluid flow. The streamlines are obtained by implementing a first order Euler scheme for solving the ordinary differential equation defined at every pixel by the corresponding simulated velocity U_x^{sim} . The solution algorithm is initialized at $x_{t_0+\Delta t}^{sim}$ where the velocity U_x^{sim} is known. The position of the pseudo-signal $x_{t_0}^{sim}$ is traced back in time for a total duration of Δt using a smaller time-step dt :

$$\Delta t = Ndt, \quad (5.9)$$

where N defines the amount and the size of the time intervals used to solve the differential equation and is a free variable. At every time-interval dt a new velocity $U_{x,dt}^{sim}$ is obtained for the intermediate position x_{dt}^{sim} and the same procedure is performed for the y -dimension in parallel. Since an intermediate position $(x_{dt}^{sim}, y_{dt}^{sim})$ may lie anywhere among the pixel centers of the original simulated velocity matrix, 2D bilinear interpolation is implemented in order to obtain the intermediate velocities $U_{x,dt}^{sim}$ and $U_{y,dt}^{sim}$. Using this method, like in the case of the experimental data, the matrices of the simulated data-set will no longer contain the velocity components U_x^{sim} and U_y^{sim} , but the calculated positions $x_{t_0}^{sim}$ and $y_{t_0}^{sim}$.

Note that although in this case the time-step is negative, the algorithm applied is the *forward* Euler method, because every new position is approximated with the

help of the derivative U_x^{sim} at the *current* location. This simple Euler scheme is adequate since Δt is relatively small. The resulting streamlines are usually of a short length, i.e. comparable to the pixel dimensions p_x and p_y . If this is not the case for some reason, i.e. if the simulated velocities are very high or if Δt is very big, a more precise solution algorithm should be considered instead, like e.g. a 4th order Runge-Kutta scheme. Similarly, bilinear interpolation requires a small pixel size. Otherwise, the usage of polynomial interpolation may be necessary.

In order to perform the local averaging of positions as described in page 64, the velocity matrices of the simulated data-set need to have a finer resolution than the matrices of the experimental data-set. If each of the experimental matrices has a resolution of $n_x^{exp} \times n_y^{exp}$, the resolution of the simulated matrices, $n_x^{sim} \times n_y^{sim}$, should be set in accordance to Eq. 5.10:

$$n_{(x,y)}^{sim} = 3^{(k-1)} n_{(x,y)}^{exp}, \quad (5.10)$$

where k denotes the refinement level of the simulated data-set and is a free variable. Thus, for every pixel in an experimental matrix, the respective simulated matrix will have q corresponding pixels according to Eq. 5.11 and Eq. 5.12:

$$m = \sum_{l=1}^{k-1} (3^{(l-1)}) \quad \text{with } k \geq 2 \quad (5.11)$$

$$q = (2m + 1)^2. \quad (5.12)$$

In Fig. 5.5 a pixel of an experimental matrix together with the respective simulated pixels is presented. The measured pixel is indicated by the solid borders whereas the simulated pixels are indicated by the dashed borders. The points represent the pixel centers that are allocated at the pixel's physical positions. The closed point indicates the center of the experimental pixel and the open points indicate the centers of the simulated pixels. The simulated matrix of the figure was generated with a refinement level of $k = 2$, so that there is a group of $q = 9$ simulated pixels that correspond to one experimental pixel. In Fig. 5.5 it can be seen that $q - 1$ pixels of the group are all within a radius of m pixels around a central element whose physical position coincides with the position of the experimental pixel. This equivalency of physical position is indicated by the location (i, j) of that central pixel in the simulated matrix. In addition, (i, j) is used in the notation of the experimental data to refer to the corresponding group of q pixels in the simulated matrix. Therefore, there is:

$$x_{t_0+\Delta t, (i,j)}^{exp} \equiv x_{t_0+\Delta t, (i,j)}^{sim} \quad (5.13)$$

If all positions $x_{t_0, (i,j)}^{sim}$ are obtained from their respective velocities as described in page 64, an average $x_{t_0, (i,j)}^{sim, av}$ may be calculated. The averaging is performed for every pixel group of the simulated matrix according to Eq. 5.14:

$$x_{t_0, (i,j)}^{sim, av} = \frac{1}{q} \sum_{g=0}^m \sum_{h=0}^m x_{t_0, (i \pm g, j \pm h)}^{sim}. \quad (5.14)$$

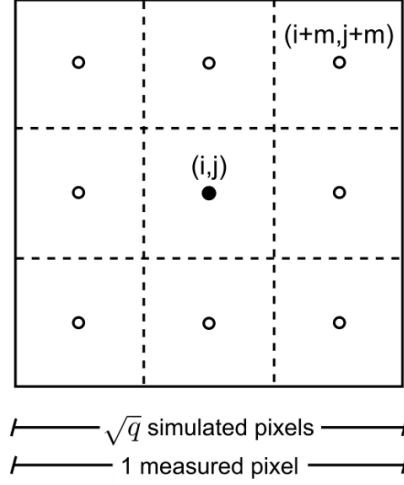


Figure 5.5: Refinement scheme for the simulated data-set for $q = 9$ and $m = 1$.

From these averaged positions, a new data-set is generated the matrices of which have the same resolution and pixel size as the matrices of the experimental data-set. Thus, the simulated and the experimental elements $x_{t_0,(i,j)}^{sim,av}$ and $x_{t_0,(i,j)}^{exp}$, originate from the same physical positions in the droplet (Eq. 5.13), and can therefore be compared directly. If the NMR data were free of experimental error and if the simulated flow exactly matched the reality, these calculated positions for $t = t_0$ would coincide. However, in the non-ideal case where the parameters of the VarIT model are not precisely known, a discrepancy between the experimental and the simulated matrices occurs. Since the data-sets that are being compared no longer contain velocities but positions on a 2D plane, the comparison between simulation and experiment is performed by calculating the distances ψ_{ij} between the respective elements of the two data-sets:

$$\psi_{ij} = \sqrt{(x_{t_0,(i,j)}^{sim,av} - x_{t_0,(i,j)}^{exp})^2 + (y_{t_0,(i,j)}^{sim,av} - y_{t_0,(i,j)}^{exp})^2}. \quad (5.15)$$

The squared sum of these values is the objective function used for solving the inverse problem. The parameters of the VarIT model must be adjusted so that the squared sum of the distances between the experimental points $(x_{t_0,(i,j)}^{exp}, y_{t_0,(i,j)}^{exp})$ and the simulated points $(x_{t_0,(i,j)}^{sim,av}, y_{t_0,(i,j)}^{sim,av})$ are minimized:

$$\Phi = \sum_{i=1}^{n_x} \sum_{j=1}^{n_y} \psi_{ij}^2 \rightarrow \min, \quad (5.16)$$

where $n_{x,y} \equiv n_{x,y}^{exp} \equiv n_{x,y}^{sim}$. In order to obtain a more tangible measure of the agreement between the simulation and the experiment, the average distance between the respective positions of the two data-sets may be calculated:

$$\Psi = \frac{1}{S} \sum_{i=1}^{n_x} \sum_{j=1}^{n_y} \psi_{ij}, \quad (5.17)$$

where S is the number of the pixels that represent the droplet. If Ψ is smaller than the experimental pixel size, $\Psi < p_x^{exp}, p_y^{exp}$, it could mean that the precision limits of the measuring method are being approached.

Since the droplet shape in the simulation may deviate from that in the experiment, S is defined as the amount of pixels contained in the set $s^{exp} \cup s^{sim}$, where s represents the set of pixels that belong to the droplet. The droplet pixels can be easily identified in a matrix since the velocity in all pixels that belong to the continuous phase is zero. However, within a data-set some pixels of the U_x -velocity matrix may be equal to zero whereas the corresponding pixels of the U_y -velocity matrix are non-zero. Therefore, for both the experimental and the simulated data-sets, s is defined as $s = s_x \cup s_y$, where s_x and s_y are the sets of non-zero pixels in the respective matrices of x - and y -velocity components. Usually such a mismatch between the U_x -velocity matrix and the U_y -velocity matrix within the same data-set occurs in the vicinity of the interface, but it is sometimes possible that inside the droplet there are pixels where both velocity components are zero. In such an occasion, the droplet borders need to be located by determining the lines and the columns of the velocity matrix where the non-zero region starts and ends. The position of each pixel then needs to be checked relative to the droplet borders in order to determine whether the pixel belongs to the droplet or to the continuous phase.

Chapter 6

Results and discussion

In this chapter the simulation results for the cases of the sedimenting and the levitated droplets are presented. The sedimenting-droplet problem (Sec. 6.1) was used as a test-case for evaluating the accuracy of the DROPS software since both experimental data and semi-empirical engineering models were available as benchmarks. The levitated droplet problem is introduced in Sec. 6.2 where its distinctive features are discussed. The simulation results are presented in Sec. 6.3, together with their quantitative comparison to the NMR measurements based on the NMR imaging function. General remarks on the behavior of the levitated droplet are then made in Sec. 6.3.2.

The simulation results on droplet sedimentation were previously presented in the publications by Bertakis et al. (2010) and Bertakis et al. (2008), but a more up-to-date discussion is provided in this chapter. Some of the results on the interfacial stagnation of the levitated droplet were published by Bertakis and Pfennig (2009) and Bertakis et al. (2009), but a thorough discussion is presented for the first time in this work. Intermediate results of this work concerning the numerical aspects of the levitated droplet problem were previously published by Nguyen (2009), who focused on the mass transfer between the droplet and the continuous phase, and Esser et al. (2009) who focused on the implementation of the XFEM method.

6.1 Code evaluation: Droplet sedimentation

The influence of the simulation parameters like mesh size and computational domain size are discussed in Sec. 6.1.1 in order to discriminate amongst the calculations those that provide the most valid results. These results are then evaluated in Sec. 6.1.2 based on the published literature as well as according to three benchmarks that were discussed in Sec. 2.1.1, namely:

- the shape regime chart for freely moving fluid particles of Clift et al. (1978),
- the circulation and oscillation thresholds presented by Mack (2001),
- the semi-empirical model of Henschke (2003).

The simulation results provide the calculated droplet position for every simulation time step, from which the corresponding droplet velocities can be obtained by numerical differentiation. If these velocities are plotted versus time, a velocity plateau is eventually reached that indicates the sedimentation velocity (v_{sed}) for a given simulation. Therefore, the droplet speed was monitored during the simulation until the droplet reached a state where either the rise velocity was constant, or it constantly oscillated around a stable value. In addition, by visualizing the zero-level of the level-set function as an isosurface, a representation of the droplet interface could be created. In this way, the droplet shape was also obtained as a function of time for each given droplet diameter.

6.1.1 Numerical simulations

The simulation parameters that can have an important impact on the obtained transient results are:

- the mesh size,
- the step size of the time discretization,
- the initial conditions of the simulation system, and,
- the distance between the wall of the computational domain and the droplet interface.

The influence of these parameters is examined in this section for ensuring that they do not affect the simulated steady-state sedimentation velocity that is compared to the experimental data. A comparison of the DROPS version with standard finite-elements and the DROPS-XFEM version is also presented in this section. The results are evaluated using the model of Henschke (2003) that was presented in Sec. 2.1.1, and specifically to the sedimentation curve of droplets with an ideally mobile interface. This is because the free-surface modeling in the sedimentation simulations does not take any interfacial stagnation into account, and its results should thus be compared against a model that makes the same assumption and is fitted to experimental data. Thus, the convergence of the simulation results to the corresponding experimental and model values for varying simulation parameters can be checked. A comprehensive comparison of the final sedimentation results to the model of Henschke (2003) is given in Sec. 6.1.2.

Time step

The timestep is a parameter that can have a considerable impact, not only on the generated results and algorithm stability, but also on the simulation duration. In this work two different timesteps are tested, one is 10^{-4} s, and the other 5.0×10^{-4} s. In Fig. 6.1 (left) the results obtained with the two time steps are shown, where it is seen that both velocity plots are slightly scattered. This scatter is an effect of the numerical differentiation of the droplet position data. Moreover, periodic scatter of high frequency is introduced by the reparametrization of the level-set function. To eliminate the scattering, and to thus increase the accuracy of the calculated droplet terminal velocity, a central moving average smoothing scheme was applied to all subsequent data. The averaging period was equal to the level-set reparametrization period, i.e. 10 time steps. Thus, the averaging scheme acts as a low-pass filter that eliminates the numerical high-frequency scatter in favor of the physical low-frequency effects.

The results are shown in Fig. 6.1 (right), where it can be seen that the curve with the smaller timestep lies above the curve with the larger timestep, but the difference is not significant. The average deviation along the whole curve was found to be 1.9%, while the average deviation at the velocity plateau was 1.5%. Therefore, it is concluded that the obtained results can be considered equivalent for terminal velocity calculations. Thus, the larger step size is used in the following simulations.

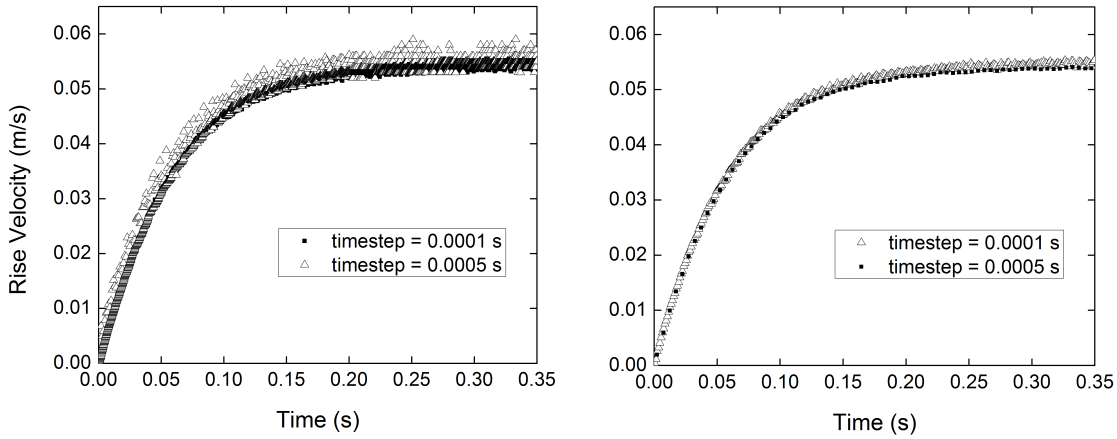


Figure 6.1: Comparison of rise velocity for different time step sizes using XFEM-DROPS for $d = 2.0$ mm, $h = 3.13 \times 10^{-4}$ m, $h/d = 0.157$, $\xi_0 = 9.0$ mm, $v_{sed} = 0.054$ m/s. Left: raw velocity data. Right: smoothed velocity data.

Initial velocity

Concerning the droplet velocity at the beginning of the simulation, two possibilities have been tested. In one case the droplet initial velocity is set to zero, and therefore

the droplet accelerates to its terminal state. In the second case the droplet is given an initial velocity that is equal to the one predicted from the Stokes' law for the given system and droplet diameter. In this case the droplet is decelerated to its terminal velocity. In Fig. 6.2 the dependency of the simulation results on the initial velocity of a droplet with a $d = 2.0$ mm diameter are shown. On the left are the results of the plain DROPS version, and on the right are the results of the DROPS-XFEM version. Both droplet velocity curves in each diagram converge to the same terminal sedimentation velocity at the same point in time, independent of the initial conditions. Therefore, the initial droplet velocity has no influence on the obtained final result.

