Out of equilibrium actuation of microprinted hydrogel objects for ultrasmall locomotor systems

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学而时习之，不亦说乎？

孔子

Learn and practice on a regular basis, isn't that pleasant?

Confucius
Summary

Self-propelling microobjects or colloids are a topical research subject for soft matter microrobots as well as for devices that mix, sort and circulate fluids. However, an artificial microswimmer that propels itself by pure body deformation is rather difficult to realize, since the deformations have to be non-reciprocal (or time-irreversible) during cyclic actuations, which is also known as the Scallop Theorem proposed by E. M. Purcell. Additional requirements to implement such a morphing microswimmer are a source of energy, sufficiently fast actuation, and a control mechanism for the repetition as well as for directing the motion.

In this dissertation, a novel class of artificial microswimmers is presented that exploit the principle of out-of-equilibrium actuation by photothermal heating. The system consists of a crosslinked thermoresponsive hydrogel poly(N-isopropylacrylamide) laden with gold nanorods. Very fast temperature jumps localized to the volume of the microgel can be achieved by laser irradiation of the gold nanorods, which convert light energy into heat with efficiency close to unity. Because the diffusion of the gel network cannot follow fast temperature changes in time, the volume change can be effectuated out of equilibrium. Under out-of-equilibrium conditions, non-reciprocal motions are expected to take place due to the deviation in the swelling and shrinking path.

The control over temperature change and rate inside a hydrogel network by photothermal heating is demonstrated, and the heating processes were shown to be distinct from the case of gold nanorods suspended in solution. Ultrasmall hydrogel objects were prepared by the PRINT (Particle Replication in Non-wetting Templates) technique, known to be effective in controlling the composition, size and geometry in the microscopic range. The actuation kinetics by photothermal heating was investigated based on a disk-shaped microgel under stroboscopic irradiations, and the actuation efficiency was estimated. Anisometric microgels have also been prepared, which demonstrated bending deformation and enhanced actuation amplitude due to the out-of-equilibrium conditions. Furthermore, bilayer hydrogel ribbons were fabricated that underwent reversible shape transformations upon swelling/shrinking. Spiral, helical or tubular geometries can be achieved depending on the initial aspect ratios of the ribbon. The helical microgels showed a response time on the millisecond scale upon photothermal actuation. The switch of the helicity can be triggered by irradiations due to the inversion of the ribbon curvature. The inversion process was found to be highly dependent on the environmental temperature and ionic species in the medium, which can be potentially utilized in sensing applications. By fine tuning of the irradiation conditions, rotational motion was achieved on both helical and spiral microgels. Analysis of the kinematics revealed non-reciprocal deformation paths under stroboscopic irradiations. When exposed to physical confinements, the helical microgels also exhibited translational motions.

The results in this dissertation point out the possibility to design the modes, sequences, and amplitudes of complex body deformations of small hydrogel objects in a precise and purposeful way. The self-propulsion of microgels by dynamic control of shapes through photothermal heating provides an exciting avenue for developing soft micro-robotics in biomedical or microfluidic applications.
Zusammenfassung

Selbstantreibende Mikroobjekte oder Kolloide sind ein aktuelles Forschungsgebiet für Mikroroboter aus weicher Materie sowie für Geräte, die Fluide mischen, sortieren und zirkulieren. Jedoch ist ein künstlicher Mikroschwimmer, der sich durch reine Körperverformung antreibt, schwierig zu realisieren, da die Verformungen während zyklischer Anregungen nicht reziprok (oder zeit-irreversibel) sein dürfen, was auch als das von E. M. Purcell beschriebene Scallop-Theorem bekannt ist. Zusätzliche Anforderungen für die Implementierung eines derartigen Morphing-Mikroschwimmers sind eine Energiequelle, eine ausreichend schnelle Anregung und ein Kontrollmechanismus sowohl für die Wiederholung als auch zum Steuern der Bewegung.


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**Motivation**

Self-propelling microobjects or colloids are a topical research subject for soft matter microrobots as well as for devices that mix, sort and circulate fluids.[1-4] These microswimmers are expected to open new avenues for a biomimetic soft matter microtechnology. Recent literature on synthetic or man-made microswimmers focuses mostly on thermo- and diffusiophoresis for the propulsion.[5-9] However, self-propelling microorganisms in nature adopt different concepts for propulsion, which are based on complex body deformations. These organisms propel by a shape deformation with distinct spatiotemporal patterns, which consists of rotational motions or cyclic beatings that are asymmetric in the forward and backward strokes. The actuation is achieved by rotary motors like in *Escherichia coli*,[10] or by dynein motors that produce bending waves like in sperms and in ciliated protozoa.[11, 12] Actually within a strict definition, directional swimming may be regarded as a forward motion by shape deformation.[13-15] The reason those microorganisms employ such complex deformation patterns is that the locomotion of microorganisms takes place at very small Reynolds numbers, $R_e \approx 10^{-4}$, where inertia becomes insignificant when compared to the viscous drag of the fluid. Under these conditions propulsion by a repeated body shape change is only possible, when the deformation is non-reciprocal (or time-irreversible). This famous problem has been pointed out originally by Purcell and is often discussed as the scallop theorem.[13, 16] Swimming

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microbes naturally follow this requirement and it is also mandatory for an artificial microswimmer using the same principle. Additional requirements for the design of such a morphing microswimmer are a source of energy, sufficiently fast action, and a control mechanism for the repetition as well as for directing the motion.

As a consequence of these multifold requirements, an artificial morphing microswimmer is well-known for its difficulty to realize. To our best knowledge, only three examples have been reported so far. One example is a flexible flagellum-like tail of magnetic particles bridged by DNA molecules and end-linked to a red blood cell as a head. The structure could be actuated and directed by an oscillating external magnetic field.[17] The second example is a biohybrid swimmer that consists of a polydimethylsiloxane filament on which cardiomyocytes have been adhered. The cardiomyocytes contract periodically and deform the filament to propel the swimmer.[18] Only recently, a rather advanced fully synthetic material design was reported where a liquid crystalline elastomer with photoisomerizable azobenzene groups was propelled by intrabody shape changes as a traveling wave along the object.[19] Irrespective of the fact, that the objects had to be sufficiently large to see the optical pattern, directed motion was fully controlled from outside. Yet, the report can be seen as a major breakthrough because the body shape deformation was caused by a peristaltic motion with the high rates, necessary for the propulsion of such small objects.

In nature, mechanical actuation is frequently caused by swelling and deswelling of hydrogels. In cases like the hydraulic opening and closing of a pine cone this is not
tied to mechanisms of living matter. Still the motion can be fast and complex.[20, 21] Again intrigued by the examples in the nature researchers developed an increasing interest in artificial hydrogel actuator systems that exploit swelling/deswelling in response to an external stimulus.[22, 23] Mostly these systems utilize the volume phase transition of polyacrylamide derivatives and focus on the shape variance between end states in equilibrium.[24] So far, dissipative internal stimulation has been reported by means of an oscillatory chemical reaction [25] and theoretically evaluated for its potential to design morphing microswimmers.[26, 27] Yet, most of these systems suffer from a slow stimulus, i.e., change in temperature, pH or ionic strength, a slow, diffusion-controlled volume response of a hydrogel, [28, 29] and the requirement for a cyclic motion that results in a net translation.

In view of this state of knowledge, it remains a challenge to devise new expedient actuation mechanisms for a morphing microswimmer with fast cyclic sequences of shape configurations leading to translational motion. It has been our objective to design an actuation principle that enables further miniaturization and is not bound to the spatial resolution of an external field variation. In the meantime, the modes of motion should be programmed by the structure and can be controlled by the energy uptake. Therefore, we focus on thin poly(N-isopropylacrylamide) microgel bodies which can undergo fast swelling and deswelling due to the small dimensions. Very fast temperature jumps localized to the volume of the thin microgel body can also be achieved by photothermal heating with gold nanorods when they are embedded within the temperature responsive PNIPAm microgel. Because volume changes are diffusion
controlled and cannot follow fast temperature changes in time, the volume change can be effectuated out of equilibrium. Under non-equilibrium conditions, non-reciprocal motions are expected to take place due to the deviation in the swelling and shrinking path. This can be exploited for the generation of propulsion, when the shape of the microgels is purposefully designed. For the fabrication of the microgels we utilize the PRINT (Particle Replication in Non-wetting Templates) technique, known to be effective in controlling the composition, size and geometry in the microscopic range.[30] This dissertation will demonstrate the control over temperature change and rate by photothermal heating, the corresponding kinetics of microgel actuation under non-equilibrium conditions, as well as the programming of motion by shape design and irradiation conditions.

References


Scope of the thesis

Chapter 1 and 2 give introductions on gold nanorods and responsive gels respectively. Their properties are summarized and recent progresses in relevant fields are briefly reviewed.

In Chapter 3 the photothermal heat generation by gold nanorods inside a hydrogel network was investigated. The temperature changes under both continuous and stroboscopic laser irradiations were measured and analyzed. The results were compared with the temperature evolution in solutions of gold nanorods, and the effects on actuation are discussed.

Chapter 4 discusses the kinetics of PNIPAm microgels driven by periodic temperature jumps via photothermal heating. The disk-shaped microgel laden with gold nanorods was irradiated stroboscopically, and the change in the diameter was measured to characterize the non-equilibrium kinetics of volume change. The efficiency of actuation was also calculated based on the Flory-Huggins theory of free energy of the gel.

Chapter 5 presents a non-spherical microgel in the pursuit of enhancing the kinetics of deformation. Due to the large aspect ratio and the non-equilibrium heating by the gold nanorods, bending was induced on the microgel under stroboscopic irradiations. The amplitude and speed of deformation were significantly enhanced with tunable
asymmetry in the kinetics, which can be potentially used for locomotion at the microscopic scale.

In Chapter 6 the effects of bilayer structure on the geometry of rectangular hydrogel microgels upon swelling are demonstrated. A shape diagram illustrates how spiral, helical, and tubular structures are formed by tuning the aspect ratio of the microgel. The reversal process of a helical microgel is investigated, which shows large deformation amplitudes and high rates of change achieved by the photothermal heating. The potential application of such microgel as a sensor is shown at the end of the chapter.

Chapter 7 reports on soft microrobots made by thin hydrogel bodies that undergo bending and torsional motions upon swelling and deswelling. The shapes of the microgels are purposefully designed, so that the kinematics of deformation can be tuned to be irreversible in the forward and backward motion. Based on this, the light-driven microgel can rotated and move forward by body deformation.

In Chapter 8 two examples of artificial microgel swimmers using the principles discussed in Chapter 6 and 7 are presented. The first is a spiral microgel fixed at one end that rotates around the fixation point. The kinematics of deformation is characterized to show the non-reciprocal deformations. The second is a helical microgel that demonstrates rotation in the free suspending state. Translational motions can also be achieved by subjecting the microgel in physical confinements.


1. Gold nanorods as heating source

Noble metal nanoparticles continue to attract attentions due to their unique optical and
electronic properties, which find wide applications in fields such as biological sensing,
nonlinear optics, diagnostics, and imaging beyond diffraction limit.[1-5] These
properties arise from the large ratio of surface area to volume, which ensures efficient
capture of incident photons. The confined photons then induce a collective oscillation
of the conduction band electrons of the nanoparticles, the so called surface plasmon
resonance.[1] The energy of the incoming photons is then dissipated either by re-
irradiation of the photon (scattering) or by conversion into heat (non-radiative).[2]
The ratio of radiative to non-radiative dissipation depends on the size and aspect ratio
of the nanoparticle, which can be tuned by synthetic methods or post-treatments.[3]
Among numerous types of noble metal nanoparticles, gold nanorods (AuNRs) are
especially intriguing due to their strong plasmonic effects in the visible and near
infrared range, high geometric tunability via synthesis, availability of various surface
modifications, and their chemical stability. Unlike spherical nanoparticle, nanorods
exhibit two SPR modes along the main axes, namely the transverse and the
longitudinal mode. While the position of the transverse band is rather insensitive to
the geometry, the position of the longitudinal band is highly dependent on the aspect
ratio of the nanorods with much stronger absorption than the transverse one.[3, 4] In
this chapter, synthetic methods of AuNRs and the general strategies for their
modification are briefly reviewed. Besides, a special focus is given to the thermoplasmonic properties of AuNRs with examples of their applications.

1.1 Synthesis and modification of AuNRs

To date, a variety of strategies are available to produce AuNRs, such as seed-mediated synthesis, electrochemical deposition, electron beam lithography, and templated synthesis.[5-9] Thorough reviews on different synthetic methods can be found in Ref. [1] and [10]. Here we briefly review the seed-mediated synthesis by wet-chemistry. This method allows preparation of AuNRs with well-defined geometry in high yield, and the as-prepared nanorods can be readily functionalized via post-modification. Furthermore, the relatively simple synthesis procedure allows for excellent tunability of the aspect ratio.

1.1.1 Seed-mediated synthesis

The forerunner of the currently popular seed-mediated synthesis is the electrochemical method, where a gold plate as anode provides gold source for the reaction.[11] Murphy and coworkers further developed the seed-mediated approach in an attempt to synthesize AuNRs by chemical reduction.[12] In this approach, Au(III) is reduced by a reducing agent (ascorbic acid) in the presence of cetyltrimethylammonium bromide (CTAB) and pre-made gold nuclei with a diameter of about 3 nm. Anisometric gold nanoparticle formation can be improved further by small amounts of silver nitrate. The aspect ratio can be varied from 1.5 to 10 by
controlling the amount of seeds with respect to the amount of chloroaauric acid. Nevertheless, the yield of rod-shaped gold nanoparticles is relatively low: as much as 40-50% of the total particles are spherical.[12]

A noteworthy modification to this method was contributed by El-Sayed et al., which dramatically improved the yield of AuNRs with a nanosphere fraction of less than 1%. [5, 10] The formation of spherical nanoparticles is significantly suppressed by using CTAB-capped seeds instead of the citrate-capped ones and by abandoning organic co-solvents such as hexane or acetone. The aspect ratio of AuNRs can be partially tuned by the concentration of either silver or gold ions. Higher aspect ratios up to 4.5 (longitudinal surface plasmon resonance, LSPR = 850 nm) can be achieved by increasing the concentration of both ions. To further increase the aspect ratio, a dual-surfactant system was applied, consisting of CTAB and benzyldimethylammoniumchloride. The longitudinal plasmon band shifted further into the near infrared region with a maximum of wavelength at 1300 nm (aspect ratio in the range of 7 - 10). However, a significant increase in the amount of nanospheres was observed under these conditions.[5] AuNRs synthesized by the seed-mediated method are shown in Figure 1.

Further advances based on seed-mediated synthesis have been made by Murray and coworkers to enhance the monodispersity of AuNRs.[13, 14] By introducing aromatic additives (salicylate) to the growth solution, uniform AuNRs in a wide range of aspect ratios were obtained at significantly reduced concentration of CTAB. The concentration of spherical particles was found to be less than 1%. Besides,
monodisperse AuNRs with aspect ratio higher than 6 (LSPR > 979 nm) can be obtained by lowering the pH of the growth solution by aromatic additives as demonstrated in Figure 1 (a) – (b). As a reason for the enhanced monodispersity, the interaction of the additives with the CTAB bilayer was indicated to mediate the binding with certain facets of the gold crystal. Formation of three-dimensional superstructures (smectic phase) from such uniform AuNRs was also demonstrated.

Figure 1. (a) – (b) TEM images of AuNRs synthesized by the seed-mediated method with aromatic additives. Scale bar: 100 nm. Adapted from Ref. [14]. (c) Photographs of the AuNR solutions of different aspect ratios and (d) corresponding UV-Vis spectra of the solutions. Adapted from Ref. [15]. (e) and (f) High resolution TEM images of AuNRs in side view.
Adapted from Ref. [16]. (g) and (h) Illustration of the proposed crystal structures of AuNRs. Adapted from Ref. [17].

The crystal structure of the AuNRs produced by the seed-mediated method has also been investigated. [16-18] In the case of synthesis with silver ions, the AuNRs are mostly single crystals with no twinning faults. [19] The long axis of the nanorod follows the $<001>$ direction, while the cross-section of the nanorod has an octagonal shape. The prevalent view about the sides of the nanorods is that they comprise alternating $\{100\}$ and $\{110\}$ facets. These are connected by $\{110\}$ and $\{111\}$ facets to the tip of the rods respectively, see Figure 1 (e) and (f). [16] However, recent results by Liz-Marzán and coworkers has shown that the side of the nanorod might also be eight equal $\{250\}$ facets with slightly different angles between them, as demonstrated by the comparison of the two models in Figure 1 (g) and (h). [17] Both models are consistent with the side view of the nanorod.

Different hypotheses have been proposed to elucidate the synthesis process. Initially, the templating effect of the rod-shaped CTAB micelles was believed to be the reason of anisotropic growth of gold nanorods, since the concentration of CTAB is above its critical micelle concentration (CMC) during the synthesis. [11, 12] Nevertheless, later studies suggest that the binding of different species, such as the silver and iodide, to the growing facets may play a far more important role in determining the shape than the soft-template of CTAB micelles. [5, 20-24] It was hypothesized that metallic silver atoms might be adsorbed preferentially on the $\{110\}$ surface due to underpotential deposition (UPD) of silver ions, thus lowering the growth rate along the $<110>$
direction.[22] Besides, the binding of silver ions in the form of \( \text{AgBr}^2^- \text{CTA}^+ \) to the gold surface could also be the main driving force of anisotropic growth according to Cortie and coworkers.[23] Moreover, El-Sayed and coworkers proposed that CTAB has a higher propensity to bind the \{110\} facets due to larger interatomic distances.[5] In any case, the growth along \(<100>\) direction is favored resulting in the formation of an anisometric geometry.

### 1.1.2 Modification methods

CTAB-stabilized AuNRs from the seed-mediated synthesis have normally poor stability in situations such as low CTAB concentration of the solution, high salt concentration (biological environment), or the presence of organic solvent.[10, 25, 26] Therefore, surface modifications of the AuNRs are indispensable to enhance their colloidal stability and to introduce functionalities for many applications. Different strategies have been developed for the modification of the nanorods, among which the thiol-gold chemistry is the most widely used method to covalently modify the gold surface by grafting a polymer brush onto it.[27-35] Both “grafting-to” and “grafting-from” approaches are possible, which differ in whether the polymer chain is preformed with functional groups or grown directly from the gold surface.[36-38] The main advantages of “grafting-to” methods are the easy protocol and better control over the molecular structure of the brushes. A disadvantage could be that the grafting density is relatively low due to the steric hindrance of already attached polymers.[38] The influence of the grafting density on the conformation of the brushes is illustrated in **Figure 2 (a).**[38, 39] The thickness of the brushes \( L \) depends on the solvent
conditions, the diameter of the segments $a$, the number of segments $N$, and the average distance between the tethering point $d$, which is summarized in Table 1.[37]

**Table 1.** Dimensions of polymer chains under different conditions.[37]

<table>
<thead>
<tr>
<th></th>
<th>Tethered polymer chain</th>
<th>Free polymer chain</th>
</tr>
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<tbody>
<tr>
<td>Good solvent</td>
<td>$L/a \approx N(a/d)^{2/3}$</td>
<td>$R_g \sim N^{4/5}$</td>
</tr>
<tr>
<td>Theta solvent</td>
<td>$L/a \approx N(a/d)$</td>
<td>$R_g \sim N^{3/2}$</td>
</tr>
<tr>
<td>Melt state</td>
<td>$L \sim N^{2/3}$</td>
<td>$R_g \sim N^{3/2}$</td>
</tr>
</tbody>
</table>

Generally for the “grafting-to” approach, thiol-containing polymers are added to the solution of CTAB-capped AuNRs, and ligand-exchange between the polymer and CTAB takes place to produce a polymer coating on the nanorods, which provides steric instead of electrostatic stabilization (for polymers containing charged groups, electrostatic stabilization is also present). The exchange is driven by the high affinity of gold surfaces to thiol-derivatives.[40-42] Nevertheless, incomplete modification of the gold surface can be the case due to the presence of CTAB bilayer, and may result in irreversible aggregation of the nanorods.[30, 42, 43] To overcome this problem, different methods are employed such as the addition of organic solvent and heating of the solution to desorb the CTAB-bilayer, which are often performed under sonication to prevent aggregation before the modification is complete.[29-31] For example, PEG-thiols can be used to fully modify the surface of AuNRs to increase their stability and biocompatibility as demonstrated in Figure 2 (b) and (c).[36]
Site selective modification of AuNRs has also been developed for directed self-assembly. E.g., the ends of the nanorods have been modified preferentially by polystyrene-thiol, while the side remains capped by the CTAB bilayer.[44] This selectivity has been attributed to the fact that the bilayer is denser on the side than on the end, which facilitates the ligand exchange only at the end of the nanorods. In addition, the thiols also bind preferentially to the <111> facet at the rod ends. By changing the solvent composition, the end-to-end self-assembly of AuNRs can be triggered to form a long chain of nanorods.[44] Review on AuNR self-assembly can be found in Ref. [10].

1.2 Thermoplasmonics and applications of AuNRs

AuNRs are capable of absorbing light and converting the energy of photons into heat. This remarkable photothermal property is due to the surface plasmon resonance, which is the collective oscillation of conduction band electrons triggered by incident light at resonant frequency.[1, 2] The photophysical processes of light-to-heat conversion have been thoroughly studied by El-Sayed and coworkers using pulsed
laser (from the femtosecond to the nanosecond). In general, the processes start with photoexcitation of electrons, the energy of which is then transferred to the lattice of the nanocrystal via electron-phonon relaxation within 0.5 – 1 picosecond, independent on the size and shape of the nanoparticle. The heat is subsequently dissipated to the surrounding via phonon-phonon relaxation within 100 ps, which results in a fast cooling of nanorod. If the laser pulse provides sufficient energy, bubbles can be generated around the gold nanoparticles. Figure 3 (a) illustrates the time scales involved in the photothermal process. The duration and energy of the laser pulse can be adjusted, enabling precise control of the relative rates of heating and cooling of the nanoparticles. Short pulses (fs) of high energy induce a huge increase in temperature of the nanorods without affecting the environment temperature because of the slower heat transfer to the environment. For example, melting of the nanorods was observed for a 100-fs laser that is much shorter than the time scale of the heat dissipation (~ 100 ps). In contrast, longer pulses or continuous waves (cw) with high intensity lead to heating of both the nanorod and the surrounding medium with an exponential type of temperature profile around the nanorod as shown in Figure 3 (b) and (c). When the cw-laser has a relatively low intensity, the temperature difference between single nanorod and the medium remains relatively small, although significant global temperature increase of the heated volume can be achieved for high concentration of AuNRs.
Figure 3. (a) Time scale of transient events on a pulsed-laser irradiated gold nanoparticle. Adapted from Ref. [52]. (b) Calculated steady-state temperature profile under continuous-wave (cw) illumination and the envelope of the temperature evolution under pulsed illumination. The inset shows the fit of the NP temperature profile in the case of a pulsed illumination. Adapted from Ref. [53]. (c) Illustration of the temperature profile over time around the NP subsequent to a fs-pulse and temperature profile around the NP under cw-illumination. Adapted from Ref. [53].

The photothermal conversion efficiency, defined as the ratio of light absorption to total extinction (comprised of scattering and absorption), is the relevant parameter when dealing with photothermal applications. In particular, the photothermal efficiency of nanorods depends on aspect ratio, size, and refractive index of the surrounding.[3] El-Sayed and coworkers calculated the absorption and scattering efficiency using Mie theory and discrete dipole approximation (DDA) method.[3, 4] Results show that for a certain aspect ratio, the efficiency can be close to unity for smaller nanorods (effective radius < 10 nm), while scattering dominates as the nanorods become larger (effective radius > 60 nm). Figure 4 demonstrates the change of absorption and scattering efficiency for AuNRs with different effective radius. As the effective radius increases, photothermal conversion efficiency decreases
significantly at fixed aspect ratio. In contrast, the aspect ratio plays a minor role in determining the ratio of absorption to scattering.[4] Experimental results corroborate this conclusion in Ref. [56], where the efficiency drops from 1 to below 0.5 as the diameter of gold nanoparticles increases from 20 nm to above 80 nm. Govorov and coworkers demonstrated a light-to-heat conversion efficiency close to 1 in a laser excited water droplet containing 20 nm gold nanoparticles.[55] The heating and cooling processes of a thermally isolated cell filled with gold nanoparticle suspension under cw-irradiation were studied by Roper and coworkers.[57] Calculations based on the heat transfer by radiation and conduction allowed for description of the temperature evolution during heating and cooling processes. The temperature change showed an exponential profile in time.[55, 57] Steady-state-temperature under irradiation can be predicted based on the heat transfer model for given laser power and nanoparticle concentration.

Figure 4. (a) – (c) Calculated spectra of the efficiency of absorption $Q_{abs}$ (red triangles), scattering $Q_{sca}$ (black circles), and extinction $Q_{ext}$ (green squares) for AuNRs with fixed aspect ratio 3.9 and effective radius $r_{eff} = 8.74$, 17.90, and 21.86 nm. Adapted from Ref. [4].

Thermoplasmonic applications of the AuNRs include but are not limited to photothermal therapy, drug delivery, plasmon-assisted heterogeneous catalysis, and
actuation of hydrogels.[58-61] In photothermal therapy, AuNRs are used as heating source to locally increase the temperature in cancer tissues, i.e. to trigger the hyperthermia of the cancer cells. The AuNRs are designed to accumulate specifically in the cancer cells by surface modification either with thiol-PEG or antibody. The LSPR band of the nanorods is tuned to be in the near-infrared region, where the body tissues have least absorption, thus allowing a penetration depth of irradiation up to a few centimeters. Both in vitro and in vivo experiments have shown feasibility of the photothermal therapy in treating tumors, while clinical trials have been initiated using gold nanoshells.[59] Besides, AuNRs are also ideal carriers of drugs with tailored pharmacokinetics. The release of a drug can be triggered at a specific location of the body by photothermal heating, thus enhancing the therapeutic efficacy of the drug. Mori and coworkers also studied the release of a model drug in a thermoresponsive hydrogel containing AuNRs, where photo-thermal heating of the nanorods induced rapid shrinking of the hydrogel and thus release of the drug.[60] Furthermore, the photothermal properties of gold nanoparticles have been utilized to control the shape of polymer composites, where heating of different metal nanoparticles with different laser lines gave rise to selective actuation of the shape.[61]

This short review demonstrates the advantages of using AuNRs as a localized heat source, whose photothermal efficiency can be tuned by synthetic methods (size, aspect ratio etc.). Besides, controlled surface functionalization enables their integration into other materials, where the procedure requires dispersion in an organic solvent without aggregation. The heat rate and temperature change can be tailored by
the pulse duration, irradiation intensity, AuNR concentration ensuring the fine tuning of the heating process.

1.3 References


2. Responsive gels

Gels are an intriguing class of materials made of cross-linked polymer networks swollen in a solvent, e.g., water in the case of a hydrogel. There are abundant examples of gels both in the nature, such as the jelly fish, and in our daily life from contact lenses to diapers. The remarkable ability of gels to swell is driven by the osmotic pressure as well as by ionic interactions, when ionic groups are present.[1] Swelling is counter-balanced by the entropic elasticity of polymer network, and this eventually defines the equilibrium swelling degree of the gel.[2, 3] Generally, the solvent is the major component of a gel, while the polymer network, though of much smaller portion, is largely responsible for the functions of the material. In this chapter, the fundamentals of gels are reviewed with a focus on their responsive behaviors that find applications in numerous areas. Recent progresses in responsive gels, especially in the field of actuation and swelling-induced deformations of gels, are summarized at the end of the chapter.

2.1 Phase transitions of gels

The phase transition of gels was predicted theoretically in 1968 by Dusek and Patterson [4] and first experimentally observed by Tanaka in 1978.[5] Thorough reviews on the phase transitions of gels can be found in Ref. [1, 3]. Various stimuli, such as solvent, temperature, ionic strength, pH, light, and electric field, have been found to induce the phase transitions depending on the chemical composition of the polymer and on the underlying monomer/solvent interactions.[1, 6-12]. While a single macromolecule undergoes a coil-to-globule transition when a stimulus is applied, a gel, as the macroscopic analog of a single polymer chain,[1, 5] exhibits a volume
phase transition (VPT), which is characterized by a dramatic decrease/increase in the volume upon the change of environmental factors.\cite{13-15} The two transitions are schematically illustrated in Figure 1.

