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1. INTRODUCTION

1.1 Motivation

Sunlight is an omnipresent source of energy on our planet. It enabled the formation of life and constantly illuminates the Earth's surface with a power of 342 Watt per square meter.¹ Therefore, it is intriguing to build systems that are able to harvest light energy and transform it into work. Performing a periodic motion from a continuous energy input that itself lacks periodicity is the working principle of so-called self-oscillators.² Well-known examples are the Carnot cycle of a heat engine and the Belousov–Zhabotinsky (BZ) reaction, however it remains challenging to engineer artificial self-oscillators, especially at micrometer scale.³

The key functions to generate a self-oscillator are a feedback mechanism and bistability, as the feedback regulates the energy input and the bistability avoids equilibration of the system.⁴ Several examples exist where scientists have shown how this principle can be applied to generate polymeric self-oscillators. Yoshida et al. have shown how the BZ reaction can be coupled to a responsive gel network to generate oscillating contractions which can ultimately be used to build a self-propelling hydrogel walker.⁵⁻⁷ Alternatively to the chemical energy supply, light-fueled actuators can be built to perform a self-sustained motion.⁸⁻¹¹ Their photoconversion mechanism is, e.g., based on the heating through liquid crystal elastomers and polymer networks liquid crystal networks (LCNs), or gold nanoparticles embedded in a thermoresponsive hydrogel.⁹⁻¹⁰ In both examples, self-shadowing is used as a feedback mechanism to switch the photothermal heating on and off, respectively. Here, we will follow a similar approach, where a thermoresponsive hydrogel with embedded gold nanorods (AuNRs) is illuminated with a laser at their LSPR (localized surface plasmon resonance) wavelength. We chose AuNRs due to their superior heating efficiency and because they can be easily adapted to the embedding matrix by interchangeable surface coatings.¹²⁻¹³ Furthermore, when AuNRs are brought in close proximity to each other, plasmonic coupling causes a shift of the LSPR, therefore reducing the heating efficiency under monochromatic illumination.¹⁴ Regarding the matrix material, the structural and thermal properties of poly(N-isopropylacrylamide) (PNIPAm) and gels thereof are well understood and provide a versatile platform e.g. to entrap or interlink AuNRs to generate photothermal actuators.¹⁵ When coupling aligned AuNRs with PNIPAm, an opto-thermal feedback mechanism is created, fulfilling the first requirement of engineering an artificial self-oscillator.¹⁶

So far, the dimensions of reported artificial self-oscillators are in the range of millimeters. In order to further miniaturize, an additional challenge occurs, as the micromachine needs to overcome the limitations of swimming at low Reynolds number. This is known as the “scallop theorem” and can be accomplished by a non-reciprocal deformation path.¹⁷ This requires control over the actuation pattern, which is interlinked with the shape of the swimmer.¹⁸⁻¹⁹ When AuNR-laden PNIPAm gels are shaped as slender objects, e.g., ribbons and coated on one side with a thin layer of gold that restricts swelling, they coil up to spiral or helical shapes.²⁰ Photothermal heating by the AuNRs enables the actuation via pulsed irradiation, which effects a temperature-induced shape change of the swimmer. Moreover, the kinetics enable transient states of the gel and therefore non-reciprocal kinematics and net displacement.^{15, 21}

The aim of this work is to create a switchable, bistable microgel that transitions with a fast, snap-like motion. Furthermore, it is investigated how a microswimmer with directional motility can be generated with the given material concept. Therefore, the capabilities of the composite material to generate work under critical conditions are evaluated, as well as the kinematics of swimming when shaped as anisometric objects. Ultimately, the combination thereof will open the pathway to generate an autonomous, i.e., a self-oscillating microswimmer.

1.2 Scope of the Thesis

Chapter 2 will give an overview of the state of the art in literature regarding plasmonic heating of gold nanorods, as well as their synthesis and surface modification. Furthermore, the behavior of thermoresponsive hydrogels is described. Ultimately, the combination of both in the application as light-driven microswimmers with non-equilibrium actuation are shown.

In **Chapter 3** the design principles to build an autonomous micromachine are summarized and discussed. This includes the generation of mechanical actuation of a thermoresponsive hydrogel by photothermal heating and the work cycle thereof. Furthermore, the implementation of an opto-thermal feedback to employ a self-controlled energy conversion mechanism is described. A concept for a mechanically bistable object is shown and demonstrated how this enables self-oscillation when combined with the feedback mechanism.

Chapter 4 reports on the shape deformation work cycle of a bilayer hydrogel ribbon under critical conditions, i.e. close to the volume phase transition temperature of the gel. It is highlighted how small temperature fluctuations effect volume changes that lead to large amplitude actuation, amplified by the curvature of the ribbon competing in two directions.

These conditions are sufficient to perform work, e.g., for stirring a dispersion of micro particles.

Chapter 5 discusses the design and characteristics of a microswimmer prepared from a bilayer ribbon with a wedge-like shape. A shape diagram shows how the taper ratio of the ribbon affects the equilibrium shape of the swimmer when swollen. Different photothermal actuation modes via stroboscopic irradiation are investigated and it is shown how the wide and short end of the ribbon, respectively, perform different kinematics. The differentiation in a 'head' (leading edge) and 'tail' (trailing edge) of the ribbon during actuation showcases the directional motion.

In **Chapter 6** the buckling and swimming of radially confined hydrogel microdisks in an annulus is discussed. When swollen, the disk transforms into a wrinkled dome shape. A scaling law is applied to confirm the correlation between the number of wrinkles and the aspect ratio of the disk. Moreover, different modes of actuation enable the accumulation or depletion of a dispersion of microparticles beneath the dome when located on a substrate.

Chapter 7 reports on how a switchable, bistable hydrogel dome can be designed, prepared and actuated. Similar to chapter 6 the wrinkling pattern indicates the state of the dome, however in this case correlates to the passive and active layer facing outwards and inwards, respectively. Bistability is therefore demonstrated by finding both states under the same conditions. It is shown how the dome can be inverted with a snapping motion through temperature change. Furthermore, the influence of the cooling rate on the speed of snap-trough transition is investigated to find that it can be as low as two milliseconds.

1.3 References

The content of chapter **1.1 Motivation** is based on the concept and ideas described in the SFB 985 project application for 'A7 – A microgel clock' and the ERC program 'Jellyclock' (ERC 695716) and parts of the content have been adapted and modified.

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2. GOLD NANOROD LADEN HYDROGELS AS PHOTOTHERMAL ACTUATORS

2.1 Abstract

Soft micro actuators are microscopic objects made of a responsive material with an incorporated energy conversion mechanism that produces a motion upon an external stimulus. Among energy conversion mechanisms, gold nanorods (AuNRs) are a popular choice due to their ease of preparation, simple coating that allows adapting to the matrix material and efficient heating capabilities. Pairing AuNRs with thermoresponsive hydrogels and purposeful shaping methods enables the fabrication of microactuators capable of swimming in water.¹⁻² This chapter will give an overview of the history and state of the art in (i) the fundamentals of the optothermal properties of gold nanoparticles and nanorods in particular (ii) the synthesis and surface modification methods to produce gold nanorods (iii) the properties of thermoresponsive hydrogels and (iv) fabrication methods and applications of thermoresponsive microgel actuators.

2.2 Opto-thermal properties of gold nanoparticles

The term nanotechnology is attributed to being proposed in a speech of Richard P. Feynman in December 1959 “There’s Plenty of Room at the Bottom” and has evolved to a flourishing field of research during the last decades.³⁻⁴ It describes the design of functional matter on a 1-100 nm scale that can be tackled in either a top-down, or bottom-up approach, respectively. Therefore, the term is quite broad and affects many fields of research such as physics, chemistry, materials science, engineering, biology and medicine.⁵ Some of the recent developments in nanotechnology, especially nanoparticles, have already become an indispensable part of consumer products in, e.g., cosmetics, antimicrobial coatings or medical products.⁶⁻⁹ Within these new developments, gold nanoparticles and in particular nanorods play an important role as they have been discovered to efficiently absorb light in order to produce heat at their resonance wavelength.¹⁰ This remote-controlled heat generation, paired with good particle stability and readily available synthesis methods make gold nanoparticles an attractive candidate for innovative concepts in thermoplasmonic applications: From biomedical applications like cancer therapy to catalysis, photovoltaics, and soft microrobotics.¹¹⁻¹⁴

Nanoparticles are well-known for showing size-scaling effects and gold nanoparticles are the most prominent example, therefore having been investigated thoroughly in recent years.¹⁵⁻¹⁷ Their exceptional optical properties have already been observed and employed by humans hundreds of years ago, albeit being unaware of their presence and origin. The most well-known example in this regard is the Lycurgus Cup, which was manufactured by the ancient Romans in the 4th century A.D. It shows the triumph of Dionysus over Lycurgus from the sixth book of Homer's Iliad, embossed in glass that has a pale green color in reflected light and a red glow in transmitted light, respectively.¹⁸ First investigations on the chemical composition of the glass have been conducted only in the middle of the 20th century. The red color was suspected to be caused by colloidal gold by indirect proof as theoretical concepts describing color effects in such dispersions already existed.¹⁹⁻²⁰ This was later confirmed using energy-dispersive X-ray spectroscopy in a transmission electron microscopy setup.²¹ The mechanism of this phenomenon was identified to be an in-phase oscillation of the metal's band electrons with the electric field of incident light, known as localized surface plasmon resonance (LSPR).^{20, 22} When bulk gold is exposed to electromagnetic irradiation, electron clouds on the surface of the metal are coherently displaced from their equilibrium position around the lattice of positively charged metal ions. Such collectively displaced electron clouds are called plasmons and in the previously described case the phenomenon is referred to as propagating surface plasmon polaritons (SPP). These oscillations occur within a certain depth, the 'skin', of the bulk metal. However, when the size of a metal particle is smaller than the thickness of this skin and smaller than the photon wavelength, the irradiation penetrates the entire metal particle and an oscillation of the electrons over the whole volume occurs (**Figure 1A**). Therefore, the effect is called localized surface plasmon (LSP) and when in resonance to the frequency of the exciting light, localized surface plasmon resonance (LSPR).²² The LSPR of gold nanoparticles is typically within the range of visible to near-infrared (NIR) irradiation, i.e. between 500 nm and 1400 nm. However, the exact wavelength of the absorbance maximum depends on the shape and dimensions of the nanoparticle, resulting in a vivid spectrum of colored dispersions.²³⁻²⁴ An increase in one dimension, e.g. the diameter of the particle, leads to a red-shift, whereas a decrease effects a blue-shift of the absorbed wavelength. Consequently, gold particles with an anisotropic shape, i.e., gold nanorods, have two absorbance maxima: Across the diameter (transversal) and the length (longitudinal) of the rod, respectively (**Figure 1B**), with the latter being less sensitive to changes in its dimension.¹⁶ The absorbance cross-section is a multiple of the particle's geometrical cross section (**Figure 1C, left**) and the range of absorbance can be tailored to the needs of an application.²⁵ The LSPR wavelength is furthermore influenced by the dielectric constant of the surrounding medium, as it alters the restoring columbic forces

of the oscillating electrons.¹⁰ If two nanoparticles are in close proximity, i.e., within 2.5 times their diameter or less, the LSPR is shifted due to plasmonic coupling.²⁶ In case of gold nanorods this coupling is sensitive to the angle between the rods, i.e., side-by-side and end-to-end alignment can be differentiated, enhancing the transverse and longitudinal LSPR, respectively.²⁷ The plasmonic oscillations are dampened by a series of relaxation processes within a time span of a few nanoseconds (**Figure 1C**). After the metal band electrons are initially excited by the incident light wave so-called hot electron-hole pairs form and redistribute non-thermally by Landau damping, i.e., by re-emission of light within the first 100 femtoseconds. Subsequently, and within up to one picosecond electron-electron scattering generates heat in the nanoparticle that is then dissipated into the surrounding medium by thermal conduction within 10 nanoseconds.²⁸ This timescale of the chain of events enables nearly instantaneous heating compared to thermal convection from an external heat source.

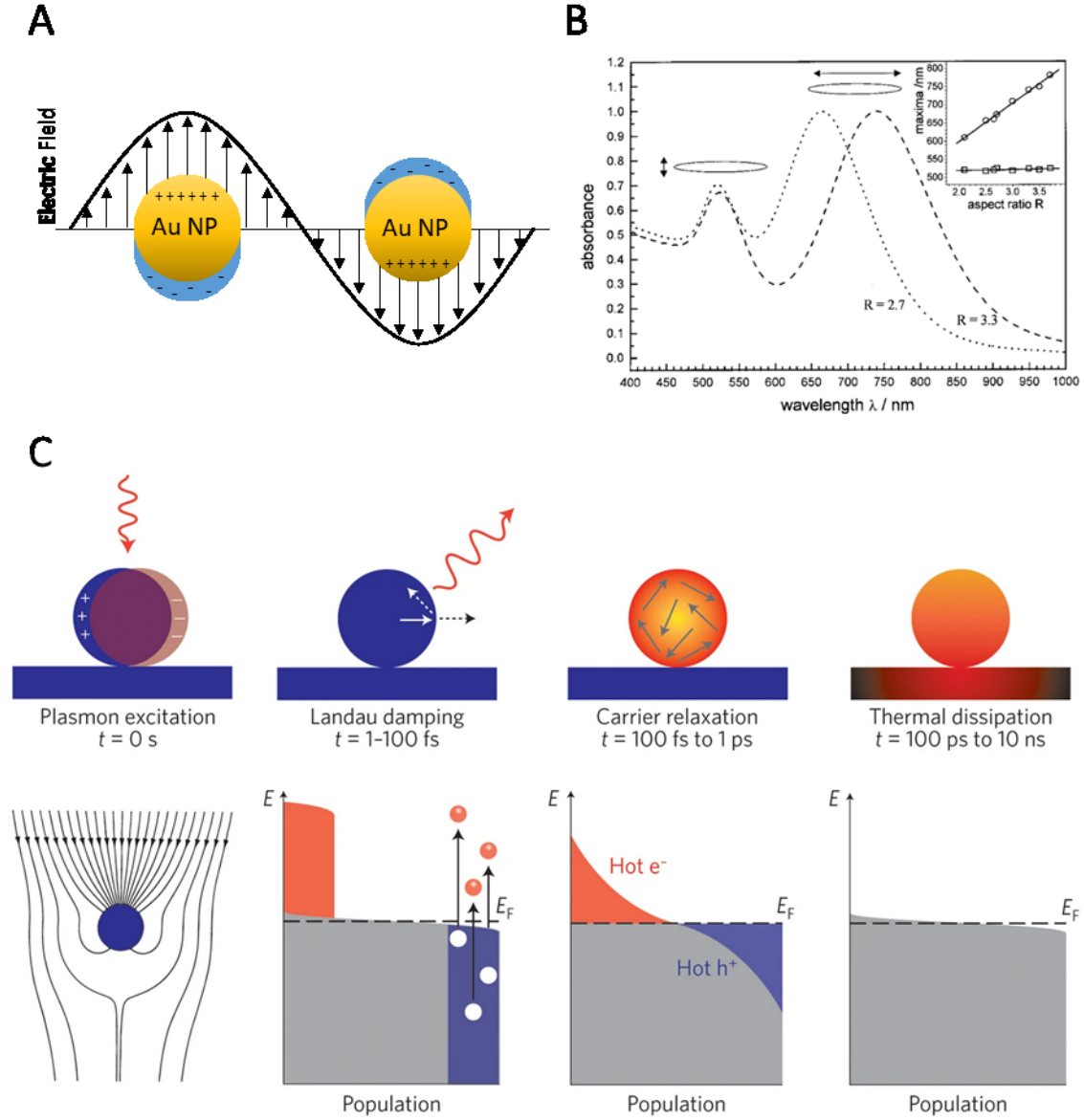


Figure 1: (A) Plasmon resonance of a spherical gold nanoparticle (Au NP): The electrons of the metal's valence band are displaced into the opposite direction of the electric field from an incident light wave. (B) Typical absorbance spectrum of gold nanorods: Two maxima, i.e., transverse (between 500-550 nm) and longitudinal (between 650-800 nm) can be found and shift with the aspect ratio (AR) of the nanorod.¹⁶ (C) Schematic drawing of the photoexcitation of the valence band electrons in a metal nanoparticle and their subsequent relaxation processes with characteristic timescales.²⁸

Nanorods are of particular interest for thermoplasmonic applications, as their surface-to-volume ratio is increased compared to nanospheres.²⁹ Therefore, the heating efficiency is increased by 60 % when transitioning from a spherical to a rod-shaped particle of similar volume and a 3:1 aspect ratio.³⁰⁻³¹ In general, the heating efficiency η of a dispersion of gold nanoparticles can be calculated from the ratio of absorbance and total extinction as

shown in Equation 1. Here, the power absorbed and converted into heat is P_{abs} , the input power is P_0 , and OD is the optical density.¹⁷

$$\eta = \frac{P_{abs}}{P_0(1 - 10^{-OD})} \quad (1)$$

Herein, the optical density OD is defined as the logarithmic ratio of incident and transmitted light intensity and can thus be evaluated experimentally by UV-Vis measurements.³²

$$OD = -\log_{10}(I_1/I_0) \quad (2)$$

Furthermore, with an increasing size of the nanoparticle the scattering contribution grows with its volume squared, whereas the absorbance scales linearly.³³ Many attempts were made to experimentally determine the heating efficiency of gold nanoparticles and values ranging from 2% up to 100 % efficiency were found.¹⁷ In conclusion, when gold nanoparticles are employed in thermoplasmonic applications, they are usually chosen for their optimal heating efficiency and tunability. Therefore, various synthesis strategies for AuNRs have been developed and ultimately complemented by a wide spectrum of surface functionalization to facilitate compatibility with the medium that is to be heated.

2.3 Gold nanorods synthesis and surface modification

Amongst the large variety of synthesis methods that nowadays exist for shape-controlled preparation of gold nanoparticles, colloidal methods are the most popular ones for the growth of gold nanorods.^{12, 15, 34-35} During the synthesis, ligands are employed that enable a precise shape control while stabilizing the dispersion of particles in the medium.³⁶ To further facilitate binding AuNRs to a substrate, oftentimes a ligand exchange is performed to incorporate a functional species with enhanced attractive forces towards the substrate.³⁷ Such immobilization results in a random arrangement of AuNRs. In contrast, coordinated patterns that exploit plasmonic properties of the rods can be synthesized directly in a bottom-up approach by template-assisted procedures.³⁸ Furthermore, selective coating of AuNRs enables self-assembly, or ultimately the generation of interactive matter by incorporating AuNRs into stimuli-responsive polymers.^{1, 39-40}

AuNR Synthesis

First colloidal gold nanoparticles were synthesized by reduction of gold(III) chloride in the presence of citrate as a reducing agent and stabilizing ligand, as published by Turkevich in 1951.⁴¹ Frens found in 1973 that the size of the AuNPs can be controlled by the citrate to gold ratio, which was based on the assumption that the nucleation and growth of particles, respectively, follow different kinetics.⁴² Whereas gold nanorods were first synthesized by electrochemical methods, in 2001 Murphy et al. capitalized on the available knowledge about the aforementioned wet chemical methods and introduced the seed-mediated synthesis of gold nanorods, demonstrating good control over the aspect ratio of the rods.⁴³⁻⁴⁴ The key to achieve this was to (i) employ hexadecyltrimethylammonium bromide (CTAB) as a ligand, as well as (ii) introduce silver ions via silver nitrate. The procedure is composed of two major operations: First, a citrate-stabilized seed solution is prepared by reducing gold to grow isotropic nanoparticles of 3 nm to 4 nm in diameter. This step was soon after improved by El-Sayed et al. who used CTAB to stabilize the seeds, suppressing the formation of spherical shapes.⁴⁵ Second, the seeds are added to a growth solution containing gold salt (chloroauric acid) and small portions of silver nitrate to then form nanorods by adding more reducing agent (ascorbic acid). The nanorods' aspect ratio can be controlled precisely between 1 and 10 by adjusting the number of seeds per *mol* of gold salt in the growth solution. The corresponding wavelength of localized surface plasmon resonance can therefore range between 500 nm and 1700 nm. During the particle growth, the silver ions induce a rod-shaped structure by forming silver bromide on the surface of the particle, therefore restricting the growth in favor of the formation of spheroids (**Figure 2 B**). As CTAB forms rod-shaped bilayer micelles, it further supports the growth of the nanorods, despite covering its surface, as it has a variable packing density and therefore directing functionality on the addition of gold. Depending on the preparation method, the AuNRs can grow with a different crystal structure, e.g., a cyclic penta-twinned crystal structure with five (111) end faces and (100) faces along the (110) axis as shown in **Figure 2 A**.⁴⁶ Furthermore, Murphy et al. found that in case of CTAB the more sparsely packed (100) face of the rods is tightly covered by the head groups of CTAB. Conversely, the (111) faces are more densely packed and therefore less favorable to host the ligand, in return favoring this face to grow by addition of further gold atoms. Via this 'zipping mechanism' the rods grow together with the CTAB bilayer by continuous insertion of new species (**Figure 2 C**).⁴⁷ In addition to the tips of the rod being less densely covered with CTAB, the curvature causes a widening of the ligands structure which further favors the insertion of 'fresh' gold salt.⁴⁸ Pérez-Juste et al. furthermore hypothesized that the directional growth of

the rods can be explained by the asymmetry of their electric field, which is indeed the case as shown in more recent studies (**Figure 2 D**).⁴⁹⁻⁵⁰

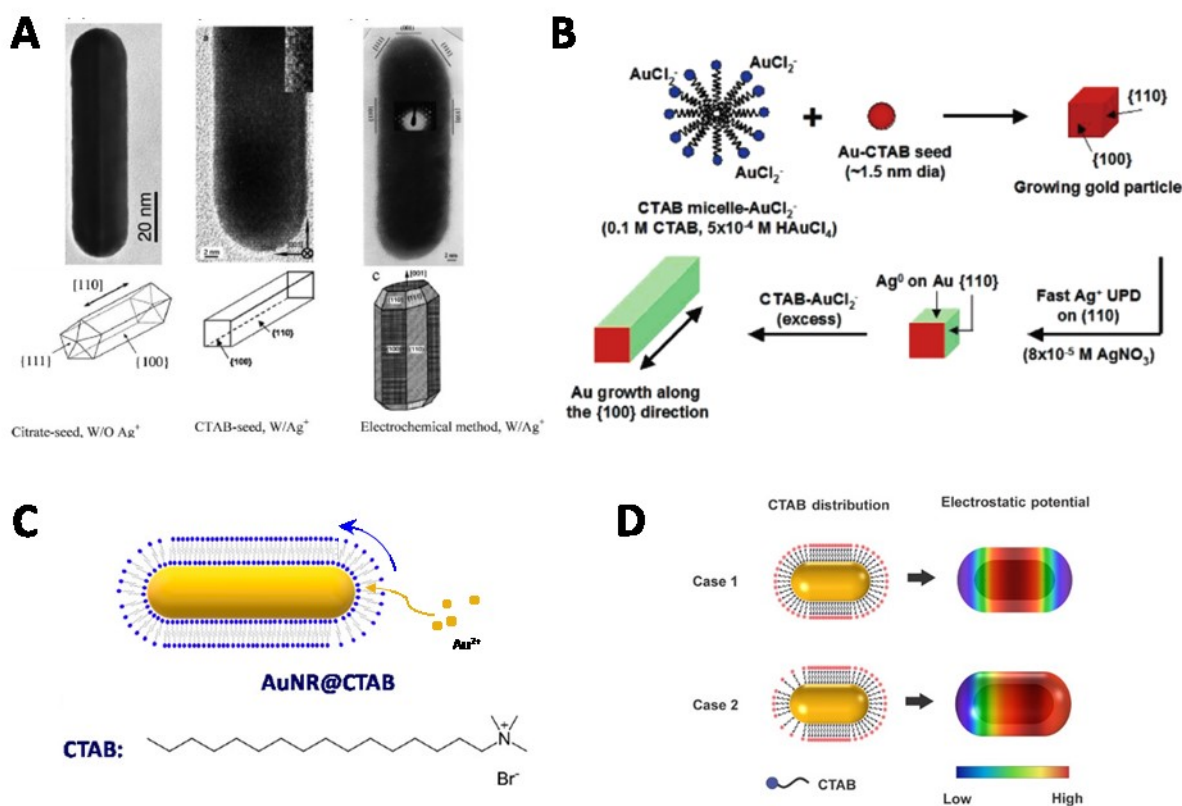


Figure 2: (A) Crystal structure and high resolution transmission electron microscopy images of gold nanorods grown via citrate-stabilized, CTAB-stabilized and electrochemical synthesis, respectively.¹² (B) Scheme for the seed-mediated synthesis of CTAB stabilized gold nanorods with silver ions to enhance the directional growth.⁵¹ (C) "Zipping" growth mechanism of CTAB insertion during the growth step of AuNRs (adapted and modified from Ref.⁵²). (D) Schematic illustration of the dipole character of CTAB-stabilized AuNRs that enhances directional growth.⁵⁰

El-Sayed and Nikoobakht published a modified version in 2003 of Murphy's seed-mediated synthesis with key changes that increase the yield of rods over spheres.⁴⁵ Instead of citrate, CTAB is employed to prepare the seed solution. Furthermore, a second surfactant (Benzyltrimethylhexadecylammonium chloride) is introduced to facilitate the higher yield in the synthesis of AuNRs with an aspect ratio of 4.6 to 10. Moreover, they demonstrated that by continuously adding growth solution, the rod's dimensions can be controlled to the desired target dimensions and thus, the target LSPR wavelength. The resulting dispersion of gold nanorods is redispersible and may serve as a basis for further functionalization, e.g., via ligand exchange, which is essential for translation to applications.

AuNR Surface-Modification

Despite being superior for a controlled growth of gold nanorods, CTAB limits their field of application as it is not compatible with all solvents and more importantly cytotoxic.⁵³ However, it is also challenging to replace as it forms a strong bond with the gold surface. To facilitate simplified handling, Brust et al. reported in 1994 a two-phase synthesis for AuNRs with dodecanethiol as ligand, resulting in an excellent stability and redispersibility.⁵⁴ A disadvantage of this method is the inability to disperse the AuNRs in water due to the lack of solubility of the alkane groups. This was tackled a few years later by Wuelfing et al. by introducing a monolayer coating of R-methoxy- ω -mercapto-poly(ethylene glycol) with thiol end-groups on the rods to facilitate aqueous solubility.⁵⁵ This so-called 'PEGylation' (PEG = poly(ethylene glycol)) became the most relevant and well-established method for functionalization of AuNRs. Furthermore, choosing the appropriate PEGylation agent, e.g. a bi-functional PEG, offers the possibility to make AuNRs water-friendly, biocompatible, or to form self-assembly.^{53, 56-58} In general, the ligand exchange is driven by the higher affinity of the end-group of the newly introduced ligand to the gold surface. Thiols have been proven to be a good choice as end-group, since they form a strong metal thiolate bond.⁵⁹⁻⁶¹ The ligand exchange on gold nanorods can be done via phase-transfer, by immobilizing the nanorods on an ion-exchange resin, or in a one-pot fashion, with the latter being the most feasible method.⁵⁶ Hostetler et al. investigated the ligand exchange of such place-exchange one-pot approach on gold clusters. They found that the exchange kinetics depend on the crystallographic site and size of both the replacing and replaced ligand.⁶² Kinnear et al. further investigated the efficiency of CTAB removal during PEGylation to minimize cytotoxicity, which resulted in a two-step procedure where CTAB excess is washed, then desorbed by solvent exchange and subsequently replaced by PEG.⁶³ The CTAB extraction step can be improved by using chloroform, and the grafting density of PEG enhanced, e.g., by introducing a C-10 spacer between PEG-chain and thiol end-group, making the AuNR chemically more robust.⁵⁷ As mentioned in Section 2.2.1 above, the binding of ligands is site-dependent and therefore enables the development of selective surface functionalization of gold nanorods. The other two major impact factors for selective functionalization are the rod's surface curvature and geometry of the grafted species. A combined control over both factors enables selective functionalization induced self-assembly of AuNRs: The rods can be tuned to show side-by-side alignment or end-to-end alignment, respectively.^{58, 64} Ultimately, this enables further possibilities to tune the optical properties by near-field coupling of the rods. Selectively introducing stimuli responsive molecules as linkers thus results in switchable optical properties of gold nanorod assemblies.⁶⁵

2.4 Thermoresponsive Hydrogel Actuators

Hydrogels are three-dimensional, cross-linked polymer networks that expand, i.e., swell, in water due to the polymer chains' hydrophilic properties. They naturally occur as gelatin or collagen, and ample possibilities exist to produce hydrogels from both naturally occurring and artificial polymers by chemical cross-linking.⁶⁶⁻⁶⁹ Bearing a large amount of liquid, the properties of a hydrogel body can be described as half-solid and half-liquid as it appears solid, however is easily deformed under shear.⁷⁰ Furthermore, functional groups can be added to the polymer backbone to prepare stimuli responsive gels that (de-)swell upon changes in pH-value, ionic strength, electric field, or temperature.⁷¹ By the incorporation of a conversion mechanism, e.g., AuNRs that transform incoming light into heat, into a thermoresponsive gel matrix an interactive material can be generated that reacts to external stimuli.⁷² Furthermore, the combination of being easily deformable and the ability to be stimuli responsive with external triggers makes such composite gel bodies a promising candidate for designing soft actuators and soft micro-robots. Hydrogels and actuators thereof can be employed as drug release carriers, photonic sensors, or for tissue engineering.⁷³⁻⁷⁶

Thermoresponsive Hydrogels

When polymer chains are dissolved in a liquid they form a random coil instead of being in an elongated conformation due to entropic and enthalpic effects, driven by monomer-monomer and monomer-solvent interactions. If such dissolved polymer is stimuli responsive, the monomer-solvent interaction can be influenced e.g. by change of the temperature which leads to a coil-globule transition of the polymer (**Figure 3 A**). The transition point is known as a polymer's upper or lower critical solution temperature (LCST/UCST), respectively.⁷⁷ LCST and UCST represent the lowest and highest temperature, respectively, of the binodal curve as shown in the phase diagrams in **Figure 3 B**. In the case of a polymer with LCST behavior, the hydrophobic interactions between the polymer chains dominate above the LCST, leading to loss of coordinated water molecules and thus phase separation.⁷⁸ This transition can be visually observed and quantified by turbidimetry, as the phase separation induces an increase of scattered light, turning the polymer solution opaque. The temperature at which this occurs is known as the "cloud point".⁷⁹ However, the phase separation proceeds continuously and nonlinearly when approaching and crossing the critical solution temperature.⁸⁰ In a hydrogel, swelling arises from the solubility of polymer chains in a similar way as for the single polymer chain. However, the osmotic pressure is counterbalanced by the polymer network's elasticity arising from cross-linking of the chains that make the polymer resist dissolution.^{66, 81-82} Above the LCST, the water molecules are expelled from the network, resulting in a two-phase mixture

which is referred to as de-swelling or collapse of the gel. The loss of water effects a drastic reduction of volume and therefore the transition is commonly known as the volume-phase-transition (VPT) of a gel. In analogy to the LCST, the transition temperature is therefore the VPT-temperature (VPTT). The phase diagrams of thermoresponsive polymers in solution and the corresponding states of their gels are shown in **Figure 3 B**.

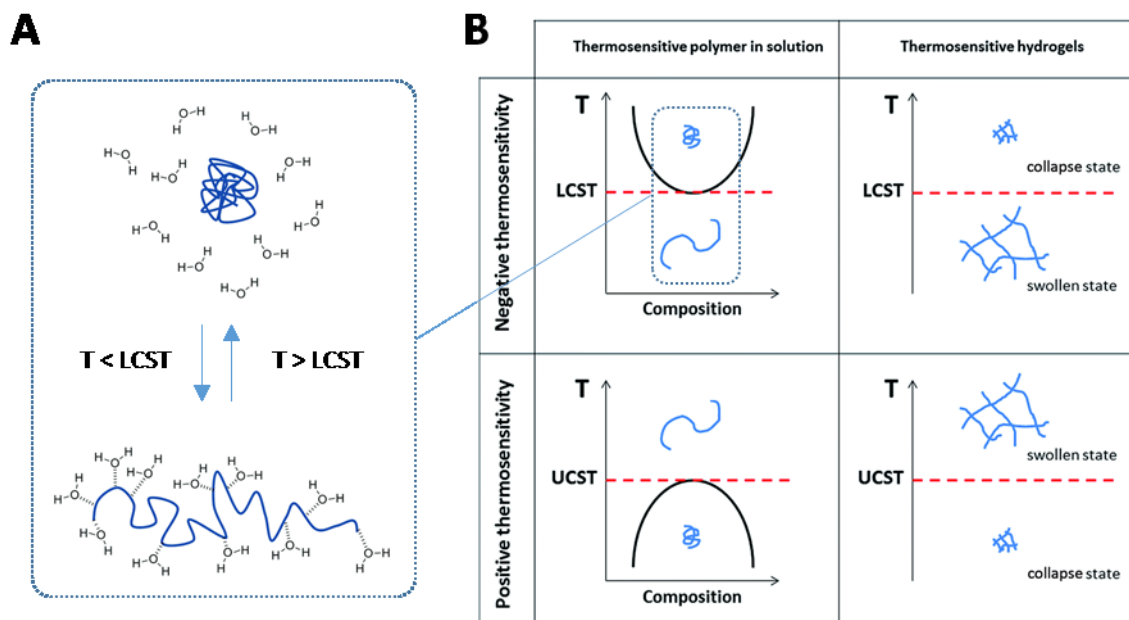


Figure 3: (A) Scheme of a thermoresponsive polymer chain in its states above and below the lower critical solution temperature (LCST), respectively. Scheme adapted and modified from Ref. [78]. (B) Schematic matrix of the LCST and UCST behavior of thermoresponsive polymers and the respective behavior if the same polymers were prepared as a gel. In the solved state the gel network is expanded, whereas it fully collapses when crossing the critical solution temperature. Adapted and modified from Ref. [83].