Note that the droplet terminal velocity obtained by the DROPS-XFEM version is slightly higher than the velocity obtained by the plain DROPS version. The deviation of the droplet terminal velocity between the two diagrams of Fig. 6.2 was found to be 6.8%.

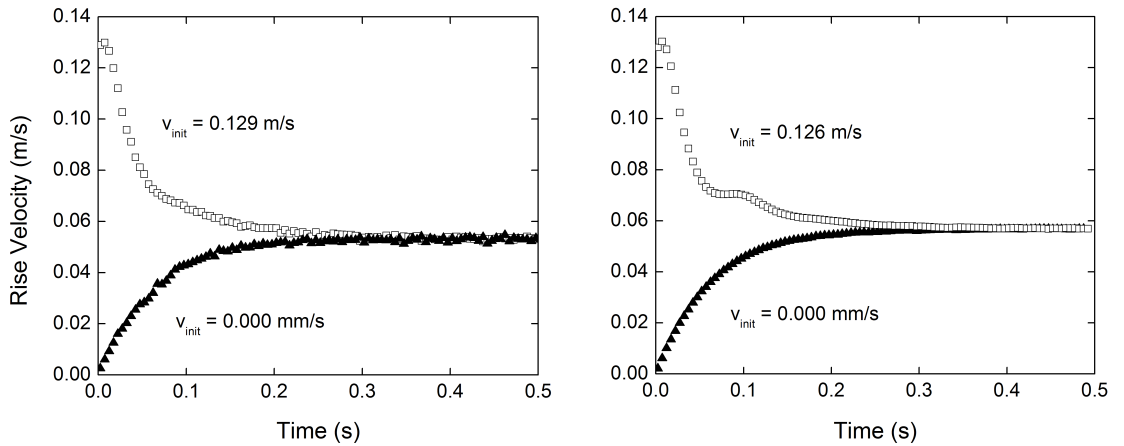


Figure 6.2: Comparison of rise velocity for different initial conditions for $d = 2.0$ mm, $h = 3.13 \times 10^{-4}$ m, $h/d = 0.157$, $\xi_0 = 9.0$ mm. Left: plain DROPS version, $v_{sed} = 0.053$ m/s. Right: DROPS-XFEM version, $v_{sed} = 0.057$ m/s.

For large droplets ($d \geq 3$ mm) a large initial velocity resulted in droplet breakup, and, therefore, the droplet sedimentation velocity could not be determined. The pattern of droplet breakup in the simulations resembles those described by Wang and Wang (2007) for large fluid particles where the droplet obtains a bell-like form. In Fig. 6.3 the simulated droplet breakup stages can be seen. The breakup starts from the top of the droplet, thus resulting in a torus-like formation, and eventually the droplet breaks up forming two daughter droplets. At this point it is important to note that the volume conservation method mentioned in Sec. 4.1.1 for the level-set function conserves only the total volume of the dispersed phase. After droplet breakup volume must be preserved for each of the two droplets. This however, is not guaranteed with the volume conservation method currently available in DROPS.

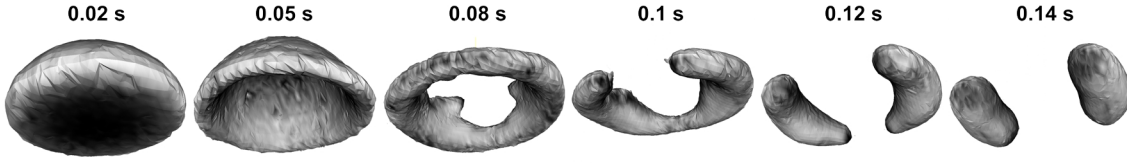


Figure 6.3: Breakup stages of a droplet simulated with the plain DROPS version for $d = 3.0$ mm, $h = 3.13 \times 10^{-4}$ m, $h/d = 0.104$, $v_{init} = 0.247$ m/s, $Re \approx 500$ as seen from below when rising. The velocity is mapped on a grey scale ranging from white (for low velocities) to black (for higher velocities).

Comparison of finite-element methods

In Fig. 6.4 the results obtained for droplets with diameters $d = 1.0$ mm and $d = 2.0$ mm using the two DROPS versions are displayed, whereas all other simulation settings like time step, initial velocity and mesh size, were identical. In these plots it is noted that the XFEM-technique results in sedimentation velocities that are systematically higher than those calculated by the plain DROPS version. As mentioned in the beginning of this section, since the sedimentation simulations do not take any interfacial stagnation into account, they should be compared against a benchmark that makes the same assumption. The validity of the simulation results is, therefore, evaluated based on the model by Henschke (2003) that is fitted to experimental data and depicts the sedimentation velocities of droplets with an ideally mobile interface.

The sedimentation velocities for $d = 1.0$ mm and $d = 2.0$ mm according to Henschke's model are $v_{sed} = 0.029$ m/s and $v_{sed} = 0.058$ m/s respectively and are presented in Fig. 6.4 using solid horizontal lines. Since the results obtained using the XFEM-version of DROPS are closer to these values, it can be concluded that they are more accurate than the results of the plain DROPS version.

The slight scatter noticed in Fig. 6.4 (left) in the data from the plain DROPS version stems from the relatively coarse grid that was used in the simulations of that diagram. Although the actual mesh size h in Fig. 6.4 (left) is smaller than in Fig. 6.4 (right), the grid in the simulations on the left is coarser in relation to the droplet size than in the simulations on the right. In addition, in Fig. 6.4 (left) it is noticed that although the same grid was used for both simulations in the diagram, the data from the XFEM-DROPS version do not show any scatter, contrary to the data from the plain DROPS version. This fact indicates that the extended finite-element technique is also less sensitive to grid resolution for the cases investigated in this work. The influence of grid resolution is presented in more detail in the next section.

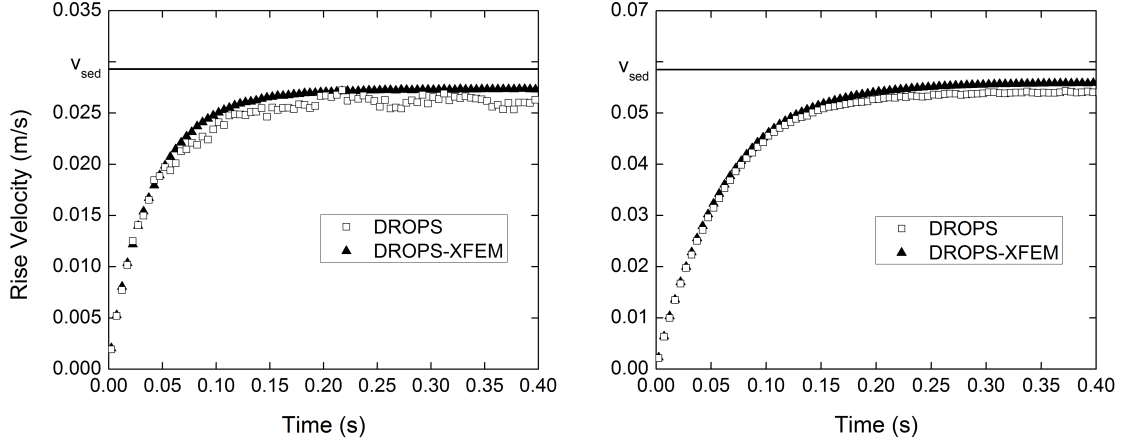


Figure 6.4: Comparison between the plain DROPS version and the DROPS-XFEM version. Left: $d = 1.0$ mm, $h = 1.25 \times 10^{-4}$ m, $h/d = 0.125$, $\xi_0 = 3.5$ mm, $v_{sed} = 0.027$ m/s. Right: $d = 2.0$ mm, $h = 1.56 \times 10^{-4}$ m, $h/d = 0.078$, $\xi_0 = 4.0$ mm, $v_{sed} = 0.056$ m/s.

Grid resolution

In Fig. 6.5 the influence of the mesh size is presented for the DROPS version with standard finite-elements for two droplets of $d = 3.0$ mm and $d = 4.0$ mm. Since the grid is configured so that the smallest mesh size is in the vicinity of the fluid interface, simulating a bigger droplet in diameter means that more of the smallest tetrahedra are necessary than in the case of a smaller droplet using the same grid configuration. For the relatively big droplets of Fig. 6.5 this means that the parallel DROPS version is needed in order to avoid very long calculation times. In this work, the mesh size at the droplet interface is used to represent the resolution of the grid and is denoted by h . Additionally, the dimensionless mesh size, defined by the fraction h/d , is used to indicate the grid resolution in relation to the droplet diameter. In Fig. 6.5 it can be seen that a finer grid results to a higher terminal droplet velocity, that is closer to the benchmark horizontal line indicating the corresponding value of the Henschke (2003) model. The benchmark lines for $d = 3.0$ mm and $d = 4.0$ mm are at $v_{sed} = 0.061$ m/s and $v_{sed} = 0.058$ m/s respectively.

In Fig. 6.6 the grid influence is tested for the XFEM version. In contrast to Fig. 6.5 it is noticed that the influence of the grid resolution is negligible between the cases studied, since a finer grid in Fig. 6.6 does not lead to any significant increase of the droplet terminal velocity. A small difference is noted only for $d = 3.0$ mm where the terminal velocity is uninfluenced, but the two curves have a slightly different shape. Concerning the agreement of the simulations with the model of Henschke (2003), we notice that the simulations in Fig. 6.6 are closer to the model than the simulations in Fig. 6.5. This difference is not only due to the different finite-element methods but also due to the size of the computational domain. This factor will be examined in the next section.

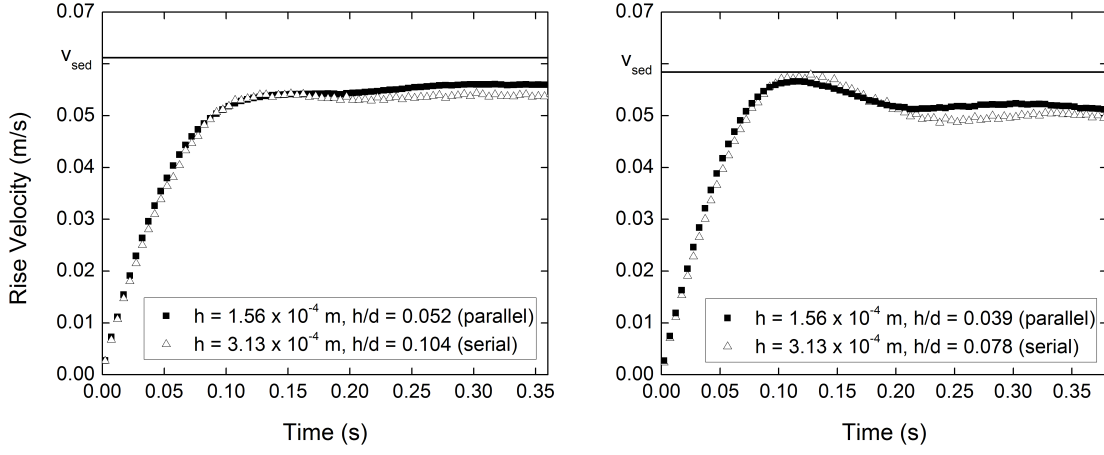


Figure 6.5: Comparison of different mesh sizes for DROPS with standard FE. Left: $d = 3.0$ mm, $\xi_0 = 3.5$ mm, $v_{sed} = 0.056$ m/s. Right: $d = 4.0$ mm, $\xi_0 = 5.0$ mm, $v_{sed} = 0.052$ m/s.

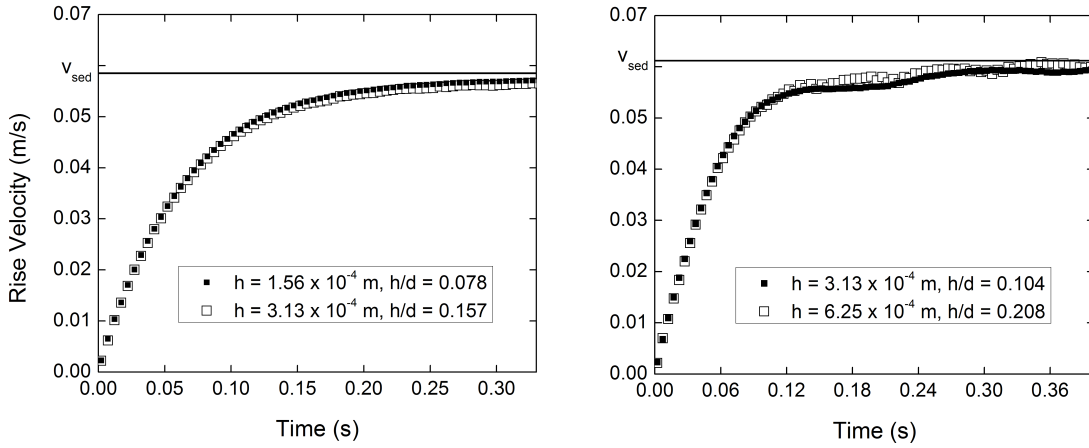


Figure 6.6: Comparison of different mesh sizes for the XFEM-DROPS method. Left: $d = 2.0$ mm, $\xi_0 = 9.0$ mm, $v_{sed} = 0.057$ m/s. Right: $d = 3.0$ mm, $\xi_0 = 8.5$ mm, $v_{sed} = 0.060$ m/s.

Wall effects

Walls can have a considerable influence on the droplet sedimentation velocity (Henschke et al., 2000; Zimmerman, 2004; Uno and Kintner, 1956). In this work the horizontal distance of the droplet interface to the computational-domain wall at the beginning of the simulation was varied. This distance is denoted by ξ_0 .

In Fig. 6.7 (left) a droplet with $d = 3.0$ mm is simulated using different computational domain sizes, namely, $\xi_0 = 3.5$ mm, $\xi_0 = 8.5$ mm, and $\xi_0 = 13.5$ mm. For $\xi_0 = 3.5$ mm both the XFEM-DROPS and the plain DROPS versions were tested, and the terminal velocity calculated by the XFEM method was found higher than the one calculated by the plain method. If the droplet distance to the computational domain wall increases to $\xi_0 = 8.5$ mm, the sedimentation velocity stabilizes to an even higher value than for $\xi_0 = 3.5$ mm. A further increase of the computational domain size to $\xi_0 = 13.5$ mm does not affect the droplet velocity, thus suggesting that a safe distance of the phase interface to the wall was achieved at $\xi_0 = 8.5$ mm.

The same test was performed for a droplet diameter of $d = 4.0$ mm, and the obtained results can be seen in Fig. 6.7 (right). The computational domain sizes were $\xi_0 = 5.0$ mm, $\xi_0 = 13.0$ mm, and $\xi_0 = 28.0$ mm. From Fig. 6.7 (right) it is seen that $\xi_0 = 5.0$ mm is too small, since a rise to $\xi_0 = 13.0$ mm leads to a rise of the droplet terminal velocity. As in Fig. 6.7 (left) for $d = 3.0$ mm, there is also expected to be a slight influence of the choice of the finite-element method, but the wall effect is dominating in this case. A further rise to $\xi_0 = 28.5$ mm had no effect on the droplet terminal velocity or the shape of the droplet velocity curve, and, therefore, it is concluded that the wall-effect has been eliminated for $\xi_0 = 13.0$ mm.