![Figure 1](image)

**Figure 1.** Illustrations of (a) the coil-to-globule transition of a single polymer chain and (b) volume phase transition of a crosslinked gel. Rod dots in (b) represent the crosslinks inside the gel.

Among the different stimuli, temperature is widely applied to trigger the phase transitions. Correspondingly, the temperature where the transitions take place is known as the lower/upper critical solution temperature (LCST/UCST) for dissolved polymer chains and as the volume phase transition temperature (VPTT) for crosslinked gels. The LCST of a polymer solution can be determined by the cloud point method, where the optical density of the sample is measured at different temperatures, or by the calorimetric method.\cite{16, 17} For a gel, the VPTT is generally measured by the equilibrium swelling method, such as the determination of the hydrodynamic radius of microgels using dynamic light scattering.\cite{18, 19}

A common example of the thermoresponsive gels is the poly(N-isopropylacrylamide) gel (PNIPAm), which swells at lower temperatures and shrinks at higher temperatures. The phase transition of PNIPAm is due to the hydrophobic interactions, which take
place when hydrophobic (nonpolar) molecules, in this case the isopropyl moieties, are in contact with water (Figure 2).[1, 6] The water molecules tend to form ordered structures surrounding the nonpolar molecules to minimize the total free energy of the system due to the lack of hydrogen bonding between them.[3, 20-23] The resultant structure of water molecules is similar to that of ice, and they are thus sometimes referred to as “ice-cages” or “ice-bergs”.[24, 25] The shielding effect of the ice-cages weakens at higher temperatures since the “frozen” water molecules melt. This results in the collapse of the gel upon increase of the temperature.[1] The hydrophobic interaction is essentially driven by entropy due to the large entropy increase when the water molecules are released from the “ice-cages”.[23] Both continuous and discontinuous phase transitions have been observed for PNIPAm gels in pure water depending on the crosslinking density and the degree of ionization, and the volume phase transition temperature (VPTT) found in literature is generally around 32 °C.[26, 27]

![Hydrophobic interactions](image)

**Figure 2.** Illustrations of hydrophobic interactions and corresponding volume phase transitions. Redrawn from Ref. [1] and [6].

### 2.2 Free energy and swelling ratio of gels

Based on the Flory-Huggins theory, the free energy of the gel describing its thermodynamic state was derived and used to predict the gel volume phase
transition.[4] According to the theory,[28, 29] the free energy of a gel \( \Delta F_{gel} \) is composed of mixing energy \( \Delta F_m \), rubber elasticity \( \Delta F_{el} \), and energy due to counterions in the gel \( \Delta F_i \). The Flory-Huggins free energy is expressed in Equation (1) to (4).[3, 28-31]

\[
\Delta F_{gel} = \Delta F_m + \Delta F_{el} + \Delta F_i
\]

\[
\Delta F_m = k_B T [n ln(1 - \varphi) + \chi n \varphi]
\]

\[
\Delta F_{el} = \frac{3\nu k_B T}{2} (\alpha^2 - 1 - ln \alpha)
\]

\[
\Delta F_i = -\nu k_B T f \ln \varphi
\]

where \( \varphi \) is the volume fraction of polymer network, \( \alpha \) is the linear swelling ratio, \( n \) is the number of solved molecules in the gel, \( \nu \) is the total number of chains in the gel, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( f \) is the number of counterions per polymer chain, and \( \chi \) is the Flory’s interaction parameter between the polymer and the solvent.

Flory and Rehner established a theory that correlates the equilibrium swelling degree of an isotropic polymer network with the crosslinking density and the solvent quality.[2, 32] It takes into account (1) the entropy of mixing polymer with solvent, (2) the elastic entropy change due to deformation of the network, and (3) the heat of mixing.[2, 33] The equilibrium swelling equation is written as following

\[-[ln(1 - \nu_2) + \nu_2 + \chi \nu_2^2] = V_1 n \left( \frac{1}{\nu_2} - \frac{\nu_2}{2} \right)\]

with \( \nu_2 \) the volume fraction of polymer in swollen state, \( V_1 \) the molar volume of the solvent, \( n \) the number of segments between crosslinks, and \( \chi \) is the Flory’s interaction parameter. Since \( \chi \) and \( V_1 \) are known for a given polymer-solvent system, one can
estimate the equilibrium swelling ratio from the density of crosslinks, or vice versa. For example, the Flory-Rehner equation has been used to acquire the apparent mesh size or crosslinking density by fitting the swelling curves of the gels.[34-36]

The Flory-Huggins theory was used to describe the phase transitions in a gel system.[4] However, it is a mean-field theory that only allows for qualitative description of the volume phase transition, and the results are not satisfactory for gels containing ionic groups. Therefore, further modifications to the Flory-Huggins theory were proposed in the attempt to quantitatively explain the phase transitions in gels.[37-40]

2.3 Kinetics of gels

Tanaka and Fillmore proposed a theory describing the kinetics of the swelling of gels.[41] The kinetics of swelling is characterized by a collective diffusion coefficient $D_{gel}$, which is defined as the ratio of longitudinal bulk modulus $E$ of the network to the friction coefficient $f$ between the polymer network and the solvent. Equation 6 describes the characteristic time $\tau$ of swelling in terms of the square of the linear size $a^2$ and the collective diffusion coefficient $D_{gel}$.

$$\tau = \frac{a^2}{D_{gel}} \quad (6)$$

The diffusion coefficient can be determined experimentally by the light scattering spectroscopy or swelling experiments.[41-43] The diffusion coefficient depends on the gel composition, and the geometry of the gel also affects the coefficient. For instance, the diffusion coefficients have been determined for asymmetric gels, where the diameter of a cylindrical gel and the thickness of a disk-shaped gel were taken as
the characteristic linear dimensions.[44] The effective diffusion coefficient have been found to be reduced to 1/2 and 1/3 of $D_{gel}$ of a spherical gel with the same characteristic dimension (diameter). For poly(acrylamide) gels, diffusion coefficients between $2.4 \times 10^{-7}$ and $4.0 \times 10^{-7}$ cm$^2 \cdot s^{-1}$ are typically found in literature.[42-44]

At the phase transition of gels, the diffusion coefficient is not constant.[3, 45] Close to the critical temperature, the collective diffusion coefficient $D_0$ diminishes, which is known as the critical slowing-down.[1, 45] Moreover, the friction between water and the gel network vanishes near the VPTT due to the formation of heterogeneous pores inside the gel.[46] This is because the VPT of gels involves binodal or spinodal decompositions (compositional heterogeneity).[13, 47-49] An additional complication arises from the finite size and presence of surfaces boundaries that leads to the formation of surface patterns (wrinkles, bubbles, etc.).[14, 47, 50, 51] The kinetics of the VPT has also been found to be a function of initial and final temperatures, the monomer concentration during the gel preparation, and the degree of crosslinking.[14, 47, 50, 52]

### 2.4 Applications of thermoresponsive gels

Since their discovery, various thermoresponsive gels have been found with a broad range of transition temperatures.[1, 53] The continuity of the phase transitions and the volume changes can also be tuned by co-polymerization or ionization.[31] Thermoresponsive gels have been utilized for various purposes, such as drug delivery,[53-57] microfluidics,[58, 59] self-shaping structures,[60-64] and soft robotics.[30, 65] Furthermore, the hydrophobicity and mechanical properties of gels also change dramatically upon the VPT, which is essential for biomedical applications.
such as tissue engineering.[66, 67] This section briefly reviews recent advances in the field of thermoresponsive gels with a focus on the actuation and the swelling-induced deformations of gels.

2.4.1 Thermoresponsive hydrogel for actuation

Since the VPTT of many hydrogels is close to the body temperature, thermoresponsive gels can be used as convenient carriers of drugs. It has been shown that a release of entrapped drugs was achieved by inducing the VPT of PNIPAm.[53, 68-70] The release and permeation of drugs depend on the physical and chemical properties of the gel network, and the release process can be influenced by the temperature changes.[71] Mori and coworkers took a step further to incorporate gold nanorods into the gel network, so that the VPT of the gel can be triggered by laser induced heating of the nanorods.[54] The shrinking of the gel under laser irradiation is accompanied by a rapid release of a model drug with a high spatial resolution.

Thermoresponsive gels have also been applied in microfluidics. Beebe and coworkers first prepared responsive hydrogel microvalves using photomasks.[72] Later the idea was extended to a PNIPAm based system with embedded gold nanoparticles, which allows for optical on/off-switching of the microfluidic valves.[73] The Aizenberg group designed self-regulating microfluidic structures made of soft high aspect-ratio microstructures and thermoresponsive hydrogel films.[74, 75] The response of the hydrogel to stimulus leads to the actuation of the microstructures, which enables a feed-back mechanism for a homeostatic system. The hydrogel structures can be also patterned by multiphoton lithography, which provides better spatial and geometric control of the gel.[76] Figure 3 (a) demonstrates one of these structures, where the
swelling/shrinking of the gel brought about localized deflection of the high aspect-ratio micropillars.[76]

![Figure 3](image-url)

**Figure 3.** (a) Microstructured gel written by multiphoton lithography on soft micropillars. (a1) SEM image of fabricated gel on the pillars. Scale bar: 5 µm. (a2) and (a3) Optical micrographs of the gel in swollen and shrunken states at low (a2) and high temperatures (a3). Scale bar: 10 µm. Adapted from Ref. [76]. (b) Self-walking of a gel actuator on a ratchet surface. The self-oscillation is driven by the Belousov–Zhabotinsky reaction. Scale bar: 600 µm. Adapted from Ref. [77]. (c) Dome-shaped hydrogel with integrated heater mesh. Local heating by the heater resulted in the deformation of the hydrogel. Adapted from Ref. [78]

Self-oscillating gels capable of autonomous motion were designed using the Belousov–Zhabotinsky (BZ) reaction. [77, 79, 80] The BZ reaction is a peculiar yet fascinating phenomenon involving the oscillation of certain chemical reactions.[79, 81] One example is shown Figure 3 (b), where the gel structure was able to walk on a ratchet structure without any external control.[77] The gel was made of a copolymer based on PNIPAm and ruthenium(II) tris(2,2'-bipyridine). When the BZ reaction takes place inside the gel, the oxidation state of Ru oscillates between Ru(II) and Ru(III), which results in the change in the VPTT of the gel due to the altered degree of ionization. Therefore, the gel swells and shrinks at a constant temperature as a
result of the oscillation of the VPTT.[77] Since the chemical wave of the BZ reaction travels through the gel, the periodic shrinking and swelling enables a peristaltic motion of the gel, and the gel was thus able to walk.[80] Figure 3 (c) demonstrates a dome-shaped thermoresponsive hydrogel with integrated heater mesh, where the shape of the hydrogel can be programmed by local heating of the mesh.[78]

2.4.2 Swelling-induced deformations

When confined from one side, the swelling of a gel film may induce different modes of deformations as shown in Figure 4.[82] When the confinement is a hard substrate which resists bending and stretching of the gel film, wrinkling or creasing takes place at the surface of the gel layer to release the compressive strain on the film surfaces.[83] Hayward and coworkers described swelling instabilities for a surface-attached hydrogel film that resulted in creasing at the surface.[84] Guvendiren et al. reported highly ordered patterns on the surface of a confined hydrogel film (Figure 4 (b)), where the pattern formation was controlled by a gradient in modulus on the surface and the crosslinking degree of the film.[85]

Bending of the gel takes place, when the confinement is soft but resists stretching/expansion of the gel layer. Timoshenko first investigated the bending of a bilayer structure (bi-metal thermostat) upon heating, where the two layers have different thermal expansion coefficients.[86] The concept was later extended to bilayers made of gels.[65, 87-91] In principle, these structures contain an “active layer” that swells or shrinks much more significantly than the other “passive layer”. When the active layer is made of a thermoresponsive gel, the bending behavior can be readily controlled by temperature change. For instance, a tubular microjet was fabricated by the rolling of a gel bilayer, where PNIPAm gel serves as the active
The inner surface of the bilayer was coated with platinum that enables catalytic decomposition of hydrogen peroxide in the environment. The formation of oxygen bubbles due to the decomposition thus propelled the tubular microjet. The propulsion can be switched off by heating the sample above 28 °C, where the tubular structure unrolled due to shrinking of the PNIPAm layer as demonstrated in Figure 4 (c).

**Figure 4.** (a) Swelling-induced deformations in confined thin films: wrinkling, creasing, and bending. Reproduced from [82]. (b) Wrinkle formation on a swollen hydrogel film tethered on a rigid substrate. Adapted from [85]. (c) Microjets formed by rolling of a thermoresponsive hydrogel bi-layer. Optical micrographs show the unrolling of the hydrogel sheet by temperature increase. Bubble formation was hindered by the unrolling. Scale bar: 100 µm. Adapted from Ref. [65]. (d) Formation of helical structures from two dimensionally patterned hydrogel sheets. The patterns are 1mm stripes with certain angles θ to the long axis of the sheet. (d1) to (d4): θ = 30°, 60°, 45°, and -45°. Scale bar: 1 cm. Adapted from Ref. [64].
Beside the bilayer structures, patterned two-dimensional (2D) hydrogel films also undergo programmed shape transformations into three dimensional (3D) structures upon swelling. Hayward and coworkers developed a technique called “halftone gel lithography”, where a PNIPAm-copolymer sheet was double-crosslinked through a halftone photomask.[61] The halftoned gel sheet buckles upon swelling due to the differential expansion of the exposed areas. In this way, 3D surfaces with constant Gaussian curvatures can be obtained by prescribing the 2D pattern of the gel sheet. Similarly, Kumacheva and coworkers designed a self-shaping structure made of 2D hydrogel sheet.[64] Alternating stripes that have different swelling properties were fabricated in the sheet by two-step photo-crosslinking with a photomask. Depending on the pattern orientation, different helices can be formed upon swelling as shown in Figure 4 (d).

The swelling induced deformation of bilayer or patterned gel structures has shown great potential in controlling the 3D geometry by the 2D design. By tuning the material properties, the internal stress of the structure can be engineered to provide various responses such as wrinkling or bending. This can be exploited as a powerful tool for the manipulation of shapes down to the microscopic scale, and the modes of actuation can be pre-programmed.

2.5 References

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3. Photothermal heating of gold nanorods: suspended in solution versus entrapped in a hydrogel

3.1 Introduction

Hydrogels are cross-linked polymeric networks that swell enormously in water. Among the huge variety of hydrogels, thermoresponsive ones have attracted special attention, since they can convert heat into mechanical deformations. This is an intriguing property that finds applications in drug release,[1-4] microfluidics,[5, 6] self-shaping structures,[7-10] soft robotics,[11, 12] etc. Poly(N-isopropylacrylamide) (PNIPAm) is the most widely studied thermoresponsive hydrogel with a volume phase transition temperature (VPTT) around 32 °C.[13] Near the VPTT, the volume is strongly dependent on the temperature. Therefore, precise control over temperature is essential for the development of hydrogel based actuator systems. Instead of conventional heating of the whole aqueous environment, local heating of hydrogel by incorporation of metal nanoparticles that absorb and convert light into heat is a novel way of local temperature control.[1, 10] Localized surface plasmon resonance of metal nanoparticles can be excited by light at defined wavelength, the energy of which is then partially dissipated as heat into the surrounding.[14] The light-induced heating is thus known as photo-thermal or thermoplasmonic effect. The advantage of local heating is the much higher rate of temperature change compared to global heating because of the smaller heating volume. Besides, the temperature can be controlled remotely with light. Therefore, understanding the temperature change due to irradiation of hydrogel containing metal nanoparticles is of paramount importance for designing photo-thermo-mechanical actuator systems.
In this study, gold nanorods (AuNRs) were utilized as the nano heating source. Among nanoparticles, AuNR is a compelling candidate because the absorption wavelength of longitudinal band can be readily tuned by varying the aspect ratio during synthesis or through post-treatment.[15-17] For example, absorption in the near infrared regime can be obtained which is highly desirable for in vivo applications.[18] Moreover, AuNRs have a large absorption cross-section as well as a high ratio of absorption over extinction.[19, 20] Both properties contribute to enhanced efficacy of photo-thermal heating. In this study, a near infrared (NIR) laser was used with a wavelength close to the maximum of the longitudinal SPR of the AuNRs, so that the photo-thermal property of AuNRs can be most efficiently exploited. Incorporation of such AuNRs within the hydrogel network was performed during the gelation process. This allows precise control of the loading by the solution concentration. Moreover, it ensures uniform dispersion of AuNRs within the network, whose average mesh size is below 5 nm.

Irradiation by near IR-light and conversion to heat has been engineered to enable temperature jumps up to more than 20 °C within less than milliseconds for microgels.[21] Because the heating is restricted to the irradiated volume, it can also cool down quickly due to the fast heat transfer to the surrounding bath once the heating is ceased. As a result, the PNIPAm hydrogel shrinks and swells periodically in response to the temperature variation. To investigate the temperature change under stroboscopic irradiation, we designed an experimental setup to monitor the temperature evolution of the AuNR/hydrogel system under both continuous and stroboscopic laser irradiation. Besides, we also assessed the heat produced by the aqueous dispersion of the same AuNRs. The differences of temperature evolution in solution and hydrogel are compared, and their effects on actuation are discussed.
3.2 Results and discussions

3.2.1 Photothermal heating of AuNR solutions

3.2.1.1 Power-dependent heating

The experimental setup is illustrated in Figure 1 (a) (for details, see the *Experimental section*). The spectra of the AuNRs and the laser are shown in Figure 1 (b). The change of temperature in an AuNR solution during irradiation is plotted in Figure 1 (c), where the on- and off-switch of the laser is marked. The temperature evolution can be fitted by an exponential decay function as shown in Figure 1 (c). Upon irradiation, the temperature underwent fast increase (~ 4 °C·s⁻¹) and slowly leveled off to reach a steady state, while the reverse process took place when the irradiation was removed, namely a fast drop followed by a slower temperature equilibration. The temperature change depending on the irradiating time or the cooling time shows a single exponential process with a characteristic heating/cooling time (τ) of 5.8 s. Details of the fit can be found in the *Experimental section*. Figure 1 (d) shows the steady state temperature increase ΔT = (T<sub>max</sub> - T<sub>0</sub>) depending on the laser powers and the AuNR concentrations. The temperature increase due to continuous irradiation of pure water was taken as reference measurement. As expected, the temperature (ΔT) increases linearly with the irradiation power with a slope defined by the AuNR concentration. Thus, controlling the density of the light absorber or the laser intensity enables tuning of the temperature.[22]
Figure 1. (a) Schematic illustration of the experiments. The rectangular capillary filled with AuNR solution was irradiated with a NIR laser. The laser spot was aligned to the immediate vicinity of the temperature sensor at an incident angle of 40°. (b) Optical spectra of the AuNR solution and the NIR laser. Arrows mark the maxima of longitudinal SPR of the AuNRs and of the laser. (c) Temperature evolution of the AuNR solution under irradiation. The dashed line is the exponential fit. Optical density (OD) of the AuNR solution is 0.76 at 808 nm normalized to an optical path of 1.0 cm. Laser power is 1.1 W at 808 nm. (d) Power-dependent temperature increase of AuNR solutions at different optical densities. Lines are the linear fit of corresponding data series. Environmental temperature ($T_0 = 19.7 ^\circ C$) was subtracted for (c) and (d).

The exponential-type temperature evolution shown in Figure 1 (c) is consistent with the heat transfer models taking into account the energy balance between the photothermal heating and the heat dissipation.[22-26] This energy balance depends on the heating volume, the thermal property of the medium, the absorption efficiency of the nanoparticles, the laser power, the interfacial area of the system, etc. Besides, the characteristic thermal time $\tau$ to reach a steady state depends only on the volume, interfacial area and thermal property of the medium.[22, 23] This is confirmed by our observation that $\tau$ remained almost constant for all the experiments in solution.
Furthermore, the measured linear increase of the temperature with power, whose slope depends on the concentration of AuNRs (see Figure 1 (d)), is in agreement with the literature report and theoretical calculations.[22, 23]

### 3.2.1.2 Photothermal heating by stroboscopic irradiation

To characterize the temperature change induced by stroboscopic irradiation, different irradiation periods were investigated as shown in Figure 2. In Figure 2 (a), the irradiation period is 20 ms, which is two orders of magnitude smaller than the characteristic time $\tau$ of the system. As a result, the temperature variations between the short on and off periods are negligible and the temperature reached a steady state after 2000 cycles. The temperature evolution is similar to the case of continuous irradiation except that the $\Delta T_{\text{max}}$ is smaller as one would expect from the reduced effective irradiation power. Indeed, the effective power $I_{\text{eff}}$ can be calculated by Equation 1, where $t_{\text{on}}$ and $t_{\text{off}}$ are the on- and off-durations of the irradiation respectively, and $I_0$ is the power of the incident laser. This leads to an effective power of 0.55 W. In practice, short stroboscopic irradiations are widely used to reduce the laser power.[23] The measured temperature increase $\Delta T_{\text{max}}$ in Figure 2 (a) is 9.8 °C, in agreement with the estimated $\Delta T_{\text{est}} = 9.3$ °C obtained by the effective power and the corresponding linear fit as noted in Figure 1 (d).

$$I_{\text{eff}} = \frac{t_{\text{on}}}{t_{\text{on}}+t_{\text{off}}}I_0.$$ (1)
Figure 2. Temperature evolution of the AuNR solution under stroboscopic irradiations. (a) 10 ms (on) – 10 ms (off). The dashed line is the exponential fit. (b) 5 s (on) – 5 s (off). Inset is the enlarged view of the temperature variation at the steady state. \( \Delta T = T(t) - T_0; \) where \( T_0 = 19.7^\circ C \). Laser power: 1.1 W, \( OD = 0.76 \) normalized to an optical path of 1.0 cm.

In Figure 2 (b) the irradiation period was 10 s with equal on/off durations. Under this irradiation condition, the temperature variation between on and off periods is substantial as the period is close to the thermal relaxation time \( \tau \) of the system. Within the first cycles, we observed an overall increase of the temperature peak and after about 4 irradiation cycles, the mean temperature reached the steady state, where it oscillated between a higher \( \Delta T_{\text{high}} = 14.0^\circ C \) and a lower value \( \Delta T_{\text{low}} = 5.2^\circ C \). The mean temperature \( \Delta T_{\text{mean}} = (\Delta T_{\text{high}} + \Delta T_{\text{low}})/2 = 9.6^\circ C \), very close to \( \Delta T_{\text{max}} = 9.3^\circ C \) estimated from the effective power.

3.2.2 Photothermal heating of hydrogel laden with AuNRs

In this section, the temperature evolution of photo-thermally heated hydrogel is studied using the same experimental setup except that the AuNRs are now incorporated into a thermoresponsive PNIPAm hydrogel. Because the AuNRs were trapped, we expect to probe heat dynamics that are coupled to the increase and decrease of the concentration of the gold nanorods as the gel network shrinks and expands. If the \( T_{\text{max}} \) (steady state temperature) is well below the VPTT and the \( \Delta T_{\text{max}} \)
\( (T_{\text{max}} - T_0) \) is relatively small, the volume change is expected to be small from the equilibrium volume-temperature dependence. **Figure 3** depicts the change of temperature in the gel under continuous (a) and stroboscopic (b) irradiations.

**Figure 3.** Temperature evolution inside the hydrogel laden with AuNRs \((OD = 1.12\) normalized to an optical path of 1 cm). (a) Continuous irradiation. Dashed line is the exponential fitting. Laser power = 134 mW. (b) Stroboscopic irradiation: 5s (on) - 5s (off). Inset is the enlarged view of temperature variation at the steady state. Laser power = 96 mW.

The diagrams resemble very much those in Figure 2 for the gold nanorod solution. Under continuous irradiation in Figure 3 (a), the temperature change follows an exponential function with a characteristic time \( \tau = 8.6 \) s. Also temperature variation through stroboscopic irradiation demonstrates similar behavior like AuNR solution (Figure 3 (b)). After 5 irradiation cycles, the temperature begins to oscillate around a mean temperature with a slightly asymmetric profile. In the temperature range far from the volume phase transition by around 10 °C, the hydrogel shrinks by only about 9% (linear dimension), and the effect of shrinking on the concentration of the light absorbers is insignificant.[13] The resultant temperature evolution still follows an exponential decay, and the photothermal heating in this case is similar to the case of AuNR solution. Within the temperature range of the maximum \( V(T) \) sensitivity, i.e. at the center of the VPTT, the temperature response upon irradiation of the solution and the gel become more distinct. This is demonstrated in **Figure 4**, where the gel was
irradiated with light intensity to achieve a higher raise in temperature in order to cross the VPTT.

**Figure 4.** (a) Temperature evolution of the hydrogel laden with AuNRs under continuous irradiation. Dashed line is the exponential fitting by assuming $\tau = 8.6$ s and $T_{\text{max}} = 26.8$ °C. OD: 1.12, laser power: 285 mW. Inset: top view of irradiated area after the laser is switched off. Ellipsoidal region is formed due to the collapse of gel, which lies directly beside the sensor. Scale bar: 500 µm. (b) Power-dependent temperature increase of hydrogel with different AuNR concentrations. Optical densities are all normalized to 1 cm optical path.

At a constant irradiation intensity (Figure 4 (a)), the temperature shows a stepwise increase with the irradiation time. According to the linear dependence of $T_{\text{max}}$ on the laser power, as already shown in Figure 1 (b), we can estimate a steady state temperature of around 26.8 °C for continuous irradiation by a laser power of 285 mW. This estimation is plotted in red dashed line in Figure 4 (a). However, the experimental data showed a further increase, distinguished as a second step. Only in the initial stage, the temperature increases as predicted by the exponential fit with $\tau = 8.6$ s. The second step starts as the temperature exceeds 25 °C, and the shrinking of gel begins to affect the photo-thermal heating process significantly. Firstly, the volume decrease of the hydrogel close to the VPTT [13] effectively increases the concentration of AuNRs per unit volume. Therefore, the temperature can reach higher values compared to the case of AuNR solution at the same power. Secondly, also the
decrease in surface area of the gel and the reduced diffusion/convection might retard heat transfer to the surrounding, both concur to enhance the heating and thus result in a higher $T_{\text{max}}$.\cite{22, 23, 26} It is worthwhile to note that the two steps are well discriminated on the time scale. The collapse-induced temperature rise only started after ca. 50s of irradiation when the temperature reached 30 °C, which corresponds to the volume phase transition of the gel.\cite{27, 28} This self-accelerating heating is brought to a halt when the volume phase transition has been crossed and the gel assumes the fully collapsed state, where no further volume decrease is possible. Indeed, more than 350 s were required for the shrinking of the hydrogel, after which the temperature reached the steady state (Figure 4 (a)). The total increase of temperature was 19.96 °C, i.e. a 2.8 time enhancement compared to the 7.1 °C. The irradiated area is fully collapsed as can be seen in the inset of Figure 4 (a), where the ellipsoidal shape of the irradiated area is imprinted into the hydrogel.

To further elucidate the self-accelerated heating effect, power-dependent measurements were performed on hydrogels containing different AuNR concentrations. The results are plotted in Figure 4 (b). Hydrogel without AuNRs was measured as noted in the graph. Again, the temperature increases linearly with the laser power with a slope that depends on the heat absorber density. However, once the laser power is high enough so that the temperature exceeds 25 °C, a sharp transition, i.e. almost 4 time increase of slope, can be observed. Temperatures measured in this regime are always above 32 °C, indicating that the hydrogel has crossed the volume phase transition. Above the collapse, the $T_{\text{max}}$ is linearly dependent on the input power.

To sum up this section, the photothermal heat generation with AuNRs in solutions or laden in hydrogels showed similar behavior for temperature well below the VPTT of
the gel (< 25 °C). The temperature ($\Delta T_{\text{max}}$) increased linearly with the laser power in both cases. The only difference is in the heating dynamics. However, the shrinking of the hydrogel increased the density of heating elements close to the VPTT, and the temperature evolution inside the hydrogel underwent a self-accelerating process. The result was a strong enhancement of the heating effect that brought about much higher steady state temperatures $T_{\text{max}}$. In contrast, the power dependence in AuNR solutions showed a single linear dependence even at $\Delta T_{\text{max}}$ higher than 20 °C (i.e. $T_{\text{max}} > 40$ °C).