Amongst thermoresponsive hydrogels, poly(*N*-isopropylacrylamide)-gels (PNIPAm) are the most prominent example and their volume phase transition behavior is well understood.⁸⁴⁻⁸⁵ The backbone of the polymer is hydrophobic, whereas the acrylamide introduces polar moieties along the polymer chain, making it water soluble. The combination of these two moieties results in formation of an LCST polymer and the LCST, and thus the VPT of its gel, is reported to be at around 32°C.⁸⁶ The VPT is a discontinuous process and the foundation for describing the thermodynamics of swelling of gels was laid by Flory and Huggins in 1941 and 1942, respectively, by describing the thermodynamics of polymer solutions.⁸⁷⁻⁸⁸ Shortly after, Flory and Rehner published their theory on swelling thermodynamics of gels.⁸¹ Further in-depth studies of the volume-phase transition of hydrogels were conducted by Toyochi Tanaka et al. between 1978 and 1999.⁸⁹⁻⁹³ According to the model developed by Flory and Rehner (FR-theory), the free Gibbs energy of a swollen gel ΔG_{sw} equals the sum of energies for mixing

of the polymer with the solvent ΔG_{mix} , the elasticity of the network ΔG_{el} , the contribution of mixing ions and electrostatic effects (for ionisable gels) ΔG_{ion} :⁹⁴

$$\Delta G_{sw} = \Delta G_{mix} + \Delta G_{el} + \Delta G_{ion} \quad (1)$$

Herein, the mixing energy and elastic energy are the main contributors to the total swelling free energy. Moreover, the mixing of a polymer chain with solvent molecules is described utilizing a lattice model, which therefore results in a purely enthalpic representation of the swelling process. It is known from other studies that the water molecules rearrange around hydrophobic molecules or moieties, in our case the polymer chain, to form an 'ice cage'. This ultimately enables the thermoresponsiveness of gels by hydrophobic interactions.⁹⁵⁻⁹⁶ In the FR theory, the thermodynamic equilibrium of the gel is assumed to be reached when the chemical potential of the solvent inside and outside of the gel body, respectively, is equal. These considerations result in the prediction of an abrupt VPT of gels. Flory and Rehner also predicted a correlation between the swelling ratio and the density of cross-links, as well as that the preparation of a gel in the presence of a diluent lowers the elastic modulus of the gel network, ultimately increasing its swelling capacity.⁸¹ The VPT behavior of a gel object was experimentally first described and thus confirmed by Kuhn et al. in 1950 for polyacrylic acid that has been cross-linked via esterification.⁹⁷ Besides temperature, stimuli like salt and acid were applied to the gel to vary its swelling ratio. Moreover, a correlation between the extent of esterification, i.e., cross-linking density of the gel, and its swelling degree was found, therefore confirming the FR-theory. The theory was later extended e.g. for charged microgels and an overview of the evolution of theoretical models for gel swelling is given in the review papers from Quesada-Pérez et al. and Dusek et al.^{94, 98-99} Regarding the application of thermoresponsive gels as actuators, the dynamics, i.e., kinetics of swelling are an important factor as they, for example, depend on the shape of the object.⁹³ In general, the characteristic swelling time τ of a spherical gel object is proportional to the diffusion coefficient D of the gel and the squared gel radius a .⁹⁰

$$\tau = \frac{a^2}{D} \quad (2)$$

Typical values for the diffusion coefficient D of e.g. PNIPAm gels are in the order of $10^{-11} \text{ m}^2/\text{s}$. Moreover, D increases with the temperature, which is in agreement with the Wilke-Chang relation.¹⁰⁰ When crossing the VPTT, the (de-)swelling process initially occurs on the surface of the gel object. This leads to internal stress in the gel network that is a function of position and time, as it reduces towards the center of the object and ultimately relaxes when reaching the new equilibrium state.⁹⁰ Such stress formation can induce, e.g., irregular surface

patterning, as observed by Tanaka et al. in shrinking gels that form surface wrinkles.¹⁰¹ Furthermore, dynamic surface patterning of PNIPAm gel objects, and a heating rate dependent VPT were reported elsewhere.^{92, 102-104} Such non-equilibrium reaction to an external stimulus enables purposefully shaped gel bodies to undergo a non-reciprocal deformation cycle, eventually facilitating motility.¹

Hydrogel Actuators

As gels are typically synthesized in emulsion polymerization they have a spherical, 'fuzzy' shape.¹⁰⁵ In order to prepare an actuator from gel, the gelation process therefore needs to be adapted to control the geometry of the object. This can be facilitated by using a hard template like a glass capillary in which the gelation reaction is performed and which is afterwards carefully removed to result in rod-shaped hydrogel. Such gel bodies were typically used in early studies, e.g., for the preparation of photo-activated gel actuators in 1986 by Masahiro Irie.¹⁰⁶ He produced rod-shaped polyacrylamide gels with leucocyanide groups that undergo photodissociation upon UV-irradiation, altering the gel's cross-linking density and thus swelling properties, allowing to induce reversible bending of the rod in combination with applying an electric field. More recently, soft lithography methods were developed that offer the possibility to produce microscopic objects with precise control over sub-micrometer sized features. A popular method was published in 2005 by Rolland et al., known as 'particle replication in non-wetting templates' (PRINT method, **Figure 4A**).¹⁰⁷⁻¹⁰⁸ Herein, an elastomeric, hydrophobic mold is prepared from a master template, then subsequently filled with a polymer precursor solution and then polymerized to solidify in the desired shape. Prefabrication of features inside the mold by partial filling with a secondary precursor solution allows the generation of AB or ABA structures that ultimately can be used for self-assembly (**Figure 4A**).¹⁰⁹ Although thermoresponsive gel bodies prepared via PRINT are employed as actuators by non-equilibrium effects as described in the previous section, a more systematic approach is found in the preparation of bilayer structures. Timoshenko demonstrated already in 1925 how a temperature change can be transformed into change of curvature by using a bilayer setup of metals with opposing expansion coefficients in the context of thermostats.¹¹⁰ This rational can be translated into a passive/active bilayer construction of expandable, soft material systems which can then be applied in bending induced self-folding polymer films.¹¹¹ Such bilayer preparation is more challenging at a micrometer scale, however can be achieved by post-functionalization after PRINT by coating the exposed side of the object in its mold.¹¹² Mourran et al. have demonstrated how an Au-coating can be applied to thermoresponsive microgel ribbons prepared via PRINT with an appropriate gel precursor solution. Post-

modification, i.e., coating with a sputtered layer of gold ultimately allows the generation of light-switchable microswimmers of various shapes (**Figure 4B**).^{1,2, 113} Upon swelling in water, the gel expands on the ‘active’ side, whereas its expansion is restricted by the gold layer on the ‘passive’ side, producing a three-dimensional shape that reverses its curvature across the VPTT. The implementation of gold nanorods ultimately enables rapid temperature changes induced by laser irradiation and continuous on-off cycles with a small range of motion enables translation of the helix. The swimming of ribbons is supported by non-equilibrium effects of (de-)swelling kinetics that can also enable translation in confined spaces by a ‘jetting’ mechanism (**Figure 4C**).¹¹⁴

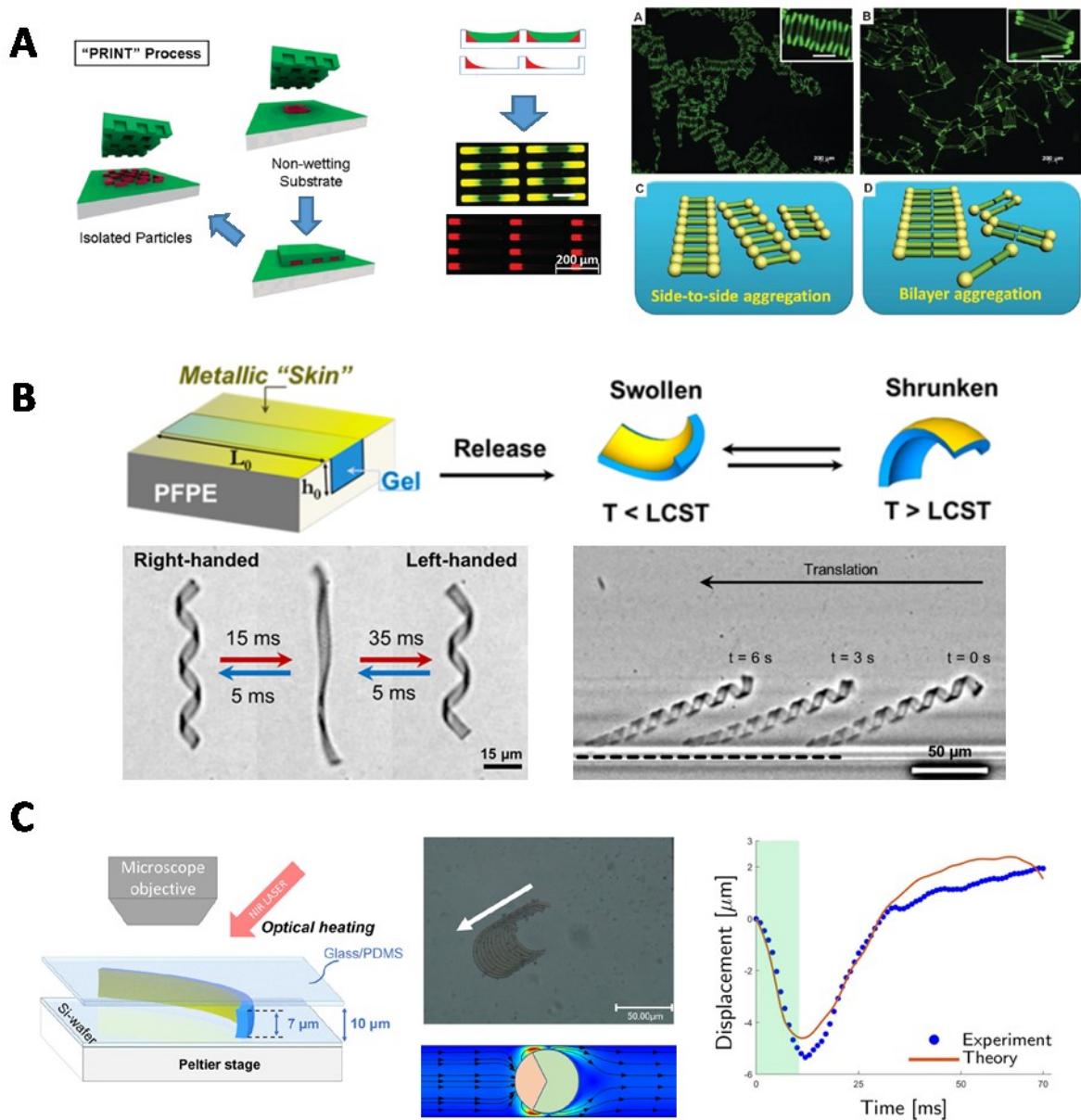


Figure 4: The PRINT method and its adaptations for self-assemblies or light driven microswimmers, respectively. (A) Left: Particle replication in non-wetting templates (PRINT). Right: The mold is filled in two steps with intermediate polymerization, enabling AB and ABA

structures that show self-assembly. Adapted and modified from Ref. [107, 109] **(B)** A thermoresponsive hydrogel body is produced via PRINT and subsequently coated with a thin layer of gold to induce 3D-bending upon swelling of the gel. The swelling induced helical structure inverts upon laser irradiation and is able to translate. Adapted and modified from Ref. [1, 115] **(C)** Jetting of bilayer microgel ribbons in confined spaces. Left: Scheme of the experimental setup for photoactuation of the ribbon. Center: Overlay of an image series showing the translation of the ribbon; Simulated flow pattern around the ribbon between the walls. Right: Experimental vs. theoretical displacement of the ribbon over time. Adapted and modified from Ref. [114].

Despite the advantage of producing a large number of particles at once, soft lithography is limited to the two-dimensional projection of shapes. However, the recent rapid developments of additive manufacturing technology opened further pathways to produce actuators with full three dimensional design freedom.¹¹⁶⁻¹¹⁹ Hippler et al. have shown how this can be applied to prepare tethered, temperature switchable bilayer actuators (**Figure 5A**, left).¹²⁰ Furthermore, they demonstrated equipping a microfluidic channel with switchable valves that can be opened and closed, respectively, by change of temperature (**Figure 5A**, right). This is an advancement over previous approaches where such valves were only realized as 2D-projected shapes, e.g. pillars in a channel.¹²¹⁻¹²² Nishigushi et al. have demonstrated how to gain spatial control at a micrometer level over the cross-linking density of hydrogels to alter their swelling properties and generate an actuator (**Figure 5B**).¹²³ In addition, gold nanorods were dispersed in the printing solution, enabling rapid photothermal actuation. On the other hand, gold nanorods can also serve as thermal initiators to prepare gels with stereolithography.¹²⁴ The disadvantage of stereolithographic methods is the limitation in certain solvent/polymer combinations as monomer units need to stay dissolved, but when polymerized should remain dimensionally stable, requiring rapid gelation kinetics.

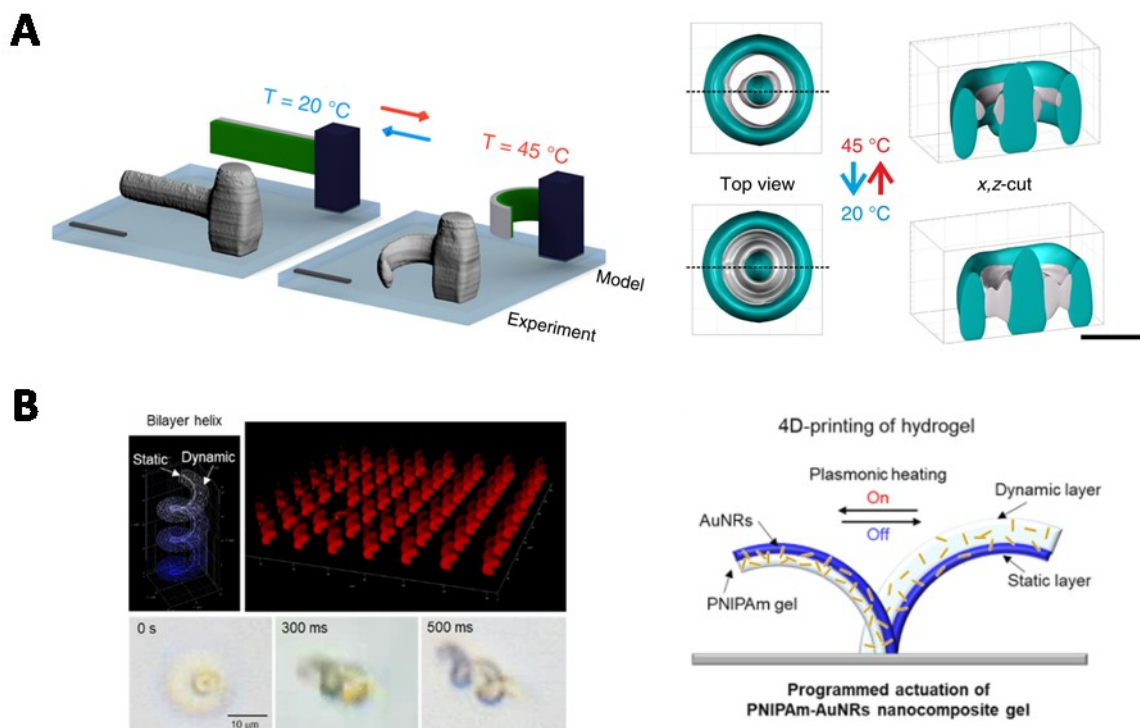


Figure 5: Examples of multiphoton lithography fabricated, PNIPAm based microactuators. **(A)** A static/dynamic bilayer actuator is constructed by controlling the cross-linking density via illumination intensity. The gold nanorods laden precursor solution allows fast (<500ms) actuation by an incident light pulse. **(B)** Left: A tethered bilayer actuator is produced by spatial control over the cross-linking density and can bend across the VPTT. Right: The same material is applied in a microfluidic channel to generate a temperature-switchable valve (scale bar: 30 μm).¹²⁰

Besides the advancements of preparation methods, the implementation of complex chemical reaction systems into the gel network has enabled autonomous regulation of the actuator's movement. This was demonstrated by Hashimoto et al. who coupled the self-oscillating Belousov–Zhabotinsky reaction (BZ-reaction) in the gel.¹²⁵ The BZ-reaction creates waves in the gel that cause peristaltic motion and ultimately enable a ribbon to translate on a ratchet-patterned surface.¹²⁶ More recently, also biological concepts were explored. For example the coupling of an enzyme reaction that drives shape morphing by self-stiffening and self-softening of hydrogels, respectively, to form self-folding origami shapes.¹²⁷ Overall, methods, materials and combinations thereof rapidly increased in variations and complexity over the past years. Actuation mechanisms are increasingly well understood, setting the foundation to further explore realization of autonomous microactuators.

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3. DESIGN OF AN AUTONOMOUS HYDROGEL MICROMACHINE

3.1 Abstract

The recent and rapid progress in additive manufacturing and lithographic methods led to a large toolbox and thus broad variety of micromachines. Through the combination of an increasing accuracy down to nanometer scale, improved miniaturization of such micromachines is facilitated. Additionally, the intelligence is increasing, i.e., the micromachines' ability to adapt or respond to external conditions, navigating or swarming behavior.¹ Their design is oftentimes inspired by the movement of bacteria and other micro-organisms or, on an even smaller scale, the kinesin molecule walking on a microtubule.²⁻³ In the following, a concept to master the key steps of building an autonomous microswimmer with self-maintained motion from a hydrogel is developed and discussed. The micromachine consists of a thermoresponsive hydrogel body that includes the following features: (i) a mechanism to transform light into mechanical energy (ii) a feedback loop to self-control energy conversion (iii) a bistable design that enables self-oscillation and (iv) a shape that facilitates directional motion.

3.2 From light to mechanical energy

The energy source for our micromachine is light and therefore a conversion mechanism is required that transforms light into a mechanical response. First studies of a photo-activated gel actuator were conducted by Masahiro Irie in 1986 on rod-shaped polyacrylamide gels with leucocyanide groups that undergo photodissociation, inducing bending of the rod in combination with applying an electric field.⁴ The bond dissociation alters the gel's cross-linking density and thus swelling properties, which generates an imbalance of the network and therefore internal stress that is partially alleviated by the bending moment of the rod. A similar effect can be achieved by photothermal heating of gold nanorods embedded in a thermoresponsive hydrogel (poly(N-isopropylacrylamide), PNIPAm) as demonstrated by Mourran et al.⁵ As described in the previous chapter, gold nanorods are efficient photothermal heaters that dissipate heat to their surroundings within <10 ns.⁶ When AuNRs are dispersed in water, the temperature of the liquid increases linearly with the incident light intensity upon irradiation (**Figure 1A**). When embedded into the PNIPAm gel network however, the increase

with intensity self-accelerates above a critical value. Above this limit, the heating is significantly more efficient compared to the aqueous dispersion as a similar slope for the increase with incident light intensity can be achieved with a 10-fold decrease in AuNR concentration. In **Figure 1B** the equilibrium swelling curve of a PNIPAm microdisk is shown in blue with the diameter D of the disk plotted as a function of temperature.⁷ The diameter decreases continuously with a steep drop across the volume phase transition temperature, which is typical for thermoresponsive gels. The photothermal actuation cycle of the same disk at an ambient temperature of 20°C is plotted in red. The irradiation causes a sudden increase in temperature and as the heat transfer is more rapid than the mass transport of water out of the microgel network, the diameter is nearly constant. As the perimeter of the gel disk collapses first due to the shorter diffusion path, a transient elastic instability in the gel is generated that causes wrinkling of the surface (image on the right in **Figure 1B**).⁷ Eventually the gel volume and thus disk diameter decreases before the irradiation is ceased. The rapid heat transfer to the surrounding liquid acts as a heat sink and enables a temperature change at nearly constant gel volume. Subsequently the gel swells and the next irradiation pulse begins, restarting the actuation cycle. The actuation efficiency of a microdisk undergoing this photothermal deformation cycle was found to be in the order of 10^{-6} as the vast majority of the heat is immediately dissipated into the surrounding liquid. Hang Zhang further demonstrated that the elastic energy of the gel disk is a function of the disk diameter and the corresponding graphs are depicted in the center of **Figure 1B**. The elastic energy reaches a peak when the disk is shrinking during irradiation and returns to the original level after reswelling. This non-equilibrium response of the gel to rapid temperature changes can be utilized to create a shape deformation hysteresis loop of a V-shaped microgel body as shown in **Figure 1C**.⁵ The internal stress of the gel causes an out-of-plane bending moment and thus three-dimensional deformation of the initially flat V. Therefore, the end-to-end distance of the V changes rapidly during actuation and is plotted as a function of time in the central graph of **Figure 1C**. A clear difference in slope can be seen between the on and off phase of the actuation cycle. The ratio between these two slopes, however, is a function of the irradiation frequency and inverts above a certain threshold.

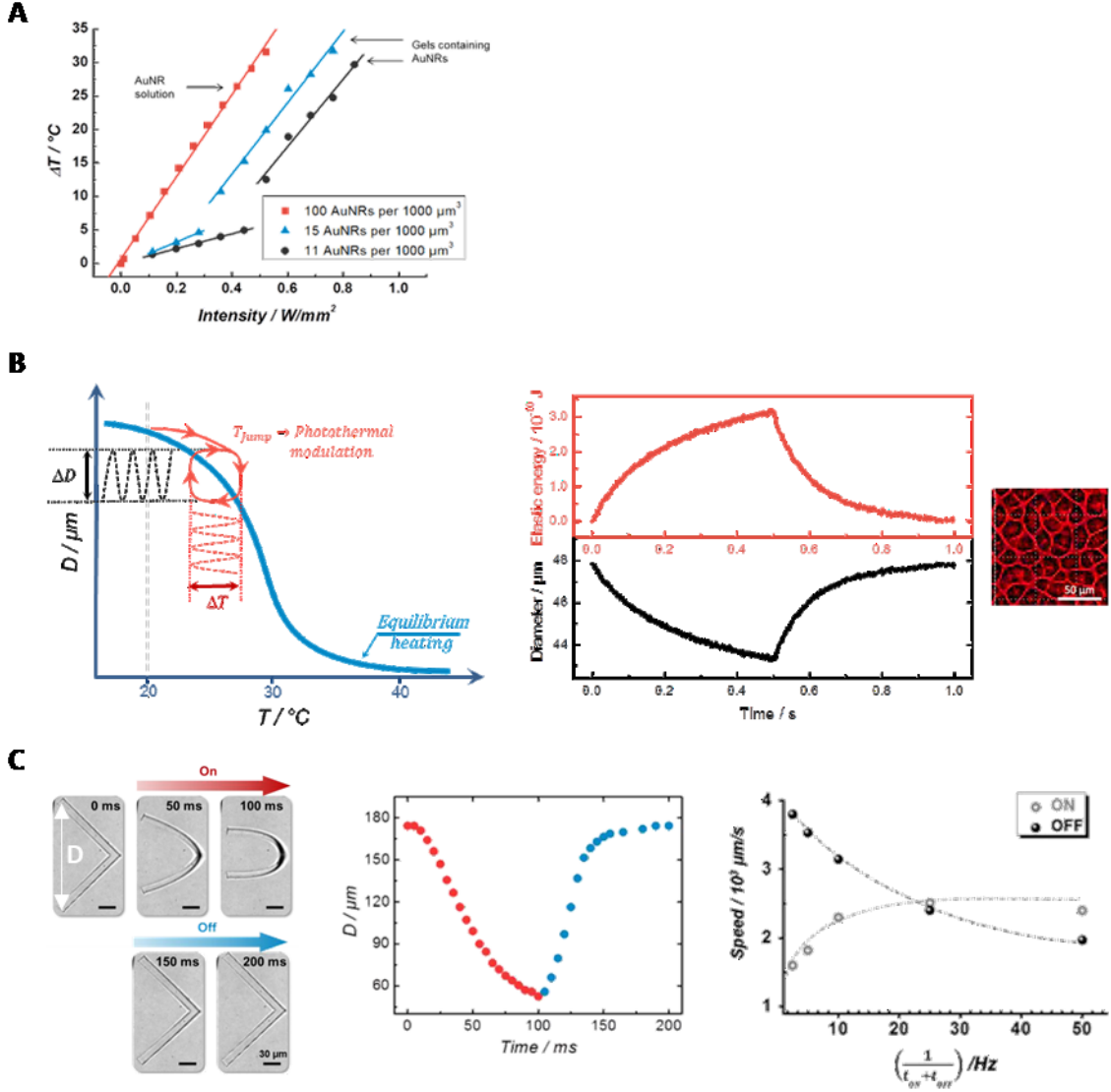


Figure 1: (A) Temperature change of an AuNR dispersion (black) and AuNR-laden hydrogels (blue and red) with different concentrations as a function of the incident light intensity. Adapted from ref. [7] (B) Left: Equilibrium swelling curve (blue) and photothermal actuation cycle by periodic irradiation (red) of an AuNR laden PNIPAm disk. The diameter D and temperature T are effectively varied during (photothermal) heating/cooling as indicated. Right: Diameter and elastic energy of the disk during one cycle. Image of the gel's wrinkled surface in its transient state during photothermal actuation. Adapted from ref. [7] (C) Non-equilibrium shapes of a V-shaped hydrogel body during one photothermal actuation cycle. The central graph shows the end-to-end distance D vs. time during the cycle (heating and cooling period in red and blue, respectively). The actuation speed during the on and off phase, respectively, as a function of the irradiation frequency. Adapted from reference [8].

The work cycle of an AuNR laden hydrogel is already depicted and described within **Figure 1B**. However, we will now focus on the key parameter that needs to be controlled to generate an autonomous system. Therefore, the ideal work cycle is illustrated in **Figure 2**. The black line represents the equilibrium swelling path of the microgel. The initial state is at a low temperature where the gel is swollen. This can be readily facilitated by photothermal heating

of gold nanorods as discussed in the previous paragraph. In order to maximize the output of the micromachine, i.e., the work, the area within the cycle needs to be as large as possible. This can be achieved if the temperature changes at constant volume and the volume changes at constant temperature, respectively. The first condition is sufficiently satisfied for the photothermal heating process as the heat conversion and transfer is much more rapid than the mass transport of water through the gel network. In the second phase the gel collapses at a constant temperature (second condition) which for PNIPAm requires a temperature change of $>10^{\circ}\text{C}$ and therefore likely falls within the regime of self-accelerated heating according to **Figure 1A**. In conclusion, heating with AuNRs is not ideal with regard to maximizing the power output. In a typical experiment the microgel object is placed in a capillary with dimensions and thus liquid volume much larger than the volume of the gel. The surrounding liquid therefore is an excellent heat sink, enabling rapid cooling at nearly constant gel volume, close to the initial temperature. The subsequent increase of volume by swelling of the gel at nearly constant temperature closes the work cycle.

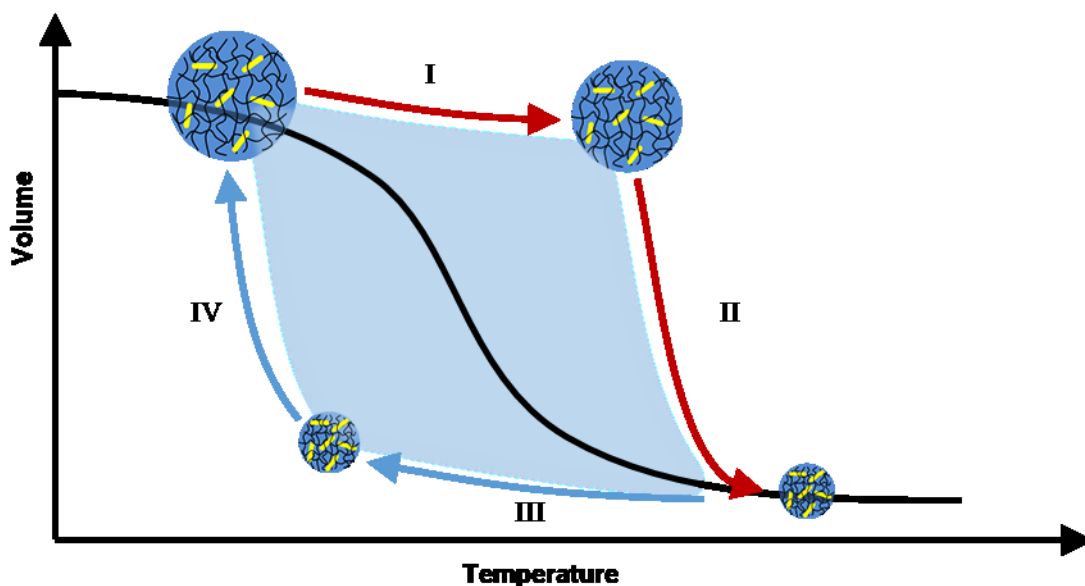


Figure 2: Schematic work cycle of the light-actuated gel microdisk made of AuNR-laden PNIPAm microgel under photothermal heating at the LSPR wavelength. Equilibrium swelling path of a microgel = black curve. Critical to maximizing the work is a constant temperature for phase I and III and a constant volume for phase II and IV, respectively. The area within the cycle (blue shade) represents the work performed, similar to a Carnot process.

The hysteresis loop of the light actuated gel microdisk in **Figure 1B** fulfills the requirements for an object to perform work and therefore demonstrates how AuNR laden hydrogels are an essential element to build a micromachine. However, this work cycle is coupled to the periodic on/off switching of the light source. In order to create a self-sustained motion under continuous irradiation, a feedback loop is necessary that can switch the energy conversion

mechanism on and off autonomously. Ideally, the switch that stops the heat generation acts instantly when the gel reaches its collapsed state in order to minimize overheating and therefore maximize the work output. In the next section, the possibility of generating such a switch by exploiting the optical properties of aligned gold nanorods in a thermoresponsive gel will be discussed.

3.3 Negative opto-thermal feedback

A feedback loop reverts the output of a system to the input, therefore altering the new output value. A negative feedback decreases the output value, whereas a positive feedback amplifies it. In general, this allows the regulation of, e.g., complex biological systems, is applied in electronic devices like amplifiers and is key to self-oscillation.⁹ Zhao et al. have demonstrated how a hydrogel body can be designed to provide a feedback that allows to perform an oscillatory motion under continuous laser irradiation.¹⁰ For our system, we aim to have an opto-thermal feedback, i.e., a mechanism that reduces heating when irradiated. Therefore, gold nanorods shall be end-to-end aligned and coupled to a thermoresponsive material that alters the distance upon irradiation, effectively reducing the heating efficiency. The alignment of nanoparticles can be achieved for example by capillary forces.¹¹⁻¹³ Flauraud et al. investigated how precise control over end-to-end distance between two AuNRs can be achieved and analyze the spectral effects.¹⁴ Besides such template assisted approach, AuNR alignment can be performed by selective surface functionalization and both pathways will be discussed in the following.

Sjören Schweizerhof demonstrated how to achieve a photoswitchable and fully reversible end-to-end alignment of AuNRs by selective surface modification of the rods.¹⁵ Therefore, thermoresponsive PNIPAm ligands are attached to the ends of the rods whereas the sides are PEGylated (**Figure 5A**, left). In a solution of sodium sulfate, end-to-end association of the rods takes place when heated and chains of rods are formed (**Figure 5A**, center). Upon cooling, the assembly reverses to a dispersion of singular rods. Both states can be distinguished by their corresponding spectra in UV-Vis-spectroscopy (**Figure 5A**, right). At 50 °C and after salt addition the LSPR wavelength of approximately 800 nm decreases continuously (thin black lines were recorded at 2 minute intervals). Furthermore, the peak shifts towards higher wavelengths, confirming the expected near-field coupling of the interlinked rods. After cooling to 20°C, the original spectrum is recovered, confirming the full reversibility of the assembly. When in the aligned state, stroboscopic irradiation at the LSPR wavelength triggers photothermal heating of the AuNRs to which the PNIPAm ligands react by ejecting water when

overcoming the lower critical solution temperature (LCST). This results in a reduced volume and thus a lower end-to-end distance between the rods, shifting the LSPR and therefore reducing the heating. The corresponding shifts in spectra and temperature of the dispersion are depicted in the graphs of **Figure 5B**.

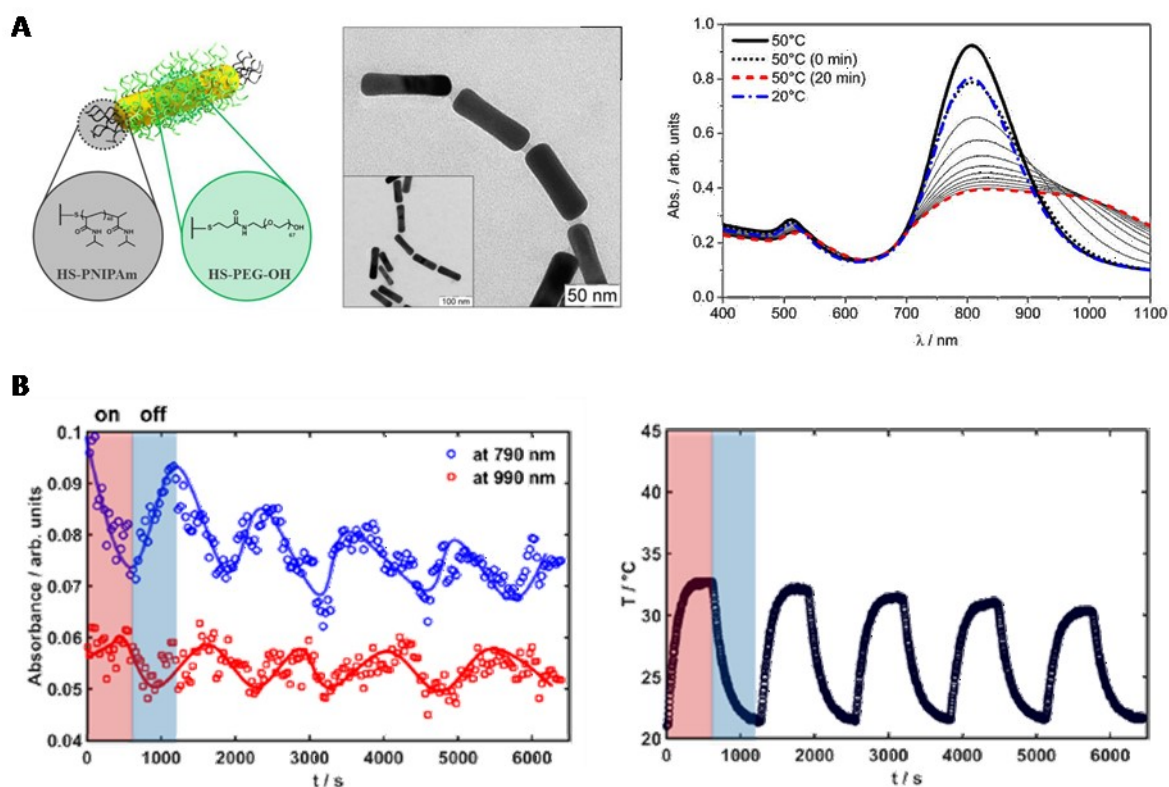


Figure 5: Selectively modified AuNRs for end-to-end alignment with thermoresponsive ligands to enable a photothermally induced shift of maximum absorbance. **(A)** Left: Sketch of an AuNR with selective side- and end-modification. Center: Transmission electron microscopy image of self-assembled AuNRs that are modified as shown in the sketch. Right: The absorbance spectra of such AuNRs as a function of time after salt addition at 50°C (reducing the maximum around 800 nm) and recovery of the end-to-end assembly after cooling to 20°C (blue). **(B)** Left: The optical absorbance at 790 nm and 990 nm, respectively, of a dispersion of the AuNRs in 150 mM sodium sulfate under photothermal heating cycles (on/off intervals as marked). Left: corresponding dispersion temperature evolution over time during the photothermal stimulation. Figure adapted from reference [15].

Despite being successful in reversible end-to-end alignment of the AuNRs and shifting the absorbance spectrum by temperature, this feedback mechanism is insufficient to reduce the heating by itself to a level where it can recover and therefore still relies on pulsed external stimulation. This problem was addressed in the work of Marcel van Dongen, who developed a method to align AuNRs on a microstructured surface and transfer them onto a PNIPAm microgel surface. In this configuration, the end-to-end distance of aligned AuNRs is coupled to the swelling degree of the thermoresponsive hydrogel. A scanning electron microscopy image

of the microstructured template and gel surface is shown in **Figure 6A**. To facilitate the transfer of the rods onto the surface of e.g. a microgel disk the PRINT method (particle replication in non-wetting templates) is applied. When bound onto a gel, the effectiveness of monochromatic laser irradiation will depend on the expansion state of the gel: In the swollen state the end-to-end distance between two rods is larger compared to the shrunken state. Under appropriate spacing of several nanometers between the rods, near-field coupling between the AuNRs occurs and any change in distance effects a shift of the LSPR wavelength. Thus, a laser irradiation wavelength can be selected that preferably heats the gel in either state. Van Dongen et al. chose a wavelength close to the maximum absorbance of a single rod (approximately 808 nm, **Figure 6C**). Under these conditions, the absorbance spectrum is close to that of a regular AuNR dispersion and photothermal heating occurs. Upon the subsequent temperature increase, the gel shrinks and the distance between the AuNRs decreases, leading to a blueshift of the LSPR wavelength. The result is a decrease in effectiveness of the photothermal heating. When observing an isotropic dispersion of AuNRs in a PNIPAm gel at 20°C and 40°C, it is found that the temperature increases at a higher rate at 40°C versus 20°C. This is due to an increase in optical density – the per-volume concentration of rods increases because the gel loses its water content. In contrast, a gel with aligned AuNRs on its surface shows reduced heating at 40°C despite the increased optical density, indicating the near-field coupling induced spectral shift of the LSPR.