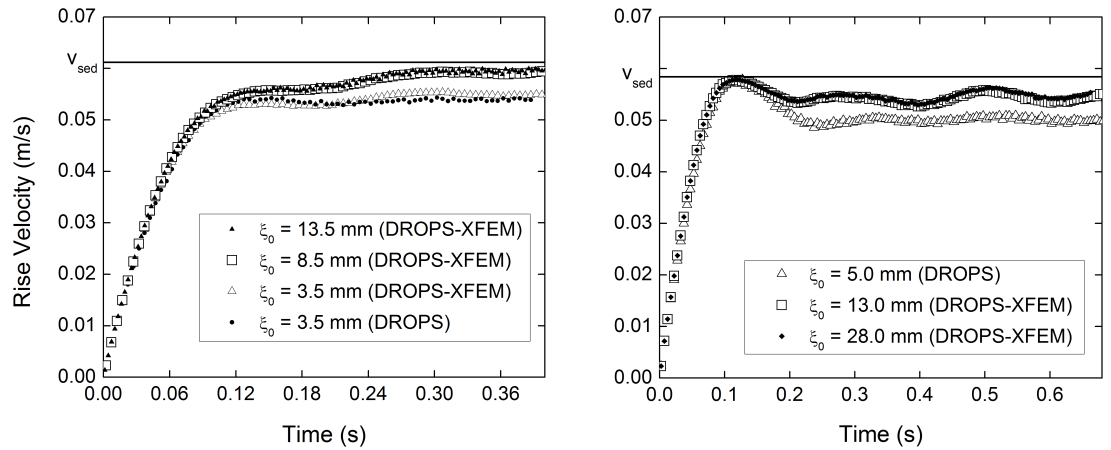


Figure 6.7: Comparison of different geometry settings for $h = 3.13 \times 10^{-4}$ m. Left: $d = 3.0$ mm, $h/d = 0.104$, $v_{sed} = 0.060$ m/s. Right: $d = 4.0$ mm, $h/d = 0.078$, $v_{sed} = 0.055$ m/s.

Independent of the geometry configuration, a strong fluctuation occurs at the beginning of the simulation for $d = 4.0$ mm. In Fig. 6.7 (right) this fluctuation can be

seen as a local peak in the velocity curve at the end of the acceleration stage. After this initial peak, the droplet reaches its terminal state. This fluctuation can also be seen in Fig. 6.9 where the shape of the droplet is captured at 0.1 s and 0.2 s. It is also noted that the sedimentation curves of smaller droplets do not exhibit this behavior. However, in both cases in Fig. 6.7 velocity oscillations are noticed around a constant velocity value, although for $d = 3.0$ mm these oscillations are very weak. In such cases, this constant mean velocity is used as the droplet sedimentation velocity. Such oscillations are not taken into account in the experiment, since the sedimentation velocity is measured as an average over a distance of 100 mm.

For both $d = 3.0$ mm and $d = 4.0$ mm the computational domain size had an influence not only on the droplet terminal velocity, but also on the shape of the velocity curves of Fig. 6.7. More specifically, the velocity oscillations are more evident in the case of the wider computational domain. This is because the no-slip condition is applied on the computational domain boundaries, the interface is allowed to move more freely when the distance between the interface and the wall increases. Thus, the sedimentation velocity rises and the velocity oscillations get stronger.

Finally, a droplet with $d = 2.0$ mm was simulated with XFEM-DROPS and two different computational domain sizes with $\xi_0 = 4.0$ mm and $\xi_0 = 9.0$ mm. The influence of the computational domain wall on the droplet sedimentation velocity in this case was only 1.4%, and the sedimentation velocity in the case of $\xi_0 = 9.0$ mm, i.e. without any wall-related effects, was $v_{sed} = 0.057$ m/s.

To these observations, it should be added that droplet deformation may have an impact on the extent of the wall's influence on the sedimentation velocity. If the droplet deforms to an oblate shape, as in the simulations of the present work, the interface will move closer to the wall, thus limiting its velocity. Considering a d/ξ_0 ratio instead of just ξ_0 may not necessarily resolve the issue for all liquid-liquid systems, since droplet deformation is dependent on the material properties. In the present work, $d/\xi_0 = 0.35$ and $d/\xi_0 = 0.31$ were sufficient for eliminating any wall-effects for $d = 3.0$ mm and $d = 4.0$ mm respectively. However, it was found that the $d/\xi_0 = 0.35$ was marginally too high for $d = 4.0$ mm. Therefore, the recommended d/ξ_0 value for the simulations discussed in this work lies between $0.31 \leq d/\xi_0 < 0.35$.

6.1.2 Evaluation of results

The data presented so far provide insight as to which factors can influence the simulation results and to what extent. Parameters such as time step, initial droplet velocity, computational domain size and grid resolution have been tested. As a result, these parameters can be safely set such that good simulation accuracy is achieved while minimizing the computational effort.

In particular it is shown that for the discretization of the discontinuous pressure the XFEM method is much better suited than the standard linear (P_1) finite element method. In the case of droplets with $d = 1.0$ mm and $d = 2.0$ mm the finest grids that were used had a smallest mesh size of $h = 1.25 \times 10^{-4}$ m, and $h = 1.56 \times 10^{-4}$ m ($h/d = 0.125$ and $h/d = 0.078$) respectively. The finest grid used for the droplets with $d = 3.0$ mm and $d = 4.0$ mm had a smallest mesh size of $h = 3.13 \times 10^{-4}$ m ($h/d = 0.104$ and $h/d = 0.078$). Any wall effects have been eliminated by using a sufficiently wide computational domain. The size of the timestep that was used was equal to 5.0×10^{-4} s. The final results of the simulations performed with the above specifications are presented in Table 6.1 together with the respective values of the Re , EO and Ar numbers.

In Fig. 6.8 these data are graphically compared to the model curve by Henschke (2003) for droplets with an ideally mobile interface that was fitted to experimental data with good agreement. Since no interfacial stagnation is considered in the simulations, the respective results are compared to the model curve that also makes the same assumption, i.e. that the interface is ideally mobile. In Fig. 6.8 it can be seen that the simulation results are in good quantitative agreement with the model curve. Consequently, the DROPS-simulations are also in good agreement with the experimental data. The experiments, as well as the fitted model, suggest a rise of the terminal velocity with increasing droplet diameter that subsequently reaches a maximum and then decays. These three curve characteristics and their corresponding locations on the diagram are all well-predicted by the simulations.

The model curve is drawn only up to the maximum droplet diameter that has been investigated in the experiments ($d = 3.48$ mm). Extrapolating the model curve beyond that point would not necessarily depict the experimental data trend, since only two experimental points are in the oscillating droplet region as shown in Table 3.2. The experimental data in this region influence the fitting of the model parameter α_{sc} , that determines the vertical position of the plateau of the sedimentation curve for oscillating droplets. After considering these facts, it can be stated that the result of the DROPS-XFEM simulation for $d = 4.0$ mm is also in agreement with the trend of the experimental data in the oscillating region.

In Fig. 6.9 the shapes of droplets with different diameters are displayed as a function of time. The smallest droplet with $d = 1$ mm constantly exhibits a spherical shape, whereas slightly bigger droplets with $d = 1.5$ mm and $d = 2.0$ mm eventually become ellipsoidal. Larger droplets with $d = 3$ mm and $d = 4$ mm are flat and oblate at their steady state, while they undergo significant changes in shape before they reach this stable form. Although the droplet shape for $d = 4$ mm and $t = 0.4$ s seems to be severely oblate, similar shapes have been previously reported by Quan and Schmidt (2006), Raymond and Rosant (2000) and Wellek et al. (1966) together with correlations of the droplet eccentricity to the Reynolds number and other dimensionless quantities.

Table 6.1: Simulated terminal velocities and dimensionless numbers for n-butanol droplets sedimenting in the continuous water phase.

d (mm)	v_{sed} (mm/s)	Re	EO	Ar
1.0	27.6	19.6	0.85	709
1.5	44	46.9	1.91	2392
2.0	57	81.0	3.40	5669
3.0	60	127.9	7.64	19132
4.0	55	156.4	13.6	45351

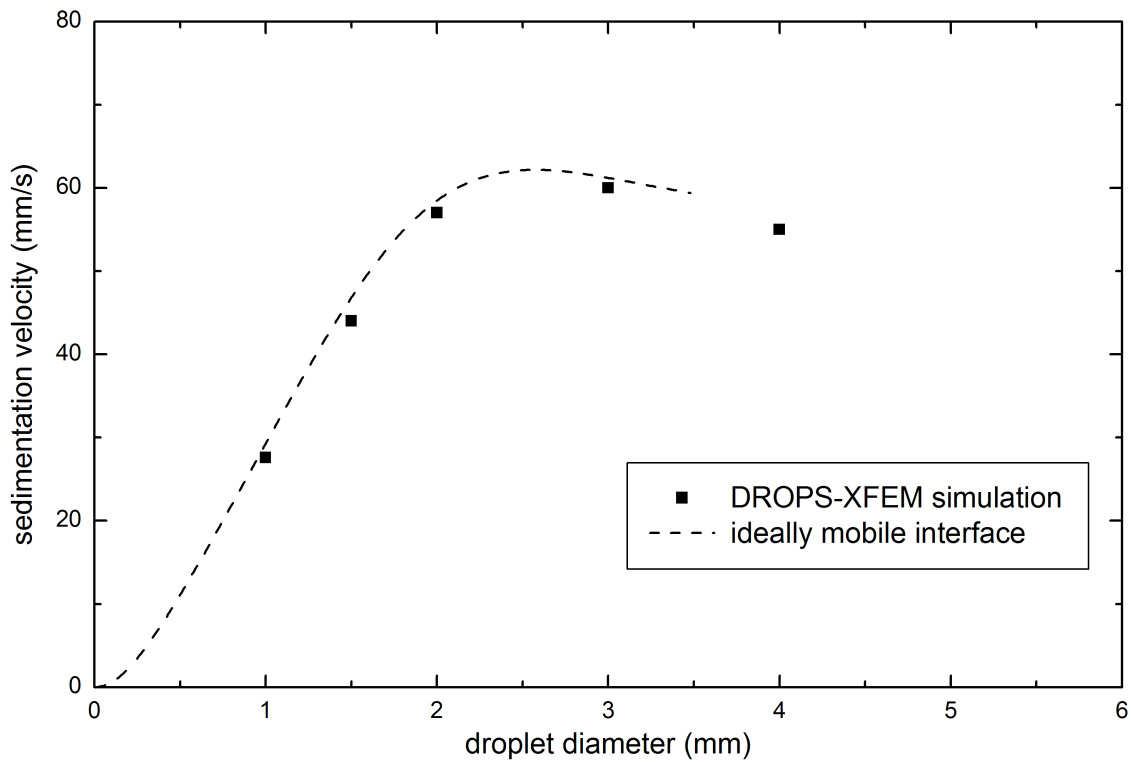


Figure 6.8: Comparison of simulation results to model curve for an ideally mobile interface.

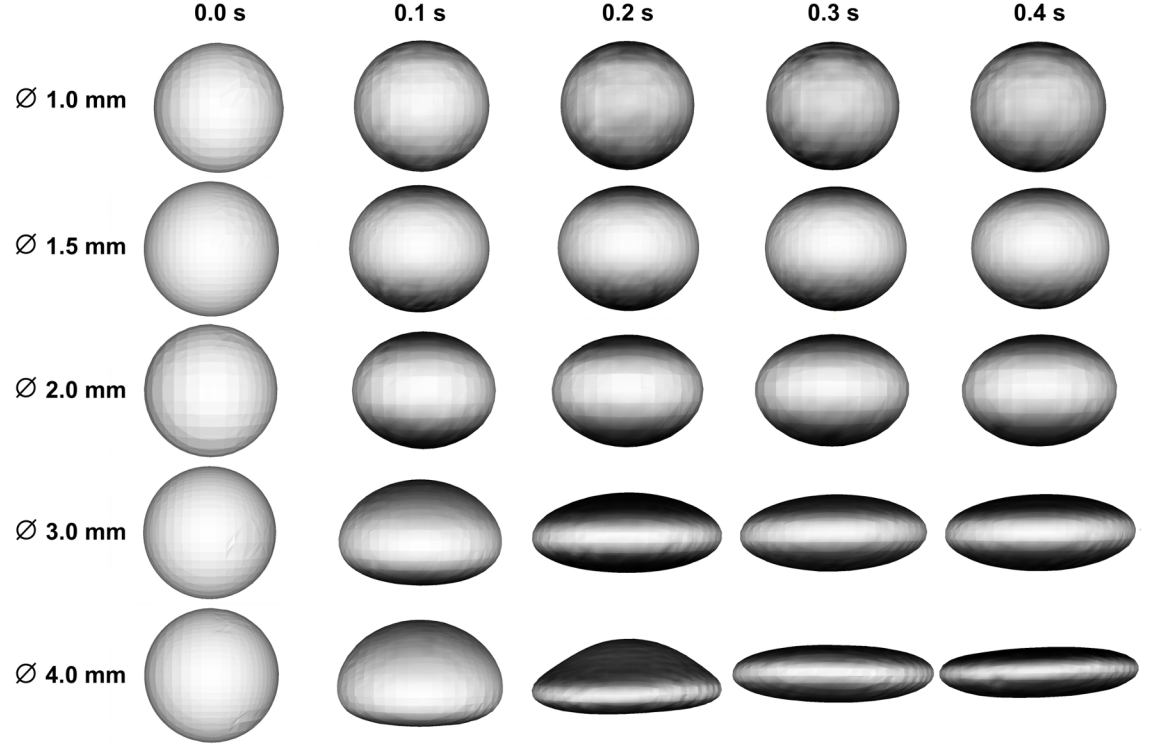


Figure 6.9: Comparison of droplet deformation at different time stages for various droplet diameters. All simulations were performed with $v_{init} = 0$.

In Fig. 6.9 it is evident that the droplet with a diameter of $d = 4$ mm becomes highly asymmetric at the beginning of the simulation before the steady state is reached. This behavior corresponds to the velocity peak noted in Fig. 6.7 (right). In the case of $d = 3$ mm it can be seen that the droplet also obtains a non-symmetrical shape for a short time period, but this phenomenon is not as apparent as for $d = 4$ mm. Although oscillations were not directly visible when the droplet had reached its terminal velocity, examination of the data in Fig. 6.7 shows that velocity oscillations do exist, but have a very short time period. These findings are in accordance to the criterion of Clift et al. (1978) concerning the droplet shape and to that of Mack (2001) concerning the droplet oscillation behavior.

Smolianski et al. (2008) performed finite-element simulations of freely rising fluid particles using the level-set method (Smolianski, 2001) and calculated the particle rise velocity as a function of time. Although fluid particles of ellipsoidal, skirted, and indented shape were simulated, low frequency oscillations like the ones of Fig. 6.7 were not observed, but very high frequency velocity oscillations were noted instead. Similar velocity oscillations were also reported by Rusche (2002) for rising bubbles. Given the form of the raw data that were presented in Fig. 6.1 (left), the importance of carefully eliminating the numerical effects from the simulated data needs to be stressed. The data smoothing scheme should not suppress the physical velocity oscillations of the larger fluid particles as might have been the case in the work of Smolianski et al. (2008).

