ISMC2019

Oral abstracts

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PLENARY TALKS

Flow and rheology at ultimate scales

BOCQUET, Lydéric, CNRS, ENS, Paris

Plenary

Soft matter is a field of scales: from the macroscales of collective response, down to the microscales of molecular motion, via intermediate mesoscopic structures. Probing material properties at ever smaller scales is thus expected to give much insights into the elementary building blocks of soft matter.

In this talk I will highlight our recent efforts to probe transport and rheology at the smallest scales. In a first part, I will explore transport oddities across individual channels with nanometric and even sub-nanometric dimensions. These experiments illustrate in particular how quantum effects may enter the game of fluid dynamics at the smallest scales. In a second part, I will discuss the rheological response of metallic nanojunctions of a few atoms in size. Their mechanical response demonstrates unexpected similarities with soft yielding materials, in spite of orders of magnitude of difference in length scale.

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Why soft solids fail’

CIPELLETTI, Luca, Montpellier

Plenary

Luca Cipelletti, University of Montpellier

Why soft solids fail

Material failure is ubiquitous on length scales ranging from a few nanometers, as in fracture of atomic or molecular systems, up to geological scales, as in earthquakes. The detection of any precursors that may point to incipient failure is the Holy Grail in many disciplines, from material science to engineering and geology. I will discuss a series of experiments probing simultaneously the microscopic dynamics and the macroscopic response of soft solids under a mechanical load. We focus on loading conditions such that the material suddenly fails after a long induction time, with little if any changes at the macroscopic level. While little changes are seen in the microscopic structure, we unveil dynamic precursors signaling plastic rearrangements well before macroscopic failure. Remarkably, dynamic precursors of failure are seen in a variety of colloidal and polymeric systems, and under various loading protocols. These experiments suggest that dynamic precursors have a great potentiality as a tool to predict and understand material failure.

Macromolecular Mechanochemistry

CRAIG, Stephen L, Duke

Plenary

In recent years, covalent polymer mechanochemistry has undergone something of a renaissance in which it has been extensively explored for a variety of purposes including (but not limited to) biasing reaction pathways, trapping transition states and intermediates, catalysis, release of small molecules and protons, stress reporting and stress strengthening materials, and soft devices. The extent to which such responses might be useful in bulk materials involves physics on two different length scales: the coupling of force to chemical reactions within an individual polymer strand, and the number of polymer strands within a network that experience various magnitudes of force. This talk will describe quantitative studies on both of these length scales, including the ability of studies on one to inform the other.

Building synthetic cells

DOGTEROM, Marileen, TU Delft

Plenary

Tough topological polymers and their applications to energy-efficient vehicles and medicine

ITO, Kohzo, Tokyo

Plenary

We have recently developed a novel type of polymer network called slidering materials by cross-linking polyrotaxane, the supramolecular architecture with topological characteristics.1) In the network, polymer chains are topologically interlocked by figure-of-eight cross-links. Hence, these cross-links can pass along the polymer chains freely to equalize the tension of the threading polymer chains similarly to pulleys. The slide-ring gel or elastomer shows quite small Young's modulus, which is not proportional to the cross-linking density and much lower than those of chemical gels with the same density. This arises from the difference in the molecular mechanism of the entropic elasticity: While the conformational entropy is mainly responsible for the elasticity in usual chemical gels or rubbers, the mechanical properties of the slide-ring gel should be inherently governed by the alignment entropy of free cyclic molecules in polyrotaxane as well as the conformational entropy of backbone polymer. This means that the softness in the slide-ring gel is due to the novel entropic elasticity, which is also expected to yield sliding state and sliding transition. Consequently, the slide-ring materials have the dynamic coupling between two kinds of entropy: the conformational entropy of strings and alignment entropy of rings. 2,3) The concept of the slide-ring gel is not limited to cross-linked gels but also includes elastomer, cross-linked polymeric materials without solvent. Accordingly it can be applied to wide area such as soft contact lens, paints, rubbers, soft actuator and so on. As a typical example, the scratch-resist properties of the selfrestoring slide-ring elastomer were adopted into the top coating on the mobile phone.4) Finally, I would like to introduce ImPACT (Impulsing Paradigm Change through Disruptive Technologies) program, which is promoting to create flexible and tough polymers by using the slide-ring materials as a key technology.

In addition, we have recently developed mass-producing, low-cost, and free-standing nanosheets using

topological self-assembly of cyclodextrins (CDs) and amphiphilic block copolymer, namely, pseudo-polyrotaxane (PPR) nanosheet by hierarchically ordered supramolecular self-assembly as shown Fig. 2.5) The PPR nanosheets were obtained by just mixing triblock copolymer andβ-CD in water. β-CDs threaded on poly(propylene glycol) segment of the triblock copolymer to form a monoclinic single crystal with a dimension of 10-20 nm thickness and a few micro meters size. The PPR nanosheet can be applied to a novel drag delivery system with cell adhesiveness.

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Biofilms: What’s in it for Soft Matter?'

MACPHEE, Cait, Edinburgh

Plenary

A Cabinet of Curiosities: Stories of Electrostatics in Soft Matter’

PERKIN, Susan, Oxford

Plenary

A Cabinet of Curiosities: Stories of Electrostatics in Soft Matter

Susan Perkin

Physical & Theoretical Chemistry Laboratory, University of Oxford, UK.

After the golden period of colloid science in the mid 20th Century, it appeared that most of what was useful to know about electrostatic interactions in (what we now call) soft matter had been found. Yet reality is more interesting: decades later, we find ourselves frequently surprised when Coulombic ‘curiosities’ emerge from experiments and theoretical work. These are in some cases quite dramatic and prompt a re-examination of assumptions, and in other cases are very subtle and hint at delicate ways to tune interactions. In this lecture I will describe and explore several of these interesting observations, including the attractive interaction between charge-patterned surfaces, oscillating charge density in electrical double layers, and anomalously long electrostatic screening lengths observed at high concentration.

Fast, Elastic, Defective, Active Matter'

RAMASWAMY, Sriram, IIS, Bengaluru

Plenary

Orientationally ordered states of active systems apparently contain the seeds of their own destruction -- an irresistible zero-Reynolds-number instability in bulk suspension, and the inexorable unbinding of topological defects in adsorbed layers. I will summarise our recent results on (i) fluid flocks stabilised by inertia; (ii) superdiffusion and flow-induced condensation in aligned suspensions; (iii) a noise-induced threshold for defect unbinding in active nematics. Venturing beyond orientational order, I will also show that smectic elasticity and defects govern the trapping phase transition of motile rods. Time permitting I may discuss results on actively forced crystals.

Pixelated Polymers: Programming Function into Liquid Crystalline Polymer Networks and Elastomers

WHITE, Tim, Colorado

Lectureship Award Plenary

Liquid crystalline materials are pervasive, enabling devices in our homes, purses, and pockets. It has been long-known that liquid crystalline materials in polymeric forms also exhibit exceptional characteristics in high performance applications such as transparent armor or bulletproof vests. This talk will generally focus on a specific class of liquid crystalline polymeric materials referred to as liquid crystalline elastomers. These materials were predicted by de Gennes to have exceptional promise as artificial muscles, owing to the unique assimilation of anisotropy and elasticity. Subsequent experimental studies have confirmed the salient features of these materials, with respect to other forms of stimuli-responsive soft matter, are actuation cycles of up to 400% as well "soft elasticity" (stretch at minimal stress).

This lecture will survey our efforts in directing the self-assembly of these materials to realize distinctive functional behavior. Most notably, enabled by the chemistries and processing methods developed in my laboratories, we have prepared liquid crystal elastomers with distinctive actuation and mechanical properties realizing nearly 20 J/kg work capacities in homogenous material compositions. Local control of orientation dictates nonuniformity in the elastic properties, which we recently have shown could be a powerful means of ruggedizing flexible electronic devices. Reflective films, prepared with the cholesteric phase, will be presented capable of concurrent shape and color change (thermochromism).

KEYNOTE TALKS

Spontaneous and driven active matter flows

CLÉMENT, Eric, ESPCI, Paris

Active Soft Matter

Spontaneous and driven active matter flows

Eric Clément, PMMH-ESPCI-Sorbonne University

Understanding the individual and the macroscopic transport properties of motile micro-organisms in various complex environments, is a timely question, relevant to many ecological, medical and technological applications. At the fundamental level, this question is also receiving a lot of attention as fluids loaded with swimming micro-organisms has become a rich domain of applications for the statistical physics of “active matter”. The existence of microscopic sources of energy borne in the motile character of micro-swimmers is driving self-organization processes at the origin of numerous original effects, new emergent phases and unconventional macroscopic properties which led to revisit standard concepts in the physics of suspensions like Brownian motion, hydrodynamics dispersion or rheological response. In this presentation, I will report on a recent full exploration of the rheological response of active suspensions and also present new experiments showing how the motility of bacteria can be controlled such as to extract work macroscopically.

Flow-Induced Crystallization of Engineering Thermoplastics

COLBY, Ralph, Penn State

Polymeric Soft Matter

Brief intervals of shear flow at rates exceeding the reciprocal of the Rouse time of the longest chains create precursors that nucleate orders of magnitude more crystals and change the morphology from ~30 μm spherulites to far smaller ~1 μm crystallites. This flow-induced crystallization (FIC) at low shear rates builds with shearing time and eventually saturates. In contrast, at much higher stress levels that might occur in processing flows, a second morphology transition to shish-kebabs is observed when a critical shear stress (~0.14 MPa for iPP) is exceeded. The shish-kebab transition is evident in subsequent oscillatory shear as a weak gel and as a sudden jump in the pressure needed to push the material through the die in capillary rheometry. Flow-induced crystallization is studied in detail for isotactic polypropylenes1-3 and poly(ether ether ketone)s4 representing flexible and semi-rigid polymers, and for Polyamide 6,6 representing a flexible polymer with strong hydrogen bonding, 5,6 to see which aspects of

FIC are universal to all polymers and which aspects are polymerspecific. The fact that the precursors are quite stable allows the sheared samples to be removed from the rheometer and studied extensively with DSC and optical microscopy, while annealing at elevated temperatures allows the study of precursor stability.

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Cavitation and Puncture: Crack Nucleation in Soft Solids

CROSBY, Al, Massachusetts Amherst

Stressed Soft Matter

Failure, or fracture, remains one of the most important, yet most challenging, topics in materials science. This challenge is especially true for soft materials, such as swollen polymer networks and biological tissues. Understanding failure in these systems is critical for developing important technologies, from robust prosthetic materials to protective gear for mitigating debilitating injuries; however, their ultra-soft nature makes quantifying failure processes difficult. Failure in soft materials can be divided into two steps: 1) crack nucleation, and 2) crack propagation. Crack nucleation, typically important for systems devoid of defects above a critical size scale, involves the mechanism of forming a void within a material. For soft materials, crack nucleation is largely associated with the onset of an instability, called cavitation. Crack propagation involves the growth of a defect, or void, and the associated energy balance of creating new surfaces within a material. Traditionally, this process is understood through the classical continuum framework of the critical strain energy release rate or critical stress intensity factor, introduced by Griffith and Irwin, respectively. While quantifying and understanding crack propagation has received significant attention due to well-established methods and precedence from hard materials science, nucleation-related mechanisms, which may be more critically important for soft materials, remain largely unexplored. Here, we present an overview, along with new, unpublished results, related to our studies of cavitation and crack nucleation in soft materials. We focus on deformations associated with needle-induced cavitation and blunt needle puncture, which provide new insight into how failure-inducing nucleating events occur in soft materials. We explore these mechanisms across a range of model swollen polymer networks, leading to the introduction of new relationships between molecular network architecture and continuum responses. The results and discussion presented here are important for enhancing our fundamental understanding of soft materials and for introducing new methods for quantifying mechanical properties of soft materials across a range of size scales.

Growing and shrinking bubbles, enhanced Ostwald ripening via mass transport in nanometer thick films

DAGASTINE, Ray, Melbourne

Interfacial Soft Matter

The individual building blocks of soft matter respond to their surrounds in a far more complicated manner than any rigid system. This allows for more flexibility in formulation and processing, but provides more challenges in understanding and studying soft matter systems relevant to a diverse range of applications. Our research group has developed novel methods using Atomic Force Microscopy (AFM) to visualize the collisions between micro-drops or micro-bubbles on the nanoscale. This is coupled with companion theoretical analyses to account for shape changes from interfacial deformation, surface chemistry, and fluid flow in these measurements.

In this presentation, we build on our existing work to better understand an additional aspect of soft matter, specifically the transport between micro-bubbles or micro-drops that can destabilise an emulsion or coarsen a foam. We present the first direct measurements of mass transfer between two adjacent nitrogen microbubbles at nanometer separation over a range of bubble radius ratios in an aqueous solution using AFM in combination with optical microscopy. The results of a numerical model coupling interface deformation, equilibrium surface forces, and mass transfer across the thin film separating the two bubbles display excellent agreement with experimental measurements. Further, we demonstrate that mass transfer is not retarded by the presence of an anionic surfactant, sodium dodecylsulfate, at the gas/liquid interface, but is reduced in the presence of a polymer monolayer. This approach may also have potential in providing a novel method to rapidly screen interfacial species with potential utility in the areas of ultrasound contrast imaging agents, oxygen carriers and therapeutic gases.

Topology, softness and rigidity in gel networks

DEL GADO, Emanuela, Georgetown University

Arrested Soft Matter

Soft matter (colloids, polymers, proteins…) often self-assembles into gels where rigidity emerges in diverse structures with a variety of mechanical features. Through the interplay between their microstructure with an imposed deformation, gels can be stretched, flow, squeezed or fractured, but controlling and being able to design such processes (think for example of soft inks for 3D printing technologies) requires a fundamental understanding that is still lacking. Interesting new insight into the emergence of rigidity and the role of the network topology can be gained through theoretical/computational approaches. I will give an overview of the novel insight gained into the aging, the uniquely wide-ranged viscoelastic spectra and the presence of a topologically controlled softness in gel networks. Such findings can help understand the nontrivial mechanical response of soft gels in different contexts, develop constitutive models and theories further, and design smart materials.

Hierarchical biomechanics: from single folded proteins to cross-linked protein networks

DOUGAN, Lorna, Leeds

Making and measuring

Our understanding of the mechanism by which the viscosity of supercooled liquids increases by many orders of magnitude is a major challenge in condensed matter physics [1,2]. To resolve this challenge, it is necessary to discriminate between incompatible theoretical approaches which nevertheless provide equally good descriptions of experimental data. The competing approaches boil down to whether the glass transition is driven by an underlying thermodynamic phase transition, or whether it is predominantly dynamical [1]. To resolve this issue, we need to equilibrate samples of sufficiently high viscosity - and therefore long relaxation times - that experimental or numerical techniques can probe suitable quantities that enable discrimination of the theories.

Here we report new developments with experiments on soft matter, which provide significant insight into the nature of the glass transition. We use super-resolution microscopy techniques to track the coordinates of colloids with a resolution that is an order of magnitude better than the state-of-the-art. The small colloids, whose coordinates we track, sample phase space a thousand times faster than in comparable studies. This means that we access effective timescales three orders magnitude larger than in previous work. With this new technique, we are able to access a new dynamical regime in thee supercooled liquid, and our results provide strong evidence in support of a thermodynamic phase transition underlying the dynamical arrest that is the glass transition [3]. We further investigate predictions of a structural-dynamical phase transition in trajectory space, which we verify with experiments [4], and provide a route to reconcile the competing theoretical descriptions of the glass transition [5].

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Phase-separation in an elastic matrix: from living cells to synthetic materials

DUFRESNE, Eric, ETH, Zürich

Living Soft Matter

Demixing on curved surfaces

KRAFT, Daniela, Leiden

Interfacial Soft Matter

Like oil in water in vinaigrette, artificial membranes composed of three or more types of lipids can undergo liquid-liquid phase separation. Unraveling the physical mechanisms behind the organization of these liquid phases in membranes may be of key importance for understanding cellular processes such as protein sorting and signal transduction, but may also provide new insights into the thermodynamics of phase separation. Previous studies on vesicles and supported lipid bilayers have unveiled a fundamental interplay between the membrane geometry and position of different lipid domains. However, the detailed mechanisms behind this coupling remain incompletely understood, because of the difficulty of independently controlling the membrane geometry and composition.

In this talk, I will show how we overcome this limitation by fabricating multicomponent lipid bilayers supported by colloidal scaffolds of prescribed shape. Thanks to a combination of experiments and theoretical modeling, we demonstrate that the substrate local curvature and the global chemical composition of the bilayer determine both the spatial arrangement and the amount of mixing of the lipid domains. Our results provide key insights into phase separation in lipid membranes and complex fluids in general.

Ionic Liquid Crystals: Controlling Self-Assembly and Function through Charge and Symmetry

LASCHAT, Sabine, Stuttgart

Self-assembled Soft Matter

Ionic liquid crystals (ILCs) are unique soft matter materials, which combine the best of two worlds, i.e. the fluidity, thermal and electrochemical stability of ionic liquids with the anisotropic physical properties of thermotropic liquid crystals. The presence of charged headgroups and counterions results in anisotropic ionic conductivity, which is very useful for applications in solar cells and battery materials.

However, the presence of charged head groups and counterions also causes problems, such as the difficult accessability of certain mesophase types, which are common among neutral thermotropic liquid crystals. Another challenge with respect to practical applications are high phase transition temperatures between mesophase and isotropic liquid, i.e. clearing points which are close to thermal decomposition. The lecture will present design strategies to overcome these limitations using symmetry considerations. ILCs possessing rare mesophases, such as tilted smectic C phases and de Vries materials with minimal layer shrinkage during the smectic A - smectic C transition will be discussed as well as ILCs showing electrooptical birefringence (Kerr effect). On the other hand the mesomorphic self-assembly can enhance linear optical properties such as fluorescence emission or photoswitchable devices. Last but not least, the molecular structure of ILCs has also implications on their interactions with biological matter. Selected examples of such bio-active ILCs will be presented.

Optimal navigation strategies of active colloids in complex environment

LÖWEN, Hartmut, Dusseldorf

Active Soft Matter

The quest for the optimal navigation strategy in a complex environment is at the heart of microswimmer applications like cargo carriage or drug targeting to cancer cells. Here, we formulate a variational Fermat's principle for microswimmers determining the optimal path regarding travelling time, energy dissipation or fuel consumption. For piecewise constant forces (or flow fields), the principle leads to Snell's law, showing that the optimal path is piecewise linear, as for light rays, but with a generalized refraction law.

For complex environments, like general 1D-, shear- or vortex-fields, we obtain exact analytical expressions for the optimal path, showing, for example, that microswimmers sometimes have to temporarily navigate away from their target to reach it fastest. Our results might be useful to benchmark algorithmic schemes for optimal navigation.

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Revealing Processability of Structured Fluids by Microfluidics

LYNCH, Matt, Proctor & Gamble

Making and measuring

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ABSTRACT

Structured fluids are used in a variety of applications including freshening sprays, detergents, cosmetics, and medicine. In particular, yield stress fluids allow the suspension of materials such as encapsulated particles, emulsions, or hydrocolloids, but flow under applied stress to allow delivery by methods such as spraying, injecting, or topical application. Critically, after the dispensing of the materials, the thixotropic properties of the fluids allow subsequent recovery of the structure. Design such systems requires understanding of the history of the applied strain, extensional properties, and flow-induced alteration in these fluids. These properties are investigated in microfluidic devices that contain expansion and contraction elements for three different types for fluids: xanthan-konjac gum as a yield stress and shear-thinning fluid, polyethylene oxide (PEO) as a Boger fluid, and a Newtonian fluid. The flow behavior of these fluids is understood combined with bulk rheology measurements.

From soft matter rheology to civil engineering

OVARLEZ, Guillaume, Solvay, Bordeaux

Processing Soft Matter

Many materials used in civil engineering (concrete, plaster, earth…) are first handled as pastes, allowing them to be placed before hardening occurs due to drying or chemical reactions. In this so-called fresh state, they display all the variety of rheological behaviors encountered in complex fluids: yield stress, thixotropy, shear-thickening…

This complexity results from the presence of both colloidal and noncolloidal particles in these polydisperse suspensions, as well as that of polymeric additives and bubbles. In addition, chemistry can already play a significant role before any hardening is observed.

In this talk, I will discuss the many insights that can be gained from the study of soft matter rheology to model the rheology of civil engineering materials and to guide their formulation.

Peeking and poking biological matter using optical tweezers in combination with single-molecule fluorescence microscopy

PETERMAN, Erwin, Vrije Universiteit

Living Soft Matter

In our lab, we have developed the combination of optical tweezers and single-molecule fluorescence microscopy as a powerful tool to study biomolecules and biomolecular complexes. Combining these two technologies allows holding a sample molecule or complex, extending or deforming it, and measuring forces acting on it, while, at the same time, visualizing it with single-molecule sensitivity. We have applied this approach to different biological systems, including DNA, whole chromosomes, cytoskeletal components and membranes.

In my presentation I will explain the concept of the technology, its potential and limitations. As an example, I will show our research on the mechanical properties of DNA and force-induced conformational transitions. In our latest studies we have addressed the change in orientation of DNA bases under mechanical stress using single-molecule fluorescence polarization measurements and we have developed a method to (quantitatively) change the supercoiling of an optically trapped DNA molecule, resulting in substantial changes in mechanical properties.

Disclosure: combined optical tweezers and fluorescence technology is patented and licensed to spin-off company LUMICKS b.v., which sells the instruments. I declare financial interest.

Towards an Understanding of the Glass Transition? Insights from Experiment and Simulation

ROYALL, Paddy, University of Bristol

Arrested Soft Matter

Our understanding of the mechanism by which the viscosity of supercooled liquids increases by many orders of magnitude is a major challenge in condensed matter physics [1,2]. To resolve this challenge, it is necessary to discriminate between incompatible theoretical approaches which nevertheless provide equally good descriptions of experimental data. The competing approaches boil down to whether the glass transition is driven by an underlying thermodynamic phase transition, or whether it is predominantly dynamical [1]. To resolve this issue, we need to equilibrate samples of sufficiently high viscosity - and therefore long relaxation times - that experimental or numerical techniques can probe suitable quantities that enable discrimination of the theories.

Here we report new developments with experiments on soft matter, which provide significant insight into the nature of the glass transition. We use super-resolution microscopy techniques to track the coordinates of colloids with a resolution that is an order of magnitude better than the state-of-the-art. The small colloids, whose coordinates we track, sample phase space a thousand times faster than in comparable studies. This means that we access effective timescales three orders magnitude larger than in previous work. With this new technique, we are able to access a new dynamical regime in thee supercooled liquid, and our results provide strong evidence in support of a thermodynamic phase transition underlying the dynamical arrest that is the glass transition [3]. We further investigate predictions of a structural-dynamical phase transition in trajectory space, which we verify with experiments [4], and provide a route to reconcile the competing theoretical descriptions of the glass transition [5].

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Mix and Melt Colloidal engineering

SACANNA, Stefano, New York

Colloidal and Granular Soft Matter

Traditionally, a chemist’s task has been to characterize and manipulate atomic and molecular building blocks. On the micron scale, however, we have the opportunity to design altogether new, colloidal, building blocks from the bottom up. This vast synthetic freedom translates into a world of assembly possibilities because while there are a set few atomic units, the colloidal periodic table is seemingly infinite. An enormous research effort is currently taking place to develop heuristics for generating three-dimensional architecture from ”soups” of intelligently designed colloids so that future materials can be imbued with intricate microscale detail.

In this talk, I will present new methods for shaping, programming, and assembling matter at the nano- and micron-scale. A particular emphasis will be given to colloidal fluids of patchy, shape-changing, and active particles.

Why "bad" is "good": Polydispersity in polymeric nanostructures

SCHMID, Friederike, Mainz

Polymeric Soft Matter

Synthetic polymers almost always have some degree of polydispersity, yet the influence of polydispersity on polymeric nanostructures has received surprisingly little attention so far. In the talk, we discuss polydispersity effects in two prominent cases of such structures - polymer brushes and self-assembled polymeric nanoparticles - using self-consistent field calculations, analytical theory, and Monte Carlo simulations. Among other, we show that monodisperse brushes correspond in some sense to a multicritical state characterized by high fluctuations. The fluctuations are reduced dramatically if the brush is slightly polydisperse. Polydispersity also influences the friction between opposing polymer brushes. In the second part of the talk, we study the size distribution of self-assembled copolymeric micelles in solution. We show that polydispersity in the copolymer constituents significantly reduces the dispersity in the micelle size distribution. Hence "ill-defined" polymeric materials may produce "better", more uniform nanoparticles.

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Law and Disorder: The unusual behaviour of ultraweak crystals

SPRAKEL, Joris, Wageningen

Colloidal and Granular Soft Matter

Squids as soft matter: evolved self-assembly of gradient-index lenses and light guides

SWEENEY, Alison, University of Pennsylvania

Self Assembled soft matter

Cephalopods are rich with evolved optical devices with sub-wavelength structure that self-assemble into: gradient-index lenses that form near-perfect images; bioluminescent light guides that provide camouflage; focusing mirrors that attract mates; isotropic diffusers for luring prey, and more. These optical devices all self-assemble from structural proteins: S-crystallins in the case of lenses, and reflectins in the case of light-guiding materials. Assembly behavior in these systems is well-rationalized by theories from soft matter, particularly those of patchy particles and surfactants. I will first explain how patchy particle theory explains the evolutionary emergence of gradient index optics in squid lenses. The second part of my talk will discuss preliminary results from self-assembling reflectin systems, including the possible conceptual linkages between S-crystallin-based self-assembling lenses and reflectin-based self-assembling light guides.

CONTRIBUTED TALKS

Active vesicles: a minimal model for cell motility

ABAURREA-VELASCO, Clara, Forschungszentrum Jülich, Institute of Complex Systems, Theoretical Soft Matter and Biophysics

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Living Soft Matter

Self-assembly is a key mechanism for structure formation in passive soft matter. In systems with intrinsic driving forces, activity crucially determines the structure and dynamics [1]. An important active system is the cytoskeleton of biological cells, a highly dynamic three-dimensional network of polar filaments and molecular motors. It provides stability and generates and transmits mechanical forces. Here, we present a generic two-dimensional model of active vesicles, where self-propelled filaments attached to rings form mechanosensitive active agents [2,3]. Using deformable, semiflexible polymer rings we find universal correlations between shape and motility. To probe the internal dynamics of the vesicles in response to stimuli, we study the effect of substrate patterning on shape and motility.\\[0.5ex]

The active vesicles show experimentally observed shapes and motion patterns reminiscent of circular-fluctuating cells, keratocytes, and neutrophils. Interestingly, explicit pulling forces only are sufficient to reproduce this cell-like behaviour. Also for the reflection of the vesicles at walls and the deflection of their trajectories at friction interfaces we find parallels to keratocytes. Our model may thus serve as a filament-based, minimal model for cell motility.

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Controlling Gel Properties by Chirality

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Self-Assembled Soft Matter

Varying the chirality of low molecular weight gelators (LMWGs) provides the exciting potential to control and define gel properties. Most LMWGs are chiral, with racemic mixtures often unable to form gels. Here, we investigate a functionalised dipeptide LMWG 2NapFF. 2NapFF forms opaque solutions at high pH and translucent gels when the pH is decreased. Gels can be formed from both solutions of either the SS and RR enantiomers . This is unsurprising, as it has been previously shown that enantiomers for this class of gelator have a similar gelation ability. However, it has been previously reported that mixtures of two enantiomers do not form gels. Surprisingly, here we have found that gels can also be formed from the mixtures as well as from the other diastereomers of 2NapFF, the SR and RS, as well as from racemic mixtures.

We show for the different chiral conformations of 2NapFF in both solution and gel form, a wide variation in properties is possible. For example, regarding the gelator solutions at high pH vastly different structures are observed via cryo-TEM. SS and RR give long thin fibres whereas, the SR and RS contain hollow nanotubes. These observations were consistent with SANS data on the systems. At high pH, different self-assembled aggregates are formed and these directly template the structures formed in the gel.

We have shown solutions and gels with different properties can be accessed simply by varying the chirality of the LMWG. A variety of techniques have been implemented to investigate these differences including SANS, SAXS, CD/LD, FT-IR, rheology, cryo-TEM, confocal and optical microscopy.

Formation of Suspended Bilayers at the Air-Water Interface: A Novel Bacterial Membrane Mimic.

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Interfacial Soft Matter

Bacterial membranes are an important drug target for the development of new antimicrobial drugs. We have created a bilayer membrane mimic, which by virtue of being suspended below a surfactant monolayer at the air-water interface has greater freedom to fluctuate than solid supported membranes.

The suspended lipid bilayers are formed by the rupture of either liposomes or proteoliposomes underneath a cationic monolayer. Fits to our recent neutron reflectivity experiments show that a bilayer coverage of 99% can be achieved and that there is a 2 nm thick water layer between the surfactant layer and the lipid bilayer. This water layer means that the suspended bilayer can fluctuate and that there is sufficient space to allow for membrane proteins to be inserted.

Forming the bilayer by rupture of proteoliposomes provides a convenient method to study/analyse membrane proteins that avoids the need to remove the detergents used in other/more established protocols. We have used proteoliposomes containing mechanosensitive ion channels of large conductance, MscL, which we express through cell free protein expression directly into POPC/POPG liposomes. MscL is a highly conserved membrane protein in gram-negative bacteria such as E. coli that protects them against osmotic shock, making it an interesting protein to investigate as a potential drug target.

Fits to the neutron reflectivity measured from the suspended bilayer formed from these proteoliposomes clearly indicates the presence of ion channels.

The MscL protein is known to gate in the presence of small amphiphilic molecules in patch-clamp experiments, though this has not yet been shown directly through scattering. By successfully incorporating this membrane protein into our less constrained bacterial membrane mimic, we have a good model to test the behaviour of MscL with already investigated amphiphilic molecules and potential antimicrobial drugs.

How to unify diffusio-phoresis, Marangoni and osmotic flows with interfacially driven transport of soft matter ?

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Interfacial Soft Matter

The characteristic of soft matter flows is the presence of interfaces between adjacent phases leading to multiple surface interactions. It is particularly the case when processing soft matter in confined geometries (microfluidics, membranes) and/or in concentrated dispersion (rheology, self-assemblies). In these systems, the transport of colloid/solvent mixture near an interface is controlled by colloid-colloid and colloid-interface interactions.

A theoretical approach of transport phenomena has been developed to take these interactions into account in momentum and mass balances (Suspension Balance Model [1]). This model makes it possible to simulate the flow of colloid-solvent mixture in presence of interacting interfaces. It determines the local variation of concentration and velocities as well as the macroscopic variation of the pressure.