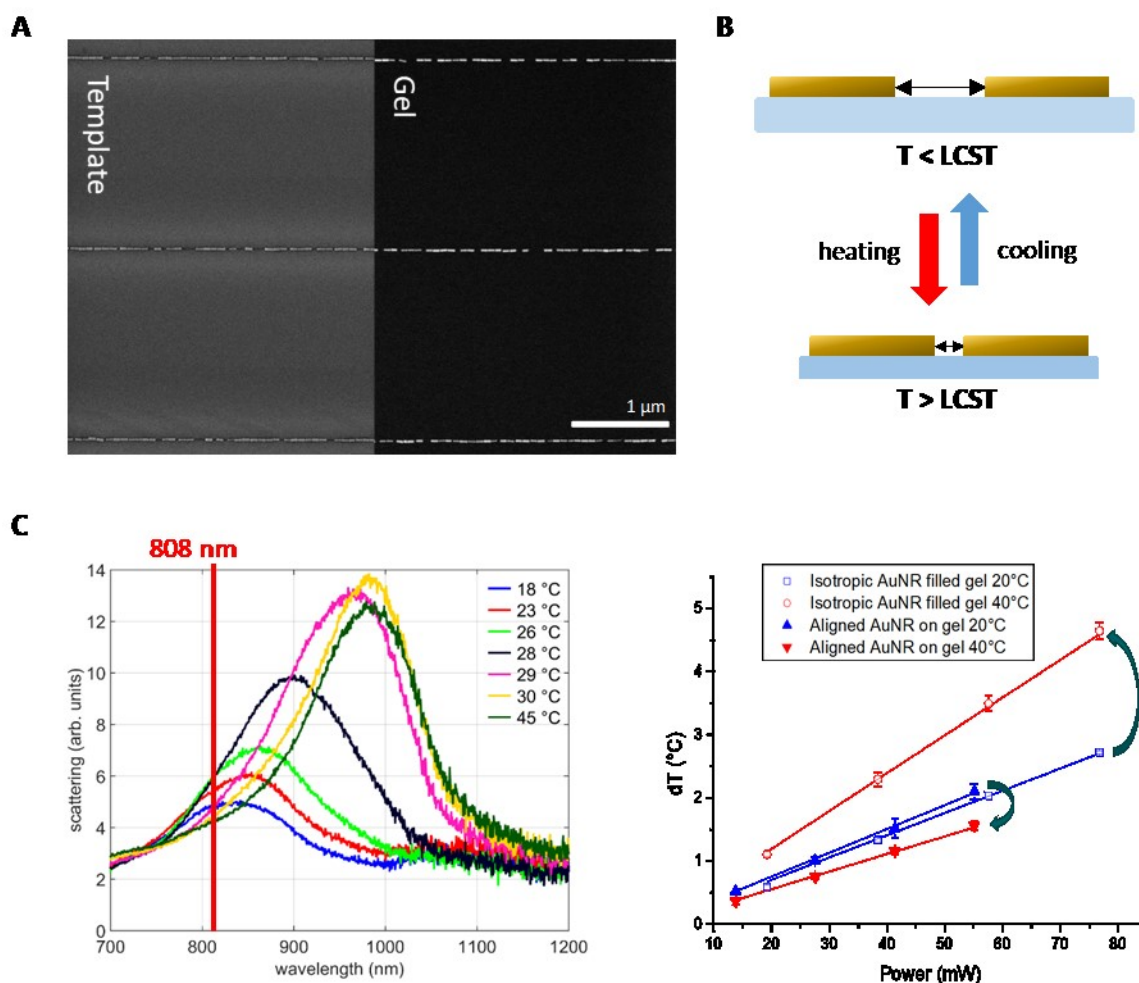


Figure 6: (A) A microstructured template with end-to-end aligned gold nanorods (left) is used to transfer the AuNRs onto a microgel surface (right). (B) Swelling induced control of end-to-end distance by (re-)swelling. (C) UV-Vis spectra of aligned AuNRs on a microstructured gel surface at different temperatures (left) and comparison of the photothermally induced temperature change at 20 °C and 40 °C of aligned versus isotropically distributed AuNRs (right). Figure 6A and 6C have been adapted from unpublished work of Marcel van Dongen and Alexander Nedilko and were created within the SFB985 A7 project, supervised by Dr. Ahmed Mourran, Prof. Dr. Gero von Plessen and Prof. Dr. Martin Möller.

Two tangible solutions were developed and discussed that can be applied to facilitate a negative opto-thermal feedback mechanism. However, a feedback mechanism by itself always drifts towards an equilibrium state, i.e., the system is dampened. In order to overcome this, a bistability mechanism needs to be implemented so that, by accumulation and sudden release of energy, the switch between the two states occurs in a rapid fashion, eventually maintaining a constant oscillation amplitude.

3.4 Bistability enabling self-oscillation

Bistability describes the ability of a system to be stable in two different states, i.e., have two local minima of free energy under the same conditions. These two stable states can correspond to two different geometrical configurations, e.g. the upwards and downwards buckling, respectively, of a clamped beam under in-plane compressive force.¹⁶ As the flat state of such structure is inaccessible, a rapid transition between the two states by snap-through buckling takes place. In the following, we discuss how to translate this principle to a free-standing microgel structure, and how the work-cycle of this micromachine can be affected by its design parameters.

The first challenge is to implement a self-activation mechanism that drives the transition between the two states. An exemplary solution has been shown by Timoshenko who investigated a bilayer metal beam with differential thermal expansion coefficients, enabling temperature-induced snap-through buckling.¹⁷ Just like the metal beam, gels also allow the sudden release of stored elastic energy resulting in rapid actuation as demonstrated by Lee et al.¹⁸ Our system shall be a bistable, dome-shaped actuator that includes an optical feedback mechanism as discussed in the previous section. In Chapter 7, a detailed description and discussion on the preparation, characterization and actuation of a snap-through buckling microgel dome is provided. For the following, we consider a bilayer microdisk with an active side, comprised of a thermoresponsive gel including an opto-thermal feedback mechanism and a passive layer, comprised of a non-responsive material. The disk is radially compressed and fixed in an annulus resulting in a dome shape by buckling. This dome is stable in two states: with the active and passive layer facing outwards, respectively. The two states and corresponding energy minima are depicted in **Figure 8A**. The compression-induced buckling makes the flat state of the disk inaccessible and therefore creates an energy barrier between the two states. Furthermore, the amount of compression defines the deflection height of the dome and therefore the height of the energy barrier. Therefore, the amount of potential energy stored before transitioning from one to the other state can be tailored. The swelling state of the gel creates a preference for the active layer to face outwards at low temperature (swollen) and to face inwards at high temperatures when the gel is collapsed. Therefore, it is the driver for the inversion of the dome and its properties are thus relevant to the transition behavior. In addition, the swellability of the gel depends on its preparation state as shown in **Figure 8B**. The radius of the disk in preparation is 30 μm , and when swollen in water expands to up to 50 μm , independent of the polymer mass fraction during gelation. However, the minimum radius when the gel is collapsed shows a strong dependence on the mass fraction, as both

decrease together. Thus, the mass fraction during preparation of the disk can be utilized to adjust the driving force for the dome inversion.

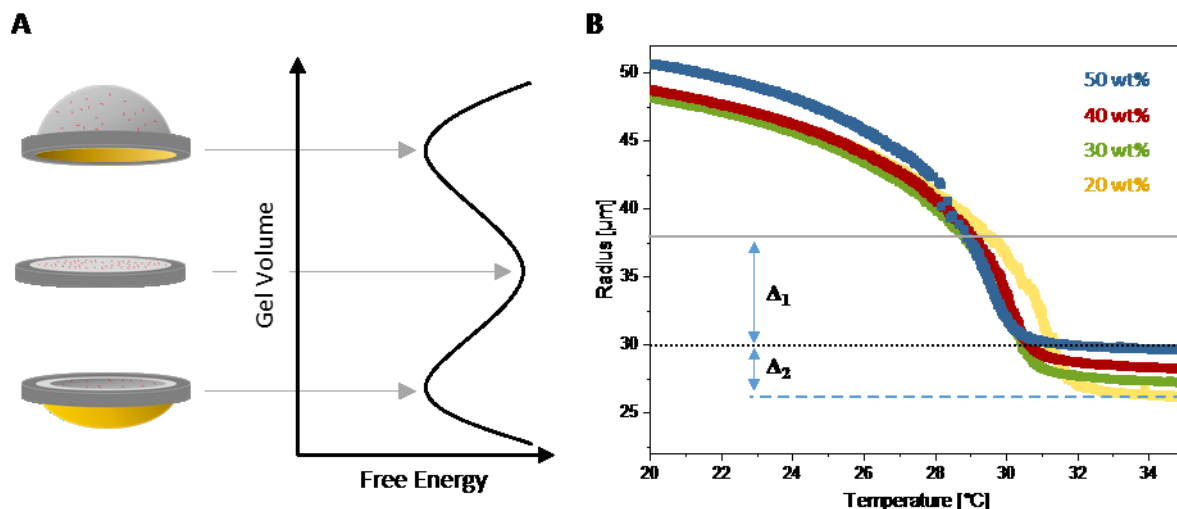


Figure 8: (A) Sketch of a radially compressed bilayer disk clamped in an annulus; the two stable states of upwards and downwards deflection (and corresponding energy minima) and the transient flat state (energy barrier separating the minima). (B) Equilibrium swelling curves of PNIPAm microdisks as a function of temperature and for different mass fractions in the preparation state. The radius of the disk and annulus in preparation state is 30 μm (dotted black line). The passive layer is applied under radial expansion (grey solid line). The dotted blue line marks the minimum radius of a gel with 20 wt% in preparation. Δ_1 affects the deflection of the passive layer, whereas Δ_2 is related to the force the gel exerts upon collapse to invert the dome.

The work cycle of a self-oscillating microgel made from a thermoresponsive hydrogel with an opto-thermal feedback and bistability mechanism is depicted in **Figure 9**. On the left, the equilibrium swelling hysteresis is shown as a black solid line with a grey dotted line indicating the range where bistability occurs. Within this temperature frame there are two possible states that the gel can be found in. For example at T_0 the two possible states correspond to the two minima in free energy as indicated by the dotted red arrows. The two minima are separated by an energy barrier, i.e., the local maximum as indicated by the light blue arrow. When the continuous irradiation of the object is started, the local plasmonic heating effects a transient state of the gel with a close to initial volume but higher temperature (solid red arrow, 'on' state). De-swelling of the gel then leads to reduced heating due to the feedback mechanism ('off' state) and therefore subsequent re-swelling until the photothermal heating ('on' state) sets in again and the process restarts itself. Because of the bistable design, the system is storing and rapidly releasing a certain amount of elastic energy while being driven across the energy barrier by the (de-)swelling forces each time it transitions between the 'on' and 'off' state. This is a key factor to avoid reaching an equilibrium state and maintain the oscillation as long as the irradiation continues.

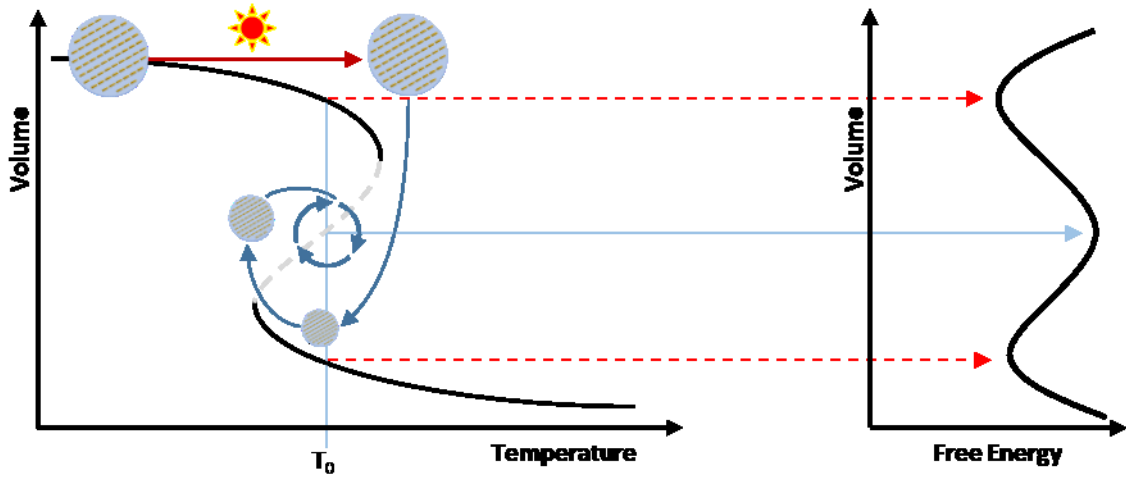


Figure 9: Schematic work cycle of a self-oscillating microgel (left) and the volume of the gel vs. free energy of the oscillator with bistability mechanism (right). Due to the bistability, the equilibrium swelling curve of the gel follows a hysteretic path upon heating and cooling, respectively (solid black & dashed grey line). Thus, at temperature T_0 the system has two stable states, i.e., two minima in free energy (follow the red dashed arrows). These minima are separated by a local maximum (follow the light blue arrow). Upon irradiation, the photothermal heating increases the temperature of the gel at near constant volume (red arrow) and the opto-thermal feedback causes reduced heating, i.e., re-swelling until the photothermal heating is re-started. The bistability enables the continuous oscillation around the local maximum of free energy.

The amount of radial compression and thus the dome's deflection height directly affects the speed of snap-through buckling which is a crucial factor to maximize the efficiency of the work cycle. In an ideal case both the energy built-up phase by shrinking and swelling of the gel, respectively, and the energy release phase by snap-through transition are as short as possible. However, as duality between the two exists, there is likely an optimum in the ratio since, e.g., the photothermal heating continues until the dome inverts, allowing more time for the gel to shrink. Furthermore, a symmetrical snap would be beneficial for a controlled self-oscillation. In contrast, asymmetry in kinematics enables swimming of microscopic structures and is therefore needed to achieve directional motion. The requirements for the latter will be further discussed in the next section.

3.5 Directional Swimming

So far, we have discussed all necessary functions of designing a self-oscillating microgel. In order to achieve a directional motion, the kinematics have to be controlled to overcome the limitations of swimming at low Reynolds number, while in addition providing a sense for directionality, i.e., distinguish between 'head' and 'tail'. Nature brought forth a flourishing variety of microorganisms that create propulsion by body shape deformation or controlled movement of flexible appendages, and inspired many scientists to mimic these in motile active matter.¹⁹ Both natural and artificial microswimmers overcome the challenges of swimming at low Re-number through non-reciprocal shape deformation cycles.²⁰ Furthermore, it was found that the locomotion of microswimmers is facilitated through exploiting viscous drag and the trajectory of swimming is influenced by the drag anisotropy.²¹ For example unlike a sphere, a spheroid does not sediment in parallel but at an angle to the gravitational field, gliding along its long axis.²² Moreover, translation can be facilitated by angular forcing of chiral objects, like helices. Koens et al. demonstrated this principle for a ribbon-shaped hydrogel microswimmer that coils up into a helix upon swelling.²³ Hang Zhang demonstrated how directional translation can be achieved with this helical swimmer by placing it into a confinement environment, i.e., a channel with a depth and width close to the dimensions of the helix's diameter.⁷ Capitalizing on this knowledge, a purposefully designed microswimmer is discussed in chapter 5, that shows anisotropy in shape and by two different modes of motion on the 'head' and 'tail', respectively. This swimmer is able to perform a directed motion without the need of a confined environment. Ultimately, the previously presented concept of a dome-shaped self-oscillator is also in favor of providing directional motion, as demonstrated in recent literature, and will be further discussed in Chapters 6 and 7.²⁴⁻²⁵

3.6 Experimental Section

Preparation of hydrogel microdisks

All listed chemicals and materials were used as received, unless stated otherwise:

Acetone (Sigma-Aldrich), Dimethyl sulfoxide (DMSO, VWR), Isopropanol (IPA, Sigma-Aldrich), N-Isopropylacrylamide (NIPAm, 97%, Sigma-Aldrich, recrystallized in hexane), N,N'-Methylenbisacrylamide (BIS, 99%, Sigma-Aldrich), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (98%, Sigma-Aldrich), Bifunctional perfluoropolyether urethane (PFPE, Mw = 4000, Fomblin® MD 40, Solvay Solexis), 2-Hydroxy-2-methylpropiophenone (97%, Sigma-Aldrich), Polyvinylpyrrolidone (PVP, 40 kDa, Sigma-Aldrich). A micro structured silicon

wafer (AMO GmbH) with an array of pillars (diameter 60 μm and height 5 μm) was used as template.

The preparation of PNIPAm microdisks was performed in a glovebox with an oxygen level of under 0.5 %. Three stock solutions were prepared: (I) For the fluorinated elastomer mold MD40 PFPE was thoroughly mixed with 1 wt% of 2-Hydroxy-2-methylpropiophenone as photoinitiator and subsequently bubbled with nitrogen for 30 min. (II) A hydrogel prepolymer solution was prepared by adding 575 mg (1 eq) of NIPAm with 7.83 mg (0.01 eq) of the crosslinker BIS and 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone as photoinitiator to an appropriate amount of DMSO that results in a mass fraction of 20 wt%, 30 wt%, 40 wt% and 50 wt%, respectively. After thorough mixing, the solution was bubbled with nitrogen for 30 min. (III) A solution of PVP in ethanol/water at a volume ratio of 7/63.

An elastomer replica of approximately 20 mm x 50 mm was prepared from the Si-master wafer by placing two pieces of double-layered of Parafilm (Bemis) onto the wafer and laying a clean glass slide on top. The interspace was then filled with solution (I) and subsequently cured by UV-irradiation (370 nm, 2 W) for 10 minutes. The 200 μm thick elastomer mold was separated from the wafer, cut into 6 mm x 6 mm squares and washed with acetone prior to its use as a mold. The process was repeated, however with an additional glass slide replacing the Si-wafer and two pieces of 4-layered Parafilm to result in a featureless film of 400 μm thickness. It is used to cover the mold during the PRINT-process. The two 6 mm x 6 mm pieces (mold and flat film) were placed into a homemade press with a quartz glass window. A 0.5 μL droplet of solution (II) was placed onto the mold and covered with the flat film by closing the press. The sample was irradiated with UV-light (370 nm, 2 W) for 10 min to facilitate PNIPAm gelation. After removing the sample from the press and glovebox, the flat film was peeled off and the mold was placed with the gel objects facing down onto a droplet of solution (III) on a cleaned and plasma activated (O_2 , 1.6 mbar, 200 Watt, 2 min) glass slide to then dry overnight.

Harvesting and sample transfer into capillaries

Capillaries with a 50 x 1000 μm rectangular cross section (VitroTubes, VitroCom) were plasma treated (O_2 , 1.6 mbar, 200 Watt, 2 min). After peeling the sample mold from the PVP, 15 μL of ultrapure water were added onto the sample. Subsequently, the microdisks detached from the glass slide by swelling in water and dissolution of the PVP. The swollen microdisks were transferred into a capillary by gently immersing it into the droplet until completely filled. Both ends were then placed onto circular glass slides (diameter: 5 mm) and sealed with two component epoxy glue (UHU Plus Sofortfest).

Bright-field Microscopy Imaging

The sample capillary was placed onto a microscope stage with temperature control. A digital microscope (VW1000, Keyence) was used to record the images of the samples. After sufficient time for equilibrium swelling at 20°C, videos of the disks were recorded at heating rates of 1°C/min from 20°C to 40°C.

Image Analysis

The recorded videos were analyzed via *Fiji ImageJ*. In order to determine the radius of the microdisk, the image sequence of the recorded videos was first thresholded and subsequently binarized. The 'analyze particles' function within *ImageJ* was used to analyze the area of the disk for each frame. From this, the radius was calculated and the value plotted vs. the number of the current frame, i.e., temperature after appropriate conversion.

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4. A CRITICAL HYDROGEL ENGINE

4.1 Abstract

Propulsion mechanisms of artificial microswimmers demand an energy supply that is oftentimes provided externally and first converted by a chemical reaction or another type of energy dissipation mechanism to then effectuate motion. We here report on a hydrogel bilayer ribbon that is able to perform work by direct conversion of changes in temperature into actuation by coupling the volume phase transition of the gel to bending deformation by differential swelling. We demonstrate the critical conditions under which a curvature inversion of the ribbon takes place across the gel's volume phase transition and how mechanical properties, i.e., build up and retarded release of stress effectuate a shape deformation work cycle. This system is prone to amplify even small alterations in temperature as large volumetric changes resulting in amplified motion. Periodic temperature changes of less than one tenth of a degree Celsius are induced by PID-controlled heating and are closely followed by oscillations in the ribbon's curvature. The work thus performed is visualized by flow lines of tracer particles that move faster than Brownian motion.

4.2 Introduction

Flagella and cilia are flexible, filament like appendages equipped with a supramolecular motor to propel microbes e.g. in search for food. Their simple rotary or back and forth motions are the major propulsion mechanism of bacteria and fueled by the hydrolysis of adenosine triphosphate (ATP). Their strokes are sufficient to generate speeds of multiple body lengths per second, despite being rather inefficient when compared to macroscopic mechanical engines.¹ One of the reasons for that is that bodies at the micro-scale have to overcome the viscous drag of the surrounding liquid and therefore deform in a non-reciprocal way.² In that regard the ability of a slender body to deform, i.e., bend or buckle is an important property and drastically influences its functionality.³ For example the red blood cell can travel through capillaries smaller than its own diameter because of its extraordinary softness, which comes from its active elastic network, the cytoskeleton.⁴

Artificial motile active matter at the microscale faces the same challenges as their natural analog and research has brought out a broad variety of concepts how to cope with these.⁵⁻⁷ Fueling mechanisms oftentimes incorporate chemical reactions like the light-induced surface

catalysis of peroxides on Janus particles, or more advanced concepts like oscillating redox-reactions embedded in a hydrogel body.⁸⁻⁹ We have previously introduced a new material system for thermally driven, artificial microswimmers that combine motor and actuator in one and can propel by body shape deformation and jetting.¹⁰⁻¹² It is comprised of a thermoresponsive hydrogel, with embedded gold nanorods that convert near-infrared (NIR) light into heat. The gel therefore acts as a heat engine, i.e., transforming local heat into volume change. Further deformation modes have also been achieved using a bilayer structure where a passive layer induces swelling gradient along the hydrogel thickness and causes out-of-plane deformations. We have investigated the material properties, shape variations and non-reciprocal actuation patterns of such microswimmers, as well as demonstrated how the bilayer actuator can be shaped to achieve a microswimmer with directed motility.¹³⁻¹⁵ As the energy input of the NIR laser irradiation is rather high compared to the effective temperature change of the gel, the efficiency is low and in the order of 10^{-6} .¹⁶ Generally, heat engines are limited in their efficiency η by the temperature of the respective cool and hot reservoir. This limit is also known as Carnot efficiency η_c and can only be reached at infinite time and thus null power. However, when the working substance undergoes a phase transition during the cycle efficiencies of η/η_c close to one can be achieved.¹⁷ At the volume phase transition temperature (VPTT) the hydrogel switches its state from hydrated to condensed, due to hydrophobic interactions.¹⁸⁻²² Therefore, it is not a phase transition in the classical sense of solid, liquid, or gaseous, however comparable effects occur: At the phase transition thermal energy is consumed to facilitate the transition of the substance to reach its new state. This is detectable as an infinite peak of the heat capacity and similarly a peak of heat capacity for gels occurs at the VPTT, however in the latter case is rate dependent.²³ Thus, when choosing a thermoresponsive gel as a working substance for a heat engine, enhanced efficiency can be expected around the VPTT. In this publication we will focus on this special case, capitalizing on our knowledge in the production of temperature driven bilayer actuators. We will highlight the extraordinary sensitivity to fluctuations of less than 0.05°C in ambient temperature at the VPTT. Therefore, the gel is monitored under periodic temperature fluctuations and we investigate the ability of the system to perform work under these conditions.

4.3 Results and Discussion

Curvature reversal hysteresis: The study focuses on a bilayer ribbon composed of crosslinked poly(*N*-isopropylacrylamide) polymer loaded with gold nanorods and sputter-coated on one side with a 2 nm gold layer. It was shaped by micromolding to a length of $L_0 = 160 \mu\text{m}$, width of $w = 5 \mu\text{m}$, and thickness of $h = 2 \mu\text{m}$. The gold layer was applied to one of the larger sides while the ribbon was still in the mold, protecting all other sides. The detailed experimental procedure can be found in the experimental section. Upon hydration with cold water, the misfit strain between the swollen gel and the nearly inextensible gold skin induces biaxial bending, evidenced by a transverse and longitudinal curvature noted as $1/R_w$ and $1/R_L$ respectively (**Fig. 1A**). The resulting shape is a circular arc that aligns easily parallel to the glass walls of the observation chamber (see **Fig. 1**). Note that the shape of such swollen ribbon depends on their length to width ratio, and thickness to width ratio, as well as the thickness of the coating.¹⁴

²⁴ The hydration state of the PNIPAm network strands decreases with temperature and above the VPTT, the hydrogel shrinks below the dimension initially set by the preparation conditions, i.e., the monomers composition and dimension of the micromold. Consequently, the misfit strain at the gold/hydrogel interface is now reversed as compared to the swollen state, thus reversing the curvature with the gold layer facing outwards. For clarity, we assign a negative sign to the curvature whenever the gold faces outwards and refer to this state as inverted (**Fig. 1A**).

Figure 1B shows the variation of curvature as a function of the arc length of the ribbon during heating and cooling at a rate of $5^\circ\text{C}/\text{min}$. This non-reciprocal deformation is due to the hysteresis that evolves during a temperature-dependent bending and curvature inversion cycle. In contrast, under a similar heating rate, quite small hysteresis was observed for a ribbon undergoing isotropic deformation, i.e. unconstrained by the gold skin (**Figure S1**). It is interesting to note that poly(*N*-isopropylacrylamide) homopolymers exhibit low hysteresis, less than one centigrade,²⁵⁻²⁶ yet in a hydrogel this can lead to marked bistability and a wide hysteresis window when swelling induces bending deformation. For more details, we have plotted in **Figure 1C** the radius of the arc during heating or cooling side by side with the relative strain of the unconstrained ribbon. This refers to the relative strain with respect to the initial length of the ribbon set by the micromold. In this respect, the temperature dependent relative strain (**Fig. 1C**) highlights to what extent the gold skin restrains the expansion of the hydrogel as well as the reversal of curvature upon collapse. Indeed, the critical relative strain causing the inversion of the curvature is of the order of $\pm 10\%$, which occurs in a range of less than two centigrade around the VPTT. Near the transition, the bilayer ribbon is almost straight, approaching the preparation state. However, a slight curvature persists with a magnitude that

depends on whether the transition temperature is approached by cooling or heating. These thermal hysteresis effects can become significant at high heating rates, for example through photothermal effects as shown elsewhere. In passing, we also note that the bilayer ribbon might be frustrated, since there is no longer a planar reference state.²⁷⁻²⁸ This has a profound impact on the stiffness of the ribbon. Nevertheless, the dependence of shape changes on the heat flow rate and path is the hallmark of a non-equilibrium process, involving (de)swelling, bending deformation and curvature reversal. The intrinsic hysteresis of the polymer and the inherent heterogeneities of the network, which are either permanent such as network imperfections, edge effects due to the finite size, including the asymmetry introduced by the gold skin, or which are transient, i.e., heating rate dependent, all combine to generate thermal hysteresis and a bistable curvature state. The dependence of the state of the system on its history, combined with a non-reciprocal bending deformation, implies that work is performed by the system on the environment during a heating and cooling cycle. Generally, in a bilayer construction the curvature is proportional to the misfit strain between the two layers.²⁹ In our case the misfit strain originates from the difference between the expansion of gel relative to the gold film. Therefore, it is coupled to the LCST behavior; hence, near the VPTT, small changes in temperature lead to large changes in volume and thus curvature. This behavior is consistent with **Fig. 1C** which shows that the curvature nearly vanishes near the VPTT.

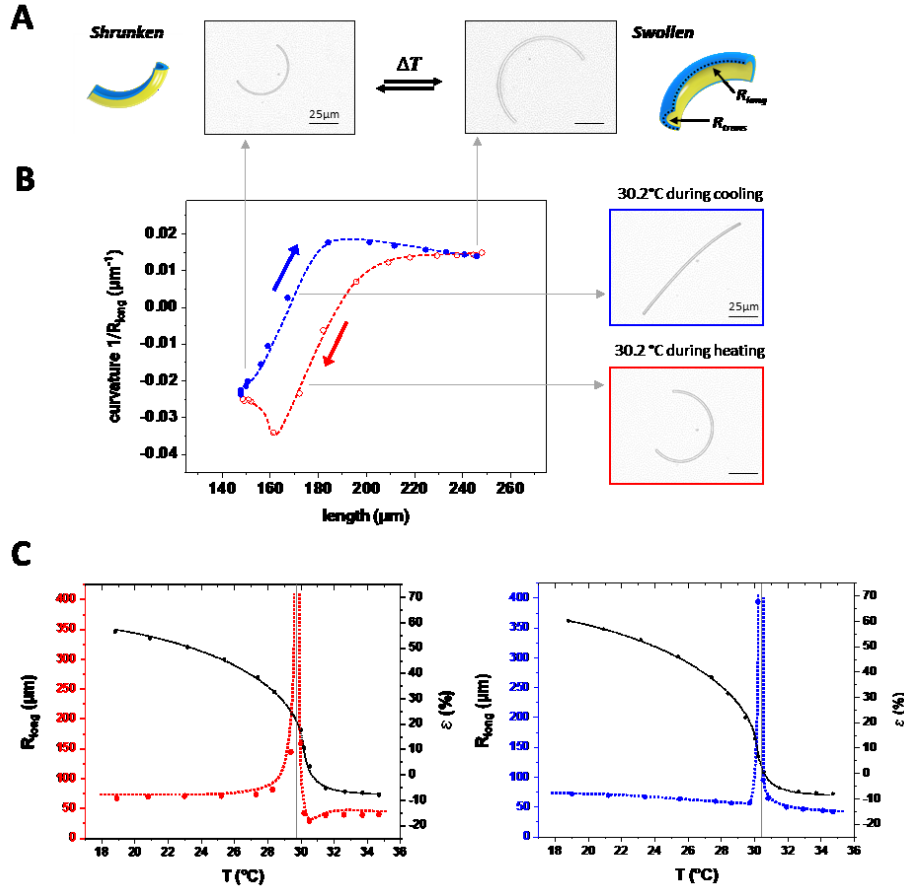


Figure 1: Quantitative relations between curvature and temperature. **(A)** Scheme and corresponding micrograph of the curvature inversion of a hydrogel/gold bilayer ribbon in water above (left, 35°C) and below (right, 20°C) the LCST of the polymer. **(B)** As the ribbon is oriented edge on, the curvature of the bending around the transverse axis, as well as the length along the centerline of the ribbon is measured during one heating and cooling ramp, respectively, between 20°C and 35°C at 5°C/min. A shape deformation hysteresis occurs due to non-equilibrium swelling effects, i.e., the shape of the ribbon depends on whether it is currently cooled or heated (top and bottom image at 30.2°C). **(C)** The equilibrium-swelling curve (black solid line) of a non-coated hydrogel shows that the expansion decreases beyond the dimensions of the ribbon as prepared, resulting in negative values of the strain ε . The so induced curvature inversion in a bilayer design generates a singularity of the radius at the inversion (dotted red and blue line for heating and cooling). At this point the system is most sensitive to small temperature variations as they effect large volume changes and thus large differences in radius. The inversion temperature T_{inv} shifts by 0.65°C between heating and cooling.

Here we attempt to exploit hysteresis to build a heat engine. The idea is to maintain the bath temperature close to the VPTT of the hydrogel, where the curvature of the ribbon is sensitive to small environment changes, and investigate to what extent tiny temperature fluctuations lead to changes in curvature, thereby stirring the surrounding water and doing work on the medium. The heating stage of the microscope maintains a constant temperature through a feedback loop (PID), which in turn generates a temperature fluctuation of $\pm 0.1^\circ\text{C}$ at a rate of up to 6°C/min. Such small temperature changes appear negligible at bath temperatures of,

e.g., 29°C, however are large enough to cause a change in the ribbon end-to-end distance d of a few tens of micrometers. Through optical tracking of the ribbon ends while measuring the surface temperature of the stage, we find that thermal fluctuations correlate directly with changes of d (**Fig. 2 A**). Indeed, a fast Fourier transform analysis of the temperature and the end-to-end distance shows that both traces fluctuate with similar frequency between 0.1-0.2 Hz (see **Figure S2** and **S3**). In addition, we note that the temperature fluctuates at a rate of up to 6°C/min, at this rate the hydrogel is thermally driven into non-equilibrium conditions, as described in the previous section. Only near the VPTT does the ribbon respond mechanically to temperature fluctuations. The amplitude of the oscillation reaches thus a maximum in a narrow temperature window within which the curvature also reverses. We report in **Fig. 2 B** the maximum oscillation amplitude Δd as a function of the bath temperature maintained around the VPTT. We scale the amplitude by the length of the as prepared ribbon L_0 , i.e. y-axis is in units of body length, and the temperature by the temperature at which the curvature reverses T_{inv} (see **Fig. 1**). For T/T_{inv} below one, the ribbon bends with the gold layer facing inwards, i.e., $1/R > 0$ and above one the ribbon is inverted, hence $1/R < 0$. Regardless of the sign of the curvature, the highest amplitude occurs at 1/10th of a degree centigrade from the inversion temperature with a magnitude up to 1/3 of the body-length. We note that for positive curvature the oscillations magnitude appears to increase steadily, whereas it decays steeply for reverse curvature. We relate this effect to the variation of the volume with temperature, which continuously decrease across the VPT and turns flat at high temperatures, as reported in **Fig. 1 C**. The enormous difference in elastic moduli and swelling ratio of PNIPAm and gold leads to bending deformation of the bilayer. The misfit strain is different below and above the VPTT, which tends to dissipate near the inversion temperature. However, this is not possible as the ribbon flat reference state no longer exists, making the bilayer sensitive to environmental changes only near the transition temperature. In a superposition of two ribbons during a ten seconds long movie section from the experiment we can further analyze the deformation path of the ribbon (**Fig. 2 C**). During opening and closing of the ribbon, respectively, it appears to be stationary at two points due to conservation of its geometrical center of mass. Actually, the geometrical center of mass is translating over time (**Fig. S 5**), however in the given timeframe the movement is so small that it is beyond our resolution. The amplitude of the oscillatory motion is largest when furthest away from these points, i.e., at the two free ends and in the center between the two stationary points. In a medium of dispersed microspheres the motion induced flow of the liquid in proximity to the ribbon is visualized. The particles follow a circular trajectory around the stationary points as indicated by the solid arrows in **Figure 2 C**. These vortices revert their directionality when the ribbon is opening and closing, respectively. Furthermore, and in agreement with our finding of a non-

reciprocal shape deformation path, this demonstrates how the system performs work on its environment.