Wegener et al. (2007a) performed experiments on toluene droplets rising in water and measured their velocity as a function of time. In their work, a behavior comparable to the one presented here is shown. For relatively small droplets, the velocity rises with time until a plateau is reached where it remains constant. The duration of this smooth acceleration stage depended slightly upon the diameter of the droplet studied, but was in general not greater than 0.5 s. This observation agrees with the results of the present work if figures 6.1, 6.2, 6.4 and 6.6 (left) are examined, where the acceleration stage of small droplets also appears to be equally short. For bigger droplets a strong peak in the droplet velocity is noted right after the acceleration region that is very similar to the peak found in the simulations of the droplet with $d = 4.0$ mm. Furthermore, after this first fluctuation, smaller oscillations around the droplet terminal velocity were also observed in the experiments of Wegener et al. (2007a), similar to the ones shown in figures 6.5 and 6.7.

Both Wegener et al. (2007a) and Gueyffier et al. (1999) as well as other authors like Petera and Weatherley (2001) and Wang et al. (2008) report acceleration stages that are in general no longer than one second in duration. However, Wegener et al. (2010) presented experimental results which show that if the droplet velocity exhibits a maximum right after the acceleration stage, it may need a considerable amount of time (>2 s) in order to reach a velocity plateau that will be characteristic of its terminal velocity. Nevertheless, the exact behavior of the droplet depends in this case not only on the droplet size, but also on the type of nozzle used for its injection. Since the droplet injection is not included in the simulations of this work, and decaying oscillations due to non-idealities of the nozzle and injection thus do not occur, it can be assumed that the real-time duration of the present simulations is sufficient for obtaining the theoretical sedimentation velocity of the droplets.

Droplet sedimentation simulations for the n-butanol+water system were also performed by Bäumlér et al. (2011) who used a finite-element code. Their droplet terminal velocity data were compared in Bäumlér et al. (2011) to the results of this work with excellent agreement. Simulations with the high-interfacial tension standard test system toluene+water were also reported in Bäumlér et al. (2011) as well as in Bäumlér et al. (2009) also showing good agreement to experimental data and semi-empirical models. The authors employed a Lagrangian front-tracking method for simulating the interface movement. Although high interfacial tensions can be readily applied when using this method, numerical effects due to the strong mesh deformation caused unnatural velocity oscillations, thus preventing the simulation of large droplets.

6.2 Simulation of the levitated droplet

In this section, the VarIT model that was presented in Sec. 5.1 will be compared to the experimental results of Sec. 3.1 using the imaging function that was described in Sec. 5.2. The model parameters, that define an interfacial tension gradient along the droplet's vertical axis, will be fitted to the experimental data so that the stagnant cap that is evident in the experimental velocity plots is reproduced by the simulation software.

In comparison to the simulation of the sedimenting droplet with the n-butanol+water test-system, the levitated-droplet problem with the toluene+water system involves additional simulation and modeling aspects that need to be taken into account. These are the following:

- the initialization of the simulation,
- the higher interfacial tension of the toluene+water system,
- the configuration of the VarIT model.

These issues will be addressed in the coming sections before the main objective of the present work, namely the fitting of the model parameters to the experimental data, can be presented. The results of all simulations that will be discussed from now on, unless explicitly stated otherwise, have been obtained using the XFEM version of the DROPS software with a timestep of 2.0×10^{-4} s and a toluene droplet with an equivalent spherical diameter of 4.0 mm ($34 \mu\text{L}$) levitated in a counter-current flow of the aqueous continuous phase.

6.2.1 Initialization

Like in the case of the sedimenting droplet, a simulation of the levitated droplet may be initialized either by setting the fluid velocities equal to zero everywhere in space, or by setting the initial droplet velocity equal to the one predicted from the Stokes' law for the given system and droplet diameter. Regardless of the option used, however, the simulations need to have a real-time duration of several seconds in order for the droplet to reach its equilibrium position in the levitation cell and its steady circulation state. Therefore, very long computational times are necessary (Rajeh, 2009). If it is also considered that the simulation results are also used to calculate the value of the objective function that needs to be minimized in order to fit the parameters of the VarIT model to the experimental NMR data, the overall duration of such a procedure that involves multiple simulation runs would be prohibitively long.

For this reason, the software package DROPS provides the additional option of using the result of a previous simulation as the initial condition for a subsequent simulation. This initialization practice does not apply to the simulation boundary

conditions and to the VarIT model parameters so that the variable surface tension and the velocity profile of the counter-current can be re-configured between the runs. The droplet position, however, that is defined by the value of the level-set function in the computational domain, is obtained from the simulation that is used as a starting point. Therefore, the droplet position can be configured explicitly only at the beginning of a simulation sequence and the position of the droplet must be equilibrated in each run. The final simulation results are independent from their initial conditions since their reproducibility from different initial states has been ascertained. Using this capability, only the transition period from one equilibrium point to the next needs to be calculated, thus making the simulations significantly shorter.

Another configuration issue of the levitated-droplet simulations concerns the velocity of the aqueous counter-current at the top of the cell that is set as an inlet boundary condition. Although the value of the counter-current velocity in the experiment is known, it corresponds to a certain set of model parameters that are unknown. In addition, since the parameters of the VarIT model influence the fluid dynamics of the system, each set of parameter values corresponds to a counter-current velocity that results to a stable droplet position within the simulation domain. An inappropriate counter-current velocity would lead to an either upward or downward motion of the droplet inside the levitation cell that could eventually result to the droplet exiting the computational domain. Therefore, each step of the iterative procedure of fitting the VarIT parameters to the experimental data also involves adjusting the counter-current velocity so that an equilibrium state is reached.

A droplet simulated without the VarIT model has a fully mobile interface, whereas in the experiment the droplet interface is partially stagnant. Therefore, the counter-current velocity at the beginning of the parameter fitting procedure is much higher than in the experiment. As the parameters of the VarIT model are changed and the discrepancy between simulation and experiment is reduced, the counter-current velocity in the simulation is also set to smaller values in order to obtain a stable droplet position. When the optimum parameter values are eventually found, the respective counter-current volume flow should also match the experimental value of 1.6 mL/s. This is because for a matching degree of stagnation between simulation and experiment, the counter-current flow should also coincide in order to obtain the same droplet position that is not a directly controlled variable in the simulation and can be explicitly set only at the beginning of the fitting procedure.

6.2.2 Interfacial tension

Although the XFEM method leads to an improvement of the accuracy of the CFD calculations and it is necessary for the simulation of the toluene+water system that features a high interfacial tension, some spurious velocities do make their appearance in the final results. These can be recognized by the fact that their vectors are at

a random angle to the liquid-liquid interface and not tangential to it as expected. These spurious currents, however, do not deform the interface and have a lifespan of only a few timesteps. In Fig. 6.10 four snapshots taken from two different simulations are presented. The simulation of the top row features a droplet with a constant interfacial tension whereas the simulation of the second row features a droplet with a variable interfacial tension. The spurious velocity vectors, that in Fig. 6.10 (right) are being indicated by white rectangles, appear and disappear typically within 2-6 timesteps.

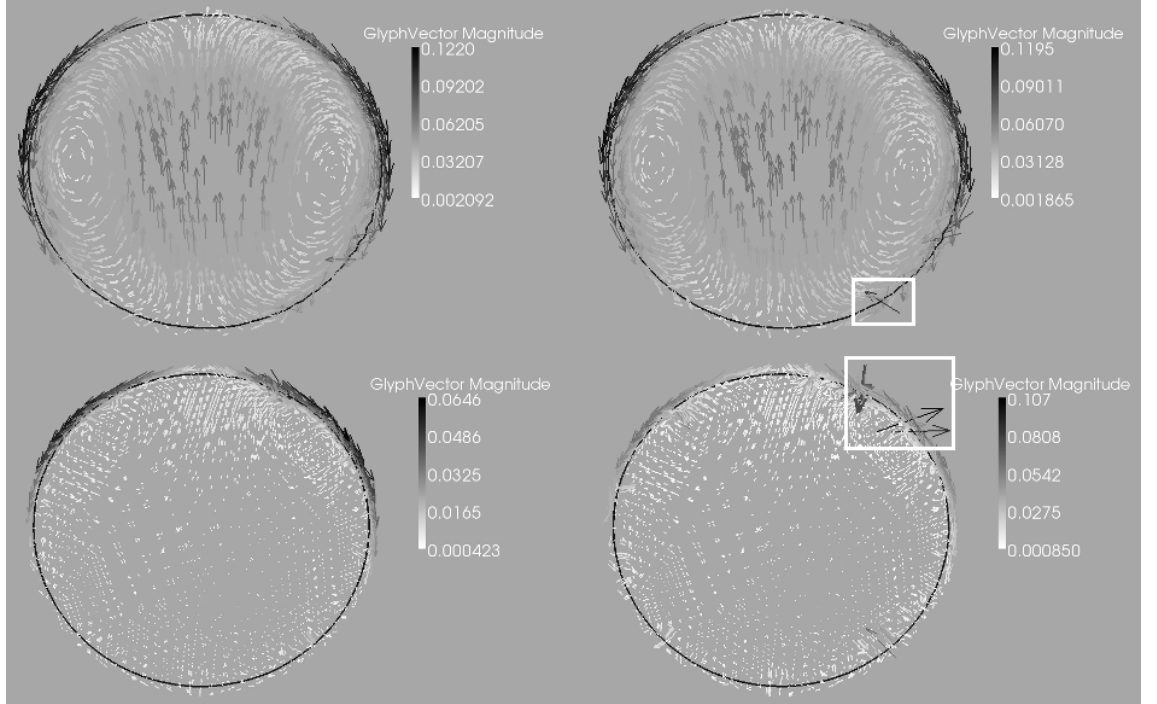


Figure 6.10: Simulation snapshots without the VarIT model (top) and simulation snapshots with the VarIT model (bottom) with $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$. No spurious velocities are initially present (left) but 0.4 ms (two timesteps) later a few spurious velocity vectors appear (right).

In addition, the interfacial tension gradient imposed by the VarIT model and the interfacial stagnation that results thereof make this numerical phenomenon more severe. In the simulation with the interfacial tension gradient (Fig. 6.10, bottom), the spurious velocities are much larger than the rest of the velocity vectors on the interface that result due to the aqueous phase counter-current. The change of the maximum velocity magnitude from $U_{int}^{max} = 0.065$ m/s to $U_{int}^{max} = 0.107$ m/s that can be noticed in Fig. 6.10 (bottom) is indicative of this fact. On the other hand, due to the overall larger velocities in the simulation without an interfacial tension gradient (Fig. 6.10, top), the spurious velocities do not dominate in such a manner. Nevertheless, due to their very short lifespan, the spurious velocities did not seem to influence the neighboring flow in either case.

In order to ascertain that the observed spurious velocities had no influence on the simulation results, the interface of each droplet was examined for local, “unphysical” deformations like those seen in Fig. 4.1. All droplets presented in this work had a smooth surface, which means that the spurious velocities could be ignored.

6.2.3 Torus inversion

The model of Huang and Kintner (1969) suggests that the surfactant concentration profile, and thus the interfacial tension profile along the droplet surface, is a step function rather than a smooth function that features a well-defined gradient. In addition, this discontinuity is expected at the position of the boundary layer separation. However, this means that at the point of the discontinuity a sharp force would appear, that in the CFD simulations of this work resulted to the velocity pattern pictured in Fig. 6.11. In that simulation, the interfacial tension gradient was placed at the droplet equator (Fig. 6.11, left) and had a total width of $\Delta\epsilon = 1.0$ mm, which corresponds to a setting that aimed to approximate a step function with a steep gradient, as can be seen in Fig. 6.12. In that simulation, the maximum of the interfacial tension gradient was $\sigma'_{max} = 2.695$ mN/m². Although the interfacial tension difference between the upper and the lower droplet part was only 5%, the resulting localized forces caused a flow strong enough to compensate the influence of the counter-current. The highest velocities on the droplet surface were concentrated at the same area as the interfacial tension jump (Fig. 6.11, middle) and acted against the counter-current flow. Thus, an inverted toroidal circulation inside the droplet appeared (Fig. 6.11, right).

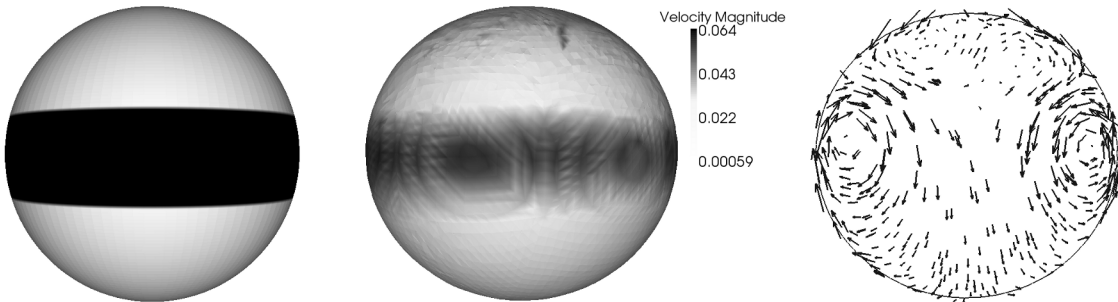


Figure 6.11: Simulation results of a droplet featuring a very steep surface-tension gradient ($y_{grad,rel} = 1.0$, $\Delta\epsilon = 0.5$ mm and $\alpha = 0.95$): Interfacial-tension gradient zone (left), velocity distribution on the droplet interface (middle) and velocity plot on a vertical 2D droplet slice (right).

Velocities induced by interfacial-tension gradients that oppose the continuous-phase flow have been previously reported in the CFD simulations of Burghoff and Kenig (2006). In that work, however, such velocities were considered physically consistent since they aimed to model the interfacial instabilities caused by mass transfer

between the droplet and the continuous phase. An inverted torus, like the one in Fig. 6.11, has not yet been reported experimentally and can, therefore, be considered unphysical under current conditions. Therefore, the interfacial-tension function, and thus also the concentration of the surfactant molecules on the droplet surface, are likely to feature a rather flat gradient rather than an steep one.

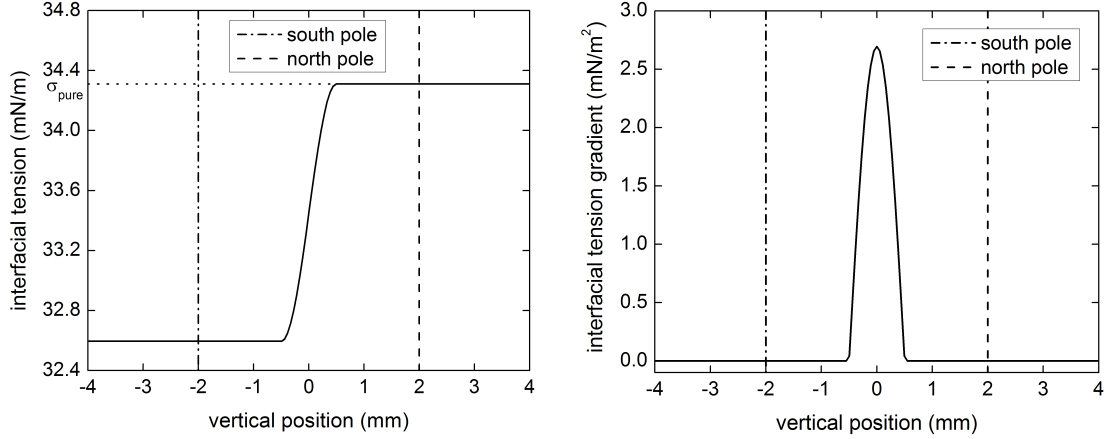


Figure 6.12: Profiles of the interfacial tension (left) and its gradient (right) along the droplet surface for $y_{grad,rel} = 1.0$, $\Delta\epsilon = 0.5$ mm and $\alpha = 0.95$.