### 3.2.3 Photothermal actuation of microgels laden with AuNRs

The consequence of the self-acceleration process was investigated on a freely suspended microgel laden with AuNRs. The microgels were fabricated via a modified PRINT technique, details of which can be found in the Experimental section.[29] We selected a disk with a diameter of 30 µm and the thickness of 5 µm in the as-prepared state. The microgel can be observed with an optical microscope, so that the swelling/shrinking of hydrogel in different conditions can be monitored. Once swollen, the microgels can reach a diameter of 50 µm at 15 °C as shown in Figure 5 (a). As the temperature increased, the diameter of the disk decreased continuously with most of the change taking place between 27 °C and 31 °C, i.e. close to the VPTT. Above 31 °C, the diameter remained almost constant at about 28 µm. Inset in Figure 5 (a) demonstrates the continuous shrinking of the microgel disk during heating. In contrast, when the hydrogel disk was heated photothermally, the shrinking process was no longer continuous. Figure 5 (b) shows the diameter change of the same microgel depending on the irradiation. With increasing laser power, the microgel shrunk since the temperature change due to photothermal heating is linearly proportional to the power. However, an abrupt decrease of diameter can be seen around 1.6 W. This
transition took place within a small window of the laser power, namely 0.1 W, after which the hydrogel disk is collapsed with only slight variation in diameter. This behavior was assigned to the self-acceleration process discussed in the last section. This process ceases only when the hydrogel is in the collapsed state.

Figure 5. (a) Temperature-dependent shrinking of disk-shaped microgel. Each point represents statistics of 10 microgel particles. Inset: Optical micrographs of the microgel from 16 °C to 34 °C. Scale bar: 30 µm. (b) Power-dependent shrinking of the microgel. Red-dashed line marks the transition.

3.3 Conclusion

By measuring the temperature change due to optical stimulation of AuNRs, we demonstrate the exponential increase of the temperature to reach a steady state. The increase of temperature is linearly proportional to the laser power, and the slope of the increase depends on the AuNR concentration. By stroboscopic irradiation with period close or larger than the characteristic thermal equilibration time $\tau$ of the system, the temperature profile follows the variation in the irradiation. For hydrogel laden with gold nanorods, the photothermal heat generation below 25 °C is comparable to that of the AuNR solution. The difference is rather in the heat dynamics but not in the steady state. This is due to the fact the volume change of the hydrogel is small below the VPTT. Once the laser power brings the hydrogel close to the VPTT, the self-
acceleration process takes place, where the shrinking enhances the temperature increase and drives the hydrogel collapse. The effect of the heat enhancement on the disk-shaped microgel demonstrated a gradual decrease of the diameter with increasing power up to a certain threshold, above which the hydrogel quickly reach the collapsed state. This study opens up the possibility for understanding the swelling kinetics and the photothermal actuation of thermo-responsive microgels.

3.4. Experimental section

3.4.1 Synthesis and modification of AuNRs

AuNRs were synthesized by a modified seed-mediated method.[15] All chemicals were purchased from Sigma-Aldrich unless otherwise mentioned. Deionized water (0.1 µS·cm⁻¹, ELGA Purelab-Plus) was used. 0.60 mL of freshly prepared ice-cold 0.010 M NaBH₄ (99%) aqueous solution was added to a mixture of water (4.2 mL), 0.20 M Cetyltrimethylammonium bromide (CTAB, 5.0 mL, 99%) and 0.0030 M hydrogen tetrachloroauric (III) acid (HAuCl₄, 0.83 mL, p.a.) under vigorous stirring for 2 min, which served later as the seed solution. For the growth solution, 0.20 M CTAB (150 mL), 0.050 M ascorbic acid (3.1 mL, 99%) and 0.0080 M AgNO₃ (3.3 ml, 99.99%) were added under stirring to 0.0010 M HAuCl₄ (150 mL). The temperature of the growth solution was kept at 25 °C in water bath. 0.875 mL of the seed solution was injected into the growth solution under rigorous stirring followed by 30 min of stirring and addition of 0.050 M ascorbic acid (2.0 mL) at a flow rate of 0.50 mL/h. Afterwards the solution was stirred for another 30 min. of AuNRs was then obtained. The resultant brownish red solution was centrifuged at 8000 rpm for 40 min in an Eppendorf Centrifuge 5810. The supernatant containing excess surfactant was
discarded, and the precipitated AuNRs were collected and re-suspended in water with a final volume of ca. 20 mL.

Thiol functional polyethylene glycol (PEG) polymer (HS-PEG-OH, Mw = 3000 Da, Iris Biotech) was dissolved in ethanol (99.8%) to produce a 2.5 mM solution. 10 mL of the solution with redisperssed AuNRs was diluted to 100 mL and mixed with the 20 mL of the ethanolic PEG solution under stirring. This solution was then sonicated at 60 °C for 30 min and at 30 – 50 °C for another 3.5 h.[30] After stirring the solution overnight, it was extracted with chloroform (ca. 120 mL, p.a.) for three times to remove the CTAB and free polymer. The extracted solution was again centrifuged for 3 times, where the supernatant was discarded each time and the sedimented AuNR-containing fraction (less than 2 mL) was diluted with dimethyl sulfoxide (DMSO) or deionized water to 45 mL. After the last centrifugation, the sedimented AuNRs were collected as a concentrated solution of PEGylated AuNRs in DMSO or water. UV-Vis spectrum (V-630, JASCO) shows that the modified AuNRs have an absorption maximum of longitudinal band at 791 nm. Analysis based on transmission electron microscope (Zebra 120, Zeiss) reveals that the AuNRs have an average diameter of 15.4 nm and length of 60.0 nm, i.e. aspect ratio of 3.90, see Figure S1. The stock solution of AuNRs was diluted to obtain different optical densities.

![Figure S1](image_url)

**Figure S1.** Left: statistics of PEGylated AuNR. Right: TEM micrograph. 120 particles were analyzed with ImageJ. Average length: 60.0 nm, diameter: 15.4 nm.
3.4.2 Preparation of hydrogel laden with AuNRs and optical density estimation

The monomer solution was prepared according to Table S1. The ratio of crosslinker ($N,N'$-Methylenebisacrylamide, BIS, 99%) and photo-initiator (2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiofenone, 98%) to $N$-Isopropylacrylamide (NIPAm, 97%, recrystallized twice in n-hexane) is 1 mol%, the as-prepared solution for hydrogel ribbons has an estimated volume of 154 µL, which results in optical densities of around 4.68 at 808 nm for ribbon 1, 1.17 for ribbon 2, and 240 for the microgel. The optical densities were normalized to an optical path of 1 cm. The solution was bubbled with argon for 5 minutes to remove oxygen.

Table S1. Composition of pre-polymer solution

<table>
<thead>
<tr>
<th></th>
<th>NIPAm</th>
<th>BIS</th>
<th>Photo-initiator</th>
<th>AuNR</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ribbon 1</td>
<td>57.5 mg</td>
<td>0.783 mg</td>
<td>1.14 mg</td>
<td>1.54 µL</td>
<td>96.56 µL</td>
</tr>
<tr>
<td>Ribbon 2</td>
<td>57.5 mg</td>
<td>0.783 mg</td>
<td>1.14 mg</td>
<td>0.385 µL</td>
<td>97.72 µL</td>
</tr>
<tr>
<td>Microgel</td>
<td>57.5 mg</td>
<td>0.783 mg</td>
<td>1.14 mg</td>
<td>79.5 µL</td>
<td>18.6 µL</td>
</tr>
</tbody>
</table>

The polymerization of hydrogel was carried out in a glove box where the oxygen level was kept below 0.2%. The monomer solution containing AuNRs was loaded into a rectangular glass capillary ((0.5 × 5 × 50) mm, Vitrocom), which was treated beforehand with O$_2$-plasma (200 W, 5 min, 1 mbar, PVP Tepla 100). The solution was cured under a UV-lamp (366 & 254 nm, 8 W, Konrad Benda) for 20 minutes. The capillary was immersed in abundant deionized water for two days to exchange the solvent. After drying in a vacuum oven at 60 °C, the hydrogel strip could be easily taken out of the capillary. The strip was then cut into rectangular segments with a length of roughly 10 mm and kept in a closed vessel for storage.

After swelling in water, the volume of the as-prepared hydrogel increased by 3.19 times at 20 °C as estimated from the swelling curve of the microgel disk. The optical
density of the hydrogel samples decreased to 1.12 for ribbon 1, 0.278 for ribbon 2, and 57.3 for the microgel (normalized to an optical path of 1 cm) correspondingly.

### 3.4.3 Photothermal heating and temperature measurement

The AuNR solution was injected into a rectangular glass capillary maintained at a constant temperature (20 °C). The rectangular capillary (1 mm × 10 mm × 50 mm, Vitrocom) was then sealed with epoxy glue at one end. The temperature-sensor (Mini-BetaCHIP-Sensor, diameter ~ 0.43 mm, Telemeter Electronics) was placed in the immediate vicinity of the laser beam to monitor the temperature of irradiated area while avoiding direct laser heating (see Figure S2 (a) and (b)). The optical density, also known as the absorbance, of the AuNR solution was determined by UV-Vis spectroscopy. In the case of the hydrogel strip containing AuNRs, deionized water was injected, and the strip was inserted into the capillary. The gel was allowed to reswell at 20 °C for half an hour before measurements. The temperature sensor was carefully inserted into the capillary to avoid bubbles and was placed on top of the hydrogel strip. The capillary was placed on a Peltier stage, which was mounted on an optical microscope (VHZ-100UR, Keyence). The Peltier stage provided controlled temperature for the samples. A silicon wafer was placed beneath the sample to reduce laser scattering resulted from the Peltier stage. As the laser source, a near infrared (NIR) laser (808 nm, 2.5 W, Roithner Lasertechnik) was used. The output power of the laser was calibrated with an optical power meter (PM200, Thorlabs). The laser irradiation had an incident angle of 40 °. The elliptical laser spot had a transverse dimension of around 1 mm, and the longitudinal dimension was parallel to the temperature sensor as shown in Figure S2 (c). The laser was modulated with 1 ms
temporal resolution. Throughout the experiments, the light of the microscope was kept off to avoid additional heating. The temperature data was recorded at 55 ms intervals.

**Figure S2.** (a) Illustration of temperature measurement in AuNR solution; (b) Illustration of temperature measurement in gel containing AuNRs; (c) Top view of the AuNR solution under laser irradiation. The elliptical laser spot is outlined. The spot is visible due to scattering from the AuNRs. The green line marks the contour of the temperature sensor. Scale bar: 500 µm.

**Figure S3** shows the temperature increase at steady state ($\Delta T_{\text{max}}$) on a hydrogel ribbon laden with AuNRs at different distances. The plot indicates the temperature profile around the irradiation spot. It can be seen that the $\Delta T_{\text{max}}$ is significantly lower (by more than 8 °C) at a distance of 1000 µm compared to 150 µm. The change of the temperature is especially strong near the irradiation spot: the $\Delta T_{\text{max}}$ decreased by more than 2 °C (~ 20 %) as the distance increased from 150 µm to 270 µm. It can be therefore reasonably assumed that the real temperature in the center of the spot may also be systematically higher than the measured temperature, even though the sensor was placed directly next to the laser spot. This is the accuracy limit presented by the physical sensor method.
Figure S3. (a) Dependence of $\Delta T_{\text{max}}$ on the distance between the laser spot and the sensor. The number density of AuNRs is 4 µm$^{-3}$. The laser intensity is 0.67 W·mm$^{-2}$. The dashed line is drawn to guide the eye. (b) Optical micrograph of the laser spot and the temperature sensor. The distance is marked.

3.4.4 Fitting of the temperature variations

The temperature variations under irradiation were fitted by exponential decay functions as shown in Equation S1 and S2. \[22, 23\]

\[
\Delta T_{\text{on}}(t) = \Delta T_{\text{max}}(1 - \exp(-Bt)) \quad (S\ 1)
\]

\[
\Delta T_{\text{off}}(t) = \Delta T_{\text{max}}\exp(-Bt) \quad (S\ 2)
\]

where $\Delta T_{\text{on}}(t)$ is the temperature change during the heating period (irradiation on), $\Delta T_{\text{off}}(t)$ is the temperature change during the cooling period (irradiation off), $\Delta T_{\text{max}}$ is the steady state temperature increase, and $B$ is the decay constant. Since $\Delta T_{\text{max}}$ is already known from the data, $B$ is the only parameter to be fitted. The fitting was done by the software Origin (v8.5). The characteristic thermal equilibration time is calculated as the reciprocal of $B$ as shown in Equation S3.

\[
\tau = \frac{1}{B} \quad (S\ 3)
\]
3.4.5 Fabrication of disk-shaped microgels and photothermal actuation

Non-wetting templates were used to fabricate the disk-shaped microgel.[31] In short, photo-lithographically patterned silicon wafer (structure size: diameter 30 µm and height 5 µm) was replicated in a glove box with perfluoropolyether-urethane dimethacrylate (PFPE, M_w = 2000, Fluorolink MD700, Solvay Solexis), which contained 1 wt% Darocure 1173 (Ciba Specialty Chemicals) as photoinitiator. The replica was used as the mold, on which monomer solution was pipetted. The mold was then pressed by a flat PFPE film under certain pressure (~ 260 kPa) to squeeze out the excess of the solution, so that only isolated microgels can be formed. The solution was cured under a UV-lamp for 20 min (366 & 254nm, 8 W, Konrad Benda) in a glove box. To transfer the as-prepared microgels, a PDMS frame (inner dimension: 1 cm × 1 cm) was bonded a on microscope slide after O₂-plasma treatment (200 W, 20 s, 1 mbar, PVP Tepla 100) to form the chamber for microgels. The chamber was filled with glycerol (99.5 %, Sigma-Aldrich), and the PFPE mold was placed in the chamber with the microgel side in contact with the glycerol. The sample was stored in a freezer at -80 °C overnight. Subsequently, the PFPE mold was peeled off while the glycerol was in frozen state, which served as the glue to transfer the gel. The glycerol was evaporated at 60 °C in vacuum (1 × 10⁻² mbar), and deionized water was added to reswell the microgel. The chamber was then closed by a cover slip to avoid evaporation. For photothermal actuation, the same setup was used as in the case of temperature measurement. The microgel was brought to the center of laser spot, and optical images were taken at different laser intensities. The microgels were analyzed by ImageJ to acquire the diameter at different temperatures or powers.
3.5 References

Chapter 4

4. Swelling/deswelling kinetics of microgels driven by stroboscopic irradiation and actuation efficiency

4.1 Introduction

Poly(N-isopropylacrylamide) (PNIPAm) is one of the most widely studied hydrogels due to its thermo-responsiveness. Cross-linked PNIPAm has a volume phase transition temperature (VPTT) at around 32 °C that is of both biomedical and practical importance.[1] PNIPAm has therefore been utilized in a diverse range of applications such as cell culture,[2-4] soft robotics,[5] self-folding structures,[6-8] drug release,[9, 10] and self-regulating systems.[11] The understanding of the kinetics of phase transition in PNIPAm is essential for the engineering of dynamic properties of the abovementioned systems. However, there exist practical difficulties to experimentally determine the kinetics with conventional methods.[12-17] For example, the size of the studied gel was generally in the range between cm and mm, which requires a time scale of swelling from hours to even a few days due to the small diffusion coefficient. This may sometimes bring about inaccurate results, when insufficient time for equilibration was used.[18] Besides, the kinetics of VPT is usually studied by temperature-jumps, meaning that the change of temperature is considered as instantaneous. Nevertheless, this is often achieved by exchanging the surrounding water that requires time and introduces heterogeneity in the gel such as pattern formation on the surface, thus hampering the time-resolved kinetic study.[13, 19]

This chapter focuses on the kinetics of PNIPAm microgels driven by periodic temperature jumps via photothermal heating. The incorporation of gold nanorods (AuNRs) into the microgel structure enables absorption and conversion of light
energy into heat. Upon irradiation, the surface plasmon resonance (SPR) of AuNRs is excited instantaneously by the incident photons.[20-22] Part of the light energy is absorbed and dissipated as heat. The ratio of absorption to extinction is defined as the photothermal conversion efficiency, which has been extensively investigated experimentally and theoretically.[21-25] The AuNRs are heated up by the absorbed light within several picoseconds. Thereafter, transfer of heat from the surface of the AuNRs to the surrounding takes place. By irradiating the sample with a laser at the SPR, where the absorption is at its maximum, the gel can be heated up almost instantaneously. This is due to the much faster local thermal equilibration compared to the global heating of the medium, since the thermal equilibration time is proportional to the square of the linear size. By utilizing a technique known as the *Particle Replication in Non-wetting Templates* (PRINT),[26, 27] micrometer-sized hydrogel particles were fabricated with precise control over their shape and composition. The small size of the hydrogel particles ensures fast kinetics, since the characteristic time $\tau$ of swelling/shrinking is proportional to the square of the smallest dimension of the material. For instance, by reducing the dimension of a spherical gel particle from 1 mm to 1 µm, $\tau$ can be brought from 6.9 hours down to 25 milliseconds ($D = 4.0 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$), i.e. a $10^6$ reduction. In the range of tens of milliseconds, photothermal modulation becomes highly desirable as it corresponds to frequencies in the range from a dozen to hundred Hz. This is a range that is relevant for natural pulsating systems such as rotating bacterial flagellum and beating muscle cells.[28, 29] A reduction in size combined with photothermal heating ensures fast and accurate modulation of the temperature. As a result, the volume of the gel can be precisely controlled. The efficiency of actuation, defined as the ratio of the stored elastic energy
to the absorbed light energy, can be calculated based on the Flory-Huggins theory of the free energy of the gel, which is shown in the last section of this chapter.

4.2 Results and discussion

4.2.1 Kinetics of swelling/deswelling in response to photothermal heating

Figure 1 (a) shows a scheme of the experimental setup, where dispersed microgels can be observed with an optical microscope. The temperature of the sample chamber was controlled by a Peltier stage maintained at 20 °C with an accuracy of ± 0.1 °C. The optical micrograph of the microgels can be easily captured from above by the microscope, which also allows for fast video record by implementing a high-speed camera. The disk-shaped microgel in swollen state at 20 °C has a diameter of 48.4 µm and a thickness of 8.1 µm (aspect ratio of 6). The average number density of AuNRs is estimated to be 2.2 particles·µm⁻³ based on the optical density of the pre-polymer solution (see the Experimental Section for more details). Figure 1 (b) illustrates schematically the cyclic change of temperature and volume (diameter) under stroboscopic irradiation. The depth of temperature variation can be controlled by the duration of the laser pulse, the laser intensity, the concentration of AuNRs etc. Because the swelling and shrinking of the gel are controlled by mass-diffusion and cannot follow the fast temperature change, the volume change strongly deviates from the equilibrium line as demonstrated by the red cycle.[30] The path of the volume change therefore doesn’t coincide with the equilibrium line, but rather adopts a Carnot-cycle-like path.
Figure 1. (a) Schematic drawing of the experimental setup. The microgels are dispersed in a chamber made by a PDMS frame and glass slides. The laser was aligned onto the field of view of the microscope objective with an incident angle of 40°. The lower panel shows the shrinking and swelling of the disk-shaped microgel upon laser modulation. (b) Illustration of the diameter variation of a disk under equilibrium heating (blue) and upon stroboscopic irradiation under non-equilibrium dynamics (red cycle). The Carnot-like cycle is achieved due to the faster heating rate compared to the rate of volume change.

Figure 2 shows the cyclic change of the microgel diameter under stroboscopic irradiation with a NIR laser (808 nm, 1.7 W·mm⁻²). The stroboscopic irradiation was performed with equal on and off durations. Time t = 0 indicates the start of one cycle of irradiation. Upon stroboscopic irradiation, the disk shrunk and swelled in a certain range with a period defined by the strobe frequency of the light. This is expected because the time for the thermal equilibration of the microgel is essentially shorter compared to the irradiation period. Using the thermal diffusivity of water ($D_{\text{thermal}} = 1.4 \times 10^{-3} \text{ cm}^2\cdot\text{s}^{-1}$) and the thickness of the hydrogel disk (8.1 µm), the typical time for the gel to reach a steady state temperature is estimated to be 0.5 ms. Considering the duration of the irradiation (> 100 ms), the thermal equilibration process can be deemed as instantaneous.
For the shortest irradiation of 0.2 s, the diameter changed periodically between 46.5 µm and 44.5 µm, namely an amplitude of 2.0 µm. The fact that the diameter did not attain the size at swelling equilibrium of 48.4 µm indicates that the gel is modulated around a steady state (see Figure 1 (b)). This is due to the shorter modulation period compared to the required recovery time of the gel. With longer modulation periods, the microgel nearly recovered its equilibrium size at 20 °C. However, the kinetics of swelling/shrinking became highly asymmetric in time. In particular, when the irradiation period exceeded 0.5 s, a fast water uptake was followed by a slow expansion when the gel swelled. In contrast, the shrinking did not show the same behavior. Specifically, the shrinking process slowed down but without reaching a plateau in the later stage. This can be attributed to the self-acceleration process discussed in Chapter 3. In brief, AuNRs are physically trapped in the mesh of
hydrogel, and their concentration increases when the volume of the gel decreases. As a result, the temperature tends to increase at constant laser intensity.[22-24] This effect is more significant for large volume changes. For example, the diameter change of 2.8 µm for 0.4 s modulation corresponds to a volume change of 16%. In contrast, the effect of the volume shrinking on the photothermal heat generation became significant for long irradiation period (2 s), which caused a reduction in volume by 35%.

Figure 3. (a) Change of the diameter at different modulation periods. ∆D is defined as the difference between maximal and minimal diameters under stroboscopic modulation. (b) Average speed in the first 40 ms after the switch of laser at different modulation periods. Dashed line is to guide the eye.

Figure 3 (a) demonstrates the amplitude of actuation ∆D at different modulation periods. The amplitude ∆D is defined as:

\[ \Delta D = D_{\text{max}} - D_{\text{min}}. \]  

(1)

\(D_{\text{max}}\) and \(D_{\text{min}}\) are the maximal and minimal diameters during stroboscopic irradiation. The amplitude increases from 0.34 µm to 6.5 µm as the period changes from 0.02 s to 2 s. It can be expected to reach an upper limit defined by the physical limits of the hydrogel between the fully collapsed and the fully swollen state at equilibrium.
In the beginning of the two periods, the diameter is always subjected to a nearly linear and rapid change and tends to slow down. The speed of this initial stage is plotted in Figure 3 (b) inferred from a linear fit of the first 40 ms of each phase. The initial speeds of shrinking and swelling differ as the modulation period increases. A nearly constant speed (~ 24 µm·s⁻¹) was observed for the shrinking process regardless of the irradiation period. In contrast, the swelling speed increased from 28.4 µm·s⁻¹ to 52 µm·s⁻¹ with irradiation period. This enhancement in kinetics can be attributed to the elastic restoring force that accumulates during the on-period and increases with longer irradiation time, i.e. larger volume change, as indicated by Flory-Huggins theory.[31, 32] The interplay of elastic force and osmotic force account for the higher speed in the swelling process.[33]

To summarize, the shrinking and swelling of disk-shaped microgels can be modulated with a NIR laser via photo-thermal heating. The duration of the stroboscopic modulation can be used to control the amplitude and kinetics of the swelling/shrinking. Shorter modulation periods result in relatively small amplitudes and symmetric kinetics, whereas larger amplitudes and asymmetric kinetics can be achieved by longer modulation periods.

**4.2.2 Efficiency of energy conversion**

In the AuNR/PNIPAm system, the energy of light is converted into heat via the AuNRs. The heat results in a change in the volume of the hydrogel and thus mechanical work. The efficiency of this process is estimated based on the elastic energy point of view.[5] The Gibbs free energy of a microgel $\Delta F$ is composed of mixing energy $\Delta F_m$, and rubber elasticity $\Delta F_{el}$ as expressed in Equation 3 – 5.[5, 31]
Since the PNIPAm gel is not charged, the energy due to counterions in the gel $\Delta F_i$ is not included.

$$\Delta F = \Delta F_m + \Delta F_{el}, \quad (3)$$

$$\Delta F_m = kT[n\ln(1 - \phi) + \chi n\phi], \quad (4)$$

$$\Delta F_{el} = \frac{3\nu kT}{2} (a^2 - 1 - \ln a), \quad (5)$$

where $\phi$ is the volume fraction of polymer network, $\alpha$ is the linear swelling ratio, $n$ is the number of solved molecules in the gel, $\nu$ is the total number of chains in the gel, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\chi$ is the interaction parameter between polymer and solvent. Assuming that the mixing energy is generally dissipated as heat, the potential mechanical work that can be restituted from actuation is the elastic energy as defined by Equation 5, i.e. the difference of elastic energy between swollen and shrunken states.

According to the equilibrium swelling curve in Chapter 3, the temperature of the hydrogel during the on-phase is around 33.2 °C, while the diameter of the disk in a fully collapsed state at laser intensity of 1.7 W·mm$^{-2}$ is 27.7 µm. This data can then be applied in the swelling curve to obtain the corresponding temperature by linear interpolation. The number of polymer chains is estimated from the volume of as-prepared microgel and the concentration of monomer in the pre-polymer solution. By assuming a degree of polymerization of 50, i.e. all the cross-linkers and monomers were consumed in the polymerization, the number of chains $\nu$ is estimated to be $1.4 \times 10^{11}$ per microgel particle. Linear swelling ratio of the gel can be easily calculated by using the diameter of the as-prepared gel $D_0 = 30 \mu m$ as reference state so that

$$\alpha(t) = \frac{D(t)}{D_0} \quad (7)$$

67
where the linear swelling ratio $\alpha(t)$ is proportional to the diameter $D(t)$. By combining Equation 7 with Equation 5, elastic energy $\Delta F_{el}$ becomes a function of diameter that can be experimentally determined. Figure 4 demonstrates the change of elastic energy during one actuation cycle exemplified by the 1 s modulation. The reference elastic energy $\Delta F_{el,0}$ is the energy immediately after the laser is activated, which causes the temperature to increase to 33.2 °C, while the diameter remains unchanged. In this case, $\Delta F_{el,0}$ can be calculated to be $9.5 \times 10^{-10}$ J, where $T = 33.2$ °C and $D = 47.8$ µm. This reference elastic energy is subtracted to obtain the real elastic energy caused by the laser irradiation as plotted in Figure 4. The maximal elastic energy achieved in the 0.5 s on-period is $3.2 \times 10^{-10}$ J, which is fully released in the off-phase via re-swelling.

![Figure 4](image)

**Figure 4.** Change of elastic energy and diameter within one cycle of laser modulation (1 s). Laser is switched off at $t = 0.5$ s.

To calculate the energy conversion efficiency, the light energy absorbed by the microgel needs to be determined. The surface area $S$ of a swollen gel is known to be 1798 µm² in the abovementioned case (diameter = 47.8 µm). Another factor needed in the calculation, which is the optical density (OD) of the microgel across the thickness, is estimated to be 0.046 at 808 nm with consideration of the swelling of the gel and corresponding dilution of AuNRs. The laser intensity $I$ is 1.7 W·mm² and the
duration of irradiation \( t_{irr} \) is 0.5 s. The total absorbed light energy \( E_{abs} \) is calculated using Equation 8 to be \( 1.5 \times 10^{-4} \) J, where the photothermal conversion efficiency of AuNR \( \eta \) is assumed to be 1 and the volume change during actuation is ignored.

\[
E_{abs} = SI(1 - 10^{-\text{OD}})\eta t_{irr}
\]  

(8)

Therefore, the efficiency of photothermal actuation, which is the ratio of elastic energy to absorbed light energy, is \( 2.1 \times 10^{-6} \), i.e. 0.00021%. One reason for the low efficiency is that most of the heat generated by irradiation is dissipated to the surrounding, since the microgel is not an isolated system. To elucidate the effect of heat dissipation on the efficiency, a microgel in an adiabatic condition is considered in the following discussion. In this situation, the energy \( E_{ad} \) needed to adiabatically heat up the microgel by 13.2 °C can be easily calculated to be \( 7.9 \times 10^{-7} \) J by applying the volume of microgel (1.4 \( \times 10^4 \) µm\(^3\)) and the heat capacity of water (4.18 J·g\(^{-1}\)·K\(^{-1}\)). The calculated energy is three orders of magnitude smaller than the irradiation energy \( E_{abs} \), which indicates that nearly 99.5% of the absorbed energy is dissipated to the surrounding. The efficiency of photothermal actuation in this adiabatic assumption would be \( 4.0 \times 10^{-4} \), i.e. 0.04%. A summary of the efficiency of different modulations is listed in Table 1. It can be seen that the elastic energy increases with \( T \), while the efficiency decreases at larger \( T \).