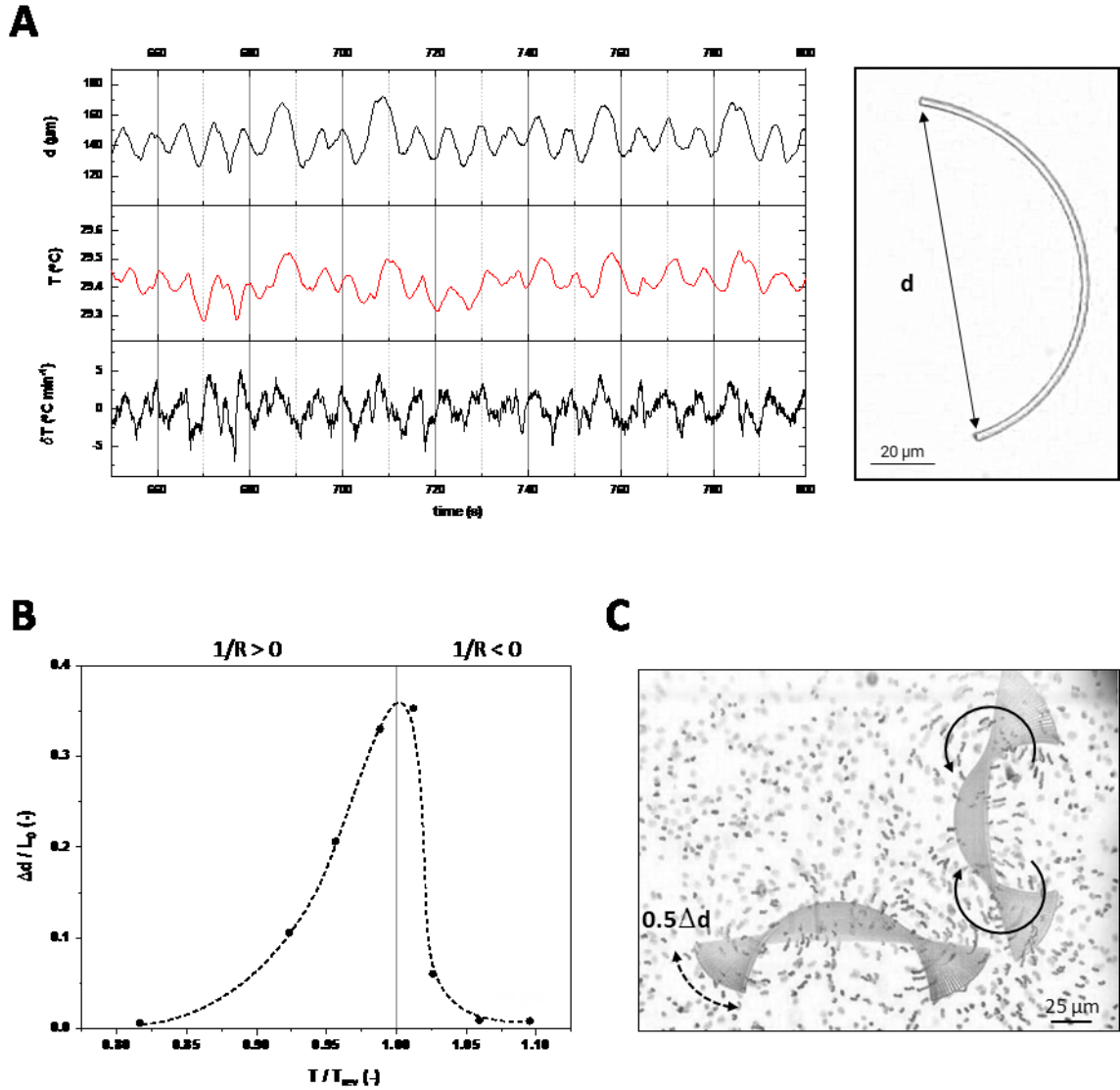


Figure 2: Oscillation of a bilayer hydrogel ribbon, thermally driven by a PID regulated temperature controller heating/cooling the environment. **(A)** During temperature oscillations (red curve) of $\pm 0.1^\circ\text{C}$ the end-to-end distance of a bilayer hydrogel ribbon reacts to tiny changes of $< 0.05^\circ\text{C}$ and closely follows the course of the temperature. The rates of T -change are of up to $\pm 6^\circ\text{C}/\text{min}$ and therefore actuate the ribbon under non-equilibrium conditions. **(B)** The maximum amplitude of the ribbons oscillation is plotted as a function of T/T_{inv} , indicating its position relative to the temperature where curvature inversion occurs. **(C)** Superposition of two ribbons undergoing an opening motion (dotted arrow) during cooling. The fluid motion is indicated by dispersed microspheres and shows circulation around the two stationary points of the ribbon (solid arrows).

In conclusion, we have demonstrated how a gold plated hydrogel ribbon converts small temperature changes into large amplitude motion. Actuation under non-equilibrium conditions creates a non-reciprocal shape deformation loop, analogue to the Carnot cycle. Overlap of the

curvature inversion and the volume phase transition enhance the effectiveness and create a system that is extremely sensitive to small temperature fluctuations. Periodic temperature oscillations with an amplitude as low as 0.05°C are sufficient to trigger strong oscillatory motion where the amplitude of the motion can reach up to 30% of the body length. Furthermore, the work performed by this system is visualized by streamline patterns of tracer particles around the ribbon. This study gives insight into the special properties of a soft microactuator system, which may be used as an artificial micro robot that can work in an environment that can e.g. only withstand a small amount of deviation from its normal conditions.

4.4 Experimental section

All listed chemicals were used as received, unless stated otherwise:

Acetone (Sigma-Aldrich), Dimethyl sulfoxide (DMSO, VWR), N-Isopropylacrylamid (NIPAm, 97%, Sigma-Aldrich, recrystallized in n-hexane), N,N'-Methylenbisacrylamide (BIS, 99%, Sigma-Aldrich), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (98%, Sigma-Aldrich), Bifunctional perfluoropolyether urethane (PFPE, Mw = 4000, Fomblin® MD 40, Solvay Solexis), 2-Hydroxy-2-methylpropiophenone (97%, Sigma-Aldrich), Polyvinylpyrrolidon (PVP, 40 kDa, Sigma-Aldrich).

Preparation of the bilayer ribbon

The production of the hydrogel ribbons was carried out in a glovebox by soft templating (PRINT³⁰) under nitrogen atmosphere ($O_2 < 0.5\%$). Gold nanorods were synthesized and surface modified prior to experiments according to literature.³¹

A prepolymer solution has been prepared, containing 575 mg (1 eq) of NIPAm, 7.83 mg (0.01 eq) of BIS as crosslinker, 11.4 mg (0.01 eq) of 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone as photoinitiator and 892 µL of AuNRs dispersed in DMSO (optical density OD = 240 at 810 nm, determined via UV/VIS spectroscopy). The solution has been bubbled with nitrogen for 30 min to remove oxygen. The precursor solution for the fluorinated elastomer mold was prepared by mixing PFPE MD40 with 1 wt% of the photoinitiator 2-Hydroxy-2-methylpropiophenone and bubbling with nitrogen for 30 min. A mold for the ribbons was casted from a silicon master wafer (AMO GmbH) containing the ribbon structure by applying a glass slide with two-layered Parafilm (Bemis) as separators on the short edges and filling the interspace, resulting in a film thickness of 200 µm. The liquid was cured by UV

irradiation (370 nm, 2 W) for 10 min and subsequently peeled from the master. A 400 μm thick film of PFPE was prepared from the same solution by filling between two glass slides that were separated by 4 layers of Parafilm on the short edges, followed by UV curing. Two pieces of (6 x 6) mm were cut from each film and placed in a homemade press with a quartz glass window. Each piece was washed in acetone before further use to remove any unreacted residues. To prepare the hydrogel a 0.5 μL droplet of the precursor solution was placed onto the mold and evenly spread by applying pressure with the flat film, thus ensuring drainage of excess liquid. The setup was placed under a UV hand lamp (366 & 254 nm, 4 W at each wavelength, Konrad Benda) for 20 min to form the gel. Afterwards, the mold was separated from the flat film and placed into a gold sputtering machine to apply approximately 2 nm thick film onto the ribbons (60 mA, 10 s, Edwards S150B). A square (25 x 25) mm cover glass was cleaned and plasma treated (O_2 , 1.6 mbar, 200 Watt, 2 min). A droplet of PVP solution (PVP, in ethanol/water, volume ratio: 7/63) was placed onto the cover glass and the mold placed onto the PVP upside down while gently applying pressure. After drying overnight the mold was ready to be peeled off to release the gel structures from it. A reference sample without a gold layer was prepared to investigate the swelling ratio of the gel when its unconfined.

Sample transfer into capillaries

Capillaries with a 50 x 1000 μm rectangular cross section (VitroTubes, VitroCom) were plasma treated (O_2 , 1.6 mbar, 200 Watt, 2 min). The mold was peeled from the PVP and a 15 μL droplet of ultrapure water was placed onto the sample. After release of the gel ribbons from the PVP, the capillary was gently immersed into the droplet until completely filled. It was then placed onto round glass slides (diameter: 5 mm) on both ends and sealed with two component epoxy glue (UHU Plus Sofortfest).

Digital microscopy imaging, tracking and temperature measurements

The sample capillary was placed on a Si-wafer to enhance contrast during imaging using a digital microscope (VW1000, Keyence). The heating stage onto which the Si-wafer with the sample was placed consisted of a Peltier element with an aluminium element towards the sample and a water cooled copper element on the opposing side, enabling heating and cooling ramps of up to 60°C/min, respectively. The temperature of the stage was regulated using xy microcontroller with a sensor in the aluminium element. Temperature on the surface of the Si-wafer was recorded by taping a sensor (Micro-BetaCHIP Thermistor Probe (MCD), TE connectivity) onto the wafer which was connected to a source meter (Keithley Dual-channel Sourcemeter 2636). The measured values were read out and recorded from the source meter with a home made excel plugin at intervals of 50 ms. In order to synchronize the video recording with the temperature measurement, a 20 ms laser pulse (808 nm, 10 W, Roithner Lasertechnik) was applied to the sensor, resulting in an immediate temperature change as well as an optical signal from the stray light of the laser to the camera. For each measurement, the temperature was set to the desired value and the sample was recorded for 30 minutes. Tracking of the ends of the ribbon was performed by using a tracking software (MotionAnalyzer, Keyence). The x and y positions of the tracking points were used to calculate the end-to-end distance of the ribbon over time. The recorded values of end-to-end distance were filtered to reduce noise using a FFT filter in *OriginLab* with appropriate limits, i.e., typically 0.05 Hz as the lower limit and 1 Hz as the upper limit. These data were then processed in a box-plot, giving the maximum amplitude of end-to-end distance by the upper and lower whiskers. The results are summarized in **Figure S2**. Heating and cooling cycle experiments were performed by applying a temperature ramp of 5°C/min for the bilayer ribbon and 1°C/min (near equilibrium conditions) for the reference sample, respectively.

Curvature Analysis with ImageJ

In order to analyze the curvature of the ribbons during cyclic heating/cooling, single frames have been extracted from the video. The image sequence was then imported in *ImageJ* and analyzed using the plugin *kappa*.³² To evaluate the curvature and length, a b-spline centerline of the ribbon was drawn and automatically calculated values of the average curvature, as well as length of the ribbon were exported as .csv files. The latter were imported in *OriginLab* to further analyze and plot the data.

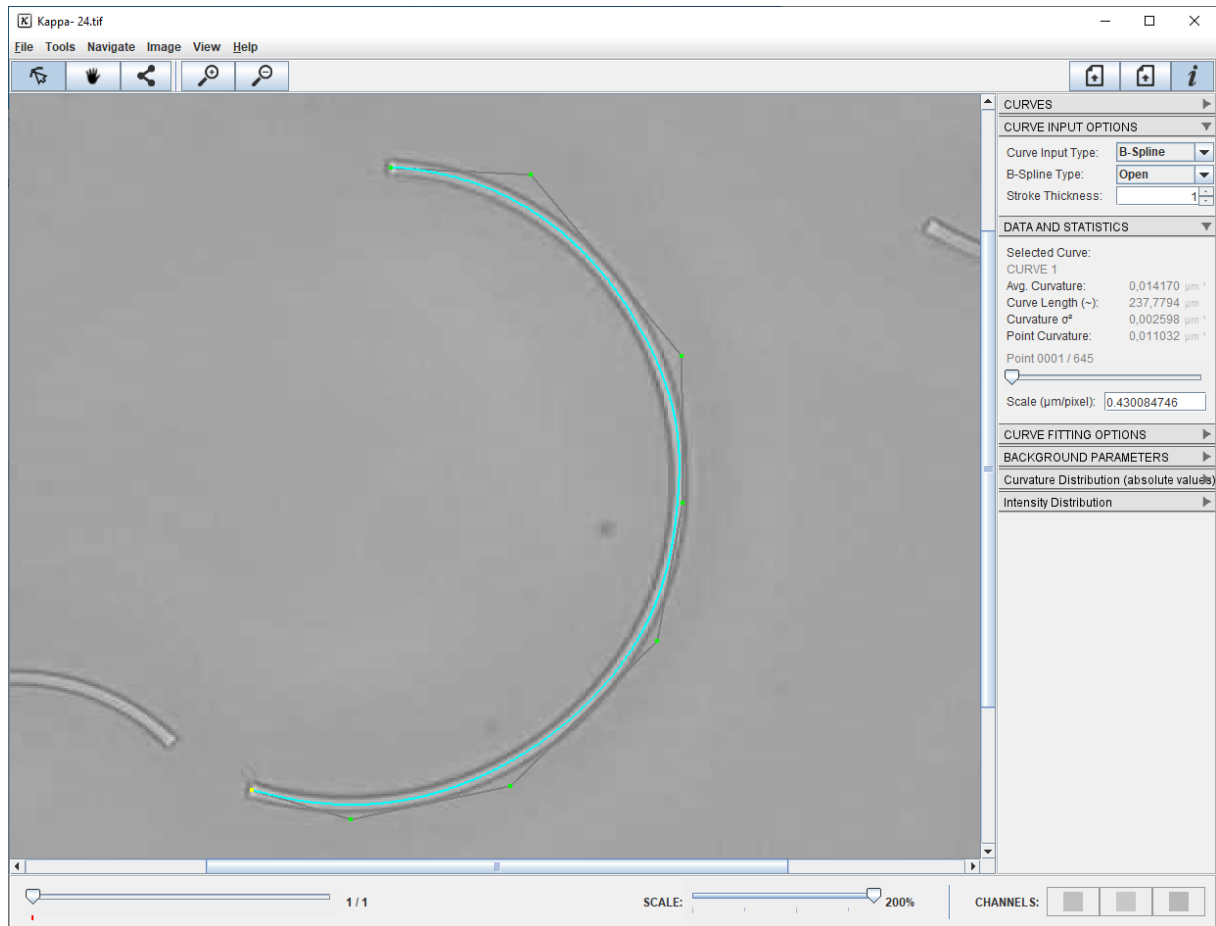


Figure 3: Curvature analysis of a bilayer ribbon in ImageJ using the plugin kappa.³² A snapshot from the video is uploaded and a centerline is manually drawn (teal line). Curvature and length of the ribbon are then calculated by the plugin and exported for further analysis.

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4.6 Experimental data

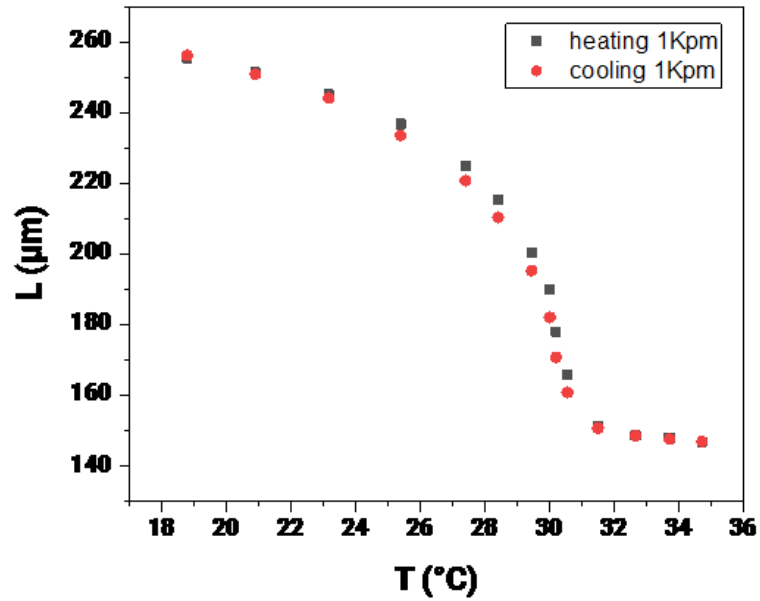


Figure S1: The length of an unconstrained (non-sputtered) hydrogel ribbon during heating and subsequent cooling at a rate of 1 K min^{-1} . Already at this rate a small hysteresis can be observed. Furthermore, it becomes clear that the dimensions of the gel in its collapsed state are below the preparation conditions of $L_0 = 160 \text{ μm}$.

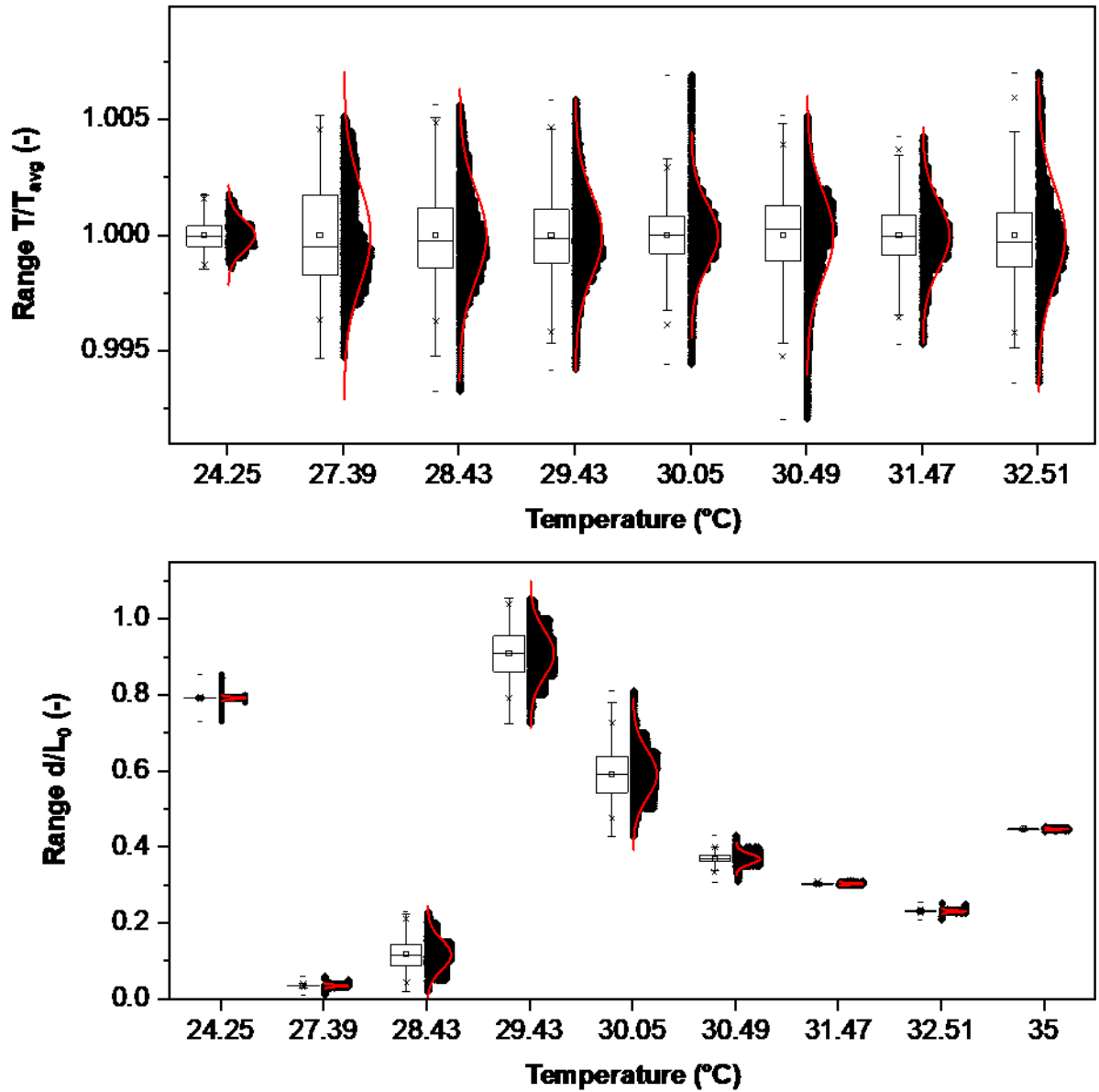


Figure S2: Statistic analysis of the oscillations in bath temperature and end-to-end distance of the bilayer ribbon. **(A)** The range of temperature fluctuations that are caused by PID regulation of the heating stage during the measurement at different temperature settings. The X-axis denotes the average temperature of the respective measurement. **(B)** Range of motion of the hydrogel arch. The Y-offset is due to the respective opening state of the ribbon arch. Whiskers are used to determine the maximum amplitude of motion in **Figure 2B**.

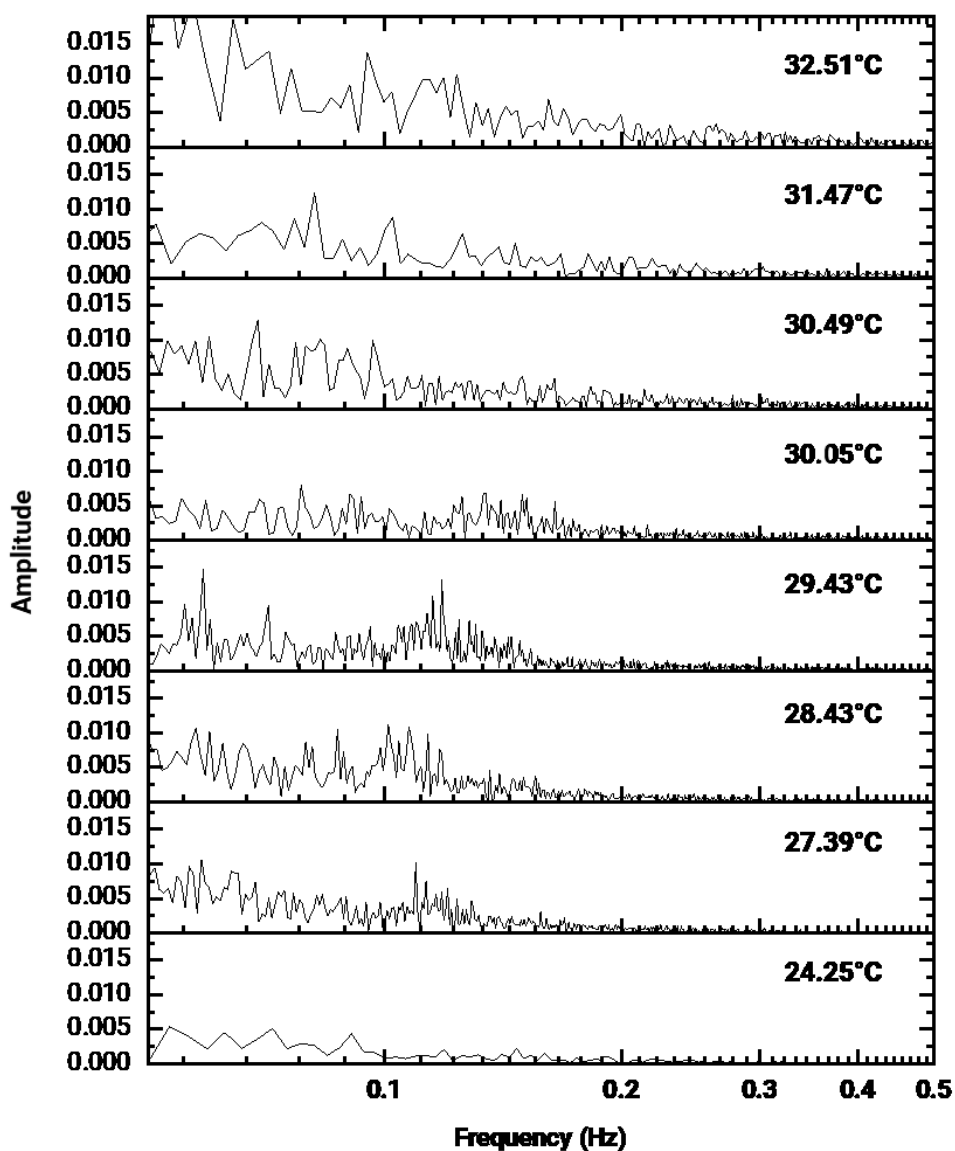


Figure S3: Frequency spectrum of the temperature oscillations after a fast Fourier transform (FFT) analysis. The inset temperature values represent the average value during the measurement interval. The majority of oscillations occur at frequencies between 0.1 Hz to 0.2 Hz corresponding to wavelengths of 5 s to 10 s.

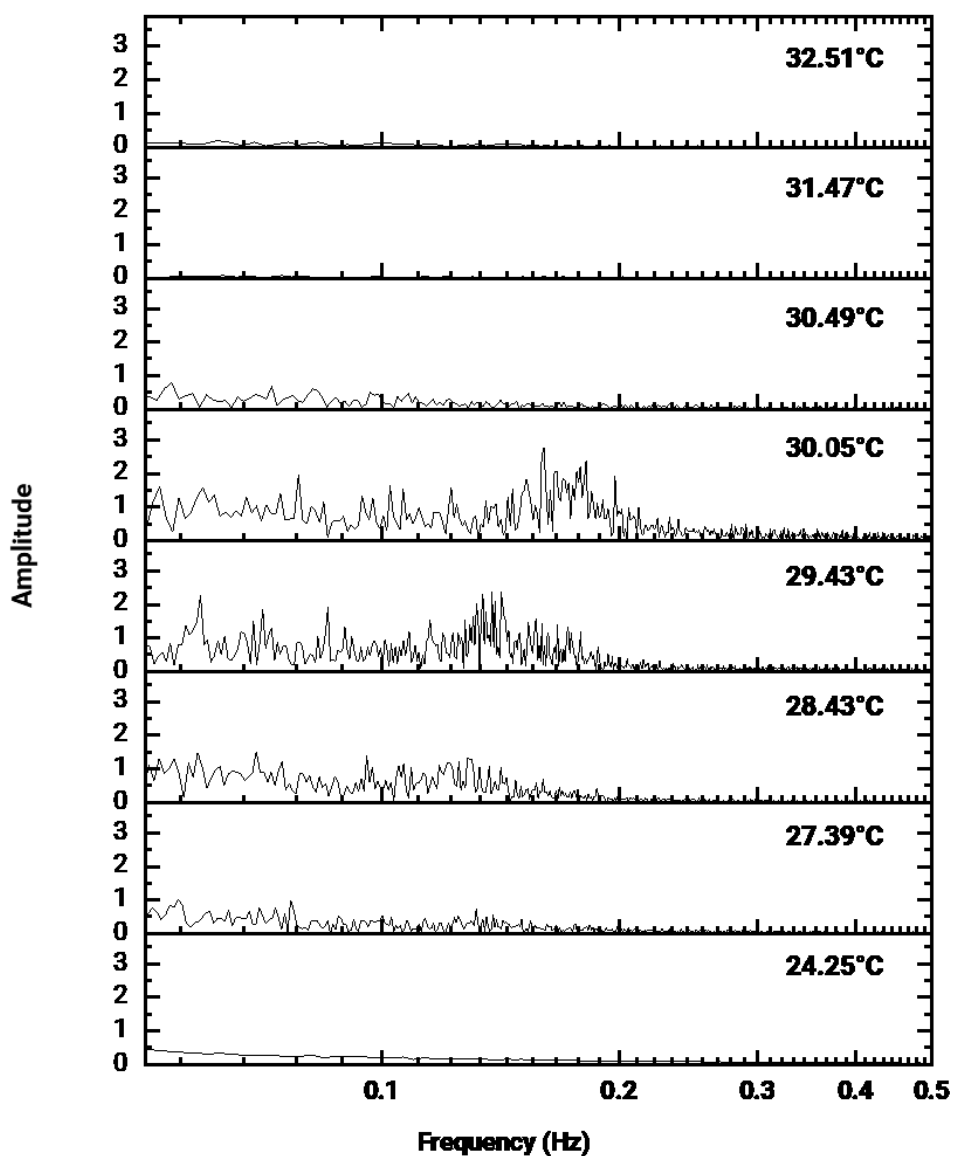


Figure S4: Frequency spectrum of the end-to-end distance oscillations after a fast Fourier transform (FFT) analysis. The inset temperature values represent the average value during the measurement interval. When none or changes in end-to-end distance close to the image resolution are detected, the spectra consequently are flat. However, when occurring the majority of oscillations appear at frequencies between 0.1 Hz to 0.2 Hz corresponding to wavelengths of 5 s to 10 s, similar to the oscillations in temperature in Fig. S2.

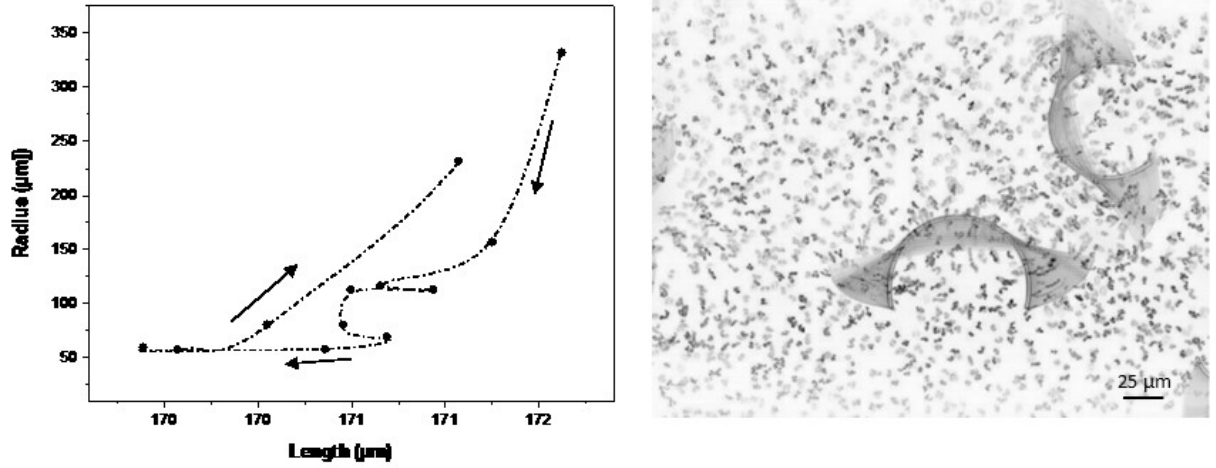


Figure S5: Motion analysis of two ribbons in a microsphere environment during a large amplitude deformation cycle **(A)** The radius of the ribbon in the center is plotted against the respective length during the same cycle. This deformation cycle almost forms a closed loop as in **Fig. 1 B**, however as the temperature fluctuates constantly many small disturbances occur. Nevertheless, both A & B here demonstrate the work that is done by the ribbon. **(B)** Superposition image of the motion cycle.

5. Microgel that swims to the beat of light*

5.1 Abstract

Complementary to the quickly advancing understanding of the swimming of microorganisms, we demonstrate rather simple design principles for systems that can mimic swimming by body shape deformation. For this purpose, we developed a micro-swimmer that could be actuated and controlled by fast temperature changes through pulsed infrared light irradiation. The construction of the microswimmer has the following features: (i) it is a bilayer ribbon with a length of 80 or 120 μm , consisting of a thermo-responsive hydrogel of poly-N-isopropylamide coated with a 2 nm layer of gold and equipped with homogeneously dispersed gold nanorods; (ii) the width of the ribbon is linearly tapered with a wider end of 5 μm and a tip of 0.5 μm ; (iii) a thickness of only 1 and 2 μm that ensures a maximum variation of the cross-section of the ribbon along its length from square to rectangular. These wedge shaped ribbons form conical helices when the hydrogel is swollen in cold water and extend to a filament-like object when the temperature is raised above the volume phase transition of the hydrogel at 32°C. The two ends of these ribbons undergo different but coupled modes of motion upon fast temperature cycling through plasmonic heating of the gel-objects from inside. Proper choice of the IR-light pulse sequence caused the ribbons to move at a rate of 6 body length /s (500 $\mu\text{m/s}$) with the wider end ahead. Within the confinement of rectangular container of 30 μm height and 300 μm width the different modes can be actuated in a way that the movement is directed by the energy input between spinning on the spot and fast forwards locomotion.

5.2 Introduction

Self propelling microorganisms such as *Euglena*, a single cell flagellate eukaryote, move by large amplitude periodic shape deformations.¹ Here, the term “large” implies an amplitude of a size of the whole organism. Interestingly, Euglenids can employ two distinct modes of locomotion. Swimming in a non-confined environment is effected by the beat of the flagellum with a regular beating period and a helical trajectory.² In a confined environment, the cell body undergoes a peristaltic motion, also called metaboly, which again is periodic and highly coordinated.³ In both cases, locomotion involves a deformation of the body or its appendages

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in an environment where viscous forces are dominant, characterized by a low Reynolds number.⁴⁻⁵ Microorganisms cope with this constraint by deformation of their body in a hysteresis sequence,⁶ which is in fact one of the challenges in the design of periodically actuated microscopic swimmers. Reconstruction of the flagellar beat as well as the metachronal motion requires a detailed spatiotemporal resolution of the complex deformations and has been subject of physical modelling.^{3, 7} Yet, it remains a challenge to image these shape deformations in detail with current microscopy techniques and recent reports focus on the evaluation of the motion trajectories⁸⁻¹² as a basis for the reconstruction of the propelling shape deformation. In contrast to these advancements, mimicry of such locomotion by synthetic objects that allow for reduced complexity and improved control of such body shape deformations is still in its infancy. It might contribute significantly to the understanding of the efficiency of such locomotion,¹³⁻¹⁴ but will also provide new capabilities for microrobotic systems that can search their own way to transport and deliver, e.g., by chemotaxis as the motility is effected by gradient in concentration, or which can mix, sort and circulate fluids.^{1, 15}

Recently we have described preparation and motility of helical ribbons that were actuated by periodic pulse irradiation with near IR-light.¹⁶⁻¹⁹ We note that ribbons are long narrow strips possessing three distinct material length scales (thickness, width, and length) which produce unique shapes unobtainable by wires or filaments. Our ribbons were typically a few tens of micrometers long, one micrometer thick and had a width of 5 micrometers. They were prepared from a thermo-responsive poly(N-isopropylacrylamide) (PNIPAm) hydrogel whose solubility decreased with temperature,²⁰ causing volumetric shrinkage. Another design feature of these ribbons is that they were heated from inside by means of near infrared light-absorbing gold nanorods (AuNRs) embedded in the hydrogel matrix. As a consequence the surrounding medium acted as a heat sink. These slender bodies fulfilled specific requirements for swimming by large periodic shape deformations, such as (i) cyclic beating motion because the swelling-collapse deformation was caused by the periodic irradiation, (ii) peristaltic motion, as the light induced volume collapse and bulge (wrinkles) were spatiotemporal inhomogeneous, and (iii) large deformation as inhomogeneous volume changes resulted in large amplitude bending motions. We could also demonstrate a strong asymmetry of the sequence of shapes during one cycle or beat. This remarkable behavior was assigned to the fact that heating and cooling of the microgel ribbons occurred faster than the corresponding volume change. Therefore, volume-temperature equilibrium state is not reached and the deformation became path and shape dependent.

We capitalize on our previous work to develop swimming microgels capable of navigation. This entails a proper choice of the shape, i.e. the design of the microgel objects must

distinguish a head and a tail. For navigation we want to control the motional mode by the light intensity and the beat period and study how the motion can respond to an obstacle or confinement. Here we describe how this can be achieved with wedge shaped ribbons with ends of different width. Upon photothermal heating, the variation in width causes different dynamic responses in volume change and bending along the centreline of the ribbon, which control the locomotion. In the first part of this report, we describe the temperature-mediated variations of the 3D shape of the microgel-ribbons under equilibrium conditions, i.e. for varying temperatures and corresponding degrees of swelling. Because of the bilayer structure, the ribbons respond to swelling by bending and the taper in width induces distinct coiled shapes. This point gives a first insight into the interrelation of the geometry and the mechanics of our elongated ribbons. In the second part, we focus on the shape variation under non-equilibrium conditions, when the wedge shaped ribbons are periodically actuated by NIR light which leads to conditions where the temperature change is faster than the diffusion controlled swelling and contraction. Finally, we discuss how the motility can be controlled by the stroboscopic frequency between moving forward and spinning on the spot. We also analyse the resulting flow in the surrounding water that causes a forward swimming motion.