6.2.4 Influence of materials and droplet diameter

The findings presented in Sec. 6.2.3 suggest that the values of the VarIT model parameters must be bounded in order to obtain meaningful results and to avoid unphysical simulation effects. During the procedure of fitting the values of these parameters to the experimental data, care has been taken to avoid flow patterns like the one pictured in Fig. 6.11. Such patterns, however, can result not only because of the value of model parameter $\Delta\epsilon$, but also because of the value of model parameter α , since both the width and the height of the interfacial tension step influence the steepness of the interfacial-tension gradient. Therefore, a series of preliminary simulations were aimed at qualitatively examining the physical influence of the model parameters on the fluid flow. For this purpose, simulations for both toluene and n-butanol droplets, levitated in water, each with a diameter of 2.0 mm were performed (Rajeh, 2009).

In the case of the system toluene+water, it was found that for $\alpha \leq 0.95$ and $\Delta\epsilon \leq 0.7$ mm the force induced by the interfacial-tension gradient was big enough to cause an inversion of the inner circulation torus as presented in Fig. 6.11. These settings correspond to a maximum interfacial-tension gradient of $\sigma'_{max} = 1.922$ mN/m². A small degree of stagnation in the lower part of the droplet was obtained using $\alpha = 0.99$, $\Delta\epsilon = 1.0$ mm and $y_{grad,rel} = 1.9$ as shown in Fig. 6.13 that corresponds to a maximum interfacial-tension gradient of $\sigma'_{max} = 0.269$ mN/m² (Fig. 6.14, right).

Similar settings were also applied to a droplet with a diameter of $d = 4.0$ mm in which the gradient was moved slightly towards the droplet equator by setting $y_{grad,rel} = 1.8$ and the interfacial-tension difference between the droplet poles was increased using $\alpha = 0.98$. Although this configuration brings the interfacial-tension gradient to a maximum of $\sigma'_{max} = 0.538$ mN/m² (Fig. 6.14, left), it had no visible effect on the internal droplet flow that remained fully circulating. The interfacial-tension gradient caused only a slight decrease of the fluid velocity magnitudes on the droplet surface near its bottom pole. This lead to a boundary-layer separation at the droplet rear in spite of the fact that the droplet featured no stagnant cap.

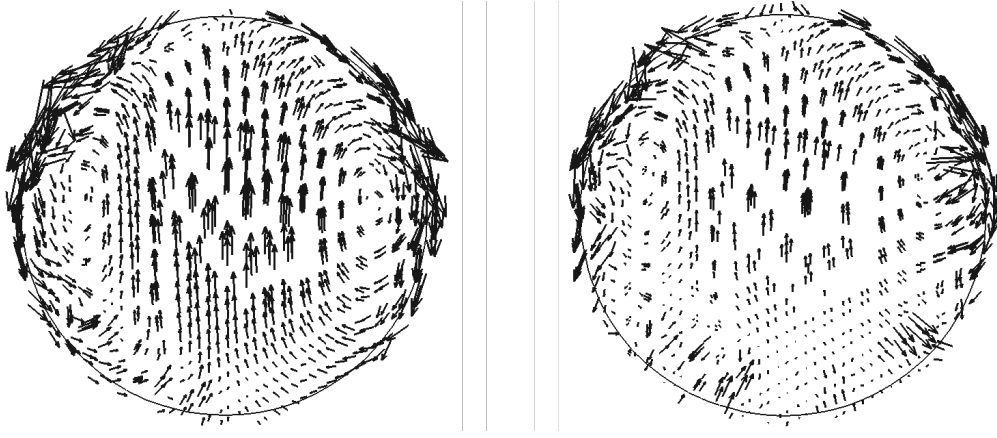


Figure 6.13: Vector plots on vertical mid-planes for toluene droplets levitated in water without (left) and with the VarIT model (right) and a diameter of $d = 2.0$ mm: for $y_{grad,rel} = 1.9$, $\Delta\epsilon = 1.0$ mm and $\alpha = 0.99$.

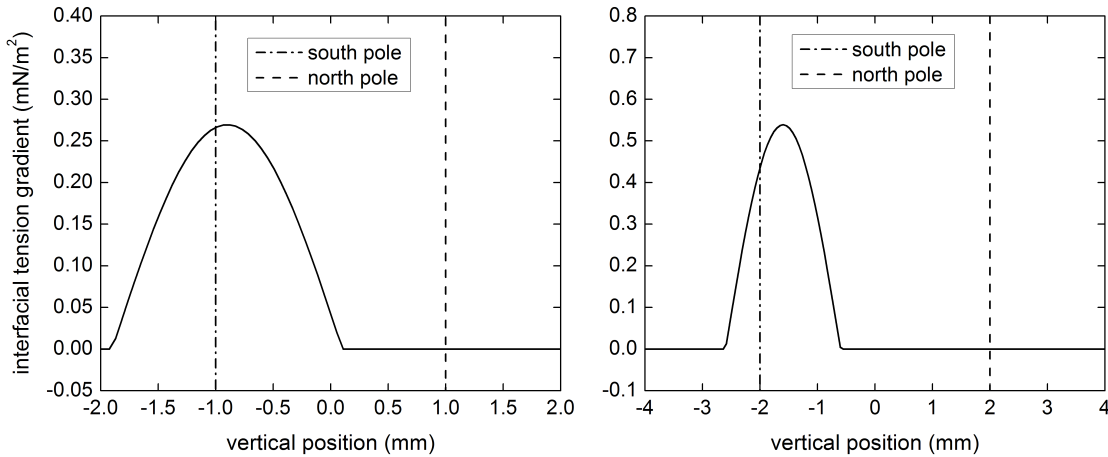


Figure 6.14: Comparison of interfacial tension gradient curves with $d = 2.0$ mm, $y_{grad,rel} = 1.9$, $\Delta\epsilon = 1.0$ mm and $\alpha = 0.99$ (left) and $d = 4.0$ mm, $y_{grad,rel} = 1.8$, $\Delta\epsilon = 1.0$ mm and $\alpha = 0.98$ (right).

Although a boundary layer separation is connected to a drag increase, the above comparison indicates the higher sensitivity of smaller droplets to impurities in comparison to larger droplets. If a small amount of a weak surface-active compound is present in the liquid-liquid system, only small droplets will be influenced, while larger droplets due to their higher buoyancy and larger relative velocity to the continuous phase will remain fully circulating.

The data considered in Sec. 6.2.3 as well as in Fig. 6.14 also suggest that the interfacial-tension gradient must be fairly wide in relation to the droplet diameter rather than concentrated at a certain location in order to obtain a stagnant cap. Therefore, during the fitting procedure, where only droplets with $d = 4.0$ mm were considered, focus was given on wide gradients with $\Delta\epsilon > 1.0$ mm. Furthermore, parameter α was bounded between $0.92 < \alpha < 0.98$ in order to maintain a strong interfacial tension gradient force that is capable of stagnating large droplets without causing an inversion of the inner circulation torus. In this work, best stagnation results for toluene droplets with $d = 4.0$ mm were obtained using $\alpha = 0.95$.

In the case of the n-butanol+water system, a droplet with a diameter of $d = 2.0$ mm was simulated using the VarIT model configured with $y_{grad,rel} = 1.0$, $\Delta\epsilon = 0.5$ mm and $\alpha = 0.80$. The results are presented in Fig. 6.15 where a simulated droplet without an interfacial-tension gradient (left) is compared to a respective simulation with the VarIT model (right) in which the droplet features a stagnant cap. In Fig. 6.16 the profiles of the interfacial tension (left) and its gradient (right) along the droplet surface are displayed. If the model parameters of the toluene droplet simulation in Fig. 6.13 are compared to the model parameters of the n-butanol droplet simulation in Fig. 6.15 it is evident that much smaller values for both parameters α and $\Delta\epsilon$ were necessary in order to obtain a stagnant cap.

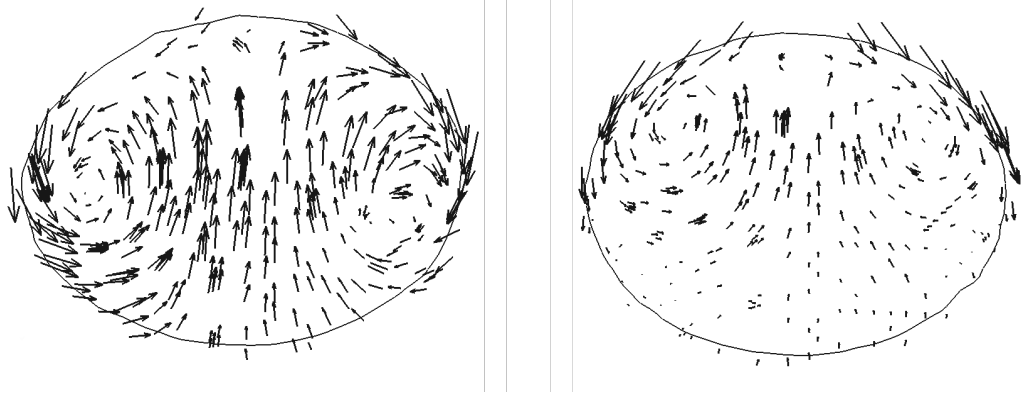


Figure 6.15: Vector plots on vertical mid-planes for n-butanol droplets levitated in water without (left) and with the VarIT model (right) and a diameter of $d = 2.0$ mm: for $y_{grad,rel} = 1.0$, $\Delta\epsilon = 0.5$ mm and $\alpha = 0.80$.

The smaller values for α and $\Delta\epsilon$ in the simulation of the n-butanol droplet correspond to a much steeper interfacial-tension gradient than in the simulation of the toluene droplet. The interfacial-tension gradient peak in Fig. 6.16 (right) reaches a maximum

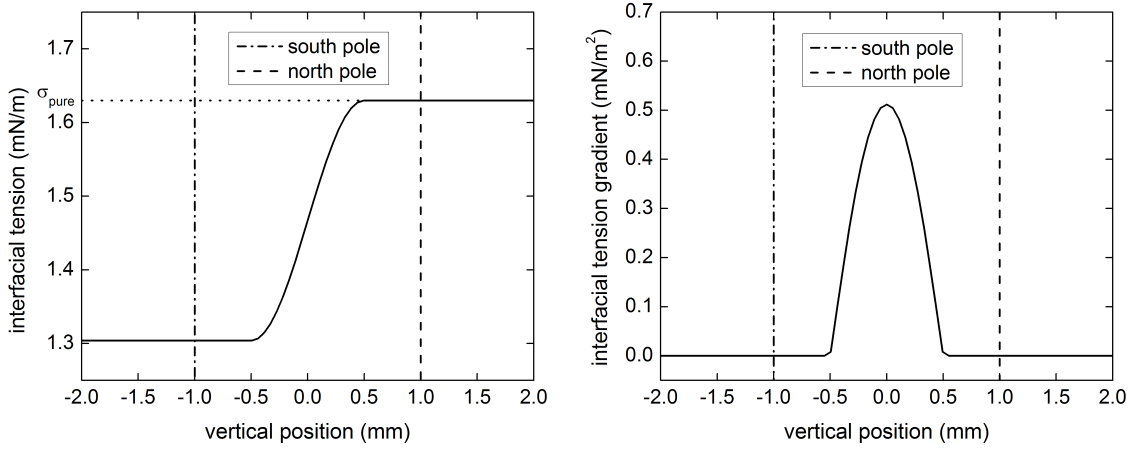


Figure 6.16: Profiles of the interfacial tension (left) and its gradient (right) along the surface of an n-butanol droplet for $d = 2.0$ mm, $y_{grad,rel} = 1.0$, $\Delta\epsilon = 0.5$ mm and $\alpha = 0.80$.

value of $\sigma'_{max} = 0.512$ mN/m² that is almost double the respective value of $\sigma'_{max} = 0.269$ mN/m² that was noted in the case of the toluene droplet. This is due to the very low interfacial tension of the n-butanol+water system, which means that a higher degree of contamination, or a stronger surfactant, is necessary in order for an n-butanol droplet to be stagnated in comparison to a toluene droplet. This result is in agreement with the postulation of Thorsen et al. (1968) according to which the higher the interfacial tension of a system, the more sensitive the system will be to contamination.

6.3 Solving the inverse problem

The values of the VarIT model parameters were manually fitted to the experimental data presented in Sec. 3.1.2 that were obtained using the FLIESSEN NMR-sequence. The objective function was based on comparing the measured and simulated fluid velocities inside the droplet by using the NMR imaging function as described in Sec. 5.2.2. In this way, the inverse problem of determining the shape and location of the interfacial-tension gradient along the droplet surface by measuring its impact on the flow was solved.

6.3.1 Parameter fitting

The fitting procedure was based on the insights of the preliminary simulations as presented in Sec. 6.2.3 and Sec. 6.2.4. An interfacial-tension gradient similar to the one in Fig. 6.14 (left) that resulted in a slight stagnation in a toluene droplet with a diameter of $d = 2.0$ mm was applied to a toluene droplet with a diameter

of $d = 4.0$ mm. In order to account for the larger droplet size, the gradient was made wider by setting $\Delta\epsilon = 2.0$ mm. The gradient maximum was also raised to $\sigma'_{max} = 0.674$ mN/m² by using $\alpha = 0.95$ and its position was set to $y_{grad,rel} = 1.8$ as pictured in Fig. 6.17. The results can be viewed in Fig. 6.18 (right) where the flow of the toluene-rich phase is visualized with the help of vectors plotted on a vertical 2D slice at the middle of the droplet. For comparison, the respective flow inside a levitated droplet without an interfacial tension gradient is pictured in Fig. 6.18 (left). The vector length is scaled according to velocity magnitude in each frame independently.

The simulated droplet in Fig. 6.18 (right) features a stagnant cap that spans approximately the lower quarter of its vertical axis. This stagnant cap is relatively small if qualitatively compared to the experimental results of Fig. 3.4 where only the upper half of the droplet was circulating. In order to obtain a larger stagnant cap, the interfacial tension gradient of Fig. 6.17. was made broader by setting $\Delta\epsilon = 3.0$ mm and the position of its center was moved towards the droplet equator at $y_{grad,rel} = 1.65$. These settings, however, did not have any significant impact on the fluid flow and the vector map of the velocities inside the droplet remained as pictured in Fig. 6.18 (right). Therefore, the interfacial-tension gradient was shifted above the droplet equator using $y_{grad,rel} = 0.8$. The interfacial-tension curve thus obtained the form presented in Fig. 6.19. This new setting did change the internal circulation of the droplet as shown in Fig. 6.20 (left). The force induced by the interfacial-tension gradient was strong enough to cause a secondary circulation torus at the lower part of the droplet in spite of the reduction of the gradient maximum to $\sigma'_{max} = 0.449$ mN/m² in comparison to the $\sigma'_{max} = 0.674$ mN/m² of Fig. 6.18 (right). An adjustment of the interfacial-gradient position below the equator at $y_{grad,rel} = 1.2$ did not have any qualitative influence on the fluid flow that remained as pictured in Fig. 6.20 (left).

The secondary circulation torus strongly resembles the inverted torus discussed in Sec. 6.2.3 and is not considered a physically valid state due to the lack of experimental evidence to the contrary in this work. According to Kück et al. (2011), however, a secondary counter-rotating torus at the droplet rear has been experimentally reported in the past (Pruppacher and Beard, 1970) and could be caused by the accumulation of surface-active components on the interface. Nevertheless, this torus can also be induced by the circulation of the continuous phase at the droplet wake as demonstrated in Brander and Brauer (1993), Waheed (2001) and Waheed et al. (2004) without any surfactant influence.