2D flow simulations of a colloid/solvent mixture through an array of interfaces will be presented. It represents the flow of soft matter through a membrane or around an object. Due to the flow through these interacting interfaces, a colloid concentration gradient appears along the interface. This concentration gradient modifies the solvent pressure near the interface [2] which, in turn, induces a flow of solvent:

- if the interface repels colloids, a flow of solvent appears toward high colloid concentration zone. Theses simulations allows then to reproduce reverse osmosis flows.

- if the interface attracts colloids, a flow of solvent appears toward low colloid concentration zone. This flow is a Marangoni flow that occurs toward low surfactant (a surfactant can be seen as a colloid with an affinity for an interface) or toward high surface tension zone.

It will then be demonstrated that the solvent flow due to diffusio-osmosis and Marangoni effects is the same consequence of colloid-interface interactions. The proposed universality between diffusio-osmosis and Marangoni flow will be extended further to include diffusio-phoresis. When the interface is mobile in a stagnant fluid, by reciprocity, the interfacial driven transport induces the move of the interacting interface. It will be shown that the direction of this displacement called diffusio-phoresis depends on the nature of the interactions: the object goes toward low concentration in the case of colloid-interface repulsion and toward high concentration in the case of colloid-interface attraction.

To summarize, the presentation will present how these four transport phenomena can be unified when considering the colloid-interface interactions. The model will explain how the colloid-interface interaction i) plays a role on the mass and momentum balance ii) generates local transport phenomena (interfacially driven transport) iii) changes the relative transport of an object and a fluid in a colloidal dispersion. In real life case, the solute and the interface combine multiple interactions: they interacts both with repulsive (leading to osmotic like flow) and attractive contributions (leading to Marangoni like flow). To open up perspectives, it will be discussed how active solute displaying patchy interactions on their surface can also lead to very specific and local transport properties.

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Lattice Boltzmann simulations of collective phenomena in microswimmer suspensions

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Active Soft Matter

Long-ranged hydrodynamic interactions often dominate the collective behaviours in suspensions of microswimmers. These phenomena include bacterial turbulence, where suspensions of pusher bacteria at sufficient densities exhibit large-scale, chaotic flows [1]. To study collective phenomena, we use large-scale (up to $N=5\times 10^6$) particle-resolved lattice Boltzmann simulations [2,3]. In this work we model the microswimmers as two point forces, representing the drag force on the body and the propulsive force from the flagella, yielding an extended stresslet acting on the fluid, while ignoring near-field effects and excluded volume interactions. The large system sizes enables us to obtain quantitative information about both the transition to bacterial turbulence and characteristic features of the turbulent state itself with high numerical accuracy.

We quantify the length- and timescales of the turbulent flows and find a sharp increase in these quantities near the transition to turbulence, followed by a decrease beyond the transition, showing that the fluid flows near the instability are characterized by long-ranged correlations and very slow dynamics. In the turbulent regime, we show that the characteristic length- and timescales saturate with system size. The observation of a characteristic lengthscale is further confirmed by the existence of a peak in the Fourier-space energy spectra of the fluid flows. We furthermore characterize the structure and dynamics of the \textit{swimmers}, showing that the lenghtscales obtained from the long-ranged orientational correlations of the swimmers show identical trends compared to the lenghtscales obtained from the fluid. Our results thus open up new possibilities for studying collective behaviour in hydrodynamically interacting microswimmer suspensions using particle-resolved simulations over unprecedented length- and timescales.

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Ageing, yielding and shear banding in an elasto-plastic model

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Arrested Soft Matter

We introduce a two-dimensional tensorial lattice-based elasto-plastic model for the rheology of yield stress fluids. The model incorporates both full force balance (including after each local plastic yielding event), and the rheological ageing behaviour that is widespread in soft glassy materials. We examine the emergence of shear bands separately in shear startup and following the imposition of a step stress. These bands are shown to be transient but very long-lived, and we characterise carefully the lifetime of the bands before a statistically homogeneous steady state is recovered. We also consider the interplay between these long-lived bulk shear bands, and avalanches of plastic events that flicker in and out of existence across the sample.

Environmental nanoparticle-induced toughening and pinning of a crack in a biopolymer hydrogel

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Processing & Stressed Soft Matter

Thanks to their meshsizes in the tens of nanometer range, polymer hydrogels can alloy with nanoparticles while preserving their structural integrity, although gaining superior functionalities for applications in tissue engineering, drug delivery, bio-sensing or catalysis. The synergy of such hybrid associations stems from the high surface-activity of nanoparticles and the stimulus-responsivity of hydrogels which can readily exchange solvent with their environment (Noselli et al. {\it J. Mech. Phys. Solids}, 2016). Exogenous nanoparticles supplied by an external solution have been shown to interplay adhesively with 3D \emph{ bulk} gels (Pardo-Yissar et al. {\it Adv. Mat.}, 2001) or 2D \emph{interfaces} (Rose et al. {\it Nature}, 2014) between gels or biological tissues. We investigate how such ``environmental'' nanoparticles interact with a moving quasi-1D \emph{crack front}, slow it down and potentially pin it. Playing with the net charge sign of polyampholyte networks, we unveil two distinct toughening mechanisms. The primary one is charge-independent and involves the hindering of poroelastic flows by a particulate clog. Transient adhesive bonding superimposes when particles and network bear opposite charges. Both mechanisms amount to a {\it fast} and {\it self targeting} (Kolmakov et al. {\it ACS nano} 2010) action of nanoparticles on the very network zone where rupture occurs, thanks to the breathing-in poroelastic flow generated by the singular stress field in the crack tip vicinity.

Tooling up to build an artificial cell

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Living Soft Matter

The biological cell is a highly autonomous, responsive and functional form of soft matter. Mimicking some of its key features in synthetic systems carries the potential for novel advanced materials and chemical technologies. More fundamentally, the endeavour of trying to create an artificial cell from its fundamental constituents may shed new light on the molecular basis of life. I will present our recent progress in developing tools for the bottom-up assembly of artificial cells.

Compartmentalisation of function within distinct organelles is a hallmark of increased functional complexity in living cells. By repurposing natural membrane remodelling complexes, we can generate new internal membrane-bound compartments within giant vesicles (a model artificial cell) that encapsulate cargo from the bulk medium. We have found that negative feedback from membrane tension is a useful mechanism to regulate this membrane remodelling activity.

Within vesicle compartments we can encapsulate autocatalytic enzyme reactions that respond to the stimulus of a metabolite in the external environment, allow communication and synchronisation between vesicles in a population and can be harnessed for clock-like switching behaviour and triggered release of bioactive compounds.

Finally, lipid bilayer vesicles are known for their relative fragility and poor endurance, which is an undesirable property in a new material. We have found that combining biocompatible lipids with more durable block copolymer systems to form hybrid membrane materials significantly enhances the longevity of these vesicles, while still providing a suitable environment for the activity of delicate biologics such as membrane proteins. One membrane protein we have investigated exhibited a greater than 10-fold increase in functional lifetime when reconstituted within a hybrid vesicle, with significant (~25% of initial) activity measured 1.5 years following initial fabrication.

Future combination of these approaches holds promise for the fabrication of robust, multifunctional and environment-responsive artificial cells.

Assembly of patterned colloids close to a patterned substrate

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Colloidal & Granular Soft Matter

Two-dimensional colloidal aggregates adsorbed to a planar substrate can be designed to realize specific structures and, thus, achieve target functionalities. The features of these aggregates depend on the balance between colloid-colloid and colloid-substrate interactions. Well-established methods for the fabrication of two-dimensional colloidal structures consist either in tuning the surface properties of the particles or in taking advantage of chemically or physically patterned substrates. Recently, these two approaches have been combined [1,2] by considering spherical patchy particles with three attractive spots, adsorbed on patterned substrates made by circular wells regularly distributed in specific lattice arrangements. We consider a similar setup in the context of heterogeneously charged systems: our investigations focus on negatively charged colloids with two positively charged polar caps adsorbed to a patterned substrate composed of alternating (negative/neutral, positive/neutral and positive/negative) parallel stripes. We show that the competition between the different lengths scales characterizing the system (i.e., the particle interaction range and the size of the stripes) and between the different directional (attractive and repulsive) interactions give rise to a plethora of distinct particle arrangements, where some well-defined trends can be observed. By accurately tuning the substrate charged motif it is possible to, e.g., promote specific particles arrangements, disfavor crystalline domains or induce the formation of percolating, open clusters [2,3]. We note that the aggregation of particles on substrates could be used to guide the crystallization of bulk crystals as well as to tailor their orientation, a process referred to as “colloidal epitaxy” [5].

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On flow, fracture and getting jammed – Failure modes in dense suspensions

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Processing & Stressed Soft Matter

Dense suspensions are a class of complex fluids that exhibit both shear-thickening and shear-jamming behavior as a response to an applied stress. These dynamic liquid-to-solid transitions have important consequences for the displacement of a dense suspension by another fluid: upon the injection of air, intricate patterns arise in the suspension, leading to flow or fracture of the material. We displace a cornstarch suspension by a pressure-controlled injection of air in a quasi-2D geometry. Depending on the concentration of cornstarch and the applied stress, we observe a variety of patterns: smooth fingering in the fluid regime and different modes of fractures, ranging from slow branched cracks to single fast fractures. Remarkably, there is a regime where, despite the application of pressure, the suspension cannot be displaced. Only upon an increase to a higher pressure, air injection occurs, leading to very thin fractures in the suspension. We hypothesize that in this regime the suspension is in the shear-jammed state. This would imply a novel way of investigating the mechanical properties of a shear-jammed material by probing its fracture behavior.

“Hot Spots” in pore scale flow through soft carbon fibre felt electrodes limit the efficiency of Redox Flow Battery operation

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Making & Measuring Soft Matter

The Vanadium Redox Flow Battery (VRFB) is one of the most promising Electro-Chemical Device (ECD) technologies for large scale local storage of renewable energy, such as wind and solar. Commercial exploitation of this technology has emerged, but a lack of fundamental understanding of VRFB operation is limiting the development of this new technology. In particular, battery longevity is a problem due to degradation of the soft graphite felt carbon fibre electrode material under electrochemical cycling. In addition, the energy density must be improved, as this is low compared to Li-ion battery performance. For these reasons, we investigated here the performance of soft carbon fibre electrode materials using a combination of computational modelling and experimental characterisation. In particular, the surface area of the porous electrode is critical to the device performance. To optimize electrochemical reactions in the electrode, the reactive surface area has to be as large as possible. In terms of micro-structure, this means that the felt fibres must be distributed homogeneously. In current VRFB technology, however, the felts are woven bundles of fibres yielding a large local variation in voids and bundles. Recently, synchrotron micro-CT scanning was used [1] to image the 3D pore structure of a graphite felt in-operando. However, the resulting alteration of the actual flow field could not be quantified, as it is very difficult to measure in-situ due to limited spatio-temporal resolution. Also, it is difficult to obtain the altered flow field from average tortuosity and porosity calculations, as the relation between permeability and tortuosity / porosity is only known empirically. Here we calculate, for the first time, the relation between flow and altered micro-structural properties using direct flow calculations in pore space images of a representative volume of a soft carbon fibre material obtained from micro-CT imaging. We present detailed spatio-temporal pore space images of a representative 3D soft fibre felt geometry, and the corresponding flow field. The flow field was calculated using our home-grown Lattice-Boltzmann (LB) code (see [2], [3] and [4]) on a big data set of 15 billion voxels using HPC facilities.

Our simulations show that the electrolyte is concentrated in local areas (“hot spots”), thus limiting electro-chemical reactions. The heterogeneity of the commercial soft carbon fibre material therefore reduces the efficiency of the electrode, as it may cause high voltage spots and therefore damage in the electrode. To mitigate problems associated with the heterogeneous nature of soft carbon fibre graphite felts, we use a rational design approach to develop new soft fibrous carbon materials with superior properties.

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Load distributions in multi-network elastomers

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Polymeric Soft Matter

Polymer architectures based on double networks provide a now well-established route to making gels and elastomers with enhanced mechanical properties (Gong et al., Adv. Mater. 2003). Recent work on double and triple elastomers has shown that this is true even when the two networks are chemically identical and only differ in the amount of pre-stretch they carry: such materials display enhanced toughness because the first network provides "sacrificial bonds" (Ducrot et al., Science 2014). We present a simple method to generate numerical models of such double and triple networks and use them in coarse-grained Molecular Dynamics simulations to assess how the stresses that arise during large deformations of these networks are distributed over the different generations of the network, and to elucidate the nature of the resulting fracture process and toughness.

How are salivary pellicles affected by surfactants of different ionic character?

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Interfacial Soft Matter

Surfactants are often used in oral health products such as toothpastes and mouthwashes. The use these compounds has been related to exacerbation of periodontal disease, initiation and progression of gingival recession and recurrent oral ulceration [1]. However, oral care products without surfactants have been unsuccessful as these components fulfil several functions [2]. They serve as solubilizing, dispersing, emulsifying and wetting agents. Moreover, they promote foaming, which is preferred by consumers since it provides a perception of cleanliness. Thus, it is of high interest [1, 3] to identify and use surfactants with the lower adverse effects. In this context, it is of great value to understand how surfactants interact with the first interfacial layer that they encounter i.e., the salivary pellicles. Salivary pellicles are (mostly) proteinaceous nm-thick films that form on any type of surface upon exposure to saliva. The role of the pellicle is manifold. Among its functions, hydration and lubrication of the underlying tissues is often listed [4]. Along with others, we have performed previous studies on surfactant-pellicle interactions e.g., [5]. However, at present there are no systematic investigations on how these interactions are affected by properties of the surfactants, such as their ionic character, or on how they alter functions fulfilled by the pellicle like hydrating and lubricating the underlying surfaces. Here we present such an study with a focus on amphoteric and nonionic surfactants, which are seen as potential substitutes for ionic surfactants i.e., those more often used in oral health products, but are also known to specially cause adverse reactions to oral tissues [6]. We have performed ellipsometry, QCM-D and neutron reflectometry investigations in order to elucidate how amphoteric and nonionic surfactants alter structural properties e.g., thickness and hydration, of salivary pellicles. Moreover, we have also investigated how these interactions alter the lubrication properties of salivary pellicles as measured with an Atomic Force Microscope.

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Soft lubrication with polymer brushes

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Processing & Stressed Soft Matter

The term « soft lubrication » was coined about fifteen years ago, when theoretical studies demonstrated that the presence of a thin and compliant layer on the surface of rigid solids could have a sizeable and non-trivial effect on the lubrication forces controlling their interactions under flow. Such an effect, which stems from elastohydrodynamics, is expected to be key to a whole range of situations in soft matter physics involving fluid-immersed deformable surfaces in relative motion. Paradoxically enough, soft lubrication has received only a very limited attention from the experimental side.

We address this point and focus on the elastohydrodynamic interactions at play, at small scales, between a flowing particle and a compliant surface. Combining microfluidics and 3D optical tracking, we show that a thin (sub-µm) and soft polymer layer bound to a surface induces, at low Reynolds number, a significant lift on microspheres flowing nearby, while this phenomenon is absent for a non-deformable surface. Such lift is observed to be stronger at larger wall shear rates and for softer polymer layers. Moreover, we show that our results are in quantitative agreement with predictions from elastohydrodynamic and polymer brush theories [1].

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External and internal deformations of colloidal crystals

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Colloidal & Granular Soft Matter

I will present experimental results concerning the mechanical deformation of two-dimensional (2D) colloidal crystals. In absence of attractive interactions, colloidal crystals spontaneously form at given area fractions and are typically littered with line and point defects that govern their mechanical properties.

The crystalline monolayers are fabricated at a flat liquid-liquid interface to exploit the soft bonds and the long-ranged dipolar interactions between particles. This strategy makes the 2D crystals easy to deform under weak forces and allow trapping and/or actuating single particles without spurious effects near contact. I will highlight the differences between three sources of deformation: (1) shear flows, (2) external driving and (3) self-propulsion. In (1), a micro-fabricated magnetic disk is manipulated by external magnetic fields to apply steady and oscillatory shear flows to the colloid-laden interface. In (2), we use an optical tweezer to drive a single colloid through the lattice at different velocities and orientations relative to the crystalline axes. In (3), we dope the crystals with few Pt-coated particles that undergo self-propulsion due to the catalytic decomposition of hydrogen peroxide in the water phase.

The experimental results pinpoint local regions and directions through which crystalline materials rearrange when they are driven out of thermodynamic equilibrium. Furthermore, we elucidate the fundamental differences between driven and self-driven colloids in dense structures.

Anisotropic self-assembly from isotropic colloidal building blocks

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Interfacial Soft Matter

Spherical colloidal particles generally self-assemble into hexagonal lattices in two dimensions. However, more complex, non-hexagonal phases have been predicted theoretically for isotropic particles with a soft repulsive shoulder but have not been experimentally realized. We study the phase behaviour of microspheres in the presence of poly(N-isopropylacrylamide) (PNiPAm) microgels at the air/water interface. We observe a complex phase diagram, including phases with chain and square arrangements, which exclusively form in the presence of the microgels [1]. Our experimental data suggests that the microgels form a corona around the microspheres and induce a soft repulsive shoulder that governs the self-assembly in this system. The observed structures are fully reproduced by both minimum energy calculations and finite temperature Monte Carlo simulations of hard core-soft shoulder particles with experimentally realistic interaction parameters [1]. Similar structures are also observed experimentally for other binary colloid and block copolymer or colloid and protein systems, suggesting that the proposed self-assembly mechanism is generic [2]. Our results demonstrate how complex, anisotropic assembly patterns can be realized from entirely isotropic building blocks by controlling the interaction potential, providing a simple but powerful platform for the design of new materials.

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Multi-scale relaxation in aging gels: from localized plastic events to system-spanning `quakes'

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Arrested Soft Matter

Relaxation of internal stresses through a cascade of microscopic restructuring events is the hallmark of many materials [1,2], ranging from amorphous solids like glasses and gels to geological structures subjected to a persistent external load. By means of Photon Correlation Imaging, a recently developed technique blending the powers of scattering and imaging, we provide a spatially and temporally resolved survey of the restructuring and aging processes that spontaneously occur in physical gels originating from arrested phase separation. We show that the temporal dynamics is characterized by an intermittent sequence of spatially--localized `micro-quakes' that eventually lead to global rearrangements occurring at a rate that scales with the gel age. Notably, these dramatic upheavals of the gel structure are heralded by a progressive acceleration of the microscopic gel dynamics that originates from recognizable active spots and then spread at a large but finite speed through the gel. Within the `slack' phase between two of these `macro--quakes', the fluctuations of the degree of temporal correlation obey a non-Gaussian statistics described by a generalized logistic distribution, while the distribution of the strongest micro--quakes within is in full agreement with the predictions of an Extreme Value Analysis. The evidence we obtained suggests a strong connection both with the stress relaxation processes taking place in earthquake sequences [3] and with recently proposed self-organized oscillator mechanisms of crystal plasticity [4].

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Microgels adsorbed at liquid-liquid interfaces: insights from realistic modelling and experiments

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Interfacial Soft Matter

A distinctive feature of microgel particles is that of being soft colloids with an internal polymeric architecture. At liquid interfaces, in particular, they deform and flatten significantly due to the balance between surface activity and internal elasticity. For this reason, recent experimental studies have shown that they are a valuable choice to stabilize smart emulsions with respect to common rigid colloids, and for the versatile patterning of surfaces [1]. Despite the clear potential this system could bring, a detailed theoretical understanding of the phenomenon is still lacking. In fact, commonly accepted models in which the internal structure is neglected or diamond-like, where polymer chains have a fixed length, are not able to reproduce this behavior, especially by the fact that the corona would not flatten out. Conversely, we have now provided a realistic model that reproduces \textit{in silico} the polymeric network of PNIPAM microgels and its properties [2], even in the presence of an explicit solvent [3].

By placing the microgel at liquid-liquid interfaces, we can now directly compare the morphology of the microgels resulting from simulations with \textit{in situ} cryo-electron microscopy measurements and AFM imaging after Langmuir-Blodgett depositions [4]. The correct modelling of the internal degrees of freedom allows for a qualitative comparison with the experimental outcomes and to report a consistent trend as a function of the fraction of crosslinkers. Most importantly, we can link the internal structure of the polymer network to their macroscopic behavior by computing their effective interactions at the interface, for which a clear dependence on the microgel structure has been recently found for microgels in bulk [5]. These are essential to develop predictive power for the use of microgels in a broad range of applications as well as in bi-dimensional soft model systems for the accurate investigation of glassy and high-density states of thin microgel layers.

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Smart Adsorption, playing with geometry to enhance selectivity

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Polymeric Soft Matter

Scaling theories are a powerful tool allowing to map properties of extremely complex systems onto simple relations, thus linking a selection of microscopic details to a subset of general features.

Polymers, due to their fractal nature, are an excellent example of systems that can extensively be described by means of scaling theories for the most diversified architectures and chemical compositions [1].

We will here illustrate how to use polymeric macromolecules for the design and realisation of the most diversified tunable smart nano-materials. In particular we will concentrate on how to exploit the polymeric nature to perform selective adsorption in solution. Starting from the single molecule properties, we will show how, by means of a combination of theoretical, computational and experimental tools, it is possible to predict the properties of complex assembled materials by only retaining a few details of the microscopic systems [2]. We will focus on selective adsorption properties presenting a hybrid theoretical/experimental approach able to discriminate and selectively adsorb solvent in solution [3]. Finally, we will compare polymeric systems with different geometries [4,5] and show how to exploit the geometry of the macromolecules to enhance the selectivity of the adsorption process and test a first principle design for a smart nano-adsorber.

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Capillary phenomena in miscible fluids

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Interfacial Soft Matter

Interfacial tension between immiscible fluids is a well-defined, well-known quantity occurring in a wide range of phenomena. By contrast, this quantity is neither easily defined nor fully understood for miscible fluids. Following the work of Korteweg in 1901 [1], an “effective interfacial tension” (EIT) is supposed to exist between miscible fluids, which stems from spatial gradients of concentration or density in a multifluid system. Nevertheless, the existence of these so-called “Korteweg stresses” is still debated [2-3], since they are hardly detectable in simple miscible liquids, where diffusion rapidly smears out interfaces.

In order to investigate EIT, we perform a series of spinning drop tensiometry (SDT) experiments. In SDT, a drop of one fluid is injected in a background fluid contained in a cylindrical capillary. The capillary is rapidly spun and one follows the evolution of the drop shape by video imaging. We modify a commercial apparatus and use fluorescent drops in order to retrieve the full three-dimensional concentration profile of the drop, allowing us to follow the dynamics of the interface with unprecedented detail.

We first investigate the model case of immiscible molecular fluids, for which we find that the time evolution of the drop shape agrees nicely with theoretical predictions [4] that where not tested so far. These results constitute a solid starting point for SDT on miscible fluids. We find that the shape of a miscible drop continuously evolves, in contrast to the saturation effect reported in previous investigations that explored a smaller temporal range. By varying systematically the compositions of the fluids, we determine that the shape of miscible drops during elongation is not only determined by the density and viscosity contrast with respect to the background fluid, but also by the chemistry of the fluids. This crucial result rules out the possibility that the drop dynamics are purely dictated by hydrodynamics and strongly hints at the existence of an effective interfacial tension.

Furthermore, we observe the onset of standing inertial waves which generates fluctuations in the drop width, as previously reported for ultralow interfacial tension systems [5]. The instability occurs for very elongated drops and depends on the drop chemistry; it provides additional evidence to the existence of effective interfacial stresses acting as a positive tension.

Our experiments strongly support the presence of an off-equilibrium EIT at the interface between miscible simple liquids, and pave the way for a thorough understanding of the very nature of Korteweg stresses.

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Reversible cluster formation, gelation and glassy dynamics in colloidal dispersions

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Colloidal & Granular Soft Matter

Particle aggregation or clustering is an obligatory step for the initiation of the phase separation or the large-scale formation of materials that exhibit a heterogeneous structure, such as gels and porous media. Nevertheless, even though the macroscopic structure of such materials depends on the shape and size of the resulting clusters or aggregates, the cluster formation at equilibrium and its corresponding morphology are not fully understood. The local morphological information is also important for the identification of the physical mechanisms for arrested states of matter, especially gels and glasses, which remains a hotly debated research topic in condensed matter physics. Due to the complex nature and different microscopic details of each particular system, a general, consistent and unified definition is of paramount importance from both scientific and technological viewpoints.

Combining molecular simulations, experimental characterizations and theoretical calculations: 1) we conclusively demonstrate that the cluster morphology in short-ranged attractive colloidal systems (SRACS) at equilibrium conditions can be uniquely determined by the reduced second virial coefficient; our findings link the reversible colloidal aggregation with the extended law of corresponding states, 2) we show that gelation in adhesive hard-sphere dispersions is the result of the rigidity percolation with coordination number equal to 2.4; these results connect the concept of critical gel formation in SRACS to the universal concept of the rigidity percolation and, finally, 3) we provide a unified description and a general overview of the different aspects of the glass transition in largely asymmetric binary mixtures of hard-spheres; we highlight the fundamental relevance in considering explicitly the dynamics of both large and small particles to properly account for the glassy scenario.

Tracking-free one- and two-point microrheology of soft materials

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Making & Measuring Soft Matter

Passive particle tracking microrheology (PT-μr) is an experimental technique that exploits the thermal motion of tracer particles to probe the local mechanical properties of small amounts of homogeneous (one-point PT-μr) and micro-structured (two-point PT-μr) soft materials [1].

While in one-point PT-μr the trajectories of single particles are analysed to extract their mean squared displacement, in two-point PT-μr the cross correlations between the mean-square displacements of two particles are studied, which provides a means to get rid of artefacts that may arise in PT-μr as a consequence of the interactions of the probes with the sample microstructure. Despite its appealing conceptual simplicity, both approaches require calibration procedures and operating assumptions that constitute a practical barrier to a wider adoption, especially in industrial environments and in particular for two-point PT-μr that requires numerous accurate measurements and a subtle analysis of the acquired data.

Here, we present a novel approach to passive one-and two-point microrheology that, not requiring particle tracking, unlocks a calibration-free, automated, operator-independent rheological characterisation of soft materials. We first show how Differential Dynamic Microscopy (DDM) [2] can be used to perform one-point microrheology of different homogeneous complex fluids [3] by relying on the multi-scale, temporal correlation study of the image intensity fluctuations that are observed in microscopy experiments as a consequence of the motion of the tracers. In addition, we show how a novel analysis based on optical flow detection, enables one obtaining accurate two-point microrheology data of entagled F-actin solutions [4].

Our results are in good agreement with PT-μr when the latter can be used. In addition, we can extract reliable information even in cases where PT-μr is not a suitable option, demonstrating tracking-free microrheology as a viable alternative and complement to PT-μr and to other rheological probes.

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Colloids Get Creative: Key to Open Crystals

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Self-Assembled Soft Matter

Open crystals are sparsely populated periodic structures, which, when composed of colloidal particles, are appealing for their variety of applications, for example, as photonic materials, phononic and mechanical metamaterials, as well as porous media [1-4]. Programming self-assembly of colloidal particles into open crystals has proved a long-standing challenge due both to the mechanical instability and lack of kinetic accessibility that colloidal open crystals typically suffer from. Building on our recent work [5-7], I will here introduce a hierarchical self-assembly scheme for triblock patchy particles to address the challenges met with programming self-assembly into colloidal open crystals [8]. The presentation will demonstrate \textit{in silico} the hierarchical self-assembly of colloidal open crystals via what we call closed clusters, which stop to grow beyond a certain size in the first stage and are thus self-limiting [8,9]. Our designer patchy particles are spherical in shape, having two attractive patches at the poles across a charged middle band – a close variant of those synthesised recently [10]. By employing a variety of computer simulation techniques, I will show that the design space supports different closed clusters (e.g. tetrahedra or octahedra with variable valences) en route to distinct open crystals. Our design rules thus open up the prospects of realising a number of colloidal open crystals from designer triblock patchy particles, including, most remarkably, diamond and tetrastack crystals [8,9], much sough-after for their attractive photonic applications. The relevant photonic band structures will be also presented.

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Bottom-up mechanisms for the emergence of swarming

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Active Soft Matter

We study moving, re-orientable agents that seek to maximise the space of accessible (visual) environments they can access in the future. The action of each agent is (re)established by exhaustive enumeration of its future decision tree at each time step: it chooses the branch of this tree leading from the present to the richest future state space. Cohesive, swarm-like motion emerges that is similar to that observed in animal systems. We develop heuristics that mimic this computationally intensive process but that could operate in real time under animal cognition. We argue that this offers a philosophically attractive, bottom-up mechanism for the emergence of swarming and could also motivate algorithms for encoding in future realisations of "intelligent" matter, able to sense and respond to the environment.

Bacterial chromosome organization: special crosslinks, confinement effects and molecular crowders play the pivotal roles.

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Living Soft Matter

Using a bead-spring model of bacterial DNA polymers of {\em C. crescentus} we show that just 33 effective cross-links at special positions along the chain contour of the DNA of bacteria {\em C. crescentus} can lead to the large scale organization of the DNA-polymer with 4.017×10^6 base pairs, where confinement effects play a key role in the

organization. The positions of the the 33 cross-links are chosen from the contact map data of C. crescentus. The DNA is modeled as flexible bead-spring ring polymer with 4017 beads, i.e. each bead represents 1000 base pairs.

We further investigate the pivotal role played by the ability of DNA molecule to release topological constraints by chain crossing to get organized at micron length scales. We observe that chain compaction induced by the crowded environment in the bacterial cytoplasm contributes to the organization the bead-spring model of the DNA-polymer.

Using Monte-Carlo simulations we show that the release of topological constraints and the crowding environment is necessary for the polymer to obtain a unique organization. We have also compared our results with the organization of a ring polymer with an equal number of cross-links but at random positions along the chain.

These studies are repeated for the chromosome of {\em E.coli} and we arrive at similar conclusions. This assures us of the robustness of our findings. [1,2,3,4].

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{\bf Publications:} \\

1. Origin of spatial organization of DNA-polymer in bacterial chromosomes.\\

Europhys. Lett., {\bf 121}, 18004 (2018).

2. Role of special cross-links in structure formation of bacterial DNA polymer.\\

J. Phys.: Condens. Matter {\bf 30}, 034003 (2018).

3. Bacterial chromosome organization I: crucial role of release of topological constraints and molecular crowders. \\ {\em J.Chem.Phys: resubmitted incorporating minor corrections as asked by referees.}

4. Bacterial chromosome organization II: few special cross-links, cell confinement, and molecular crowders play the pivotal roles.\\ {\em J.Chem.Phys: resubmitted incorporating minor corrections as asked by referees.}

Bistability in wall aggregation of active Brownian particles.