**Table 1.** Efficiency of photothermal actuation at different modulation periods

<table>
<thead>
<tr>
<th>( T / s )</th>
<th>( \Delta F_e / 10^{10} ) J</th>
<th>( E_{abs} / 10^4 ) J</th>
<th>Actuation efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.4</td>
<td>0.29</td>
<td>( 4.7 \times 10^{-6} )</td>
</tr>
<tr>
<td>0.4</td>
<td>2.0</td>
<td>0.62</td>
<td>( 3.2 \times 10^{-6} )</td>
</tr>
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<td>1.0</td>
<td>3.2</td>
<td>1.5</td>
<td>( 2.1 \times 10^{-6} )</td>
</tr>
<tr>
<td>2.0</td>
<td>4.6</td>
<td>3.2</td>
<td>( 1.4 \times 10^{-6} )</td>
</tr>
</tbody>
</table>
4.3 Conclusion

In this chapter, the kinetics of swelling/shrinking of a photothermally modulated AuNR/hydrogel system was studied, and the efficiency of actuation was estimated. Near infrared laser of 808 nm was used to excite the longitudinal SPR of AuNRs, which then dissipated as heat to the surrounding, i.e. to the thermoresponsive hydrogel. This results in the shrinking of hydrogel due to the volume phase transition. Since the AuNRs, as a heating source, are localized only inside the microgel, a rapid increase or recovery of temperature can be achieved once the laser is switched on or off; the change of temperature then causes the hydrogel to shrink or swell. Cyclic actuation of the hydrogel is realized by stroboscopic modulation of the laser intensity. Based on the thermal diffusion calculation, the time for the microgel to reach a steady state temperature is estimated to be in the order of sub-millisecond, while the swelling/shrinking of the microgel has a characteristic time of more than one second. The difference in orders of magnitude of the two processes means that the temperature change can always be considered as instantaneous. The duration of the stroboscopic modulation determines the amplitude and kinetics of the swelling/shrinking. At shorter periods, the kinetics of actuation is rather linear and symmetric with small amplitudes, whereas the kinetics becomes non-linear and asymmetric with larger amplitudes at longer periods. The asymmetry is also reflected by the initial speed of the swelling/shrinking process, which shows significant divergence at longer periods. The efficiency of actuation, which indicates the ability of the system to exploit light energy for mechanical work, is estimated to be in the order of $10^{-6}$ based on the consideration of elastic energy. One reason for this negligible number is the huge loss of energy due to heat dissipation to the environment.
4.4 Experimental section

4.4.1 Synthesis of AuNRs and estimation of number density

AuNRs were synthesized and modified as described in Chapter 3. The concentrations of AuNRs and the composition of the monomer solution are the same as used in Chapter 3. The monomer solution for microgels had an optical density of 240 at 808 nm (optical path = 1 cm). The number density of AuNRs in the monomer solution was calculated according to Equation 1 to 3, where $T$ is the transmission, $\sigma$ is the extinction cross-section of AuNRs, $n$ is the number density of AuNRs, $l$ is the optical path, and $OD$ is the optical density.

$$T = e^{-\sigma nl} \quad (1)$$

$$OD = -\log T \quad (2)$$

$$n = 2.3 (OD / \sigma l) \quad (3)$$

By assuming $\sigma$ to be ~ 6100 nm$^2$ at the wavelength of 808 nm for the AuNRs used in the present study,[34] the number density can be calculated to be 9.1 particles·µm$^{-3}$ for the $OD = 240$ solution. The diameter of the gel increases from 30 µm to 48.4 µm upon swelling at 20 °C, which leads to a 3.19 fold volume increase. Therefore, the concentration of AuNRs after swelling can be calculated to be 2.2 particles·µm$^{-3}$. The optical density decreased to 57.3 correspondingly.

4.4.2 Fabrication of disk-shaped microgels

Microgel particles with well-defined shapes were fabricated using non-wetting fluorinated elastomer molds as the template.[26] In a glove box, a cleaned microscope slide was placed on top of a diced silicon master (2 cm × 2 cm) produced by
photolithography (AMO GmbH, Aachen, Germany, see **Figure S1**). Two layers of parafilm (Bemis, total thickness \( \sim 200 \mu \text{m} \)) were used as spacers. Perfluoropolyether-urethane dimethacrylate (PFPE, \( M_w = 2000 \), Fluorolink MD700, Solvay Solexis) was mixed with 1 wt\% Darocure 1173 (Ciba Specialty Chemicals) and injected into the interspace until it was filled. Subsequently, the PFPE was cured for 20 min by UV irradiation (Konrad Benda lamp 366 & 254 nm, 8 W) in an argon protected atmosphere. After curing, the PFPE film was carefully peeled off and cut into suitable size (6 mm \( \times \) 6 mm). A flat thick layer of PFPE (0.4 mm) was prepared by the same protocol on a microscope glass slide.

![Figure S1](image)

**Figure S1.** Optical micrograph of the silicon master. Etching depth: 5 \( \mu \text{m} \).

Microgel objects were fabricated using PFPE as the molds as illustrated in **Figure S2**. A home-made press with a quartz window was used for the molding, and all steps were carried out in a glove box with less than 0.2\% \( \text{O}_2 \) in the atmosphere. The monomer solution (1 \( \mu \text{L} \)) was pipetted on the microstructured PFPE which was then covered by a flat PFPE layer. To squeeze out the excess of the solution, the quartz window was pressed on the PFPE mold by applying a weight (\( \sim 260 \text{ kPa} \)). The microgels were cured by 20 min UV-irradiation, after which the mold was peeled off from the flat film.
Release of the microgels from the mold was achieved by peeling them off with the help of a sacrificial adhesive layer. Microscope slides (Corning glass) were cut into 25 mm × 25 mm squares and cleaned by sonication in isopropanol. From a PDMS film (500 µm, Sylgard 184, Dow Corning) square frames were cut with an outer dimension of 15 mm × 15 mm and an inner dimension of 10 mm × 10 mm. The glass slide and the PDMS frame were activated by O₂ plasma (200 W, 20 s, 1 mbar, PVP Tepla 100) and then bonded together. Glycerol (99.5%, 15 µL) was pipetted in the PDMS trough, and the PFPE mold was placed in the trough with the microgel objects in contact with the glycerol. The trough was then stored in a freezer (-80 °C) overnight, and the PFPE mold was peeled off from the frozen glycerol, which served as an adhesive. The glycerol was subsequently evaporated at 60 °C under vacuum (10⁻² mbar), leaving only microgels in the PDMS trough. Deionized water was added to reswell the microgel.

In order to load the microgels into a capillary, one end of a plasma-treated (O₂, 200 W, 5min, 1 mbar) rectangular capillary (0.05 mm × 1.0 mm × 50 mm, Vitrocom) was immersed into the trough, so that dispersed microgel objects were sucked in by the capillary force. The ends of the capillary were sealed and fixed on a microscope slide by a 2-component epoxy adhesive (UHU GmbH).
4.4.3 Photothermal actuation and observation of disk-shaped microgels

The capillary containing microgels was placed on a peltier stage mounted on an optical microscope stage (VHZ-100UR, Keyence). The temperature of the capillary was controlled with an accuracy of ± 0.1 °C. NIR laser (808 nm, 2.5 W, Roithner Lasertechnik) was focused to the centre of field of view with an incident angle of ~40 °. This results in an elliptical footprint as seen in Figure S3. The size of the irradiated area was chosen to be much larger than the irradiated microgel objects and the irradiation is considered as homogeneous for the whole object. The mean laser intensity, 1.7 W·mm⁻², was calibrated by an optical power meter (PM200, Thorlab). The laser was modulated with a temporal resolution of 1 ms. Videos were recorded by a high speed camera (Miro M310, Phantom) at a speed of 1000 frames per second (fps). A short pass filter (700 nm, OD 4, Edmund optics) was used to block the scattered NIR light and to protect the camera. Acquired videos were contrast-enhanced and analyzed with the open-source software ImageJ.

![Laser spot](image)

**Figure S3.** Optical micrograph of the footprint of the laser spot, scale bar: 200 µm. To demonstrate the laser spot, the microscope light was switched off.

4.4.4 Analysis of actuation dynamics

To obtain the dynamics of the disk-shaped microgel, videos were processed by ImageJ (Version: 1.50c) as demonstrated in Figure S4. The videos were first converted into 8-bit grayscale (Figure S4 (a)), and then a threshold was applied to
subtract the background (Figure S4 (b)), leaving only the boundaries of particles visible. By defining the analysis parameters (size range, circularity etc.), the boundary of the microgel could be detected using the “Analyze Particles” function. Geometrical information of the disk such as circularity, perimeter, and area was thus obtained. The diameter \(D\) of the disk was calculated by \(D = 2\sqrt{\frac{S}{\pi}}\) from the acquired area \(S\). The geometry analysis is plotted in Figure 1.

**Figure S4.** Illustration of the geometry analysis using ImageJ. (a) Original micrograph in 8-bit format; (b) thresholded micrograph, and (c) automatic detection of disk geometry.

4.5 References


5. Triggering bending deformation by non-equilibrium actuation of anisometric microgels

5.1 Introduction

Photothermal heating of microgel via gold nanorods enables temperature jumps that drive the swelling/deswelling of the microgel out of equilibrium as demonstrated in Chapter 4. The actuation is achieved by both the material design, i.e. incorporation of AuNRs into geometrically defined PNIPAm microgels, and the optimization of external stimulus, i.e. irradiation of a near infrared (NIR) laser at the absorption maximum of the AuNRs. The NIR irradiation results in heating that is localized within the microgel without affecting the temperature of the medium. Nevertheless, the effected deformation of the disk-shaped microgel discussed in the last chapter was basically isotropic, and the amplitude of actuation was limited to 4% - 14% change of the linear dimension. To achieve enhanced amplitudes and kinetics of the actuation, anisotropic deformations, such as bending and torsion, are more desirable. These kinds of pronounced deformations can be indeed induced by small changes in volume, when the structures are purposefully designed.[1-17]

In this chapter, we designed L-shaped microgels that have two arms of equal lengths with the goal of enhancing both the amplitude and the kinetics of the deformation by inducing bending of the microgel. The microgels were fabricated by the Particle Replication in Non-wetting Template (PRINT) technique.[18] The PRINT offers immense freedom in designing the shape, composition, and dimension of microparticles.[18, 19] The microgel was actuated by stroboscopic irradiations with a NIR laser, and the results are contrasted to equilibrium heating/cooling cycles.
5.2 Results and discussion

The response of the L-shaped microgel to temperature changes is illustrated in Figure 1 (a) by the end-to-end distance ($D$) of the two arms. The shrinking of the hydrogel at increasing temperatures resulted in the decrease in $D$. The slope is steepest when the temperature is close to the VPTT ($\sim 32 ^\circ C$). Above the VPTT, however, the hydrogel was fully collapsed, and the $D$ remained nearly constant. The total decrease in $D$ is roughly 40% between 20 °C and 40 °C. Since the microgel was always in equilibrated state, it underwent isotropic volume changes as seen in Figure 1 (b), where the shape of the microgel is preserved throughout the heating/cooling process. This is a clear indication that no significant structural heterogeneities are present inside the microgel.

![Figure 1](image)

**Figure 1.** (a) Change in the end-to-end distance ($D$) of the L-shaped microgel with temperature. The line is drawn to guide the eye. Inset: schematic illustration of the L-shaped microgel with corresponding dimensions. Not drawn to scale. (b) Optical micrographs of the L-shaped microgel at different temperatures. The isotropic volume change was induced by heating/cooling along the equilibrium line.

In contrast, the L-shaped microgel responded to the photothermal heating by bending like a tweezer, when the volume change of the gel was effectuated by a fast temperature change and was thus fully out of equilibrium. The shrinking kinetics of the gel in this case, which depends on the surface to volume ratio, varied in the
different sections of the gel due to the limited mass transport rate. Therefore, the shrinkage is particularly heterogeneous in the corner that connects the two arms (see Figure 2).[20] We have indeed found that heterogeneity arises when the hydrogel is photothermally actuated as demonstrated by the inset of Figure 2 (a), where a tethered hydrogel film wrinkled on the surface under strong irradiation.[20] The bending of the microgel is reminiscent of the bilayer structures, where the two layers have different expansion ratios, and the bending can be triggered by changes in temperature or humidity.[5, 10, 21] However, the bilayer structures are fundamentally different in terms of equilibrium state and kinetics. The large aspect ratio of the L-shape ($L/h = 20:1$) further amplifies the bending of the structure as can be seen in the huge bending deformation (Figure 2 (a)) of more than 150 µm within 200 ms.

Figure 2. (a) Change in the end-to-end distance during one cycle of irradiation (200 ms on – 200 ms off). Inset shows the wrinkled surface of a tethered hydrogel film under laser irradiation.[20] Reproduced with Permission. (b) Optical micrographs of the L-shaped microgel under stroboscopic irradiation as in (a). Enlarged inset is the schematic illustration of the deformed corner of the microgel.

Figure 3 shows the deformation kinetics of the L-shaped microgel at different stroboscopic frequencies. The change in $D$ during one cycle of laser modulation is plotted together with the optical micrographs. The microgel was actuated by the 20 ms – 20 ms laser irradiation in Figure 3 (a). Due to the short recovery time, the
microgel was still slightly deformed before it began to shrink under irradiation. This is reflected by the $D$, which has a maximum of 145 µm during the stroboscopic actuation, compared to 194 µm in a swollen microgel. In the initial 2 ms of irradiation, the $D$ remained constant, after which the microgel started to bend with $D$ decreasing from 145 µm to 102 µm. Fitting of the linear region shows a slope of $2.6 \times 10^3$ µm·s$^{-1}$. The off-period is characterized by a similar linear change, where the $D$ increased at a speed of $2.3 \times 10^3$ µm·s$^{-1}$ without any delay. The bending speeds are almost 100 times higher than the isotropic volume change of the disk-shaped microgel ($30$ µm·s$^{-1}$) discussed in Chapter 4.

Figure 3. (a) Change in the end-to-end distance ($D$) during one irradiation cycle (on - off). (a) 20 ms – 20 ms; (b) 50 ms – 50 ms; (c) 100 ms– 100 ms; Irradiation starts at $t = 0$ ms. Right panel shows optical micrographs of the microgel at different points in time.
With longer irradiation periods, as shown in Figure 3 (b), the bending kinetics becomes non-linear and asymmetric. Again a 2 ms delay can be observed followed by a linear decrease of $D$. After 25 ms, the speed slowed down, and the $D$ finally reached 76 µm. Once the laser was switched off, a relatively slow recovery can be seen, after which a fast linear increase of distance took place till 85 ms. The distance change then relaxed slowly in the final stage of recovery.

As the irradiation period increases, the kinetics between the bending and the recovery processes became significantly asymmetric (Figure 3 (c)). For the irradiation periods of 100 ms – 100 ms, the deformation began with a relatively slow decrease in the $D$ followed by a linear decrease, and slowed down again in the later stage. The off-period is characterized by a distinct kinetics: the initial recovery stage was fast and linear with slow relaxation towards the end. In the first half of the off-period, the microgel already recovered its flat L-shape, as demonstrated by the optical micrographs. The reason for this fast recovery is the coupling between osmotic pressure and elastic restoring force, which was accumulated in the shrinking process. The elastic energy was particularly enhanced by the irradiation-induced heterogeneity. Once the heterogeneity was reduced by releasing the elastic energy in the fast linear recovery, slower swelling driven by collective diffusion of the gel network dominated the kinetics illustrated by the second half in the off-period.

The amplitude of the deformation, defined as the maximal change in the $D$, and the highest speed of the deformation are plotted in Figure 4. In general, the amplitude and speed show similar tendency compared to the disk-shaped microgel. The amplitude increased with the irradiation period and was limited by the physical constraint of swelling/shrinking of the gel network at longer periods. The highest
speeds of the bending (on) and recovery (off), acquired by fitting the linear regions in Figure 3, are plotted in Figure 4 (b).

![Figure 4](image)

**Figure 4.** (a) Amplitude of bending at different periods of stroboscopic irradiations. Dashed line is drawn to guide the eyes. (b) Highest speed of deformation at different periods of stroboscopic irradiations. The speed was measured by fitting the linear regions in Figure 2. Dashed lines are drawn to guide the eyes.

The change of the two speeds diverts significantly as the irradiation time increases. A decreasing speed (from $2.6 \times 10^3$ to $1.8 \times 10^3 \, \text{µm}\cdot\text{s}^{-1}$) was observed for the bending process. In contrast, the recovery speed increased from $2.3 \times 10^3 \, \text{µm}\cdot\text{s}^{-1}$ to $4.0 \times 10^3 \, \text{µm}\cdot\text{s}^{-1}$ with irradiation period. It is noteworthy that both speeds are almost two orders of magnitude higher than that of the isotropically swelling/shrinking microgels (*Chapter 4*), which reflects the enhancement in kinetics due to bending deformation.

To explain the origin of the delay time, we performed additional experiments on bar-shaped microgels as shown in **Figure 5**. The duration of the delay on the L-shaped microgel is found not to be significantly dependent on the irradiation conditions as summarized in **Table 1**. In contrast, the response of a bar-shaped microgel proved to be instantaneous under similar irradiations (Figure 5 (a)). The length changed immediately after the irradiation was switched on/off. It is worth noting that the deformation in this case is dominantly due to the isotropic swelling and shrinking of
the network leading to a small amplitude of 2 µm. In principle such volume change also existed in the L-shaped microgel for the initial 2 ms. However, its effect was completely overdamped by the huge bending deformation.

![Figure 5](image)

**Figure 5.** (a) Change in the length of a rectangular microgel under stroboscopic irradiation (50 ms – 50 ms). Irradiation started at t = 0 ms. Upper panel: illustration of the as-prepared dimensions and the microgel under optical microscope. (b) Optical micrographs showing the bending of a bar-shaped microgel under stroboscopic irradiation (100 ms – 100 ms). The laser irradiation started at t = 0 ms. Upper panel: illustration of the as-prepared dimension of the microgel. Laser intensity: 1.7 W·mm⁻² for both (a) and (b).

From the comparison of the two different gels, it can be concluded that the change in the end-to-end distance is mainly due to the bending of the structure, since the change in the volume of the gel takes place instantaneously and has significantly smaller amplitudes. As discussed above, the bending is caused by the heterogeneity within the gel during the shrinking process. Therefore, certain degree of shrinking would be needed to trigger the bending. The delay time of the L-shaped microgel is thus assigned to the time during which the gel shrunk with minor change in the D. The change in the volume of the bar-shaped microgel in the first 2 ms, calculated from the length change, is demonstrated in Table 1, where the shrinking degrees in length of
the microgel are listed for different modulations. Because the dimensions of the bar-
shape and the L-shaped microgels are similar, especially in the thickness and width, it
can be assumed that the kinetics of volume change is roughly identical under the same
irradiation conditions. This leads to the conclusion that the change in the linear
dimension of the microgel between 0.27% and 0.29% (~0.84 vol%) is sufficient to
bring about the bending of the L-shaped microgel. Note that the bar-shaped microgel
didn’t show observable bending because of its much smaller aspect ratio \(L/h = 10\)
compared to the L-shaped microgel. This is associated with the observation that a
longer bar-shaped microgel \(L/h = 16\) indeed experienced bending deformation under
the similar irradiation conditions (Figure 5 (b)).

<table>
<thead>
<tr>
<th>Modulation</th>
<th>Delay time / ms</th>
<th>Shrinking degree in 2 ms / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 ms - 20 ms</td>
<td>2 ± 1</td>
<td>0.27 ± 0.09</td>
</tr>
<tr>
<td>50 ms – 50 ms</td>
<td>2 ± 1</td>
<td>0.27 ± 0.06</td>
</tr>
<tr>
<td>100 ms – 100 ms</td>
<td>2.5 ± 2.5</td>
<td>0.28 ± 0.09</td>
</tr>
<tr>
<td>200 ms – 200 ms</td>
<td>2.5 ± 2.5</td>
<td>0.29 ± 0.09</td>
</tr>
</tbody>
</table>

5.3 Conclusion

By designing the shape of the microgel, photothermal heating enables bending
deformation and allows the investigation of the kinetics on an L-shaped microgel. The
maximal deformation speeds, characterized by the change of end-to-end distance of
the two arms, were \(2.6 \times 10^3 \mu \text{m}\cdot\text{s}^{-1}\) and \(4.0 \times 10^3 \mu \text{m}\cdot\text{s}^{-1}\) respectively, compared to \(25\)
\(\mu \text{m}\cdot\text{s}^{-1}\) and \(52 \mu \text{m}\cdot\text{s}^{-1}\) in the case of isotropic deformation of the disk-shaped microgel
discussed in Chapter 4. The significant enhancement can be attributed to the
anisotropic deformation of the gel, which is the result of heterogeneity inside the
microgel induced by the fast photothermal heating, combined with the high aspect
ratio of the microgel structure. Short irradiation of 20 ms – 20 ms leads to linear and almost symmetric bending kinetics, whereas non-linearity and asymmetry in the deformation kinetics increases with longer irradiations. The asymmetry is to be attributed to the elastic restoring force that plays a key role in the re-swelling process with a higher bending rate and distinct kinetics. The amplitude of non-equilibrium actuation can be tuned by the irradiation period: longer modulations bring about larger amplitudes. Accumulation of minor shrinkage is needed to trigger the bending of the L-shaped microgel, which results in the delay of 2 ms upon irradiation. This study demonstrates that the kinetics and amplitude of actuation can be strongly enhanced by tailoring the geometry of the microgel, so that anisotropic deformation, i.e. bending, can be achieved. The resultant enhancement and asymmetric kinetics are potentially advantageous for applications that require non-reciprocal deformation to generate effective flow, e.g. artificial microscopic swimmers and microfluidic devices.

5.4 Experimental section

5.4.1 Fabrication of microgel particles

PEGylated AuNRs were synthesized as described in Chapters 3 and 4. The monomer solution containing AuNRs was prepared according to Table S1. The ratios of crosslinker (N,N’-Methylenebisacrylamide, BIS, 99%) and photo-initiator (2-Hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone, 98%) to the monomer N-Isopropylacrylamide (NIPAm, 97%, recrystallized twice in n-hexane) are both 1 mol%. The as-prepared solution has an optical density of around 240 at 808 nm (optical path = 1 cm).
In a glove box, a cleaned microscope slide was placed on top of a diced silicon master (2 cm × 2 cm) produced by photolithography (AMO GmbH, Aachen, Germany, see Figure S1), and two layers of parafilm (Bemis, total thickness ~ 200 µm) were used as spacer. Perfluoropolyether-urethane dimethacrylate (PFPE, Mw = 2000, Fluorolink MD700, Solvay Solexis), mixed with 1 wt% Darocure 1173 (Ciba Specialty Chemicals), was then injected until the space was fully filled. Subsequently, the PFPE was cured for 20 min by a UV lamp (366 & 254 nm, 2 × 4 W, Konrad Benda) under argon protection.

After curing, the PFPE film with replicated reliefs was carefully peeled off from the silicon master and cut into suitable size (6 mm × 6 mm). The flat PFPE film was prepared with the same protocol using a transparent microscope glass slide instead of the silicon master. A home-made press with quartz window was used for the molding of microgel, and all steps were carried out in glove box with less than 0.2% O₂. 1 µL of the monomer solution was pipetted onto the replicated PFPE film, which was then covered with a flat PFPE film. Weight was applied on the PFPE film through the quartz window to ensure suitable pressure (~ 260 kPa) to remove the excess of the solution, so that only separate microgel elements were formed. UV irradiation was carried out for 20 min to cure the hydrogel, after which the weight was removed, and the mold was peeled off from the flat film. The prepared microgels have certain stickiness to the mold after curing, so that a transfer step is needed to release the microgels.
Figure S1. (a) Optical micrograph of silicon master with L-shape. Scale bar: 200 µm. (b) L-shaped microgel on a conductive tape under scanning electron microscope (Hitachi S4800). Scale bar: 20 µm.

For the transfer, microscope slides (Corning glass) were cut into 25 mm × 25 mm squares and cleaned by sonication in isopropanol. 500 µm thick PDMS film (Sylgard 184, Dow Corning) was cut into square frame with an outer dimension of 15 mm × 15 mm and an inner dimension of 10 mm × 10 mm. Both the cleaned glass slide and the PDMS frame were activated in O₂ plasma (200 W, 20 s, 1 mbar, PVP Tepla 100) and then bound together to form an open trough. 15 µL of glycerol (99.5%) was pipetted in the chamber, and the PFPE mold with hydrogel particles was placed upside down in the chamber carefully to avoid bubbles. The whole chamber was then stored in a freezer (-80 °C) overnight. Transfer of the microgels was achieved by peeling off the mold carefully, with frozen glycerol serving as adhesive to release the microgel from the PFPE mold. The glycerol was subsequently evaporated at 60 °C under vacuum (10⁻² mbar), and deionized water was added to re-swell the microgel. The microgels were finally loaded into a plasma-treated (O₂, 200 W, 5 min, 1 mbar) rectangular capillary (0.05 mm × 1.0 mm × 50 mm, Vitrocom) by immersing one end of the capillary in the chamber, so that microgels were spontaneously loaded into the tubing by capillary force. Both ends of the capillary were then sealed and fixed on a clean microscope slide by a 2-component epoxy adhesive (UHU GmbH). Scanning electron micrograph of one L-shaped microgel is shown in Figure S1 (b), where the gel is
released from PFPE mold with a conductive tape. Other shapes of microgels were fabricated in the same way with different silicon masters, and the dimensions of the mold are defined as the as-prepared dimensions.

### 5.4.2 Actuation and analysis of microgels

The capillary containing microgels was placed on a Peltier stage for temperature control, which was mounted on the sample stage of an optical microscope (VHZ-100UR, Keyence). A silicon wafer was placed beneath the sample to enhance the optical contrast. The temperature of the sample was controlled with an accuracy of ±0.1 °C at 20 °C. NIR laser (808 nm, 2.5 W, Roithner Lasertechnik) was focused to the middle of the field of view with an incident angle of ~ 40 °. The laser intensity in the center is 1.7 W·mm⁻², which was calibrated by an optical powermeter (PM200, Thorlab). The laser modulation has a temporal resolution of 1 µs. Videos were recorded by a high speed camera (Miro M310, Phantom) at the speed of 1000 or 200 frames per second depending on the laser modulation. A short pass filter (700 nm, OD 4, Edmund optics) was used to block scattered laser light and to protect the camera.

To acquire the equilibrium swelling curve of the microgel, the temperature of the Peltier stage was adjusted correspondingly, and photos were taken with the microscope camera (Keyence VHX 1000) after equilibration for 5 min at each temperature. Acquired videos were processed and analyzed by the open-source software ImageJ (version 1.50C). The end-to-end distance of one actuation cycle was manually measured with ImageJ and plotted in the figures shown in this chapter.

To acquire the length change of the bar-shape microgel shown in Figure 5 (a), the same protocol of image analysis was used as in Chapter 4. In brief, the images were first converted into 8-bit format and then thresholded to show the contour of the bar-
shaped microgels in binary images. The area of the microgel was then measured using the *Analyze Particles* function of ImageJ. The length of the microgel was calculated by assuming a rectangular shape with an aspect ratio \((L/w)\) of 5.

### 5.5 References

6. Dynamic switching of helical microgel ribbons

6.1 Introduction

Hydrogels whose constituent polymers are characterized by a lower critical solution temperature in water are known to undergo a volume phase transition. The gel collapses reversibly when either the temperature is raised or the solution conditions are changed (pH, ionic strength etc.).[1, 2] Depending on the geometry of the hydrogel body, such objects can morph between different shapes.[3-8] Applications have been explored widely, exemplarily for encapsulation,[4] drug delivery,[9] tissue engineering,[10] and microfluidics.[11] Furthermore, feedback loops have been proposed for self-regulating chemical micro reaction systems.[12] Repetitive volume changes offer intriguing perspectives to design micro swimmers and other locomotors, as has been demonstrated theoretically [13, 14] as well as by a chemically fueled microgel walker.[15] Recently we have realized experimentally a light driven morphing microswimmer. The principle is based on the ability of microscopic hydrogel objects to undergo complex large amplitude motions when the volume change is coupled to distortion modes under non-equilibrium conditions.[16] The latter point is important when a repetitive cyclic deformation is driving a directed motion and enabling the microsystem to perform work. By a proper combination of different deformation modes a cyclic process with forward and backward strokes can be distinguished, as a result at small Reynolds numbers directed rotations and even forward movement can be effectuated. This was demonstrated by a helical hydrogel.