5.3 Results and discussion

Shape variation by swelling and consecutive bending.

A key element of our experiments is given by the transformation of volume changes to large amplitude bending. In order to achieve this we made thin hydrogels ribbons with a bilayer composition. As described before, the ribbons were prepared by micro-molding and UV-cross-linking of N-isopropylacrylamide and N,N'-methylene-bis(acrylamide) dissolved in DMSO.²¹ For the design of the geometry, we used lithographic techniques. An elastomer made from perfluoro-polyether was employed for the fabrication of the mold.²² At 32°C the hydrogels undergo a volume phase transition due to lower critical solution behavior. In order to impart a temperature-dependent bending, the polymer ribbons were sputter coated on one side by a 2 nm thick layer of gold when they were still in the mold. When such bilayer is released into cold water, the hydrogel objects swell and expand relative to the metallic layer. Obviously, stress accumulation at the metal /hydrogel interface causes bending towards the side of the gold layer, as shown in **Figure 1A**. Remarkably, an inversion of the curvature occurs when the hydrogel transforms from the swollen state at low temperature to the collapsed state at elevated temperature.

Modeling of bilayer bending as a consequence of equibiaxial misfit strains is well established in the literature.²³⁻²⁶ As long as the surface of the bilayer sheet is kept constant, bending in two directions must be isometric, i.e. the Gaussian curvature κ is constant. This condition is fulfilled if one of the principle curvature is zero, $\kappa = 0$. As consequence the expansion or shrinkage of a rectangular hydrogel/gold-film bilayer tends either to form a long tube (bending around the long axis of the rectangular ribbon) or a spiral (bending normal to the width of the ribbon). Elasticity of the bilayer structure enables biaxial bending, $\kappa > 0$, corresponding to some bulging as depicted in Figure 1a. For large curvatures, however, the energy required for elastic deformation is too high and the ribbon only bends around one direction (tube or spiral). Limited biaxial bending can still be found at sides of the ribbon. Because these double bending sides are longer in the case of a spiral, formation of a spiral is energetically more favorable for a long ribbon. This edge effect causes the ribbon to wind up as a helix, with the helix direction controlled by small misfits of the geometrical long axis and the stresses which result from imperfections in geometry and homogeneity of the helix.²⁵ **Figure 1B** demonstrates such shape variations for a our rectangular hydrogel/gold-film bilayer samples with different length-to width-to-height ratio at equilibrium swelling at 20°C, i.e., at fixed swelling degree. For the shape diagram in **Figure 1B**, we normalized the length and thickness to the width $w = 5 \mu m$. As expected, the ribbons form spirals which transform into helices when the aspect ratio was increased or when the thickness was reduced. Unexpectedly, we observed formation of tubes for thin and long ribbons although spiral conformations should be preferred at high aspect ratios. However, the evolution of a tube may be guided by irregularities in the swelling process, e.g. variations in height along the ribbon, release from the mold, or dog ear formation at the end of the ribbon. Spontaneous curvature perpendicular to the long axis will create a geometric obstruction or barrier to reaching the spiral shape. The tubes, which we observed, were bent like a banana demonstrating some biaxial bending influence. Important for this work here is the transition from a spiral to a helical conformation whereas the main principle curvature is controlled by the h/w ratio. For a square cross-section ($h/w = 1$), the bending around the transverse direction dominates, while small h/w ratios favor the helix formation.

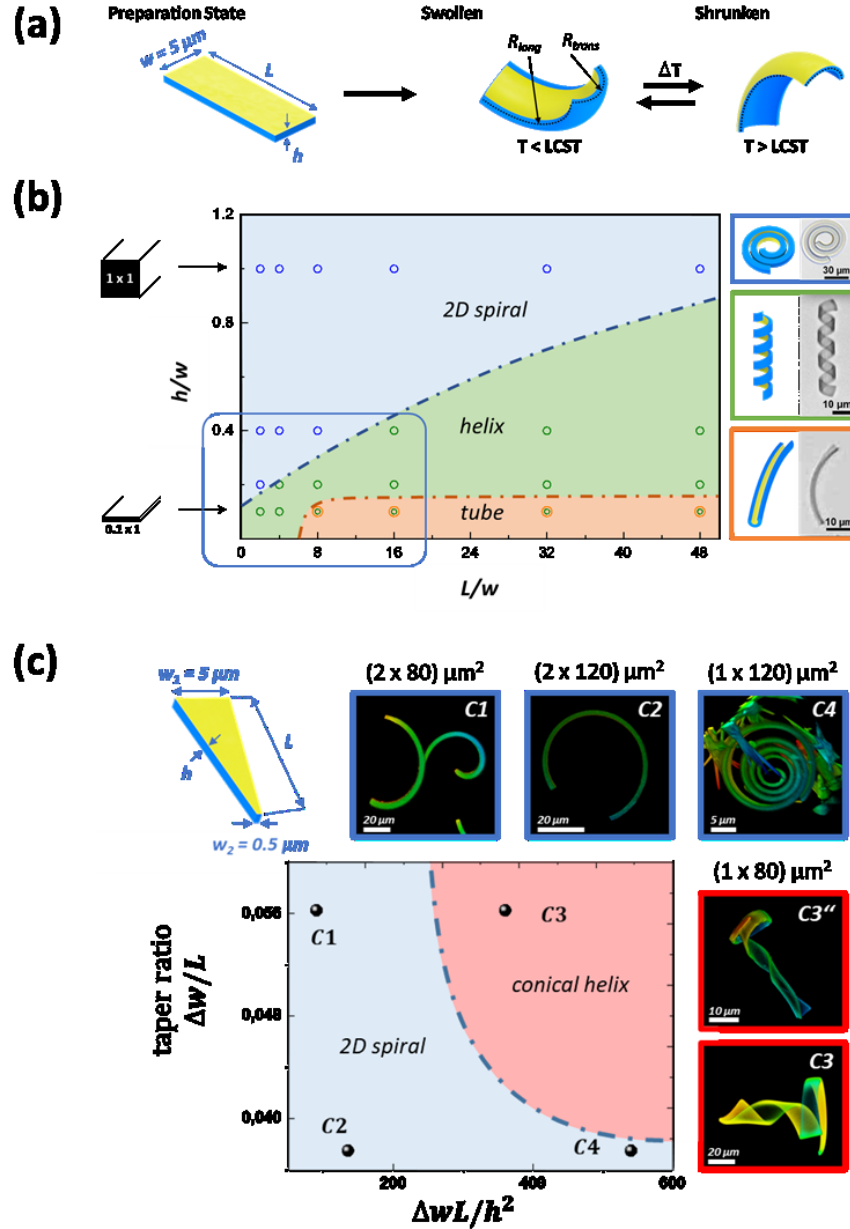


Figure 1: (A) The scheme shows a bilayer hydrogel ribbon with a thin gold layer (two nanometres-thick layer applied by sputter coating). At low-temperature, this inextensible layer restricts the swelling of the PNIPAm hydrogel and causes the ribbon to bend biaxially inwards. At high temperatures, the curvature is reversed. (B) Shape diagram of swelling caused conformations of rectangular bilayer strips of varying length L (x-axis) and thickness h (y-axis), normalized to a constant width of $w = 5 \mu\text{m}$. For a square cross-section, the ratio of thickness to width is equal to unity ($h/w = 1$). Points in the graph present the conformations, we found experimentally for the equilibrium-swollen structure at 20°C . Discontinuous lines are hypothetical boundaries between different structures. (C) Conformations of bilayer ribbons, that were cut in a wedge shape along their length like it is illustrated by the drawing. Points in the graph denote experimentally found equilibrium structures in water at 20°C shown in the corresponding confocal micrographs: C1 (2×80) μm , C2 (2×120) μm , C4 (1×120) μm , and C3, C3'' are (1×80) μm (additional structures are presented in Fig. 2). We limited our investigation to two lengths of 80 and 120 μm , respectively, as well as two thicknesses of 1 μm and 2 μm . The width of the wedge like ribbons was altered from 5 μm at the wider end to 0.5 μm at the narrow end.

The graph plots the taper ratio of the ribbon against Föppl–von Kármán number as a geometric parameter accounting for the tendency of thin sheets to bend. The dashed line is a hypothetical boundary between spiral and conical helix.

When the bilayer hydrogel ribbon is cut to a wedge-shape, the bending preferences varies along the length of the ribbon and can span different areas of the diagram in **Figure 1B**. The insets C3 and C3'' in **Figure 1C** depict confocal microscopy images, showing that such objects can combine spiral and helical elements, which results in the formation of a cone like 3D conformation. As the cross-section varies from square to rectangular along the ribbon long axis, the transverse bending becomes more important, favoring a 3D helical over the 2D spiral shape.²⁷ For the samples C1 and C2 the equilibrium shape is a two-dimensional spiral in which the narrow tip bends tightly while the wider end opens radially. When the thickness was reduced, the curvature increases resulting in a spiral structure similar to a clockwork spring, as shown in image C4 of **Fig. 1C**. C3 in **Figure 1C** shows the transition from a spiral to a helix. Hence, the images demonstrate a remarkable shape variation between the ribbons and even within one ribbon. Note that in the case of a 2D spiral, the narrow end was oriented to the core of the spiral where the curvature is maximum (**C4**). When, however, the ribbon adopted the 3D cone conformation, obviously controlled by the curvature of the wider end, its narrow end pointed to the outside of the spiral that developed at the base of the cone (C3, C3'' including all the conical configurations in **Figure 2**). In order to classify the different conformations we plotted the taper ratio ($\Delta w/L$) of the ribbon against Föppl–von Kármán number ($\Delta w L/h^2$) which is a geometric parameter determining how easily a sheet bends.^{28,29} The dashed line is a hypothetical borderline between the spiral objects and the 3D cone objects. In the case of the ribbon in C3 with a length of 80 μm and a thickness of 1 μm , the narrower end only bends around the transverse axis (uniaxial bending) ; while the conformation at the wider end gets controlled by the longitudinal and transverse axis (biaxial bending). This approach to data presentation was derived from the consideration that the 2D spiral should be controlled by the gradient in curvature and, as the ribbon width is increased, bending in the transverse direction plays an increasing role and results in an apparent stiffening of the ribbon,³⁰ which we consider to be proportional to the gradient in width $\Delta w/L$.³¹ So far, we limit our analysis of the bending of the wedge like ribbons to the description of the experimental observation. Rigorous modelling of the bending is beyond the scope of this work with its focus on the non-equilibrium actuation.

The examples demonstrate, how the stresses caused by swelling can be exploited to realize distinct geometric variations of the shape of such hydrogel objects. Actually we found that the conformation of the objects is susceptible to structural variations that are even less

pronounced. The accuracy of the micro-molding has a variance of about 100 nm³² (mainly determined by templating a silicon micromold to a perfluoropolyether mold, from which the object is obtained). Relative to the small thickness of the ribbons of 1 or 2 μm , this can cause significant variations in bending. **Figure 2** shows four 3D cone conformations observed for four wedge shaped ribbons that have been prepared in the same fabrication batch (80 μm long, 1 μm thick and a width of 5 and 0.5 μm at the two ends resp.) The comparison demonstrates that the combination of a helical and a spiral element is strongly influenced by small variations, which we cannot control so far. However, because we can study the temperature response of such objects individually, these variations enable us to observe their effects on the motility or to find efficient swimmers, as it will be shown below.

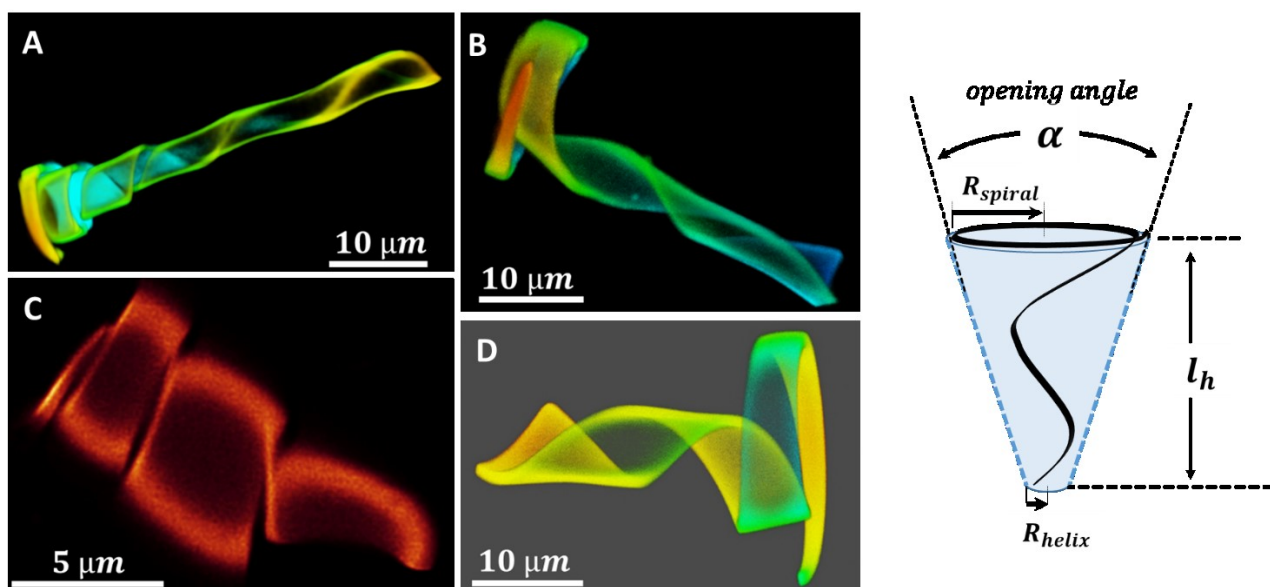


Figure 2: Four typical 3D cone conformations (20°C in water) which were obtained by one microlithographic fabrication batch. The batch was directed to yield ca. 50 % ‘identical’ hydrogel ribbons of 80 μm in length, 1 μm height and a width of 5 μm and 0.5 μm at the two ends. However, as the images demonstrate, small variations in the dimensions of the ribbon can cause significant differences in the 3D conformations. We classified these variations qualitatively by four groups: Type A, a helix that widens at the end to a short spiral element; Type B and D: a widening helix with a spiral at the end whose length is roughly identical to the length of the segment that forms the helix; and Type C, only a helical element. The drawing shows the parameters that describe the conical helix. The images refer to other figures as follows: A = C’’’; B = C3’’; C = C’; D = C3.

Temperature response and NIR-light actuation

So far, we looked at the equilibrium state of the wedge shaped ribbons in water at low-temperature as caused by the swelling of the hydrogel. **Figure 3** shows a series of optical microscopy images at raising temperature obtained for sample C in **Fig. 2**. As the degree of

swelling decreased at elevated temperature, the two ends changed their shapes in different ways. The spiral end became straight, while the wider end even underwent the first steps for a helix inversion. Hence, the design of a wedge shaped bilayer ribbon does not only demonstrate how different shape deformations can be combined within the body of single object making a distinction for its “head” and “tail”, but both ends of the wedge shaped ribbon respond also differently to temperature changes. Together, these two features are helpful but not sufficient to cause locomotion of such small objects.

As mentioned in the introduction, directed motility of such micro-objects in water, i.e., swimming, occurs at low Reynolds numbers and requires a cyclic but asymmetric or hysteresis sequence of shapes. Such a hysteresis shape response is only found under non-equilibrium conditions. Theoretical models for microswimmers that undergo locomotion by shape deformation are based on a retarded volume or shape response, e.g. by assuming instantaneous temperature changes³³ or by snap buckling³⁴. In other words, out of equilibrium actuation ensures that the shape deformation cycle does not comprise time reversible steps. Consequently, a net flow in the surrounding fluid is generated, resulting in a displacement of the body. In the case of a thermo-responsive hydrogel, hysteresis of the heating and cooling response can be expected at fast heating and cooling rates, whereby stress generation is coupled to the diffusion of the water out of and into the gel objects. Thus, transient stresses are built up within the gel because its volume cannot respond quickly enough to the temperature.³⁵⁻³⁷

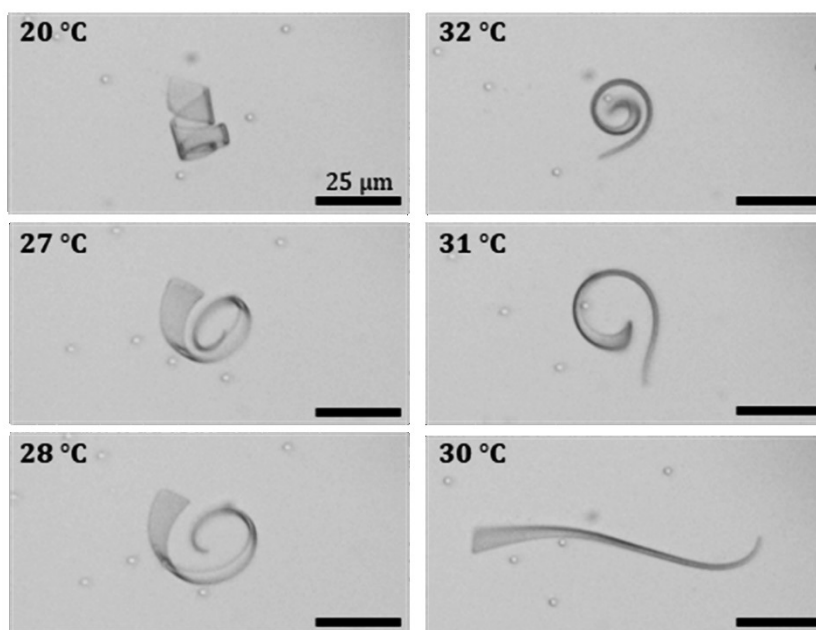


Figure 3: Optical micrographs of a tapered bilayer ribbon, 80 μm long and 1 μm thick, whose shape changes during a quasi-static rise in temperature. At 30°C, close to the volume phase transition temperature, the ribbon unwinds whereby the wider end begins to bend in the opposite direction than the tip. Above 30°C, the curvature gradually reverses.

In our work, we used gold nanorods as heating elements inside the microgel objects for the required fast raise in temperature. Typically, we incorporated nine nanorods per cubic micrometer of the gel. Their average dimensions are 60 nm length and 15.4 nm diameter.¹⁶ These nanorods are superior heating elements when they are irradiated by NIR-light. They convert the incident light to heat nearly by 100 % within nanoseconds.³⁸⁻³⁹ Thus, the heating rates are controlled solely by the thermal diffusion in the aqueous gel and thus mainly by the average distance between Au nanorods in the gel particles and the light intensity. By light pulses, the temperature can be raised by several degrees within milliseconds. When the IR-irradiation stops, the small microgel objects cool down rapidly as the heat is transferred by the same thermal diffusion to the surrounding water, acting as a huge heat sink.⁴⁰

Our previously reported rectangular helical microgel ribbons had a constant radius.¹⁷ When heated by NIR-light pulses both ends reacted the same way (the irradiation was almost homogeneous over the whole sample). Heating resulted in unwinding and even reversal of the helix. The cyclic deformation showed a hysteresis in the shape sequence upon fast heating and cooling, as the actuation occurred at non-equilibrium conditions.^{16, 19} When confined between two planes the gel-objects rotated around their long as well as around their normal axis. When one end touched a flat wall, we observed a net translation along this wall.

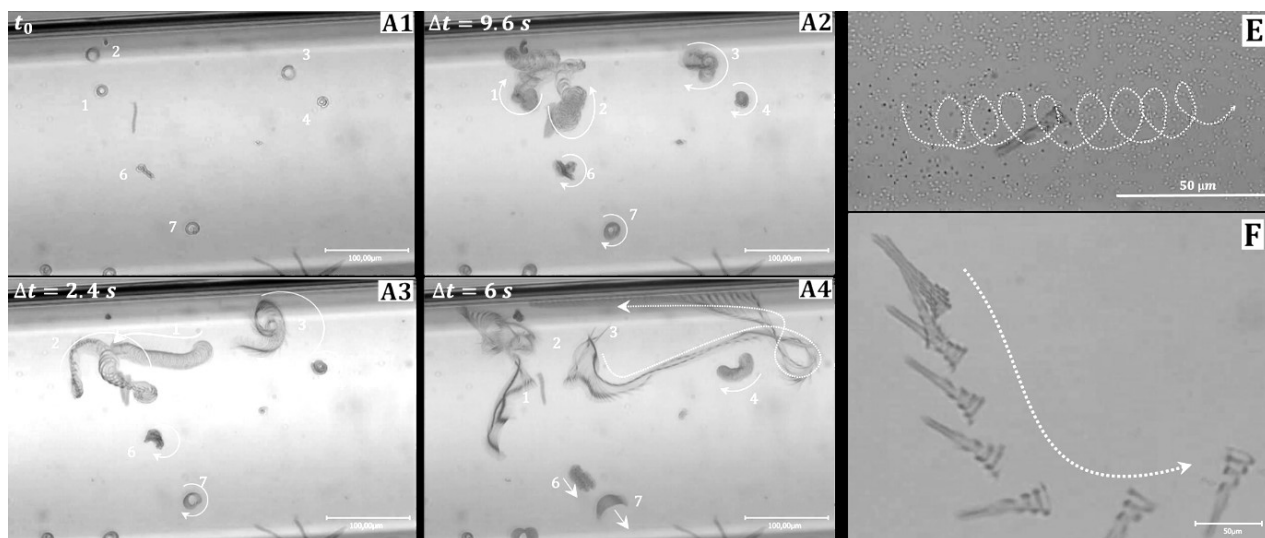


Figure 4: (A1-4) A low-magnification optical micrograph reconstructed by the superposition of images at different time intervals enabling tracking the trajectories of different helical swimmers, in this case they were weakly confined as the gap was 30 μm high, thus larger than the helices dimensions. The period was 11 ms whereby irradiation was during 3 ms and the recovery for 8 ms. The image shows 3 conical helices of the type D in Figure 2, marked by numbers (1-3). When the conical helix got oriented with its wider part towards the glass wall, it spins at the spot (situation A1-2 in the image), whereas when it moving forward, the velocity was roughly 500 $\mu\text{m/s}$ (situation A3-4). (E) Shows the motion trajectory of a Type B conical helix, which resulted from the combined rotational and translation modes when irradiating for 1 ms

and 8 ms recovery cycles. **(F)** The object resembles the one in **Fig. 2B/C**. Also this one moves forward with its wider part ahead. Different than the one in **A1-4**, it could not change its direction abruptly and just turned in a wide bend as a consequence of a forward motion and rotation, most likely because of the effect of the two glass walls. Obviously **E** and **F** demonstrate rather stable modes of motion within the confined space of the rectangular capillary).

Because the new conical hydrogel objects reported here have distinguished ends, we expected to observe a forward motility even under non-constrained conditions, when their shape variation was actuated by fast heating-cooling cycle under non-equilibrium conditions. This is indeed the case as demonstrated in **Fig. 4**. This figure depicts three examples of ribbons that formed conical helices in water at 20°C. They were observed swimming in a rectangular capillary with a 300 µm wide and 30 µm high lumen when they were actuated by short NIR-light pulses separated by a defined recovery time. Taking into account that the length of the conical helices is between 10 and 50 µm and that the extended ribbon spans 80 µm, the hydrogels are confined in their movement parallel to the direction of observation. They move rather freely within the observation plane, but they cannot freely turn around the normal axis. Within the gap between the upper and the lower glass wall, we observed, however, that they can swim against gravity and their mode of motion could change, when they encounter the upper wall. In some cases, we observed hydrogel-objects spinning at the spot as they hit the glass-wall (**Fig. 4 A1**). In other cases the conical objects swam forward within the xy-plane. **Figure 4A 3-4** demonstrates the forwards motion of cones with a low temperature conformation like the one shown in **Fig. 2D** with the spiral end ahead. When the hydrogel got oriented with its cone axis perpendicular to the top/bottom side of the capillary it got stuck for some time as the wider part is moved against the wall (**Fig 4A 1, 2, 3**). Eventually the hydrogel could escape this situation and started to move forward parallel to the horizontal capillary walls with a displacement velocity of ca. 500 µm/s (6 body lengths per second). A different response is shown in **Figure 4E** for **A/B** type conical helix (see **Fig. 2**). Clearly, the object moved also with its wider part ahead but it followed a cycloidal trajectory. A different situation is depicted in **Figure 4F** for an object that resembled the one in **Fig. 2A/D**. Also this one moves forward with its wider part ahead. Different than the one in **Figure 4A**, it could not change its direction abruptly. However, it follows a curved trajectory as the consequence of a forward motion combined with rotation. Obviously **Figs 4 E** and **F** demonstrate rather stable modes of motion within the confined space of the rectangular capillary.

The examples demonstrate for all three conical helix objects a common forward motion component with the wider end as the head. They also show that small variations in the geometry in combination with the spatial confinement can cause sideways and rotational components of the motion. **Fig 5** shows a series of stroboscopic images of the light actuated

object displayed in **Fig 2D**. They were observed swimming in a rectangular capillary with a 200 μm wide and 20 μm high lumen. In this case, the cone could not orient perpendicular to the wall. This results in sudden reorientation of the micro-object when it collides with the walls. We did not observe any adhesive contacts, which would permanently tether the helix to the glass. Clearly the helix turns in clockwise direction, most likely because of the leverage effect of the friction at the wider spiral head. Such a directed rotation can easily explain the forward motion in analogy to the rotating flagella of bacteria such as *escheria coli*.⁴

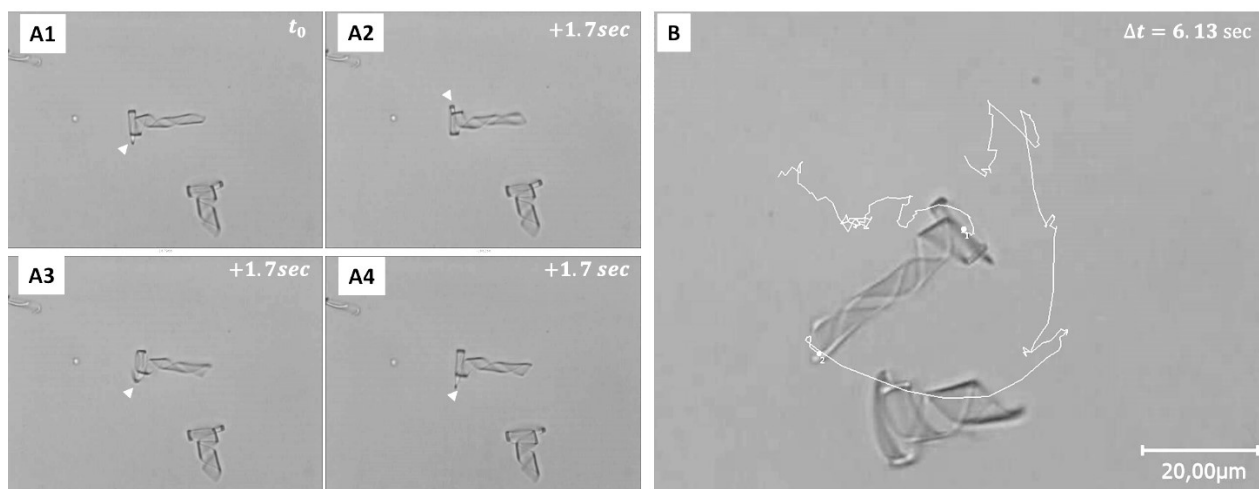


Figure 5: (A1-4) sequence of images of the conical helix shown in Figure 2 D, when actuated by 200 μs long NIR-pulses followed by a recovery time of 800 μs . The time between images was 1.7 s, which corresponds to 5170 light pulses during which the helix spins counter-clockwise around the helical axis and makes one revolution. (B) Trajectory of the helix after 67 s indicating that while it spins, it translates and rotates clockwise. Note that the motion is strongly biased by the glass surface because, in this case, the capillary was only 20 μm high.

Control of the motility by the energy input such as the NIR-irradiation sequence

So far we have demonstrated the differentiation between a head and a tail of the conical helix and shown that it can be actuated to undergo directed motion by pulsed NIR-light. Going a step further, we hypothesize that the coupling of different motional modes within one object can be controlled by the pulse rate and the intensity of the NIR-irradiation. As a consequence, we expected that the motion can be directed by the choice of the pulse sequences. In **Fig. 4** we depicted the motility at relatively short irradiation pulses (3 ms on / 8 ms off). Within the confinement of a flat channel, we observed a fast lateral swimming mode, during which the helix got practically fully extended (**Sequence Fig4 A3-4**). **Fig. 6** demonstrates the movement

of such a conical helix under irradiation (10 ms on / 10 ms off). The helix axial length was 30 μm with a radius of the spiral at the wider end of 12 μm and 4 μm for the radius of the helix at the narrow end. It is shown in a situation when it got confined in one direction as the truncated coil oriented perpendicular to the upper wall of the capillary. As already described in **Figure 4**, this blockade of a forward motion restricts the cone to rotate slowly around its long axis while the spiral end and the helix unwind and wind during the heating-cooling cycles. The vertical orientation enabled us to track the rotation of the extremities of the cone around its long axis and thus to measure the time dependence of the cone's radii. The inset in **Figure 6A** depicts the view along the axis of the truncated coil through the spiral end which is in contact with the wall. The main image in **Fig. 6A** shows a superposition of the cone as it rotates clockwise without changing its position during an actuation cycle of 20 s. The outer radius marks the trajectory of the end of the spiral, while the inner radius marks the trajectory of the eye of the helix. Variation of the sequence of actuating light pulses effects the amplitude of the opening of the coil. When we chose the irradiation frequency in a range so that the cone remained entrapped in its orientation, we could analyse the rate of the rotation around the long axis of the cone. The variation of the angular velocity for different irradiation sequences is depicted in **Figure 6B** (light-on and light-off times were kept identical and summed up to the full period). The double-log diagram indicates that the rate of the motion can be regulated over a range of two orders of magnitude from roughly one revolution per minute at low and high frequencies to more than one revolution per second for the 20 ms actuation cycle. **Figure 6C** shows, how the radii of the head and the tail varies during a full actuation cycle for the 20 ms actuation period, which corresponds to the maximum amplitude of the opening of the helix. The diagram demonstrates a more or less simultaneous opening of the helix and the spiral during heating, while the helix segment re-twisted almost instantaneously when the light was switched off accompanied by comparable slow rewinding of the spiral. Clearly, the deformation cycle is non-reversible with the area under the curve being related to the work produced by the rotor.

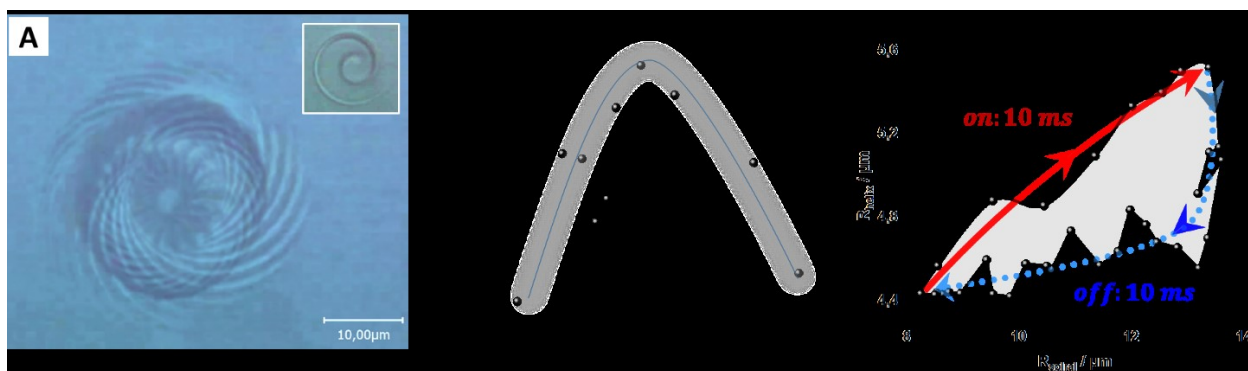


Figure.6: (A) Overlay of optical micrographs that demonstrates the clockwise rotation of a truncated coil with its long axis oriented perpendicular to the capillary wall above it when it has

been actuated by light on and light off sequences of 10 + 10 ms. This orientation is kinematically preferred when the actuation is chosen to maximize the amplitude of the oscillation whereby the rotation velocity is maximum. The axial length of the conical helix was 30 μm and the glass capillary was 30 μm high and 300 μm wide. The main image shows a superposition of the conical helix as it rotates clockwise. The outer radius marks the trajectory of the head of the conical helix, while the inner radius marks the trajectory of the tail. The inset contains a snapshot of the view along the axis of the conical helix through the wide end which is close to the wall. **(B)** The variation of the angular velocity depending on the irradiation period. **(C)** The radius of the tail R_{helix} (or inner radius) as a function of the radius of the wider head.

Figure 7A-B show the movement of the same conical helix while it was tilted towards the capillary wall by an angle of 47°. ⁴¹ In this sequence, the light actuation period was 1.6 ms. Under these conditions, the amplitude is so small that the helix conformation appears optically unchanged. However, it moved steadily around an imaginary axis with the head oriented inwards. **Figure 7A** shows the tracking points (white dots) to trace the rotation of the helix. The white traces depicted in the overlay **image 7B** show the trajectory of these points after a full rotation around the imaginary axis, which lasted about 24 s, taking 15000 actuation cycles. Due to the different displacements during one actuation cycle of the ribbon at the head and the tail, and the corresponding friction effects on the fluid, a torque is created (on the fluid) causing a clockwise rotation of the helix around its axis.

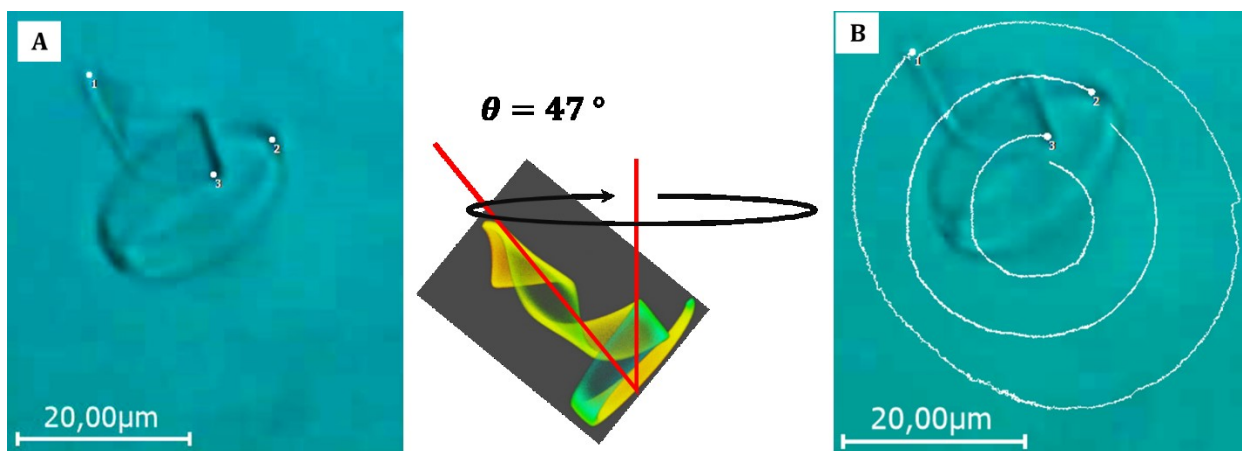


Figure 7: **(A)** Inclined configuration of the conical helix with respect to the glass surface. **(B)** Shows clock-wise rotation path after 24 seconds under irradiation with 800 μs pulse and 800 μs recovery time. The rotation velocity was 23 deg/s. The drawing illustrates the tilt angle.