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Active Soft Matter

Active Brownian particles phase separate into high-density clusters at sufficiently large motilities. They also aggregate to form large clusters on a rigid wall. We show that by tuning the wall properties, one can change the geometry of active aggregates from a connected, continuous cluster to disjointed clusters. The breakup of the continuous cluster into smaller clusters is related to large fluctuations in the interfacial width, caused due to enhanced particle currents at the wall. We also show that for a range of particle motility, both the geometries co-exist for the same parameter values and the aggregates occasionally switch from one geometry to the other. As the transition in cluster geometry is similar to surface tension driven, morphological transition in equilibrium fluids, we explore similar description to understand the stability of different shapes of aggregates in this non-equilibrium system.

Demonstrating stress transfer between networks in multiple network elastomers with mechanochemistry

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Processing & Stressed Soft Matter

When Spiropyran (SP) is activated by a force above 240 pN, it can turn into merocyanine (MC), change its light absorption and become fluorescent. SP was used here as a molecular probe to sense the transmission of stress between sequentially synthesized interpenetrated networks of multiple network elastomers[1][2]. SP was separately incorporated as a crosslinker into the first, second and third network of multiple network elastomers. In uniaxial extension, the three types of materials have identical mechanical properties but exhibit a color change at different levels of stretching. SP in the first network changed color in the region where random sacrificial bond breaking occurs, while SP in the second network only changed color after the first network was extensively damaged and necking was observed. SP in the third network was not activated before macroscopic fracture. The color changes demonstrate directly how the macroscopic load is transferred from one network to the next in these hierarchically prestretched multi-networks. In fracture experiment, the fluorescent signal of MC is present in a small volume in front of the crack tip for the materials in which SP is located in the second network but not for the materials where SP is in the third network. The fluorescent signal around the crack tip confirms the presence of two levels of damage at the crack tip: a first region further away from the tip where random sacrificial bonds breakage occurs and the load is still carried by the first network alone and a second region very close to the tip where the load is transferred to the second network before finally breaking causing crack propagation.

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Under the Smectic Blanket: Biaxial, Twist- and Splay-bend nematics revealed destabilizing the Smectic phase of Hard Boomerangs

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Self-Assembled Soft Matter

In 1970, Freiser [1] showed that systems of biaxial particles can undergo a transition to the biaxial nematic phase (N_b), a nematic phase in which both particle axes are aligned along two mutually orthogonal directors. In the following years, the N_b phase was predicted for various hard particle models: parallelepipeds, spheroplatelets, boomerangs, cuboids, prisms and rhombi. Despite the numerous theoretical predictions, the N_b phase resulted to be extremely elusive in experiments, its stability hindered by the competition with positionally ordered phases: only in 2004, more than 30 years after Freiser's prediction, the first experimental evidences of stable N_b phases were claimed for systems of "banana-shaped" bent-core mesogens [2,3].

These claims encouraged further studies on bent-core mesogens, kindling a "banana-mania" which led to the discovery of more than 50 novel liquid crystal phases, such as the twist-bend nematic phase N_{TB}. The existence of a N_{TB} phase was first postulated by Meyer [4] in 1976 as the result of the geometric frustration arising from bend deformations of the nematic director. Meyer realized that such frustration could be resolved via a complementary deformation of twist or splay, thereby postulating the existence of the twist- and splay-bend (N_{SB}) nematic phases. Later, Dozov [5] predicted the stability of the N_{TB} and N_{SB} phases for banana-shaped particles. Contrary to the N_{TB} phase, found in systems of banana-shaped particles both in experiments and computer simulations, no evidence of a stable N_{SB} phase has yet been reported in literature, raising doubts on its very existence.

The attribution of the rich phase behaviour of bent-core mesogens to their shape is questioned by a computational study of hard boomerangs by Lansac \textit{et al.} [6], who found large regions of smectic phase (Sm) in spite of exotic nematic phases, contributing to a fragmented picture inconclusive about the role of shape in the stabilization of N_b, N_{TB} and N_{SB} phases.

By means of an extensive theoretical and computational study of various models of bent particles, we show that the N_b, N_{TB} and N_{SB} phases of hard boomerangs are metastable with respect to the Sm phase. However, we find that if the positional order is destabilized, via polydispersity in the particle lengths or curvature in the particle shape, N_b, N_{TB} and N_{SB} appear as stable phases, thereby connecting the previous theoretical, computational and experimental results in a unified and consistent picture. More remarkably, we also report the first evidence of a stable N_{SB} phase.

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Temperature Dependent Aging and Yield of Drilling Fluids

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Processing & Stressed Soft Matter

Drilling fluids are designed to fulfil many functions over a wide range of temperature and pressure. Key amongst these functions are (i) providing a hydrostatic balance between the wellbore and formation during drilling, and (ii) carriage of the drilled cuttings to the surface. Hydrostatic balance is usually achieved by “weighting” the fluid, that is adding dense particles so that the overall fluid density is comparable to the formation density. Hence the fluid comprises both dense particles that are part of the formulation and less dense particles, i.e. the cuttings. For both sets of particles, when the circulating drilling fluid stops, they should remain suspended; i.e. the fluid is required to be viscoplastic. Typical formulations containing at least an oil, a brine emulsion and a clay together with emulsifiers and dispersants exhibit the full range of complex behaviour observed for simpler attractive colloid systems seen in the literature: aging, double yield, gel collapse and intermittency. Here we focus on the double yield behaviour. We find that, as a function of temperature the formulations exhibit a switch between a single yield behaviour and a double yield behaviour in both oscillation and shear-startup. Moreover, interpretation of MS-DWS reveals correlated changes in the detailed structural lengthscales. We tentatively interpret these results to indicate a crossing of the binodal boundary in the usual interaction strength – volume fraction phase space whereby the system switches between amorphous percolating gel and arrested phase separating gel states.

WAVE FRONT PROPAGATION SPEEDS IN A BACTERIOPHAGE - BACTERIA SYSTEM

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Active Soft Matter

Wave fronts are realised in many biological situations, and indeed a large number of physical systems. An understanding of such front propagation has applications to predicting the invasion rates of viruses into a healthy population, or the escape speed of a healthy species from an infected area. These applications are particularly important considerations for the use of bacteriophages (phages), viruses which predate on bacteria, to curb the populations of pathogenic bacteria. Given the serious threat of antibiotic resistance to the healthcare system in the future, phage therapies have been proposed as a potential solution. Understanding the spatial dynamics of the virus and bacteria will be vital information in the effort to control infections. To this end, a system of \textit{T4} bacteriophages invading a population of \textit{Escherichia coli} in a 1D channel were modelled using a system of coupled partial differential equations. In contrast to previous studies, which have either omitted spatial dynamics or considered stationary bacteria with other coupled fields (i.e. nutrient or phage concentration) to diffuse, the dynamics in this system assumes stationary phages and motile bacteria. This essentially assumes the bacteria swim and are not prone to significant biofilm formation as is often realised practically. This was investigated numerically and was found to display wave fronts converging to constant spreading speeds in all cases considered. Intriguingly, the viral infection can invade the population of \textit{Escherichia coli} in the absence of diffusion purely by commandeering the hosts. Furthermore, there appears to have been very few examples in the literature of fronts converging to constant propagation speeds into states which are growing exponentially. It was unexpected that the bacteria concentration exhibited near self-similar solutions whereas the phage concentration did not. With applications to food waste reduction and wound dressing, the bacteria were then modelled as propagating in a constant background of bacteriophages. The dynamics were again found to converge to solutions with wave-fronts tending to an asymptotic speed. Surprisingly, it was found that wave fronts in this scenario were significantly slower than the wavefront speed of the phage invading an exponentially growing population of bacteria. The numerical simulations are supplemented by analytic predictions of the asymptotic front speed. The ability for bacteria to evolve phage resistance is an important consideration in making more realistic predictions and was incorporated into the model. In addition to this, 2D simulations were also performed to investigate spreading on surfaces.

High dynamic range, bio-inspired stress-sensing in polymers

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Processing & Stressed Soft Matter

Stress-sensing in polymeric materials is an important tool in monitoring material integrity and in the study of their failure mechanisms. In recent years, the field of polymer mechanochemistry has established new routes to make polymeric materials that are able to report on their own stress, by tapping into the usually destructive mechanical forces on polymer chains to realise productive transformations. These materials allow us to relate macroscopic stresses to molecular-level processes.

Here, we present a bio-inspired stress-sensor for polymeric materials which contains two mechanochromic components: a spiropyran, which produces a (fluoro)chromophore under mechanical activation, and a photonic colloidal elastomer, which responds to force with a shift in its photonic bandgap as a result of the deformation of the crystal lattice. The structure is inspired by the skin of some cephalopods, which comprises tunable absorptive and photonic pigments. The combination of mechanophores expands the dynamic range of stresses in the material that can be monitored, as the photonic elastomer is responsive to smaller applied strains, whilst the spiropyran activates at a relatively high applied strain. We demonstrate how this sensor can be used for imaging stresses in mechanical situations in which the polymeric material exhibits a wide range of stresses, such as in the vicinity of a stress concentrator, or inclusion.

Hard times for hard spheres: Enhanced crystallization of the Laves phase from soft colloids.

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Colloidal & Granular Soft Matter

The binary $MgCu_2$ Laves phase consisting of a diamond and pyrochlore sublattice represents the best example of a colloidal crystal with an omnidirectional photonic band gap in the visible region at low refractive index contrasts. Although the Laves phase (LPs) has been shown to be stable for a binary hard-sphere mixture with a size ratio ranging from 0.76 to 0.84, colloidal LPs have never been observed to spontaneously crystallize in computer simulations nor in experiments with micron-sized colloids.

Here we show how softness changes this game. We find that the crystallization of the Laves phase is enhanced by a slightly soft-particle interaction, and we explain the absence of crystallization of the Laves phase in binary hard spheres by investigating the structure and dynamics. Since the free-energy differences among the three types of LPs – $MgCu_2$, $MgZn_2$ and $MgNi_2$ – are extremely small ($< 0.001 k_BT$ per particle), a random stacking of the different polymorphs is often obtained. Here, we reveal that the number of stacking faults can be reduced by using a seed of the target crystal structure.

General methodology to identify the minimum alphabet size for heteropolymer design

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Polymeric Soft Matter

The design of self-assembling systems is one of the most promising fields to build new smart materials, with applications ranging from energetics to catalysis and biomimetic scaffolding.

Heteropolymers are essential examples of self-assembling systems, where the final structure is determined \textit{via} a variable pattern (sequence) of a fixed alphabet of chemically different building blocks along the chain. The design is the process necessary to identify a sequence that drives the polymer to fold into a chosen target structure. In nature, proteins are the most versatile example of heteropolymers, and their outstanding self-assembling properties demonstrate the power of the so-called \textit{bottom-up} approach to self-assembly.

The technology for the synthesis and manipulation of synthetic heteropolymers is already advanced, and it is nowadays possible to synthesise polymers made of up to 7 different monomers with complex pattern arrangements (e.g. block copolymers). In previous publications, we have demonstrated that it is possible to design heteropolymer precisely to fold into target structures. The essential elements to allows the beginning of a new era of experimental polymer design are the identification of optimal building blocks and the minimum number of such building blocks to achieve the design.

\textbf{In this work, we introduce a general methodology to estimate the minimum number of building blocks (i.e., the alphabet size) necessary to design a heteropolymer. }The definition of the minimum alphabet $q_{min}=e^\omega$ was first given in the Random Energy Model (REM) (for a review see Pande \textit{et al.} Rev. Mod. Phys. 2000). ω is the conformational entropy per monomer of the system, defined as the logarithm of the total number of accessible, compact conformations per monomer. A direct calculation of ω for an off-lattice heteropolymer was never presented before and this work present the first example of such calculation.

\textbf{Hence we obtained the q_{min} for a generalised heteropolymer model and its dependency on the number of direction interactions per monomer and the size of the target conformational space.}

We verify that the directional interactions reduce ω, by introducing a methodology to calculate ω for off-lattice polymers based on the REM, and we confirm the theory by comparing with designability characterisation results in previous works. Then, by enlarging the ensemble of possible target structures, we calculate the larger q_{min} needed to design less favoured structures. Thus, we show how much variability of different structures can be ensured for different numbers of patches, to individuate the best candidates with the highest variability of different conformations.

\textbf{We use our results to identify optimal chemical monomers for the synthesis of designable heteropolymers.} We classified conventional synthetic polymers according to the number of potential backbone hydrogen bond per monomer. Such results provide a guideline for future experiments as they indicate explicitly which chemical species can be used to construct designable backbones. \textbf{In particular, we identified polyurea, polyamide and polyurethane residues as optimal candidates. }

Surface Active Microgels: a step towards soft stabilisers

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Arrested Soft Matter

Microgels are soft particles composed of cross-linked networks of polymers. A unique property of microgels is their ability to swell when dispersed in specific solvents. The size of microgels varies from several micrometers (‘swollen’) down to nanometers (‘unswollen’). ‘Unswollen’ microgels bear similarities to hard colloids, however, when ‘swollen’ they act as soft particles. The rheology of microgel suspensions can be tuned by causing the microgels to swell or de-swell. The ability to manipulate the rheology of suspensions has led to microgels being abundant in a number of industrial applications such as food, pharmaceuticals and cosmetics [1].

In this work we studied a commercially available microgel which is composed of a polymer called Sepimax Zen [2]. Sepimax Zen is a block copolymer which has both hydrophobic and hydrophilic components and acts as an associative thickener. In this work we studied the microgel in bulk to understand how the microgel particles influence the rheology of suspensions.

Microgel suspensions were analysed using a combination of rheology and various microscopy techniques. Our results reveal the microgel particles go through distinct structural changes as polymer concentration is increased. In the dilute regime (‘swollen’) microgels do not interact whereas in the concentrated regime they start to interact and deswell, eventually behaving as a ‘soft-set glass’. This attraction being due to the hydrophobic parts of the Sepimax Zen molecules. These changes directly affect bulk properties of the suspensions such as yield stress and viscosity.

Given Sepimax Zen’s amphiphilic nature, future work will focus on how microgels behave at interfaces. Sepimax Zen was found to stabilise oil-in-water emulsions against creaming and coalescence. Initial findings indicate that this behaviour is distinctly different to hard particles most probably due to this unique properties of the microgel particles [3].

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Domain formation in compaction of a semiflexible polymer

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Polymeric Soft Matter

Packaging configurations of a semiflexible polymer chain inside a constraining enclosure are relevant in different contexts, spanning a range of problems from physical virology such as nanoscale energetics of genome packing in bacteriophages, and then all the way to macroscopic elasticity of thin wire morphologies in spherical cavities. The usually assumed optimal solution to this packing problem is a single spool configuration.

Here we show, using analytical field theory and molecular dynamics simulations, that for a long, thin, worm-like chain polymer confined to a spherical cavity the single spool configuration is not optimal. Instead, the optimal (minimal bending energy) packing is given by a configuration best described by 3 perpendicular concentric spools.

Moreover, including non-linear elasticity effects, corresponding to DNA, yields an even richer behaviour with a single polymer forming a mixture of spool-like and nematic-like domains.

These findings are consistent with experimentally observed domain formation of DNA packing in viral capsids.

Microscopic pathways for stress relaxation in repulsive colloidal glasses

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Arrested Soft Matter

Generally, when a disordered system is carried in the glassy state, a certain amount of residual stresses will be trapped in the glass's volume. The presence of such residual stresses can influence various physical properties, sometimes with extreme results like for example in the historical case of prince Rupert's drops. However, the interplay among these stress fields and the microscopic dynamics is still an open research field. It is known that the dissipation of internal stresses is at the origin of the particle mobility at small length-scales in many different systems close to or fully in the glassy state, e.g. metallic glasses [1], colloidal glasses or collapsing gels [2]. Typically, the residual stress field is randomly distributed across the sample volume, but what happens when it possesses a definite symmetry?

In this talk I will present XPCS results obtained on a colloidal glass of repulsive silica nanoparticles dispersed in a water-lutidine 2.6 mixture. We observed that even in this class of materials the residual stress field gives rise to a very rich phenomenology in the observed dynamical properties as the presence of compressed relaxation functions and ballistic dynamics. Moreover, thanks to the relatively small number of particles in the scattering volume, we were able to characterize dynamical heterogeneities as a function of both lag time and exchanged wave-vector [3]. The picture which emerges is one where the macroscopic stress stored in this colloidal glass relaxes via the cooperative motion of groups of particles with a characteristic size of the order of ten particle diameters.

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Inter-protein forces as a cell-membrane organization principle

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Living Soft Matter

Several mechanisms have been proposed in the biophysics and biology literature to account for the existence of protein nanodomains (or nanoclusters) in biomembranes, as evidenced by electronic microscopy, single-molecule tracking fluorescence microscopy, and more recently super-resolution microscopy. Here we focus on the role of nanometer-range inter-protein forces mediated by the membrane. They arise from both to its elastic properties and its rich lipid composition. We show that such forces are capable of explaining many properties of nanodomains, among which their typical size and their biologic specificity, without necessarily appealing to a pre-existing lipid micro-phase separation. However, the role of lipids remains essential because they contribute to the specificity of interactions and thus to the biological specialization of domains. We propose analytic arguments together with numerical ones, using a multi scale approach where we compare results from a mesoscopic vesicle model (with Monte Carlo sampling) and coarse-grained molecular dynamics (MARTINI force field). We discuss the role of the different physical parameters (membrane tension, spontaneous curvature, line tension between phases). The role of membrane recycling is also discussed in this context.

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Confocal microscopy study of the interaction between particle-stabilised droplets and a solidification front

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Interfacial Soft Matter

Particle-stabilised or Pickering emulsions are widely used in the food and personal care industries and are present in common household products such as homogenised milk and food spreads [1]. In addition, Pickering stabilisation has been suggested as a method of increasing product shelf life over surfactant stabilisation [2]. It is therefore important to characterise the behaviour and stability of Pickering emulsions subjected to processes used in industry and everyday life.

Freezing is one process of interest as it is used both for product transport and the extension of shelf life. In particular, directional freezing is notable as a technique used in applications such as materials processing and production of aligned porous structures because of the enhanced level of structural control via tunable crystal growth directions and velocities [3].

Using confocal microscopy combined with a directional freezing temperature stage, we investigate the behaviour of particle-stabilised water droplets interacting with a hexadecane solidification front. The interaction is imaged in 4 dimensions (xyzt), allowing us to observe the movement of particles on the droplet interface as a droplet is trapped by the freezing front. We then study the effects of the interfacial particles on the dynamics of the droplet engulfment in the front. Our results show that droplets with a low surface coverage of particles are not engulfed as easily as those with a high surface coverage. In addition, droplets are typically deformed during engulfment as they are not immediately surrounded by the solid upon contact but are rather partially trapped and stretched as a result of the moving front. This suggests that the primary mechanism behind droplet engulfment is the trapping of individual particles on the droplet surface rather than the droplet as a whole.

Apart from illuminating the stability of particle-stabilised emulsions under one specific industrially relevant process, more generally our results highlight the importance of interfacial particles in determining emulsion droplet behaviour during interactions with a freezing continuous phase. This is one key factor in determining whether the advantages of Pickering stabilisation still stand in the context of any freezing process.

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Microscopic Force Measurements in Colloidal Gels

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Arrested Soft Matter

\begin{confabstract}

Understanding transmission of microscopic stresses in colloidal gels is crucial to unravel the origin of gel collapse, design colloidal networks with superior mechanical properties and therefore increase the shelf life of commercial products.

In this study, we employed colloid-polymer mixtures as model system and performed three-dimensional particle-resolved characterisation using confocal microscopy\cite{Zhang}. Due to the solvatochromic dye used in the system, fluorescent signals from colloidal oil droplets and interfaces are able to be distinguished and separately detected, this enables us to identify contacts between droplets. From confocal images we used particle tracking algorithms to track coordinates of particles and contacts, and calculated interdroplet forces based on the size of deformation area\cite{Brujic}\cite{Princen}. From interdroplet forces, we computed stress tensor for each particle, and found force chains, which tells how stresses are transmitted, in the gel. We also performed local structural analysis using Topological Cluster Classification (TCC) and packing anaysis for all gel samples, in order to find the correlation betwee force distributions and structural characteristics\cite{Malins}.

\end{confabstract}

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Nanocomposites Drying : Structural Evolution from Solution to Solid

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Polymeric Soft Matter

Nanocomposites Drying : Structural Evolution from Solution to Solid

Keywords : Nanocomposite, Polymer, Silica, Drying, Structure.

The dispersion of nanoscale inorganic fillers within a polymer matrix may potentially lead to a significant improvement of some of its mechanical properties. One of the methods used to prepare these nanocomposite materials relies on solvent evaporation. We chose a system based on a polymer, poly(methacrylic acid), silica nanoparticles and water. In this system, the polymer conformation can be tuned from compact coils to extended coils by changing the pH whereas the polymer-silica interactions are controlled using different surface modifications on silica nanoparticles.

The purpose is to monitor the drying of these materials and to study their evolution towards the solid state. The results obtained should help understanding the mechanisms involved during drying, their impact on the charge organization and on the mechanical behavior of the final nanocomposites.

Phase diagrams of polymer-silica mixtures in solution were determined in order to define the conditions under which phase separation occurs. Every phases were then characterized by Small Angle X-ray Scattering (SAXS) which allowed us to get information about silica’s organization.

A drying study was also performed at the nanoscale, in-situ structural characterizations were carried out by SAXS during the drying process. A characteristic peak related to the silica nanoparticle organization appears above a critical silica concentration. These structures are strongly depending upon system’s parameters. Either a compact structure or a fractal structure is obtained according to polymer conformations, that is compact coils or extended coils conformations respectively. The compacts structures are very similar regardless of the silica nanoparticles used while the fractal structures show a fractal dimension depending on pH and on the nature of the silica nanoparticles in use.

Next step of this work will be to correlate the structural properties of the solid materials to their mechanical characterization.

A geometric model for the erosion and fragmentation of polymers in the ocean.

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Polymeric Soft Matter

Pollution of the ocean by plastic litter has become a major environmental problem : when mismanaged, plastics enter the environment where they undergo degradation and fragmentation into microplastics that are now ubiquitous in all aquatic compartments. In addition to the fact that microplastics are impossible to remove from the marine environment, they are even more damaging for the ecosystems than the macroscopic waste.

The fate of polymers in aquatic environment depends both on abiotic phenomena (UV, mechanical stress), and on biotic ones, due to the colonization of plastics by micro-organisms. A primary step for bio-degradation is the constitution of a biofilm and reduction of the polymer chain length via exo-enzymes produced by bacteria from the biofilm. Once polymer chains are short enough, they can be assimilated by bacteria. While abiotic phenomena lead to the damage and fragmentation of a polymer by oxidation and hydrolysis mechanisms, creation of structural defects and fracture propagation, it is generally admitted that only biotic phenomena will result into the complete bio-degradation of a polymer, i.e. its conversion into biomass, water and CO2. In the marine environment, many questions remain about the relative kinetics of abiotic and biotic degradation and their respective impact in terms of fragmentation. For instance, several papers have recently reported that the size distribution of particles collected in the ocean between 5mm and a few hundreds of microns, does not seem to correspond to a single-kinetic fragmentation process.

We studied the enzymatic erosion process in semi-crystalline polymers to understand the potential fracture and fragments generation in relation to the formation of erosion patterns. Being specifically interested in the role of heterogeneities at the scale of a few nanometers to a few micrometers, we used a polymer of a given chemical composition and monitored its morphology through its change in crystallinity ratio, everything else remaining constant. We used the well-known model system PDLLA/proteinase K. Enzymatic erosion kinetics were measured through weight loss experiments and erosion patterns were observed over time through atomic force microscopy (AFM) and SEM.

In order to interpret the results, we combined a simple two-phase geometric erosion model with the well-known Michaelis-Menten model for enzymatic kinetics. Our geometric erosion model is based on the evolution of the erosion front with time induced by the erosion rate difference between crystalline and amorphous regions. This new model accounts very well for the experimental results and unexpectedly predicts that after a lag time, the final erosion rate will be the one of the fastest eroding phase. Moreover, we observed a morphology-dependent release of fragments, which the model is also able to predict. In particular, one observes the release of spherulites as long as they are smaller than a critical size determined in the model.

Some important consequences relevant for the understanding of the formation of micro-plastics in the ocean can be drawn from these results.

Sorting cells in microfluidics based on their intrinsic properties

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Processing & Stressed Soft Matter

Sorting cells based on their intrinsic properties is a highly desirable objective, since changes in cell deformability are often associated with various stress conditions and diseases. Deterministic lateral displacement (DLD) devices offer high precision for rigid spherical particles, while their success in sorting deformable particles remains limited due to the complexity of cell traversal in DLD devices. We employ mesoscopic hydrodynamics simulations and microfluidic experiments to better understand flow properties of red blood cells (RBCs) traversing through different DLD devices. In particular, we demonstrate prominent advantages of sharp-edged obstacles for probing deformability properties of RBCs. Furthermore, we will illustrate how single cell dynamics governs its motion through DLD devices, which can serve as a possible sorting strategy. Interestingly, good sensitivity to changes in intrinsic properties of RBCs requires fine-tuning of flow conditions, including flow strength and device geometry. We expect that similar mechanisms should be applicable for the development of novel DLD devices that target intrinsic properties of many other cells.

Colloidal SU-8 polymer rods for three-dimensional confocal imaging and optical tweezing

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Making & Measuring Soft Matter

Colloidal rod-like particles have been used as a powerful model system to study liquid crystalline (LC) behaviour. Already a wide range of colloidal LC-forming systems have been developed including TMV and fd-virus particles, PMMA ellipsoids, boehmite rods, and silica rods. In recent years, confocal microscopy has become an increasingly popular technique to obtain three-dimensional (3D) real space information on the structure and dynamics of concentrated colloidal dispersions. This technique has also been applied to study dense suspensions of rods including PMMA ellipsoids [1], silica rods [2] and fd-virus particles [3]. However, the small dimensions of fd-virus particles, the large mass density of the silica rods and the limited yield and deviation from the ideal rod-like shape of the PMMA ellipsoids, make 3D confocal experiments with tuneable effects of gravity at the single particle level cumbersome.

Here, we describe the bulk synthesis of fluorescent colloidal SU-8 polymer rods with tuneable length and diameter that are stable in both aqueous and apolar solvent mixtures. The colloidal SU-8 rods are prepared by shearing an emulsion of SU-8 polymer droplets [4] and then exposing the resulting non-Brownian rods to ultrasonic waves, which breaks them into colloidal rods with typical lengths of 3.5 - 10 μm and diameters of 0.4 - 1 μm. By varying the composition of the solvent mixture, both the difference in refractive index and mass density between the particles and the solvent can be independently controlled. This enables the use of colloidal SU-8 rods in both 3D confocal microscopy and optical trapping experiments, and even in experiments combining both techniques. We demonstrate this by imaging the liquid crystalline phases and the isotropic-nematic interface formed by the colloidal SU-8 rods. In addition, we show the optical trapping of single SU-8 rods in water and the simultaneous optical manipulation and confocal imaging of multiple rods in the isotropic phase.

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Optimizing dissipation in active matter: dynamical phase transitions, clustering and collective motion

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Active Soft Matter

In contrast with systems driven by an external field, energy dissipation in active matter is local and independent for each particle. This leads to new dynamics and phases, such as clustering with purely repulsive interactions and collective directed motion. While these phenomena have been studied extensively, understanding how the local dissipation affects the collective dynamics, and its connection with entropy production [1, 2], has remained an elusive goal.

Based on methods of large deviations, we explore how tuning the dissipation, as an independent parameter, modifies the emerging collective behavior. This amounts to a change of ensemble where individual trajectories are biased in terms of their dissipation. By deriving an auxiliary dynamics which effectively realizes the dissipation bias, we put forward a microscopic mechanism which promotes clustering at low dissipation [3]. Moreover, the direct sampling of the biased ensemble reveals the emergence of a collective moving state at high dissipation, despite the absence of aligning interactions [4]. We combine heuristic and analytic arguments to rationalize the dynamical phase transitions between these states.

Overall, our results shed a new light on the control of collective properties by local dissipation. They open the door to the search of new phases and dynamics, as well as unexpected transitions between them, in biased ensembles of active matter.

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Structure and Dynamics of Single-Chain Polymeric Nanoparticles under Shear Flow in Dilute and Concentrated Solution

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Polymeric Soft Matter

Understanding the flow properties of macromolecular objects in solution is a problem of broad interest due to its relevance in many areas of soft matter, engineering, and biophysics as, for example, microfluidics, extrusion, or blood flow. There is nowadays strong evidence that the nonequilibrium conformations and reorientational dynamics under shear flow have a strong, and sometimes even dramatic, dependence not only on the concentration and shear rate but also on the specific macromolecular topology.

We use a multiscale hydrodynamics simulation approach to study, for the first time, single-chain polymeric nanoparticles (SCNPs) under shear flow. SCNPs are a new class of macromolecular objects, synthesized through purely intramolecular cross-linking of single polymer chains, with enormous potential for use as, e.g., biosensors, catalysts, drug delivery vehicles or rheological agents. They are topologically polydisperse, exhibiting a broad range of architectures from nanogel-like networks to sparse irregular multi-loop objects [1]. We investigate the case of unentangled, irreversible SCNPs (permanent cross-links) over the whole concentration range, from high dilution to crowded solutions (40% of volume fraction). SCNPs emerge as a novel class of macromolecular objects with response to shear distinct from other systems such as linear chains, star polymers, rings, or dendrimers. This is evidenced by the observed set of scaling exponents for the shear rate dependence of the SCNP static and dynamic properties (components of the inertia tensor, orientational resistance, rotational frequency, viscosity, etc) [2]. Surprisingly, these exponents are, at most, marginally dependent on the specific topology of the SCNP (globular or sparse), suggesting that they are inherently related to the network-like character of the molecular architecture and not to its specific connectivity. At high shear rates the dynamics of the sparse SCNPs is dominated by tumbling motion. Coexistence of tumbling and tank treading is observed for the most globular SCNPs [2].

SCNPs in solution show shear thinning at all concentrations. The concentration dependence of the scaling properties of SCNPs under shear flow exhibits remarkable differences with those of more simple topologies as unentangled linear chains or star polymers. Whereas for the latter the scaling exponents are marginally dependent on the concentration [3,4], two clearly different scaling regimes are found for the SCNPs below and above the overlap concentration. This finding is inherently related to the conformational changes experienced by the sparse SCNPs in equilibrium concentrated solutions [1], which are characterized by an entropically driven collapse to the so-called fractal globular state, as opposite to the milder transition from self-avoiding to gaussian conformations in linear chains or stars.