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2 This chapter is adapted from the publication: H. Zhang, A. Mourran, and M. Möller, Dynamic switching of helical microgel ribbons. Nano Letters, 2017. 17(3): p. 2010-2014. Authors’ contributions: AM and MM designed the project. HZ carried out the experiments and collected the data. All authors analyzed and interpreted the data. HZ prepared the draft. AM and MM critically revised the manuscript.
ribbon whose helix pitch and diameter oscillated due to light-controlled heating from inside. Temperature jumps causing heating were induced by heating embedded gold nanorods via irradiation at \( \lambda = 808 \text{ nm} \), the maximum of the longitudinal plasmon resonance band.

In this work we report helix reversal of a microscopic poly(N-isopropylacrylamide) hydrogel ribbon, poly(NIPAm), coated by a thin gold layer and affected by the volume phase transition. Particular emphasis is put on the large amplitudes and large rates of the changes that can be achieved, as well as on a comparison of the changes under equilibrium and non-equilibrium conditions. Like in our previous report, fast temperature rises are achieved by heating the microgel from inside with the help of embedded gold nanorods that convert IR-light efficiently to heat. Subsequent fast cooling is enabled by the small dimensions of the ribbon kept in water at constant temperature. The volume change of the hydrogel layer is triggered by deswelling and reswelling and thus diffusion controlled. Hence its rate is several orders of magnitude smaller than the temperature change and the resulting deformations require milliseconds to seconds. As a consequence the helix deformation can take place under non-equilibrium conditions. We will demonstrate the enormous sensitivity of the deformations rate and amplitude that can be achieved. Next we explore the interplay between geometry and swelling properties of the microscopic bilayer structure comprising single hydrogel layer. Finally we shortly discuss the potential of these responsive systems for sensing applications.
6.2 Results and discussion

6.2.1 Shape selection through misfit strain

The helices are formed from a bilayer ribbon consisting of a poly(NIPAm) hydrogel layer, on which a 2 nm thick gold layer was sputtered. The dimensions were length $L = 80 \mu m$, width $w = 5 \mu m$, and height $h = 1 \mu m$. Upon swelling in water, expansion and stretching of the gel layer is restricted by the gold skin, which itself can be stretched barely. Hence, the structure is a bilayer ribbon in which one layer expands relative to the other.[17] As a consequence, swelling and deswelling of the hydrogel causes stresses which, in turn, lead to bending of the bilayer. The bilayer micro ribbon has been prepared by crosslinking polymerization of NIPAm in DMSO solution in micromolds as described elsewhere.[16] In that situation swelling at low temperatures ($< 30 ^\circ C$) causes concave bending towards the gold layer and deswelling at high temperatures ($> 32 ^\circ C$) causes convex bending. Deswelling is effected either by warming the surrounding water, at low rate to keep the structure in equilibrium, or by an internal temperature jump caused by plasmonic heating of embedded gold nanorods (diameter 15 nm and length 60 nm; $c = 9 \text{ AuNRs}/\mu m^3$) with laser light as mentioned above. The gold skin contributes an additional heating effect. In the case of a temperature jump, the deformation follows non-equilibrium transition path. The microgel can be considered as being prestressed and thus is capable of a rapid release of the elastic energy. Figure 1 shows the geometrical parameter space describing the configurations generated by bending or buckling of a bilayer ribbon depending on its dimensions. Depending on the interplay of stretching and bending, the ribbons adopt a distorted equilibrium configuration that breaks the planar symmetry. For a given material composition, the stretching energy, accounting for in-plane deformations, is linear in the ribbon thickness $h$ while the bending energy is cubic in $h$.\[18\] These
dependences entail that bending is more favorable for thinner films and for large $h/w$ values ribbons coil up like a spiral spring.

Figure 1. Shape diagram of bilayer ribbons with different cross-sections and lengths and the corresponding schemes of minimum energy configurations. The length and the thickness are normalized to the constant ribbon width. Symbols mark the configurations found for ribbons coated with a 2 nm gold skin after swelling the poly(NIPAm) at ambient temperature in water. For details of the film preparation see ref [16]).

Wide and thin sheets adopt a cylindrical configuration. Coiling of ribbons with an intermediate $h/w$ ratio is directed by the interplay of the two bending modes, resulting in a pronounced non-zero Gaussian curvature. A small gold-coated rectangular sheet will acquire a dome like (elliptic) natural curvature upon swelling or deswelling of the hydrogel layer. For longer ribbons the principle curvatures become more unequal and the ribbon bends along a preferred direction set by the misfit in strain, including edge effects.\cite{19, 20} It tends to adopt a helical configuration as wound around a cylinder. For a given ratio of $L/w$ ratio, we observe a two-dimensional spiral, a cylindrical helix, and a cylindrical tube as the ribbon becomes thinner. The sense of the helix is determined by small mismatches between the main stress axis and the long axis of the
stripe. These are caused by inhomogeneity in thickness, shape, or bulk structure.[21, 22]

6.2.2 Shape changes during equilibrium heating

As mentioned already the poly(NIPAm) ribbon was prepared by sputtering a gold layer onto a planar ribbon, and it bends upon swelling in opposite directions below and above the volume phase transition temperature (Figure 2 (a)). Indeed, a reversal of the curvature is observed upon heating/cooling, markedly at temperatures around the volume phase transition temperature. Figures 2 (b) - (d) summarizes the observed temperature dependent changes of the helical configuration of the bilayer ribbon under equilibrium conditions. At 20 °C, the ribbon shown in Figure 2 (b) forms a tight right handed helix. As the temperature is raised the helix widens and uncoils until it approaches the fully stretched state at about 31 °C. At higher temperatures a reversed helical conformation is formed that coils up more strongly as the temperature is increased to 50 °C. Hence we observe a remarkable helix reversal as a function of temperature, that can be understood from the flat reference state of the gels, as defined by the preparative conditions,[16, 23] in combination with the metallic skin that restricts isotropic swelling and shrinkage at low and high temperatures, respectively. Figure 2 (c) depicts uncoiling and coiling of the helix as measured by its radius as a function of the temperature and under equilibrium conditions. As the helix unwinds upon raising the temperature from 20 to 30.5 °C its radius $R$ increases. When the temperature is raised further the helix coils up in reversed sense, the radius decreases again approaching asymptotically the configuration of the collapsed hydrogel layer. Remarkably, the strain difference between the left and right helix is of the order of 10%, much of which accumulates in less than 2 °C. For comparison we plot the
relative change in length $\varepsilon$ for an unconstrained hydrogel ribbon (no metallic skin) of the same dimensions. The “skinless” ribbon continuously shrinks with temperature.

Figure 2. Helix reversal of a bilayer hydrogel ribbon around the volume phase transition. The volume change is constrained by a 2nm thick metallic skin at one side. (A) Scheme of the fabrication and swelling/deswelling deformation of the micro-ribbon. The ribbon was prepared in a mold of perfluorinated ether elastomer from a monomer solution in DMSO by photopolymerization.[16] Still in the mold a 2 nm gold layer was sputtered on top of the hydrogel. When the hydrogel ribbons are suspended, swelling causes convex buckling controlled by the temperature resp. the solvent quality. (B) Optical micrographs of the coiled ribbon. At low temperatures a tight helix is formed. Upon deswelling of the hydrogel layer the helix undergoes an inversion in handedness (scale bar: 15 µm); (C) Variation of the helix radius with temperature (full symbols), and expansion in length $(L - L_0)/L_0$ of an unconstrained (without metallic skin) micro-ribbon (open symbols). (D) Curvature (R and L) versus misfit strain relative to the ribbon thickness.

The steep change of the helix radius within a narrow temperature range, less than 1 °C is striking. The high sensitivity of shape and diameter resp. results in a well-
developed singularity. This shows up clearly Figure 2 (d) where \( 1/R \) is plotted versus the \( \varepsilon/h \), where \( \varepsilon \) is the relative change in length of the free hydrogel (open symbols in Figure 2 (c)). This behavior is similar to Timoshenko’s bending of a bimetallic strip. In that case the curvature is proportional to the misfit in strain of the two layers and inversely proportional to the thickness of the strip.[18] Here we take the equilibrium expansion of the unconstrained hydrogel ribbon as an approximation for the misfit in strain between top and bottom side of the bilayer ribbon. Figure 2 (d) indicates that the experimental data follow rather well a linear relationship. The alteration of the slope of the \( 1/R \) versus \( \varepsilon/h \) relation at the helix inversion transition is in agreement with the change in bending modulus and thickness of the ribbon at the volume phase transition. Hence, although the volume phase transition of the nonionic hydrogel is continuous, it is sufficiently steep to cause an even more sharp transition in the bending behavior.

6.2.3 Dynamics of helical switching

The transformation described so far occurs at slow temperature changes and thus under conditions where the system can follow the equilibrium transition. However, the plasmonic heating allows a sudden change of temperature that is in first instance localized to the volume of the hydrogel. This temperature change can be effected within milliseconds, which is short with regard to both the diffusion time for swelling and deswelling and the time for elastic bending of the ribbon. The latter is controlled by polymer relaxation and the retardation due to the viscous drag exerted on the moving ribbon.[24, 25] In the following we shall discuss this dynamic behavior.
Figure 3. (A) Optical micrographs of the helical microgel in one cycle of actuation (80 ms on – 12 ms off). Laser irradiation starts at $t = 0$. Scale bar: 15 µm. (B) Radius of a right-handed helix (R) as a function of the irradiation duration. Left panel: recovery upon cooling after a light pulse of 80 ms. Irradiation was performed at 808 nm at an intensity of 1.7 W/mm². The light intensity was enough to revert the chiral structure within 30 ms. The extra irradiation time (50 ms) effected recoiling to a left-handed (L) helix. The recovery process upon cooling takes place in a time interval of one tenth compared to the irradiation-driven helix inversion.

Figure 3 demonstrates the helix uncoiling and reversal as observed by light induced heating. The temperature of the water was externally regulated at 20 °C, significantly below the volume phase transition temperature of poly(NIPAm). The optical power has been set to cause the helical ribbon to fully unwind and reverse its chirality. The results depicted in Figure 3 demonstrate that uncoiling and reversal of the helix can be achieved within 90 ms (Figure 3 (a) and (b) right panel). This time is still long compared to the thermal diffusion time but remarkably short for this complex motion. An even faster response is observed when the irradiation is ceased and the ribbon cooled down by the surrounding bath. A minimum of only 12 ms is needed to fully recover the initial helical state. Hence the off-time needed to recuperate the initial
state (Figure 3 (b), right panel) is nearly an order of magnitude shorter than the on-time of the reversal process (Figure 3 (b), left panel).

Let us consider the deformation to be a diffusion limited process. Then the rates for the uncoiling-coiling deformation should be related to the collective diffusion coefficient $D_p$ of the water in the gel and to a diffusion length $\Delta h$. The latter corresponds to the shortest path for the water molecules to get out or into the gel, i.e., the height of the ribbon which is its smallest dimension. With $D_p \sim 2 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, the minimum time for swelling/deswelling of a 1 µm thick ribbon by 40% (corresponding to the volume change upon coiling or uncoiling, see Figure 2 (c)) would require $\tau_p = 8 \text{ ms}$.\[26, 27\] This value is close to the time needed to fully rewind the helix during cooling and fully unwind it during irradiation. The rewinding of the helix after helix inversion during irradiation, i.e. above the volume phase transition, requires a longer time of about 50 ms. This retardation effect indicates, that the diffusion of water out of the gel above the collapse temperature is probably significantly hindered, e.g. by a skin effect. Such a skin effect is not expected upon reswelling. Even at high temperatures, dehydration is only partial and the polymer volume fraction does not exceed 80%. Yet unwinding the helix upon cooling takes only 5 ms, a shorter time than the estimated on from diffusion. These differences indicate that the process does not follow the equilibrium swelling/deswelling trajectory. Non-equilibrium dynamics are also seen when we consider the changes near to the helix inversion point. According to the equilibrium trajectory in Figure 2 (c), most of the change in the radius of the helix takes place within an expansion/contraction interval of maximum 10%. Within this interval the response should be even faster, in the range of 1 ms. However the helix reversal took 5 ms upon cooling and more than 10 ms upon
heating/irradiation most probably the drag force acting on the moving ribbon could retard the large amplitude motion within this range.

6.2.4 Sensing by helical switching

In order to check the non-equilibrium deformation path we plot in Figure 4 the variation in the helix length against its diameter for the slow helix reversal transition from Figure 2 and for the fast helix reversal effected by a pulsed irradiation with laser light. Observation of the two geometrical parameters, length $L$ and radius $R$, allows to record differences deformation mode of the ribbon during the transformation. Figure 4 depicts a huge difference of the trajectories for the equilibrium transformation and the light-induced transformation. While the former follows the same trajectory upon heating as upon cooling, the transformation effected by the light pulse depends strongly on the time parameters of the experiment and the trajectories upon heating and cooling. Obviously, these differences in the mechanical response are related to the ribbon deforming under non-equilibrium conditions. It is prestressed and as such altered in its mechanical properties. During the deformation cycle the prestress changes dynamically. The dynamics can be altered by changing the heating and diffusion rates. By varying the heating cooling cycle (irradiation and bath temperature) the dynamic non-equilibrium can be optimized for maximum deformation. However, it will also be strongly dependent on the gel properties. Variation of the swelling/deswelling properties of the gel, e.g. by ionic strength of the medium, by pH or by binding of an analyte will certainly alter the response characteristics.
Figure 4. Plots of radius $R$ versus length $L$ for the bilayer ribbon during helix reversal. (A) shows the deformation cycle under equilibrium conditions. (B) depicts the deformation cycle for the same bilayer ribbon for the helix inversion cycle under non equilibrium plasmonic heating (80 ms heating interval followed by a 12 ms cooling period). The huge difference in the geometrical trajectory demonstrates the effect of the prestressed state of the ribbon when it is not in its equilibrium configuration.

The comparison demonstrates an enormous sensitivity of the mode of the motion on the way it is affected. Particularly under non-equilibrium conditions the spatiotemporal path can be altered dramatically. Most importantly, this is a cyclic process which can be repeated without changing the response of the hydrogel as long as it is not degraded by ageing. Here this effect is demonstrated on the example of a helix forming ribbon. Although helix inversion by itself is an intriguing observation, it shows especially that the complex interplay of the different deformations can be mastered rather accurately. Moreover, it demonstrates the transformation of a small amplitude change, swelling/deswelling to a large amplitude change that can be observed easily. This principle can be transferred to hydrogel with other geometries and response modes. Short time reactions under non-equilibrium conditions allow fast and repetitive observation of the dynamics characteristic for the specific object. We expect that the response does not only depend on the actuation/irradiation mode, but also on the gel properties. In the present case the actuation and response of the gels can serve as sensing element whose sensitivity can be optimized by the actuation
mode. The nonequilibrium response offers the possibility to sense, by amplitude or frequency sweep, the uptake of an analyte either on the surface of the gold layer or within the gel.

**Figure 5** provides preliminary measurements for detecting small changes in bath temperature or also variation in salt concentration in the medium. We monitor the change in the environment by observing unwinding of the helix in response to a given irradiation frequency. We quantify the sensor property by measuring the helix extension time denoted by $t_1$ (see insert Fig 5A). We found that this parameter is more sensitive that the helix deformation path, in particular in the case of salt-sensing. Indeed, the non-linear dependence of the extension time with the bath temperature indicates a sensitivity range of one tenth of degree. Remarkable, is the salt sensitivity of the extension time which is in the millimolar range. Our measurement is order of magnitude sensitive in comparison to scattering techniques.[28] To use these helical ribbons as selective chemical sensor would requires tethering “receptors” to the helices by chemical of physical activation of their surfaces.

![Figure 5](image)

**Figure 5.** Time required for unwinding of the helix for a given irradiation time depending on the bath temperature (A) and depending on the sodium sulphate concentration (B). The irradiation frequency was on/off 120ms/30ms. A detailed description of the measurement is in the supporting information.
6.3 Conclusion

In conclusion, we have demonstrated experimentally the significance of confined swelling in shaping a flat bi-layer microgel. Through water uptake, the microgel layer expands and deforms by bending into a three-dimensional structure in order to reduce the stresses in accordance with the geometric constraints. We focused on the cylindrical helix and explored in detail the interplay between the geometry and the mechanics. A key point is the strong dependence of the helical radius (curvature) on the ribbon thickness; leading to an interplay of the bending stiffness and the helix radius. This turns out to be of great advantage as it provides versatility in controlling the helix geometry through the fabrication parameters. Even more appealing is the temperature-sensitivity of the gel, which provides an unparalleled control of the helix geometry. This has not only been explored through external heating, but also by internal photothermal heating enabling force-free unwinding and reversal of the chirality of the helix. Our approach offers unique possibilities to probe the deformation dynamics in a regime where inertia is negligible and water viscosity with the ensuing drag force prevails. By photothermal heating the diffusion of water can be modulated with respect to the bending deformation in less than 1 ms. This allows to store or to initiate the release of elastic energy which is subsequently converted into kinetic energy. The latter is dissipated by the fluid leading to motion with a characteristic timescale in the ms range. These new possibilities of morphing three-dimensional microgels with fast dynamics may find applications in fields such as soft-robotics, microfluidics, and artificial microswimmers.
6.4 Experimental section

6.4.1 Synthesis and modification of AuNRs

Gold nanorods were synthesized by a seed-mediated method.[29] All chemicals were purchased from Sigma-Aldrich if not otherwise mentioned. Deionized water (0.1 \(\mu\)S·cm\(^{-1}\), ELGA Purelab-Plus) was used. For the seed solution, 0.60 mL of freshly prepared ice-cold 0.010 M NaBH\(_4\) (99%) aqueous solution was added to a mixture of water (4.2 mL), 0.20 M Cetyltrimethylammonium bromide (CTAB, 5.0 mL, 99%) and 0.0030 M hydrogen tetrachloroauric (III) acid (HAuCl\(_4\), 0.83 mL, p.a.) under vigorous stirring for 2 min. For the growth solution, 0.20 M CTAB (150 mL), 0.050 M ascorbic acid (3.1 mL, 99%) and 0.0080 M AgNO\(_3\) (3.3 mL, 99.99%) were added under stirring to 0.0010 M HAuCl\(_4\) (150 mL). The temperature of the growth solution was kept at 25 °C in water bath, and 0.875 mL of seed solution were injected under rigorous stirring followed by 30 min of stirring and addition of 0.050 M ascorbic acid (2.0 mL) at a flow rate of 0.50 mL/h. Afterwards the solution was stirred for another 30 min. The resultant brownish red solution of AuNRs was centrifuged at 8000 rpm for 40 min in an Eppendorf Centrifuge 5810. The supernatant containing excess surfactant was discarded, and the precipitated AuNRs were collected and re-suspended in water with a final volume of ca. 20 mL.

Thiol functional polyethylene glycol (PEG) polymer (HS-PEG-OH, Mw = 3000 Da, Iris Biotech) was dissolved in ethanol (99.8%) to make a 2.5 mM solution. 10 mL of the solution with redispersed AuNRs were diluted to 100 mL and mixed with 20 mL ethanolic PEG solution under stirring. This solution was sonicated at 60 °C for 30 min and subsequently for another 3.5 h at 30 – 50 °C.[30] After stirring of the solution overnight, it was extracted three times with chloroform (ca. 120 mL, p.a.) to remove CTAB and free polymer. In a second purification step, the extracted solution was
centrifuged for 3 times, each time the supernatant was discarded and the sedimented gold-containing fraction (less than 2 mL) was diluted with dimethyl sulfoxide (DMSO) to 45 mL. After the last centrifugation, the sedimented gold-containing fraction was collected as a concentrated solution of PEGylated AuNRs in DMSO. The modified AuNRs had a longitudinal absorption band maximum at 791 nm (UV-Vis spectrum, V-630, JASCO). Transmission electron microscopy (Libra 120, Zeiss) revealed that the AuNRs had an average diameter of 15.4 nm and length of 60.0 nm, i.e. an aspect ratio of 3.90, see Figure S1.

![Figure S1](image)

**Figure S1.** (a) UV-Vis spectrum of PEGylated AuNRs with inset of TEM micrograph (500 × dilution in water, optical path = 1 cm, scale bar: 100 nm). Optical density (OD) at 791 nm = 1.288, OD at 808 nm = 1.258. (b) Statistics of PEGylated AuNR, 120 particles were analyzed with ImageJ. Red curve is the Gaussian fitting.

### 6.4.2 Fabrication of AuNRs filled microgels

**Table S1** summarizes the composition of the solution for the preparation of microgels. Crosslinker \((N,N'\text{-Methylenebisacrylamide, BIS, 99\%})\) and photo-initiator \((2\text{-Hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone, 98\%})\) were added at a ratio of 1 mol\% relative to \(N\text{-Isopropylacrylamide (NIPAm, 97\%, recrystallized twice in n-hexane)}\). After addition of an appropriate volume of the gold nanorod solution, the light extinction maximum is at 791 nm (longitudinal plasmonic band of the AuNRs). For an optical path length of 1 cm, it resulted in an optical density of 240 at 808 nm.
Table S1. Composition of monomer solution

<table>
<thead>
<tr>
<th></th>
<th>NIPAm</th>
<th>BIS</th>
<th>Photo-initiator</th>
<th>AuNR</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microparticles</td>
<td>57.5 mg</td>
<td>0.783 mg</td>
<td>1.14 mg</td>
<td>57.5 µL</td>
<td>40.6 µL</td>
</tr>
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</table>

The number density of AuNRs in the monomer solution was calculated according to Equation 1 to 3, where $T$ is the transmission, $\sigma$ is the extinction cross-section of AuNRs, $n$ is the number density of AuNRs, $l$ is the optical path, and $OD$ is the optical density.

$$T = e^{-\sigma nl} \quad (1)$$

$$OD = -\log T \quad (2)$$

$$n = 2.3(OD/\sigma l) \quad (3)$$

By assuming $\sigma$ to be $\sim 6100 \text{ nm}^2$ at wavelength of 808 nm for the AuNRs used in the present study,[31] the number density can be calculated to be $3.8 \mu m^{-3}$ for $OD = 100$ solution and $9.1 \mu m^{-3}$ for the $OD = 240$ solution.

The microgel ribbon was fabricated in a non-wetting template made of perfluoropolyether (PFPE), which is the negative replica of a photo-lithographically patterned silicon wafer.[32] In a glove box, a cleaned microscope slide was placed on top of a diced silicon master ($2 \text{ cm} \times 2 \text{ cm}$) produced by photolithography (AMO GmbH), while two pieces of bilayer parafilm (Bemis, total thickness $\sim 200 \mu m$) were used as spacers. Details of silicon masters with $5 \mu m$ etching depth can be found in Figure S2. Other silicon masters are of the same structural design but different etching depths. Perfluoropolyether-urethane dimethacrylate (PFPE, $M_w = 2000$, Fluorolink MD700, Solvay Solexis) was thoroughly mixed with 1 wt% Darocure 1173 (Ciba Specialty Chemicals), which is the photoinitiator. The mixture was then
injected between the glass slide and silicon master until the space was fully filled. Subsequently, the PFPE was cured for 20 min under a UV lamp (366 & 254nm, 2 × 4 W, Konrad Benda) in an argon atmosphere. After curing, the PFPE film was carefully peeled off from silicon master and cut into suitable size (6 mm × 6 mm). The flat PFPE film was prepared by the same protocol between two microscope slides.

![Figure S2](image)

**Figure S2.** Optical micrographs of the silicon masters. The shown masters have an etching depth of 5 µm. The width is 5 µm for all the ribbons. The lengths from (a) to (f) are 10 µm, 20 µm, 40 µm, 80 µm, 160 µm, and 240 µm, respectively. Scale bar: 20 µm.

The fabrication procedure is illustrated in **Figure S3**. A home-made press with quartz window was used for the molding of microgel, and all steps were carried out in a glove box (O₂ < 0.2%). The monomer solution (0.5 µL) was first pipetted on the replicated PFPE film, which was then covered by a flat PFPE film. A weight was applied on top of the flat film to generate suitable pressure (~ 260 kPa) to the mold. The pressure ensures that only separate elements were formed. The microgels were cured by 20 min of UV irradiation (366 & 254nm, 4 W of each wavelength, Konrad Benda). Afterwards the weight was removed, and the mold was peeled off from the flat film. Bi-layered microgels were produced by sputtering a thin gold film (~ 2 nm)
on the sample with a sputter coater (30 mA, 20s, Edwards S150B). The affinity between gold and amide group, as well as physical entrapment provides strong adhesion of the metal layer to the gel surface.[33] Indeed, no delamination of the metal layer was observed throughout all our experiments. The prepared microgels have certain stickiness to the mold after curing. Therefore, an extra step to transfer and release the microgel is needed.

Figure S3. Illustration of the microfabrication process. (a) Micropatterned silicon master; (b) Replicated PFPE mold; (c) Molding of microgel particles; (d) Transfer of microgel particles on adhesive layer (yellow); (e) Released microgel particles in water.

Microscope slides (Corning glass) were cut into squares (25 mm × 25 mm) and cleaned with sonication in isopropanol. 0.5 mm thick PDMS film (Sylgard 184, Dow Corning) was cut into square frame with outer dimension of 15 mm × 15 mm and inner dimension of 10 mm × 10 mm. The cleaned glass slide and the PDMS frame were activated in O₂ plasma (200 W, 20 s, 1 mbar, PVP Tepla 100) and then bound together to form an open chamber. Glycerol (15 µL, 99.5%) was pipetted in the chamber and the PFPE mold with hydrogel particles was placed upside down in the chamber. The whole chamber was then stored in a freezer at -80 °C overnight. Transfer of the microgels was achieved by peeling the PFPE mold off, where the frozen glycerol served as adhesive. The glycerol was subsequently evaporated at 60°C under vacuum (1 × 10⁻² mbar), leaving only microgels in the PDMS chamber.
Deionized water was added to reswell the microgel. To load the microgels into capillary, one end of a plasma-treated rectangular capillary (0.05 mm × 1.0 mm × 50 mm, Vitrocom) was immersed in the chamber, so that the microgels can be spontaneously sucked in by capillary force. The ends of the capillary (200 W, 20 s, 1 mbar) were then sealed and fixed on a microscope slide with a 2-component epoxy adhesive (UHU GmbH).

### 6.4.3 Actuation and observation of microgels

The capillary containing microgels was placed on a home-made Peltier stage for temperature control. The Peltier stage was mounted on an optical microscope stage (VHZ-100UR, Keyence). The temperature of sample was controlled with an accuracy of ± 0.1 °C. Images were taken after the sample was equilibrated for more than 5 min at different temperatures. The images of the microgels were adjusted with ImageJ; the radius and length of the helical microgel were measured manually.

The swelling degree of a ribbon-shaped microgel without sputter coating was measured at different temperatures with the same experimental setup shown above. Three characteristic images are shown in Figure S4. The length of the ribbon was measure with ImageJ. 10 different microgel particles were measured at each temperature to acquire the swelling curve in Figure 1. The linear swelling degree is acquired by normalizing the length of the ribbon at different temperatures to the length of the mold, i.e. 80 µm. The optical contrast is relatively low, since the refractive indices of hydrogel and water are close.
Using the experimental setup mentioned above, the helical microgel was actuated with a near infrared (NIR) laser (808 nm, 2.5 W, Roithner Lasertechnik) which was focused to the middle of field of view with an incident angle of ~ 40 °. This results in an elliptical footprint (~ 1 mm × 1.5 mm) with an intensity of 1.7 W·mm² as calibrated by an optical power meter (PM200, Thorlab). The laser was modulated with 1 ms temporal resolution. Videos were recorded with a high speed camera (Miro M310, Phantom) at 1000 or 2000 frames per second. A short pass filter (700 nm, OD 4, Edmund optics) was used to protect the camera from scattered laser. Acquired videos were contrast-enhanced and analyzed with ImageJ.