As mentioned above the confined situation displayed in **Figure 6A** is characteristic for the 20 ms irradiation period at the maximum of the deformation amplitude and rate. At short irradiation times, the small deformation amplitude did not stabilise the spinning of the helix with its axis orthogonal to the surfaces. The orthogonal orientation is also less stable for longer irradiation periods. Actually the 20 ms period coincides with the timescale of the diffusion of the water molecules in and out of the gel. ⁴² Apparently, the orthogonal orientation

of the helix is stabilized only because of the actuation (kinematic stability) and that it should be possible to direct the locomotion by changing the pulse period. That is indeed possible, as demonstrated in the following. **Figure 8** presents an example, how the swimming can be directed by the modulation of the irradiation. In **Figure 8A**, the time dependent superposition of the images of two conical helices is depicted as they were irradiated by a 2 ms *on* and 8 ms *off* sequence (the time between two images was 300 ms). At this irradiation, the conical helix opened only slightly and rotated around its long axis, alike those shown in **Figure 6**, whereas the time for a full rotation lasted 18 s. The image sequence displays different positions of the arc of the spiral as it rotates in one case clockwise and in the other case counter-clockwise. Whether the conical helix rotates clockwise or counter-clockwise is controlled by the handedness of the helix which in turn is determined by small asymmetries in the structure of the wedge shaped ribbon.¹⁶ When the irradiation time was increased from 2 to 4 ms, while the cooling time was kept constant at 8 ms, the ribbon unwound to nearly full extension and did not have sufficient time to recover its helical conformation. Instead it started to wag like a flagellum, obviously combined with a rotation around its long axis. The main image in **Fig. 8B** presents the observation of the forward movement of two of such ribbons actuated in their extended state. We displayed a superposition at different times with a time interval of 396 ms. We clearly identify the forward swimming of the extended ribbon with its wider end ahead at a velocity of 20 $\mu\text{m/s}$. The example shows how the rather unpretentious geometry of the wedge like bilayer ribbon in combination with a light actuated shape transformation induce directed motility of these micro-objects and how this motion can be stirred in a remarkable way by the control of the energy input. By the choice of the irradiation sequence, we could command the agitated ribbons to rotate around at a place and order them to swim forward when the irradiation sequence was switched. Here the velocity of the forward motion resulted to 20 $\mu\text{m/s}$ ($\frac{1}{4}$ body length/s), which is comparable to the non-confined swimming of a *Euglenia*.²

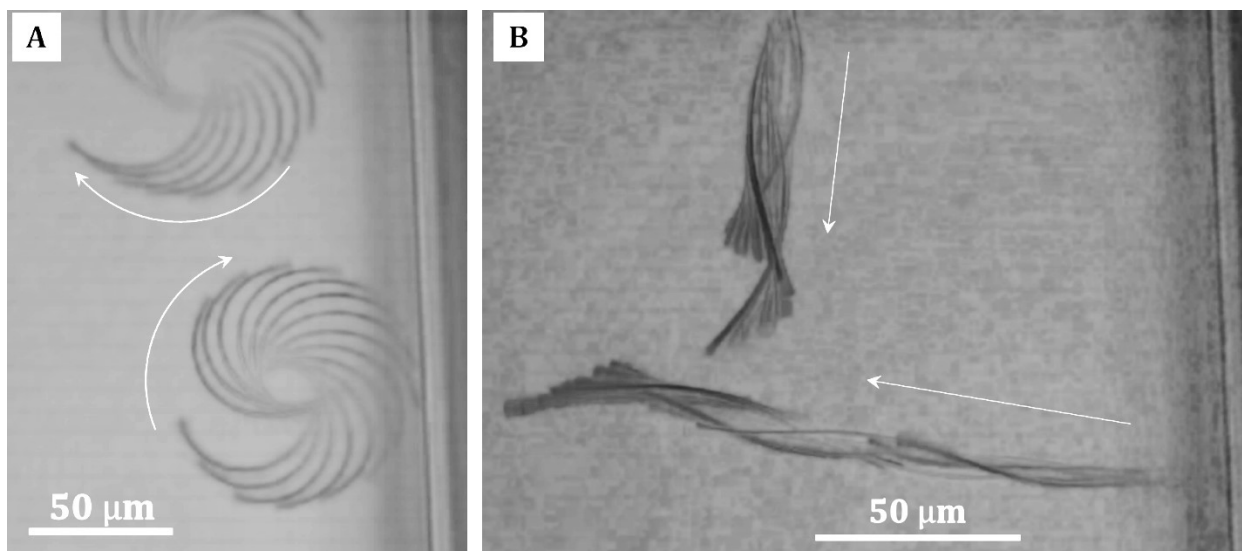


Figure 8: (A) overlay of images with an interval of 300 ms showing the typical deformation and the trajectories of the tapered ribbon while it spin clockwise under an irradiation period of 10 ms (2 ms on and 8 ms recovery) (B) while for a strobe period of 12 ms (4 ms irradiation and 8 ms recovery) it translate by undulation of the body, in this case **overlay** images with an interval of 396 ms it helps to show a wavelike motion.

We have mentioned above that swimming of such thermoresponsive hydrogel microobjects in Newtonian fluid requires a hysteresis motion cycle, which in turn entails shape deformation at non-equilibrium conditions. Such body deformation performs work on its environment because it causes a circulation of the surrounding fluid. We visualized the flow of the surrounding liquid for the swimmer in its forward moving state shown in **Figure 8B** by following the traces of some small colloidal particles. This has been possible as we have been able to observe the extended swimmer in action while it was tethered either with its narrow end or with its wide end to a wall and could not move out of the image area.

In this case we did not use a rectangular capillary for the microscopic observation, but watched the ribbons in a compartment imprinted in a thin layer of polydimethylsiloxane rubber that was sealed by a thin cover glass yielding a square water cavity of $(500 \times 500) \mu\text{m}^2$ and 30 μm in height. We assume that the ends were tethered to the edge of the silicone cavity by hydrophobic interaction and with the help of the cover glass.

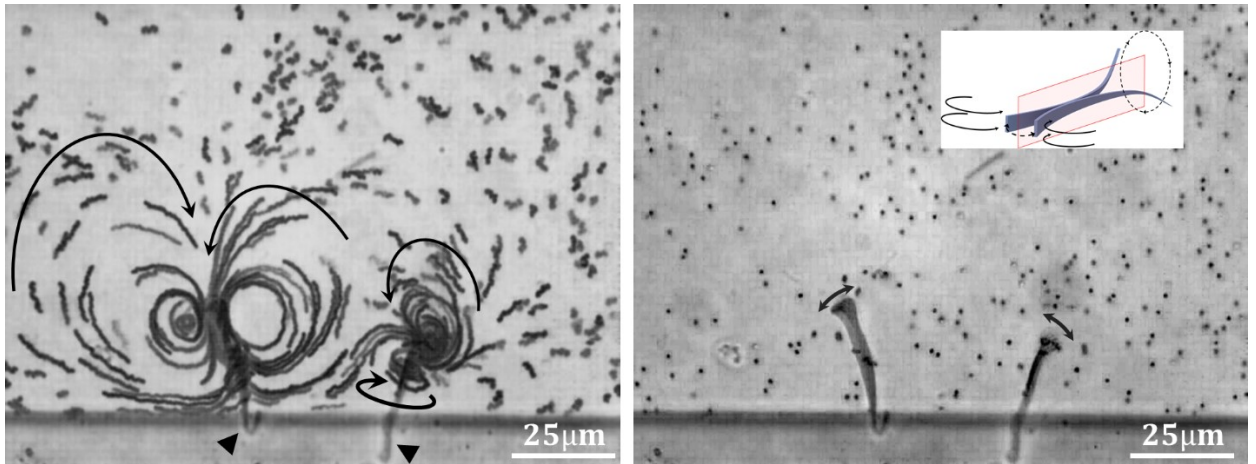


Figure 9: The flow direction and the streamlines pattern of tracer micro particles generated by two tethered tapered ribbons during actuation (4 ms pulse and 12 ms recovery). The triangles indicate where the ends got bound to the polydimethylsiloxane wall of the compartment. Left: the ribbon was attached by its narrow end and the arrows describe the direction of the flow, Right: the ribbon was attached by its wider end and the arrows describe the direction of movement. The inset illustrate possible streamline during actuation of a free ribbon.

Figure 9 shows two distinct patterns of flow lines induced by the periodic deformation of either the widest part (**left**) or the narrow tip (**right**) of the tapered ribbons which got tethered to the silicone edge by their opposite ends. For the free ends we now can see the flow in the surrounding water. The arrows indicate the respective flow direction. The flow lines are clearly distinct and different for the two ends. Hence they indicate different modes of motion for the wider and the narrower end of the wedge shaped ribbon. While the wide end of the ribbon undergoes sideways flapping indicated by the very well developed vertical vortices, the narrow end evidently demonstrates also a rotational component around the main axis of the ribbon combined with the wagging of the tail. In a first attempt we describe the motion like it is depicted in the scheme in **Figure 9B**. How and whether the coupling of these modes of motion, flapping and rotational wagging could cause the forward motion in the direction of the wider end is a question beyond the scope of this publication. Certainly the model in **Figure 9B** gives a base for advanced mathematical modelling of the observed motility of the freely swimming ribbon.

Conclusion

Complementary to the quickly advancing understanding of the swimming of microorganisms, we demonstrated rather simple design principles for systems that can mimic swimming by body shape deformation excluding propelling by a rotary motor. Firstly, and actually compelling by the laws of thermodynamics, in case of reciprocal shape changes the actuation

must follow a nonequilibrium path. Secondly, directional swimming that distinguishes between forward and backwards movement does not only require a swimmer with a 'head' and a 'tail' but should also involve coupling of different modes of motion. Thirdly, coupled modes of motion allow to control and direct the locomotion by the energy input modulation as the different modes can be actuated to different extent. All three points became possible by the fact that we could drive the motion from inside the object by plasmonic heating to which the gels respond by volume changes that transform to different bending modes. While these bending mechanisms are predefined by the bilayer structure of the ribbons, they are controlled by the deviation of the actuation from the equilibrium swelling/shrinking path.

Based on these points, we have been able to design a micro-swimmer that swims forward in the direction of the flapping end. This might appear counterintuitive, however the forward thrust can only be understood by the coupling of this motion with the one of the tail. It may be speculated that the flapping head stabilizes the direction of the forward thrust of the tail. A more detailed analysis should be a subject of hydrodynamic modelling. The forward speed was determined up to 6 body length/s, which is comparable to the rates measured for bacteria *Thiovulum majus*.⁴³

It should be noted that the locomotion of our microswimmer is in fact not fully autonomous, but still controlled from the outside, i.e., by the energy uptake and thus the width of the irradiation pulses and the delay between them. A fully autonomous swimmer would require a mechanism such that the swimmer itself will control the switching between energy uptake and relaxation. This task has not been addressed here. For a light driven swimmer this might be achieved by orientation or temperature sensitive light absorption. Alternatively, the swimmers could be driven by an intermittent chemical reaction. Such a metabolic energy source remains subject of topical investigations.⁴⁴⁻⁴⁵ Most chemical transformations are too slow to cause non-equilibrium situations within small open objects when stress generation is diffusion limited.⁴⁶ Hence, chemical non-equilibrium in living organisms is typically controlled by membranes and pores.⁴⁷ An exception is given by coupling the oscillatory Belousov-Zhabotinsky (BZ) reaction to the volume change of gels and stress generation, whereas the reaction itself is heterogeneous in space,⁴⁸ Within a gel beam, the oscillation can cause bending deformation,⁴⁹ transport, and peristaltic pumping.⁵⁰ This behaviour was modelled with multiphysics simulations of three-dimensional poroelastic systems coupled to the Oregonator model.⁵¹⁻⁵³ It has been shown that the propagation of a Belousov-Zhabotinsky reaction-diffusion front in a submillimeter gel disk induces local changes in the curvature of the disk that result in periodic 3D flapping.⁴⁴ It will be interesting how such autonomous and periodic

buckling deformation propagating along the thin body could be combined with the multi-mode design of the swimmers described in this report.⁵⁴

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5.4 Experimental section

Microgel particles were fabricated by the so-called particle replication in a non-wetting template technique in short PRINT.²² It is based on a template made of perfluoropolyether elastomer.

Preparation of the perfluoropolyether template: A cleaned microscope slide was placed on top of a diced silicon master (5×2.5) cm, produced by photolithography (AMO GmbH), where two pieces of two-layered parafilm (Bemis, total thickness of ca. 200 μm) were used as spacers. The Perfluoropolyether-urethane dimethacrylate liquid (PFPE, Mw = 2000, Fluorolink MD700, Solvay Solexis) containing 1 wt% 2-Hydroxy-2-methylpropiophenone (Sigma Aldrich) was then injected into the space, ensuring its filling. Subsequently, it was exposed to a UV radiation (366 & 254 nm, 4 W at each wavelength, Konrad Benda) for 20 min under argon atmosphere. After curing, the PFPE elastomer was carefully peeled from the silicon master. The micro structured PFPE replicas were cut into suitable size of (6×6) mm^2 . A flat featureless PFPE film with a thickness of 400 μm was prepared according to the same protocol.

Fabrication tapered bilayer ribbons laden with AuNRs: 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 monomer which was recrystallized twice in n-hexane before utilization. A typical monomer solution thus contains NIPAM (575 mg), BIS (7.8 mg), photo-initiator (11.4 mg), and AuNR dispersion in DMSO (981 μL). The nanorods concentration was assessed by the optical density of the dispersion and it was 240 measured at the maximum wavelength of absorbance and an optical path of 1 cm. The typical number density was 9 nanorods/ μm^3 , with nanorods having a longitudinal absorption maximum at around 800 nm, very close to the laser irradiation wavelength of 808 nm. For fluorescent labeling, Nile red was added at a molar ratio of approximately 1:1000, relative to NIPAm. The fabrication procedure of microgel particles is the same as used in our previous reports.²¹ A homemade press with a quartz

window was used for the molding of microgel, and all steps were carried out in a glove box (with an oxygen content $O_2 < 1\%$). A drop of the monomer solution (0.5 μL) was deposited on the PFPE replica and subsequently covered by the flat PFPE-film. A weight was applied to generate suitable pressure (ca. 260 kPa) and ensure drainage of excess of monomer solution. This leads to filling of the microstructure and results in disconnected elements without residual film in between. Subsequently, the assembly was exposed to UV radiation (366 & 254 nm, 4 W at each wavelength, Konrad Benda) for 20 min. Subsequently, the weight was removed and the mold was peeled off from the flat film. The bilayer microgels were produced by sputtering a thin gold film (ca. 2 nm) while the microgels are still in the mold using a sputter coater (30 mA, 10 s, Edwards S150B). To transfer the samples, a droplet of 714 g/L solution of Polyvinylpyrrolidone (PVP, 40 kDa) in ethanol/water (volume ratio: 7/63) was placed on a clean (25 x 25) mm cover glass, followed by the mold facing upside-down. The sample was then left to dry overnight.

Microscopic investigations and light actuation

For microscopic investigations, the PFPE-film was peeled and a droplet of ultrapure water (0.055 $\mu\text{S/cm}$, Purelab Plus UV) was applied to release the objects from the glass surface. The samples were then collected into plasma-cleaned (O_2 , 40 mL/min, 200 W, 5 min, PVA TePla100) capillaries (Vitrocom) and sealed at the ends using two-component epoxy glue (high strength epoxy resin, RS Pro). The temperature was controlled with an accuracy of $\pm 0.1^\circ\text{C}$, using a water cooled Peltier element mounted onto the microscope stage. Infrared LASER-irradiation (808 nm, 10 W, Roithner Lasertechnik) was applied at an incident angle of 45° , giving an elliptical spot size of approximately (2 x 1.5) mm. Videos with high temporal resolution of up to 1 ms were recorded using a digital microscope (VW-9000D, Keyence) with a high speed camera. The motion of the elements was tracked, using MotionAnalyzer (Keyence).

Confinement space and map of the flow field

An (8 x 8) array of square cavities, each with a width of 500 μm and a height of 30 μm was imprinted in PDMS rubber. To that purpose, a master was designed using computer-aided design (CAD) software (Inventor, Autodesk) and produced in a multiphoton lithography setup (Photonic Professional GT, Nanoscribe GmbH) with a 25x immersion objective (numerical aperture (NA), 0.8; Zeiss) and IP-S photoresin (Nanoscribe GmbH). The slicing and hatching distance were 1 μm and 0.5 μm , respectively. The laser power was set to 100 % and scanning speed at 100 mm/s. Substrate adhesion was enhanced by pretreatment of the glass slide with plasma (O_2 , 40 mL/min, 200 W, 5 min, PVA TePla 100) and subsequent incubation overnight in

a 1 % solution of 3-(Trimethoxysilyl)propyl acrylate (Sigma-Aldrich) in acetone. The structure was replicated in 0.2 mL PDMS (Sylgard 184, Dow Corning) using (300x300) μm square capillaries (Vitrocom) as spacers between the master and a glass slide to give a total film thickness of 600 μm . After removing the PFPE film from the sample, 4 μL of ultra pure water were pipetted to transfer it onto a plasma treated (20 x 20) mm Silicon wafer and left to dry. Afterwards, 1.5 μL of the microsphere tracer dispersion (FluoSpheres®, 1.0 μm , Invitrogen, diluted with ultrapure water at a 1:10 volume ratio) was added and the elements trapped by covering with the plasma-activated (O_2 , 30 mL/min, 100 W, 30 s, PVA TePla 100) PDMS-replica, followed by a clean (25 x 25) mm cover glass. Finally, the assembly was left on the microscope stage at 30-40°C until excess liquid was fully evaporated.

Confocal laser scanning microscopy

The investigated elements were collected with ultra pure water into rectangular glass capillaries, as described before. To enhance usability, the capillaries were additionally fixed to a microscope slide using clear nail polish (fisher scientific). The confocal laser scanning microscopy images were recorded using a Leica TCS SPE microscope with a 100x magnification objective (HC PL APO CS2 100x/1.4 Oil). Emission wavelength of 503 nm has been applied and the corresponding fluorescence signal has been detected at 508 – 584 nm.

Curvature analysis

The curvature of the conical helices was analyzed using confocal images. Therefore, Z-stack measurements were converted into color depth coded 3D models using the LASX software (Leica Microsystems CMS GmbH). The perspective of observation was rotated to a view along the helix axis (see **Fig. S1i-ii**). The resulting 2D image was exported and loaded in *ImageJ*, where further analysis was done using the Kappa plugin for curvature analysis.⁵⁵ Color depth coding in the image was used to identify the wide end of the ribbon. Starting at this point, a B-Spline was drawn, following the edge of the ribbon towards the thin end. The curvature of the B-spline was extracted and plotted against the length, where 0 μm denotes the starting point on the wide end (**Fig S1 iii**). The mean curvature of each conical helix was calculated by averaging all values. A linear fit was applied to the curvature profile, describing the gradient in curvature along the length of the ribbon by the slope m .

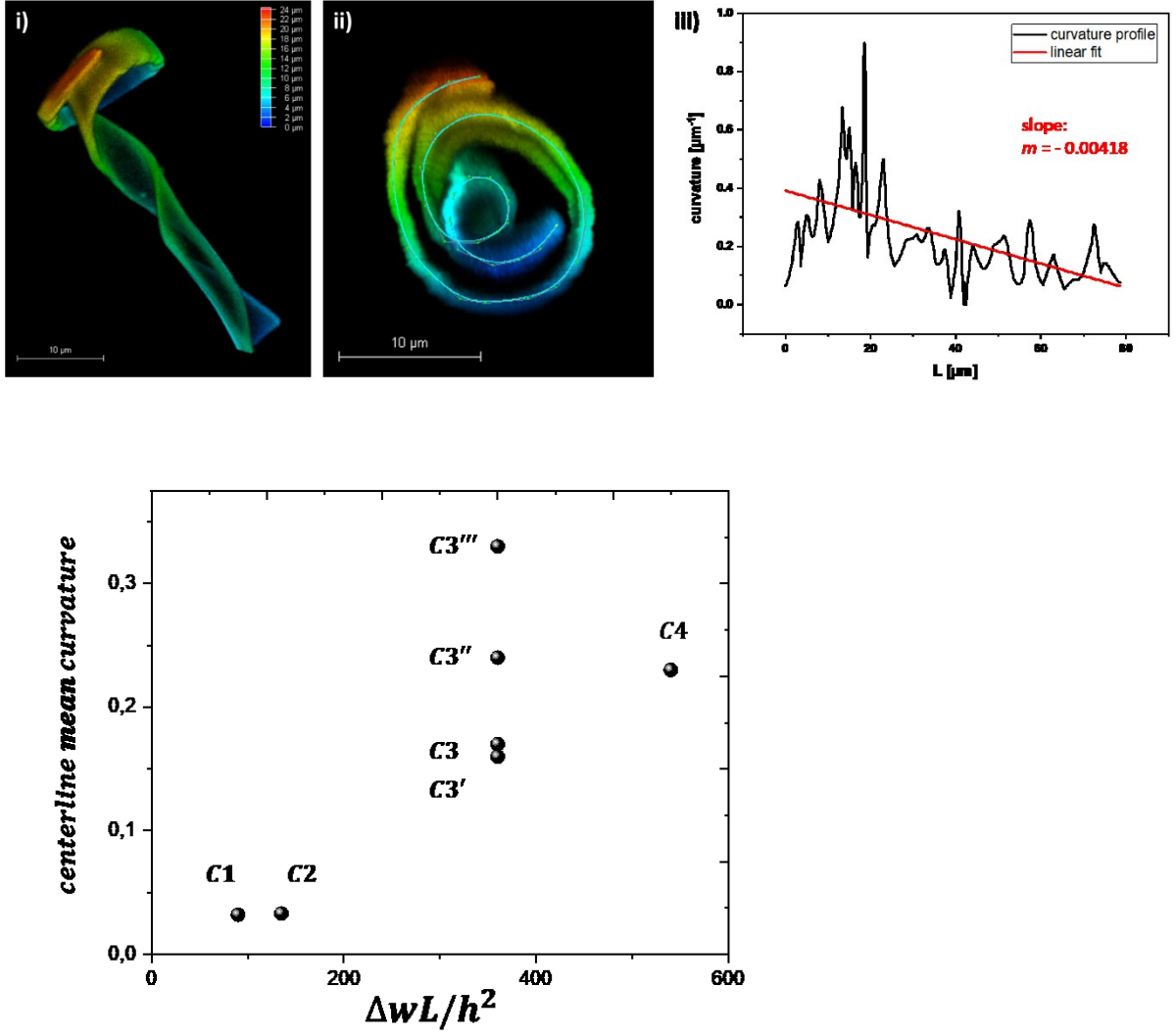


Figure S1: Curvature analysis of a conical helix. (i) A 3D model of a Z-stack measurement from laser scanning microscopy experiment is composed using LAS X software (Leica Microsystems CMS GmbH). (ii) The 3D image is rotated to view the object along the axis of the helix. Subsequently, a 2D image is recorded, imported in ImageJ, and a B-Spline is drawn along the edge of the ribbon (blue line). (iii) The resulting curvature is plotted against the length of the ribbon from the wide end ($w = 5 \mu\text{m}$, $L = 0 \mu\text{m}$) to the thin end ($w = 0.5 \mu\text{m}$, $L = 80 \mu\text{m}$). The slope m of the linear fit describes the gradient in curvature of the object. In order to classify the different conformations we also plotted the mean curvature measured along the length of the ribbon against $\Delta wL/h^2$ Föppl–von Kármán number which is a geometric parameter how easily a sheet bends.

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6. MORPHING AND SWIMMING OF A HYDROGEL DISK WITH AN INEXTENSIBLE ANNULUS

6.1 Abstract

Buckling deformations play a major role in shaping cells and microorganisms and enable ample functionalities and complex tasks like morphogenesis or swimming, which remain challenging to mimic in artificial soft matter.¹⁻⁴ In this study we demonstrate (i) how a hydrogel microdisk undergoes a swelling induced shape evolution into a dome with a periodic wrinkling pattern and (ii) the ability of such dome to swim at low Re-number by photothermal actuation. The dome shape is realized by limiting the lateral expansion of the disk with an inextensible annulus. Through variation of the radius of the disk, relative to the width of the annulus, we found that the maximum height of the dome increases linearly with the radius of its base. The wrinkles are evenly distributed along the azimuth and their number scales as a power-law of the disk's aspect ratio. In this regard the gel disk reacts similarly to the radial confinement like thin shells or capsules do when deforming under external load.⁵⁻⁶ By embedding near-infrared (NIR) light-absorbing gold nanoparticles in the hydrogel network, we enable the photothermal heating of the gel beyond equilibrium conditions. Upon irradiation, wrinkles vanish and the dome flattens. Once the irradiation is stopped, the disk recovers its wrinkled dome state. In cyclic deformation experiments, translation of the dome in proximity to the substrate is observed, independent of the incident light angle and with a preferred directionality of the swimmer relative to its body axis. As we show, this motility is enabled by a non-reciprocal actuation path that is visualized in an environment of microspheres: the particles can be depleted or accumulated, respectively, by modulating the actuation frequency.

6.2 Introduction

Objects made of soft, elastic material are oftentimes shaped by stress fields, which can come from confinement, load forces or differential expansion like growth and swelling. The induced stress is partially released by buckling instabilities, causing a global shape change of the object as a result of geometric incompatibility.⁷⁻⁸ One of the most prominent buckling instabilities one can observe is wrinkling patterns, which naturally occur across a large scale: from centimeters in the human brain cortex; to millimeters in leaves, flowers, fruit, or skin; to micrometer in seeds; to nanometer in vesicles or pollen.⁹⁻¹¹ Understanding the mechanical

response of soft materials to external stimuli and stress fields is of utmost importance to develop functional materials that mimic biological functions like morphogenesis, or create actuators driven by external fields. Applications can be therefore be found in health care, e.g. to promote cell adhesion by surface structuring, in material science where the optical properties of a material are tailored, or in industry for flexible electronics, as well as anti-counterfeiting.¹²⁻¹⁵

The key property that unifies structures undergoing wrinkling deformations is the slenderness of the object, i.e., one dimension being much larger than the other two. Typical examples for objects that are prone to wrinkling are sheets, shells, or capsules. In these simple cases the elastic energy can be described by the Föppl–von Kármán equations which balance the stretching and bending energy of the material. Both contributions scale with the thickness t of the object as $1/t^3$ for stretching and $1/t$ for bending, respectively, meaning that stretching is energetically more costly than bending.¹⁶ A simple experiment to demonstrate this is trying to wrap a sheet of paper onto a sphere: wrinkles are formed by bending of the paper, as a way to alleviate the imposed stress of the geometrical confinement and adapt to the spherical shape. The wrinkles in this case are distributed along the azimuth and can be characterized by a wavelength λ , the lateral distance between two maxima of deflection, and the vertical distance between a maximum and minimum deflection of a wrinkle, called amplitude A .¹⁷ Wrinkling patterns also occur on caps and shells, by indentation with a rod or a pressure difference. In the first case, wrinkles form perpendicular to the direction of the load force and the number of wrinkles depend on the indentation depth.¹⁸ For shells it was found, that the amount and rate of pressure difference determine the shape. With an increasing pressure single or multiple dimples form on the surface prior to wrinkling, and for an increasing rate of pressure difference, the number of wrinkles increases.¹⁹ In all the cases mentioned, the number of wrinkles was found to scale either as a function of the thickness of the membrane, the amount of force applied, or the curvature it has to adapt to. Therefore, the number of wrinkles can be used as a way to measure either material properties like Young's modulus, or changes in the environment of an object.²⁰⁻²¹ Similar to geometric compaction by load forces, stress induced wrinkles are formed by swelling of a material when its expansion is confined in at least one dimension. For instance, a rectangular hydrogel stripe can be bound with one edge to a stiff substrate. Above a critical swelling ratio, the strain mismatch between soft and stiff substrate cause buckling and thus wrinkling of the gel strip. The amplitude and wavelength of the wrinkles are then a function of the gel's swelling degree.²² The nature of hydrogels as a crosslinked, three dimensional polymer network offers additional possibilities to tune the mechanical properties of a material. For instance changing the mesh size by varying the cross-linking density directly affects the swellability of the gel, as it is balanced by the elastic

properties of the polymer network.²³⁻²⁴ Furthermore, the cross-linking density can be locally varied, allowing to program a certain shape that the object is morphing into when its swollen or collapsed, respectively.²⁵⁻²⁷ Given a swellable disk: If the cross-linking density is higher at the perimeter, the local stiffening leads to buckling into a dome shape due to expansion of the inner part when the gel is swollen. When shrinking however, the less densely crosslinked gel can contract more than the rim, leading to a saddle-like shape.²⁷ When bound to a curved surface, its curvature adds an additional degree of complexity that affects the wrinkling behavior of the disk.²⁸ In this regard, our case where a swellable hydrogel disk is confined by an annulus with a curvature of $1/R_i$, several aspects affecting the wrinkling behavior are combined. Furthermore, responsivity to an external stimulus like pH, light, or temperature can be introduced to a gel by choosing the corresponding monomer or post-modification of the polymer.²⁹⁻³² Among thermoresponsive polymers, poly(*N*-isopropylacrylamide) (PNIPAm) is the most prominent one and widely used due to its superior properties.³³⁻³⁵ The lower critical solution behavior of PNIPAm leads to a volumetric change when fabricated as a crosslinked gel, known as the volume phase transition.³⁶⁻³⁷ We capitalize on this behavior and translate the volume change into a mechanical actuation by generating anisometric bodies. Shaping of the gel is therefore done by replication in non-wetting templates (PRINT)³⁸ and swelling is restricted by applying a passive coating to generate a temperature-reversible curvature.³⁹ This method allows precise fabrication of soft micro actuators. Due to their dimensions in the micron range their Reynolds number in water is much smaller than one.⁴⁰ Thus, the fundamental challenge of microswimmers is to overcome the drag from the high viscosity of the fluid, e.g. by generating non-reciprocal kinematics.⁴¹ To facilitate this, we implement gold nanoparticles into the gel network for plasmonic heating, i.e., locally generating heat in the gel by irradiating with near infrared (NIR) light. This heat is transferred throughout the polymer network orders of magnitude faster than the mass transport of water out of the gel, causing non-equilibrium states that are otherwise inaccessible.⁴² Accompanied by self-acceleration this strongly affects the dynamics of the gel, forming a skin layer on the gel that causes a shape hysteresis for heating/cooling cycles.⁴² Cyclic irradiation therefore leads to a net flow and thus translation of the swimmer, which can be directed under the right pulse sequence and swimmer geometry.⁴³ For disks however, simply applying a passive layer is insufficient to produce a microswimmer due to its rotational symmetry. Instead, the disk has to be morphed into a different shape, e.g. by a passive annulus, and equipped with a second feature to create non-reciprocal kinematics.⁴⁴

In this work, we prepare a gold nanorods laden PNIPAm hydrogel disk that is confined in its planar expansion with an annulus such that swelling of the thermoresponsive gel leads to buckling into a dome shape. We first investigate the wrinkling behavior of this dome, as the

number and position of wrinkles give a hint on the stress distribution in the gel. We then show how to control the wrinkling behavior of the disk by varying the geometrical parameters, i.e., the aspect ratio of the disk. Furthermore, pulse sequences of NIR irradiation are applied and the deformation of the dome is studied from two observation angles to identify the kinematics of the object. Finally, we investigate how the orientation of the dome relative to the substrate affects its trajectory when swimming and demonstrate how manipulating the pulse sequence can be utilized to either gather or deplete particles in an environment of dispersed microspheres.

6.3 Results and Discussion

Wrinkling analysis under equilibrium conditions

The microgel disks with an inextensible annulus were composed of a poly(NIPAm)-based hydrogel disk that is surrounded by an acrylate rim. The typical dimensions are a thickness of $t = 5 \mu\text{m}$ and a radius R_i between $5 \mu\text{m}$ and $80 \mu\text{m}$. The objects were fabricated by combining soft lithography (particle replication in non-wetting templates, PRINT) with multiphoton lithography (MPL), as illustrated in **Figure 1**. The detailed procedure can be found in the experimental section. Briefly, a micro-structured silicon master (disks with variable radius) was replicated in a UV-curable, fluorinated elastomer (PFPE). Subsequently, a passive acrylate annulus was fabricated via MPL. The dimensions of the annulus were adapted to the dimensions of the mold, allowing us to vary the aspect ratio of the hydrogel disk either by choosing master structures with the appropriate diameter of the disks, or decreasing the inner radius of the rim. A gold nanorods laden NIPAm solution was then added to the mold, excess solution removed by pressing with a featureless film of PFPE, and polymerization initiated by UV irradiation. As a result, the PNIPAm disk and the polyacrylate annulus are covalently interlinked. After transfer of the sample onto a glass slide with the help of sacrificial PVP solution, the sample was collected in a capillary for microscopic investigations.

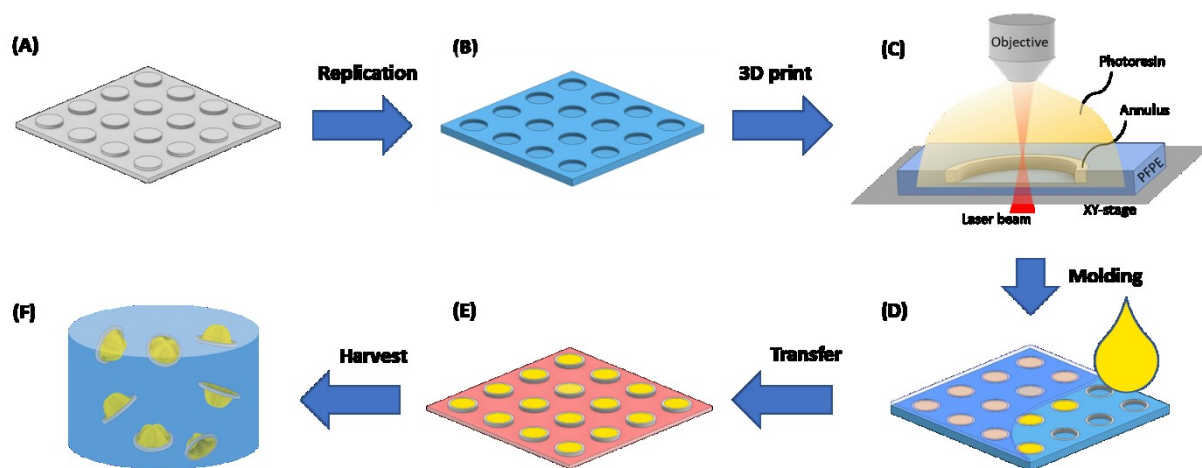


Figure 1: Shape programming of a microgel disk by combining soft lithography technique with multiphoton lithography (MPL). A silicon master (A) is replicated using fluorinated elastomer to create a mold (B) for the microdisks. (C) The inextensible annulus is implemented by MPL using an acrylate based resin. (D) The gold nanorods laden microgel is then formed from solution (yellow) by UV-curing. For microscopic investigation the samples are first transferred to a glass slide using PVP (red) as adhesive (E), and then harvested into capillaries (F).