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Tracking the Molecular Organisation of Water and Alcohol Mixtures at Hydrophobic Solid Interfaces

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Self-Assembled Soft Matter

Mixtures of water and alcohol are used in many fields where they play vital roles as solvents, reagents, in catalysis, surface treatments and in fuel cells. We have recently shown that at the interface with a hydrophobic solid such as highly oriented pyrolytic graphite (HOPG), water-methanol mixtures spontaneously nucleate stable supramolecular assemblies at room temperature [1]. Despite being only physisorbed on the surface of the graphite, these structures are robust, being stabilized by an extended network of hydrogen bonds. Their presence can dramatically affect the properties of the interface, potentially leading to significant consequences for applications using graphitic material immersed in aqueous solutions where methanol can spontaneously form [2]. There is hence a need to better understand the properties, evolution and molecular arrangement of these structures, as well as their stability in different environments.

Computational analysis of the monolayers indicates the alcohol-water assemblies have a wide variety of energetically favourable configurations with low free energy barriers for transitions between them [1]. Perturbing the system in a controlled manner could therefore shift the molecular self-assembly in new, desirable directions.

In this work we demonstrate that by doping the system in a controlled manner it is possible to direct the self-assembly of small hydrogen bonding molecules down different energetic pathways to create reproducible structures unique to the composition of the interfacial liquid. We explore the effect of adding potassium chloride, disodium hydrogen phosphate, phosphate buffered saline (PBS) and larger monohydric alcohols on the development and evolution of molecular structures. Using atomic force microscopy to map these structure in-situ with high-resolution we identify different supramolecular patterns and gain insights into the molecular arrangements. Three-dimensional scanning force microscopy (3D-SFM) [3] is then used to explore the hydration profile of the interfacial liquid and demonstrate the 3D structure of the multi-molecule assemblies. The experimental results are complemented by molecular dynamics simulations to verify our 3D picture of the interfacial liquid.

Our results reveal the importance of the alcohols in the molecular assemblies as well as an interesting competition between the intermolecular hydrogen bonded network and interactions with the surface. We believe that this research will have an exciting impact on the ever evolving field of controlled molecular self-assembly and nanoscale surface treatments.

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Strongly heterogeneous motion at the depinning transition in dense dispersions

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Arrested Soft Matter

We study the force driven motion of microscopic probe particles in glasses using experiments, simulations and mode coupling theory. We show that structurally homogeneous glasses, displaying only weak dynamic heterogeneities in the quiescent state, are dynamically heterogeneous when the motion of the particles is driven by an external force. Our experiments are performed on a near-ideal model system for hard sphere dispersions. Beyond a threshold force we observe intermittent dynamics and bimodal displacement distribution functions. For smaller forces, linear response connects the particle mean displacement and quiescent mean squared displacement. Our findings highlight the important differences between quiescent and driven motion in crowded environments.

In the experiment a polystyrene probe particle is immersed in an emulsion glass composed of droplets of the same size and pulled with a laser line trap [1]. For sufficiently dense emulsions, the hard-sphere like droplets mutually hinder their motion so that they are effectively arrested and form a glass. With active microrheology we can study the local analogue of yielding: For large forces the probe can break free and delocalize. We characterize the strongly intermittent motion. In theory or simulation, the motion of the probe particle is characterized by a time-dependent probability distribution, the so called van Hove function. It correlates the positions of the particle for different times. It is calculated based on stochastic dynamics, simplified in a Zwanzig-Mori approach, and approximated within mode coupling theory [2]. Additionally, Langevin dynamics simulations are performed.

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Random-packed structures of rings as a model system of Soft Matter problems

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Polymeric Soft Matter

Unraveling the packing structure of dense assemblies of semiflexible rings is not only fundamental for the dynamical description of polymers rings but also key to understanding biopackaging, such as observed in circular DNA inside viruses or genome folding.

In this work, we use X-ray tomography to study disordered packings of rubber bands in cylindrical containers. Using advanced computational tools we detect and study the rings configurations in the packings, characterizing the system at geometrical and topological level. The degree of entanglement in the structures is quantified through minimal surfaces and generalized Voronoi tessellations, allowing the identification of band's threadings and neighbors.

We found that packings of short bands conform a liquid-like disordered structure, with short-range orientational order and a minor influence of the container. On the contrary, for longer rings, confinement forces the band's folding and the rings interpenetrate and entangle. Most of the systems are found to display a threading network which percolates the system. Interestingly, for long bands whose diameter doubles the diameter of the container, we found that all bands interpenetrate each other, in a complex fully-entangled structure.

Phase transition behaviour in single solid-supported lipid bilayer

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Living Soft Matter

Solid-supported lipid bilayers (SLBs) are widely used tools in biological- and technological-oriented studies, for the investigation of interactions and molecular processes involved in cell functioning, diseases and for sensing applications. Coexistence of ordered and disordered domains, structural and dynamical coupling between leaflets and the structural responses to changes in the environmental parameters such as temperature, are of fundamental interests in all these scientific fields. Moreover, SLBs are one of the prototype of natural self-assembling systems.

We applied time- and temperature-resolved neutron reflectometry for the real-time characterization of the structural changes taking place across phase transitions in SLBs. This new method allowed to determine the presence of an isothermal phase transition, characterized by a symmetrical rearrangement of lipids molecules in both bilayer leaflets, followed by a thermotropic phase transition characterized by an independent melting of the two leaflets. Contrary to recent results on similar samples by atomic-force microscopy we demonstrate that the presence of a substrate equally increases the enthalpy of melting for both SLB leaflets with respect to that reported for free standing bilayers. These results are of extreme importance for the further understanding of cooperative structural dynamics in SLBs and for their use in biophysical and biological studies, as for example, for the investigation of thermally activated processes as the lipid flip-flop.

Unjamming overcomes kinetic arrest in terminally differentiated cells and promotes collective motility of carcinoma

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Living Soft Matter

Even though densely packed cell in tissues are normally in a jammed, solid-like state, key biological processes, such as wound healing, branching morphogenesis and cancer invasion, involve collective migration of cells and cellular rearrangements. One recent unifying framework to account for the biophysical changes leading to the acquisition of collective motility and enabling structural remodeling is the so-called unjamming transition [1] by which a solid tissue can locally flow to allow for the collective motion of small groups of cells that retain an epithelial phenotype, i.e. that maintain adhesion with neighboring cells. Importantly, the same mechanisms capable of overcoming the jammed, kinetically arrested state of late stage aggressive tumors may also promote dissemination and cancer metastasis without the need to invoke changes of identity and complex transcriptional rewiring programs, as in the well-known epithelial to mesenchymal transition scenario [2]. The biomolecular machinery behind unjamming, its physiological and clinical relevance remain, however, largely unexplored.

Here, we combine biophysical and biochemical analysis with numerical modelling to investigate the unjamming transition in a variety of epithelial 2D and 3D collectives: monolayers [3-5], differentiated normal mammary cysts [6-7], spheroid models of breast ductal carcinoma in situ (DCIS), and ex vivo slices of orthotopically-implanted DCIS [7]. In all cases, unjamming, initiated by the elevation of the small GTPase RAB5A, a master regulator of endocytosis, occurs via the acquisition of a flocking-like coordinated motility mode that in 3D takes the form of a collective rotation of the cell assembly.

Beyond accurately characterizing the biochemical pathway that drives unjamming, we also investigate the consequences of the resulting highly coordinated collective cell motility when cells are in confined 2D and 3D geometries. By reconstructing the spatial distribution of the fluctuating mechanical stresses induced in the matrix and by monitoring its microstructural remodeling, we show that collective motility invariably translates into a significant mechanical action on the extracellular matrix, providing a physical mechanism to initiate and enable collective invasion and dissemination.

The microscopic role of deformation in the dynamics of soft colloids

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Arrested Soft Matter

Unraveling the glass transition and jamming in soft colloidal systems remains a challenge for modern soft matter physics. An important open question is whether softness controls the dynamics in such dense conditions [1]. Numerical simulations represent a strong ally to elucidate this problem, but in most cases softness is tuned by modifying the pair-potential parameters allowing particles to overlap to a certain extent, while neglecting crucial aspects that contribute to the elastic properties of realistic particles. This makes the concept of "softness" in simulations and experiments very different. To fill this gap, I will discuss a new model of 2D elastic polymer rings with tunable softness which undergo substantial deformation at high densities. The ability to deform has a strong impact on the dependence of the relaxation time on the packing fraction which changes from fragile-to-strong. In addition, dynamics is controlled by an intermittent particle motion that gives rise to a compressed exponential decay of the self-intermediate scattering function. This behavior can be rationalized in terms of deformed rings that act as internal source of stress, in agreement with previous works on colloidal gels[2]. This simple model thus provides microscopic insights into two mechanisms which are of deep interest in soft matter: the fragility dependence on softness and the occurrence of a compressed exponential decay in dynamical correlation functions [3].

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The microscopic origin of the rheology in supramolecular entangled polymers

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Polymeric Soft Matter

Supramolecular polymers offer enhanced properties as stimuli- and/or thermo-responsiveness due to transient interactions between the monomeric building blocks provided by supramolecular “functional” groups. Thus this class of polymeric materials is used for various applications that require a precise control of the mechanical behavior as sensors, coatings, shock absorbers or construction materials. A prerequisite do design this interactive materials in a reasonable manner is a fundamental understanding of the underlying physical processes. Via a multi-methods approach it was managed for the first time to relate the macroscopically observed mechanical response, detected by small amplitude oscillatory shear rheometry (SAOS), to its physical origin, using urazole functionalized entangled polyisoprene as a model system. The Gaussian chain conformation of the randomly functionalized chains was proven by small-angle neutron scattering (SANS). The temperature dependent lifetime of the urazole H-bonds and the related activation energy of the dissociation process was investigated by broadband dielectric spectroscopy (BDS), while differential scanning calorimetric measurements (DSC) were used for a detection of the glass transition behavior. The H-bond lifetimes (dielectric α^*-process) and the rheological response in terms of the loss modulus G'' differ by 2 orders of magnitude in time. Within the concept of a compact random walk, where the random walker (urazole group acting as a sticker) undergoes multiple returns to its starting point and following the concept of theoretical proposed renormalized sticky bond lifetimes, we quantitatively solve this longstanding and unexplained large discrepancy: While the bond opening gives rise to the dielectric response, for rheological relaxation the association with a new partner is relevant. This takes place only after multiple returns to the original binding partner [1],[2].

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Unipletion in colloid--polymer mixtures

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Polymeric Soft Matter

Addition of polymers to a colloidal dispersion modulates the interactions between the colloids. The precise effect on the colloidal phase behaviour sensitively depends on the effective colloid--polymer interactions. We present a theoretical framework to predict the phase behaviour of colloid--polymer mixtures for varying affinities between colloid and polymer, leading to either polymer depletion to adsorption. For certain conditions, polymers are neither depleted nor adsorbed: the polymer concentration is essentially constant up to the colloidal surface, a condition which we term ‘unipletion’. Near this condition, the calculated phase diagrams reveal a stable--unstable--restabilisation transition with increasing polymer concentration. Similar effects have been reported experimentally, for instance as a function of temperature [Feng \textit{et al.}, \textit{Nat. Mat.}, 2015, \textbf{14},61–65], which may modulate the effective polymer--colloid affinity. Understanding unipletion opens up the possibility of preparing highly dense, yet stable, colloid--polymer mixtures.

Investigating the aging of model liquid infused porous surfaces

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Interfacial Soft Matter

Slippery liquid infused porous (SLIP) surfaces are a new breed of bio-inspired materials that are being explored as anti-fouling coatings for use in the medical and marine industry. Despite their success as self cleaning surfaces, they are still poorly understood and more work is needed to understand the complex interactions between the porous matrix, the infused liquid and any fouling particles or droplets. In particular understanding how the surfaces age when they are subjected to external perturbations would be useful when considering the environments that SLIP surfaces are required to function in. An example may be that of a SLIPs coating for a ocean liner which would be required to survive the mechanical stresses of waves as well as the corrosive behaviour of the saline environment.

Here, a model liquid infused surface is used, fabricated with commercially available hydrophobic nano-particles (Glaco Mirror Coat™ [1]) and infused with silicone oil. This allows low cost surfaces to be easily made as test-pieces to study SLIP surface behaviour. Using a combination of atomic force microscopy (AFM) and contact angle measurements, the surfaces are studied in detail to investigate the impact of ageing on the surface performance and nano-structure.

It is found that when the surfaces are exposed to prolonged pressure perturbations or to saline solutions the surfaces become less reliable and exhibit high variability in contact angle measurements. The surface struggles to retain its self healing properties, leading to a patchy oil layer, which affects the contact angle of a droplet on the surface by increasing the surface roughness and inducing pinning. Comparing this model system to other SLIP surfaces may be useful in predicting the effect of certain environmental pressures on SLIP surfaces and explain some of the behaviours observed.

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Chirality-Controlled Self-Assembly via Topological Defects

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Self-Assembled Soft Matter

Chirality plays an important role in science from enantiomeric separation in chemistry to chiral plasmonics in nanotechnology. However, the understanding of chirality amplification from chiral building blocks to ordered helical superstructures remains a challenge. Here, we demonstrate that topological defects, such as screw dislocations, can drive the chirality transfer from particle to supramolecular structure level during the self-assembly process (1). By using a model system of chiral particles, which enables direct imaging of single particle incorporation into growing crystals, we show that the kinetic pathway is the key parameter for monitoring, via the defects, the chirality amplification of the self-assembled structures from racemic to predominantly homohelical. We provide an explanation based on the interplay between geometrical frustration, racemization induced by thermal fluctuations, and particle chirality. Our results demonstrate that screw dislocations not only promote the growth, but also control the chiral morphology (2) and therefore the functionality of soft and hard materials.

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Model of ciliated-cell collective behavior and mucus transport in bronchial epithelium

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Living Soft Matter

In the lungs, the airway epithelial surface is covered by mucus, a viscous fluid providing a physiological barrier against foreign inhaled particles and pathogens. As a result of active ciliary beating on the epithelium, the mucus is transported along the bronchial tree until its elimination by swallowing or expectoration. This process, referred to as mucociliary clearance, is a crucial mechanism for the self-defense of the respiratory system; its deficiency is related to chronic respiratory diseases as severe asthma, chronic obstructive pulmonary disease and cystic fibrosis.

The effective transport of mucus requires a coherent large-scale organization of the ciliary activity. Especially, a long-range alignment of the beating orientation is expected. Yet ciliated epithelia can exhibit non-homogeneous and transient patterns of beating orientation. In addition, recent experiments have suggested that hydrodynamic interactions can have an important impact on the emergence of such patterns.

A simple physical model is proposed to address the possible emergence of large-scale beating-orientation patterns due to hydrodynamic interactions. The mucus flow is assumed to be two-dimensional, in a plane parallel to the epithelium. The effect of ciliary beating is modeled by local momentum sources, whose orientation is driven by an alignment rule with respect to the nearby flow. The flow is modeled by the Navier-Stokes equations and predicted using numerical simulations.

Model solutions exhibit several patterns, including a swirly pattern similar to that observed experimentally and a fully aligned pattern that is optimal for mucus transport. This supports that the flow can carry the necessary information for large-scale organization. The possible emergence of preferential directions is studied, and the implications for the comprehension of natural systems is discussed.

Jamming in star polymer solutions and melts

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Arrested Soft Matter

The properties of star polymers are governed by arm size and branching functionality. They can be viewed as the extreme case of grafted nanoparticles when the core size tends to zero. In solution, osmotic pressure pushes the solvent inside the particles causing a tenfold increase of the hydrodynamic size, similar to what is observed in microgel particles. These features make star polymers ideal model particles for the study of soft colloids, offering the ability to explore the whole range of concentrations, from dilute solution to the melt.

Here, we report unexpected rheological features arising for the extreme case of very high branching functionality (f≈900) and very short arm size (Ma=5.8 kg.mol-1). Comparing the melt properties of these very dense stars with data available in the literature for lower branching functionalities, we find that their dynamics is characterized by remarkable properties: the absence of terminal regime in the accessible terminal window; a low frequency plateau modulus which is approximately 10 times smaller than the value at the polymeric plateau. We attribute these properties to the colloidal jamming of the stars.

We further investigate the dynamics of the stars when solvent is added, down to the liquid state. We find a striking resemblance to jammed microgel suspensions at intermediate concentrations, while the high concentration regime is distinct, probably because of the interpenetration of the star polymers that eventually leads to the formation of entanglements. Their transient shear response exhibits distinct polymeric and colloidal features, such as two stress overshoots, two yield stresses/strains and a Herschel-Bulkley behaviour which set them apart from other soft colloids such as microgels. These results reveal how the interplay between different ingredients of softness – particle elasticity, entanglements and osmotic compression – is essential to colloidal matter.

Understanding the helix pitch of the equilibrium cholesteric CNC phases

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Self-Assembled Soft Matter

Cellulose nanocrystals (CNCs) are nanorods of crystalline cellulose that can be easily dispersed in water, thanks to their negative charged surface groups. CNCs are emerging as a new class of functional material due to their fascinating ability to form liquid crystalline phases–of chiral nematic type, N*– after reaching a critical concentration. The chiral nematic phase is characterized by a long-range orientational order of the particles with a helical modulation of the director in which they align. The local alignment orientation is referred to as the director and the distance for which the director rotates until it completes a full rotation is known as pitch, p.

The number of experimental studies on helix formation in CNC suspensions is rather small, all reporting a decrease in p with increasing the particle concentration, w. Unfortunately, at a threshold w_g ≈ 10 wt.%, the macroscopic CNC suspension gets arrested into a gel state, with w_g lower than the threshold for reaching 100% liquid crystalline state. The latter situation is a limitation for a deeper study since the helix formation is restricted only to a narrow CNC concentration range.

However, due to the notorious dispersity in aspect ratio, the phase separation is accompanied by a spontaneous fractionation: rods with high aspect ratio preferentially enter the N* phase, whereas the short rods remain in the isotropic fraction. By repeating this liquid crystal formation-driven fractionation, we have succeeded in significantly reducing CNC dispersity and extent the chiral nematic regime, allowing the access to a broader CNC concentration range.

We found that the aspect ratio largely impacts the transition from the isotropic to the N* phase. However, p seems not to be significantly affected. Therefore, the changing p within this regime suggests that it is the increasing concentration of counterion–attracted by the negative surface charges–that drives the change, which is confirmed in our experiments.

Acoustic confinement of swimming bacteria

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Active Soft Matter

Studies on Acoustic Manipulation of active biological objects like bacteria or microalgae are still rare because of various difficulties. First, it is difficult to control biological parameters like motility, concentration and the culture environement. Second, Reproducibility of experiments relies on intrinsic biological variables and is still a challenge to ensure well-controlled physical parameters. In this work we present a study of bacteria in levitation to understand the process of aggregation or clustering in function of concentration and motility. We describe the process of aggregation under acoustic field with frequencies between 1 and 2 MHz in an acoustic resonator. Wild type e-Coli bacteria are focused at the nodal plane of a standing wave generated beteew the two parallel plates bounding the resonator. The manipulated volumes are hundreds of microliters. We demonstrate differences in the aggregation process in function of bacteria motility. Using PIV (Particle Image Velocimetry) measurements we observe collective large-scale structures forming in aggregates. Collective effects are thus starting to be explored in acoustic levitation, in quasi 2D configurations, without interactions with solid walls.Bacteria are confined in layers of several bacteria size thickness and the cluster can be several hundred of micrometers wide. A typical experiment lasts 20 min, which is the typical replication time of the bacteria. The size and shape of bacteria clusters are function of the acoustic energy distribution, acoustic average energy and on bacteria concentration. We consider in our experiments an acoustic energy large enough to confine the bacteria, i.e. the acoustic radial force is larger than the thrust induced by the swimming of each bacteria. This acoustic confinement will certainly allow in the near future to experimentally study the thermodynamics of active matter by allowing the determination of the swim and active pressure, for instance.

Defect dynamics and reconfigurable flows in confined active soft matter

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Active Soft Matter

Active nematics are non-equilibrium analogues of traditional liquid crystals, where the long-range orientational order is continuously disrupted by events of nucleation, chaotic motion, and annihilation of topological defects. Such dynamical states are sustained by continuous energy consumption. It is well established, both from theoretical predictions and experimental evidence, that, for unconstrained geometries, both defect density and flow patterns are linked to an intrinsic activity-dependent length scale. In previous experiments with a tubulin/kinesin active nematic, we shown that patterning of the soft substrates that support the active material leads to changes in the geometry of the self-sustained flows [1], but always dominated by the same intrinsic length scale, that may even change its role but not its scaling with material parameters [2,3].

We present here experiments where the same active material is laterally confinement either in straight, circular, or ring-like narrow channels, and we show that activity plays a secondary role under strong confinement. While the channel width emerges as the new relevant length-scale, flows adapt to the geometrical constraints by forming surprisingly ordered patterns where activity-induced defect nucleation can be inhibited, and flow symmetry can be broken thus generating net transport.

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Using sequential gelation as a method to direct gel structure and mechanics

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Arrested Soft Matter

We investigate the collective behavior of suspended thermoresponsive microgels, that expel solvent and subsequently decrease in size upon heating. This collapse is accompanied by a change in interaction behavior, switching from soft repulsive at low temperatures to attractive at higher temperatures. Using a mixture of two differently thermoresponsive microgels, we demonstrate that different structures can form depending on the heating profile used. Using confocal imaging, we observe that a fast heating profile yields homo-gelated structures which exhibit a random distribution of the two particle types, with all particles having collapsed simultaneously. If a slower heating profile is applied, we observe a sequentially gelated core-shell structure. During the formation of these core-shell structures, a monolayer of secondary particles deposits upon a primary particle gel scaffold, and gel structures can be reproduced using Brownian dynamics simulations. We have developed a toolbox of image analysis methods that quantitatively analyzes and compares these simulated structures and experimental systems. In addition to structural analysis, we investigate mechanical behavior with oscillatory rheology. We show that the secondary particle deposition enhances the structural integrity of the previously formed single species gel, with the final structure exhibiting higher elastic and loss moduli than its compositionally identical homo-gelled counterpart. Furthermore, we demonstrate that aging processes in the scaffold before secondary microgel deposition govern the final mechanical properties of the bigel. These systems thus allow us to design colloidal gels where mechanical and structural properties can be finely tuned.

Toward the creation of 2D or 3D clusters of cells in acoustic levitation

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Living Soft Matter

Today, three dimensional (3D) cell cultures tend to replace 2D conventional method because of their more relevant tissue-mimicking characteristics. Indeed, the 3D cell architecture (spheroïd, organoïd, etc) and the microenvironment is closer to In Vivo physiological behaviour [1], [2]. The main difficulties remain in creating a scaffold compatible with the targeted cells and tissue. Bioprinting is one the great objective for tissue engineering. For instance, stereolithography is a 3D printing technology where the freestanding object is built layer by layer with a photosensitive polymer resin through the projection of a UV image in the top plane. In recent promising work, stereolithography has been applied to create 3D hydrogel structures to guide cells like hepatocytes [3]. Nevertheless, ideally, scaffold-free methods are needed. We propose a new method combining a microfluidic channel and the acoustic radiation force (ARF) to structure and to control the shape of stem-cells aggregates. In a standing wave cavity the cells can be trapped in a central cluster. After a short temporary period and using the proper parameters, the cluster is close to a circular monolayer levitating in the surrounding fluid. The control of the medium flow and of the ARF allows various manipulations. For example, it is possible to structure the circular monolayer with different 2D stratifications of cells into the acoustic nodal plane. The result is a cluster with type 1 cells at its center, surrounded by a ring of type 2 cells. Other layers can be added, leading to a concentric multi-annular monolayer. Modifying the geometry of the cavity or the acoustic frequency can also increase the number of cell clusters, leading to a superposition of monolayers distributed along the height of the cavity. This new approach opens a new way of fabricating complex 3D multilayers spheroids or organoïds.

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Investigating DNA-based dendrimers: theory and experiment

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Polymeric Soft Matter

Dendrimers are synthetic macromolecules possessing a highly branched and regular internal structure. Recently, Luo and his co-workers at Cornell University synthesized dendrimer-like DNA (DL-DNA) via enzymatic ligation of Y-shaped DNA building blocks [1]. These charged DNA-based dendrimers are novel macromolecule aggregates, which hold high promise in bringing about targeted self-assembly of soft-matter systems in the bulk and at interfaces. Being charged, these dendrimers are -- in contrast to their neutral counterparts -- conformationally responsive.

Inspired by these findings, we present a joint theoretical-experimental study of this novel class of macromolecules. We employ a bead-spring model in order to describe such dendrimers of varying generation numbers and performed Molecular Dynamics simulations (MD) to determine equilibrium properties and conformational characteristics of all-DNA dendrimers. The obtained results are compared to static (SLS) and dynamic light scattering experiments (DLS) [2]. While the results from MD simulations show favorable agreement with the experimental results, e.g., with SLS data for the radius of gyration, R_g, and with DLS data for the hydrodynamic radius, R_H, they also provide a host of additional information and insight into the molecular structure of DL-DNA at the same time. For instance, our computational results show that DL-DNA molecules are rigid objects with low internal bead concentration and a high percentage of absorbed counterions. We also examine the salt-responsiveness of these macromolecules, finding that despite the strong screening of electrostatic interactions brought about by the added salt, the macromolecules shrink only slightly, their size robustness stemming from the high bending rigidity of the DNA-segments.

In order to simulate large ensembles of DL-DNA, we calculate a coarse-grained potential for the dendrimers within the framework of the introduced model. This is achieved by employing an approach based on the Widom particle-insertion method as well as the umbrella sampling method [3]. With this coarse-grained potential at hand, we investigate the bulk behaviour of DL-DNA systems. These findings are essential to determine if DL-DNA is a viable candidate for the experimental realization of cluster crystals in the bulk, a novel form of solid with multiple site occupancy [4].

The study of these charged dendrimer systems is an important field of research in the area of soft matter due to their potential role for various interdisciplinary applications, ranging from molecular cages and carriers for drug delivery in a living organism to the development of dendrimer- and dendron-based ultra-thin films in the area of nanotechnology [5-6].

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Ions can generate large membrane curvatures

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Interfacial Soft Matter

Biological membranes are built up from asymmetric bilayers. This asymmetry is associated both with the molecular composition of the two leaflets and with differences in the cytosolic and periplasmic solutions containing macromolecules and ions. There has been a long quest for understanding the effect of ions on the physical and morphological properties of membranes. Here, we elucidate the changes in the mechanical properties of membranes exposed to asymmetric buffer conditions and the associated curvature generation. As a model system, we employed giant unilamellar vesicles (GUVs) whose membranes were asymmetrically exposed to an interior sugar solution and an exterior salt solution. The GUVs were aspirated into a micropipette, beads were attached to the GUV membranes, and these beads were then pulled by optical tweezers, thereby generating membrane nanotubes. The assay allowed us to measure the spontaneous curvature and the bending rigidity of the bilayer membranes in the presence of different ions and sugar. At high sugar/ NaCl, KCl conditions, we observed softening of the membranes and significant negative spontaneous curvatures due to ion depletion. This effect is negligible at low sugar/ KCl, NaCl. In the case of LiCl, we observed a noticeable spontaneous curvature even at low concentration due to ion adsorption. Our findings, reported in Nano Lett. 18, 7816−7821 (2018), reveal the reshaping role of alkali chlorides on biomembranes.

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Mosaics of patchy rhombi: from close-packed arrangements to open lattices

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Self-Assembled Soft Matter

Mosaics of patchy rhombi: from close-packed arrangements to open lattices

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Two dimensional functional materials with tunable structural properties have important applications at all length scales, ranging from the molecular to the colloidal regime. Due to their porous nature, the utilization of metal-organic frameworks (MOFs) and - recently - covalent organic frameworks (COFs) as filters, catalysts and gas storage units is well established at the molecular length scale. The structural versatility of organic molecules resulted in over 20.000 reported MOF and COF structures over the course of the last 20 years. Still in its infancy but certainly as exciting, research into colloidal surface patterned materials builds on recent advancements in the fabrication of colloidal building blocks. The production of colloidal units with arbitrary shape and size and the possibility to tune and direct interactions between the units offer previously unthought-of perspectives in surface science as a whole.

In this zoo of molecular and colloidal building blocks, our work [1] gives design directions for the production of materials with tunable porosity and lattice geometry. In specific, our model - hard rhombi with localized interactions sites - has been proven to mimic the steric and attractive interactions of tetracarboxylic acids, small rigid organic molecules with functional carboxylic groups [2,3]. Through choosing particular ?patch topologies? - the specific placement of the patches on the rhombi edges - we are able to assemble tilings with identical lattice geometry but varying porosity from a close-packed arrangement to a highly porous, open lattice. Moreover, by playing with different patch identities we can select and stabilize otherwise competing tilings, such as the kagome versus a rhombic pore lattice.

We are confident that the design principles we found through exploring various tuning parameters will guide the way to building new interesting materials. In particular, the ability to fine tune the lattice porosity leads us to speculate about lattices that can dynamically and reversibly switch between close-packed and open structures. The colloidal junctions as explored by Kraft et al. [4] might prove to be the experimental realization of these dynamically switchable tilings.

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Ionic Coulomb blockade as a fractional Wien effect

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Interfacial Soft Matter

Ionic transport is key to numerous processes from neurotransmission to ultrafiltration. The recent advances in nanofluidics have allowed tremendous progress in the exploration of ionic and fluid transport at the ultimate scales. However, artificial porins are still far from reaching the considerable richness and subtlety of the biological ionic machinery, which exhibits advanced functionalities such as high selectivity, ionic pumping, and electrical and mechanical gating. A key step towards such functionalities is achieving active control of ionic transport. In particular, the realisation of single ion transport that is tuneable by an external gate -- the ionic analogue of the famous electronic Coulomb blockade (CB) -- would open considerable new avenues in this pursuit. Despite several claims of ionic CB signatures in experiments and simulations, the understanding of this effect has never gone beyond the electronic analogy, ignoring the particularities of electrolyte systems at room temperature.

We explored theoretically the many-body dynamics of ions confined in a charged nanochannel and obtained analytical predictions demonstrating that ionic conduction is allowed only at discrete values of a gating charge. This result is analogous to the electronic CB, and it is in full agreement with numerical simulations. Surprisingly, this classical quantisation of ionic transport takes its root in the dissociation of 'Bjerrum pairs', through a mechanism reminiscent of Onsager's Wien effect. Our findings open the way to novel nanofluidic functionalities at the single-ion level. As a proof-of-concept, we demonstrate an ionic-CB-based ion pump inspired by its electronic counterpart.