### 6.4.4 Estimation of equilibration time and temperature

The characteristic equilibration time of temperature change inside a microgel particle depends strongly on the size of the particle with a power law \( \tau = l^2 / D \), since it is essentially a thermal diffusion process. Utilizing the thermal diffusivity of water at 25 °C, i.e. \( D_{\text{thermal}} = 0.14 \text{ mm}^2\cdot\text{s}^{-1} \), the characteristic time of thermal equilibration can be approximated for the rectangular tubing (thickness ~ 50 µm) to be roughly 0.18 s.
and for the microgel ribbon (H \sim 1 \mu m) to be around 7 \mu s. This can be compared with the diffusion process of gel network that results in volume change, which has a diffusion coefficient \( D_{\text{diffusion}} \sim 2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \) at \( \Delta T = 3 \text{ °C} \) (\( \Delta T \) is the difference between set temperature and LCST) [1] and is thus orders of magnitude slower than the thermal equilibration. For instance, it can be estimated that 25 milliseconds are needed for the gel to shrink by 0.5 \mu m under the abovementioned condition. It can also be concluded that the thermal equilibration is always much faster than the volume change inside the microgel due to the huge difference between the two types of diffusivity, so that the temperature change can be considered as an instantaneous process when dealing with the volume change of the gel. Besides, the response dynamics can be strongly enhanced by reducing the dimension of the hydrogel, owning to the fact that the characteristic time of swelling depends on the square of the characteristic length of the microgel.[34]

**Figure S5.** Change of pitch versus temperature at equilibrium. Inset: helix at equilibrated state upon laser irradiation. Scale bar: 15 \mu m.

Upon laser irradiation, the temperature of the microgel is increased, so that it undergoes inversion of helicity. At steady state upon irradiation, the inverse helix has a pitch of 11.4 \mu m which corresponds approximately to the data point at 34 °C (pitch:
11.3 µm) in Figure S5. This indicates that the temperature reached is roughly 34 °C by the laser irradiation.

6.4.5 Effects of salt and temperature on the actuation

The helical microgels were loaded into a shorter capillary (length = 2 cm, height = 50 µm) as described before, and the ends of the capillary were kept open. The capillary was then placed on a microscope slide for observation. The videos were immediately captured to avoid significant water evaporation by a high-speed camera with a frame rate of 2000 fps. Subsequently, the capillary was immersed in abundant Na₂SO₄ solutions (99.0%, 0.01M and 0.02M). After equilibration of the ions inside the capillary (> 48 hours), the same helix was used again for video record at the same modulation. The videos of the helix under 120 ms – 30 ms stroboscopic modulations can be found in supporting videos. This modulation was chosen as it provides inversion of the chirality at different salt concentrations.

For the temperature-dependent experiments, the capillary containing microgel was sealed by epoxy glue and fixed on a microscope slide. The bath temperature was controlled by the peltier stage beneath the slide with an accuracy of ± 0.1 °C. Videos were recorded by the high-speed camera with a frame rate of 2000 fps. The stroboscopic modulation was 120 ms (on) – 30 ms (off). The time for the helix to reach the fully stretched shape (t₁) was measured using ImageJ. The error bar in Figure 5 is resulted from the temporal resolution of the video and the inaccuracy in determining the frame of helical inversion.
6.5 References


7. Soft microrobots by non-equilibrium actuation via plasmonic heating

7.1 Introduction

Self-propelling microobjects or colloids are a topical research subject for soft matter microrobots as well as for devices that mix, sort and circulate fluids. [1-4] These microswimmers are expected to open new avenues for a biomimetic soft matter microtechnology. Recent literature on synthetic or man-made microswimmers focuses mostly on thermo- and diffusiophoresis for the propulsion. Yet, examples of self-propelling microorganisms in nature teach us also other concepts for propulsion based on complex body deformations. These organisms propel by a shape deformation with distinct spatiotemporal patterns, which consists of a rotational forward movement or a cyclic beating comprising a distinct forward and reverse stroke. The actuation is achieved by rotary motors like in Escherichia coli,[5] or by dynein motors that produce bending waves like in sperms and in ciliated protozoa,[6, 7] as well as whole body deformations as observed for marine phytoplankton Eutreptiella gymnastica.[8]

Actually within a strict definition, directional swimming may be regarded as a forward motion by shape deformation.[9-11] For the sake of clarity we will use the term ‘morphing microswimmer’ here for locomotion by shape deformation. In contrast to a macroscopic swimmer, such locomotion of small, lightweight microorganisms must take account of the fact that it takes place at very small Reynolds numbers, Re \(\approx 10^{-4}\). In a Newtonian fluid and at Re < 1, inertia and

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3 This chapter is adapted from the publication:
Authors’ contributions: AM and MM designed the project. HZ carried out the experiments and collected the data. All authors analyzed and interpreted the data. HZ prepared the draft. AM and MM critically revised the manuscript.
momentum become insignificant when compared to the viscous resistance of the medium. Under these conditions propulsion by a repeated body shape deformation is only possible, if it is not based on identical forward and backward strokes. Precisely, this involves cyclic shape deformation whereby any point on the body traces a loop in space thanks to the different shape configurations in each half-cycle. This famous problem has been pointed out originally by Purcell and is often discussed as the scallop theorem.\cite{9} In order to fulfill this requirement a body deformation must be composed from different deformation modes that follow a different time dependence on the forward and the shape recovery stroke, such like bending and torsion or orthogonal bending modes. (see also \cite{12} for a review) Swimming microbes naturally follow this requirement and it is also mandatory for an artificial microswimmer. Additional requirements for the design of such a morphing microswimmer are a source of energy, sufficiently fast action, and a control mechanism for the repetition as well as for directing the motion.

As a consequence of these multifold requirements, an artificial morphing microswimmer is notoriously difficult to realize. To our knowledge, only three examples have been reported so far. One example is a flexible flagellum-like tail of magnetic particles bridged by DNA molecules and end-linked to a red blood cell as a head. The structure could be actuated and directed by an oscillating external magnetic field.\cite{13} The second example is a biohybrid swimmer that consists of a polydimethylsiloxane filament on which cardiomyocytes have been adhered. The cardiomyocytes contract periodically and deform the filament to propel the swimmer.\cite{14} Only recently, a rather advanced fully synthetic material design was reported where a liquid crystalline elastomer with photoisomerizable azobenzene groups was propelled by intrabody shape changes as a traveling wave along the
object.[15] Irrespective of the fact, that the objects had to be sufficiently large to see the optical pattern, directed motion was fully controlled from outside. Yet, the report can be seen as a major breakthrough because the body shape deformation was caused by a peristaltic motion with the high rates, necessary for the propulsion of such small objects.

In view of this state of knowledge, it remains a challenge to devise new expedient actuation mechanisms for a morphing microswimmer with fast cyclic sequences of shape configurations leading to translational motion. It has been our objective to design an actuation principle that enables further miniaturization and is not bound to the spatial resolution of an external field variation and where on one side the modes of motion are programmed by the structure and on the other side can be controlled by the energy uptake. For this purpose we focused on a rotating helix as shown in the scheme of Figure 1. Different than in the case of the bacterium Escherichia coli, the flagellum cannot simply rotate because we lack a suitable rotary motor. So the forward propulsion must be generated by conformational changes, i.e. body shape variations, which in turn can be exploited for rotation. Necessarily such a body shape deformation must comprise a cyclic process at whose end the object is again in its starting conformation. The first deformation, e.g., unwinding of the helix, must be followed by shape restoring deformations that are not reverse in space in order to cause the required disparity in the viscous forward and backward drag. As pointed out above, this requires conformational changes that are composed from different modes that follow a different time dependence on the forward and the shape recovery stroke. We will demonstrate below, that the combination of different deformation modes can be achieved by exploiting the transformation of volume changes to bending modes as it is well known for heterogeneously structured objects.[16-18] In order to achieve the
necessary disparity in the forward and the backward mode we operate the system strongly off equilibrium, under conditions where small variations in the input of energy cause strong variations in the response. A key point has been to achieve fast and repetitive response without changing the state of the environment. For this, we exploit the light effectuated thermal response, i.e., swelling/deswelling, of a purposefully designed hydrogel body. We demonstrate that the out of equilibrium response can yield precise and fast shape deformations with rigorous and versatile control of complex motility modes as it will be needed for mobile microscale robots.

Figure 1: Illustration of the locomotion generated by non-reciprocal deformations of the helix.

Mechanical actuation in nature is frequently caused by swelling and deswelling of hydrogels. In cases like the hydraulic opening and closing of a pine cone this is not tied to mechanisms of living matter. Still the motion can be fast and complex.[19, 20] Intrigued by these examples researchers developed an increasing interest in artificial hydrogel actuator systems that exploit swelling/deswelling in response to an external stimulus.[21, 22] Mostly these systems utilize the volume phase transition of polyacrylamide derivatives and focus on the shape variance between end states in equilibrium.[23] So far, dissipative internal stimulation has been reported by means of an oscillatory chemical reaction [24] and theoretically evaluated for its potential to design morphing microswimmers.[25, 26] Yet, most of these systems suffer from a
slow stimulus, i.e., change in temperature, pH or ionic strength, a slow, diffusion-controlled volume response of a hydrogel, [27, 28] and the requirement for a cyclic motion that results in a net translation.

In this context we focus on thin poly(N-isopropylacrylamide) microgel bodies that undergo bending and torsional motions upon swelling and deswelling. Very fast temperature jumps localized to the volume of the thin microgel body are achieved by photothermal heating with gold nanorods that have been embedded within the temperature responsive poly(N-isopropylacrylamide) (PNIPAm) microgel. Irradiation by near IR-light and conversion to heat has been engineered to enable jumps in temperature by up to more than 20 °C within milliseconds and less (see Experimental section). Because the heating is restricted to the inner volume of small microgel objects, they also cool down quickly by fast heat transfer to the surrounding bath when the heating is ceased. Because swelling and shrinkage are diffusion controlled and cannot follow fast temperature changes in time, the volume change can be effectuated out of equilibrium. Under non-equilibrium conditions, the time dependent volume change is controlled by the actual dimensions of the microgel, i.e. the diffusion path, and varies with the dimension of the microgel object. As a consequence volumetric changes of anisometric gels tend to be inhomogeneous. The resulting stress results in shape deformations and the accumulation of elastic energy that is released with a delay. In principle, all these different effects can be well controlled, i.e., temperature change and its rate, dynamic inhomogeneity in swelling and shrinking, as well as their transformation to bending and torsional modes, and, finally, the built up of elastic stress, that is released in a retarded manner. Below we will demonstrate by the example of a simple hydrogel ribbon in water, how to control the actual motion, i.e., volume change, bending, and torsional motions in their
direction, amplitude, and speed. This can be done in such a way, that the ribbon not only adopts a purposeful spatial configuration, but also undergoes cyclic variations in its spatial configuration that follow a different forward and backwards path in space and thus creates a thrust to propel the microgel body in water.

7.2 Results and discussion

Microgels were fabricated by the PRINT technique, known to be effective in controlling the composition, size and geometry (Figure S2 and S3).[29] The gelation reaction was carried out in micromolds with a homogeneous DMSO solution of NIPAm monomer, crosslinker (N,N'-Methylenebisacrylamide), photoinitiator and Au-nanorods. The maximum of the longitudinal plasmon absorption was at 791 nm. The later were grafted beforehand with poly(ethyleneglycol), PEG. The PEG-brush enables dispersion and trapping of the nanorods within the PNIPAm mesh. The number density of the gold nanorods was adjusted to 9 AuNRs per cubic micrometer, which corresponds to a volume fraction of < 0.01% and an average rod to rod distance < 500 nm. When the gel objects as prepared with DSMO were brought into cold water, a better solvent than DMSO, they swelled by 61% (in one dimension, e.g. length). When the water was heated above the collapse temperature they shrunk by 9% relative to the as-prepared state. Based on the degree of swelling in water and the molar ratio of crosslinker to monomer, we estimate the degree of polymerization between crosslinks to about 70 monomer units corresponding to \(<r> = 5 \text{ nm}\). This mesh size was confirmed by infiltration experiments with vitamin B12, cytochrome C and blue dextran yielding colored gels only for the two smaller dyes (see Experimental section). Suspended gel microobjects were studied by optical
microscopy regarding their reaction to laser light with a spot diameter of about 1 mm. The large spot diameter ensures homogeneous irradiation of the much smaller objects. For experimental details and the image analysis, we refer to the *Experimental section*.

### 7.2.1 Response of a microgel disk under stroboscopic irradiation

In order to evaluate the response of the gels we studied laser actuation of a hydrogel disk with an as-prepared diameter of 30 µm and a thickness of 5 µm. Corresponding to the concentration of 9 AuNRs per cubic micrometer, the OD in the normal direction was 0.12. Upon slow heating from outside, the equilibrium diameter changed continuously, corresponding to the volume phase transition of the nonionic hydrogel. Upon irradiation by laser-light at 808 nm and as the power was slowly increased, the diameter showed a sharp transition from the swollen to the collapsed state at an irradiation power of 1.7 Watt·mm$^{-2}$ (see *Experimental section Figure S8* (a) & (b)). The sharp transition can be expected because the volume concentration of heating elements (AuNRs) increased upon the collapse. When the disk was stroboscopically irradiated at high laser power (1.7 Watt·mm$^{-2}$) and frequencies in the range of 0.5 to 5 Hz, heating intervals were too short to raise the temperature sufficiently for a full collapse. Because of the fast heat transfer to the outside of the gel body, the intervals between the illumination times allowed efficient cooling (the water temperature was controlled externally at 20 °C, a temperature well below the transition temperature of the PNIPAm gel). In order to gain insight into the course of temperature changes during stroboscopic irradiation we mounted a thermistor in a capillary filled with a solution of AuNRs as well as in a corresponding gel layer (*Experimental Section Figure S7*). For a solution, the temperature varies sinusoidal with time as depicted in *Figure 2 (a)* as it can be expected because of the ultrafast light to heat conversion in the nanorods (ps) and the fast heat transfer to the
surrounding water (ns). In a gel, the temperature tends to increase in an accelerated manner, because the increase in the density of the nanorods (Experimental section Figure S7). Figure 2 (b) depicts the volume change as expressed by the variation in the diameter of the gel disc. For the smallest on-off frequency, the maximum change in diameter of 7 µm at 0.5 Hz corresponded to a $\Delta T \leq 6.2 \, ^\circ C$ according to the equilibrium volume phase transition curve (Experimental section Figure S8). Volume change starts with high rate and then slows down within the actual actuation cycle. The observation that the volume change and the temperature change are obviously not synchronized, although they occur in phase, gives a first indication that the volume transition change takes place out of equilibrium. The non-equilibrium dynamics becomes even more evident, when one considers the frequency changes of the initial rates of the shrinkage and expansion of the disc diameter. While the rate upon shrinkage does not change (20 µm·s⁻¹), the rate upon expansion is largest for long stroboscopic intervals (37 µm·s⁻¹).

A strong deviation from the equilibrium transition course might be surprising taking into account that according to the collective diffusion model,[27] the time needed to transport water molecules out of a gel of 5 µm thickness, that shrinks linearly by 10 % can be estimated to about 25 ms. Such a short diffusion time should allow near-to-equilibrium repetitive actuation amplitudes for irradiation cycles within the range of one second and even less. However, another cause for non-equilibrium dynamics became evident when we imaged the surface of a quickly shrinking hydrogel film by a confocal microscope. Upon irradiation the surface of the film started to wrinkle as shown by the scattering contrast in Figure 2 (c, insert). Wrinkling indicates the formation of a skin layer as it is expected when the water escapes the surface layers more quickly than from the inner volume of the microgel object. The wrinkles and
thus the denser surface layer only vanished when the gel was practically fully collapsed. The denser surface layer controls the diffusion of water out of the gel and thus its collapse. In contrast, reswelling is promoted by the elastic stress of the swollen outer gel layers. Hence, even for the only 5 µm thick disks we can realize volume variations that do not follow the equilibrium volume/temperature transition but yield a dissipative Carnot-Cycle as depicted in Figure 2 (d).

**Figure 2.** (a) Temperature variation in an AuNR solution under modulated irradiation. The modulations have equal on/off durations. Laser intensity: 0.34 W·mm⁻², optical density of the solution at 808 nm: 76.4 (measured on a cuvette with an optical path: 1 cm), for an irradiated volume of the solution of 1 mm³, the number density of AuNRs is 2.9 µm⁻³. (b) Diameter variation of a disk-shaped microgel (as-prepared diameter: 30 µm, thickness: 5 µm) under modulated irradiations. (c) Variations of the initial expansion and contraction speeds with the strobe frequency. The inset depicts a confocal image taken in reflection mode of the surface of a substrate-supported hydrogel layer showing a transient instability as it evolves during an intense irradiance. (d) Illustration of the diameter variation of a disk under equilibrium heating (blue line) and upon stroboscopic irradiation under non-equilibrium dynamics (red cycle). A Carnot-like cycle results as the temperature changes faster than the volume.
7.2.2 Bending deformation induced by heterogeneous volume changes

Morphing rates of 40 μm·s⁻¹ are already in the range of natural pulsating systems like a beating heart cell or microorganisms like a paramecium.[30] Even faster rates can be realized, if the volume change is exploited to cause bending deformations. This is demonstrated below at the example of an L-shaped microgel object with arms that were much longer than their thickness (Figure 3). In order to effectuate bending or buckling the volume change must, however, be locally different within the hydrogel object. Hence, concave bending will be observed, if the upper side of a sheet expands less than its lower side. Heterogeneous volume changes and thus bending can be effectuated, when the swelling or shrinkage is kinetically controlled, i.e. out of equilibrium. This is demonstrated in Figure 3 (a) and (b). When the L shaped object was collapsed by slow temperature raise under equilibrium conditions, it shrunk homogeneously without bending (Figure 3 (a)). If, however, the collapse was effectuated by fast temperature changes under non-equilibrium conditions, shrinkage varied throughout the structure depending on the surface to volume ratio in the different sections of the L-shaped body and the L responded by bending the arms together like a tweezers (Figure 3 (b)). Here shrinkage is particularly anisometric for the volume element that connects the two arms (a more detailed analysis is reserved to a special publication). The different states of the L-ribbon in Figure 3 (b) depicts the deformation cycle as observed upon stroboscopic irradiation with periods of 0.05 – 0.05 s. The time-dependence of the variation of the end-to-end distance, denoted as ΔA, demonstrates a remarkably large distance variation of 156 μm at 2.5 Hz and 122 μm at 5 Hz. The peak velocities were close to 2000 μm·s⁻¹ at an on/off period of 20 ms and lower at lower frequencies (Figure 3 (d)). Also in this case, the rates of the shape variation depend strongly on the irradiation frequency. While at high frequency,
the rate of expansion was slower than the rate by which the ends were moved together, at low frequencies, the expansion was nearly four times faster.

The data from Figures 2 and 3 demonstrate that the course and the rate of the shape change depends on the rate and the depth of the temperature jump but also on formation of diffusion barriers, as the factors which determine the deviation from the equilibrium transition line.

**Figure 3.** (a) Optical micrographs of the L-shaped microgel in equilibrated state at different temperatures. (b, c, d) Photothermal actuation of an L-shaped hydrogel ribbon (arm length = 100 μm, width 10 μm, thickness 5 μm). (b) Characteristic optical images at different stages of the configurational transformation under laser modulation. The modulation has equal on/off periods (50 ms each). (c) Variation of the end-to-end amplitude as a function of time during irradiation and recovery. (d) Speed of the motion of the ends towards each other and away from each other.
7.2.3 Helical micromotor

Having understood qualitatively the intriguing motion, that can be achieved by the fast heating and the non-equilibrium response and taking advantage of the amplification of the amplitude of motion when a volume change is transformed into bending, we designed a microgel object that can undergo bending also under equilibrium conditions. This should allow an even more rigorous and broader control of the motion. Ribbon or stripes of the AuNR equipped hydrogel were coated with a gold skin of a few nanometers in thickness. Different than in the case of the L-shaped ribbon, the coated hydrogel will bend also under equilibrium conditions when the swelling is changed compared to the state when the gold skin was applied (as prepared in the mold). Swelling in cold water causes expansion of the hydrogel layer, while the gold layer is in first instance invariant. The volume collapse of the hydrogel at elevated temperature causes shrinkage of the hydrogel compared to the initial state. In the first case the gold surface is bent in a convex way, in the second case in a concave way. Because bending can occur into the two main directions,[31] i.e. the 80 µm long axis and the 5 µm short axis, an elliptical double curved dome shape is expected as shown in Figure 4.

Figure 4. The helix direction is controlled by the two principle curvatures and the mismatch of $\varphi$ towards the length axis of the ribbon. The optical micrograph shows the helical microgel at 32 °C.
For such a stripe and depending on the width to length ratio and the thickness of the two layers, it is well known, that bending can be preferentially around the long axis of the stripe, resulting in the formation of a tube or around the short axis, resulting in the formation of a two-dimensional spiral. In intermediate situations causes formation of a helix. Whether the helix turns right or left handed depends on small mismatches of the main stress axis and the long axis of the stripe [16] caused by inhomogeneity in the thickness, the bulk structure or even edge effects.[32, 33] We have controlled whether a spiral or a helix was formed by the thickness of the applied gold skin (see also Experimental section Figure S9). Figure 5 (a) depicts optical micrographs of the helix formed by a hydrogel ribbon with a thickness of 1 µm, a width of 5 µm, and a length of 80 µm that was coated on one 5µm × 80µm face by a gold layer of 2 nm thickness. In cold water the hydrogel expanded in volume by a factor 5 and the particular ribbon formed a right handed helix with the gold layer facing inside. In the particular case shown in Figure 5 (a), the helix length at 20 °C was 72 µm compared to a contour length of 80 µm, and the helix comprised three turns.

When the temperature was raised slowly the hydrogel layer contracted and the helix pitch increased from 5 µm at 20 °C to 31.9 µm at 30.5 °C. The same transformation could be effectuated dynamically when the sample was irradiated by laser light at 808 nm. Because the plasmon resonance of the gold skin is shifted to lower wavelength it contributed at 808 nm only 0.092 to the optical density of the 1 µm thick microgel layer containing 9 AuNRs per cubic micrometer, OD = 0.024. Taking into account that the heat conversion efficacy of the gold nanorods is at least an order of magnitude larger than that of thin gold layer,[34, 35] we consider that the heating effects were
only slightly enhanced by the gold layer, also gradients in swelling within the 1 µm thick hydrogel layer can be neglected.

Comparison of the optical micrographs in Figure 5 (a), i.e., before internal heating by light and 5ms after switching on the irradiation, demonstrates the response of the helical shape. The change can be characterized quantitatively by the time dependence of the total length and the diameter of the helix. This is shown in Figure 5 (b) for a cycle within a repetitive heating and cooling sequence with an on-time of 16 ms followed by an off-time of 20 ms at 808 nm and 1.7 W·mm⁻²; the external temperature was set to 20 °C. Each on-off cycle comprises two deformation modes, contraction involving volume change, and bending which occurs at a nearly constant volume. Upon heating the helix unwinds, within 15 ms, and at the onset of cooling, it snaps back within 8 ms to its initial radius. The fact, that the shape conversion can be effectuated by raising the temperature of the bath in equilibrium (see Figure 5 (c)) as well as by dynamic heating from inside allows evaluation of the temperature during the irradiation caused temperature changes. The minimum and maximum helix stretching in the stroboscopic irradiation cycle ΔL = 76 - 72 µm corresponded to a ΔT of less than 10.5 °C (see Figure S11).

The minimum response time for swelling and deswelling the hydrogel layer by 100 nm in thickness (10 vol%) can be estimated form the diffusion coefficient of water to be less than 1 ms. The slower response times observed in the experiment indicate retardation by the formation of a diffusion controlling skin layer and by the viscous drag on the ribbon. Both effects do cause deviation from the in-equilibrium transition path. The conclusion that the deformations occurs off-equilibrium is confirmed by the geometrical description of the cycle in Figure 5 (d). The figure maps the changes in
the diameter relative to length during one power-on and recovery stroke as recorded with a time resolution of 1 ms. During the first 2 ms of irradiation, the helix even contracted in length with a minor change of its diameter. By contrast, during the remaining 14 ms of irradiation, the helix unwound and the diameter increased while the length extended to approach the contour length of the ribbon. Once the light was switched off, again an initial length contraction was followed by twisting of the helix at rather constant length. It can be noted that the sandwich structure of a metal-film on a hydrogel enabled on one side an improved control and predictability of the volume-to-bending deformation and that on the other side, the motion can still be manipulated by non-equilibrium effects even for the rather thin hydrogel film.

Figure 5. Actuation characteristics of a microgel ribbon helix under stroboscopic irradiation. (a) Micrographs from time-lapse videos of the helix during irradiation. (b) Instantaneous helix length and diameter during one irradiation cycle. Red indicates when the light is on while the blue corresponds to when the light is off. (c) The temperature dependent pitch change of the helix in equilibrated state. (d) Time evolution of the angular displacement as measured by a time-resolved sequence of time-lapse videos over 5 cycles. (d) The trajectory of the shape
deformation in phase space: the helix length vs. diameter during a 16 ms-power stroke followed by 20 ms-recovery period at intervals of less than 2 ms. (*) indicates the starting point at 20 °C.

In summary, Figure 5 (d) shows that not only the time dependencies of the forward and backward motion are different, but also that the geometrical paths are different. Such a non-reciprocal deformation has been cited above as an essential condition for swimming at low Reynolds numbers. Indeed photothermal switching resulted in a quite remarkable double rotation of the helix, which fulfilled the expectation for a directed swimming motion: this is most evident, when the morphing helix is confined in the rectangular capillary for microscopic observation. The confinement within two glass surfaces forces the helical ribbon to stay in the observation plane, but furthermore, the helix presents a freely swimming object. Irradiated by the 16/20 ms on-off sequence, the helix rotates around an axis normal to the long axis and with a much higher rate around its long axis. In Figure 6 (a), the rotation angles have been denoted Ω and θ. Movies of the actuated helix are presented in the Experimental section. Figure 6 (b) depicts the time dependence of Ω and θ with regard to the on-off steps. The rotation around the normal of the main axis of the helix clearly displayed a sequence of forward and backward steps with a backward step that was smaller than the forward step. The averaged velocity of multiple steps resulted to 31 °/s. For the rotation around the principal axis of the helix, we expect that it is composed of forward and backward steps. Winding of a right handed helix is effectuated by right hand twist. Correspondingly unwinding of a right handed helix requires a left handed twist. So the helix should also rotate around its long axis in an oscillatory way. Although it is difficult to determine the rotational direction in an unambiguous way from the optical micrographs, this is in agreement with the captured videos that give evidence about a forward and backward turn. For the net rotation we determined an
angular velocity of $590 \pm 50^\circ/s$ from the time lapse video. Evidently, the chirality of the helix defines the direction of rotation. Noteworthy here is that the ratio of the mean angular velocities correlates to the diameter of the helix divided by its length, thereby suggesting coupling between the two orthogonal rotations.[36]

**Figure 6.** (a) Upon periodic irradiation and the associated fast heating and cooling, the gel object revolved simultaneously around two principal axes of the cylindrical helix denoted by the angle $\Omega$ on the long axis and $\theta$ around the normal to the long axis at the center. (b) Time evolution of the angular displacement for both rotations as measured by a time-resolved sequence of optical micrographs. See the Experimental section for details. Each On/Off cycle of irradiation lasts 36 ms, and the laser is on for 16 ms.

If the helix ribbon in water, i.e. at very low Reynolds number, undergoes a net rotation into one direction, it should necessarily translate forward. This is the mechanism of flagellar propulsion observed for many microorganisms. In the case discussed above the thrust is, however, diverted to a rotation around the normal axis. Microorganisms control the directionality by the drag of their body and by employing counter-rotating couples of flagella. In an analogous approach we succeeded to navigate the oscillating helix by contact to a flat wall that obstructs the rotation around the axis normal to the helix direction. **Figure 7** demonstrates how the rotational motion of the helical ribbon is directed to yield a straight forward motion.
The helical ribbon translates along the wall at a velocity of 24.7 \( \mu m\cdot s^{-1} \), a rate that is comparable with that of helical bacteria such as \textit{Spirochaeta}.\cite{37, 38}

![Figure 7](image)

\textbf{Figure 7.} Directing the rotational motion to a linear translocation when the oscillating helix is confined close to a flat wall that impedes the rotation around the axis normal to the helix direction. In this case, the helical ribbon translates along the wall at an on/off frequency of 10/20 ms and a light intensity of 1.7 W\cdot mm\(^{-2}\). The speed of the longitudinal movement was 24.7 \( \mu m\cdot s^{-1} \) — a rate comparable to that of slow microorganisms. The helix contour length is 160 \( \mu m \), the dashed line indicate the wall position.