The hydrogel network was synthesized to present a linear swelling factor of 1.7, measured between a water bath temperature of $T = 20 \text{ }^{\circ}\text{C}$ and the dimensions of the disk as prepared. In an unconfined environment, a hydrogel disk prepared with a radius of $30 \mu\text{m}$ will therefore have a radius of $51 \mu\text{m}$ in the swollen state at $20 \text{ }^{\circ}\text{C}$. However, as the disk in the present case is

covalently bound to the surrounding annulus, its swelling is restricted in the lateral direction, as well as along the perimeter. As a result, a compressive load is built up upon swelling of the gel. This stress leads to out-of-plane buckling of the disk, forming a dome-shaped structure as shown in **Figure 2**. This dome has a base radius R_i , equal to the inner radius of the annulus, and a deflection height h (**Fig. 2A**). Due to the geometric compaction, wrinkles are formed along the azimuth in order to partially release the stress of the disk. **Figure 2B** shows a confocal micrograph of such a dome, providing a detailed three-dimensional view. The wrinkles are evenly distributed along the azimuth, which becomes clearly visible when observed in top-view where they form a dark contrasted line (**Fig. 2C**). The wavelength of wrinkles is calculated by dividing the perimeter length of the gel disk by the number of wrinkles n . Domes with a radius of $R_i = 50 \mu\text{m}$ typically show four or five wrinkles, i.e., a wavelength of $\lambda = 39 \mu\text{m}$ or $\lambda = 31 \mu\text{m}$, respectively.

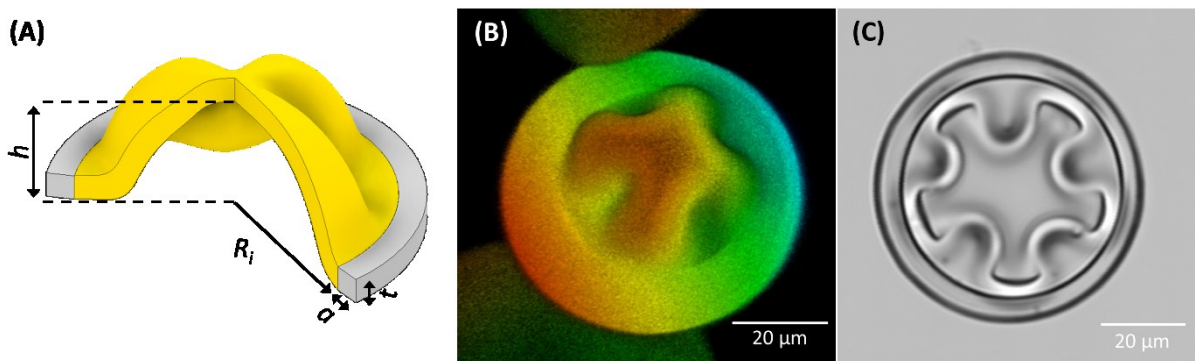


Figure 2: An initially flat microgel disk with an inextensible annulus swells and morphs into a dome-like shape with wrinkles along the azimuth. **(A)** A schematic representation of a gel disk with a thickness t , that has morphed into a wrinkled dome with a base radius R_i and deflection height h . The width of the annulus is given with a . **(B)** The 3D structure as observed by confocal microscopy with a color-coded depth. Wrinkling of the dome can be observed along the azimuth. **(C)** Bright field image of a wrinkled dome when seen from top. The regular distribution of the wrinkles can be seen more clearly and is used to calculate the wavelength λ , which is typically $31 \mu\text{m}$ or $39 \mu\text{m}$, respectively, for $R_i = 25 \mu\text{m}$.

To investigate how such wrinkling patterns evolve with the geometry of the object, we systematically varied the disk radius R_i ($5 \mu\text{m} \leq R_i \leq 90 \mu\text{m}$), while keeping the thickness constant at $t = 5 \mu\text{m}$. We found that swelling causes the disks to morph into a wrinkled dome, regardless of the initial radius. With an increasing radius of the disk, an increase in the number of wrinkles can be observed (**Fig. 3D**). When the radius is sufficiently large, i.e. $R_i > 70 \mu\text{m}$, wrinkles occur in a less regular fashion and areas with deflection of the gel below the plane of the annulus are observed. In top-view these features become visible as irregularities in the wrinkling pattern where the dark contrasted lines reach much further towards the center of the disk than usually (see **Fig. 3D**, rightmost object). The deflection height of the domes was measured using 3D images from confocal laser scanning microscopy (CLSM) experiments.

The results of the measurement are summarized in **Figure 3A**, where the deflection height h is shown as a function of the disk radius R_i . The height of the dome scales proportional with the radius of its base at a factor of 1.07. This suggests that the dome has the envelope of a hemisphere as $R_i \approx h$. Assuming that energy in stretching of the material is minimal compared to bending of the hydrogel, the scaling factor for the disks expansion is expected to be similar to the swelling factor of a free disk. To compare this to experimental results, the arch length s of the dome was measured using the vertical slices of the 3D images obtained by CLSM. Plotting s versus R_i , a linear relationship with a slope of 1.7 was found. Thus, the swelling factor of the free disk is conserved, despite the deflection into a dome shape and the formed wrinkling pattern. Increasing the radius R_i while keeping the thickness constant, effectively lowers the aspect ratio t/R_i . Since the bending energy is more sensitive to changes in thickness than stretching of the disk, an increasing number of wrinkles for a decrease in aspect ratio is expected and experimentally confirmed. We find that the number of wrinkles approximately scale with the aspect ratio with a power of -0.5. This value is comparable to other studies investigating soft domes or shells under load, as well as for bi-axially compressed disks, which all have confirmed theoretic considerations for typical scaling of deformations in thin sheets.⁵

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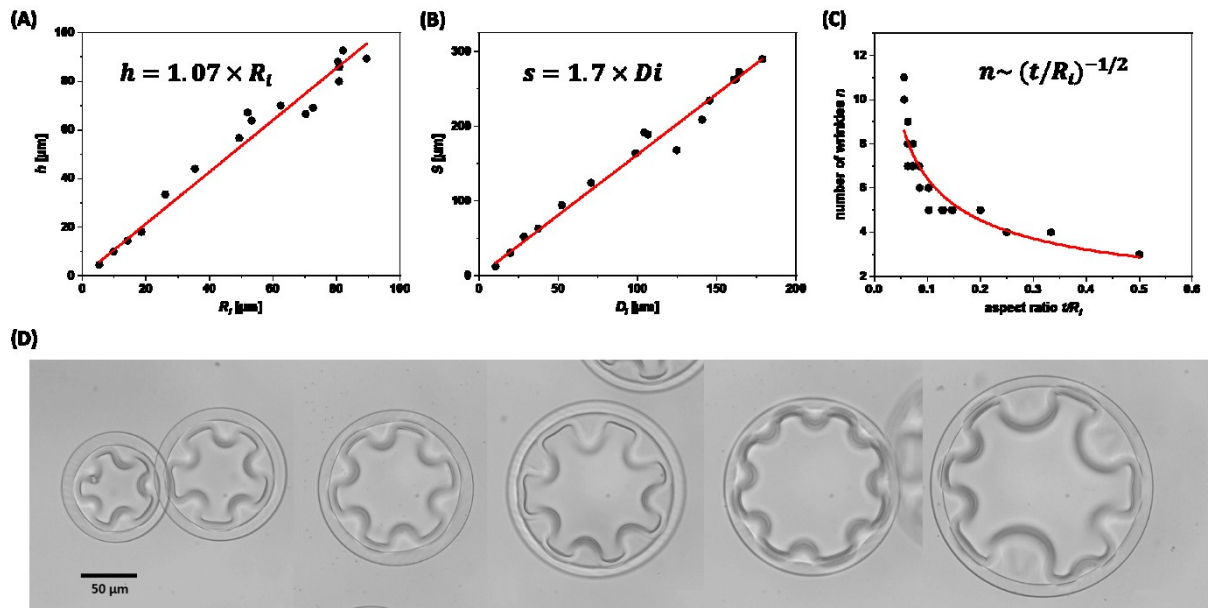


Figure 3: Scaling of the height (A), arch length (B) and number of wrinkles (C) with the geometrical parameters of the microdisk. **(A)** The height of the dome increases linearly with the disc radius at a factor of ~ 1 . Thus, the envelope is a hemisphere. **(B)** The linear scaling factor of 1.7 of the contour length is similar to the swelling factor of a free disc. **(C)** Increase in the diameter of the disc at constant thickness leads to a higher number of wrinkles. As expected from theory, the number scales with the aspect ratio as power of -0.5. **(D)** Corresponding micrographs of the objects swollen at 20°C with an increasing R_i from left to right.

Photothermal actuation and motility

We trigger localized plasmon resonance of the gold nanorods by applying laser irradiation of NIR light ($\lambda = 808$ nm). The generated heat is immediately transferred throughout the hydrogel network, surpassing the LCST of PNIPAm within milliseconds and causing the gel to collapse. This induces a shape change in the object as the swelling-induced radial compression of the disk within the annulus is released. In top-view it can be seen how the wrinkling pattern disappears during irradiation (**Fig. 4A**, left column). When the light source is turned off, heat dissipates into the surrounding liquid, allowing the gel to recover its swollen state by taking up water from its environment. This brings back the original shape with the characteristic wrinkling pattern, while the position of the wrinkles is conserved in the structure. Furthermore, we observe how the deflection of the dome changes under irradiation, by using capillaries with a square cross-section and tilting the objective of the microscope by 90° into a horizontal position (**Fig. 4A**, right column). The microgel dome is found with its annulus on the glass substrate, sealing the opening of the dome and causing a reflected image on the substrate. During irradiation, the deflection decreases and simultaneously the Z-position of the annulus is increasing. The original state of the dome is recovered after reswelling of the gel. The side-view observation also allows us to quantitatively study the response of the gel to the irradiation. Therefore, we measure the deflection height of the dome by tracking the position of the annulus and the top of the dome. The deflection height is evaluated for increasing pulse widths of $t_{on} = 100$ milliseconds up to $t_{on} = 1.5$ seconds. The results are plotted as deflection versus time in **Figure 4B**. The irradiation is started at $t_0 = 0$ s and the different widths of the pulses are color-coded. A higher decrease of deflection is observed for an increase in pulse width, and a minimum of deflection of $h = 3$ μm is reached at a pulse width of 1.5 seconds. This may indicate that the disk does not shrink to full extent. However, this can also be explained by a slight tilt of the object during the actuation, as well as the accuracy of the measurement of $\pm 10\%$. When comparing the maximum speed of collapse to the maximum speed of recovery, the latter was found to be two times slower. Unlike the immediate response of the gel when turning on the light source, the deflection does not immediately start to increase when the irradiation is stopped. Instead, we found that there is a characteristic delay of the recovery for each pulse width. We attribute the origin of this delay to residual heat in the setup. The interaction between the glass substrate and the dome is visible, when irradiating the sample with constant cycling of on- and off-times for a longer time period (seconds to minutes). As shown in the side-observation (**Fig. 4A**), the dome lifts itself up from the surface during collapse. This motion is induced by the flow beneath the dome, pushing towards the substrate. Over a longer time period of cyclic irradiation, a translation of the dome along the surface of the substrate is observed, with the trajectory of translation independent from the angle of the incident light (**Fig. 4C**). Occasionally the domes were found tilted on the glass

substrate with the opening facing towards the bulk liquid (**Fig. 4C** and **S1**). In this configuration translation velocities of $\sim 3 \mu\text{m/s}$ were observed, which is much faster than the domes with the opening facing down translating at $\sim 1 \mu\text{m/s}$ (for continuous cycles of $t_{\text{on}} = 250 \text{ ms}$ and $t_{\text{off}} = 600 \text{ ms}$). Due to the change in orientation the dome no longer has to overcome gravitational forces when translating. Upon recovery, both surfaces of the dome are facing bulk liquid and no preferred uptake can be established. In conclusion, the translation of this object in an unconfined environment has a preferred swimming direction with the opening of the dome forwards and along its rotational axis of symmetry, which is consistent with theoretical studies of a similar system.⁴⁴ As described before, a dome located with its opening towards the substrate is lifted up and returns back during actuation. By controlling the irradiation frequency, i.e., pulse width and ratio between irradiation and recovery, the gap size and amount of liquid that can enter or exit beneath the dome is controlled. In an environment of dispersed microspheres and under cyclic irradiation for $t_{\text{on}} = 150 \text{ ms}$ and recovery of $t_{\text{off}} = 500 \text{ ms}$, depletion of the particles beneath the dome is observed. By changing the pulses to $t_{\text{on}}/t_{\text{off}} = 200/600 \text{ ms/ms}$, microspheres accumulate beneath the dome over time. This effect demonstrates the non-equilibrium conditions under which the microgel is actuated.

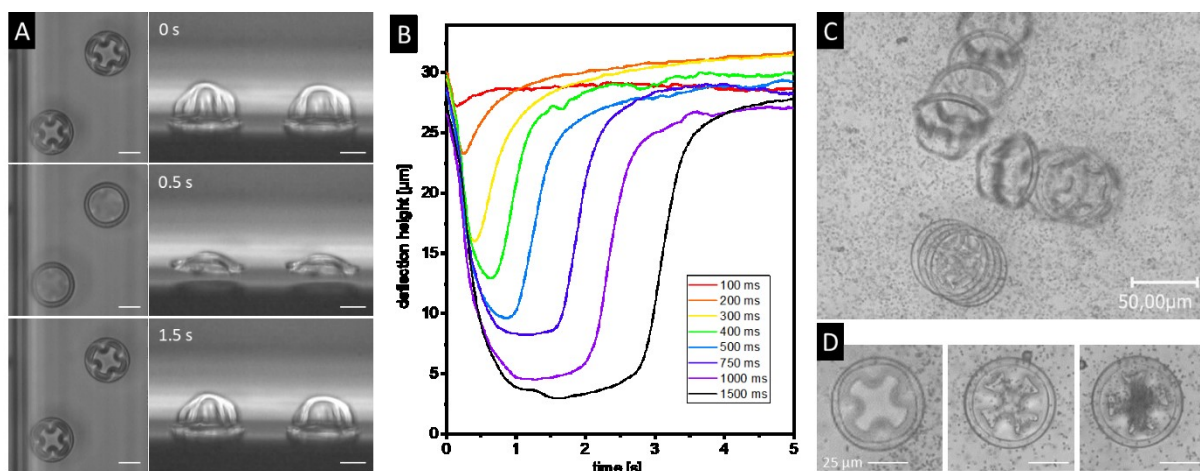


Figure 4: (A) Side observation (left column) and top-view (right column) of a collapsing dome, induced by NIR irradiation for 0.5 s and its subsequent recovery. (Scale bar is $25 \mu\text{m}$.) (B) The evolution of decreasing dome deflection with increasing irradiation times from 0.1 s to 1.5 s. (C) Superposition of three domes under pulsed NIR irradiation, translating at different speeds and in directions independent of the incident light. (D) In a medium of dispersed polystyrene beads, depletion (left) and accumulation (right) are achieved by adjusting the irradiation frequency. Center image: The dome in its original state as reference.

6.4 Conclusion

We have demonstrated how a PINPAm microdisk morphs into a wrinkled dome when its swelling is confined by an annulus and how this system performs directional motility under cyclic NIR irradiation. Despite the swelling induced buckling to a wrinkled dome shape, the swelling ratio of a free disk is conserved. Analysis of the number of wrinkles showed, that it scales with the aspect ratio of the disk to the power of -0.5, consistent with theory for the deformation of thin, soft objects. Gold nanorods embedded in the hydrogel enable rapid heat generation by NIR irradiation, which is quickly transferred to the gel network, deswelling the disk. This leads to flattening of the dome and we found a two times faster recovery upon cooling when the irradiation is stopped, suggesting a hysteresis in the kinematics that enables swimming of the dome at low Re-number. When actuated by a laser pulse, the dome is lifted upwards against gravity when facing the substrate with its opening, which we assign to water from beneath the dome being pushed towards the substrate. Cyclic actuation leads to translation of the dome independent of orientation of the dome on the substrate or the incident light angle. Most importantly, a preferred direction of motility with the opening of the dome forwards has been identified. By modulating the irradiation frequency, we were able to deplete or accumulate of microspheres beneath the dome while translating, demonstrating the work that is performed, as well as its potential as a micromachine carrying load and dispersing it on demand.

6.5 Experimental section

The following chemicals were used as received, unless stated otherwise:

1-Methoxy-2-propanyl acetate (PGMEA, Sigma-Aldrich), Isopropanol (IPA, Sigma-Aldrich), Acetone (Sigma-Aldrich), Acryloxyethyl thicarbamoyl rhodamine B (Sigma-Aldrich), N,N'-Methylenbisacrylamide (BIS, Sigma-Aldrich), Dimethyl sulfoxide (DMSO, Sigma-Aldrich), Bifunctional perfluoropolyether urethane (PFPE, Mw = 4000, Fomblin® MD 40, Solvay Solexis), 2-Hydroxy-2-methylpropiophenone (Sigma Aldrich), IPL-780 (Nanoscribe GmbH), N-Isopropylacrylamide (NIPAm, 97%, recrystallized in hexane), 4'-(2-hydroxyethoxy)-2-methylpropiophenone (98%)

The preparation of the template, as well as the synthesis of the microgel was carried out under nitrogen atmosphere in a glovebox.

Direct laser writing (DLW)

The micro-structured silicon master wafer was replicated using PFPE, containing 1 wt% of the UV-curable photoinitiator 2-Hydroxy-2-methylpropiophenone. Therefore, the interspace of a glass slide and the wafer was filled with the solution and cured under UV-irradiation (370 nm, 5 W) for 10 minutes. Afterwards the mold was separated from the wafer and inextensible acrylate rings were then implemented using a direct laser writing (DLW) setup (Photonic Professional GT, Nanoscribe GmbH, Germany) with an oil immersion 63x objective (numerical aperture (NA), 1.4; Zeiss, Germany). Therefore, a (5 x 5) mm piece of the PFPE mold was placed on a glass slide and a droplet of the photoresist IPL-780 was added. As laser source, a femtosecond laser (emission wavelength, 780 nm; pulse width, 120 fs; and repetition rate, 100 MHz) was employed. The annulus was designed using computer aided (CAD) design software (Inventor, Autodesk) and exported as stl-file. The outer diameter was chosen to be 5 μm larger than the diameter of the respective mold to ensure the adhesion of the annulus. The files were converted to printable document formats using DeScribe software (Nanoscribe, Germany), where slicing and hatching distance were set to 0.3 μm and 0.2 μm , respectively. The writing speed was varied from 20 – 70 mm/s, at a fixed laser power of 80%. After the writing process, excess photoresist was removed by incubation in 1-Methoxy-2-propylacetate (PGMEA) for 10 min and subsequent incubation in Isopropanol for 3 min.

Preparation of PNIPAm microdisks

The monomer solution for the microgel contained 500 mg NIPAm, 6.8 mg crosslinker BIS, 9.9 mg photoinitiator 4'-(2-hydroxyethoxy)-2-methylpropiophenone and 500 μL DMSO as solvent, containing the PEGylated gold nanorods (total optical density (OD): 240). The synthesis and surface functionalization of the gold nanorods has been described elsewhere.³⁹ Rhodamine B has been added at a molar ratio of approximately 1:1000 relative to NIPAm to fluorescently label the gel. Onto the (5 x 5) mm mold equipped with the annulus structure from DLW, 0.5 μL of the prepolymer solution were added. By covering the mold with a flat piece of PFPE (total thickness of 400 μm) and gently applying pressure, excess liquid was drained. The solution was then cured under UV irradiation (366 & 254 nm, 2 x 4 W, Konrad Benda). The two films were then separated and the mold was placed upside-down into a droplet of 20 wt% PVP-solution to transfer the sample on a plasma-cleaned glass slide. The sample was then left to dry overnight.

Microscopic investigations and photothermal actuation

The PFPE-mold was peeled from the glass slide and subsequently a droplet of ultrapure water (0.055 $\mu\text{S}/\text{cm}$, Purelab Plus UV) was applied to release the hydrogel objects from the PVP. Plasma-cleaned (O_2 , 40 mL/min, 200W, 5 min, PVA TePla 100), rectangular capillaries

((0.1 x 2) mm, Vitrocom) were used to collect the sample, and sealed at the ends using two-component epoxy glue (UHU® Plus Sofortfest). For side-view observations, capillaries with a (300 x 300) μm square cross section (Vitrocom) were used. The temperature was controlled using a peltier element mounted onto the microscope stage, with an accuracy of ± 0.1 °C. Plasmonic heating was induced by infrared LASER-irradiation (808 nm, 10 W, Roithner Lasertechnik). The incident angle of 45° resulted in an elliptical spot size of approximately (2 x 1.5) mm. Videos with high frame rates were recorded with a high speed camera connected to the digital microscope (VW-9000D, Keyence). For flow-studies, a dispersion of polystyrene microspheres (FluoSpheres®, 1.0 μm , invitrogen) was prepared by dilution in ultrapure water at a 1:10 volume ratio. The dispersion was then used instead of ultrapure water to release the sample and collect the gels in capillaries as described before.

Confocal laser scanning microscopy

The disks were collected with ultra pure water into rectangular capillaries, as described before. To enhance usability, the capillaries were additionally fixed to a microscope slide using clear nail polish (fisher scientific). The confocal laser scanning microscopy images were recorded using a Leica TCS SPE microscope with a 63x magnification objective (HC PL APO CS2 63x/1.3 Glyc). Emission wavelength of 520 nm has been applied and the corresponding fluorescence signal has been detected at 539 - 662 nm.

6.6 References

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6.7 Appendix

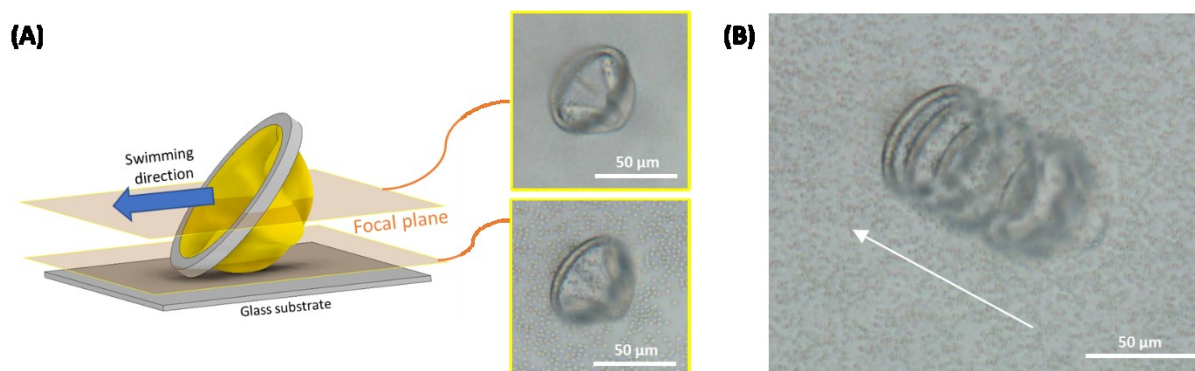


Figure S1: Directional motility of a microgel dome. **(A)** Sketch of a tilted dome on the glass substrate. The plane of the glass substrate is identified by focusing on the glass beads (diameter 2 μm) as these settle down due to gravity (lower image). From there, the focus is pulled upwards to validate the orientation of the dome with its opening towards the bulk, as the rim now is in focus like indicated in the sketch and the beads are blurred/out of focus (upper image). **(B)** For multiple irradiation cycles a translation of the dome from the bottom right to the top left corner of the image is observed and visualized by superposition of the images. A translation towards the opening of the dome can be identified.

7. A SWITCHABLE, BISTABLE MICROGEL DOME WITH ULTRAFAST SNAPPING MOTION

7.1 Abstract

In nature, snapping motions can be found in a variety of plants and animals where it is vital for their reproduction or nutrition.¹⁻² Scientists have thoroughly investigated the design principles of such features and translated them to develop shape-morphing materials with advanced functionality.³⁻⁵ We here demonstrate how a microscopic actuator can be synthesized that facilitates a fully reversible millisecond snap. We describe our design approach for a bistable hydrogel dome and show how this concept is realized using advanced lithographic methods: A microscopic bilayer disk is generated by soft lithography, radially compressed and fixed in an annulus via direct laser writing. The bilayer is buckling into a dome, whose deflection can be controlled and eventually inverted by temperature through deswelling and swelling, respectively, of the thermoresponsive gel. The stress distribution of the disk is indicated by a characteristic wrinkling pattern and therefore allows to conclude on the orientation of the bilayer inside the annulus. Furthermore, the invariant annulus generates an energy barrier between the two possible states of the dome, leading to bistability and eventually enabling a shape deformation hysteresis with a snapping transition. We study the fully reversible deformation pathway of the dome from top- and side-view during temperature change driven actuation. Variations in the rate of temperature change demonstrate the sensitivity of the system and under rapid changes induced by photothermal heating, we are able to expedite the snap-through times to two milliseconds.

7.2 Introduction

Rapid motions enable carnivorous plants to trap small insects with their lobes and other plants to spread their seeds by shooting them into the air.⁶⁻⁸ These motions can be even faster than the hydraulic movements of a plant, i.e. swelling induced, when being coupled to mechanical instability. As a result the snapping velocity can touch the border of the physically possible.⁹ In this context, snap-buckling plays an important role as it creates the most rapid, non-destructive mechanism of actuation.¹ It is therefore extensively studied in case of the venus flytrap where the snap is driven by a curvature inversion of the lobes.⁷ Typical timescales of a closing leaf are less than half a second in this case, however can be as low as tens of milliseconds in the waterwheel plant.⁸ Mimicking such mechanisms offers new possibilities to create shape-morphing matter that can be employed in various applications such as micro-electromechanical systems (MEMS), soft actuators and functional optical elements.^{5, 10-12}

Snap-buckling is a mechanical instability caused by a geometric constraint that creates an energy barrier between at least two states with minima in elastic energy.^{1, 13} It is therefore strongly linked to bistability, i.e., the ability of a material or object to have two stable states under the same conditions.¹⁴ The energy barrier separating these two states allows the build-up of stored elastic energy during transition. The subsequent rapid discharge then causes a sudden shape change of the object.¹ Typical examples for structures that show snap-buckling behavior under various conditions are clamped elastic beams and indented or pressurized capsules and shells.¹⁵⁻¹⁶ The property that unifies these examples is their slenderness, i.e., being much smaller in one spatial dimension. The elastic response of slender objects is largely affected by the thickness and bending is preferred over stretching as it scales with the thickness to a power of three, compared to a linear dependence on stretching. As a result, out-of-plane buckling is preferred over compressed, flat configurations to minimize elastic energy.¹⁷ However, shells and capsules follow other rules for buckling compared to plates, as they are curved and bending and stretching are coupled as every change curvature from the initial state induces stress in the material.¹⁸⁻¹⁹ Furthermore, the geometrical parameters of the shell or capsule determine the amount of elastic energy that can be stored, therefore influencing the snap-through transition.¹⁵⁻¹⁶ A snap-through is typically induced by a load force e.g. indentation with a rod or by differential pressure and often accompanied by the formation of circumferential waves.²⁰⁻²⁴ In the case of bilayer shells differential swelling can be used to induce snap-buckling. However, such bilayer design increases the complexity of the system as the thickness ratio between the two layers, the respective elastic properties of the different materials and their swelling properties are relevant.²⁵ Eventually, snapping enables

non-reciprocal motion, i.e., a shape deformation hysteresis and therefore fulfills a fundamental criterion for microscopic objects to swim.²⁶⁻²⁷

In previous studies we have demonstrated how thermoresponsive hydrogel/gold bilayer objects can be synthesized and employed as light-driven microswimmers.²⁸⁻²⁹ These artificial systems are, just as the snapping plants, limited in their actuation speed by the diffusion of water through their body.³⁰⁻³² Consequently, non-equilibrium effects occur in the hydrogel body during rapid temperature changes and are sufficient for shape deformation induced propulsion.³³ However, the actuation speed of soft objects can be further enhanced when driven by elastic instability.³⁴ Whilst the implementation of a snap-buckling mechanism into hydrogel actuators has been explored, it has not yet been mastered on a micrometer scale.^{4, 34-35} Furthermore, and to our best knowledge, the implementation as a freely swimming microscopic system performing a self-activated snap-buckling motion has been described but never realized.²⁶

In this work, we solve this challenge by transforming a microscopic hydrogel bilayer disk into a switchable, bistable dome. Therefore, poly(N-isopropylacrylamide) (PNIPAm) micro disks are prepared via soft lithography and coated with a passive layer. Subsequently applied equibiaxial compressive strain is conserved by an invariant annulus generated by in gel direct laser writing.³⁶ Immersing the object into water leads to swelling of the gel and consequently out-of-plane buckling of the bilayer disk into a dome shape with a characteristic wrinkling pattern along the azimuth. Driven by this (de-)swelling of the thermoresponsive hydrogel layer, we precisely control the deflection height of the dome by setting the temperature of the medium. The radial compression of the disk makes the flat state energetically unfavorable, therefore leading to a snap-through transition during curvature inversion. We study the deformation path of a heating/cooling cycle and the effect of heating and cooling rates on the actuation speed.

7.3 Results and Discussion

In our design approach we are capitalizing on our knowledge about swelling induced bending of bilayer hydrogel objects composed of thermoresponsive PNIPAm hydrogel sputtered with a layer of gold. The limited expandability of the coated surface induces bending e.g. around the length and width of a ribbon, respectively, leading to formation of a helix, 2D spiral or tube, respective of the cross section.³⁷ Furthermore, any change in temperature and therefore volume of the gel is translated into a change of curvature of the ribbon in response to balancing of stretching and bending energies from the interfacial stress. Due to the given preparation

conditions the gel shrinks below the dimensions as prepared when raising the temperature above the LCST of the polymer. Consequently, the curvature of the bilayer is reverted with the coated layer facing outwards.³⁸ A bilayer disk as employed in the bistable dome design (**Figure 1**) therefore also reverses curvature across the LCST, however without bending around a preferred axis due to its radial symmetry. When applying radial compression to such disk and subsequently fixing it in an annulus, the disk has to buckle out of plane forming a dome-like shape. Given that the passive layer is nearly inextensible and incompressible, this will furthermore enable buckling at temperatures above the LCST of the hydrogel, where the diameter of the gel disk is smaller than the opening of the annulus. The ability of the gel to be much larger or smaller than the passive layer consequently creates a preferred state of the dome with the gel facing inwards and outwards, respectively. A scheme and corresponding energy diagram of the two possible states of such dome is shown in **Figure 1**, where the deflection of the dome is plotted as a function of the free energy. We refer to a dome with the passive layer facing outwards as the regular state (solid line) with positive values for the deflection and to the gel layer facing outwards as the inverted state (dashed line) with negative deflection. Under any condition, i.e. temperature, there are two possible states of the dome which are represented by the two minima in free energy of the curve. Both of the two cases depicted represent a different state of the gel, i.e., in each case the depicted one is much more stable than its inverted version, corresponding to the much smaller minimum in free energy. As the ratio between the two minima depends on the swelling of the gel and thus temperature, a dynamic system is created. The same accounts for the energy barrier between the two possible states, as it is additionally a function of the dome's geometry and the larger the deflection of the dome, the higher the energy barrier for inversion.

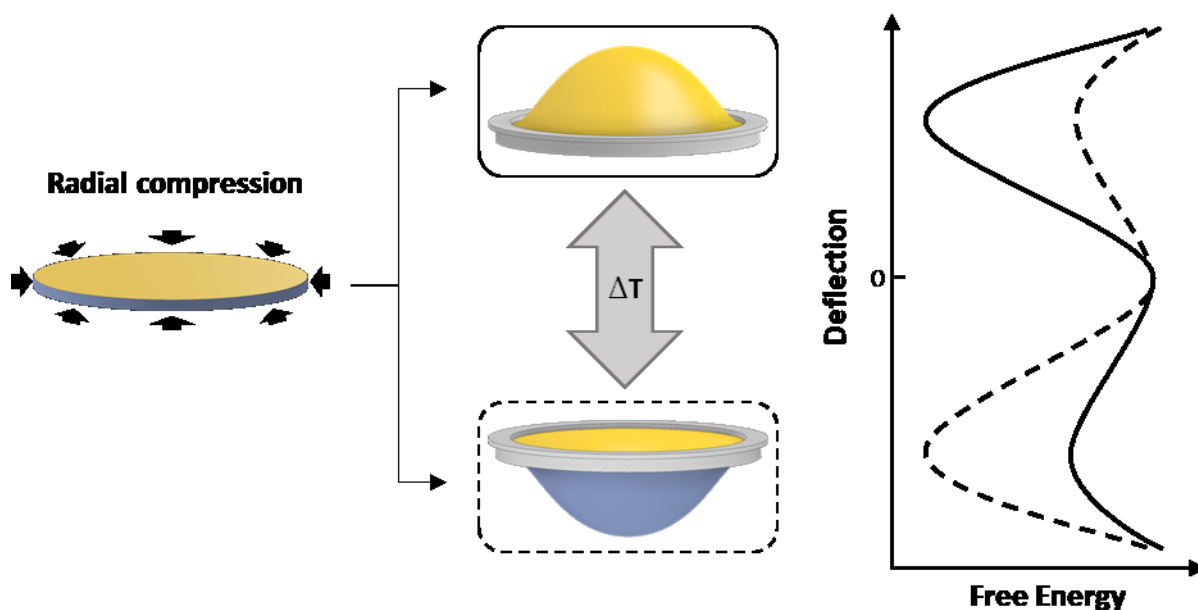


Figure 1: Scheme of our design principle for a bistable microgel dome. By radial compression of a bilayer disk consisting of polyacrylate (yellow) and thermoresponsive hydrogel (blue) and subsequent fixation it in an annulus, strain induced buckling of the disk leads to formation of a dome shape. Two possible states emerge with the passive layer facing outwards and inwards, respectively. Depending on the swelling state of the gel, and therefore temperature, one state is preferred over the other, represented by a minimum in free energy that is smaller than its counterpart. Thus, a dynamic system is created and the energy barrier between the two states enables a snap-through buckling transition. Eventually this leads to hysteretic bistability of the dome.

In order to produce the bistable microgel domes, we utilized a precise and well established soft lithography technique (PRINT³⁹) to produce microgel disks and by adding further steps generated a bilayer that is radially compressed and eventually equipped with an annulus to conserve the compressive force. A scheme of the procedure is illustrated in **Figure 2** and a detailed description can be found in the experimental section. Briefly, hydrogel microdisks with a radius of $R_i = 30 \mu\text{m}$ and thickness of $t = 2 \mu\text{m}$ were formed by gelation of a *N*-isopropylacrylamide (NIPAm) precursor solution in a fluorinated elastomer mold, previously replicated from a silicon master wafer. The mold containing the gel disks was then clamped onto a chuck, allowing to apply a uniform, planar expansion of 15%, increasing the radius of the disk to $34.5 \mu\text{m}$. In this stretched state, the sample was coated with a thin layer of gold by sputtering, generating a barrier to the acrylate applied in the following step. Therefore, an UV-curable acrylate monomer solution in DMSO was applied by pipetting, resulting in pinning of droplets to the surface of the hydrogel disks after removing excess liquid. Evaporation of the solvent lead to spreading of the liquid monomer on the disks surface and by UV-irradiation the

polymerization was initiated, eventually forming the passive layer. The strain was then released causing the mold to compress the bilayer disks. In order to conserve the compressive force, an annulus was added by in-gel direct laser writing.³⁶ The outer diameter and height of the annulus exceed the size of the mold, generating a 'step' that aids to identify the orientation of the dome during microscopy experiments as the larger diameter faces towards the passive layer (indicated by an arrow in the top right image of **Figure 2**). After completion, the objects were extracted by a sacrificial PVP adhesive and harvested into capillaries using ultrapure water. The square cross-section of the capillaries allowed microscopic investigation in top view and at a 90° angle in order to evaluate the height of the domes.