The fact that in Fig. 6.18 (right) a stagnant cap is noted whereas in Fig. 6.20 (left) an inverted torus is present, in spite of the interfacial tension gradient being less steep, can be explained by considering the overall shape and positioning of the interfacial tension gradient curve together with the interfacial velocities of the each droplet. In Fig. 6.17 (right) the interfacial tension gradient is mostly decreasing and spans only the lower half of the droplet. By contrast, the interfacial tension gradient in Fig. 6.19 (right) extends along the whole droplet surface. This means

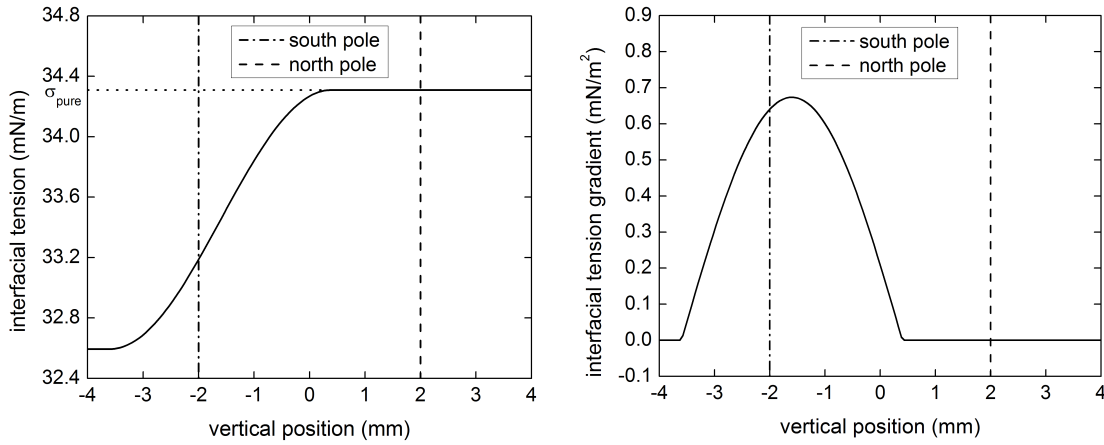


Figure 6.17: Profiles of the interfacial tension (left) and its gradient (right) along the droplet surface for $y_{\text{grad,rel}} = 1.8$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$.

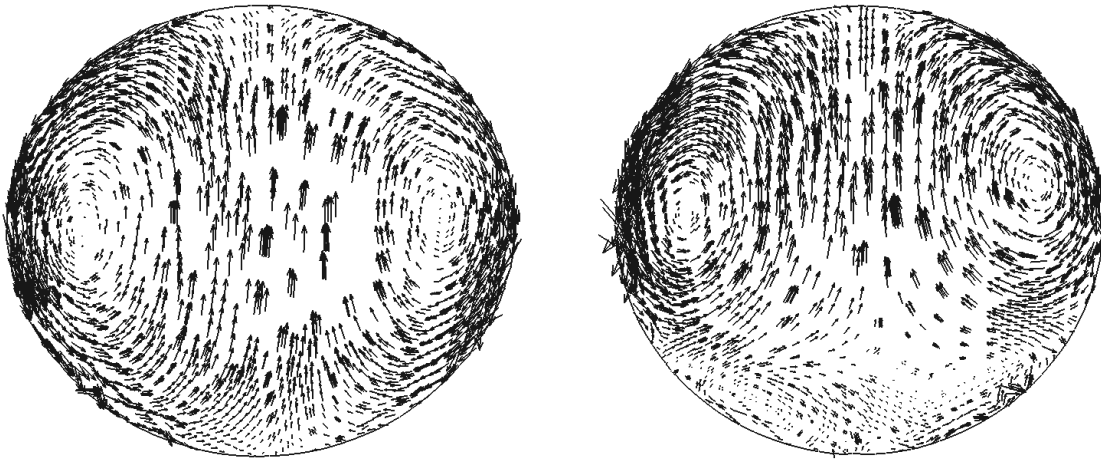


Figure 6.18: Velocity vectors on a vertical 2D slice from the droplet middle for a droplet without an interfacial tension gradient (left) and for $y_{\text{grad,rel}} = 1.8$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$ (right).

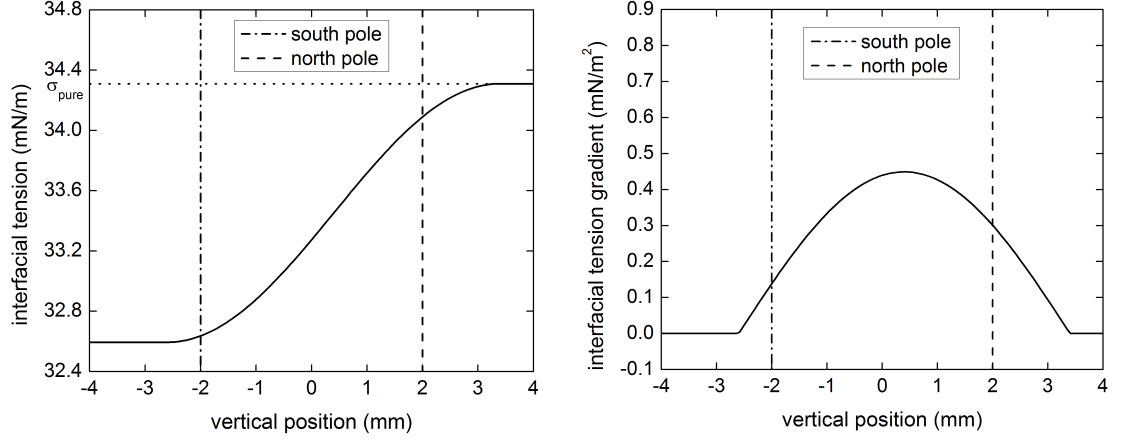


Figure 6.19: Profiles of the interfacial tension (left) and its gradient (right) along the droplet surface for $y_{grad,rel} = 0.8$, $\Delta\epsilon = 3.0$ mm and $\alpha = 0.95$.

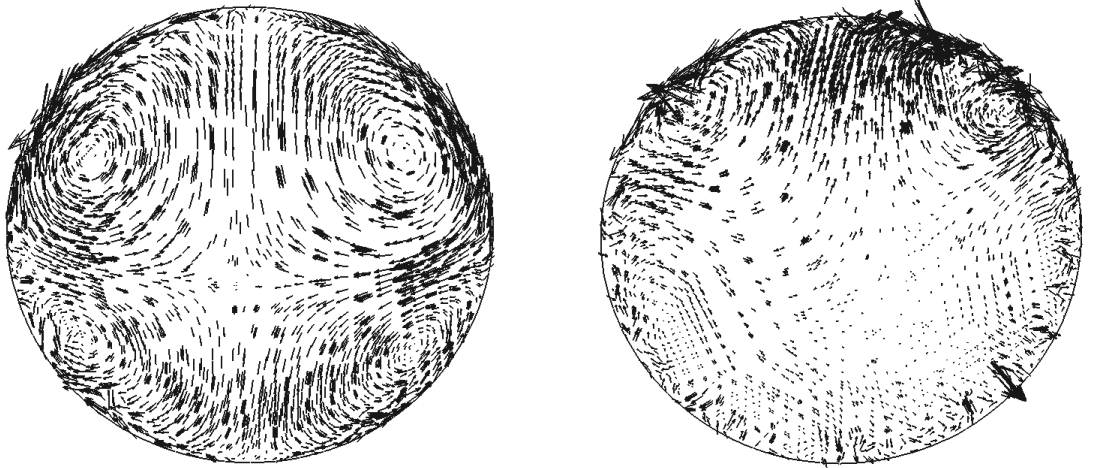


Figure 6.20: Velocity vectors on a vertical 2D slice from the droplet middle for $y_{grad,rel} = 0.8$, $\Delta\epsilon = 3.0$ mm and $\alpha = 0.95$ (left) and for $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$ (right).

that the force of the continuous phase counter-current on the upper droplet half is left undisturbed for $y_{grad,rel} = 1.8$, $\Delta\epsilon = 2.0$ mm whereas a significant portion of that force is canceled out by the interfacial tension gradient when it is made wider by using $y_{grad,rel} = 0.8$, $\Delta\epsilon = 3.0$ mm. Thus, the portion of the interfacial tension gradient acting on the lower droplet half (Fig. 6.19, right) results to a force strong enough to cause a secondary inverted torus.

This fact is confirmed by the respective interfacial velocities that are pictured in Fig. 6.21. In the figure, the fluid velocities are plotted on the droplet surface according to their magnitude using a constant scale from 0.0 m/s to 0.1 m/s. It can be seen that the interfacial velocities on the upper droplet half for $y_{grad,rel} = 0.8$ and $\Delta\epsilon = 3.0$ mm (Fig. 6.21, right) are indeed much smaller than those for $y_{grad,rel} = 1.8$ and $\Delta\epsilon = 2.0$ mm (Fig. 6.21, left). Therefore, a smaller interfacial tension gradient in the lower droplet half is capable of inverting the inner circulation in that region.

These findings suggest that in order to obtain a larger stagnant cap, an interfacial tension gradient is needed that will not stretch to the droplet rear, so as to avoid an inverted internal circulation. The gradient, however, needs to be steep enough in order to compensate the force of the counter-current flow and cause stagnation. Therefore, the interfacial tension gradient was moved higher and was made narrower by setting $y_{grad,rel} = 0.5$ and $\Delta\epsilon = 2.0$ mm as shown in Fig. 6.22. The result of that simulation can be seen in Fig. 6.20 (right), where it is noticed that the velocity pattern inside the droplet is in good qualitative agreement with the experimental results in Fig. 3.4. The influence of parameter α was examined by testing the values $\alpha = 0.94$ and $\alpha = 0.96$ while keeping the values of $y_{grad,rel} = 0.5$ and $\Delta\epsilon = 2.0$ mm constant. In the first case, the steeper interfacial tension gradient caused a small inverse flow at the vicinity of its maximum, whereas in the second case the force imposed by the interfacial tension gradient was not strong enough to result to a stagnant cap.

The imaging function that was presented in Sec. 5.2.2 was used to compare all the simulations presented above to the first two frames of the experimental data of Fig. 3.4. The value of the objective function Φ as well as the average discrepancy per pixel Ψ , that were defined in Eq. 5.16 and Eq. 5.17, were used to perform a quantitative comparison between simulation and experiment. In Table 6.2 a summary of the imaging function results is given, where it is evident that simulation #4 features the smallest Φ -value. In Fig. 6.23 an overview for all simulations of Table 6.2 is shown, where the averaged velocity magnitudes are presented (left), together with plots of the discrepancy ψ_{ij} between the simulation and the first experimental frame (middle) and streamlines based on the averaged velocity magnitudes (right). The averaging was performed in order to reduce the simulated velocities to a form that is directly comparable to the experimental data according to Sec. 5.2.1. In Fig. 6.23 it can be seen how the successive adjustment of the VarIT model parameters increases the size of the stagnant cap, thus bringing the flow pattern inside the droplet closer to the one depicted in the experiments. In addition, the simultaneous decrease of the fluid velocities inside the droplet also leads to an improved quantitative agreement

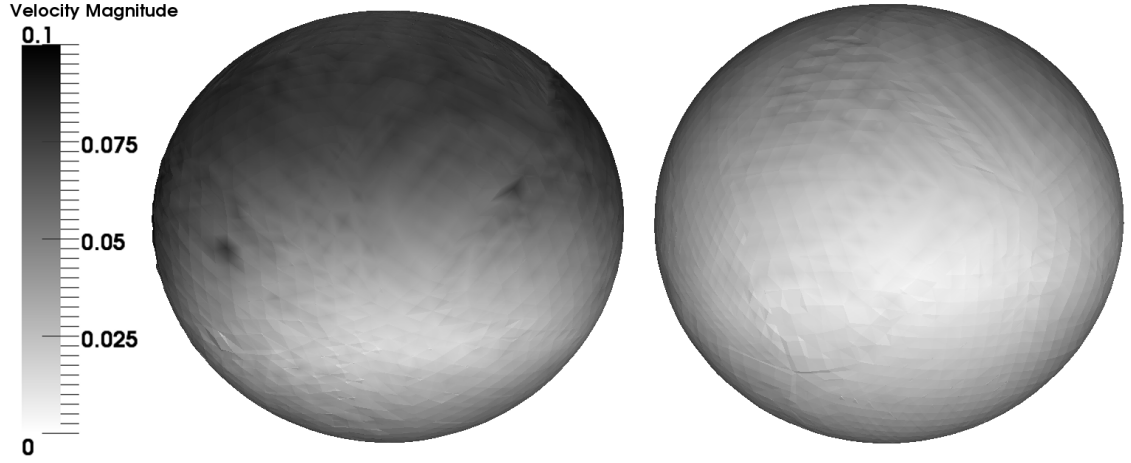


Figure 6.21: Droplet surface colored by velocity magnitude for $y_{grad,rel} = 1.8$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$ (left) and for $y_{grad,rel} = 0.8$, $\Delta\epsilon = 3.0$ mm and $\alpha = 0.95$ (right).

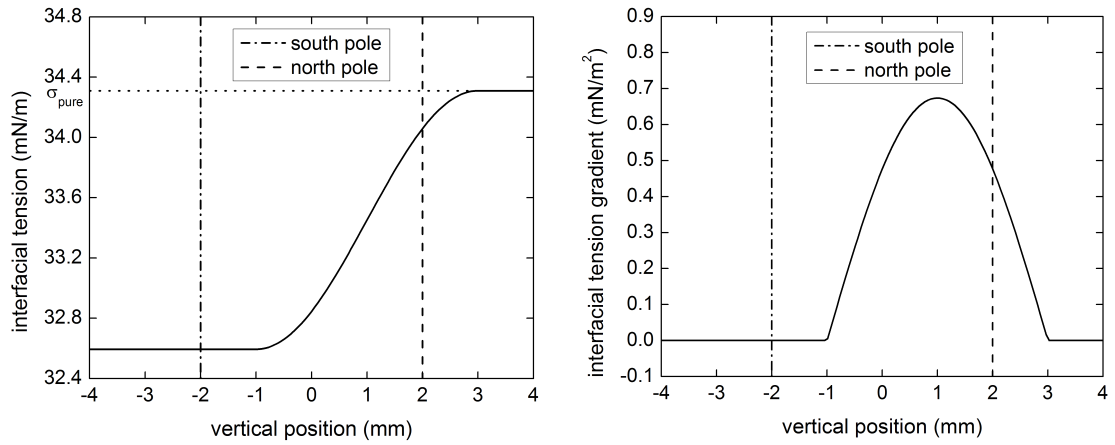


Figure 6.22: Profiles of the interfacial tension (left) and its gradient (right) along the droplet surface for $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$.

of the simulation and the experimental data. From Table 6.2 and Fig. 6.23 it can be concluded that simulation #4, performed using $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$, is also in good quantitative agreement with the experimental results.

Table 6.2: Values of the objective function for different parameter sets. The indices 1 and 2 denote the 1st and the 2nd experimental frame of Fig. 3.4 respectively.