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Structure of colloidal dispersions under shear probed by X-ray cross-correlation analysis

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Colloidal & Granular Soft Matter

Colloidal dispersions under the influence of shear forces show interesting behavior such as shear thinning or shear thickening, that is a reduction or increase of the sample's viscosity with increasing shear rates. The differences in the rheological properties can be attributed to structural changes, i.e. variations of the local order within the system. Here, we present the results of a small-angle X-ray scattering (SAXS) study on concentrated dispersions of monodisperse, spherical silica nanoparticles under shear. The technique of X-ray cross-correlation analysis (XCCA) is used to extract information about the local order of the sample beyond the static structure factor and simple pair-correlations.

The results show that the shear thinning behavior is accompanied by the emergence of local structural motifs with a 6-fold symmetry. It can be shown that with increasing shear rates the magnitude of local 6-fold order is increasing which can be quantified using XCCA. When further increasing the shear rates the samples tend to form crystallites resulting in the observation of a shear thickening behavior.

Mechanical Properties and Failure of Physically Assembled Polystyrene-Polyisoprene-Polystyrene Gels ina Mid-block Selective Sol Mechanical Properties and Failure of Physically Assembled Polystyrene-Polyisoprene-Polystyrene Gels in a Mid-block Selective So

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Processing & Stressed Soft Matter

Failure of physically assembled gels is a complex process and depends on the gel structure. Here, we investigate the mechanical properties and failure behavior of a physically assembled gel system composed of poly(styrene)-poly(isoprene)-poly(styrene) [PS-PI-PS] in mineral oil, a midblock selective solvent. The gel network consists of collapsed PS endblock aggregates acting as physical crosslinks, while PI midblocks remain in the solvent bridging those aggregates. The gel architecture, as captured by the small angle x-ray scattering, has been tuned by varying the polymer volume fraction and midblock length but keeping the endblock length almost constant. For a longer midblock length, entanglement of PI chains has been anticipated. Tensile testing experiments reveal a rate dependent mechanical properties, particularly for the samples with entangled midblocks. The energy release rate (G) for fracture scales linearly with the crack-tip velocity indicating a velocity toughening effect in these gels. The G values and their velocity dependence strongly depend on the polymer concentration and chain length. These gels fail as a result of the endblock pullout from the aggregates and the pullout process involves an entropic penalty associated with the midblock stretching, friction with other endblocks in aggregates, and the enthalpic penalty associated with placing the endblock in a non-favorable solvent. We attempt to incorporate all these factors in determining a theoretical estimate for G and compare that with the experimentally observed values.

Tribological properties of nanoconfined ionic liquids at metallic interfaces

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Interfacial Soft Matter

Room Temperature Ionic Liquids (RTILs) are emerging materials for application in energy storage and lubrication. Due to their solvent-free nature, the behaviour of RTIL strongly deviates from classical liquid description and even the characterization of their bulk properties remain unclear. Further confinement of RTIL down to the nanoscale gives rise to exotic interfacial features resulting from the strong fluid-surface electrostatic interactions, thus highly dependent on the electronic nature of the surfaces. The mechanical and frictional properties of RTIL confined with insulating surfaces have been extensively studied, but still need to be explored for metallic surfaces.

Here, we use a tuning-fork based dynamic Surface Force Tribometer to probe the rheological and tribological properties of RTIL confined between extended gold surfaces. Confining the RTIL down to the nanoscale we observe a mechanical response reminiscent of a confinement induced capillary freezing over a wide contact area. By varying the imposed nanometric shear deformation, we unveil the yielding behaviour of the interfacial solid phase, characterized by a transition from an elastic to a plastic regime, and exhibiting striking similarity with glassy materials. The dissipation to sliding velocity dependence further evidences the glassy nature of the explored feature and locates dissipative events away from the surface. Considering applications in lubrication, our findings highlight that RTILs act as a phase-changing lubricant, the metallicity of the surfaces inducing the formation of an interfacial solid phase carrying load and eventually protecting the surfaces from direct contact.

Reentrant transitions of adaptive dsDNA colloids

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Colloidal & Granular Soft Matter

We present the two-dimensional state diagram of aqueous dispersions of hairy colloids composed of a polystyrene core grafted with an extended double-stranded DNA (dsDNA) corona. At fixed grafting density and in the low salt regime, a series of reentrant transitions between locally disordered and ordered states is observed with increasing the number density of colloids. This unusual behavior can be linked with the adaptive nature of the dsDNA corona: the order/disorder reentrances coincide with particle squeezing due to crowding-induced compression: In the low salt regime the osmotic dsDNA corona adapts its size and shape in order to optimize the particle packing to the available area, and no interpenetration of the coronas is observed. We additionally investigate changes of the state diagram associated with variations of the parameters controlling the degree of size and shape variation of the colloids: grafting density, chain length and salt concentration. We compare our results with those of MD simulations based on interaction potentials proposed for star polyelectrolytes, and with results of the liquid drop model.

Group formation and cohesion of active particles with visual perception-dependent motility

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Active Soft Matter

Collective phenomena emerge when individuals vary their behaviour depending on that of their peers. Usually, individuals respond to perceived stimuli by moving according to a certain rule, e.g. avoiding neighbours or aligning with others. Analysing the consequences of these individual perception-response rules at the group level is thus crucial to understand, predict, or reproduce a given collective behaviour. The formation of cohesive groups is frequently observed in living systems and is often thought to result from a delicate balance of repulsive, aligning, and attractive interactions. However, the variety of conditions for which group formation is observed suggests the existence of robust cohesion mechanisms, that can apply at various length scales and noise levels.

Here we show that the mere action of moving when crowded regions are in sight can be sufficient to create and maintain the cohesion of a group. This mechanism is robust provided that individuals have a long-range and anisotropic “vision-like” perception of their peers and respond to it by increasing the magnitude of their velocity. This principle is tested in a real system of light-responsive active particles, whose velocities can be individually varied using an external feedback loop. When the perception is restricted to a narrow field of view, particles gather into cohesive non-polarised groups, without requiring active reorientations. For wider fields of view, cohesion may be achieved by lowering the response threshold. Confirmed in simulations, we show that this cohesive active fluid state results from a generic instability of the density when the motility increases as a function of a long-range and anisotropic perception. This motility-induced cohesion mechanism may not only be relevant for the self-organisation of living systems but may also be used as a robust and scalable procedure to aggregate artificial robots in absence of centralised control.

Phase transitions on non-uniform curved surfaces: Coupling between phase and location

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Interfacial Soft Matter

Curvature of a surface necessarily disrupts the packing of any particles adsorbed on it, and has dramatic consequences for the structures, thermodynamics and kinetics of the assembly. Important effects reported to date include the stabilisation of defects in ground-state crystals [1]; the formation of branched, ribbon-like crystals [2]; and the possibility of complicated, location-dependent nucleation pathways [3]. In our work, we have studied how surfaces of non-uniform curvature change the phase behaviour of such systems. We observe that, when confined to a surface of varying curvature, the phase transitions of clusters of attractive colloids are accompanied by a global translation across the surface. For example, on the surface of a torus there are four stable states, which can be identified not only by the cluster's phase (gas, liquid, or crystal) but also by its geometry and location on the surface.

We present free energy landscapes that display these minima, and dynamical simulations of the transitions between them. We explain the phenomena by appealing to three effects of curvature: The modification of the perimeter of a cluster by the underlying geometry; the frustration of crystals in regions of large Gaussian curvature; and the attraction of liquid clusters to highly curved regions due to more favourable second-nearest-neighbour interactions. These phenomena are general, as we demonstrate by applying the same principles to an egg-box-like surface.

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Confinement-induced transition between wave-like collective cell migration modes

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Living Soft Matter

The structural and functional organization of biological tissues relies on the intricate interplay between chemical and mechanical signaling. Whereas the role of constant and transient mechanical perturbations is generally accepted, several studies recently highlighted the existence of long range mechanical excitations (i.e., waves) at the supracellular level. Here, we confine epithelial cell monolayers to quasi-one dimensional geometries, to force the establishment of tissue-level waves of well-defined wavelength and period. Numerical simulations based on a self-propelled Voronoi model reproduce the observed waves and exhibit a phase transition between a global and a multi-nodal wave, controlled by the confinement size. We confirm experimentally the existence of such a phase transition, and show that wavelength and period are independent of the confinement length. Together, these results demonstrate the intrinsic origin of tissue oscillations, which could provide cells with a mechanism to accurately measure distances at the supracellular level.

Misalignment between magnetic dipole moment and cell axis in the magnetotactic bacterium Magnetospirillum magneticum AMB-1

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Living Soft Matter

Magnetotactic bacteria synthesize magnetosomes, which are nanometer-sized, membrane bound, magnetic crystals made of either magnetite or greigite. Magnetosomes are often aligned in one or several chain(s) inside the cell, conferring to the cell a permanent magnetic dipole moment. As a result, magnetotactic bacteria align with external magnetic fields such as the geomagnetic field. While most quantitative studies of the trajectories of magnetotactic bacteria heavily rely on the premise that the cells' magnetic dipole moment is aligned with their direction of motility, this assumption has never really been challenged. We used phase contrast microscopy to image non-motile cells of Magnetospirillum magneticum AMB-1 and reconstructed, for each individual cell, the rotation of the cell axis around its magnetic moment. Using this technique, we determined the orientation of the magnetic moment relative to the cell body's helical framework for many individual cells and obtained an average misalignment of 6° with a strong cell-to-cell variability. This misalignment is large enough to significantly affect the measurement of the magnetic moment based on statistical analysis of cell orientations in an external magnetic field. We therefore propose a method to correct for this misalignment, which leads to a non-biased measurement of the magnetic moment of single cells from their orientation distribution. The average magnetic moment measured with this method is in excellent agreement with the value obtained from the analysis of electron microscopy images. Our results imply that the orientation and motion of magnetotactic bacteria placed in an external magnetic field is more complex than generally assumed and should be studied at the single-cell level.

Pressure-stimulated supercrystal formation in nanoparticle suspensions

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Self-Assembled Soft Matter

Ordered nanoparticle assemblies can exhibit unique physical properties. Understanding the formation process of such supercrystals allows one to preserve and tailor these properties by, e.g., changing the nanoparticles size, shape, material and coatings. Typical approaches to control the superlattice formation are based on controlled evaporation of the solvent, however, such self-assembly processes are often too slow to achieve homogeneous crystallization conditions. An alternative, yet largely unexplored way to achieve homogenous crystallization is by application of hydrostatic pressure.

Here, we demonstrate the crystallization of nanoparticles in aqueous solution induced by pressure as revealed by small-angle X-ray scattering (SAXS). Our sample system studied consists of gold nanoparticles coated with a PEG-based ligand, which exhibits colloidal stability even at high particle concentrations [1]. Upon applying hydrostatic pressure on these concentrated suspensions, we could follow the deswelling of the ligand layer by SAXS, which allows tuning of the interparticle nteractions from repulsive to attractive [2]. With this approach, the effect of PEG-ligand layer modifications (thickness, grafting density) on its structure can be studied [3]. Recently, we could show that when changing the solution properties by addition of salt, pressure-induced supercrystal formation takes place [4]. This reversible transition can be reasoned with the combined effect of salt and pressure on the solubility of the organic PEG shell that passivates the nanoparticles.

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Relaxation of weakly self-propelled particles dramatically changes at glass transition

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Arrested Soft Matter

We study experimentally the response of a dense sediment of Brownian particles to low levels of self-propulsion. We observe that relaxation of the ergodic supercooled liquid is monotonically enhanced by activity. By contrast the nonergodic glass shows an order of magnitude slowdown at low activities with respect to passive case. Fluidization is recovered at higher activities due to collective motion. Analyzing particle trajectories, we find that the mechanism responsible for relaxation in a passive glass, i.e. cooperative rearrangements, becomes less efficient as soon as weak self-propulsion is introduced. We attribute this behaviour, specific to the nonergodic glass, to rotation-diffusion coupling. Our results show that a nonequilibrium glassy system does not follow a simple path on the conventional liquid-glass phase diagram and that loss of ergodicity dramatically affects active systems.

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Bottom-up Synthesis of Polymeric Micro- and Nanoparticles with Regular Anisotropic Shapes

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Making & Measuring Soft Matter

Shape-anisotropic polymeric micro- and nanoparticles are of significant interest for the development of novel composite materials, lock-and-key assemblies, and drug carriers. Current syntheses techniques require external confinement in microfluidic devices, or lithographic methods associated with significant infrastructure and low productivity. Therefore, new methods for efficient scale-up of production are in high demand.

Here, we describe a bottom-up synthesis of shape-anisotropic polymeric particles, based on a combination of emulsion drops self-shaping upon cooling [1-2] and UV-triggered emulsion polymerization. Particles obtained via the proposed method could have regular anisotropic shapes, such as polygonal platelets with different numbers of edges (typically three, four or six edges), as well as fibrilar shapes with tuneable aspect ratios. The method is compatible with a variety of monomers and functional modifications of the particles, such as composites with magnetic nanoparticles, oil soluble additives, and so on.

Polymerization of the self-shaping drops allowed us to study much smaller drops, which were previously inaccessible by the optical microscopy. We obtain polymeric particles as small as ~50 nm and going up to millimetre scale in at least one dimension [3].

We also describe post-synthetic surface modifications that lead to temperature sensitive hierarchical superstructures. The synthesis procedure has great potential in efficient nano-manufacturing as it can achieve scalable production of the above shapes in a wide range of sizes, with minimum infrastructure and process requirements, and little maintenance of the equipment.

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SWITCHABLE 3D MORPHING CONFIGURATIONS BY STIMULI RESPONSIVE HETEROGENEOUS HYDROGEL

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Making & Measuring Soft Matter

Novelty

This paper demonstrates the creation of heterogeneous layered structures of hydrogel that are used to demonstrate switchable 3-dimensional shape deformation configurations, responding to various external stimulation.

Background

Morphing soft materials responding to external stimulation (e.g. electrical, mechanical and chemical) have promising applications in various fields, such as flexible electronics, biomedical transducers and soft robotics. One of the desirable developments is to make the self-shaping process controllable and programmable, at least for specific configurations.

Wang et al. (Angew. Chem. Int. Ed., 56, 15974) has demonstrated 3D shape control through planar (flat) patterned, homogeneous swell-able hydrogels. “Pre-designed” complex deformations were demonstrated by the periodically patterned hydrogel blocks made from multi-step lithographically. The shape morphing was then generated due to elastic mismatch between non-swelling substrate and swelling gel blocks.

Whilst patterned homogenous layered structures can provide “pre-designed” 3D shapes, the post-swelling configurations are fixed. For reconfigurable morphing structures which dynamically change shapes responding to stimulation, heterogenous structures are desired.

Uniform heterogenous bio-content deposition was achieved previously by droplet microfluidics utilizing surface wettability (hydrophobic/philic patterns) by the authors (Appl. Phys. Lett., 99, 073703). We can achieve heterogenous hydrogel layers through applying such technology to assemble hydrogel droplets with various mechanical and responsive properties. This could then be combined with hydrogel-based 3D morphing technology, which brings the great potential of next generation re-configurable, stimuli-responsive, morphing soft transducers.

Methodology and Experiment

The state of the art of this work are demonstrated from the following two aspects:

- Heterogeneous hydrogel blocks patterned and layered by controlled surface wetting at hydrophobic and hydrophilic boundaries.
- Reconfigurable 3D morphing response to the stimulation inputs such as changing ionic concentration and temperature of the solution this hydrogel structure is immersed in.

The hydrogel used are Poly(Acrylamide-Sodium Acrylate), created from poly-acrylamide (PAAm) network with Sodium Acrylate (SA) which contains free positive sodium ions.

The gel swelling will happen when immersed in PBS (phosphate buffered saline) solution depending on ionic concentration of the gel and the solution. Other stimulation such as temperature, electrical potential and physical constrains will all affect the swelling behaviour.

To structure and shape the hydrogel, hydrophobic/hydrophilic patterns were created – with patterned Parylene-C hydrophobic area and hydrophilic silicon dioxide (SiO2) patterns, both on smooth silicon substrates.

Functional (swell-able) hydrogel droplets/blocks were then deposited on this Parylene-SiO2 surface, shape-controlled by hydrophobic/philic boundaries, and squeezed into “button” shape by non-functional soft substrate (e.g. non-swelling gel) before cross-linked to form the desired heterogeneous structure.

Results

Initial reconfigurable gel deformation was achieved when the heterogeneous hydrogel structure was immersed in PBS solution, the gel started bending. When the PBS concentrations changed (0.1M to 0.01M), the hydrogel structure re-shaped from “S” shape to “C” shape.

More complex 3D morphing functions can be achieved with additional hydrogel functional blocks – to be carried out as near future work.

Structure and elasticity of the endothelial glycocalyx

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Polymeric Soft Matter

Endothelial glycocalyx (EG) is a nanostructured coating, namely a sugar-rich thin layer covering the luminal surface of blood vessels. EG layer constructed around grafted polysaccharide chains, which form an interlinked polymer brush. Despite being just several hundred nanometres thick in capillaries, EG has an enormous impact on a number of vascular functions, playing a major role in sieving and mechanotransduction processes, as well as in the chemical control of the endothelial cell environment. The details of structural organization of EG, however, are not yet fully understood. In this work, we study mechanical properties and function of EG using a multiscale molecular simulation. Following Weinbaum et al. [1], we introduce a bush-like model of EG ultrastructure, where the glycan fibers are modelled using semi-flexible bead-spring chains [2]. We then quantify the EG elasticity (e.g. response to the flow and AFM tip indentation), density distribution and permeability to the blood constituents, as well as its mechanotransduction function under flow.

The main findings of our work can be summarized as follows. The bush-like structure is by far more efficient in transducing the shear stress to the cytoskeleton while is efficiently dampens the normal stresses. Given the length of the glycan fibers, density, and the ratio of their bending energy to thermal fluctuations, the variation in density and the surface roughness of the EG layer are expected to yield significant effects. In particular, parts of the layer with an average density of less than 50% of the grafting density may be over 150-nm thick for a 400-nm-tall EG. Therefore, the EG should not be considered as a uniform density layer with a single elastic constant, and moreover, this conclusion applies to any EG model or polymer brush with long filaments. Secondly, our theoretical model allows us to take into account thermal fluctuations and the non-uniform density distribution of the glycans. The model predicts force profiles that are consistent with simulation results and experimental observations [2]. Finally, we also quantify the contribution of hyaluronic cross-linkers to the EG elasticity and the effect of the EG in a disease on the layer permeability.

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Condensation and demixing in solutions of DNA nanostars and their mixtures

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Self-Assembled Soft Matter

The pivotal role played by DNA in biology cannot be understated. Its outstanding pairing specificity, embodied by the famous Watson-Crick mechanism, is at the core of its biological functionality. Exploiting such a specificity in synthetic applications, an idea which dates back to the seminal work of Ned Seeman in the 1980's, provides researchers from many different fields, ranging from nanotechnology to material science, with a new, powerful tool [1].

DNA can be used in colloidal systems as a coating agent, but also on its own to self-assemble all-DNA materials with controllable properties. In particular, short DNA strands with carefully designed sequences can self-assemble into well-defined constructs at intermediate temperature. These DNA constructs (nanostars) can, in turn, bind to each other in a controlled fashion to form higher-order structures. Recent experiments have demonstrated that DNA nanostars can be employed as experimental realisations of patchy particles [2, 3], which have shown promising properties as theoretical and numerical model systems for the synthesis of new soft materials such as empty liquids, reentrant gels and open crystals.

Here we present a novel mixed numerical/theoretical approach to efficiently evaluate the phase diagram of these objects. Combining input information based on a realistic coarse-grained DNA potential with the Wertheim association theory we derive a parameter-free thermodynamic description of these systems. We apply this method to investigate the phase behaviour of single-component and mixtures of DNA nanostars with different number of sticky arms, elucidating the role of the system functionality and of salt concentration. The predicted critical parameters compare very well with existing experimental results for the available compositions [4,5]. Our approach takes into account DNA-DNA interactions in a realistic fashion and therefore is very general and can be easily extended, e.g. to investigate the behaviour of all-DNA systems that incorporates DNA nanotechnology motifs such as hairpins and strand displacements.

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Monitoring Self-Assembly of Nanocrystal Superlattices by Time- and Space-Resolved SAXS

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Self-Assembled Soft Matter

In this study, we investigate the time-resolved self-organization of colloidal PbS nanocrystals into highly ordered superstructures upon controlled solvent evaporation using in situ synchrotron small-angle X-ray scattering (SAXS). The specially designed sample environment is used to study the evaporative assembly from a colloidal solution of PbS nanocrystals by SAXS in transmission mode. For the first time for the investigated system we observe a self-assembled hexagonal closed-packed (hcp) superlattice formed in a solvent vapor saturated atmosphere as an intermediate state between a disordered colloidal suspension and the final body-centered cubic (bcc) superlattice obtained upon complete solvent evaporation. The detailed evolution of the crystal structure with time provides key results for understanding the assembly mechanism and the role of ligand–solvent interactions during the crystallization process. Additionally, we demonstrate that X-ray cross-correlation analysis (XCCA) of Bragg reflections is a powerful method to access information on precursor structures in the assembly process, which is not evident from conventional SAXS analysis. The presented results are important both for fundamental research and for directed fabrication of nanocrystal superlattices.

Controlling efficiently active soft matter with light: from optical microfibers to photokinetic cells

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Active Soft Matter

Obtaining full control of matter at the micron scale is a major challenge in the science of soft materials. In this context, light represents the ideal tool to control the dynamics and structure of colloids at the single particle level because the electromagnetic field can be "sculpted" with sub-micron resolution. However, when light momentum is used directly to apply forces to micro-structures, the resulting efficiency is often much lower than the maximum theoretical limit. In the first part of the talk I will show how we have been able to fabricate colloidal motors, made up of optical microfibers, which have a light-to-work conversion efficiency that surpasses all strategies explored so far [1]. In the second part of the talk, I will focus on cells that are able to convert light into chemical energy which, in turn, feeds flagellar motility. It has been shown that the local density of a bacterial suspension, composed by these photokinetic cells, can be controlled by using structured light fields [2]. I will show how we could produce high-resolution grey-scale density patterns by using a E. coli strain, with minimal genetic modifications, overcoming the limitations posed by the slow response of swimming speed to light [3]. I will underline how exploiting biological photokinesis is a much more efficient strategy than controlling colloidal density profiles using light momentum directly. As an example of dynamic driving of these systems, I will discuss some recent theoretical results indicating that a net flux of photokinetic model particles can be obtained by using periodic shifting light patterns [4]. These light-induced currents show some universal features in all active particles models (active Brownian, run and tumble, etc.), such as an unexpected flow inversion (happening at specific values of the pattern shifting speed) which has been observed in genetically modified E. coli bacteria [5].

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Jamming and yielding in an athermal dense suspension of amorphous particles

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Processing & Stressed Soft Matter

Dense suspensions are ubiquitous in nature. Flow of dense suspensions show an array of striking non-linear flow properties. Understanding such rich flow behaviour is not only interesting from the fundamental point of view, but also crucial for many large scale industries. Many dense suspensions show yielding behaviour: they behave like a solid below a critical stress \cite{Bonn} called the yield stress (σ_y) but transforms into a liquid above σ_y. Using oscillatory shear rheology and in-situ optical imaging, we study the yielding behaviour of a suspension formed by mixing hydrophilic amorphous particles with a hydrophobic solvent. Due to the solvent mediated attractive interactions, the particles form fractal clusters. The space filling nature of fractals gives rise to a yield stress for packing fractions (ϕ) well below their isotropic jamming point ϕ_J \cite{Peters}. We study the stress response of the system for a wide range of applied strain amplitudes ($0.0001 < \gamma_0 < 1$) for a fixed frequency. Higher harmonic analysis reveals that the system is highly non-linear almost over the entire strain range. Consequently, the linear elastic (G') and viscous (G'') do not reliably capture the mechanical response of the system. We estimate the energy dissipation for one complete cycle of oscillation from the area of the Lissajous plots (intra-cycle stress vs strain) over the entire range of $\gamma_0 $. Remarkably, we find that the normalized dissipated energy shows a non-monotonic behaviour: it goes through a minimum at an intermediate $\gamma_0 $ and saturates at a maximum value for larger values $\gamma_0 $. Similar behaviour is observed for all values of ϕ that show yield stress. Our results suggest that with increasing applied strain, the system first reorganizes to form a more elastic solid-like state that dissipates minimum energy and then get fluidized at higher strain values when the energy dissipation increases. We also observe persistent shear banding over the entire range of strain variation. The width of the shear band (d) remains almost independent of strain amplitude up to the intermediate values of $\gamma_0 $, but in the fluidized region, d increases rapidly with γ_0. Our experiments present an interesting avenue to probe the yielding behaviour of highly non-linear, disordered systems.

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Correlation length of bacterial turbulence

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Active Soft Matter

Dense suspensions of swimming bacteria display remarkable properties such as the appearance of collective motion, i.e. local bacterial ordering associated with a characteristic correlation length-scale, reminiscent of turbulent flow behaviour. Here, we investigate this phenomenon as a function of system-size and bacterial concentrations using video microscopy over large fields of view (up to 3mm X 4mm). Using particle image velocimetry, we calculate the spatial correlation of the velocity vectors and extract a characteristic length scale L. At sufficiently, high bacterial concentrations, we found the length L is proportional to the smallest system size, i.e. here the height of the glass capillary. However, we found no saturation of L towards large system-sizes and L can reach ~500 µm, which is ~5x larger than the currently largest L reported for bacterial suspensions. This suggests the absence of an intrinsic length-scale of dense populations of such ‘pusher-like’ swimmers.

Design and synthesis of catalytically active CoFe2O4@Pt nanostructures

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Active Soft Matter

The controlled motion of active micro- and nanostructures in aqueous solutions is of interest for both fundamental research and emerging biomedical applications. Nature has inspired numerous designs founded on the swimming patterns and self-propulsion of biological swimmers. Mimicking these features might thus enable the design of active structures that propel themselves by taking up energy from their surroundings and transforming it into directed motion.[1] Within this approach, considerable research is focused on the design of catalytically active and geometrically asymmetric Janus particles.[2] In general, the advantage of these systems lies in the possibility to catalyze chemical reactions at only one side of a particle, thereby producing a driving force that impulses it forward resulting in a self-propelled object. Herein, we present novel heterofunctional CoFe2O4@Pt nanostructures activated through a novel chemical fuel system based on the catalytic reduction of borohydrides. The nanostructures are prepared via a seed-mediated growth process, which entails a stable interface linkage between the CoFe2O4 and Pt domains.[3] The propulsion is generated by a concentration gradient considering fuel and reaction products in the vicinity of the catalytic nanoobject, and by railing their direction using a homogeneous magnetic field. This investigation includes the systematic synthetic approach implemented to prepare nanostructures in a size range smaller than 50 nm, the development of a new fuel system and the real-time tracking of the motion using dark-field light scattering microscopy.

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Active apolar doping determines routes to colloidal clusters and gels

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Active Soft Matter

Collections of interacting active particles, self-propelling or not, have shown remarkable phenomena including the emergence of dynamic patterns across different length scales, from animal groups to vibrated grains, microtubules, bacteria, and chemicalor field-driven colloids [1,2]. Burgeoning experimental and simulation activities are now exploring the possibility of realizing solid and stable structures from passive elements that are assembled by a few active dopants [3]. We show that such an elusive task may be accomplished by using a small amount of apolar dopants, namely synthetic active but not self-propelling units. We use blue light to rapidly assemble 2D colloidal clusters and gels via nonequilibrium diffusiophoresis, where microscopic hematite dockers form long-living interstitial bonds that strongly glue passive silica microspheres. By varying the relative fraction of doping, we uncover a rich phase diagram including ordered and disordered clusters, space-filling gels, and bicontinuous structures formed by filamentary dockers percolating through a solid network of silica spheres. We characterize the slow relaxation and dynamic arrest of the different phases via correlation and scattering functions [4]. These findings provide a pathway toward the rapid engineering of mesoscopic gels and clusters via active colloidal doping.

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Sheared colloidal gels: Effects of having a viscoelastic matrix

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Arrested Soft Matter

The balance between hydrodynamic and interparticle forces determines the microstructure of colloidal dispersions and their rheology. In a viscoelastic suspending medium, the occurrence of normal stress differences particularly affects the hydrodynamic forces acting on single particles and aggregates. In the present study, the role of a viscoelastic medium was investigated experimentally by studying weakly aggregated PMMA particles of 1 μm diameter in PDMS at volume fractions around the percolation threshold. Viscoelasticity was introduced by using branched PDMS. A cone partition plate geometry was used to measure the magnitude and sign of first and second normal stress differences, based on which information on the pair distribution could be derived. Subsequently, a fast high resolution rheo-confocal setup was used to monitor both microstructure and rheological behavior simultaneously. On the one hand, performing stress jump experiments, viscous and elastic stress contributions stemming from the different components could be analyzed as a function of the medium viscoelasticity. On the other hand, by means of the high speed confocal microscope, using counter-rotating plates and structured illumination optics, we could study the structural evolution during steady state and transient flows on the flow-vorticity plane over a wide array of length scales. The first result was the formation of dense particle aggregates, tumbling as a whole and orienting in the vorticity direction, as expected for attractive particles. The main effect of the viscoelastic matrix is the densification of these clusters, which is affecting the effective volume occupied by the particles. The latter affects the steady state stresses, but also the long-term diffusivity and recovery of the microstructure. Moreover, changing the viscoelasticity of the matrix affects network morphology as well as strength of a colloidal gel.

Chain-length dependent relaxation dynamics and glass-formation in polymers

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Arrested Soft Matter

We present experimental and computational results on the effects of molecular size, monomer chemistry, and flexibility on the relaxation behaviour of glass-forming polymers. We show experimental data from broadband dielectric spectroscopy, calorimetry, and oscillatory rheology together with RIS computer simulation calculations. We discuss the length-dependence of molecular relaxation dynamics, chain conformation and shape; and relate these features to the glass transition temperature. We discuss the links between glass-formation in small molecules and oligomeric/polymeric glass-formers and the dependences on polymer chemistry and flexibility.

A minimal-length approach unifies rigidity in under-constrained materials

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Processing & Stressed Soft Matter

Under-constrained systems are floppy, however they can be rigidified by forcing them into a regime of geometric incompatibility. We show that under-constrained materials exhibit generic elastic behavior close to this transition, which is independent of the microscopic structure and the disorder in the system. Phrasing the condition of geometric incompatibility in terms of a minimal length function, we obtain analytic expressions for the elastic stresses and moduli. We numerically verify our findings by simulations of sub-isostatic spring networks as well as 2D and 3D vertex models for dense biological tissues. For instance, we obtain exact expressions for the magnitudes of bulk modulus and shear modulus discontinuities at the rigidity transition, several scaling relations of the shear modulus, and the magnitude of the anomalous Poynting effect. Moreover, we show that the ratio of the excess shear modulus to the shear stress is inversely proportional to the critical shear strain with a prefactor of three, which we expect to be a general hallmark of rigidity in under-constrained materials induced by geometric incompatibility. This could be used in experiments to distinguish whether strain-stiffening as observed for instance in biopolymer networks arises from nonlinear characteristics of the microscopic material components or from effects of geometric incompatibility.