\textbf{7.3 Conclusion}

In conclusion, we have shown for the purposefully shaped micro-hydrogels that the kinematics of a cyclic body shape variation can be tuned to differentiate between the forward and the backward motion. Thus, the first deformation stroke (upon heating) is not reciprocated by the second deformation stroke (during cooling), even though the cycle ends up at its starting configuration. Based on this, we have designed a light-fueled and light-controlled microswimmer that can rotate and move forward by its body deformation. Swimming by body shape deformation is distinguished by versatility and control from the motion of a compact body that is self-propelled by thermophoresis\cite{39}, diffusiophoresis,\cite{40} or jetting.\cite{41} Hence, the data shown so far point out further perspectives to design the modes, sequences, and amplitudes of complex body deformations of small hydrogel objects precisely and purposeful.
Moreover, the locally controlled plasmonic heating exploited in this study for microgel actuation can be easily transferred to liquid crystalline elastomers.[15] Consequently, the self-propulsion of microgels by dynamic control of shapes through photothermal heating provides an exciting avenue for developing soft micro-robotics in biomedical or biomechanical applications. In first instance, this approach may be useful for designing new microfluidic devices that can mix, sort and circulate fluid.

In detail, plasmonic heating of purposefully shaped micro hydrogels with embedded gold nanorods enabled a highly differentiated control of shape deformation. Regulation of the length, intensity and sequence of IR-light pulses, allows controlled motion sequences. As the objects are heated from inside, fast upward but also fast downward temperature jumps are feasible. The latter is possible, because the bath around the micro hydrogels is not heated and can dissipate the thermal energy with negligible or imperceptive warming. As a consequence, the volume change can be operated at non-equilibrium conditions, because of the imparity of heat and mass diffusion rates as well as because of heterogeneous shrinking dynamics. As a consequence one can control not only the time response but also the transformation of volume changes to bending and distortion modes. Pre-stressing to a helical ribbon could be devised by covering a hydrogel micro-ribbon with a thin gold layer. Swelling or deswelling of the hydrogel layer caused formation of a helical configuration. The pre-stressed state deformed already at small changes in the volume and thus provided a more accurate and sensitive control of the kinematics of the movement. On the one hand, the actual movement of the helical ribbon can be manipulated by adjusting the imbalance of the temperature jump rates and the shrinkage/swelling response rates. On the other hand, the response rate depends also on the path of motion, i.e., the viscous drag is influenced by the orientation of the anisometric microgel relative to
the direction of motion. For example, a forward stroke with the ribbon oriented face-on to the motion direction will experience a different viscous drag than a backward stroke, when the ribbon is oriented edge-on relative to the motion.

7.4 Experimental section

7.4.1 Synthesis and modification of AuNRs

Gold nanorods (AuNRs) were synthesized by a seed-mediated method.[42] All chemicals were purchased from Sigma-Aldrich if not otherwise mentioned. Deionized water (0.1 µS·cm⁻¹, ELGA Purelab-Plus) was used. For the seed solution, 0.60 mL of freshly prepared ice-cold 0.010 M NaBH₄ (99%) aqueous solution was added to a mixture of water (4.2 mL), 0.20 M Cetyltrimethylammonium bromide (CTAB, 5.0 mL, 99%) and 0.0030 M hydrogen tetrachloroauric (III) acid (HAuCl₄, 0.83 mL, p.a.) under vigorous stirring for 2 min. For the growth solution, 0.20 M CTAB (150 mL), 0.050 M ascorbic acid (3.1 mL, 99%) and 0.0080 M AgNO₃ (3.3 mL, 99.99%) were added under stirring to 0.0010 M HAuCl₄ (150 mL). The temperature of the growth solution was kept at 25 °C in water bath, and 0.875 mL of seed solution were injected under rigorous stirring followed by 30 min of stirring and addition of 0.050 M ascorbic acid (2.0 mL) at a flow rate of 0.50 mL/h. Afterwards the solution was stirred for another 30 min. The resultant brownish red solution of AuNRs was centrifuged at 8000 rpm for 40 min in an Eppendorf Centrifuge 5810. The supernatant containing excess surfactant was discarded, and the precipitated AuNRs were collected and re-suspended in water with a final volume of ca. 20 mL.

Thiol functional polyethylene glycol (PEG) polymer (HS-PEG-OH, Mw = 3000 Da, Iris Biotech) was dissolved in ethanol (99.8%) to make a 2.5 mM solution. 10 mL of
the solution with redispersed AuNRs were diluted to 100 mL and mixed with 20 mL ethanolic PEG solution under stirring. This solution was sonicated at 60 °C for 30 min and subsequently for another 3.5 h at 30 – 50 °C.[43] After stirring of the solution overnight, it was extracted three times with chloroform (ca. 120 mL, p.a.) to remove CTAB and free polymer. In a second purification step, the extracted solution was centrifuged for 3 times, each time the supernatant was discarded and the sedimanted gold-containing fraction (less than 2 mL) was diluted with dimethyl sulfoxide (DMSO) to 45 mL. After the last centrifugation, the sedimanted gold-containing fraction was collected as a concentrated solution of PEGylated AuNRs in DMSO. The modified AuNRs had a longitudinal absorption band maximum at 791 nm (UV-Vis spectrum, V-630, JASCO). Transmission electron microscopy (Libra 120, Zeiss) revealed that the AuNRs had an average diameter of 15.4 nm and length of 60.0 nm, i.e. an aspect ratio of 3.90, see Figure S1.

**Figure S1.** (a) UV-Vis spectrum of PEGylated AuNRs (500 × dilution in water, optical path = 1 cm). OD at 791 nm = 1.288, OD at 808 nm = 1.258. (b) Statistics of PEGylated AuNR aspect ratio with inset of TEM micrograph (scale bar: 50 nm), 120 particles were measured with ImageJ.
7.4.2 Fabrication of AuNRs filled microgels

Table S1 summarizes the composition of the solution for the preparation of microgels. Crosslinker (N,N'-Methylenebisacrylamide, BIS, 99%) and photo-initiator (2-Hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone, 98%) were added at a molar amount of 1% relative to N-Isopropylacrylamide (NIPAm, 97%, recrystallized twice in n-hexane). After addition of an appropriate volume of the gold nanorod solution, the light extinction maximum is at 791 nm (longitudinal plasmonic band of the AuNRs). For an optical path length of 1 cm, it resulted in an optical density of 240.

<table>
<thead>
<tr>
<th>Microparticles</th>
<th>NIPAm</th>
<th>BIS</th>
<th>Photo-initiator</th>
<th>AuNR</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.5 mg</td>
<td>0.783 mg</td>
<td>1.14 mg</td>
<td>57.5 μL</td>
<td>40.6 μL</td>
<td></td>
</tr>
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</table>

The number density of AuNRs in the monomer solution was calculated according to Equation 1 to 3, where \( T \) is the transmission, \( \sigma \) is the extinction cross-section of AuNRs, \( n \) is the number density of AuNRs, \( l \) is the optical path, and \( OD \) is the optical density.

\[
T = e^{-\sigma nl} \quad (1)
\]
\[
OD = -\log T \quad (2)
\]
\[
n = 2.3(OD/\sigma l) \quad (3)
\]

By assuming \( \sigma \) to be \( \approx 6100 \text{ nm}^2 \) at wavelength of 808 nm for the AuNRs used in the present study,[44] the number density can be calculated to be 3.8 \( \mu \text{m}^{-3} \) for \( OD = 100 \) solution and 9.1 \( \mu \text{m}^{-3} \) for the \( OD = 240 \) solution.
Microgel particles with a well-defined shape were fabricated using non-wetting fluorinated elastomer molds as the template.[45] In a glove box, a cleaned microscope slide was placed on top of a diced silicon master 2 cm × 2 cm produced by photolithography (AMO GmbH, Aachen, Germany, see Figure S2). Two layers of parafilm (Bemis, total thickness ~ 200 µm) were used as spacers. Perfluoropolyether-urethane dimethacrylate (PFPE, Mₖ = 2000, Fluorolink MD700, Solvay Solexis) was mixed with 1 wt% Darocure 1173 (Ciba Specialty Chemicals) and injected into the interspace until it was filled. Subsequently, the PFPE was cured for 20 min by UV irradiation (Konrad Benda lamp 366 & 254 nm, 8 W) in argon atmosphere. After curing, the PFPE film was carefully peeled off and cut into suitable size (6 mm × 6 mm). A flat thick layer of PFPE (0.4 mm) was prepared by the same protocol on a microscope glass slide.

Figure S2. Optical micrographs of silicon masters, scale bar: 50 µm. Inset (a): FESEM image of PFPE replica of the corresponding structure. Etching depth: (a) 5 µm; (b) 1 µm; (c) 5 µm; (d) 1 µm.
Microgel objects were fabricated by means of the PFPE molds as illustrated in Figure S3. A home-made press with quartz window was used for the molding and all steps were carried out in a glove box with less than 0.2% O₂ in the atmosphere. The monomer solution (1 µL) was pipetted on the microstructured PFPE which was then covered with a flat PFPE layer. To squeeze out excess of the solution, the quartz window was pressed on the PFPE mold by applying a weight (~ 260 kPa). The microgels were cured by 20 min UV-irradiation. Subsequently the mold was peeled off from the flat film. When needed, a thin gold film was coated on the microgel with a sputter coater (~ 2 nm, 30 mA, 20 s, Edwards S150B).

**Figure S3.** Fabrication and transfer of microgel particles.

Release of the microgels from the mold was achieved by peeling them off with the help of a sacrificial adhesive. Microscope slides (Corning glass) were cut into (25 × 25) mm² squares and cleaned with sonication in isopropanol. From a PDMS film (500 µm Sylgard 184, Dow Corning) square frames were cut with outer dimension of (15 × 15) mm² and inner dimension of (10 × 10) mm². The glass slide and the PDMS frame were activated by treatment with O₂ plasma (200 W, 20 s, 1 mbar, PVP Tepla 100) and then bonded. Polyvinylpyrrolidone in water (40 kg·mol⁻¹, 30 wt%, 15 µL) was pipetted in the thus formed trough and the PFPE mold containing the microgel objects was placed upside down in the trough. The whole trough was then dried at room
temperature overnight. After peeling off the PFPE mold, the PVP layer served as an adhesive to collect the microgels. Subsequently, deionized water was added to dissolve the PVP film and release the microgel. In an alternative procedure, we used glycerol (99.5%) instead of the PVP-solution, and the microgel objects in the PFPE mold were brought in contact with the glycerol. The trough was then stored in a freezer (-80 °C) overnight, and the PFPE mold was peeled off from the frozen glycerol. The glycerol was subsequently evaporated at 60 °C under vacuum ($10^{-2}$ mbar), leaving only microgels in the PDMS chamber. Deionized water was added to reswell the microgel.

In order to transfer the microgels into a capillary, one end of a plasma-treated ($\text{O}_2$, 200 W, 5min, 1 mbar) rectangular capillary ($0.05 \text{ mm} \times 1.0 \text{ mm} \times 50 \text{ mm}$, Vitrocom) was immersed in the chamber so that water dispersed microgel objects were sucked in by the capillary force. The ends of the capillary were sealed and fixed on a microscope slide with 2-component epoxy adhesive (UHU GmbH).

**7.4.3 Photothermal actuation and analysis of microgels**

The capillary containing microgels was placed on a peltier stage for temperature control mounted on an optical microscope stage (VHZ-100UR, Keyence). The temperature of the capillary was controlled with an accuracy of ± 0.1 °C. NIR laser light (808 nm, 2.5 W, Roithner Lasertechnik) was focused to the centre of field of view with an incident angle of ~ 40 °. This results in an elliptical footprint as seen in **Figure S4**. The size of the irradiated area was chosen to be larger than the irradiated microgel objects and the irradiation is supposed to be homogeneous for the whole objects. The mean laser intensity, $1.7 \text{ W} \cdot \text{mm}^{-2}$, was measured with an optical power meter (PM200, Thorlab). The laser was modulated with 1 ms temporal resolution.
Videos were recorded with a high speed camera (Miro M310, Phantom) at a speed of 1000 or 2000 frames per second (fps). A short pass filter (700 nm, OD 4, Edmund optics) was used to block and protect the camera from NIR light. Acquired videos were contrast-enhanced and analyzed with the open-source software ImageJ.

Figure S4. (a) Optical micrograph of the footprint of the laser spot, scale bar: 200 µm. To demonstrate the laser spot, the microscope light was switched off. (b) Illustration of the helical microgel inside the capillary (not drawn to scale). The two rotations of the microgel are marked correspondingly.

Figure S5 is the superposition of 3 frames using the “Image calculator” function of ImageJ. To eliminate the edge effect of the capillary, a bandpass filter was applied to the video of the translating helical microgel with ImageJ. The results before and after transformation are shown in Figure S5.

Figure S5. (a) The original overlapped image captured with the high speed camera. (b) The same image after processing with a bandpass filter. Scale bar: 50 µm.
The dynamics of the microgel disk were analyzed with ImageJ following the procedure shown in Figure S6. The videos were first converted into 8-bit grayscale (Figure S6 (a)) and then we apply a threshold to subtract the background (Figure S6 (b)), leaving only the boundary of particle visible. The “Analyze Particle” function was used to acquire geometrical information, e.g. of a disk, such as circularity, perimeter and area. The diameter $D$ of the disk was calculated from the acquired area $S$ with $D = 2 \sqrt{\frac{S}{\pi}}$.

The L-shaped microgel was also analyzed with ImageJ, where the distance between the arm ends was manually measured. For the helix the diameter and length were manually measured with ImageJ to produce the kinematics of the deformation within one cycle.

![Image](image.png)

**Figure S6.** Illustration of geometry analysis using ImageJ. (a) Original micrograph in 8-bit format; (b) thresholded micrograph and (c) automatic detection of disk geometry.

### 7.4.4 Temperature measurements of AuNR solutions and gels

One end of a rectangular capillary (1 mm × 10 mm × 50 mm, Vitrocom) was sealed by epoxy glue and the tubing was filled with AuNR solutions. In the case of the hydrogel stripe, deionized water was injected and the stripe was inserted into the tubing which was left at 20 °C for half an hour to swell. Temperature sensor (Mini-BetaCHIP-Sensor, diameter ~ 0.43 mm, Telemeter Electronics) was inserted into the
tubing and was placed in the center of the capillary or on top of the hydrogel stripe as shown in Figure S7.

**Figure S7.** (a) Illustrations of the experimental setup for temperature measurement in AuNR solution (upper) and gel containing AuNRs (lower). (b) Intensity dependent temperature increase in the equilibrated state. The $\Delta T$ in solution is linearly dependent on the intensity, while there are two regimes in the gels containing AuNRs. For the comparison of the gold nanorod solution with the nanorod loaded gels, it must be noted that the number density of gold nanorods has to be increased when the heated volume is decreased as it is the case for dispersed microgel objects in order to compensate for the larger heat loss to the environment for smaller volumes. $\Delta T$ depends on the surface area of the system as shown in Equation S1.[46] The abrupt change in the slope of the gel sample is due to the shrinking of the gel at higher temperatures, which increased the effective concentration of the AuNRs.

The capillary was placed on a Peltier stage mounted on an optical microscope (VHZ-100UR, Keyence). The Peltier stage was controlled by customized software to provide required temperature for the sample. A silicon wafer was placed beneath the sample to reduce laser scattering resulted from the Peltier stage. As laser source, a near infrared (NIR) laser (808 nm, 2.5 W, Roithner Lasertechnik) was used which can be focused via optical lens. The output power of the laser was calibrated with an optical power meter (PM200, Thorlabs). The laser irradiation has an incident angle of 40 ° and was focused to the direct vicinity of the temperature sensor, yet without direct contact. The laser was modulated with a temporal resolution of 1 ms. During the measurement, the light of the microscope was kept off to avoid additional heating. The data was recorded at 55 ms intervals.
\[ \Delta T = \frac{I(1 - 10^{-OD})\eta}{hs} \]  

(S1)

where \( I \) is the laser intensity, \( OD \) is the optical density in the optical path, \( \eta \) is the photothermal efficiency, \( h \) is the heat transfer coefficient, and \( S \) is the surface area perpendicular to the heat conduction. For the same AuNR/gel system, only \( OD \) and \( S \) depend on the size of the system. Therefore, when the size of the system increases, a lower concentration of AuNRs is needed to reach the same temperature as in the case of a smaller size.

7.4.5 Confocal microscopy of the tethered gel film

To prepare gel films tethered to a substrate, glass slides (Corning, Germany) were firstly cut into pieces of around 2 cm \( \times \) 2.5 cm in size and cleaned by sonication for 5 min in destilled water, isopropanol and acetone. Prior to the silanization, the glass substrates were activated by UV/Ozone treatment for 15 min. Silanization was done in a desiccator with an evaporating petri dish inside, which was filled with 300 \( \mu \)L of 3-(Trimethoxysilyl)propyl acrylate. The desiccator was first evacuated to \( 8 \times 10^{-2} \) mbar and left closed for 2h. Then the petri dish was removed, and the desiccator was further evacuated to \( 1 \times 10^{-3} \) mbar for 2h to remove the excess of silane. The glass substrates were then stored in a dark vessel in the glove box.

The monomer solution for the film was prepared according Table S1, except that less amount of AuNR was added, so that the resultant optical density of the solution at 808 nm is roughly 100. The decrease in the volume of AuNR solution was compensated by adding more DMSO, so that the concentrations of other components were kept the same. The solution was then injected between a clean galss substrate and the silanized glass slide using a Kapton film (25 \( \mu \)m) as the spacer. The polymerization of NIPAm
was accomplished by UV-irradiation (365 nm, 150 mW·cm$^{-2}$) for 15 min. After polymerization, the glass substrates were then separated, and the one with tethered hydrogel film was stored in abundant deionized water overnight to exchange the solvent and to swell the gel.

The characterization was carried out by a Leica SP8 confocal microscope. The laser was focused to the field of view with an estimated intensity of around 30 W·mm$^{-2}$. The film had a swollen thickness of roughly 42 µm. The laser was modulated with an on/off period of 0.7 s / 0.3 s (1 Hz). The wrinkles appeared after 3 cycles of irradiation as shown in Figure 2. The false-color image was captured by the reflection mode using the laser line of 514 nm.

### 7.4.6 Free swelling of disk-shaped microgels

The diameter of the disk-shaped microgel was measured at different temperatures as shown in Figure S8 (a). The swelling ratio at 20 °C can be estimated to be roughly 61% by comparing the diameter at 20 °C (48.4 µm) with the as-prepared diameter (30 µm). Figure S8 (b) shows diameter of the microgel depending on the laser intensity. The plot can be used to estimate the temperature of the gel during photothermal process.

![Figure S8](image-url)

**Figure S8.** Swelling of the disk-shaped microgel freely suspended in water. (a) The equilibrium diameter of the microgel as a function of temperature. 30 microgels were...
measured, and the values were averaged. (b) Change of the microgel diameter depending on the laser power.

7.4.7 Swelling response of a metal-hydrogel bilayer ribbon

We assessed the influence of the metallic layer on the microgel swelling by optical microscopy analysis of a ribbon with \( w = 10 \, \mu m \) in width, \( t = 5 \, \mu m \) in thickness and \( L = 200 \, \mu m \) lengths. Figure S9 shows the effect of the thickness of the sputtered metallic coating on the microgel geometry. For thin metallic layer constrained swelling induces bending of the ribbon to form a spiral with one and half turns. By measuring the inner contour length, the linear swelling ratio of the coated surface can be estimated to be 32% compared to 61% of the free-swelling gel, which demonstrates the confining effect of the skin. The effect becomes stronger as the coating becomes thicker. The swelling ratio of the gel with 2 nm coating decreases to 14%, while the curvature of the spiral structure decreases to produce two full turns of the spiral. With thicker coating of 12 nm, the ribbon assumes a helical shape with even smaller curvature, which indicates increased internal stress.

![Figure S9](image)

**Figure S9.** Influence of the coating thickness on the geometry of the gel. The dimensions of the original gel ribbon: \( 5 \, \mu m \times 10 \, \mu m \times 200 \, \mu m \). Coating thickness from (a) to (c): 1 nm, 2 nm, and 12 nm. The micrographs are taken after the microgels were equilibrated at 20 °C. Scale bar: 20 \( \mu m \).
The spectrum of the 2nm Au coating was measured on a PNIPAm thin film (100 µm), which was bound on a glass substrate and coated with 2 nm Au. **Figure S10** shows the results. It can be seen that the film has an optical density of 0.092 at 808 nm, which indicates that the Au coating may also absorb light and generate heat.

![Figure S10. UV-Vis spectrum of the Au coating (2 nm).](image)

**Figure S10.** UV-Vis spectrum of the Au coating (2 nm).

### 7.4.8 Porosity determination of the gels

Based on the swelling ratio and the molar ratio of the cross linker to the monomer we estimates a degree of polymerization between the cross-link of ca. 70 monomer unit with a mesh size of roughly 5 nm.[47] In addition, we checked the permeability of the gels for model compounds. Gels with the same composition as used for microgel were prepared in a glass capillary. After UV-polymerization, the gels were equilibrated in water for 48 hours at room temperature and subsequently immersed in different aqueous dye solutions for 24 hour. The dyes used are vitamin b12, cytochrome c, and blue dextran (2000 kDa), all purchased from Sigma-Aldrich. The vitamin B12 and cytochrome penetrated and colored the gel, while the blue dextran stained only the outer most the surface of the gel. From the observation it can be estimated that the pore size of the gel is larger than the hydrodynamic diameter of vitamin B12 (1.48 nm) and cytochrome C (3.4 nm), but smaller than that of the blue dextran (75 – 81 nm).
We also probed the optical density at 808 nm of the gel containing AuNRs and did not observe any leaking over long times when the gel was in contact with water.

7.4.9 Estimation of the temperature variation through actuation cycles

Figure S11. (a) Change of the helical pitch during adiabatic heating. Curve is to guide the eye. (b) Optical snapshot of the helix with a pitch of 31 µm due to 16 ms laser irradiation. Scale bar: 15 µm.

Figure S11 shows the equilibrium pitch of the helical bilayer microgel at different temperatures. For comparison Figure S11 (b) depicts the helix after 16 ms irradiation with laser light at 808 nm as described in Figure 5c at the end of the cycle. The helix has a pitch of 31.3 µm which corresponds approximately to the data point at 30.5 °C (pitch: 31.9 µm).

7.4.10 Measurement of the θ and Ω rotation

The rotation around the θ and the Ω axis was analyzed based on the snapshots from the optical observation as shown in Figure S12. For the in-plane (θ) rotation, the orientations of the helix at different stages of the irradiation were compared. For the on-period, a 3 ± 0.5 ° anticlockwise rotation was measured as demonstrated in Figure
S12 (a). The backward rotation in the off-period was measured to be \(-2 \pm 0.5^\circ\) in the clockwise direction, so that the resultant effective rotation is \(1 \pm 0.5^\circ\) per cycle. The deviation is due to the optical resolution of the video.

![Image of optical micrographs showing rotational movement](image)

**Figure S12.** (a) Optical micrographs of the helix showing the \(\theta\) rotation. The in-plane rotation during on-period is \(3 \pm 0.5^\circ\), and the rotation during the off-period is \(-2 \pm 0.5^\circ\). The effective rotation per cycle is thus \(1 \pm 0.5^\circ\). (b) Optical micrographs of the helix showing the \(\Omega\) rotation. \(t_0\) is the end of the on-period when the laser was switched off. After two milliseconds the helix recovers and it can be estimated that the recovery results in a backward rotation of roughly \(90^\circ\) around the \(\Omega\) axis as can be seen from the orientation of the end of the helix.

For the \(\Omega\) rotation around the long axis, the helix at the beginning of the irradiation period cannot be used to acquire the orientation in the long axis due to its closed shape and the limited optical resolution. Therefore, the fully opened helix at the end of the irradiation was compared with the partially closed state in the off-phase, which revealed a backward rotation of roughly \(90 \pm 30^\circ\). Although the helix further winds in the off-phase, the subsequent deformation is relatively small and so is the \(\Omega\) rotation. Thus the \(\Omega\) rotation in the first 2 ms of the off-period can be roughly considered as the
backward rotation of the whole off-period. The effective rotation per cycle demonstrated a net rotation of 21° per cycle (590 ± 50° per second). Therefore, the rotation of the on-period was estimated to be 111° (90° + 21°), which is plotted in Figure 6. Since the Ω rotation was acquired based on the in-plane projection, the data has an error bar of 30° in Figure 6.

7.4.11 Estimation of diffusion controlled response time for homogeneous swelling/deswelling

The coupling of the motions of polymer and solvent determines the characteristics of the gel kinetics,[27, 51] and τ_p specifies the response time. It is related to the collective gel diffusion coefficient D_p (which takes into account solvent diffusion, polymer chain motion, and polymer friction) and the path length of the diffusion:

\[ \tau_p = \frac{d^2}{D_p} \] [52]

With \( D_p \approx 2 \times 10^{-11} \, m^2/s \) and for a small contraction (\( \Delta d = 1 \mu m \)) corresponding to a small temperature change 3 °C, the response time is expected to be in the millisecond range (~ 100 ms), and the water can be expelled smoothly. However, in the case of a large temperature jump, the imbalance in the rates of the temperature and volume change causes strong instabilities accompanied by heterogeneity which destabilizes the hydrogel structure. [52]

7.5 References

8. Artificial microgel swimmers

8.1 Introduction

Microorganisms are ubiquitous in our world. Locomotion of microorganisms, mostly in the form of swimming, is an essential part of their life: in the pursuit of food such as Escherichia coli,[1] to escape from predators such as Paramecium,[2] or to spread progeny in the case of spermatozoa. To fulfill those complex tasks, the microorganisms have developed fundamentally different locomotion strategies than those from the macroscopic world. On the microscopic scale the viscosity dominates over inertia in water.[3, 4] From the viewpoint of fluid dynamics, the microorganisms live in an environment where the Reynolds Number (Re) is small. The latter is defined by Equation (1), where $\rho$ is the density of the fluid; $v$ is the maximum velocity of the object travelling through the fluid; $L$ is the characteristic length of the object; and $\mu$ is the dynamic viscosity of the fluid.

$$ Re = \frac{\rho v L}{\mu} = \frac{\text{inertial force}}{\text{viscous force}}. $$ (1)

Therefore the Reynolds Number is the ratio of inertial force to viscous force exerted on a swimming object. For microorganisms, the $Re$ is in the order of $10^{-4}$, so that inertia can be practically neglected.[3] In this regime, the Navier-Stokes equation simplifies to the Stokes equation as shown by Equation 2, where the $\eta$ is the viscosity, $p$ is the pressure in the fluid, and $u$ is the flow field.

$$ \eta \nabla^2 u - \nabla p = 0, \text{ and } \nabla \cdot u = 0. $$ (2)

The absence of time-dependent terms in this equation sets the limit for microorganisms that their strokes have to be time-irreversible in order to generate
effective locomotion, as specified by the Scallop theorem.[3-7] Beating of the cilia and rotating of the helical flagella, which are flexible filaments capable of active deformation, are the two major mechanisms of the microorganism propulsion.[3]

The study of locomotion of microorganisms can be traced back to more than sixty years ago,[8] while great interests have been triggered in the past decade due to advances in the experimental techniques [9, 10] and in the microscale fabrication methods.[5, 11, 12] Various artificial microswimmers have been fabricated and investigated, as they provide handy tools to understand the fundamentals of swimming at Low Reynolds Number,[5, 13, 14] to promote biomedical applications,[15, 16] as well as to achieve microscopic manipulations.[11, 17] Diverse designing principles have been employed to construct artificial microswimmers such as magnetic swimmers,[5, 11, 17, 18] microjets,[12, 19-22] diffusiophoretic swimmers,[23-27] light driven microswimmers,[14, 28-30] and biohybrid microswimmers.[31-34] Nevertheless, artificial microswimmers that achieve locomotion by pure body deformation in the absence of external force/torque are seldom found in literature. This is due to the difficulties in both precise microfabrication and proper actuation mechanisms. Therefore, a new system has to be developed to overcome these difficulties. In this regard, we designed morphing microswimmers that exploit the principle of non-equilibrium actuation by photothermal heating.