#	$y_{grad,rel}$	$\Delta\epsilon$ mm	α	Φ_1 μm^2	Ψ_1 $\mu\text{m}/\text{pixel}$	Φ_2 μm^2	Ψ_2 $\mu\text{m}/\text{pixel}$
1	-	-	-	47024426.4	84.7	48099657.1	85.8
2	1.8	2.0	0.95	23985802.1	58.7	25255635.9	59.9
3	0.8	3.0	0.95	3208229.6	20.8	3517453.2	21.7
4	0.5	2.0	0.95	1155359.3	10.7	876805.6	9.6

A discrepancy between the simulation and the experiment can be located in the shape of the interfacial velocity distribution along the upper part of the droplet. If the first frame of the experimental data series in Fig. 3.4 and simulation #4 in Fig. 6.23 are considered, it can be seen that although the size of the stagnant cap is accurately described, the velocity peaks along the interface in the mobile part of the simulated droplet have a different shape than those in the experiment. The interfacial velocities on both sides of the two-dimensional experimental and simulated data are depicted in Fig. 6.24 for a more detailed comparison.

In Fig. 6.24 (left) simulation #4 is compared to the first frame of the experimental time-series, whereas in Fig. 6.24 (right) the same simulation is compared to the second experimental frame. Starting from the front stagnation point at the droplet's top pole, the interfacial velocities in both the simulation and the experiment increase sharply towards the droplet's bottom pole until a velocity peak is reached. The simulation accurately depicts the position of this peak along the vertical axis. In the experiment, after this peak the velocity magnitudes drop abruptly, thus indicating the beginning of the stagnant interfacial area. In the simulation, however, a gradual decrease is noted, which suggests that the interfacial tension gradient might be rather small at that point.

Concerning the peak's height, a larger discrepancy between the simulation and the experiment seems to be present in Fig. 6.24 (left). This, however, is because the experimental data exhibit an unsymmetry that is not reproduced by the simulation. The measured velocities on the peak of the right side of the droplet are 85% higher than the peak velocities on the left side of the droplet. The velocity magnitudes of both peaks in the simulation are in good agreement with the left peak in the experiment, but not with the right peak. This unsymmetry is also evident in the respective vector plot of Fig. 3.4 where also a horizontal velocity vector is present on the right of the droplet, which is not conforming with the trend of its neighboring vectors. In addition, this unsymmetry diminishes with time and could be attributed

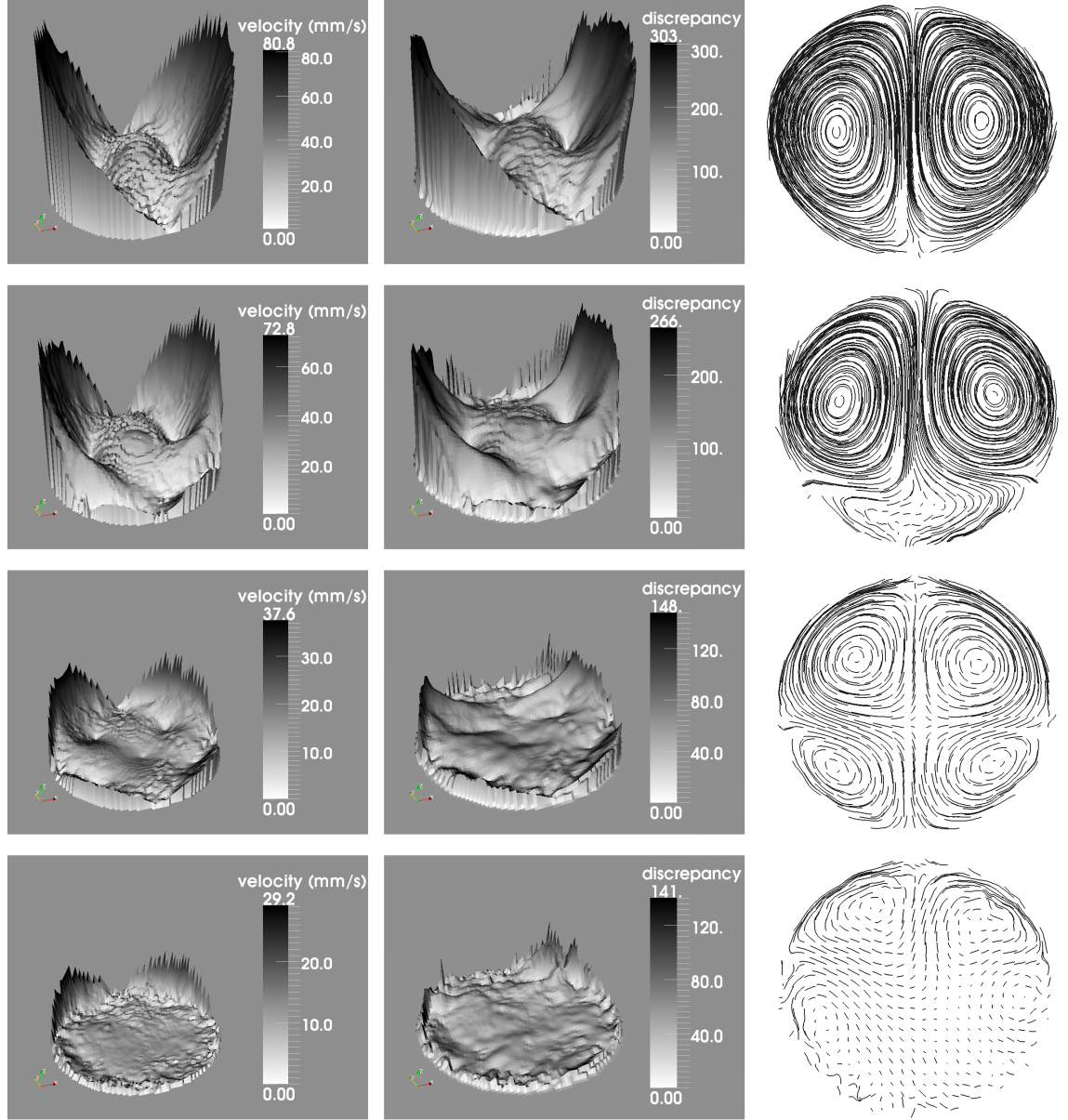


Figure 6.23: Velocity magnitudes inside a levitated droplet simulated with XFEM-DROPS (left), plots of the discrepancy ψ_{ij} between the simulation and the experiment in μm (middle) and streamlines (right) for simulations #1, 2, 3 and 4 (from top to bottom).

to the droplet not being perfectly stable during the experiment. In Fig. 6.24 (right) the simulation is compared to the second experimental frame and can be seen that the agreement between the heights of all peaks is much better due to the improved symmetry in the experimental data.

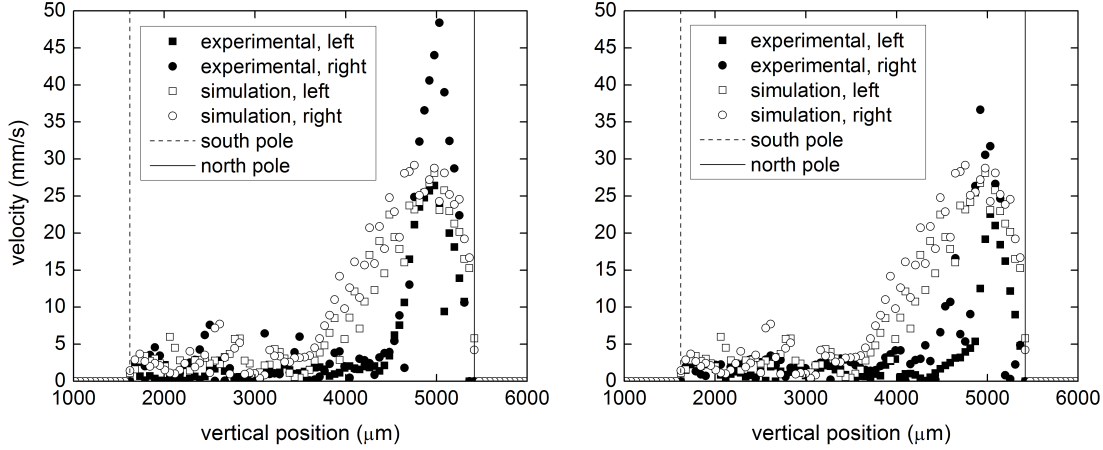


Figure 6.24: Comparison between the interfacial velocities of simulation #4 and the first frame (left) as well as the second frame (right) of the experimental data.

The better match of simulation #4 with the 2nd experimental frame in terms of interfacial velocity can also be quantitatively observed in the values of the objective function Φ_1 and Φ_2 in Table 6.2. However, variable Ψ that expresses the average discrepancy per pixel in units of distance and is also presented in Table 6.2, shows that the difference between simulation #4 and both experimental frames has fallen much below the pixel size of the measured data, which was $55 \mu\text{m}$. Therefore, the difference between the simulation and the experiment is comparable to the experimental accuracy, which makes the further analysis and fitting of the simulation difficult. Also, as seen in Fig. 6.23 (middle column), almost all discrepancy peaks have been eliminated and the flow in the main body of the droplet is simulated with good accuracy.

The agreement between the interfacial velocities of the simulation and the experiment in this work is an improvement over the one presented by Groß-Hardt (2007) that explicitly divided the droplet interface into an ideally mobile and a completely stagnant part. In order to further improve the correlation between the experimental and the calculated data, an unsymmetrical interfacial-tension gradient could be considered. Both Ponoth and McLaughlin (2000) and Li and Mao (2001) performed simulations using the adsorption/desorption model and report interfacial-tension functions that feature a minimum slightly above the rear droplet pole. This minimum emerges from the desorption of the surfactant at the vicinity of the bottom pole that lowers its concentration and therefore a small increase in the interfacial tension is noted. This local increase of the interfacial tension causes a negative interfacial tension gradient that favors a fluid flow in the same direction as the counter-current.

This would allow a finer adjustment of the interfacial tension curve and would eliminate the danger of creating an inverse circulation torus in the droplet. However, it would also import additional model parameters that must be fitted to the experimental data.

6.3.2 Discussion of results

In this section, the simulation with the fitted VarIT model will be further analyzed in order to examine its physical significance and meaning. More specifically, the impact of the interfacial stagnation on the flow of the continuous phase around the droplet will be evaluated. The fitted parameter values of the VarIT model will be interpreted in terms of interfacial concentration of contaminants as discussed in Sec. 5.1.2.

External flow around the droplet

The interfacial tension gradient does not only influence the fluid motion inside the droplet, but it also has an effect on the flow of the continuous phase as well. Fig. 6.25 presents a comparison of the external flow around the droplet between simulations #1 and #4 of Table 6.2, i.e. the simulation without the VarIT model (Fig. 6.25, left) and the simulation that presented the best fit to the experimental data (Fig. 6.25, right). In the figure, the droplet surface and the continuous phase streamlines are colored according to the minimum and the maximum velocity magnitudes on the interface. The decreased mobility in the lower part of the droplet with the VarIT model and the uniform surface velocity of the droplet without the interfacial tension gradient can be observed.

In addition, a circulation wake in the continuous phase behind the partially stagnated droplet is noticed, that is absent in the simulation of the droplet with the ideally mobile interface. The existence of this wake has been postulated by various authors in the past (Huang and Kintner, 1969; Andrews et al., 1988) and implementations of various models have also predicted its appearance for cases of contaminated droplets and bubbles (Groß-Hardt, 2007; Liao and McLaughlin, 2000; Cuenot et al., 1997; Li and Mao, 2001). Together with the decreased interfacial mobility, the circulation wake contributes in making the macroscopic behavior of a fluid particle more like that of a solid sphere by increasing its drag coefficient. The formation and the size of the trailing circulation wake is, for both ideally mobile and solid particles, dependent on the Re -number of the flow as well as on the viscosity and the density ratios of the continuous and the dispersed phase (Waheed, 2001). In this work, the Re -number in the simulation of the toluene droplet without an interfacial-tension gradient was $Re = 213.5$. The simulations of Campergher et al. (2006) show a rigid sphere at $Re = 200$ to feature a trailing wake, which demon-

strates the tendency of a contaminated droplet to behave like a solid particle, rather than a fluid one.

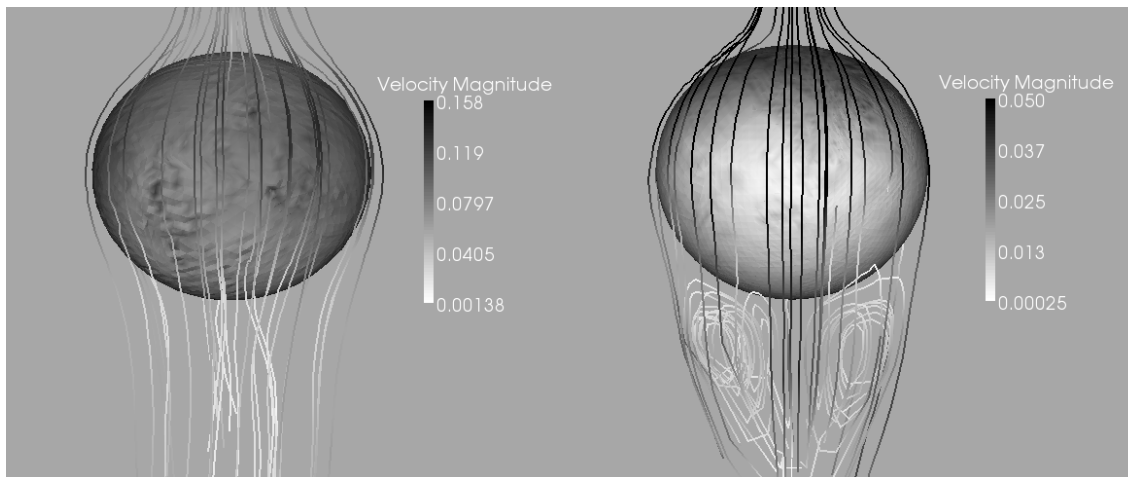


Figure 6.25: Comparison of continuous phase streamlines and droplet surface mobility between a simulation without variable interfacial tension (left) and the simulation fitted to the experimental data (right).

The drag increase was also evident in the velocity of the counter-current, that had to be adjusted during the parameter fit in order to allow the droplet to reach a stable position in the simulation cell. Since a no-slip boundary condition was applied at the wall, a velocity profile was used for defining the inlet of the continuous phase. Thus, the counter-current velocity can be described based on the maximum value of that profile. The velocity of the counter-current in the simulation pictured in Fig. 6.25 (left), that was fully circulating, was 110 mm/s. The simulation shown in Fig. 6.25 (right), that featured a stagnant cap, was performed with a counter-current velocity of 80 mm/s. This difference indicates the extent of the drag increase caused by the partial immobilization of the interface and the trailing circulation wake. The counter-current velocity of 80 mm/s corresponds to a volume throughput of 1.63 mL/s. The respective experimental value was 1.6 mL/s, which shows the good agreement between the simulation and the experiment concerning the overall droplet drag.

Physical interpretation of the interfacial-tension gradient

In Fig. 6.22 (left) it can be noticed that the interfacial tension at the droplet's top pole is smaller than the interfacial tension of the liquid-liquid system in the absence of surfactants:

$$\sigma_{top} < \sigma_{pure}.$$

According to the discussion in Sec. 5.1.2, this state corresponds to the case in which the droplet is fully covered with surfactants, but there is still a gradient of surfactant

concentration along the interface. In addition, the interfacial tension gradient at the upper droplet edge is non-zero, which means that the surfactant concentration starts increasing immediately.