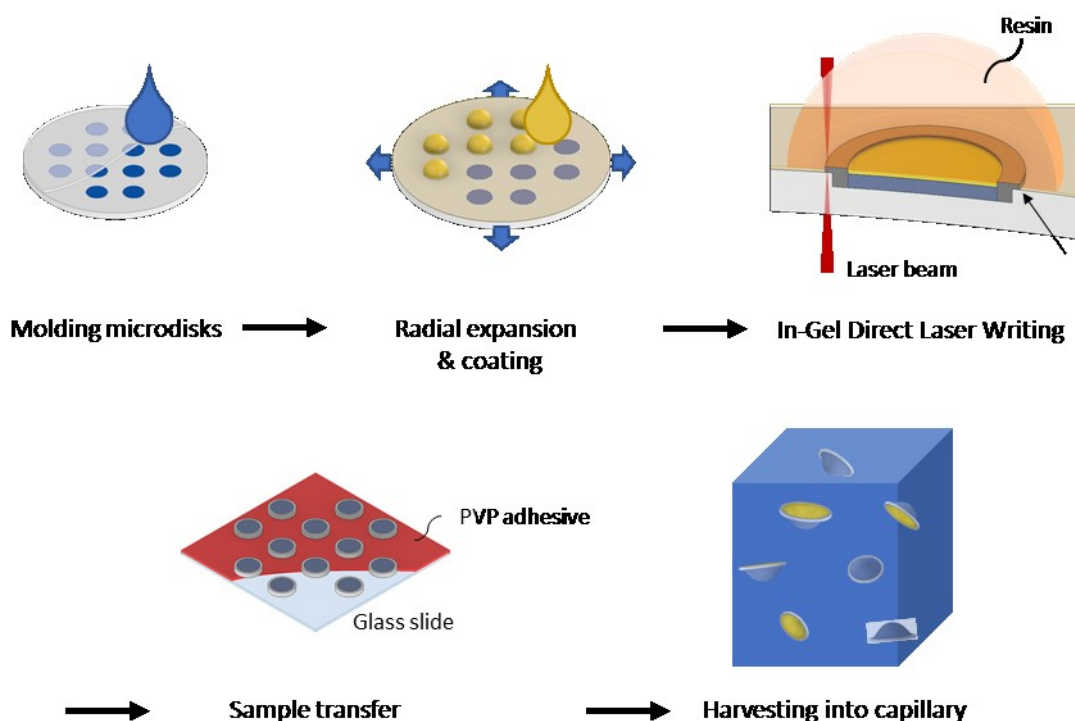


Figure 2: Scheme of the fabrication process of radially compressed bilayer microdisks with an inextensible annulus. After molding via PRINT³⁹ the hydrogel disks are radially expanded and subsequently coated with gold and reactive acrylate to form the passive layer. After release of the strain, the compression of the bilayer disk is conserved by in-gel direct laser writing³⁶ of an invariant annulus. The sample is then transferred using PVP adhesive and eventually collected into capillaries with a square cross-section.

Upon swelling in water at 20°C the hydrogel isotropically expands with a linear swelling factor of 1.7 compared to the collapsed state at 35°C. As the annulus restricts the lateral expansion, a radial compressive force is generated that transforms the bilayer disk into a dome shape by buckling (**Figure 3 A**). This dome has a base radius R_b given by the inner radius R_i of the

annulus of $R_b = R_i = 25 \mu\text{m}$ and a height of $h = 18 \mu\text{m}$. With an arc length of $63 \mu\text{m}$ the gel layer of the dome is expanded by a factor of 1.26 which is significantly less than the unconstrained gel. The passive layer is larger by a factor of 1.1 compared to as prepared dimensions and therefore extensible as well. Due to the preparation process the annulus has an outer diameter larger than the mold towards the side where the acrylate has been coated. Therefore, we observe two circular contrast lines in top view (**Figure 3 B**), the dark and larger one ($R = 32.5 \mu\text{m}$) along the outer perimeter of the annulus and the bright, smaller one ($R = 30 \mu\text{m}$) with an offset towards the center of the disk, both indicated by arrows. Furthermore, a regular pattern of wrinkles is formed along the azimuth. These wrinkles occur due to the geometric incompatibility of the expanded disk buckling into the envelope of a spherical cap. The resulting excess material from adapting to this shape increases from center towards the perimeter and wrinkles in order to partially release stress, as it is more prone to bending than being compressed. In addition, swelling induced wrinkling occurs along the perimeter as the gel is bound to the annulus.⁴⁰ As discussed previously in Chapter 6, the wrinkling pattern of such microgel domes indicates the stress of the clamped hydrogel layer and varies e.g. with its aspect ratio of the gel disk. At 20°C we observe distinct wrinkling patterns that we utilize to categorize the domes in two types that differ in wavelength λ and amplitude A of the wrinkles. In type I, shown in the upper row of **Figure 3B**, we typically count six or eight wrinkles. The wavelength of $\lambda = 26 \mu\text{m}$ and $\lambda = 20 \mu\text{m}$, respectively, is calculated by dividing the inner perimeter length of the annulus by the number of wrinkles. The amplitude is typically $A = 15 \mu\text{m}$, however, in case of the left image the amplitude of two opposing wrinkles is much higher. The effected bilateral symmetry of the dome indicates inhomogeneity in the stress distribution of the compressed disk. In contrast, the dome on the right image shows radial symmetry in its wrinkling pattern, reminiscent of the outline of a four-leaf clover. Wrinkles with an amplitude much smaller than $15 \mu\text{m}$ that occur close to the rim and pairwise between single wrinkles with $A = 15 \mu\text{m}$. In type II (bottom row of **Figure 3 B**), the wrinkling pattern is radially symmetric and although the wrinkling number of $n = 7$ barely differs from the previous type, it is accompanied by a much smaller amplitude of $A = 9 \mu\text{m}$. The wrinkles furthermore only occur in close proximity to the rim and occasionally defects interrupt the radial symmetry (left image). Upon first contact with water only domes with wrinkling pattern type I were observed (Appendix, **Figure A1**). Since the sample is transferred in such orientation that the gel will make contact with water first, the deflection of the dome is therefore biased with the gel facing outwards. However, after transfer of the sample into a capillary all patterns presented in **Figure 3 B** were observed. We hypothesize that these wrinkling patterns are typical for the two possible states that the dome can form as described in **Figure 1**, i.e., with the gel facing outwards (wrinkling type I) and inwards (wrinkling type II), respectively. This hypothesis will

be confirmed in the section where we discuss the response of the dome to fast heating by NIR-Laser light pulses. Furthermore, we conclude that at ambient temperature there is no preference in the buckling orientation of the bilayer. This is in contrast to the bending behavior that we have usually observe in hydrogel/gold bilayer structures where the gel always faces outwards at $T < \text{LCST}$.

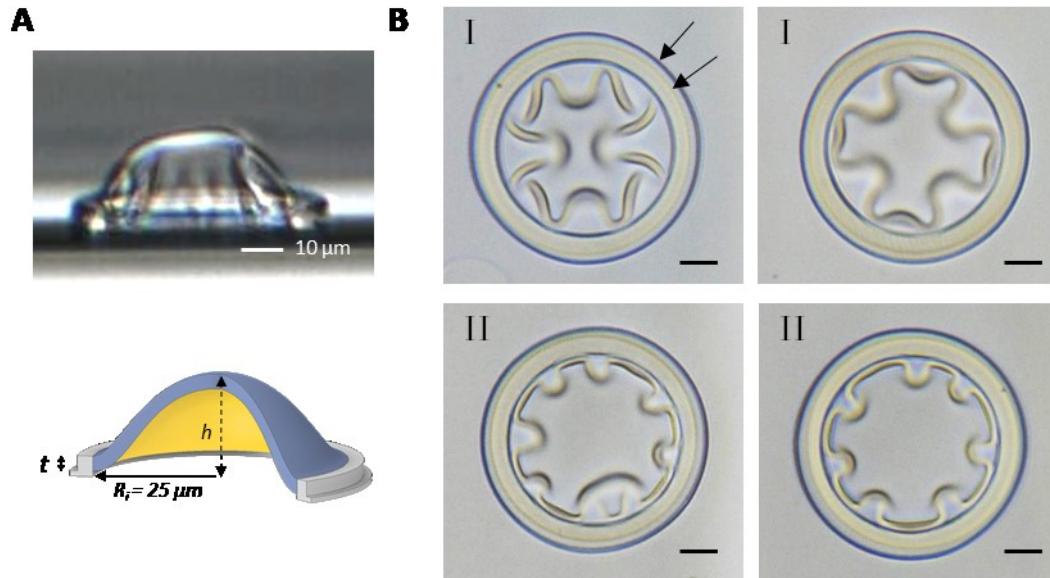


Figure 3: Microscopy images and cutaway drawing of a compressed bilayer disk that has morphed into a dome-like shape. **(A)** Bright field microscopy image of such dome in side observation. Cutaway drawing of the hydrogel/passive (blue/yellow) bilayer dome with an initial disk thickness t , annulus opening radius R_i and height h . **(B)** Top view microscopy images of the typical wrinkling patterns: Type I for domes with the hydrogel facing outwards and type II for domes with the passive layer facing outwards.

In the following, we will analyze the behavior of the compressed bilayer disk in response to cycling the bath temperature between 20°C and 45°C at a rate of 5°C min⁻¹. Therefore, the sample is observed in side view in order to determine the height of the dome as a function of the bath temperature (**Figure 4 A**). At the starting point of 20°C (top left image) the deflection height is $h = 18 \mu\text{m}$ and continuously decreases with increasing temperature with a moderate slope. When approaching 30°C the volume phase transition of the gel causes a steep decline in height until the dome is almost flat at 32°C ($h = 2 \mu\text{m}$). Beyond this point, the deflection height is no longer large enough to be measurable with good accuracy. Assuming the passive layer is invariant, a compression rate of 15% as employed in our experiment, and that the dome forms a radial arch, a deflection height of $h = 12 \mu\text{m}$ should be sustained throughout the collapsed state of the gel. However, as we have described in the previous section, the passive

layer is actually expandable and therefore allows deflections as low as we observe it above the LCST of the gel. Furthermore, the step on the edge of the annulus faces with the wider side upwards (indicated by arrow). Therefore, the dome initially has been in a state with the passive layer facing outwards, i.e., in the reversed state. This is in contrast to our usual observation of unconstrained bilayers where the gel bends towards the passive layer at temperatures below the LCST, as its surface area is larger than the passive layer. The height of the dome upon inversion during heating is not measurable, however an inversion is clearly visible in the angled perspective on the dome. Because the dome is very shallow above the LCST, the energy barrier consequently is low and allows only small amounts of elastic energy to be stored and thus released, i.e., the corresponding snap is hardly noticeable. Upon cooling, the dome gradually begins to deflect in the opposite direction with the gel facing outwards, therefore tilting on the glass substrate. The deflection reaches a minimum of less than $-20\text{ }\mu\text{m}$, which is a higher value than in the reversed state. We assign this to the ability of the gel to expand more freely. After reaching the minimum at 24°C the dome starts to partially invert, causing an increase in h until the partial inversion follows an S-shaped curve perpendicular to the plane of the annulus. The dome eventually recovers its original state and height of $18\text{ }\mu\text{m}$ in a rapid motion within a few milliseconds. This behavior of a partial inversion before a complete snap-through is typical for deep arches e.g. formed by compressed elastic beams that show a snapping inversion.¹⁶ With regard to the unusual behavior of hydrogen/gold bilayer objects bending with the gel facing inwards at low temperatures, we hypothesize that the reason for the here observed behavior is the way in which the bilayer is bound to the annulus. This is schematically drawn as a cross section close to the annulus in **Figure 4B**. The bilayer is prepared in a 'neutral position', i.e., parallel to the opening of the annulus. When moderately swollen at 30°C , the surface of the gel is larger than the passive layer, causing buckling of the bilayer with the gel towards the larger curvature. When further lowering the temperature to 25°C the swelling degree of the gel increases. This results in a higher deflection of the dome and therefore a higher curvature of the bilayer in proximity to the annulus' wall. However, as the hydrogel expands isotropically, the force perpendicular to the passive layer is increased as well (indicated by orange arrow). This induces bending of the passive layer towards the opposing side to minimize curvature, which is energetically more favorable due to the higher stiffness of the passive layer compared to the gel (scheme on the far right). Eventually this mechanism then leads to the snap-through inversion of the dome.

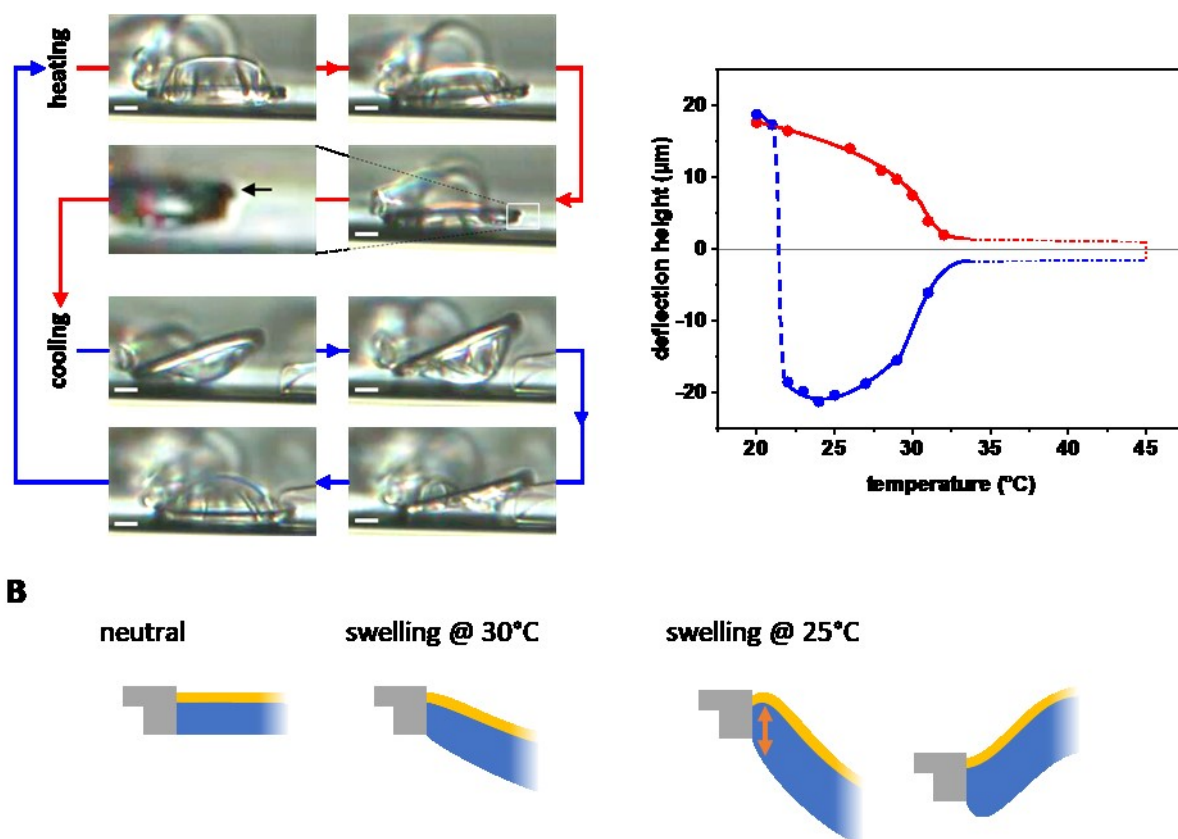


Figure 4: (A) Left: Image series of a dome in side observation during a temperature cycle between 20°C and 45°C at a heating and cooling rate of 5°C min⁻¹. Scale bar: 10 μm . Right: The corresponding plot of the deflection height of the dome vs. the temperature during one cycle. (B) Scheme of the cross-section of the bilayer bound to the annulus as prepared (neutral) and for different temperatures, i.e., swelling degrees.

In order to investigate the effect of fast heating and cooling rates on the snapping behavior the sample was locally heated by near-infrared Laser irradiation (wavelength: 808 nm, 10W) at a pulse width of two seconds, which is sufficiently long to fully collapse the gel. This method enables heating rates of >10°C s⁻¹ assuming an increase in the gel temperature from 10°C to 35°C within 2s. As the sample is heated locally while supported by an aluminium block the heat dissipates quickly when ceasing the irradiation, resulting in equally fast cooling rates. Videos of the same sample and object were recorded at a rate of 1000 frames per second in top view and at a 90° angle. A selection of the corresponding image series for one full heating and cooling cycle is shown in **Figure 5 A**. Upon irradiation the deflection of the dome decreases and it lifts up from the substrate. As this is similar to the behavior we have observed previously in 'monolayer' hydrogel domes (Chapter 6), we assign this motion to a fluid flow towards the substrate. Furthermore, the wrinkling pattern disappears when the gel is collapsed and a deflection is no longer noticeable. After the irradiation is ceased, the gel re-swells and a regular dome state is formed. Similar to the previous experiment (**Fig. 4**) a partial inversion of

the dome occurs after the dome has reached its maximum deflection in the regular state. Subsequently, the dome snaps into its initial state within three milliseconds. Furthermore, we observe a difference in the time delay between ceasing of the irradiation and the snap for the two observation angles. As the two videos were recorded in separate experiments, this demonstrates how the built-up stress can be released in small portions before the actual snap, e.g. by a different way the wrinkles deflect, and hence influences the deformation pathway. Typical examples that we found of how the swelling induced stress is released by the formation of wrinkling patterns before the snapping transition occurs are shown in **Figure 5B**. In the first case (left image series) one wrinkle extends further towards the center than the others, creating a groove along the diameter of the gel disk. In the second example (right image series) the typical clover-like wrinkling pattern initially forms and then starts to be distorted rotationally around the center of the dome. Additionally to these variations that affect the delay upon the snap-through transition, we investigated the influence of the cooling rate on the snap-through time. Therefore, we stepwise adjust a bath temperature between 10°C and 25°C while keeping the irradiation pulse constant in an intensity and duration that is sufficient to completely collapse the gel. The resulting graph is shown in **Figure 5C**, where we plot the snap-through time as a function of the bath temperature. At 10°C the fastest snap of 2 ms occurs and increases to 4 ms at a bath temperature of 20°C. Above the latter, the time increases rapidly to 18 ms at 24°C. For any higher temperature the dome remains in its regular state, i.e., the dome is stabilized in its state which is in line with the previous experiment (**Figure 4**). We concludes that the higher the cooling rate, the more the partial release of stress is suppressed, ultimately enhancing the speed of the snap-through.

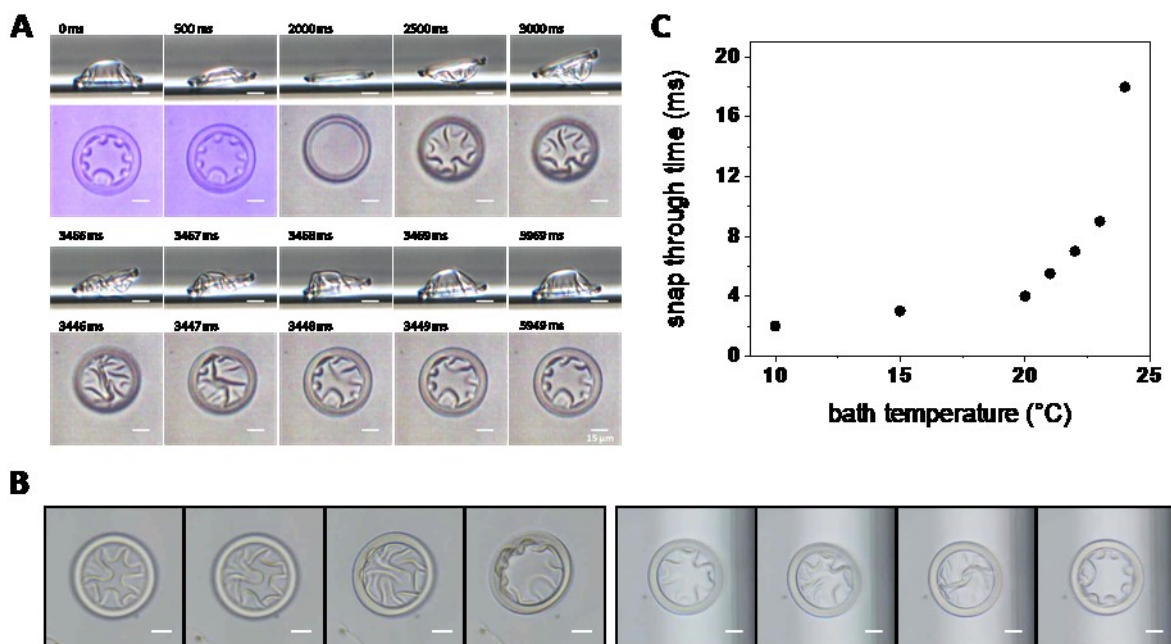


Figure 5: Photothermal heating of a bilayer dome by NIR laser irradiation. Scale bars: 15 μm . (A) Image series of a dome in top view and at a 90° angle during irradiation (pulse width 2 s) and subsequent cooling. (B) Image series of domes that show different wrinkling patterns during the cooling phase. (C) Snap-through time as a function of the bath temperature at a constant irradiation intensity and duration.

7.4 Conclusion

In this study, we presented a design principle for a light-switchable, bistable microgel dome, how it can be realized with advanced lithographic methods and characterized its properties by microscopy analysis. This design features a bilayer with an active/passive functionality given by a thermoresponsive PNIPAm hydrogel disk that is coated with a polyacrylate layer. Furthermore, this bilayer is radially compressed and fixed in an inextensible annulus. Buckling of the bilayer into a dome shape is accompanied by two possible states with the gel facing inwards and outwards, respectively. The annulus creates an energy barrier separating these two states, setting the foundation for a bistable system. Upon swelling in water, domes with two types of wrinkling patterns were observed and identified to be characteristic for the dome's state. Type I is a clover like pattern with six to eight wrinkles of different amplitude and wavelength that occurs when the hydrogel faces outwards. Type II, the inverted dome, has seven wrinkles that are similar in wavelength and amplitude with the latter being much smaller than in type I. When heating and cooling the sample at a constant rate of 5°C min⁻¹ we found a bistability hysteresis with the maximum of deflection being slightly higher when the gel faces outwards. Upon heating, the curvature of the dome inverts with a snapping transition when the

deflection is very shallow, whereas during cooling a rapid snapping motion with a large amplitude is observed. Analysis of the dome at low temperatures from the side revealed that the gel layer faces inwards. We hypothesize that the stabilization of the dome in this state is due to the binding of the passive layer close to the annulus. Furthermore, we have realized fast heating and cooling rates by NIR laser irradiation and shown how the wrinkles influence the delay between ceasing the irradiation and the snap-through by providing a way to alleviate stress during the snap-trough transition. By controlling the bath temperature, we investigated the influence of the cooling rate on the snap-through time, which was 18 ms at a bath temperature of 25°C and quickly declined to a minimum of 2 ms at 10°C. The switchable bistability of this micro-object has potential to enable autonomous microswimmers when coupled with a feedback mechanism and eventually may create self-oscillation.

7.5 Experimental Section

Materials

All listed chemicals were used as received, unless stated otherwise:

Acetone (Sigma-Aldrich), Dimethyl sulfoxide (DMSO, VWR), 1-Methoxy-2-propanyl acetate (PGMEA, Sigma-Aldrich), Isopropanol (IPA, Sigma-Aldrich), N-Isopropylacrylamide (NIPAm, 97%, Sigma-Aldrich, recrystallized in hexane), N,N'-Methylenbisacrylamide (BIS, 99%, Sigma-Aldrich), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (98%, Sigma-Aldrich), Bifunctional perfluoropolyether urethane (PFPE, Mw = 4000, Fomblin® MD 40, Solvay Solexis), 2-Hydroxy-2-methylpropiophenone (97%, Sigma-Aldrich), IPL-780 (Nanoscribe GmbH), Tetraethylene glycol dimethacrylate (90%, Sigma-Aldrich), Pentaerythritol triacrylate (Sigma-Aldrich), Polyvinylpyrrolidone (PVP, 40 kDa, Sigma-Aldrich).

Experimental Procedures

Preparation of hydrogel microdisks

Microdisks made of PNIPAm hydrogel were prepared via the particle replication in non-wetting templates (PRINT⁴¹) method under nitrogen atmosphere ($O_2 < 0.5\%$). The mold was casted from a silicon master wafer (AMO GmbH) containing a regular pattern of pillars with a height of 2 μm and diameter of 60 μm . For the replica, PFPE MD40 was mixed with 1 wt% 2-Hydroxy-2-methylpropiophenone as photoinitiator, thoroughly mixed and bubbled with nitrogen for 30 min before use. 60 μL of this solution were applied onto the silicon master wafer and carefully covered with a cover glass, resulting in a circular shape of the liquid between the two surfaces. By using two square capillaries with an outer width of 200 μm (VitroTubes, VitroCom) as spacers, an equivalent film thickness was achieved. Subsequently, the sample was irradiated with UV light (370 nm, 2 W, 10 min) to cure the solution. After separation, the mold was washed in acetone to remove any unreacted residuals. A featureless film was prepared by stacking two cover glass slides using four layers of Parafilm (Bemis) as spacers, filling the interspace with the UV-curable PFPE MD40 solution and illuminating it for 10 min (370 nm, 2 W). This film was cut into (6 x 6) mm square pieces that were washed in acetone before use.

For the hydrogel a prepolymer solution was prepared, containing 1000 mg (1 eq) of NIPAm, 13.6 mg (0.01 eq) of BIS as crosslinker and 19.8 mg (0.01 eq) of 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone as photoinitiator mixed in 1382 μL DMSO. Oxygen

was removed by bubbling with nitrogen for 30 min. The circular elastomer mold was placed onto the lower part of a homemade press and a square piece of the featureless film was placed onto the quartz glass window of the upper part. A 0.5 μL droplet of the prepolymer solution was placed onto the mold and covered with the flat film, ensuring complete filling of the mold and drainage of excess liquid. The sample was irradiated with UV light (366 & 254 nm, 4 W at each wavelength, Konrad Benda) for 20 min. Afterwards the featureless film was removed and the sample was transferred for further processing.

Applying radial strain and coating

In order to radially strain the gel disks in the mold, the latter was first clamped onto a sprocket chuck (**Figure S1 A**). The setup was then placed in the center of the microscope stage and 20 μL DMSO were applied. In this way the gel is plasticized which allows it to expand while opening the sprocket by turning the scroll ring. The desired expansion was applied and verified by measuring the diameter of the disks in the mold with a digital microscope (VW 1000, Keyence). After removing the DMSO, the setup was transferred into the chamber of a sputter coater (Edwards S150B) and coated under argon atmosphere for three seconds. It was then transferred into a glovebox to apply the acrylate coating. Therefore, 500 mg TTEGDA, 500 mg PETA and 10 mg photoinitiator 2-Hydroxy-2-methylpropiophenone were dissolved in DMSO and bubbled for 30 min to remove oxygen. 20 μL of this solution were applied onto the sample, covering the central area of the mold where the strain is equally distributed. After achieving full coverage of the desired area, the liquid was immediately removed again by aspirating with a pipette, leading to selective pinning of droplets on the gel's surface (**Figure S1 B**). After evaporation of DMSO for 5 min, the remaining thin layer of the prepolymer mixture was cured by UV-light irradiation for 5 min (370 nm, 2 W). DMSO was then applied again to plasticize the gel and the strain was released by closing the sprocket and unclamping the mold.

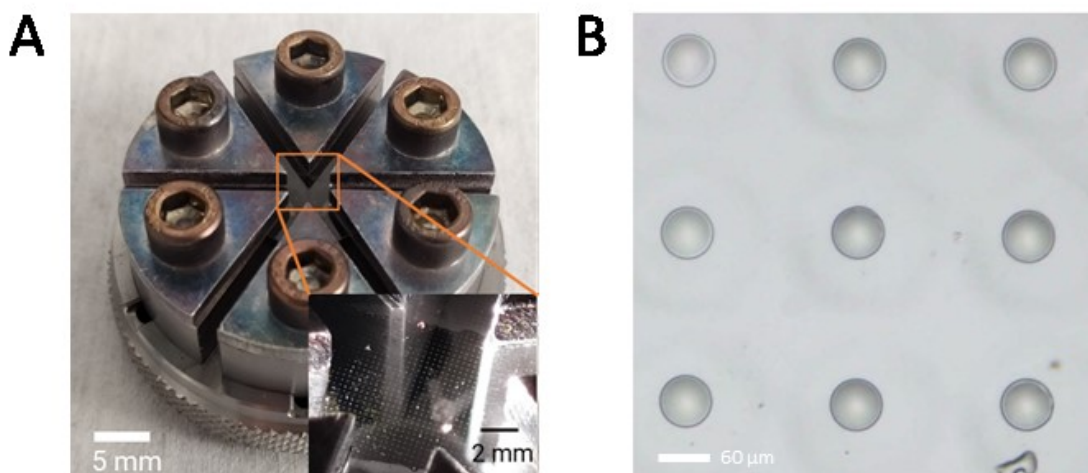


Figure S1: (A) Manual stretching device for radial expansion of the PNIPAm hydrogel microdisks. A circular elastomer mold is fixed onto the clamping segments of the sprocket chuck by six plates that are tightened with screws. Turning the scroll ring opens the chuck, thus stretching the film and expanding the diameter of the gels. The inset shows a close up of the mold where microdisks are visible as small bright spots. (B) Droplets of the acrylate prepolymer solution selectively pinned on the hydrogel disks in their PFPE mold.

Annulus preparation

In order to conserve the compressive force that the mold exerts on the bilayer disk, an inextensible annulus was added to the structure by in-gel direct laser writing.³⁶ Therefore, the photoresin IPL-780 (Nanoscribe) was evenly spread on the sample and left to diffuse into the gel for 15 min. The sample was then transferred to a multiphoton lithography setup (Photonic Professional GT, Nanoscribe GmbH) with an oil immersion 63x objective (numerical aperture (NA), 1.4; Zeiss, Germany) and a femtosecond laser (emission wavelength 780 nm; pulse width 120 fs; repetition rate 100 MHz). The annulus was designed using computer aided design software (Inventor, Autodesk) and the exported .stl-file was sliced into a printable format using DeScribe (Nanoscribe, Germany) with a slicing and hatching distance of 0.3 μm and 0.2 μm, respectively. Furthermore, the outer dimensions of the annulus were designed to overlap with the edges of the mold. After manual alignment of the laser with the disk, the annulus was printed at a laser power of 80-90% and writing speed of 20 mm/s. Afterwards, the sample was immersed in 1-Methoxy-2-propylacetate (PGMEA) for 10 min, followed by Isopropanol for 3 min to remove unreacted resin.

Harvesting and sample transfer into capillaries

To harvest the sample, a (25 x 25) mm glass slide was plasma treated (200 W, 40 mL/min, 10 min, PVP Tepla 100) and a droplet of a solution from Polyvinylpyrrolidone (PVP, 40 kDa, 2.5 g) dissolved in an ethanol/water mixture (volume ratio 7/63, 3.15 mL) was added. After placing the mold upside down into the PVP glue and carefully applying pressure, the sample was left to dry overnight. The PFPE mold was then peeled from the PVP glue and a 25 μ L droplet of ultrapure water was added to release the objects. Capillaries with a 300 μ m square cross-section (VitroTubes, VitroCom) were plasma treated (O_2 , 1.6 mbar, 200 Watt, 2 min), immersed in the droplet with one end to take up the dispersed objects and subsequently sealed on both ends with two component epoxy glue (UHU Plus Sofortfest).

Characterization Methods

Bright-field Microscopy. The samples were evaluated using a digital microscope (VW1000, Keyence). This setup also allowed an observation at a 90 degree angle. Therefore, the light source was mounted in a transmission configuration. Videos with a framerate of up to 1000 fps were recorded using a high speed digital camera (VW 9000, Keyence) and analyzed using the complementary software (MotionAnalyzer, Keyence).

Temperature control. The temperature of the samples was regulated using a Peliter element mounted on the microscope stage and controlled by a microcontroller. This setup allowed to perform heating and cooling ramps, respectively, at steady rates of e.g. 5°C/min. In order to locally apply heating rates of >60°C/min, pulses of near-infrared light LASER irradiation (808 nm, 10 W, Roithner Lasertechnik) were applied. Here, the large heat capacity of the aluminium block of the Peltier element ensured rapid cooling of the sample whenever ceasing the LASER irradiation.

7.6 References

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7.7 Appendix

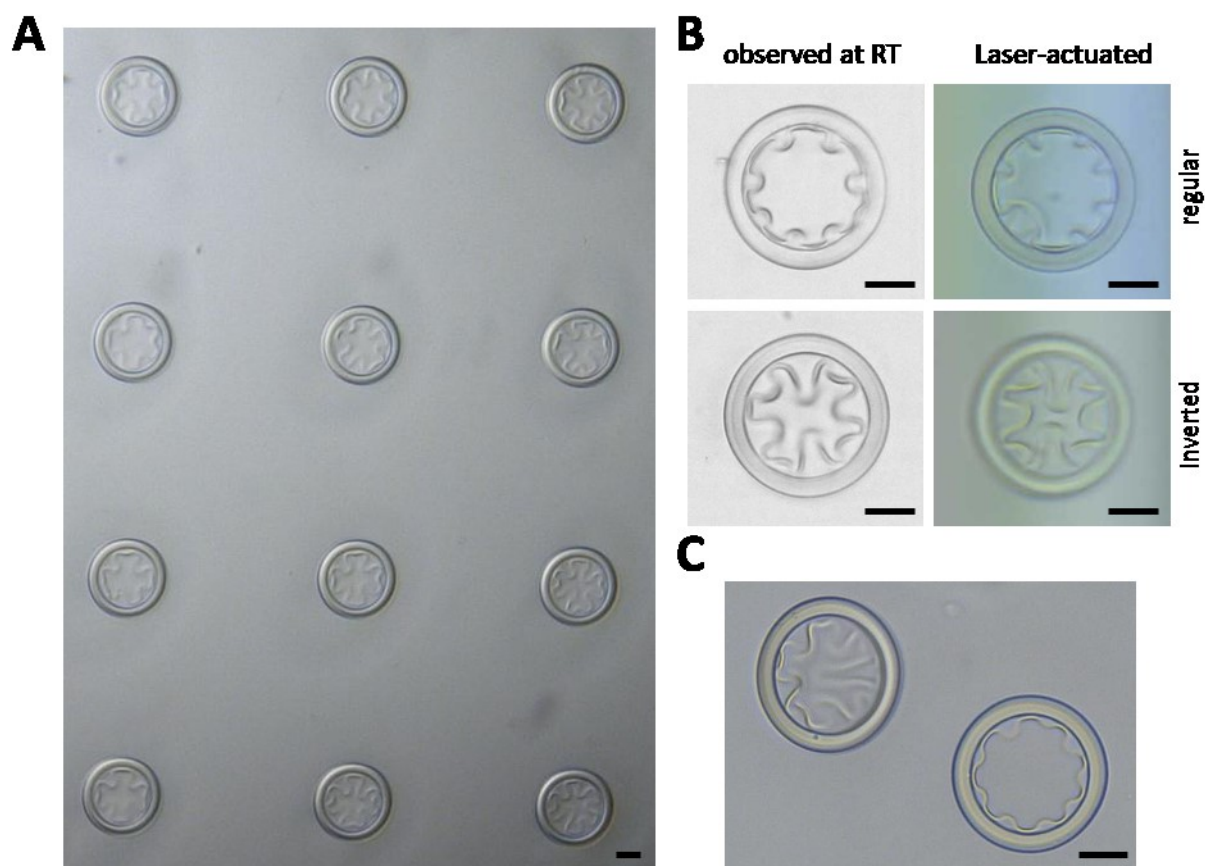


Figure A1: Micrographs of bilayer domes. Scale bars: 20 μm . **(A)** A fresh sample upon first contact with water. All domes are facing in the same direction with their hydrogel layer and show a similar wrinkling pattern. **(B)** The two typical wrinkling patterns as observed after transfer into a capillary at room temperature (left column) and the wrinkling patterns observed during photothermal heating (right column), with states regular (passive layer outwards) and inverted (gel layer outwards) assigned. **(C)** Coexistence of the two states of the bilayer dome at room temperature in one sample.

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