In this chapter, we present a novel type of artificial microswimmers that swim by non-reciprocal deformations. The body of the microswimmer consisted of a crosslinked thermoresponsive hydrogel poly(N-isopropylacrylamide) (PNIPAm) laden with gold nanorods (AuNRs). Since AuNRs can convert light energy into heat with a photothermal efficiency approaching unity, the microswimmer can reversibly change
its volume when irradiated by a near-infrared (NIR) laser.[35-37] As already demonstrated in previous chapters, microfabrication of the hydrogel particle with the help of the PRINT technique in a non-wetting template, i.e. perfluoropolyether (PFPE) mold, allows accurate and uniform replication of the designed shape. The photothermal heating by AuNRs provides precise modulation of the local temperature of the microgel particle. Furthermore, three dimensional shapes, such as helix or spiral, can be achieved by introducing a bilayer structure, which provides large deformations upon small changes in the volume. This is a desirable feature for applications like micromotors. The non-equilibrium actuation by thermoplasmonics ensures the asymmetry in the deformation path, which eventually leads to propulsion of the microgels. In the following sections, two types of artificial microswimmers were fabricated based on the bilayer design, and their behaviors are studied depending on the geometry, light modulation, and environments.

8.2 Results and discussion

8.2.1 Spiral microrotor

The two dimensional spiral was formed from a bilayer ribbon consisting of a poly(NIPAm) hydrogel layer, on which a 2 nm thick gold layer was sputtered. Upon swelling in water, expansion and stretching of the gel layer is restricted by the gold skin which strongly resists stretching. Hence, the structure is a bilayer ribbon in which one layer expands relative to the other.[38] As a consequence, swelling of the hydrogel causes stresses which, in turn, lead to bending of the bilayer. This is demonstrated in Figure 1 (a) with an optical micrograph showing the resultant spiral structure at 20 °C. As the temperature increases, the spiral microgel unbends due to the shrinking of the hydrogel layer, which brings the microgel towards its original
straight shape. This is demonstrated in Figure 1 (b) by the increase of the inner radius, while the shrinking of the gel is reflected by the decrease of the length. The dependence of the radius on the shrinking degree is shown by the curvature of the spiral plotted against the \( \varepsilon/h \) (Figure 1 (c)), where \( \varepsilon \) is the relative change in length to the as-prepared state (200 \( \mu m \)) of the spiral ribbon and \( h \) is the thickness of the ribbon. The dependence is rather linear, which is similar to Timoshenko’s bending of a bimetallic strip. In that case the curvature is proportional to the misfit in strain of the two layers and inversely proportional to the thickness of the strip.[39] It is also worth noting that the slope is close to the one of a helical microgel shown in Chapter 6.

![Figure 1](image)

**Figure 1.** (a) Illustration of the swelling of bilayer hydrogel ribbon. Right panel: optical micrograph of the spiral rotor in swollen state at 20 °C with the inner radius marked by \( R \). (b) The change of the spiral length and the radius with temperature. (c) Curvature (1/R) of the spiral versus strain \( \varepsilon \) relative to the ribbon thickness \( h \).

To fabricate the microgel rotor, a silica microsphere (diameter ~ 10 \( \mu m \)) was attached to one end of the microgel as shown in the optical micrograph of Figure 2 (c). The spiral was confined edge-on between two glass surfaces in the way that the
microsphere can freely rotate without significant lateral displacement (see the Experimental Section for more details). Upon stroboscopic irradiation, the spiral underwent bending/unbending deformations as demonstrated in Figure 2 (a).

Figure 2. (a) Superimposed optical micrographs of the spiral rotor under stroboscopic irradiation. Left: on-time (0.5 s); right: off-time (0.5 s). Laser intensity: 1.7 W·mm$^2$ at 808 nm. (b) Superimposition of micrographs of the spiral rotor under stroboscopic irradiation (0.5 s – 0.5 s). From right to left: at 0 s, 1 s, 2 s, 3 s, and 4 s. (c) Optical micrograph of the spiral rotor during recovery. The length of the center line ($L$, red-dashed line) and the tangential angle ($Theta$) are marked correspondingly. (d) Change of the $L$ vs. $Theta$ during one cycle of irradiation (0.5 s – 0.5 s). Arrows mark the direction of change, and dashed lines are drawn to guide the eye.

Figure 2 (a) shows a shape-superimposition during half a second irradiation and a recovery for half a second. The period was chosen based on the characteristic time for the water to diffuse in and out of the microgel with a thickness of 5 µm, which is in the range from sub-second to a few seconds (see estimation in Chapter 4). [40, 41] The spiral continuously unfurls to an almost straight shape within 0.5 s irradiation as
seen in the optical micrographs. At the end of each irradiation cycle, the microgel recovered its spiral shape with slight anti-clockwise rotation with respect to the initial position. The Reynolds Number of the spiral microgel can be estimated to be around $10^{-2}$ using the width of the microgel as the characteristic length (10 µm) and a typical velocity of 1000 µm·s$^{-1}$. After few cycles, the rotation of the spiral can be clearly observed as shown by the superimposed images taken at the beginning of each cycle in Figure 2 (b). The spiral exhibited a net anticlockwise rotation around the microsphere with an average speed of 22 degrees per cycle.

As discussed previously, one necessary condition for the swimming at Low Reynolds Numbers is that the deformation path in one cycle must be time-irreversible, which means that the deformation should follow different paths in the shape space.[3-5] Indeed, it can be observed from the superimposition in Figure 2 (b) that the deformation sequence during the recovery stroke is different than the power stroke, and the evolution of curvature differs as well. Two geometric parameters were selected to characterize the deformation: the length of the center line ($L$) and the tangential angle of the free end as illustrated in Figure 2 (c).[42] The evolution of these two parameters is plotted in Figure 2 (b) with the $L$ as X-axis and $theta$ as Y-axis, so that the resultant plot demonstrates the time-independent deformation during one cycle. Unbending of the spiral structure under laser irradiation resulted in a decrease of the length from 258 µm to 222 µm and a decrease of $theta$ from 142 to -203 degrees. The continuous decrease in $L$ is due to the shrinking of the gel, while the change in the $theta$ indicates the local deformation of the spiral. The microgel is close to the straight shape at the end of the irradiation (Figure 1 (b)). In contrast, the recovery stroke (off-time) adopted a distinct path than the one in the power-stroke. The steady increase in the length during the off-time is due to the swelling of the
hydrogel layer upon cooling. In the meantime, the \( \text{theta} \) increased continuously to more than 150 degrees. This value is larger than the starting point in the cycle due to the net rotation of the spiral. The non-reciprocal deformation can be attributed to the combination of non-equilibrium actuation and bending of the bilayer.

The influence of irradiation period on the spiral net rotation was also investigated (Figure 3). For short irradiation period, such as the 0.1 s – 0.1 s, the spiral microgel wasn’t able to wind back due to the short recovery time. The actuation amplitude, defined as the displacement of the free end, before and after irradiation, is rather small in this case. Nevertheless, the asymmetry of the motion kinematics during an

![Figure 3](image-url)
irradiation cycle is still distinguishable in Figure 3 (a) with a net rotational motion of 1.6 degree·s\(^{-1}\) (see Figure 3 (d)). Longer irradiation periods increase the motion amplitude and enhance the asymmetry in the motion kinematics as shown in Figure 3 (b) and (c). Figure 3 (b) shows a significantly larger amplitude as well as asymmetric kinematics compared to Figure 3 (a) with a much higher rotational speed, i.e. 16.7 degree·s\(^{-1}\). The longest irradiation period was 2 s. Note that at the end of the irradiation, the ribbon slightly bent in the opposite direction. Obviously, the shrinkage of the hydrogel resulted in a negative curvature of the bilayer (see discussion on the inversion of curvature in Chapter 6). The angular velocity in this case is 8.8 degree·s\(^{-1}\).

In Figure 3 (d), the angular velocity of rotation shows a maximum of 22 degree·s\(^{-1}\) at the \(t_{on}\) of 0.5 s. This is in an interesting correlation with the amplitude of actuation summarized in Table 1, where the largest amplitude appears also at the 0.5 s – 0.5 s. At this irradiation period, the spiral microgel already reached a fully stretched state, so that the amplitude didn’t further increase upon longer irradiation. The angular velocity thus decreased, even though the rotation per cycle at the \(t_{on}\) of 1.0 s is close to the 0.5 s.

<table>
<thead>
<tr>
<th>Irradiation period (on - off)</th>
<th>Amplitude ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ms - 100 ms</td>
<td>69</td>
</tr>
<tr>
<td>200 ms – 200 ms</td>
<td>127</td>
</tr>
<tr>
<td>500 ms – 500 ms</td>
<td>148</td>
</tr>
<tr>
<td>1000 ms – 1000 ms</td>
<td>146</td>
</tr>
</tbody>
</table>

To sum up this section, a spiral rotor has been successfully fabricated by attaching a microgel-bilayer to a microsphere, which was confined between two glass surfaces. This enabled free rotation at relative fixed position. Stroboscopic irradiation is applied to actuate the microgel using thermoplasmonic heating of the incorporated gold
nanorods. Non-reciprocal deformations were observed during the actuation, which bring about rotational motion in the Low Reynolds Number regime where the microgel rotor operates. The reason of such deformations can be attributed to the non-equilibrium swelling/shrinking kinetics of the gel and bending deformations. The net rotation per cycle depends on the irradiation and the amplitude of deformation and has a maximum of 22 degrees per cycle at $t_{on} = 0.5$ s. Change of angular velocity has the same tendency with a maximum at $t_{on} = 0.5$ s.

8.2.2 Helical microswimmer

As demonstrated in Chapter 6, the geometry of microgel bilayer can be readily tailored by changing its aspect ratio (width and length to thickness). Long and thin bilayers tend to form helical structures due to the minimization of elastic energy.[43] With an initial dimension of $1 \mu m \times 5 \mu m \times 80 \mu m$ (or $160 \mu m$) of the bilayer, helical microgels can be obtained that are capable of responding to temperature change in a precise and reversible way. The helix unwinds as temperature increases and eventually reverses its chirality above the VPTT. By photo-thermal heating via stroboscopic irradiation of a NIR laser, the helical microgel can be actuated by a frequency from 10 to 100 Hz. Due to the small dimensions that allows tuning of the kinetics of expansion (mass diffusion), the microgel provides a suitable platform for actuation with high temporal precision for soft-robotic applications. In this section, we focus on the locomotion of the helical microgel by stroboscopic irradiation.
The deformation of the helical microgel in response to the external heating is demonstrated in Figure 4 (a). At 20 °C the helix is tightly wound, so that it appeared optically as a tube with a diameter of 4.3 µm and a length of 61 µm. As the temperature increases to 30 °C, the microgel reveals its helical structure by slight unwinding, which increases the diameter and the pitch, while the total length remains unchanged. The helix is right-handed below the VPTT, see Chapter 6. For the photothermal actuation, the microgel was irradiated with a NIR laser (20 ms on and 10 ms off). The change of pitch within one cycle is shown in Figure 4 (b). Laser irradiation starts at t = 0 ms and ends at t = 20 ms as marked by the red dashed line. At this period, the change of the helical parameters is relatively small in contrast to
the case of chirality switch. Similarly as shown in Chapter 5, fast recovery was observed when the laser was switched off, which is quantified by the change of the helical pitch. The fast, millisecond response is the result of both photo-heating and the small dimensions of the microgel. Heating from the inside of the microgel with a thickness of 1 µm requires a thermal equilibration time in the order of microseconds (see discussion in Chapter 3), meaning that the temperature of the microgel can become homogeneous within a few microseconds upon irradiation. Moreover, the reduced dimension of the microgel leads to significant decrease of the characteristic time of mass diffusion. Upon irradiation, the pitch increases almost linearly at a speed of 1.7 µm·ms\(^{-1}\) to reach a maximum of 41 µm. Once the laser is switched off, the pitch first undergoes a fast recovery at a speed of 9.9 µm·ms\(^{-1}\) in the first 3 ms and then relaxes during 7 ms to recover the initial pitch (6.8 µm).

Stroboscopic irradiations lead to cyclic deformation of the helix, which lays the foundation of performing work continuously at microscopic scales. Indeed, anticlockwise rotation of the helix in the horizontal plane was observed at this modulation. The rotation is shown in Figure 4 (c) as a superimposed image, which demonstrates a rotation of 36 degrees in 16 cycles of actuation, i.e. 2.3 degrees per cycle on average. As seen in the superimposition, the rotation of the helix is rather stable throughout the modulation, meaning constant speed of rotation. The rotation within each cycle was analyzed with the help of high speed videos as demonstrated in Figure 4 (d), where the on-time is red-shaded. To characterize the degree of rotation, the central axis of the helix was taken as reference, since the helix alters its contour during actuation. From the plot it is clear that the helix underwent a step-wise rotation. During the on-time, the helix rotates anticlockwise by 6 ± 0.5 degrees, whereas during the off-time it rotated clockwise by 4 ± 0.5 degrees, leading to an anticlockwise
rotation of $2 \pm 0.5$ degrees in one cycle. By repeating the irradiation cycles, step-wise rotation can be achieved with an effective angular velocity of roughly $75$ degree·s$^{-1}$.

**Figure 5.** (a) Change of diameter and length of the helix during one cycle of actuation (20 ms on – 10 ms off). The deformation path is marked by 1, 2, 3, and 4 in the graph. The laser is switched off at 3. Dashed lines are drawn to guide the eye. (b) Optical micrographs of the helix at different points of time highlighted in (a).

In order to investigate the kinematics of the present system, we characterized the kinematics of helix during actuation by two simple geometric parameters, i.e. length and diameter. The results are shown in **Figure 5**. In the on-time, the helix starts from point 1 and undergoes a deformation through point 2 to 3, where the laser is switched off. In the off-time, the kinematics of the helix follows the path through point 4 back to 1 during the off-time. The start of on-time is accompanied by a decrease in length by 1 µm, while the diameter increases insignificantly during the same period of 1 ms. Afterwards the length and the diameter increase almost linearly to 65.4 µm and 14.4 µm respectively. In contrast, the off-time begins with a large reduction in diameter, i.e. from 14.4 µm to 7.5 µm in 2 ms, whereas the length stays nearly constant. The length begins to drop significantly in the following 8 ms, from 64.7 µm to 56.8 µm, as the diameter returns to its original state (4.8 µm). In this way, a full cycle of actuation is completed, where the helix follows a different route back in the off-time compared to
the on-time. The deformation in the power-stroke (on-time) is thus non-reciprocal compared to the recovery stroke, which gives rise to the different rotation degrees as shown in Figure 4 (d); a net rotation is therefore achieved. The asymmetric kinematics can be directly seen in Figure 5 (b), where micrograph 1 and 3 are the helix in the beginning of on- and off-time respectively, and micrographs 2 and 4 demonstrate the geometry of helix in the middle of both processes. By comparing the micrograph 2 with 4, the asymmetric kinematics in the two processes can be seen: the helix has much less turns and significantly larger pitch in micrograph 2 than in micrograph 4, reflecting the huge difference between power- and recovery-stroke. The asymmetric deformations demonstrated by the helical microgel are the result of the non-equilibrium actuation by photothermal heating as shown in the previous chapters.

The rotation of helix represents an intriguing class of microscopic locomotion that can be achieved by our artificial microswimmer. Nevertheless, many applications require also translational motion of the microswimmer rather than pure rotation, drug delivery for instance.[17] Moreover, microswimmers in the real world have to frequently cope with complex environment such as spatial confinement (water/air interfaces, physical boundaries, and so on). To further explore the possibilities in regard to these considerations, the helical microgels were exposed to two different types of geometrical confinements. The first type is a flat wall normal to the surface (Figure 6 (a)), while the other one is a rectangular channel with a width comparable to the diameter of the helix (Figure 6 (b)).
Figure 6. Helical microgels in different confinements. (a) Time sequence of helical microgel swimming along the wall of a rectangular capillary. Upper panel illustrates the orientation of the helix to the wall; the other two surfaces of the capillary are not displayed for clarity. Black dotted line in the micrograph marks the boundary of the wall. Red dashed lines show the position of the helix. Irradiation period: 5 ms – 10 ms. Laser intensity: 1.7 W·mm\(^{-2}\) at 808 nm. To reduce the edge scattering, the images were processed by a bandpass filter with ImageJ. (b) Time sequence of helical microgel swimming on a micro-patterned silicon substrate. Upper panel illustrates the helix on the microstructure. Red dashed lines show the position of the helix. Width and depth of the rectangular groove are 5 µm and 1.6 µm. Dimensions of the microgel: 1 µm × 5 µm × 80 µm. Modulation: 4 ms – 6 ms. Laser intensity: 1.7 W·mm\(^{-2}\) at 808 nm.

In Figure 6 (a), the wall of the rectangular capillary was used as a confinement. Since the height of the tubing (40 µm) is much larger than the diameter of the helix (less than 5 µm), and the microgel settles at the bottom of the capillary due to its higher density compared to water, the influence of the upper surface of the capillary can be neglected. The wall of the capillary can thus be considered as a two-dimensional flat confinement as illustrated in Figure 6 (a). One limitation of this experimental setup is the light scattering (both for microscope light and for laser) due to the presence of edges, which results in a shadowed area close to the wall as can be seen in the micrographs. Consequently, a longer microgel (160 µm) has to be used for this
experiment, since the actuation would be difficult to control for shorter microgels when they come close to the capillary edge. Cyclic irradiations with short period were applied, so that the amplitude of actuation is kept small, so that no inversion of the chirality is involved. In this case, the frequency of actuation can be relatively high (67 Hz). Instead of rotation, translation of the microgel along the wall was observed with a swimming speed of 127 µm·s\(^{-1}\), i.e. one body length per second as shown in Figure 6 (a). The speed is comparable to that of natural microswimmers such as *Paramecium* and human sperms.[2] Interestingly, the orientation of the microgel is not parallel to the swimming direction: a constant angle of approximately 25 degrees to the wall was observed, which indicates a steady interaction with the wall. The interactions can be direct physical contact with the wall and/or hydrodynamic interaction between the two objects, and the effects of confinements have been widely found to alter the swimming pattern of microswimmers.[7, 23, 24, 44-46] Therefore, the transition from rotational to translational motion near the wall could be mainly attributed to the interactions with the wall. Besides, it can be seen in the micrographs that the helical microgel assumed a conical shape during stroboscopic irradiations, which could be due to the edge scattering of the laser. This asymmetric geometry could also contribute to the translational motion of the microgel as it breaks the geometric symmetry of the microgel. In summary, translational motion of the helical microgel was achieved by exposing the microgel to a flat wall; both the interactions with the physical boundary and the gradient of laser illumination may have brought about the translational motion of the microgel.

Figure 6 (b) illustrates the situation of a helical microgel in extreme case of confinement in a rectangular microchannel, which has a width comparable to the helix’s diameter. The microchannel was fabricated by photo-lithography on a silicon
wafer with a width of 5 µm and depth of 1.6 µm. Since the width is larger than the diameter of the helix in the swollen state (4.3 µm), the helix fits into the microchannels as seen in the micrographs, where the helix is aligned along the microchannel. The small depth of the channel relative to the helix diameter minimizes the shielding of the laser and enables relative uniform irradiation of the microgel. Although the depth of the channel is smaller than the diameter, it is still sufficient to physically confine the helix, provided that the deformation of the microgel does not exceed the channel width. Indeed, irradiations longer than 5 ms lead to the release of the microgel from the microchannel, because the diameter exceeded 5 µm. In this case, rotation of the helix was observed on top of the channels. Therefore, stroboscopic irradiation with on-time of 4 ms and off-time of 6 ms was applied, and the time sequence of the helical microgel is shown in Figure 6 (b). Due to the short modulation period, actuation of the helix can barely be seen, as the microgel is tightly wound in an almost tubular configuration throughout the experiment. The actuation amplitude is therefore sufficiently small, so that the helix was able to stay inside the channel. Under these conditions, the helical microgel translates to the right of the frame at a speed of 5 µm·s⁻¹ (20 µm in 4 s). The trajectory of the swimming follows the channel orientation. Since the irradiation on the microgel can be considered as uniform, the reason of translational motion can be attributed to the physical and hydrodynamic interactions between the microgel and the confinement. The speed of translation is relatively small compared to the helix swimming near the wall, presumably due to the small actuation amplitude and large friction between the microgel and the channel. This experiment demonstrates the possibility to steer the swimming direction of the microgel in a narrow confinement, even when the microgel is only able to rotate on a flat surface. Wider and deeper micro-channels, which allow larger actuation
amplitude, might be useful to enhance the swimming speed of the helix, provided that the channel is not too wide for the microgel to lose its orientation.

8.3 Conclusion

Through spontaneous bending of a bi-layer microgel upon swelling, spiral and helical microgels were fabricated that can be photothermally actuated with high temporal (millisecond) and spatial (micrometer) accuracy. The geometry of the microgels can be dynamically morphed by stroboscopic irradiation, which provides a facile tool to perform work at a microscopic scale.

Non-reciprocal deformations were achieved at various irradiation periods for the spiral microgel: the recovery stroke followed a different path compared to the power stroke. As a result, rotational motions of the structure were observed in the *Low Reynolds Number* regime. The maximal angular velocity of the spiral rotor is 22 degree·s⁻¹ at a frequency of 1 Hz with equal on- and off-time, and the rotation per cycle increases with the irradiation period.

In an unconfined state, the investigated right-handed helical microgel demonstrates an anti-clockwise rotational motion with an irradiation period of 20 ms on - 10 ms off. The pitch of the helix increases almost linearly with time in the on-time at a speed of 1.7 µm·ms⁻¹, while the off-time is divided into a fast recovery regime of pitch at 9.9 µm·ms⁻¹ in the first 3 ms and a slow equilibration regime in the following 7 ms. The rotation has an angular velocity of roughly 75 degree·s⁻¹, where the power stroke brings about an anti-clockwise rotation of 6 ± 0.5 degrees in the on-time, while the recovery stroke is characterized by a clockwise rotation of 4 ± 0.5 degrees in the off-time. Kinematic analysis shows that the deformations of helix are indeed non-
reciprocal during the modulation, which eventually leads to the directed motion of the helix. By exposing the helical microgels to physical confinements, e.g. a flat wall or a microchannel, translational instead of rotational motion can be triggered by laser irradiation. The helix translates along the flat wall at a constant angle of 25 degrees to the swimming direction with a maximal velocity of 176 $\mu$m·s$^{-1}$, while the swimming speed inside the channel reaches 5 $\mu$m·s$^{-1}$.

The present study opens the new avenue for artificial microswimmers that can be remotely actuated by near-infrared laser with temporal resolution down to milliseconds and spatial responsiveness in the micrometer range. Both rotational and translational motions can be achieved by tailoring the input signal of actuation (i.e. laser modulation), the geometry of the microgel (via self-shaping), and the environmental factors such as physical confinements. The system can be potentially exploited for biomedical and microfluidic applications, which lays the cornerstone for the development of novel soft micro-robotics.

8.4 Experimental section

8.4.1 Synthesis of AuNRs and fabrication of microgels

Gold nanorods were synthesized and modified as described in Chapter 3 and 4. The PEGylated AuNRs have an absorption maximum at 791 nm in water. The monomer solution containing AuNRs was prepared with the same composition as used in Chapter 4, which results in an optical density of 240 at 808 nm (optical path = 1 cm). The fabrication of the microgel is illustrated in Chapter 4 and 6. Photo-lithographically patterned silicon masters (AMO GmbH, Aachen, Germany), which are shown in Figure S1, were replicated using the non-wetting elastomer PFPE.
Metallization of the microgels was carried out for both samples, where a thin gold layer (~ 2 nm) was sputter-coated on one surface of the microgels. Subsequently, the microgels were transferred into a trough constructed by a PDMS frame and a glass slide as described in Chapter 5; the transfer was done by using frozen glycerol as adhesive, so that no residues of polymers, which would otherwise alter the viscosity of water, were present in the final solution. After re-hydration, the microgels self-fold to form different geometries depending on its initial aspect ratio (see Chapter 6).

Figure S1. Optical micrographs of silicon masters. (a) 10 µm × 200 µm rectangles, etching depth: 5 µm. Scale bar: 100 µm. (b) 5 µm × 80 µm rectangles, etching depth: 1 µm. Scale bar: 50 µm. (c) 5 µm × 160 µm rectangles, etching depth: 1 µm. Scale bar: 50 µm.

To fabricate the rotor, spiral shaped microgels (initial shape shown by Figure S1 (a)) were mixed with 10 µm non-modified silica microparticles (Creative Diagnostics, US), and the microgels were actuated by modulated NIR laser (0.5 s - 0.5 s) for 5 min for thorough mixing. To fix the microparticles, several layers of round coverslips (diameter: 10 mm) were first glued in the center of a 18 mm × 18 mm coverslip with epoxy adhesive, which was then used to cover the PDMS chamber containing microgels as illustrated in Figure S2. In this way, the spiral microgels can be confined in the space between cover slip and glass substrate; the solid microspheres were thus clamped by the two surfaces, while the attached soft microgels can be actuated. The spiral microgel, which had a microsphere attached to one end, was selected for the current study.
Figure S2. Illustration of the chamber containing spiral rotor.

For the helical microswimmer in the second section of this chapter, silicon masters in Figure S1 (b) and (c) were replicated to provide the non-wetting mold. The fabricated microgels were first transferred into the PDMS chamber with the same method described above and then loaded into a plasma-treated (200 W, 5 min, 1 mbar, PVP Tepla 100) rectangular capillary tubing after re-hydration (dimensions of the tubing: 0.05 mm \( \times \) 1.0 mm \( \times \) 50 mm for the 1 \( \mu \)m \( \times \) 5 \( \mu \)m \( \times \) 80 \( \mu \)m microgel, and 0.04 mm \( \times \) 0.8 mm \( \times \) 50 mm for the 1 \( \mu \)m \( \times \) 5 \( \mu \)m \( \times \) 160 \( \mu \)m microgel, Vitrocom). The capillary tubing was sealed and fixed on a microscope slide with epoxy glue for observation.

For the experiment with microchannel confinement, the re-hydrated helical microgels (1 \( \mu \)m \( \times \) 5 \( \mu \)m \( \times \) 160 \( \mu \)m) were pipetted on top of a silicon wafer, which is photographically patterned with continuous channels with width of 5 \( \mu \)m, depth of 1.6 \( \mu \)m, and spacing of 10 \( \mu \)m (AMO GmbH). A PDMS frame was placed on the silicon wafer to confine the liquid containing microgels, which was then covered by a coverslip to prevent evaporation.

**8.4.2 Actuation and observation of microgels**

The samples were placed on a Peltier stage for temperature control mounted on the sample stage of an optical microscope (VHZ-100UR, Keyence). A silicon wafer was placed beneath the sample to enhance optical contrast. The temperature of the Peltier stage was controlled with an accuracy of \( \pm \) 0.1 °C. Near infrared (NIR) laser (808 nm, 2.5 W, Roithner Lasertechnik) was focused to the middle of field of view with an
incident angle of roughly 40 °. The elliptical spot has a diameter of around 1 mm, and the resulted laser intensity in the center of the spot is roughly 1.7 W·mm⁻². The laser was modulated by a custom-made software, which provides 1 ms temporal resolution. For the spiral rotor, videos were recorded by the microscope camera at a frame rate of 27 frames per second, while a high speed camera (Miro M310, Phantom) was used for the helical microgel under actuation, which can reach a frame rate of 2000 frame per second. The helical microgel in microchannel was recorded by the microscope camera. A short pass filter (700 nm, OD 4, Edmund optics) was inserted between the lens and camera to filter scattered laser. The setups for the helix in confinements are shown in Figure S3.

**Figure S3.** Schematic drawing of the experimental setup. (a) The helical microgels loaded in a capillary. (b) The helical microgels on a microstructured silicon wafer. The laser was aligned onto the field of view of the microscope objective with an incident angle of 40°.

### 8.4.3 Video analysis

Acquired videos were enhanced and analyzed by ImageJ (V1.50c). Superimpositions of the images were achieved by the *Image Calculator* function. Figure 1 (c) is the superimpositions of thresholded images, to which individual colors were given using *Channel Tools* of the ImageJ. To acquire the change in shape of the spiral, the images were inverted, and the contour was fitted by the plugin *Ridge Detection*. The process is shown in Figure S4 (a). The coordinates of the fitted curve were then exported and
analyzed by Origin. The length of the center line can be easily calculated by adding up the lengths between adjacent points, while the tangential angle of the free end was measured by linear fitting of the points at the end. In principle the tangential angle on any point of the center line can be calculated based on the fitting. As an example, the tangential angle at the half length of the spiral is plotted in Figure S4 (c), which shows a qualitatively similar shape as the one in Figure 2 (d).

![Figure S4](image)

**Figure S4.** (a) Fitting of the spiral microgel using ImageJ. (b) Tangential angle (theta) at the half of the centerline. (c) Change in the theta with the half length of the center line.

### 8.5 References


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