Topological Tuning of Polymer Dynamics

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Polymeric Soft Matter

Understanding the dynamics of dense solutions of polymers with non-trivial topologies remains an outstanding challenge in polymer physics. For instance, in plain contrast to their simplicity, unknotted and unconcatenated ring polymers in dense solutions display a dynamics that is markedly different from that of their linear counterparts [1].

In this talk, I will review recent work revealing that (quasi) topological interactions called "threadings" affect the dynamics of these systems and I will discuss how they can lead to the formation of a topological glass, i.e. a frozen state that can occur only in systems of polymers that must preserve a topological invariant [2,3].

Finally, I will also discuss recent experimental and numerical work focused on studying the behaviour of chimeric polymers, i.e. ones that simultaneously display both linear and circular architectures along the backbone, such as tadpole-shaped polymers [4].

I will show that the dynamics of these chimeric polymer systems can be finely tuned by adjusting the relative size of linear and circular elements and that it can be even slower than the reptation of linear chains.

This work contributes towards achieving a better understanding of how polymer topology can be designed in order to achieve the next generation of polymeric soft matter with topology-tunable rheology.

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Label-free, spatio-temporal monitoring of cytosolic mass, osmolarity and volume, in living cells

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Living Soft Matter

Microorganisms adapt their biophysical properties in response to changes in their local environment. However, quantifying these changes at the single-cell level has only recently become possible, largely relying on fluorescent labeling strategies. In this work, we utilize yeast (Saccharomyces cerevisiae) to demonstrate label-free quantification of changes in both intracellular osmolarity and macromolecular concentration in response to changes in the local environment. By combining a digital holographic microscope with a millifluidic chip, the temporal response of cellular water flux was successfully isolated from the rate of production of higher molecular weight compounds, in addition to identifying the produced compounds in terms of the product of their refractive index increment (dn/dc) and molar mass. The ability to identify, quantify and temporally resolve multiple biophysical processes in living cells at the single cell level offers a crucial complement to label-based strategies, suggesting broad applicability in studies of a wide-range of cellular processes.

Influence of surfactant dynamics on the length scale of avalanches in foam coalescence

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Processing & Stressed Soft Matter

Foams, which are collections of gas bubbles dispersed in an aqueous phase, are intrinsically unstable. One of the mechanisms leading to the destabilization of foams consists in the rupture of the thin liquid film between two bubbles, which leads to bubble coalescence. It was shown that for dry foams below a critical liquid fraction, coalescence events evolve as an avalanche process, where hundreds of bubbles break at the same time. The critical liquid fraction depends on the surfactant concentration; therefore, it was suggested that these avalanches phenomena are due to surfactant depletion during the rapid stretching of liquid films in the T1 process [1]. Another reported mechanism suggests that the film ruptures when the amount of the liquid available during T1 rearrangement is not sufficient at the critical liquid fraction [2].

The role of the diffusion and the adsorption/desorption kinetics of the interface stabilizers is not understood yet. In this work we investigate the coalescence avalanches of foams stabilized by amphiphilic molecules while varying their size from short-chain surfactants to long polymer macromolecules. It enables us to vary both the diffusion rate of the stabilizers and their interfacial kinetics. To study the coalescence process, we produce a column of foam for which we measure the time evolution of the liquid fraction by its electrical conductivity and simultaneously observe the coalescence events with a camera.

We find that in contrast to short-chain stabilizers, in the case of macromolecular surfactants the length scale of the avalanches is much lower, of the order of several bubbles. Moreover, for macromolecular surfactants, the critical liquid fraction for coalescence is higher than the one measured for standard surfactants. Our results suggest that the diffusion time of the stabilizers, which is longer for the macromolecular surfactants, controls the value of the critical liquid fraction. Furthermore, we show that the length scale of the coalescence events is related to the gradient of liquid fraction in the foam, which is controlled by the drainage rate.

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Capillary Rheo-SANS: Measuring the rheology and nanostructure of soft matter at high shear rates

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Processing & Stressed Soft Matter

The self-assembly of complex fluids containing surfactants, polymers, inorganic nanoparticles, and proteins can change significantly when subjected to flow at high shear rates. These extreme flow environments can alter or damage precious nanoparticles during purification, formulation, and application. To better understand these flow-induced effects, a new Capillary Rheo-SANS device combines a unique capillary rheometer with small angle neutron scattering (SANS) techniques to simultaneously measure the rheological properties and nanostructure at high shear rates. The device can measure pressure drops up to 500 bar and viscosities at shear rates up to 1,000,000 s-1, while requiring relatively small sample volumes (1-2 mL) to perform SANS measurements on biological and deuterated samples. As a demonstration of the device capabilities, the rheology and nanostructure were measured for a variety of model nanoparticle systems, including worm-like micelles, concentrated silica suspensions, and the NIST monoclonal antibody. Ongoing work aims to increase measurement precision, to extend the lower and upper shear rate boundaries, to provide wide-ranging temperature control, and to measure highly viscous samples such as polymer melts, pastes, and slurries.

Dynamics of soft and permeable particles suspensions

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Colloidal & Granular Soft Matter

Concentrated suspensions of soft particles have interesting dynamic properties determined by an intricate interplay of direct (i.e. elastic and electro-steric) and solvent-mediated

hydrodynamic interactions (HIs). Salient examples studied theoretically in the present work

are microgels, i.e. solvent-containing cross-linked polymer networks of colloidal size [1-3],

and core-shell particles consisting of a dry core and a shell of grafted polymers [4]. Ionic

microgels, in particular, are very sensitive to environmental conditions such as temperature,

ionic strength and concentration which allows for controlling their size and interaction.

Using a generic annulus model to account for the solvent permeability and HIs of non-ionic

soft particles, we calculate concentration-dependent transport properties including wavenumber dependent diffusion functions, self-diffusion coefficients and high-frequency

viscosities, in good agreement with dynamic light scattering and simulation data for non-ionic microgels [2], and hybrid core-shell particles [4]. The theoretical results are used in addition to scrutinize the validity of generalized Stokes-Einstein relations between diffusion and viscoelastic properties. The effects of the concentration-dependent de-swelling of ionic microgels on structural and dynamic suspension properties are explored [1] using, respectively, a Poisson-Boltzmann cell model and a thermodynamic perturbation method [3] to determine the equilibrium microgel size. The latter is a salient ingredient in our calculation of static pair correlation functions and structure factors used, in turn, for calculating dynamic properties including the hydrodynamic function and collective diffusion coefficient. For a quantitative assessment of de-swelling effects, results for static and dynamic properties are compared with corresponding findings for a reference suspension with fixed microgel size.

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Collective dynamics in a mixe lipid bilayer

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Interfacial Soft Matter

Biomembranes composed of lipids and proteins are a dynamic platform for a variety of cell functions. In order to understand such functions, the hierarchical structure and dynamics of cell membranes need to be addressed, as the structural scales span from molecular scales to the size of cell while the dynamics span sub ps (molecular motions) to seconds (deformations of the entire cell). Our group mainly employs neutron scattering techniques to explore structure on nanometer scales and dynamics in nanoseconds, which encompasses both molecular motions and collective membrane fluctuations. Recently we showed that some of the collective membrane fluctuations, such as bending and thickness fluctuations, can be accessed by neutron spin echo spectroscopy and the relaxation time relates to the elastic and viscous properties of the membranes. These membrane mechanical properties play a vital role in controlling cell functions such as endocytosis, vesicular trafficking and cell division. In this contribution, we employ the technique to explore structure and dynamics relationship in a mixed lipid bilayer with a same headgroup chemistry but varying alkyl tail lengths, specifically a mixture between dimyristoyl- and distearoyl-phosphatidylcholine. These molecules have different alkyl tail lengths by 4 carbons in each tail and their phase transitions differ by 30 °C, thus the system shows phase separation between solid and fluid membrane regions over a wide-temperature window. The measurements of the bending fluctuations in the coexistence region showed a gradual change in the effective bending modulus with changing temperature and composition. By calculating the area fraction of solid phase in the membrane, we found that the effective bending modulus scales with the area fraction and is explained by a theory without any free parameters. To the best of our knowledge, this result is the first verification of the theory by an experiment. Furthermore, dynamics in the fluid phase showed that the membrane properties are not simply additive quantities of pure components. The mixed membranes are more dynamic than either of their constituents, as evident from the decrease in the bending and area compressibility moduli as well as the membrane viscosity compared to the pure component membranes. In addition, we found that these properties are scaled with the area per lipid, which were calculated from a combination of

specific volume and structure (membrane thickness) measurements. The results clearly show a synergy between structure and dynamics in a model lipid bilayer, and that this synergy can be understood by measuring thermally activated equilibrium dynamics.

Effective Interactions and Dynamics of Active Colloids in Phase Separating Medium

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Active Soft Matter

Janus colloids suspended in phase separating critical liquid mixtures have been used to realize model active colloids [1]. An active motion analogous to self-diffusiophoresis is initiated with the onset of phase separation of the solvent mixture. To gain a deeper understanding of the mechanism behind this active motion, we have performed systematic investigation of the evolution of interparticle interactions and dynamics of Stoeber silica and silica-nickel Janus colloids in quasi-binary mixtures of 3-methylpyridine (3MP) and heavy water/water (W). The partial structure factor of colloid interactions and intermediate scattering functions describing the particle dynamics were simultaneously obtained using ultra-small angle X-Ray Scattering and X-ray photon correlation spectroscopy measurements at ID02 beamline, ESRF. The multi-speckle analysis allowed dissecting the evolution of interactions and dynamics along the vertical and horizontal directions.

Both critical and off-critical mixtures were investigated. The phase separation was induced by a rapid jump of temperature from the one-phase to the two-phase region of the solvent mixture. In the critical case, the phase separation occurs via spinodal decomposition while in the off-critical case it could take place by nucleation and growth or spinodal decomposition depending on the magnitude of the temperature-jump. Macroscopically, Stoeber silica particles almost completely migrate to the 3MP-rich phase [2] while Janus particles tend to accumulate near the liquid-liquid interface and eventually dropping to the W-rich phase [3]. These differences are attributed to the preferential wetting of 3MP on the silica particles.

Static interactions showed a clear difference between Stoeber and Janus particles [2,3]. The former displaying little change of interactions since the aggregating region is rapidly bypassed during the temperature-jump. Janus particles tended to become attractive and formed clusters. Upon completion of the phase separation, these clusters partly re-dispersed manifesting the dynamic nature of the clustering. Particle dynamics displayed more spectacular variations dominated by strong velocity fluctuations. With Stoeber particles, the dynamics is completely governed by the advection of colloids to the 3MP phase. The velocity fluctuations gradually decayed with the coarsening of the phases. Whereas Janus particles displayed velocity fluctuations initially but they were rapidly suppressed by the dynamic clustering. The behavior is qualitatively similar whether the phase separation occurs via spinodal decomposition or by nucleation and growth. The differences are in the onset and decay rate of the velocity fluctuations.

The measured intermediate scattering functions can be factorized to advective and diffusive terms using a similar function used to describe colloid dynamics during sedimentation [4]. An important difference is that the advective dynamics observed here is nearly isotropic with some intermittency. As expected, the decay rate of velocity fluctuations is proportional to the magnitude of the temperature-jump. The active motion is a result of the phoretic dynamics driven by the preferential wetting.

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The effect of interfacial viscosity on the dynamics, rheology, and breakup of droplets

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Interfacial Soft Matter

In this talk, we discuss the dynamics of droplets with a thin layer of viscous, insoluble surfactant whose mechanics are described by interfacial viscosity, i.e., a Boussinesq-Scriven constitutive law. We develop analytical theories to quantify droplet shape under flow in the limit of weak deformation, to a sufficient level of approximation where one can extract information about non-linear rheology and droplet breakup. In shear flow and extensional flows, we calculate how interfacial viscosity alters the extra stress of a dilute suspension of droplets. We also perform detailed studies to quantify how shear and dilatational viscosities influence droplet breakup and droplet migration in wall-bounded shear flow. In particular, our calculations indicate interfacial viscosity significantly alters the critical capillary number of breakup, which depends non-trivially on droplet deformation. In the second part of the talk, we will discuss a peculiar result that is related to the translational speed of a droplet with interfacial viscosity. It turns out interfacial shear viscosity plays a minimal role in modifying droplet drag when its shape is spherical. We discuss physical mechanisms and scaling theories that explain this observation, discussing results for both the steady-state drag and unsteady drag (i.e., Basset forces and/or added mass). All these theories highlight the extent to which surface viscosity alters droplet dynamics, and we conclude by providing preliminary results on how viscoelastic membranes (which are commonly found in armored droplets and/or polymer films) and surface tension gradients alter the dynamics mentioned above. We find that interfacial rheology plays a significant role in all of the effects mentioned here, which is important in understanding the stability and dynamics of emulsions.

Dynamics of non-spherical particles in non-Newtonian fluids with applications to microfluidic separations

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Tai, Cheng-Wei (Purdue University); Wang, Shiyan (Purdue University)

Processing & Stressed Soft Matter

In wall-bounded flows of polymeric fluids, particles experience normal stresses that give rise to cross-stream migration. For example, particles migrate to the center of a straight channel in elastically dominant (Boger) fluids, while particles in shear thinning and/or inertially dominant fluids focus in well-defined patterns closer to the channel wall. This phenomenon has shown promise as a passive, continuous, high-throughput method to fractionate suspensions by size and stiffness. For example, researchers have found that adding long-chain polymers to biological suspensions can improve the separation of red blood cells from platelets and white blood cells, as well as isolate sub-micron exosomes from serum. These viscoelastic lift forces can be tuned by modifying the polymer concentration and molecular weight, and one can use a wide variety of cheap, biocompatible polymers for such applications (e.g., PVP or hylauronic acid). In this talk, we perform a combination of theories, simulations, and microfluidic experiments to quantify the cross-stream migration of non-spherical particles in polymeric fluids. We first develop pencil-paper theories to quantify the polymeric forces on particles of arbitrary shape in a second order fluid (i.e., the slow flow limit of any viscoelastic flow). The expressions we obtain for force and torque are valid for arbitrary particle shape, which allows us to perform detailed studies on how cross-stream migration and particle tumbling is altered by fluid elasticity and particle aspect ratio for spheroidal shapes. We will discuss how to extend these studies for more complicated fluid rheologies (i.e., shear-thinnnig fluids), as well how to explore the effect of channel confinement, which modify the tumbling dynamics of the particles and hence their migration behavior. We conclude the talk with experiments where we suspend spheroidal particles of different sizes/shapes in elastic and shear-thinning fluids, and flow them through microfluidic channels. Statistics of particle location and orientation are gathered using a combination of microscopy and holography. These mechanistic studies will illuminate how to rationally design viscoelastic flows to segregate suspensions containing fiber-like and platelet-like particles, which find use a wide variety of contexts.

Arresting colloidal model systems

NIKOLAENKOVA, Anna, Utrecht University

VAN DER WEE, Ernest (Utrecht University); BAESJOU, Patrick (Utrecht University); IMHOF, Arnout (Utrecht University); VAN BLAADEREN, Alfons (Utrecht University).

Arrested Soft Matter

The possibility to “stop time” in a colloidal system is a very powerful tool for experimental analysis. When using confocal laser scanning microscopy (CLSM), mobile particles move during the scanning of the sample, resulting in incorrect 3D information. This makes it difficult or even impossible to image a dynamic system or a process in 3D. However, arrested systems can be scanned as slow as needed to get very accurate data. Here, we show that arresting colloidal model systems is possible for both PMMA and silica particles: with interactions ranging from (almost) hard to very soft (screening length >> particle size) and dipolar. By the addition of a monomer and initiator to the dispersion and a subsequent exposure to a bright short UV pulse, we effectively arrest the various self-assemblies, including ones formed in the presence of an electric field, at time scales of 0.1 s. We show a number of examples obtained with this new technique, in which there is no fundamental limit on the number of particles that can be analyzed in 3D.

Polymeric nanoparticles aplenty

NIKOUBASHMAN, Arash, Johannes Gutenberg University Mainz

Tatiana Morozova (Johannes Gutenberg University Mainz); Nannan Li (Princeton University); Athanassios Z. Panagiotopoulos (Princeton University)

Making & Measuring Soft Matter

Tailored nanoparticles are increasingly sought after for many scientific and technological applications, such as optoelectronic devices and selective catalysts. However, both research and commercialization of these materials has been impeded by the lack of suitable fabrication techniques. One promising approach for overcoming this hurdle is flash nanoprecipitation, where (soft) nanoparticles are assembled through rapid micromixing of polymers in solution with a miscible poor solvent. This continuous process allows for high yields as well as precise control over particle size and morphology. We employed multiscale simulations of this process to understand its underlying mechanisms and to efficiently explore parameter space. We first performed explicit solvent molecular dynamics (MD) simulations of a bead-spring polymer model to study the microscopic properties of the fabrication process. Then, we fed the MD data into a kinetic Monte Carlo algorithm to reach macroscopic length- and timescales. We discovered that the nanoparticle size can be reliably tuned through the initial polymer concentration and the mixing rate. Further, we were able to fabricate a wide variety of structured colloids, such as Janus and core-shell particles, when polymer blends were used in the feed stream.

Advanced modelling of microgel structure across the volume phase transition

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Colloidal & Granular Soft Matter

Thermoresponsive microgels are soft colloids that have been frequently employed in experiments with the aim of shedding new light on notable phenomena such as crystal melting, nucleation, depletion, jamming and glass transitions. These spherical particles are made of crosslinked polymer chains usually organized in a disordered core-corona geometry [1], but current synthesis and characterization techniques are also able to produce and investigate particles with non-trivial shapes and density distributions. Despite the increasing experimental interest, numerical simulations have been unable so far to properly take into account their complex internal degrees of freedom.

In this contribution[2], we introduce an advanced coarse-grained model of microgels that is able to reproduce the laboratory behaviour extensively. With this aim, we employ a numerical self-assembly protocol of patchy particles that captures the polymeric essence of the disordered network. We target specific experimental density distribution by introducing and adjusting designing forces during the assembly process acting on crosslinkers. We characterize the structure and the swelling behaviour of our numerical microgels, directly comparing with measurements obtained in x-ray scattering experiments, finding quantitative agreement across the Volume Phase Transition.

This work allows to shape realistic microgels in computer simulations with the desired topology, bridging the gap between experiments and simulations and paving the way for future investigations concerning particle-particle interactions, elasticity and phase behaviour.

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Assembly of clathrates from tetrahedral patchy colloids with narrow patches

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Self-Assembled Soft Matter

The assembly of tetrahedral patchy particles has attracted much attention over the last years. These studies were both motivated by the desire to obtain diamond crystal (a material with interesting photonic properties for applications), but also by the usefulness of these simple models to understand the behaviour of tetrahedral molecular liquids such as water.

In this contribution, we revisit the assembly of colloidal tetrahedral patchy particles.

Previous studies have shown that crystallization depends more critically on patch width than on interaction range: particles with patches narrower than 40° crystallize readily and those with wide patches form disordered glass states. Here we find that patch width also determines the structure of the crystal formed. Whereas particles with intermediate patches crystallize into diamond, those with narrow patches (with width $\approx 20^{\circ}$) assemble quite frequently into clathrates. These clathrates can adopt either sII structure (whose free energy is lower than that of sI) or consist of disordered aggregates of icosahedral three shell clusters containing one hundred particles. Thermodynamic stability is not behind the formation of clathrates for particles with narrow patches, as sII is not thermodynamically more stable than diamond in any region of the parameter space. An explanation for the assembly of clathrates comes instead from a structural analysis of the fluid which shows that the probability of formation of pentagonal rings increases as patch width gets narrower. Cluster free energy calculations suggest that the similarity between the tetrahedral angle on the particles and the internal angle of a regular pentagon is behind the preferential formation of pentamer rings in highly directional tetrahedral particles.

These results shed light on the propensity of water molecules to form a significant fraction of five member rings in liquid water. These pentagonal rings were proposed as candidates of low-density regions of topologically distinct from the nucleating ice-like (diamond) structures, providing resilience to crystallization. Our results are also relevant for those seeking to produce open colloidal crystals.

Here we provide a rather simple route to the assembly of complex clathrate structures.

Self-assembly of type I collagen fibrils in solution

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Self-Assembled Soft Matter

Type I collagen is an important constituent of many biological tissues, such as skin and bone. The collagen fibril is characterised by the highly organised arrangement of the molecules in staggered parallel arrays that give rise to a periodicity of 67 nm and the characteristic banding pattern. Fibril formation is a multi-scale, self-assembly process that is driven by electrostatic interactions between the molecules, leading to fibrils that can be several microns long. Little is known, however, about the self-assembling mechanisms and dynamics of the molecules into fibrils in solution. This issue is fundamental to understanding the structural basis of imperfect fibril formation in congenital disorders such as osteogenesis imperfect, as well as the mineralisation mechanisms during bone formation. Here, we use cryo-transmission electron microscopy (cryoTEM). This technique is a powerful tool to study collagen assembly at the nano-scale, since it provides the opportunity to take snapshots of collagen fibril formation at a variety of stages, in its native, hydrated state.

Collagen dissolved in 50 mM HCl pH 2 was added to 50 mM Tris buffer pH 7.4 containing NaCl 150 mM at 37 °C to a final concentration of 500 mM to trigger the self-assembly. The process was monitored by spectrophotometric measurements at 440 nm and samples were collected at different time points and frozen for cryoTEM analysis.

Samples collected at 5 minutes showed that the self-assembly process started with the slow aggregation of the molecules. After 7.5 minutes, the molecular aggregates started to self-organise into fibrils, leading to the formation of disorganised, loosely packed fibrils after 10 minutes. The typical bands of the collagen fibril only started to appear after 15 minutes, with the fibrils becoming more organised and more compact, and the gap and overlap regions were fully visible after 20 minutes. At this stage, the fibrils still exhibited narrow disorganised regions at the edges, with molecular aggregates still associating and contributing to the growth in fibril width. After 45 minutes the fibrils were fully assembled.

In conclusion, our results show that the self-assembly of collagen molecules into fibrils starts with the formation of molecular aggregates, leading to their association into disorganised arrays of molecules and fibrils, which further self-organise into a highly ordered fibril with the periodic 67 nm banding pattern. We are currently conducting molecular dynamics simulations to further understand the mechanisms of this process.

Active matter and active materials: Emerging behavior in intrinsically out of equilibrium systems

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Active Soft Matter

Flocks of birds, schools of fishes, or bacterial colonies constitute examples of living systems that coordinate their motion. In all these systems their constituent elements generate motion due to energy consumption and can exchange information or react sensitively to chemical cues in order to move together or to react collectively to external signals. Artificial systems, such as nanorobots, exploit the heterogeneous compositions of their surface to displace as a result of the heterogeneous chemical processes that take place in the presence of appropriate chemical substances.

All these systems are intrinsically out of equilibrium in the absence of any external driving, and their collective properties result as a balance between their direct interactions and the indirect coupling to the medium in which they displace. The mechanical balance that determines the states they develop spontaneously make these systems very versatile and have a natural tendency to for large scale aggregates. An understanding on the basic principles underlying the emergence and self-assembly on active systems poses fundamental challenges: How do the relevant entities interact with each other? Can we identify universal, generic principles associated to the main features in the self assembly and emergent behavior of intrinsically out of equilibrium systems? Are there mechanisms that can be shared by living systems and synthetic, active materials?

I will consider simple statistical models to address fundamental aspects of active systems and will analyze the implications that self-propulsion has in the emergence of structures in suspensions of model self-propelled particles. I will discuss the potential of schematic models to address fundamental questions that still remain open, such as the connection of the effective phase diagram and pressure with effective equilibrium concepts. These approaches allow to understand the transformations that characterize these systems as effective phase transitions out of equilibrium.

Anisotropic Dynamics and Kinetic Arrest of Dense Colloidal Ellipsoids in the Presence of an External Field Studied by Differenti

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Arrested Soft Matter

Anisotropic dynamics on the colloidal length scale is ubiquitous in nature. Of particular interest is the dynamics of systems approaching a glass or a kinetically arrested state. The failure of classical techniques for investigating the dynamics of highly concentrated and turbid suspensions near an arrest transition has contributed towards the limited experimental information available up until now. Exploiting the recent developments in the Differential Dynamic Microscopy (DDM) technique, we herein report the first experimental study on the anisotropic collective dynamics of colloidal ellipsoids (made up of magnetic hematite cores and silica shells) over a wide concentration range approaching kinetic arrest. We combine our dynamics results with small-angle X-ray scattering and rheological measurements to relate the collective short and long time diffusion coefficients with the structural correlations and the evolution of the zero shear viscosity as the system approaches an arrested state. We find that the short time diffusion coefficient scales with the inverse of the structure factor while the long time diffusion coefficient varies as the inverse of the zero shear viscosity. As the particles are made up of magnetic hematite cores and silica shells, we moreover use an external magnetic field to control the orientational degrees of freedom of the particles to investigate the field effects on their anisotropic dynamics. We find that at high field the anisotropy in dynamics increases with an increase in concentration. We demonstrate that DDM can now be used as a versatile technique to overcome the impediment encountered with the classical methods.

Polymer dynamics and the new high-resolution J-NSE at MLZ

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Making & Measuring Soft Matter

The neutron spin echo (NSE) provides among all spectrometers the ultimate energy resolution in quasi-elastic thermal and cold neutron scattering spectroscopy. In terms of Fourier-time (τ) – or equivalently in terms of the accessible energy (E) – high resolution means the extension of τ (respectively E) into to the regime of microseconds (neV). In 2017 the Juelich neutron spin echo at MLZ went through a refurbishment of the secondary spectrometer: The old copper, main-precession coils have been replaced by a new set of fringe-field compensated, superconducting magnets that were realized following the results obtained for the design of ESSENSE, the proposed high-resolution NSE spectrometer at the ESS. One of the most innovative characteristics of the coils is their optimized geometry that maximizes the intrinsic field-integral homogeneity along the flight-path of the neutrons and that enhances the resolution of a factor 2.5, as the first experiments could already confirm. The installation of the new magnets was finalized in September 2017 and since 2018 the J-NSE is back in user program. The new configuration yields an improved resolution that may be exploited to reach larger Fourier-times and/or to benefit from significant intensity gains if shorter neutron wavelengths are used at a given Fourier-time. Thus the new J-NSE Phoenix meets the needs to look into the microscopic dynamics of soft- or –biological matter with enhanced and new quality. Here we present the results on the performance of the spectrometer after the refurbishment and some selected examples from the realm of polymer dynamics that largely rely on the enhanced properties of the new J-NSE.

Direct visualization of comb polymer dynamics in unentangled semi-dilute solutions using single molecule studies

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Polymeric Soft Matter

Branched polymers play a key role in modern technology and advanced materials. Despite their increasing importance, our current understanding of the non-equilibrium dynamic behavior of these topologically complex polymers is limited and is largely based on bulk rheological and experimental scattering data. Owing to their complex molecular architectures, comb-shaped polymers exhibit rich dynamic behavior that is not fully understood at the molecular level. To address this, we study the dynamics of single branched polymers in non-dilute solutions using single-molecule fluorescence microscopy (SMFM). In particular, we use a hybrid enzymatic-synthetic approach to synthesize DNA-based branched polymers (comb polymers) that contain a long backbone with multiple side branches grafted at various positions. The backbone and branches are dual-labeled to allow their simultaneous but separate imaging. Following synthesis, we directly study the relaxation and transient stretching dynamics of single comb polymers in non-dilute solutions of linear unlabeled polymers in extensional flow and compare them to the dynamics of comb polymers in ultra-dilute solutions. Interestingly, the dynamic behavior of comb polymers is markedly different in non-dilute polymer solutions, which reveals changes in molecular-scale dynamics due to chain branching and chain-chain intermolecular interactions. We further study the effects of background concentration and polymer topology on comb polymer dynamics in order to elucidate the non-equilibrium behavior of topologically complex polymers. Overall, our work shows that single polymer dynamics can be used to provide a direct link between polymer microstructure and bulk rheological properties.

Orthogonal superposition rheometry of model colloidal glasses with short-ranged attractions

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Arrested Soft Matter

Attractive colloidal glasses are unique as the dynamical arrest is due to a combination of entropic crowding effects and formation of attractive bonds. When such systems are subjected to flow, the dynamics of the system are activated in a way which differs from hard sphere glasses which melt through a ‘convective cage release mechanism’ [Jacob et al, Phys Rev. Lett. 2015]. Here, we investigate the microscopic dynamics by measuring the relaxation spectrum during flow using orthogonal superposition rheometry. A small amplitude oscillatory shear deformation is imposed perpendicularly to a steady shear flow and the superposition moduli are measured. At low Péclet number a crossover frequency of the elastic and viscous superposition moduli is detected which represents the relaxation time associated to shear-induced escape of particles from their frustration (localization) under flow. For the repulsive glass, this is related to shear-induced cage renewal of particles due to flow. For attractive glasses, however, when particles escape their localized length (bonds), move with no further hindrance with the escape time that is independent of attraction strength and interestingly, although counterintuitively, it is faster than that in a purely repulsive glass. This is attributed to the fact that in attractive glasses, particles are localized at much shorter length scales due to bonding. At high Peclet number flows, a second low frequency crossover between elastic and viscous moduli is observed and a low frequency elastic dominated response emerges, possibly reflecting a caging due to hydrocluster formation, similar to the mechanisms acting in binary mixtures of hard-sphere glasses where bigger particles are caged by smaller ones. At high frequencies both the elastic and loss moduli probed orthogonally increase relative to the quiescent state due to anisotropic cage deformation that slows down short-time in-cage dynamics.

Brownian dynamic simulations are utilized complementary to probe the underlying microscopic dynamics by measuring the mean square displacements (MSD) under flow. The generalized Stokes-Einstein (GSE) relation is used to extract from the MSD the moduli under shear, which are then compared to the experimental orthogonal superposition moduli.

Thermophoresis in self--associating systems

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Interfacial Soft Matter

Due to its exquisite sensitivity to interfacial properties thermophoresis, i.e., particle motion driven by thermal gradients, can provide novel, exclusive, and often surprising information on the structural properties of colloidal or macromolecular fluids and on particle/solvent interactions at the nanoscale. By using an all--optical thermal excitation technique, Thermal Lensing, we show that thermophoresis can be profitably exploited to investigate the self--association of an amphiphilic block copolymer, poloxamer P407, which takes place above a concentration--dependent critical micellization temperature (cmt). In particular we show that, around and above the cmt, the direction of the poloxamer thermophoretic motion displays a remarkable double sign inversion, which is fully correlated with a peak in the thermal expansivity of the solution marking the progressive dehydration of the propylene oxide groups of P407 and their incorporation into the micellar core. This rather puzzling behaviour of the thermophoretic mobility and of the Soret coefficient in the P407 micellization region can tentatively be explained by properly taking into account the temperature--dependent balance between micellized and nonassociated poloxamer chains.