Another scenario can be tested if the upper plateau of the model curve is set to $\sigma_{max} = 34.57$ mN/m and the same parameters of the VarIT model are used to configure the interfacial tension gradient, i.e. $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$. This setting ensures that the interfacial tension at the droplet's top pole is equal to the interfacial tension of the pure system:

$$\sigma_{top} = \sigma_{pure} = 34.31 \text{ mN/m}.$$

In Fig. 6.26 the respective interfacial tension curves are displayed for comparison. Physically, the second scenario describes the case in which the droplet's top pole is free of surfactants, although the droplet is still fully contaminated. This could be due to a different amount of surfactant in the system, or, if two systems with different species of surfactant are compared, to a different adsorption/desorption behavior of the surfactant on the droplet surface.

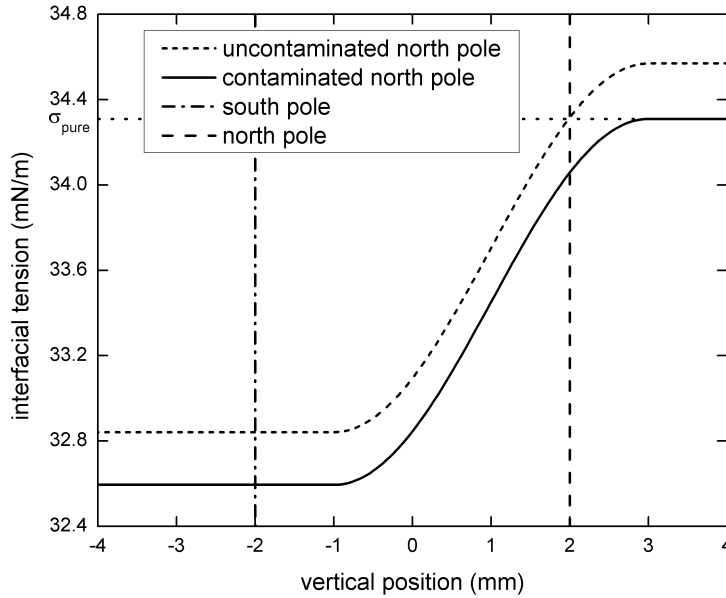


Figure 6.26: Profiles of the interfacial tension along the droplet surface for different degrees of contamination for $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm, $\alpha = 0.95$.

In both of the above cases, the interfacial tension curves feature the same gradient that is pictured in Fig. 6.22 (right). Since it is the interfacial tension gradient, rather than the interfacial tension itself, that produces the force that opposes the counter-current, the two curves shown in Fig. 6.26 are expected to have a very similar effect on the internal circulation of the droplet. This was confirmed by a DROPS-simulation, the results of which are presented in Fig. 6.27 that depicts the velocity vectors on a vertical 2D slice from the droplet middle for the two curves of Fig. 6.26.

The simulation results in Fig. 6.27 (left) obtained using the solid curve of Fig. 6.26 where $\sigma_{top} < \sigma_{pure}$ and the simulation results in Fig. 6.27 (right) obtained using the dashed curve of Fig. 6.26 where $\sigma_{top} = \sigma_{pure}$ show the same velocity pattern.

As long as the overall reduction of the interfacial tension is relatively small, so that the droplet form does not change, similar translations of the interfacial tension curve along the vertical axis will lead to the same result since the interfacial tension gradient would remain unaffected. Practically, this means that only the interfacial-tension *gradient* curve can be unambiguously determined based on the apparent droplet stagnation, and not the curve of the interfacial tension itself. The interfacial tension profile along the droplet surface may vary as shown in Fig. 6.26. Furthermore, even if an exact relation is known that describes the interfacial tension as a function of surfactant concentration, the concentration profile of surfactant on the droplet can only be approximated, because the same interfacial stagnation can be caused by more than one interfacial-tension curves. This also affects adsorption/desorption models that parametrically describe the surfactant concentration profile on the droplet and thus calculate the interfacial-tension curve. Since different interfacial-tension curves can result to the same stagnation pattern, more than one parameter sets may be obtained that fit the measured data. In contrast, the VarIT model parameters $y_{grad,rel}$, $\Delta\epsilon$ and α directly describe the interfacial-tension gradient and should be unique for a given degree of stagnation.

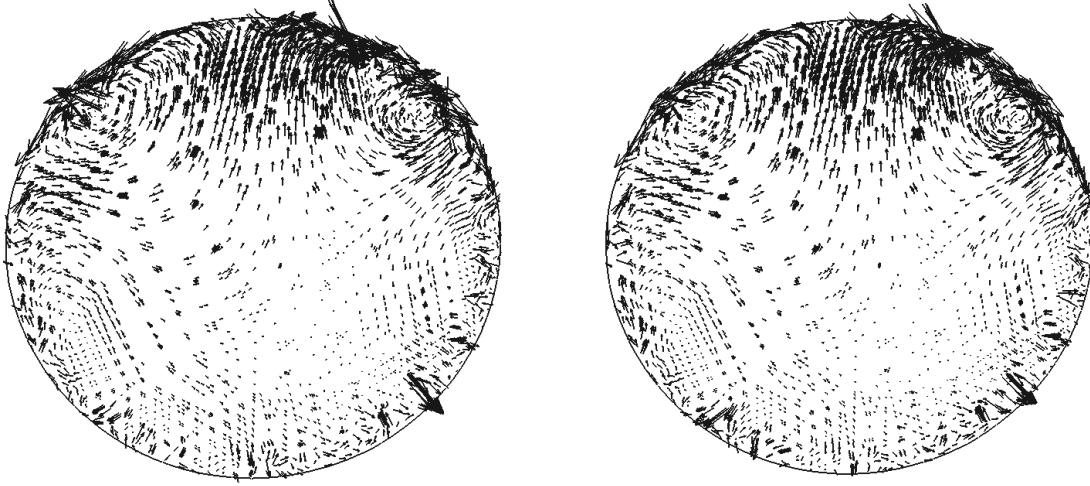


Figure 6.27: Velocity vectors on a vertical 2D slice from the droplet middle with $y_{grad,rel} = 0.5$, $\Delta\epsilon = 2.0$ mm and $\alpha = 0.95$ for $\sigma_{top} < \sigma_{pure}$ (left) and $\sigma_{top} = \sigma_{pure}$ (right).

Chapter 7

Summary

The state of-the-art modeling techniques for designing liquid-liquid extraction columns focus on the properties of single droplets and the processes in which they are involved, like sedimentation, coalescence and mass transfer. The semi-empirical models that are used in the calculations are based on fitted parameters that require experimental measurements. In addition, the phenomena observed in the experiments are very complex in nature, thus making the interpretation of the results and, thereby, the reliable design of extraction apparatuses, a non-trivial matter.

The liquid-liquid interface often plays a very dominant role in describing the behavior of droplets, but it has not yet been fully investigated. This work is a follow-up of the work by Groß-Hardt (2007) and aimed in developing and testing an interfacial tension model for simulating the effect of surface-active impurities on the internal flow of single droplets. The project was part of the Collaborative Research Center CRC-540 of the RWTH Aachen University. The simulations were performed with the CFD-program “DROPS”. For validating the interfacial model, the experimental setup proposed by Groß-Hardt (2007) was used. The software and the experimental results were respectively provided by partner-projects of the Chair of Numerical Mathematics and the Institute for Macromolecular Chemistry.

Surface-active contaminants influence the movement of a droplet inside a continuum by changing the internal circulation of the droplet. Due to the relative motion between the droplet and the continuous phase, the surfactant molecules are swept towards the droplet rear, which causes a concentration gradient on the interface. As a result, a respective interfacial-tension gradient is also present, that induces a force that opposes the counter-current flow and a stagnation of the rear droplet part appears. The droplet is thus separated into a circulating upper part and a lower stagnant part, which is commonly referred to as the “rigid cap”.

The developed model (VarIT) simulates this phenomenon by explicitly defining an interfacial-tension gradient with the help of three adjustable parameters that describe the width, steepness and position of the interfacial tension jump along the

droplet surface. The model does not make any *a priori* assumptions concerning the extent of the interfacial stagnation, but lets the internal circulation and the rigid cap result from the force balance on the interface that is calculated by the CFD-software. The parameters of the interfacial-tension profile need to be adjusted so that the flow in the droplet best fits the experimental data. In addition, the model does not require that the droplet remains spherical and no assumption is made concerning the value of the interfacial tension at any point on the droplet surface.

For fitting the model parameters, the velocities of the internal droplet flow were measured using NMR-velocimetry techniques and the simulated and the experimental data were compared quantitatively. For this purpose, an NMR-imaging function was used, that reduces the simulated 3D data-set into a 2D matrix by averaging in the 3rd dimension and transforms the velocity vector data of both the simulation and the experiment into transpositions of signal. In this way, the measuring technique is imitated and applied to the simulation results and the objective function is calculated.

The CFD-tool DROPS was evaluated based on simulations of single n-butanol droplets freely sedimenting in an aqueous continuum. The study was performed in the droplet diameter range from 1.0 to 4.0 mm, that includes spherical, deformed and oscillating droplets. The droplet terminal velocity was calculated from the transient simulation results and compared to the sedimentation model by Henschke (2003) that was fitted to experimental data. The influence of the mesh size, the simulation timestep, the droplet initial velocity, and the distance of the droplet interface to the walls of the computational domain was investigated and eliminated from the final results. Two different discretization methods were also compared, namely the conventional finite-element technique and the “extended finite-element” (XFEM) method, that improves the resolution of the pressure jump across the interface. It was found that the DROPS-XFEM version provides the most accurate results and was used in all subsequent simulations. The overall agreement of the simulation, the model of Henschke (2003) and the experimental data was found to be good.

The parameters of the VarIT model were fitted to the NMR-results obtained for a toluene droplet with $d = 4.0$ mm levitated in an aqueous counter-current, but for evaluating the overall behavior of the model, n-butanol and toluene droplets of $d = 2.0$ mm were also simulated. The fitting procedure was performed using a droplet without any interfacial stagnation as a starting point and by adjusting the model parameters so that the qualitative and quantitative discrepancies with the experiment were reduced. The end-result and the experimental data show good agreement.

The present study is the first to obtain an experimentally validated interfacial tension gradient along the droplet surface using a variable interfacial tension model and high-resolution velocimetry data obtained with a non-invasive technique.

Appendix

Appendix A

Material properties

Table A.1: Physicochemical data of the mutually saturated phases of toluene and water according to Misek et al. (1985).

property	phase	
	aqueous	organic
density ρ (kg/m ³)	998.781	867.493
viscosity μ (10 ⁻³ Pa·s)	1.029	0.596
interfacial tension σ (mN/m)	34.31	

Table A.2: Physicochemical data of the mutually saturated phases of n-butanol and water according to Misek et al. (1985).

property	phase	
	aqueous	organic
density ρ (kg/m ³)	986.51	845.44
viscosity μ (10 ⁻³ Pa·s)	1.39	3.28
interfacial tension σ (mN/m)	1.63	

Nomenclature

Greek letters

α	interfacial-tension reduction factor
$\mathbf{T}$	stress tensor
$\Delta\epsilon$	width of the interfacial-tension gradient
Δt	velocity encoding time
Δx	transposition of signal along the x -axis
Δy	transposition of signal along the y -axis
$\Delta\rho$	absolute density difference between continuous and dispersed phase
δ_Γ	Dirac δ -function with support on Γ
Γ	interfacial surface
Γ_s	surfactant concentration on the interface
Γ_∞	surfactant concentration on the saturated interface
κ	curvature of interfacial surface
μ	dynamic viscosity
Ω_1	droplet domain
Ω_2	continuous-phase domain
Φ	objective function
ϕ	level-set function
Ψ	average distance between simulated and measured signal positions at $t = t_0$
ψ	distance between simulated and measured signal positions at $t = t_0$

ρ	density
σ	interfacial tension
σ'	interfacial-tension gradient along the y -axis
σ'_{max}	maximum value of the interfacial-tension gradient along the y -axis
σ_{max}	the maximum interfacial tension
σ_{min}	interfacial tension decreased by surfactants
σ_{pure}	the interfacial tension of the pure system
σ_{top}	the interfacial tension at the droplet upped edge
θ	auxiliary variable
ξ_0	horizontal distance of droplet interface to computational-domain wall at the simulation beginning

Superscripts

av	averaged property in the imaging function
exp	experimental data
max	maximum value in a dataset
sim	simulation data

Subscripts

c	property of the continuous phase
$circ$	property of droplet with internal circulation
d	property of the dispersed phase
def	property of deformed droplet
int	property on the droplet interface
os	property of oscillating droplet
$rigid$	property of droplet with no internal circulation
$sphere$	property of spherical droplet
x	property along the x -axis

y	property along the y -axis
z	property along the z -axis

Roman letters

$\acute{f}$	rigid to circulating-droplet transition factor
K'_{HR}	corrected Hadamard-Rybczynski factor
$\mathbf{D}(\mathbf{u})$	deformation tensor
$\mathbf{I}$	identity matrix
$\mathbf{n}$	unit normal at the interface
$\mathbf{u}$	velocity vector
$\mathcal{I}_\Gamma$	indices of tetrahedra intersected by the interface
∇_Γ	tangential gradient along the interface
Ar	Archimedes number
C_D	drag coefficient
c_s	surfactant concentration in the continuous phase
dt	time-step used in the imaging function
Eu	Eötvös number
f	correction term for Hadamard-Rybczynski factor
f_Γ	surface force
g	earth's acceleration
H	Heaviside function
h	smallest mesh-element size
K	Langmuir adsorption coefficient
k	imaging function refinement level
K_{HR}	Hadamard-Rybczynski factor
m	imaging function pixel averaging radius
Mo	Morton number

N	number of time-steps used in the imaging function
n	resolution of a data-set used for fitting
p	pressure
P^{int}	a point on the phase interface with cartesian coordinates $(P_x^{int}, P_y^{int}, P_z^{int})$
p_i	pixel size along axis i
q	amount of simulation pixels corresponding to one measured pixel
Q_h	standard finite element space
Q_h^Γ	extended finite element space
q_i	nodal basis functions
q_i^Γ	additional basis functions of XFEM space
R	ideal gas constant
Re	Reynolds number
S	amount of droplet pixels during the implementation of the imaging function
s	amount of droplet pixels in a matrix of a data-set
T	absolute temperature
t	time
t_0	signal encoding time
U	velocity
v_{init}	droplet velocity at initial simulation time step
v_{sed}	droplet sedimentation velocity
x	coordinate on the x -axis, space alias
y	coordinate on the y -axis
y_{bary}	absolute vertical position of the droplet barycenter
$y_{grad,rel}$	vertical position of the interfacial-tension gradient relative to the droplet barycenter
y_{grad}	absolute vertical position of the interfacial-tension gradient
y_{test}	auxiliary variable
y_{top}	vertical position of the droplet upper edge

Variable groups

$$Re = \frac{d\rho_c v_{sed}}{\mu_c} \quad \text{Reynolds number}$$

$$Eo = \frac{d^2 g \Delta \rho}{\sigma} \quad \text{Eötvös number}$$

$$Mo = \frac{\mu_c^4 g \Delta \rho}{\rho_c^2 \sigma^3} \quad \text{Morton number}$$

$$Ar = \frac{d^3 g \rho_c \Delta \rho}{\mu_c^2} \quad \text{Archimedes number}$$

$$\Delta \rho = |\rho_c - \rho_d| \quad \text{Density difference between continuous and dispersed phase}$$

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