Dial-a-plume: Localised Photo-Bio-Convection On Demand

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Active Soft Matter

Microorganismal motility is often characterised by complex responses to environmental physico-chemical stimuli. Although the biological basis of these responses is often not well understood, their exploitation already promises novel avenues to directly control the motion of living active matter at both the individual and collective level.

Here we leverage the phototactic ability of the model microalga {\it Chlamydomonas reinhardtii} to precisely control the timing and position of localised cell photo-accumulation, leading to the controlled development of isolated bioconvective plumes.

This novel form of photo-bio-convection allows a precise, fast and reconfigurable control of the spatio-temporal dynamics of the instability and the ensuing global recirculation, which can be activated and stopped in real time.

A simple continuum model accounts for the phototactic response of the suspension and demonstrates how the spatio-temporal dynamics of the illumination field can be used as a simple external switch to produce efficient bio-mixing.

Dynamics of a forced large colloidal particle in a bath of colloidal hard spheres: Simulations and theory

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Colloidal & Granular Soft Matter

We study the dynamics and friction coefficient of a large colloidal tracer in a bath of colloidal hard spheres by Langevin dynamics simulations and theory. The tracer is pulled with a constant force, F, through the bath, which has a volume fraction of 0.50. The friction coefficient of the tracer is obtained from its stationary velocity, using the relation $F=\langle v \rangle \gamma_{eff}$. Important finite size effects are observed: the inverse friction coefficient depends linearly on the inverse system size for small and intermediate sizes (systems up to 8000 bath particles), while the it is constant for larger sizes, providing the "bulk" friction coefficient. This coefficient grows with the tracer size faster than linearly, i.e. faster than the Stokes' law. To rationalize this result, a theoretical model is proposed and solved, where the Navier-Stokes equation is modified to include the friction with the solvent. The theory agrees quantitatively with the simulation results.

The effects of the tracer on the bath are also studied, showing hydrodynamic tails that decay faster than $1/r$, as predicted for a Newtonian solvent. Our model, on the other hand, predicts a hydrodynamic tail which decays as $1/r^3$, in agreement with the simulations. However, the finite size of the bath particles induces a typical length scale (smaller than the hydrodynamic tails) in the bath which is not captured by the mean field model: the bath density and velocity oscillate in phase.

The dynamics of the tracer is also studied by means of the mean squared displacement, which reflects the viscoelastic behaviour of the bath. Diffusion at long times is observed both in the direction of the external force and perpendicular to it, with a diffusion coefficient that decays with increasing tracer radius faster than $1/a_t$. The Stokes Einstein relation, however, is fulfilled, with the friction coefficient obtained from the stationary velocity.

Biomcompatible hydrogels: formation and structure

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Wouter G. Ellenbroek (Eindhoven University of Technology)

Polymeric Soft Matter

Hydrogels are polymer networks that can absorb up to 99% of water; their structure is similar to that of the extra cellular matrix (ECM), and this makes them attractive synthetical material for biomedical materials/applications.

Hydrogels that contain a combination of reversible and irreversible crosslinks can exhibit novel properties, such as enhanced toughness, easier processability and even the ability to self-heal. We investigate microscopic design principles for self-assembling hydrogels with reversible crosslinks through coarse grained simulations, motivated by recent experimental results for tetra-PEG hydrogels assembled by click-chemistry and supramolecular hydrogen bond interactions.

We determine how the concentration of reversible and irreversible crosslinks influences the gelation and mechanical properties of the resulting network.

Operation Windows for Interfacial Rheometry

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Making & Measuring Soft Matter

The interfacial rheology of liquid interfaces can become complex if surface active species such as surfactants, particles or proteins are present at the interface. The broad interest in these complex interfaces covers topics from foam or emulsion stability to structural design in food or understanding the behavior of phospholipids as lung surfactants and is still an active area of research.

Measuring the interfacial rheology can be very challenging. Confining soft matter to a fluid interface leads to very thin layers of material, therefore resulting in a very weak mechanical response which might be insufficient to be measured accurately. This inherently soft response combines with other important challenges, including instrument inertia, sample inertia (momentum diffusion), subphase flow (Boussinesq limits), contact line imperfections, and alignment errors. In this work, we study this list of experimental challenges and derive equations for the operating limits of various macroscopic rheometers including the interfacial needle shear rheometer, the double wall ring and the bi-cone geometry. We experimentally investigate the limitations defined intrinsically by the instrument as well as the ones emerging from the properties of the interface of interest. The results provide cautionary examples and guidelines for anyone measuring interfacial rheology with these techniques.

The identified operation windows are applied at various phospholipid monolayers of DOPC and DPPC.

Functional Multicomponent Protein Networks with Tunable Domain Size

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Making & Measuring Soft Matter

The ability to self-assemble protein molecules offers the attractive opportunity for the design and synthesis of new multicomponent materials with novel properties[1]. Our goal is to create materials where the characteristics of engineered proteins (electronic or light-harvesting properties) can be scaled-up to the size of devices by assembling them in a network with tuneable behaviour. However, to exploit the opportunities offered, we need to be able to control the assembly into the desired architecture[2] whilst retaining protein functionality and avoiding protein denaturing. Here we address this challenge with a model system of the fluorescent proteins enhanced green fluorescent protein (eGFP) and mCherry, to monitor their stability –and thus their functionality -throughout the process. We used techniques of self-assembly manipulation inspired by soft matter[3] where intraprotein and salt-protein interactions[4] are controlled to yield the desired architecture. Thus, the methodology followed focus of exporting specific interactions of trivalent ions and protein surface modification (cationisation) to provide and control the specificity of protein-salt interactions. It consisted on forming a primary eGFP gel by adding yttrium chloride followed by its surface decoration with mCherry using ammonium sulphate. The structure obtained is the aimed bicontinous network where the individual protein domains are clearly distinguished and both proteins preserved their functional structure (the fluorescence was not lost). Moreover, by adding different amounts of one of the proteins, we were able to modify the percentage of the individual domains forming the structure. To our knowledge, this type of biomaterials has not been reported before and thus our studies set a precedent for a new methodology to obtain innovative biomaterials with potential medical and technological applications.

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An electric field responsive colloidal metamaterial

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Colloidal & Granular Soft Matter

We developed colloidal cubes of 1.6 micrometre in size, that have a permanent magnetic dipole moment and respond to magnetic as well as to electric fields. Without an electric field, a rhombic crystal structure is observed [1]. However, upon applying an electric field, under the appropriate conditions, the rhombic structure becomes unstable and a new structure with multiple zig-zag chains forms. In this presentation, it will be shown that an intriguing property of this transition is that the material exhibits a negative Poisson ratio. This behaviour points to a new class of ‘colloidal metamaterials [2].

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Correlations and forces in sheared fluids with or without quenching

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Arrested Soft Matter

Spatial correlations play an important role in characterizing material properties related to non-local effects. For instance, they can give rise to fluctuation-induced forces. At equilibrium, the range of correlations in fluids is typically bounded by the correlation length. Out of equilibrium, conservation laws have been found to extend correlations beyond the correlation length, leading, instead, to algebraic decays.

I shall discuss our recent systematic study of the correlations and forces in fluids driven out of equilibrium simultaneously by quenching and shearing, both for non-conserved and conserved Langevin-type dynamics. We identify which aspects of the correlations are due to shear, due to quenching, and due to simultaneously applying both, and how these properties depend on the correlation length of the system and its compressibility. Both shearing and quenching lead to long-ranged correlations, which, however, differ in their nature as well as in their prefactors, and which are mixed up by applying both perturbations.

The correlation functions can be used to compute non-equilibrium fluctuation-induced forces in the presence of shear, with or without quenching. Since shearing breaks the symmetry of correlation functions, the forces display a rich phenomenology. For instance, forces between inclusions embedded in the fluctuating medium can be stronger or weaker compared to their counterparts in unsheared systems, and they generally do not point along the axis connecting the inclusions.

Since quenches or shearing appear to be realizable in a variety of systems with conserved particle number, including active matter, we expect these findings to be relevant for experimental investigations.

Learning force fields from stochastic trajectories

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Making & Measuring Soft Matter

From nanometer-scale proteins to micron-scale colloidal particles, particles in biological and soft matter systems undergo Brownian dynamics: their deterministic motion due to the forces competes with the random diffusion due to thermal noise. The random diffusion not only blurs the dynamics, but fundamentally alters it, making the disentanglement of deterministic forces from diffusion a challenging problem. Indeed, we show that the rate with which information about the force field can be extracted from a Brownian trajectory is fundamentally bounded. We then propose a practical procedure, Stochastic Force Inference, which uses the information contained in a trajectory to approximate force fields. The technique extends to the evaluation of out-of-equilibrium currents, giving a lower bound on the entropy production rate, as well as to the inference of heterogeneous diffusion coefficients. It can be readily used with a limited amount of data, and, all in all, offers a solution to the inverse problem of Brownian dynamics.

Repulsion, attraction and contact in dense suspensions

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Processing & Stressed Soft Matter

Particle contacts, and the constraints induced by these contacts, are key to understanding non-Newtonian flow and jamming in dense suspensions. Numerical simulations and mean-field models based upon stress-induced transitions between lubricated and frictional contacts have had remarkable success reproducing the shear thickening rheology of dense suspensions, however in real experimental systems the precise nature of these frictional contacts remains ambiguous.

Using charge-stabilized silica spheres, where particle interactions can be easily tuned through the fluid ionic strength, we employ a combination of bulk rheology and single-particle atomic force microscopy (AFM) to probe the nature of these contacts. Directly measuring the forces between a silica sphere and silica surface with AFM, we can access both the finite ranged interactions as well as the force at contact, defined by a constant compliance region in the AFM force-displacement curve. As the fluid ionic strength increases from low to moderate values, both the force at contact from AFM and the onset stress for shear thickening decrease. This agrees with expectations from numerical simulations, though the force at contact from AFM lies slightly below the contact force predicted from the onset stress. As the ionic strength further increases, in the bulk rheology shear thickening becomes obscured by an increasing yield stress, while the particle interactions measured in AFM transition from repulsive to attractive at short distances. Together, these results indicate that the frictional contacts formed in dense, shear thickening suspensions represent true solid-solid contacts.

Polymer foams by using microfluidics

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Polymeric Soft Matter

Due to their interesting properties, polymer foams are widely used in different fields from food industry to industrial engineering. The weight is low as well as the density, exibiting so an high surface area. Polymer foams can be produced in different ways, and since they are used widely all over the globe the technologies to produce foams are continuously being improved. In the present study, microfluidic strategies are used to develop 3D, solid, highly monodisperse polymeric foams incorporating metal oxide nanoparticles. In a one-step flow focusing microfluidic approach, polymeric liquid foams are generated starting from bubble by bubble formation. As the concentration of the bubbles increases, they self-assembly and they form a foam, stabilized by a surfactant. As the liquid drains due to the gravity, spherical bubbles turn into polyhedral shapes giving dry foams. In the meanwhile, thanks to the addition of crosslinker for the polymer, foams are solidified via stable chemical crosslinking/polymerization processes. The use of bio-polymers plays the role of a stabilizing agent allowing us to obtain a more concentrated dispersion of nanoparticles to incorporate inside the foam. Size and shape of the cells, as well as thickness and texture of the cell walls (i.e films and plateau borders) have been tuned varying different parameters such as polymer concentration, flow rates, the size of the flow channels and also the drying procedure.

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Soluble surfactant spreading: How the amphiphilicity sets the Marangoni hydrodynamics

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Interfacial Soft Matter

The way surfactants arrange in bulk and at interfaces are related to their amphiphilicity, which is the balance between their hydrophilic and hydrophobic parts and which can be quantified by introducing the critical micellar concentration (cmc). Surfactants are also at the origin of dynamical effects: local gradients of interfacial concentrations create the so-called Marangoni flows. Here we report various results illustrating the coupling between the surfactant amphiphilicity and these Marangoni flows.

We investigated in detail a spreading configuration, where a local excess of water-soluble surfactants is locally sustained at the surface of a pure water pool, and follow how these surfactants both spread at the interface and diffuse in bulk.

We first measured the features of the interfacial flow - maximal distance and maximal speed - for different types of surfactant, and as a function of all experimentally available parameters, as well as for two different geometrical configurations [1,2]. For all the measured quantities, we have found a good agreement between the data and our hydrodynamical model. In particular, the cmc turns out to be a key element in such experiments, though performed under dynamical conditions.

We also characterized the flow field inside the water layer using particle image velocimetry and we observe the existence of a vortex ring localised just below the free interface. Moreover, we demonstrated that this vortex ring can be strong enough to deform this interface. The suction of the interface triggers a Rayleigh-Taylor instability whose dependence on experimental parameters we investigated and rationalized.

Finally, we also report flows and deformations resulting from the deposition of a water soluble surfactant at a bare oil-water interface [3]. Once the surfactant is deposited, we show that the oil-water interface is deformed with a water bump rising upward into the oil. This counter-intuitive bump of water rising through the oil layer has radial and vertical extent depending on the surfactant, and both the density and viscosity ratios. Our proposed model explains these features, and finally allows us to relate this vertical deformation to the oil-water interfacial tension profile.

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Self-propelled particles in 3D: phase behaviour and dynamics

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Active Soft Matter

Many of the experiments investigating collective behaviour in an assembly of self-propelled particles have been carried out in 2D. Here, we report for experimental observations of 3D collective behaviour in a suspension of self-propelled Janus colloids. Half metal-coated Janus particles are suspended in a water/glycerol mixture and self-propelled under an AC electric field [1, 2, 3].

The particles are fluorescent, such that it is possible to obtain 3D trajectories using a confocal microscope. We uncovered a complex phase behaviour depending on the position in the parameter space – packing fraction, Peclet number, and strength of the interaction between particles which controlled by the frequency of the electric field – that we studied extensively with the dynamics. In particular, we observed an unusual active nematic phase where particles form chains parallel to the electric field but travelling in the orthogonal plane – a feature only allowed in 3D. These experiments bring a new insight for understanding what happens when the confinement in one direction is suppressed, and potentially open some novel routes to the self-assembly of colloidal particles.

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Crack Propagation Behaviour of Polyurethane Thermoplastic Elastomers in Cyclic Fatigue

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Processing & Stressed Soft Matter

Requirements of waste reduction and environmental sustainability caused a renewed interest for thermoplastic elastomers (TPE's). TPE's are an interesting class of re-processable materials with intermediate properties between those of conventionally vulcanized elastomers and thermoplastics, such as, flexibility, high reversible extensibility, easy shaping and fast processing. Although TPE's have seen a fast diffusion in the last 20 years, few studies have appeared on the cyclic behaviour in fatigue(Mars & Ellul, 2017). TPE's are typically composed by at least two components at the operating temperature: a hard and solid component and an elastomeric soft component(J.W.C Van Bogart, A. Lilaonitkul, 1979). The presence of phase separation (at the submicron scale) between those two components provides physical crosslinking and dissipative mechanisms so that TPE's can be used without any chemical crosslinking and in unfilled state.

We investigated the crack propagation in cyclic fatigue of two commercial polyurethane/ester multi-block copolymers (TPU) with similar Young Modulus and strain lower than 100%. The cyclic fatigue resistance of the materials were characterized by the crack propagation rate per cycle (dc/dn) in a pure shear sample as function of the applied energy release rate G in each cycle (Thomas 1959) . The fracture energy for monotonic load was evaluated with the same pure shear geometry adopting the procedure used by Rivlin and Thomas (Rivlin & Thomas, 1953) at different temperatures and strain rates.

For one of the TPUs the cyclic loading results in almost no propagation with a clear blunting of the crack accompanied by a progressive damage ahead of the crack, even for thousands of cycles at moderate level of applied strain. In similar conditions, the second tested TPU shows an evident propagation of the initial crack at a rate that is comparable to that obtained for conventional filled elastomers (Mzabi, Berghezan, Roux, Hild, & Creton, 2011). The difference in the fatigue behaviour of the two TPU cannot be explained by obvious differences in the monotonic fast fracture that is instead quite similar for both TPU.

The observed crack blunting in one of the TPUs confirms that the details of the TPU's architecture resulting in a microphase separation can result in a very good resistance to crack propagation in cyclic conditions. However the sole knowledge of the fracture energy of the TPU in monotonic loading is not sufficient to predict their lifetime in repeated cyclic loading. This suggests that additional or different dissipation mechanisms are active in the two TPU’s ahead the crack tip when they operate under cyclic stress condition. To address this question we will map by Digital Image Correlation(Roux, Réthoré, & Hild, 2009) the strain field in front of the crack tip.

Silk: A natural example of a sticky entangled polymer

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Self-Assembled Soft Matter

Natural silk is produced by the Bombyx Mori silk worm from an “aquamelt” of randomly coiled proteins, which upon applying elongational flow and extraction of water rapidly undergoes a transition to a solid fibre with outstanding mechanical properties. This process is remarkably more efficient than the spinning of synthetic polymers in terms of both energetic costs and solvent recycling, but remains poorly understood. We show, using quantitative modelling of the linear viscoelastic response of the silk feedstock, that this aquamelt may be viewed as a supramolecular polymer netwerk, where the protein is topologically entangled and uses salt bridges as reversible crosslinks. Our findings provide a viable starting point to physically understand the “flow-induced self-assembly” of silk fibres.

Nanoscale optical imaging of individual and densely packed microgel colloids

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Colloidal & Granular Soft Matter

Microgels are among the most studied colloidal and polymeric systems of the past two decades. Swelling thermosensitive, poly(N- isopropylacrylamide) microgels by lowering the temperature provides a unique mechanism for controlling the porosity and size of colloidal particles on the nanoscale. As a consequence, these smart microgel particles are being considered for applications ranging from viscosity modifiers and sensing to drug delivery and as models for the glass and the jamming transition. Here, we present results from in-situ two-color superresolution microscopy of dye-labelled submicron sized pNiPAM microgels [1]. We first demonstrate direct STochastic Optical Reconstruction Microscopy (dSTORM) to image single microgels in two and three dimensions, at different stages of the volume phase transition, with a lateral optical resolution of 30nm [2]. We find that the swelling behaviour observed in real space matches quantitatively with results from traditional light scattering measurements in reciprocal space. Next, we study dye labelled tracer microgels embedded in dense microgel suspensions. As we increase the packing density we map out the different contributions that allow the dense packing of the soft microgels, due to deformation, interpenetration and compression. Moreover, we can observe shape changes, such as faceting, in dense microgel systems where particles are compressed by the presence of its neighbours [3]. This is all but impossible with other nanoscale imaging techniques used to date (AFM, Cryo-TEM). Based on the detailed understanding of the local structure and morphology we can model the macroscopic elastic properties of dense suspensions over a large range of densities [4]. Interestingly, our results suggest that the friction between the microgels is reduced due to lubrification mediated by the polymer brush-like corona before the onset of interpenetration.

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The structural colors of random assembled monodisperse colloids

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Making & Measuring Soft Matter

The color of materials usually originates from a combination of wavelength dependent absorption and scattering. Controlling the color without the use of absorbing dyes is of practical interest, not only because of undesired bleaching but also regarding minimization of environmental and health issues. Color control without dyes can be achieved by tuning the material's scattering properties in controlling size and spatial arrangement of scatterers. These structural colors can arise from ordered or disordered assemblies of colloids. Periodically ordered colloidal structures such as opals where iridescent colors arise from Bragg diffraction are well established[1]. Their colors are, however, strongly dependent on the angle of view because of the periodicity of interparticle distance giving rise to narrow diffraction maxima. For certain applications in coatings, paints, as well as cosmetics, this angular dependency is undesirable. The disorder counterpart, photonic glasses (PGs)[2], have become of interest as these possess isotropic properties and can produce angle-independent structural colors. Still, a limited range of colors was produced so far by self-assembly of monodisperse spheres to PGs. The lack of a quantitative description of the range of isotropic structural colors in PGs has hindered the potential of these low-cost structures for real life applications.

Here, we show that a recently developed quantitative scattering model[3] can fully capture the observed isotropic structural colors of PGs produced so far. The model takes into account resonant Mie-scattering, short-range positional correlations, optical near-field coupling of randomly packed, spherical scatterers as well as the sample's internal reflection at the boundary. The model predicts the reflectance spectra and the expected sample color solely from the scatterer size, refractive index, filling fraction, structural order and sample thickness and shows that a full, repeating color spectrum in PGs can be obtained. To compare the reflectance spectra calculated by the model we prepare optical thin films of PGs by random aggregation of non-absorbing, monodisperse colloidal polystyrene (PS) spheres and measure their spectral reflectance over the entire visible spectrum. By varying the colloidal scatterer size we can obtain blue, green, red and purple colors repeatably, as predicted by the model. In addition, changing the effective sample thickness enables us to tune between vivid colors and white broadband reflectance. The good agreement between the model and experiment for PS PGs enables us to map the parameter space and to predict the range of color hues for different refractive index photonic materials. We show that in higher index PGs e.g. made of titania colloids[4] even saturated yellow, magenta, blue, and green can be achieved over four decades of sample thickness. Clearly, this model provides a theoretical handle to make use of PGs for structural colors in industrial applications.

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Modification of wave velocity in a string fluid

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Colloidal & Granular Soft Matter

Complex or dusty plasmas consist of microparticles embedded in a low-temperature plasma. The microparticles acquire high charges by collecting plasma particles and strongly interact with each other. Since they are suspended in a low pressure background gas, the damping of their movement is much weaker than, for instance, in colloids, so that studies of complex plasmas complement those of colloids.

Here we present complex plasma experiments performed in the PK-4 Laboratory on board the International Space Station. The heart of this laboratory is formed by a U-shaped glass tube in which a direct current (DC) plasma is produced with a driven and a grounded electrode. The microparticles can be trapped by switching the polarity of the driven electrode at a time scale that is much smaller than that of the particle dynamics.

The polarity switching also induces ion fluxes which follow the electric field almost instantaneously. These ion fluxes cause the formation of space charges downstream from the microparticles, which lead to the formation of microparticle strings, analogous to strings forming in electrorheological fluids.

Here, we numerically demonstrate that the velocity of waves moving through this string fluid depends on the Mach number of the ions. For this purpose, we perform a Molecular-Dynamics simulation of the (negatively charged) microparticle movement with a potential that includes, in addition to the usual interaction via Yukawa potential, a positive space charge in downstream direction mimicking the wake formation. We excite a shock wave travelling through the system by pushing it on one side with a piston, and observe the velocity of the travelling wave.

We compare the results of this simulation to a slow wave mode observed in experiments in the PK-4 Laboratory: In these experiments, the microparticles were trapped in the discharge and formed a string fluid. Self-excited waves appeared which had an unusual waveform and propagated slowly compared with the usual dust acoustic wave mode.

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What controls the response of soft microgels to overcrowded environments: cross-link density or architecture?

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Colloidal & Granular Soft Matter

Soft, adaptive microgels can be compressed, deformed, or interpenetrated in concentrated suspensions. The prevalence of one of these mechanisms of responding to a crowded environment has usually been related only to the amount and distribution of crosslinks within the polymer network. Here, we report that introducing a solvent-filled cavity can enhance deswelling of microgels more than reducing the crosslink fraction. The study is based on small-angle X-ray and neutron scattering, where we probe concentrated suspensions of (i) regular, (ii) ultra-low crosslinked, and (iii) hollow poly(\textit{N}-iso\-propyl\-acryl\-amide) microgels embedded within a matrix of regular crosslinked microgels. Our experimental findings are supported by Monte Carlo simulations of mixtures of microgels modeled by combining the Flory-Rehner theory of polymer networks and Hertz effective pair potentials. We conclude that crosslink content alone cannot be used to define microgel softness, but that microgel architecture is another key property that affects softness.

Fluid flow and motility control initial bacterial colonization on curved surfaces

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Living Soft Matter

The vast majority of microorganisms are exposed to fluid flow, whether in natural environments, the human body, or artificial systems. However, despite the pervasive occurrence and implications of a fluid dynamic environment, its influence on the transport and attachment of bacteria to surfaces (1–3) remains poorly understood, especially in complex geometries that best describe real systems. We will show that fluid flow and surface geometry greatly influence transport and surface colonization by swimming microorganisms such as \textit{Pseudomonas aeruginosa} and \textit{Escherichia coli} (4). Using a combination of microfluidic experiments and numerical modelling, we will demonstrate that flow preferentially promotes bacterial attachment on specific regions of curved surfaces, i.e., on the leeward side of isolated cylindrical pillars and directly after the apexes of regular and randomly corrugated surfaces. Colonization is tightly linked to bacterial motility, which increases the attachment rates by two orders of magnitude compared to the case of non-motile bacteria or passive particles. Moreover, for relatively low flow rates (i.e., for fluid velocities not greater than 10 times the swimming speed of bacteria) a simple scaling law for the pillar capture efficiency is found, which means that the density of adhered bacteria is independent of the size of the pillar. In contrast, for high flow rates, the behavior of motile bacteria is equivalent to that of passive particles, for which the attachment rate per unit surface decreases with increasing pillar dimensions. Taken together, these results underscore the importance of fluid flow in governing bacterial colonization and biofilm formation under common environmental conditions, with significant ecological, industrial, and clinical implications.

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Material properties of hybrid lipid-polymer vesicles: towards artificial systems for enhanced membrane protein function

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Self-Assembled Soft Matter

Vesicles are spherical structures comprised of fluid enclosed by an amphiphilic bilayer. They have many applications from acting as microreactors and sensors, to drug delivery vectors and models for a cell membrane. However, biological membranes generally consist of a mixture of amphiphilic lipids, glycoproteins, glycolipids and membrane proteins, making this environment very difficult to replicate in artificial membrane models. Membrane proteins in biological membranes perform specific functions and their functionality can be sensitive and responsive to their membrane environment. In incorporating functional membrane proteins within artificial vesicles, we are interested in how engineering the properties of the membrane can be used to simultaneously optimise the functionality of membrane proteins and the overall properties of the vesicle.

Lipids and amphiphilic block copolymers are each common materials for fabrication of synthetic membrane vesicles in the form of liposomes and polymersomes, respectively. However while liposomes are biocompatible, they have poor long term stability: the reverse is true of a polymersome, which has higher mechanical stability and durability but poor or unknown biocompatibility. We hypothesise that by using a hybrid membrane, the best properties of both a polymersome and liposome can be combined.

Phospholipid, POPC, combined with different copolymers, were used to explore how the properties of the vesicles change with composition. Spectrocopic approaches to determine the proton permeability of these membranes show that increasing polymer composition decreases membrane permeability. Through correlative combination of cryo-TEM and SAXS, we are refining models for the hybrid membrane structure: increasing polymer content increases membrane thickness, and hybrid membranes exhibit membrane asymmetry. Further work is underway to determine rheological (FRAP) and mechanical (flicker spectroscopy) properties of hybrid membranes in GUVs.

Recent work is starting to uncover important advantages in using hybrid vesicles for membrane protein reconstitution, including enhanced protein folding and significantly extended functional lifetime. Understanding how the composition of a membrane affects its properties could help find what properties govern protein folding, structure and stability, therefore these hybrid membranes could be used to enhance membrane protein function and durability in artificial systems.

An old tool for a new problem: tunable electrostatic adsorption via Pnipam microgels

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Self-Assembled Soft Matter

What are the fundamental mechanisms for the adsorption of charged polymers onto oppositely charged surfaces? This recurring question is at the heart of current challenging applications in surface coating and crucial to unravel various phenomena of complexation relevant for cellular and viral biophysics. Understanding electrostatic self-assembly and adsorption still represents a fundamental problem of great interest in soft matter and many theoretical studies, using different approaches, have been published [1,2,3].

Although electroadsorption phenomena have been studied in a variety of polyelectrolyte-colloid or colloid-colloid mixtures, all previously reported works dealt with particles or polymers with fixed charge densities, or charge distributions that could not be changed without varying the ionic strength or the pH of the suspending medium. Despite of that, the most natural, though unexplored way to physically tailor colloidal charge density is to exploit the responsiveness of colloids to an external stimulus, the latter affecting their size and so their charge distribution.

Thermoresponsive poly(N-isopropylacrylamide) (PNiPAM) microgels, whose synthesis is initiated by charged groups, are characterized by a well-known thermodynamic volume phase transition (VPT). By controlling the microgel volume, the VPT affects dramatically microgel charge density and thus can enhance the electrostatic adsorption of oppositely charged polyelectrolytes (PE) [4] or nanoparticles (NP).

We have exploited this unique features of charged PNiPAM microgels to study their complexation with oppositely charged biopolymers and model nanoparticles. By combining electrophoresis, light scattering, transmission electron microscopy (TEM) and dielectric spectroscopy (DS) we have studied this complexation and its effect on the stability of microgel suspensions. We have shown that the VPT of the microgels triggers a large polyion adsorption only if polyion chains are “short enough” and always determines the onset of microgel reentrant condensation for increasing PE or NP concentrations, as opposed to a continuous enhancement of colloidal aggregation observed for increasing monovalent salt content. We show unambiguously that PniPam microgels, often considered as model neutral soft colloids, behave as strongly charged colloids especially at high T (>33 oC), where they phase separate in proximity of the isoelectric point, while their stability stays almost unaffected by PE or NP adsorption at lower temperatures.

Our results pave the way for a new route of controlled self-assembly and show how electroadsorption triggered by microgel VPT opens new intriguing scenarios for both fundamental soft matter and for the conception of smart new materials for optical devices.

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Biologically Active Liquid Crystal Droplets

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Interfacial Soft Matter

A facile method for fabricating protein-sequestered liquid crystal microemulsion droplets based on the uptake of surface-engineered protein-polymer surfactant (PS) core-shell nanobioconjugates will be described in the talk. Uptake of myoglobin (Mb-PS), bovine serum albumin (BSA-PS), Zn-porphyrin myoglobin (ZnIX-Pr-Mb-PS), horseradish peroxidase (HRP-PS) and glucose oxidase (GOx-PS) occurs without structural or functional degradation, and gives rise to sequestration within the interior or at the surface of 4-cyano-4/-pentyl biphenyl (5CB) nematic droplets depending on the net surface charge of the protein-PS conjugate. We use differences in uptake behaviour to achieve the spontaneous positional assembly of multiple proteins in the LC droplets, and demonstrate the use of spatially separated GOx and HRP enzymes to produce LC droplets capable of housing an enzyme cascade reaction. Our method opens a pathway for the development of bioactive liquid crystal droplets and could have potential applications in the optical sensing of biomolecular substrates.

Slowing down supercooled liquids by manipulating their local structure

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Arrested Soft Matter

Recent research on a variety of glass formers has demonstrated that local structural ordering plays a key role in the dynamics of glassy liquids. In particular, the local packing of particles defines the cages which particles need to escape in order for the system to relax its structure. Here, we use this observation to tune the glassy dynamics of a model glass former using short-range directional (``patchy'') interactions [1]. Starting from a dense binary-hard sphere mixture, we use computer simulations to explore the glassy dynamics of patchy particles with a wide range of geometries. We find that out of all geometries, particles with icosahedral symmetry are uniquely capable of facilitating dynamical arrest. These particles greatly enhance the number of icosahedral cages in the system, drastically impacting the relaxation rate of the system. In contrast, other patch geometries disrupt the icosahedral cages, resulting in faster dynamics. As icosahedral structures are also known to suppress the formation of long-ranged crystals, boosting their prevalence in a supercooled liquid is likely to lead to an excellent glass former. Our results open the door to controlling the dynamics of dense glassy systems by selectively promoting specific local structural environments.

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Dynamics of Membrane Wrapping of Microparticles

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Interfacial Soft Matter

Biological membranes partition eukaryotic cells into different compartments, each of which having its own function and integrity. Moreover, some organelles are characterized by very complex membrane shapes, which seem to confer to them, at least partly, their function. The regulation of biological membrane geometries is therefore crucial.

In vivo, proteins are most probably the main actors of membrane deformation. The underlying physical mechanisms of protein-membrane interactions are not comprehensively understood. 3D membrane geometries can be observed in protein-free systems as well. As the result of the adsorption of particles for example [1,2]. The adsorption of inert particles could thus enable reproduction of the essential physics of membrane deformation by bound proteins. Many numerical and simulation works have predicted how particles behave when adsorbed to membranes [3,4]. However, corresponding experimental data is lacking

We observe experimentally how micron sized particles bind and subsequently are enveloped by lipid membranes. The lipid membranes are characterized by a bending rigidity κb and a membrane tension σ, which is near zero in our experiments. The polystyrene particles used experience an adhering force introduced by depletion interactions. Both the adhesion energy and particle size can be varied continuously in our system without changing the underlying composition. Due to depletion interactions being used, the experimental system is also independent of the choice of particle material or specific lipid composition of the membrane. We observe the extent of wrapping of the particle over time and see the particle being taken up and effectively recoiling over a distance of one particle radius.

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Nanoparticle engulfment by bilayer membranes with compositional asymmetry

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Interfacial Soft Matter

We study the mechanical and curvature-elastic properties of bilayer membranes with compositional asymmetry by molecular simulations. The compositional asymmetry is controlled by the mole fraction ϕ_1 of lipids with a bulky head group in one of the bilayer leaflets. As we increase the mole fraction ϕ_1 of the bulky-head lipids, we observe a remarkable evolution of the stress profile across the bilayer and a strong increase in the first moment of this profile. In order to extract the spontaneous curvature from this moment, we also determine the bending rigidity of the bilayer. The resulting spontaneous curvature is found to be quite large compared to other molecular mechanisms for bilayer asymmetry. [1] The generated curvature leads to the formation of nanobuds, which provide new membrane compartments, in close analogy to cellular budding processes. Bilayers with compositional asymmetry can also be used to elucidate the influence of spontaneous curvature on the engulfment of nanoparticles. [2] Different morphologies of engulfment process is being studied by controlling tension in the membrane as well as the spontaneous curvature. This study has a potential application of understanding the cell environments that facilitate endocytosis and exocytosis. \\

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Adhesion remodelling upon cell shrinking

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Living Soft Matter

What happens to adhering cells when they expel water through their membranes; is adhesion lost or are the cell contacts being remodelled? It turns out these questions are of wide biological relevance- from osmotically shrinking cells to formation of lumen in embryos. To get a quantitative understanding we use a biomimetic model system, consisting of giant unilamellar vesicles (GUV's) coupled to a supported lipid bilayer or to other GUVs via strong biotin-neutravidin links, or via much weaker and biologically relevant cadherin bonds. Upon osmotic vesicle shrinking, the adjacent membranes locally disconnect and deform into water-filled pockets, also observed in cells. We are able to show that the adhesion bonds are sheared away from the disconnecting membranes, and later recover with time. The size, distribution and recovery dynamics are dependent on the magnitude of the osmotic shocks, and the strength and density of adhesion contacts.

Small-scale fracture in soft solids

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Processing & Stressed Soft Matter

Understanding how small flaws and cracks in soft solids nucleate and grow is important for a wide variety of processes, from general failure and fatigue, to adhesion, cavitation, and the design of new, soft, tough materials. These develop in a very different way to larger cracks, instead typically expanding elastically into smooth-walled, almost circular cavities before they start to extend. However, their growth is still not well understood — in part as there have been very few experimental studies on such flaws because of the difficulties of controllably making small, microscopic flaws in soft solids.

I will show how we use a new phase-separation technique to controllably grow and shrink small flaws in soft silicone solids. By combining sample stretching with this phase-separation technique, we are able to investigate in detail how these flaws grow by damaging the surrounding materials. Our results suggest that this growth process occurs at a constant driving pressure, is scale-free, and is independent of the material parameters that normally govern large crack growth. We propose a new phase diagram for flaw growth in soft materials with scale-free growth occurring below a fixed, material length-scale.

Resonant motion of magnetocapillary swimmers: lattice-Boltzmann simulations

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Active Soft Matter

Magnetocapillary swimmers are a system of three or more rigid magnetic particles trapped at a gas/fluid interface. Stable particle ensembles emerge as a result of equilibrium between the attractive capillary and the repulsive magnetic forces, while the motion of such a swimmer is induced by a modulation of the magnetic field.

A single triangular magnetocapillary swimmer is studied numerically using a hybrid method combining the pseudopotential lattice Boltzmann method and the discrete element method [1]. We first investigate the equilibrium properties of a single, two and three particles at the interface to match the parameters of the experiment [2].

Next, we demonstrate a controlled motion of the swimmer formed by three particles. It shows a sharp dependence of the average center-of-mass speed on the frequency of the time-dependent external magnetic field. Inspired by these experiments, we interpret the resonance by the optimal frequency centered around the inverse viscous time of a spherical particle. It is also shown that the resonance frequency grows and the maximum average speed decreases with increasing inter-particle distances at moderate swimmer sizes. The findings of our lattice Boltzmann simulations are supported by bead-spring model calculations [3].

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How active forces influence nonequilibrium glass transitions

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Arrested Soft Matter

Physical intuition suggests that increasing departure from equilibrium due to active forces fluidifies a glassy system. We falsify this belief by devising a model of self-propelled particles where increasing departure from equilibrium can both enhance or depress glassy dynamics, depending on the chosen state point. We analyze a number of static and dynamic observables and suggest that the location of the nonequilibrium glass transition is primarily controlled by the evolution of two-point static density correlations due to active forces. The dependence of the density correlations on the active forces varies

non-trivially with the details of the system, and is difficult to predict theoretically. Our results emphasize the need to develop an accurate liquid state theory for

nonequilibrium systems.

Stress management in composite biopolymer networks

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Living Soft Matter

Living tissues are mechanically supported by collagen networks, which need to be soft enough to allow for cell migration and proliferation, yet stiff at high deformation to prevent tissue rupture. The nonlinear mechanical response of single-component collagen reconstituted systems has been widely investigated[1,2]. However, in natural tissues, fiber collagen networks are embedded in a softer and charged matrix. Here[3], we combine rheology experiments and simulations to study the mechanical response of a biomimetic model system composed of the two paradigmatic tissue components: collagen and crosslinked hyaluronic acid (HA). We observe a synergistic mechanics characterized by an enhanced stiffness in the linear regime and a delayed strain-stiffening, strongly dependent on HA concentration. Additional measurements reveal that the presence of HA does not affect the structure or composition of the collagen networks and thus the changes in the mechanical response should be a result of a purely mechanical interaction between the fibre network and the HA matrix. Furthermore, close monitoring of the polymerization process shows that during the crosslinking of the HA matrix a negative normal stress builds up, indicating that the HA matrix wants to contract. Laser ablation experiments confirm the mechanical coupling between the collagen fibres and the HA matrix and suggest that the compressive stresses arising from the HA matrix are transferred to the collagen fibres. By developing a minimal computer model, we demonstrate that the compressive stress of a matrix is alleviated by the bending of the collagen fibres and plays a key role in the altered mechanical response. Deformation of these networks reveals that internal stresses and elastic reinforcement, both generated by the matrix, together with the fibre rigidity tune the composite response. In addition, we show that the effects of the matrix can be captured in an effective single fibre network model. We are able to rationalize the underlying physical mechanisms: the suppression of non-affine deformations causes mechanical enhancement in the linear regime; whereas the isotropic compression of the fibre network is responsible for the delayed strain stiffening. Our findings not only elucidate how biology combines polymers with complementary properties to finely-tune the mechanics of living tissues, but also provide a new avenue for the design of synthetic elastic materials. In fact, we showed that internal stress generation, which can for example be implemented in a synthetic material by using a pH- or temperature-responsive component, introduces a powerful control knob to tune the mechanical response of composite networks.

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Low Dose Antibiotics Can Cause Bacterial Aggregation

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Living Soft Matter

Bacterial aggregation is believed to be an important factor in disease as well as being industrially relevant. In this project, we find that low-dose antibiotics can cause aggregation. Specifically, we show that clustering can happen in high-density bacterial populations, triggered by a very low concentration of antibiotic. We find that a very different bacterial response is obtained depending on the type of antibiotic that is used, and we quantify the dynamical process of cluster formation using a combination of microscopic, spectroscopic and microbiological methods. Our results support a picture in which cluster formation happens due to the release of DNA by antibiotic-induced cell lysis [1].

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Distributions of first passage times reveal underlying free energy landscapes

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Colloidal & Granular Soft Matter

The concept of an energy landscape is central to the understanding of a wide variety of phenomena, ranging from the role of catalysts in chemical reactions to how proteins fold or molecules translocate across cell membranes. Here, a fundamental problem is to establish links between the dynamics of these complex processes and the energetic interactions that drive them. The problem of how molecules explore their energy landscapes, i.e. how an energy landscape leads to specific particle dynamics, has been extensively debated in theoretical and computational studies. In contrast, few methods exist to address the inverse problem of uncovering an energy landscape from a dynamic measurement. This is in spite of the fact that experimentally it is often details of the dynamics, rather than the energy landscape that are obtained, making the solution of this inverse problem crucial in the correct interpretation of experimental data. Conclusively establishing these quantitative links in experiment, however, is extremely challenging, as few experiments allow for the detailed knowledge of both the potential energy landscape and the particle dynamics required to verify proposed theories.

Here, we use a colloidal model channel system with a fully controllable potential landscape to experimentally probe these links for one-dimensional transport processes. In particular, we obtain the full first-passage time distributions for escape of a colloidal particle from a channel containing multiple potential minima. We demonstrate that the short-time regime of the distributions exhibits a power-law scaling that reflects both the number and the depth of the potential minima crossed by the particle before exiting the channel. Remarkably, this is consistent with theoretical predictions for a one-dimensional network of discrete states, indicating that a continuous potential landscape can be mapped onto this sequence of states. Furthermore, we consider the exponential decay of the first-passage time distributions at long times and show that the decay constants can be used to estimate both mean first-passage times and splitting probabilities for the process, which are again in good agreement with analytic theoretical predictions. As such, our method verifies that a purely dynamical measurement of the first-

passage time distributions can be used to uncover quantitative features of an underlying potential energy landscape, suggesting a new method of investigating the molecular mechanisms of complex processes.

Time-resolved charging dynamics of confined electric double layer

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Interfacial Soft Matter

Understanding the structural and dynamic response of an electric double layer (EDL) to external perturbation is central to myriad processes ranging from electrical energy storage by porous electrodes to controlling interfacial phenomena through tuning of surface interactions. In equilibrium, the EDL at a charged surface screens the associated electric field, with an exponential decay length (i.e., Debye length). Though, whenever changes in the surface potential (or charge) occur, the ionic atmosphere of the EDL rearranges to a new equilibrium configuration to neutralize the new surface charge, a dynamic process known as EDL charging. While this process is well understood for planar surfaces and macroscopic porous electrodes, to our knowledge, no measurements of EDL charging dynamics within a single nano-pore – the basic element of such electrodes - have been reported to date.

Here we describe a novel approach by which the dynamic behavior and charging time of EDL confined within an individual nano-slit (<< 1 μm) between two surfaces can be studied, following a potential-step applied to one of the surfaces [1]. This is done, using a surface force balance (SFB) combined with a custom-designed electrochemical cell [2], through monitoring the transient change of the forces between the confining surfaces due to an instantaneous electric field arising from the EDL perturbation, which decays as the EDL charges.

We showed that EDL charging time within the nano-slit is of order 0.5-2 sec, far slower than the time of order 0.03 sec characteristic of charging an unconfined surface in our configuration. In addition, we found that charging time increases at smaller slit thickness (increased confinement) and decreases with increasing ion concentration in the electrolyte solution. These findings are in line with the transmission-line model which describes the charging dynamics of an EDL within a nanopore, suggesting that the process of EDL charging within the nano-slit is largely limited by diffusion of ions from the bulk reservoir to which the nano-slit is coupled - this was further confirmed by measuring longer charging times for ions with smaller diffusion coefficients.

These results indicate that our novel approach provides a general means for probing EDL charging dynamics within a single nanopore in a controlled-fashion, where the nano-slit dimension and the nature of its surroundings and of its surface may be independently varied.

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Aggregation of colloidal particles in the presence of hydrophobic anions

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Colloidal & Granular Soft Matter

Colloidal properties including charging and aggregation behavior are studied in aqueous suspensions of amidine latex (AL) and sulfate latex (SL) particles containing sodium tetraphenylborate and NaCl. In monovalent salt solutions, AL is positively charged, whereas SL is negatively charged. Electrophoretic mobility measurements demonstrate that adsorption of tetraphenylborate anions leads to a charge reversal of AL particles. At higher concentrations, both types of particles accumulate negative charge. For AL particles, the charge reversal leads to a narrow fast aggregation region and an intermediate regime of slow aggregation. For SL particles, the intermediate slow regime is also observed. These aspects can be explained with classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO). Another regime of fast aggregation is observed at intermediate concentrations, and the existence of this regime can be rationalized by an additional attractive non-DLVO force. We suspect that this additional force is caused by surface charge heterogeneities. Although similar attractive forces were recently observed with direct force measurements the present data are the first ones that demonstrate the importance of such attractive non-DLVO forces in particle aggregation.

Preserving the cavity of hollow microgels by introducing charges into the polymeric network

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Making & Measuring Soft Matter

Hollow microgels have the potential to meet one of the key challenges in biomedical research: The design of nano-carriers allowing for triggered uptake, storage and release of drugs. Microgels are nanometer sized crosslinked polymers swollen in a good solvent. Temperature-sensitivity of the polymer enables temperature-controlled permeability of the shell. However, until now only hollow uncharged microgels were realised, where the cavity is mostly filled with polymer in the swollen state of the microgel. Only increasing the crosslinking density leads to defined hollow structures, but is accompanied by a loss of stimuli-sensitivity. Introduction of charges into the polymeric network improves the swelling properties of microgels due to the repulsion of similar charges and the increased osmotic pressure within the gel network. Using ionisable co-monomers for the synthesis, the swelling properties of hollow microgels are improved by additional sensitivity to pH and osmotic stress. This advanced responsiveness of such microgels makes them promising candidates for drug delivery systems.

In this work, we report on the swelling of hollow charged microgels in dependence of pH, ionic strength and temperature. Such microgels are synthesized via copolymerisation of N-isopropylacrylamide and dimethylitaconate onto sacrificial silica cores in a seed and feed precipitation polymerisation. Subsequently, sodium hydroxide is used to etch the silica cores and to saponify the ester groups to acidic groups introducing negative charges into the shell. Small angle neutron scattering is used to reveal the internal structure of these microgels. Complementary results on their swelling behaviour are obtained via super-resolved fluorescence microscopy. Additionally, their overall structure is explored using dynamic and static light scattering. Based on the use of an ionisable co-monomer, we are able to unveil the influence of charges on the structure of hollow microgels. Changing the pH induces ionisation of the microgel, and thus leads to a charged network.

We obtain an increased swelling towards the outside along with an increased internal cavity of the hollow microgel for the charged state compared to the uncharged state. Increasing the ionic strength in the ionised state of the microgel leads not only to a decrease in the overall size, but also influences the fuzziness of the network. The preservation of the cavity of the microgel in its charged state is obtained for temperatures above and below the volume phase transition temperature of poly(N-isopropylacrylamide) and for ionic strengths in the range of 0.1 mM to 50 mM.

Binary Hard Sphere Icosahedral Quasicrystals

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Self-Assembled Soft Matter

About 6 years ago our group started research at developing methodologies to structure matter at multiple length scales by Self-Assembly (SA). Presently, we see the induced SA of particles inside slowly drying droplets dispersed in an emulsion system and the resulting supraparticles (SPs) as a powerful generally applicable methodology of hierarchical SA. We found that making the shape of the particles the dominant factor in the SA is the most versatile way to use this route also for complex particle shapes and mixtures of particles. One of our first findings by both experiments and computer simulations was that spherical particles self-assembled inside a spherical confinement do not have their equilibrium bulk face centered cubic, close packed, crystal arrangement, but instead adopt an icosahedral symmetry. It turns out this icosahedral symmetry is the lowest free energy state up until roughly 100.000 particles [1]. Icosahedral packings are known not to be able to regularly pack in 3D space and are known e.g. for clusters of atoms interacting through a Lennard-Jones potential. However, it was not known that shape and thus entropy alone would favor this symmetry as well when it is induced by the spherical confinement. In recent work, we have extended our results to include the effects of particles shape (e.g. using rounded cube shaped particles) [2], rod-shaped particles [3], plate-shaped and binary particle systems. We will discuss how these changes affect the SA and how such SPs can be analyzed quantitatively on the single particle level in 3D by electron microscopy tomography [1-4]. We will also show our first more applied work on creating lasing SPs with tunable light emission [5] for which the emission properties are modified by Mie Whispering Gallery Modes. For a binary mixture of hard particles that form so-called MgZn2 Laves Phase crystals in bulk we find 3D icosahedral quasicrystals to be induced by the spherical confinement (unpublished work) allowing us for the first time to determine on the single particle level in 3D the structure of a quasicrystal and with computer simulations study how these systems nucleate and grow.

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Characterizing and controlling elastic turbulence in a viscoelastic fluid

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Polymeric Soft Matter

The properties of viscoelastic solutions are exceptionally applicable on the micron scale.

For example, in microfluidic devices mixing and heat transfer are strongly enhanced.

This is due to elastic turbulence [1], which bears similar qualities as inertial turbulence. The relevant dimensionless number characterizing viscoelastic fluids is the Weissenberg number, which compares the polymer relaxation time to the characteristic time of the flow dynamics.

Numerical solutions of the Oldroyd-B model in a two-dimensional Taylor-Couette geometry display a supercritical transition from the laminar

Taylor-Couette flow to the occurrence of a secondary flow [2]. The secondary flow is turbulent and caused by an elastic instability beyond a

critical Weissenberg number. The order parameter, the time average of the secondary-flow strength, follows the scaling law $\Phi \propto (\mathrm{Wi} - \mathrm{Wi}_c)^{\gamma}$ with $\mathrm{Wi}_c=10$ and $\gamma = 0.45$ and the power spectrum of the velocity

fluctuations shows a power-law decay with a characteristic exponent.

We also present first results on controlling the elastic instability through an oscillating rotation of the outer cylinder of the Taylor-Couette cell,

with a frequency close to the characteristic relaxation time of the dissolved polymers.

Finally, we address the three-dimensional geometry of the von Karman swirling flow between two parallel disks, which was used in Ref. [1].

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Biomimetic folding particle chains

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Making & Measuring Soft Matter

In analogy to how the sequence of amino acids determines the folded 3-D structure of proteins, we aim to control the folding of colloidal polymers via the sequence of particle types [1,2]. These colloidal strings mimic biological polymers, but can be observed in real-time on the monomer level by optical microscopy. Our simulations suggest that the prerequisites to determining a specific folded structure are a) a sequence of different isotropic interactions b) combined with an attractive directional interaction between the colloids [2]. We show how microfluidics can be used in combination with AC electric fields to assemble flexible colloidal strings [3] while controlling the sequence of particle types. The particle-particle interactions are determined by the individual surface chemistries and by the solvent composition. The interaction potentials between different patchy particles and the resulting folding behaviour of strings of particles can be studied using both confocal and holographic microscopy.

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Vertically-vibrated granular rods: topological defects and influence of imposed geometry

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Colloidal & Granular Soft Matter

We analyse liquid-crystalline ordering in vertically vibrated, quasi-two-dimensional monolayers of steel rods lying on a horizontal circular cavity, which project on the plate as rectangles. As a result of inelastic collisions between rods and the cavity walls, energy is transferred to the horizontal plane and the monolayer exhibits some characteristics typical of thermally excited equilibrium systems. After an initial transient regime, low aspect (length-to-breadth) ratio particles, at high packing fractions, frequently form globally tetratic arrangements with C4 symmetry. This symmetry, which is incompatible with the circular geometry of the cavity, is restored by the creation of four point defects with a total topological charge of +4. The defects, which are located close to the boundary at the corners of a square, exhibit slow dynamics which we investigate. Also, we study the modification of this behaviour induced by the presence of central obstacles of varying shape and size. Obstacles weaken the interaction between defects and favour the formation of smectic domains separated by blade-like interfaces sometimes connecting the inner and outer walls through a line. Obstacles also induce strong unidirectional rotation once a particular configuration stabilizes. We have developed ways to track the evolution of defects and studied the impact of clustering in the stability of the different patterns observed. Comparison of the structure and dynamics with simulation of thermally equilibrated particles allows us to investigate the similarities between non-equilibrium excited granular matter and the corresponding thermal systems.

Shape is coupled to diffusion for flexible colloidal chains

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Colloidal & Granular Soft Matter

Flexibly linked colloidal particles can self-assemble into a variety of structures, such as finite sized colloidal molecules, elongated polymer-like chains and floppy crystals. Because of their freely-jointed nature, chains of these particles serve as experimental models for flexible molecules such as proteins and polymers. Using colloid supported lipid bilayers and complementary DNA linkers, we tune the interactions between particles to form self-assembled chains of three spheres (flexible trimers). Interestingly, we find that the short-time translational and rotational diffusion coefficients depend on the instantaneous cluster shape. Additionally, we investigate how shape changes couple to the full diffusion tensor. Our findings may aid in understanding the diffusive behaviour of other materials that continually change their shape while moving, such as short polymers and intrinsically disordered proteins.

Hydrodynamic coupling between artificial cilia

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Living Soft Matter

Hydrodynamic interactions play a crucial role in the synchronisation of biological cilia. Here we experimentally and numerically studied a model system consisting of two artificial cilia at the low Reynolds number regime. The active cilium was driven by an oscillating external magnetic field and the non-magnetic passive cilium pivoted around its base in response to the fluid flow. When placed in the vicinity, the passive cilium followed the motion of the active one due to hydrodynamic interactions, yet with a reduced amplitude. We determined the coupling coefficients as a function of the separation between the cilia and the direction of forcing. The

results are in very good agreement with simulations using the Rotne-Prager approximation in the presence of a no-slip boundary.

Bacteria as living patchy colloids: Phenotypic heterogeneity in surface adhesion

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Living Soft Matter

Controlling the adhesion of bacteria to surfaces is of high biomedical relevance. Once adhered, individual cells can colonise surfaces to form biofilms that are hard to eradicate, posing serious infection risks and problems in hospital equipment, implant organs, water purification systems, and numerous other situations. Despite all this, many aspects of bacterial surface adhesion related to bacteria-surface interactions are still poorly understood. Recently, we have investigated the adhesive properties of individual Escherichia coli cells near glass surfaces from recorded microscopy videos [1]. Using high-throughput image-recognition and tracking algorithms we followed many cells within the population and carefully analysed their dynamics at the surface in time. We have observed strong phenotypic heterogeneities: a fraction of cells remained unadhered whereas others were able to adhere with an adhesion strength that in itself displayed phenotypic heterogeneity. We explain our observations with a patchy colloid model where cells bind with localized, adhesive patches. The strength of adhesion is determined by the number of patches: Nonadherers have zero patches, weak adherers bind with only a single patch, and strong adherers bind via a single or multiple patches. We discuss possible implications of our results for controlling bacterial adhesion in biomedical and other applications.

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Active filaments: Emergent conformational and dynamical properties

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Active Soft Matter

Conversion of internal energy or utilization of energy from the environment is a key feature of active matter, and gives rise to intriguing emerging structural and dynamical properties [1]. This particularly applies to soft matter systems, e.g., comprised of filaments or polymers, due to the tight coupling between nonequilibrium fluctuations and conformations [2]. This renders active soft matter a promising new class of materials. There are various realizations of active polymers. ATP-dependent enzymatic activity-induced mechanical fluctuations drive molecular motion in the cytoplasm of bacteria and eukaryotic cells and affect the properties of DNA molecules. Linear polymers, e.g., filamentous actin or microtubules of the cell cytoskeleton are propelled by tread-milling and motor proteins. In addition, the dynamics of passive colloidal particles and polymers is enhanced in a bath of propelled filaments [3,4].

Using analytical calculations and computer simulations, we analyze the conformational and dynamical properties of self-propelled linear and ring polymers, both, with (wet) [5] and without (dry) hydrodynamic interactions (HI) [3,4]. For the analytical calculations, we consider a Gaussian semiflexible polymer with active sites modeled by an Ornstein-Uhlenbeck process (active Ornstein-Uhlenbeck particle, AOUP), where the active velocity changes in a diffusive manner. In simulations, we employ a bead-spring linear phantom or self-avoiding polymer with active monomers (active Brownian particles, ABPs), where the propulsion direction obeys a random process. In the simplest case (no HI), this equivalently corresponds to either a self-propelled polymer or a passive polymer exposed to a colored noise environment. In the absence of HI, active leads to a swelling of flexible and, at intermediate activities, shrinkage of semiflexible polymers followed a reswelling at large activities. Two aspects govern this behavior, a direct increase in the conformational fluctuations by activity, and decreasing relaxation times with increasing activity. Moreover, activity yields a drastic acceleration of the polymer dynamics, both the center-of-mass and the intramolecular dynamics [3]. Interestingly, hydrodynamic interactions result in an enhanced shrinkage of polymers - even flexible polymers shrink at moderate activities and swell to a less extent than polymers in absence of HI [5]. Intriguingly, the properties of dilute solutions of active polymers depend on the nature of the active force. Wet polymers exposed to external colored noise swell stronger than dry and wet self-propelled ones. This is a consequence of an intriguing coupling between polymer conformations and HI, which is induced by the nonequilibrium process.

The predicted novel features by activity are essential for the function of, e.g., biopolymers, and might be exploited in synthetic systems for the rational design of new materials with tailored properties, e.g., for dynamical pattern formation and clustering, or viscosity modifiers.

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Shear-stress relaxation in free-standing polymer films

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Arrested Soft Matter

Using molecular dynamics simulation of a polymer glass model we investigate free-standing polymer films focusing on the in-plane shear modulus μ and the shear-stress relaxation modulus G(t) as a function of temperature T, film thickness H and sampling time t. Various observables, such as the glass transition temperature T_g, are seen to vary inversely with H demonstrating thus the (to leading order) linear superposition of bulk and surface properties. Confirming the time-translational invariance of our systems, μ is shown to be numerically equivalent to a second integral over G(t). As shown from the respective standard deviations, this is especially important for large times and for temperatures around the glass transition. Both μ and G are found to decrease continuously with T and a jump-singularity is not observed. Using the successful time-temperature superposition scaling of μ and G the shear viscosity can be estimated for a broad range of temperatures.

Unique mechanics of biopolymer microgels prepared inside artificial cells

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Self-Assembled Soft Matter

Biopolymer microgels, small gels of micrometer size, have been widely used for food, cosmetic, and biomedical applications because of their high biocompatibility and fast response to external stimuli. However, the properties of “single” microgels had not been well characterized due to limitations of measurement methods [1]. We recently revealed the unique mechanical properties of single microgels prepared inside microdroplets covered with a lipid layer, which has been used as artificial cells. In this presentation, we will explain two topics on the mechanical properties of single microgels different from the bulk gels.

The first topic is surface elasticity of gelatin microgels prepared inside lipid droplets. By using micropipette aspiration [2-3], we have revealed that the surface elasticity of the microgels gelled inside small droplets with $R < 50$ μm becomes 10 times higher than that of the bulk gels. Structural analysis demonstrated that the smaller microgels contained more β sheets in the structure than the bulk gel. The β-sheet rich structure can be the higher elastic origin of the gelatin microgel than the bulk gel. This finding indicates that the confinement size of gelling polymers becomes a factor in the variation of elasticity of protein-based microgels via secondary structure changes [4].

The second topic is the mechanical properties of droplets with the skeletal structure of DNA gels. Recent advances in DNA nanotechnology have made it possible to build a variety of DNA-based materials [5]. We used branched DNA nanostructures and mechanically stabilized lipid droplets to solve the fragility which is problematic in application. Due to the electrostatic interaction between DNA and lipid membrane covering the droplets, the branched DNA nanostructures spontaneously form skeletal network beneath the membrane. By using micropipette aspiration, we have demonstrated that the skeletal structure of DNA increases the viscoelastic properties of the lipid droplets [6].

The recent progress in fabrication and characterization of single microgels will bring important framework for design and functionalization of gel-based materials, and provide novel insights of scale-effect during gelation on gel mechanics.

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Dynamics of Viscoelastic Filaments based on Onsager Principle

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Processing & Stressed Soft Matter

When a polymer solution is uniaxially stretched and held fixed at both ends, the solution quickly separates into droplets connected by strings and takes the beads-on-string structure. The string then becomes thinner by capillary forces. Here we develop a theoretical framework on viscoelastic fluids based on Onsager variational principle and apply it to the dynamics of viscoelastic filaments. We show that the beads-on-string structure is a thermodynamic quasi-equilibrium state, and derive an equation for the coexistence condition in the pseudo-equilibrium state. Using the condition, we solve the evolution equation analytically and show that the string radius and the tensile stress vary exponentially as predicted by the classical theory of Entov and Hinch [J. Non-Newtonian Fluid Mech. 72, 31 (1997)], but the prefactor for the tensile stress is different from their theory and agrees with the numerical solutions of Clasen et al. [J. Fluid Mech. 556, 283 (2006)].