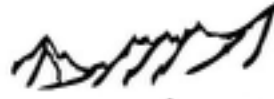Network dynamics :

Synthesis, structure and mechanical properties

Les Houches, 26th Feb - 1st March

Book of abstracts

Monday

Brittle-to-Ductile transition in fractal colloidal gels

M. Milani, E. Cavaletti, K. Ahmad, C. Ligoure, <u>L</u>. Cipelletti, **L. Ramos**

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Due to their complex disordered structure, colloidal gels are exquisite models to capture the behavior of amorphous solids under mechanical stresses and are relevant for various applications: from food industry to the manufacturing of ceramics.

We produce millimetric beads of colloidal gels made by controlled aggregation of nanoparticles into disordered network-like structure with tunable characteristic length scale and elastic modulus, which typically varies from 1 kPa to 1000 kPa. We couple mechanical measurements and imaging to investigate the yielding of the beads in compression in boundary free conditions.

The mechanical response display features akin to brittle-like or ductile-like behavior depending on the sample elastic modulus and on the compression rate, which we vary over more than three orders of magnitude. Beads of hard materials compressed at fast rates exhibit a brittle-like response and are observed to fracture abruptly producing distinct macroscopic pieces of seemingly intact gel. By contrast soft beads compressed at slow rates exhibit a ductile-like behavior and deform smoothly keeping their integrity during the all compression process. Our experiments evidence the interplay between material elasticity, plasticity and poroelasticity in the yielding of beads of colloidal gels.

Measuring elastic heterogeneities in colloidal gels

<u>David Richard</u> & Mehdi Bouzid

Adhesive particles dispersed in a suspension can self-assemble into a rigid percolating gel network. In this numerical study, we investigate the elasticity of gels formed from a continuous quench with a competitive interaction between a short-range attraction and long-range repulsion. Using finite-size scaling as well as measuring vibrational properties at the rigidity transition, we demonstrate that the elasticity of purely adhesive particles is controlled by bending modes and fall within the theoretical framework developed by Kantor and Webman. In parallel, we characterize the magnitude of mechanical heterogeneities in a variety of gels that feature different pore and strand sizes. Here, we employ two complementary methods, namely, the linear response of dipole forces and the random walk on fractals. Together, we are able to rationalize the rapid change of the shear modulus as a function of the particle concentration, quench rate, and repulsion strengthDirect Confocal Imaging of Fracture Precursors in Casein Gel

Network and entanglement contributions to elasticity of rubbers.

<u>Carsten Svaneborg</u>

We perform Molecular Dynamics simulations of Kremer-Grest model polymer networks representing PDMS polymers. Using primitive-path analysis and phantom primitive-path analysis, we obtain information about the relative importance of network structure and topological entanglements. We will also present preliminary work on generating polymer models with a well controlled topological state.

Direct Confocal Imaging of Fracture Precursors in Casein Gel

Mathieu Leocmach

Due to their heterogeneous nature, gels show a complex, yet characteristic delayed yielding behavior under the application of sub-critical stress. This makes us interested in understanding what are the signs or precursors existing within the material before the final catastrophic failure. Scattering studies hint toward microscopic changes well before failure [S. Aime et al., PNAS, 115, 14 (2018)]. What we are interested in is the direct real-space observation of the gel microstructure under shear. For this, we have designed our own setup ICAMM [A. Singh at al., Meas. Sci. Technol., 32 125603 (2021)], which can be integrated with a confocal microscope and has precision in stress application and measurement up to 6 mPa on an area as wide as the field of view of the microscope. This setup enables simultaneous shear experiments and 3D image acquisition of the whole sheared volume. Using a 3D implementation of a dense optical flow algorithm on the confocal images of the sheared gel, we are able to obtain the local strain rate field and thus, detect and have statistics on structural precursors (strand breaking events).

Understanding the physical nature of chromosomes in living cells

Antoine Coulon

Our understanding of genome organization and nuclear architecture have greatly progressed in the past few decades, thanks to advances in sequencing-based technologies for mapping chromosomal contacts and in microscopy-based technologies for visualizing chromosome folding and dynamics. However, beyond visualization, the ability to physically manipulate chromosomes inside a living cell holds great potentials to reveal what passive visualization cannot. I will present a new technology we have developed for direct mechanical manipulation of chromosomes inside living cells with magnetic forces [Keizer et al. 2022]. I will discuss what this approach taught us about the physical nature and material properties of interphase chromosomes, as well as the challenges and opportunities that lie ahead. Keizer et al. 2022 https://doi.org/10.1126/science.abi9810

Photon correlation imaging of polymer network fracture

Nicholas Orr

Network-forming materials are ubiquitous and appear in industrial products such as tires, food and cosmetics as well as composing the cytoskeleton within the cells of living organisms. They are lightweight and display desirable properties such as optical transparency and reversible deformability up to large strains. However, the microscopic mechanisms protecting a network against macroscopic fracture and the processes that control crack growth are still poorly under-stood. A deeper understanding is needed to fully exploit the potential of polymer networks in advanced and novel material design. In recent years a general phenomenon has emerged where materials composed of an interpenetrated stiff filler network and a soft matrix network display toughness far greater than either constituent [1,2]. Herein we adapt photon correlation imaging [3] (PCI) to reveal the microscopic rearrangements within poly(ethyl acrylate), PEA, networks [4] during deformation by extension and fracture (see figure 1). We examine how such rear-rangements differ in a simple PEA network and in double network composed of two interpene-trated PEA networks, one stretched and stiffer with respect to the other. We find that rearrange-ments in the double networks occur over larger distances strain windows thereby serving to re-duce stress at a crack tip and hinder its propagation.

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Structural and mechanical properties of bio-inspired polymer networks

Virginie Hugouvieux **(1)** and Walter Kob (2)

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We use molecular dynamics simulations to study the structural and mechanical properties of bead-spring polymer networks. In this study we deal with systems which are biologically-relevant as they result from the action of enzymes, i.e. biological catalysts. The latter convert repulsive monomers into attractive ones and hence, starting from a polymer solution, trigger the formation of a physically-crosslinked polymer network. This gel has a remarkably regular mesostructure in the form of a cluster phase. We simulate uniaxial tension of these networks. The evolution of their structural and mechanical properties during deformation is monitored by computing quantities such as the anisotropic pair correlation functions, Poisson's ratio, elastic moduli and stress-strain curves, and the effects of temperature and system composition (i.e. fraction of attractive monomers) are investigated.

Tuning mechanical properties of collagen networks using a stress-ramp during gelation

Lens M. Dedroog 1, Minne P. Lettinga 2, Kamal Tripathi 7, Erin Koos 3, Anja Vananroye4, Olivier Deschaume 1, Carmen Bartic1, Yovan de Coene 5, Wim Thielemans 6 and **Mehdi Bouzid** 7

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Collagen is one of the main building blocks of the mammalian extracellular matrix, due to its ability to form tough structures with a wide variety of non-linear mechanical properties allowing it to support multiple tissue types. The mechanical properties of collagen gels have been extensively studied under static conditions, however, in nature gelation will mostly take place in the presence of flow. Here we show how the elastic modulus of collagen hydrogels can be increased up to one order of magnitude by applying an stress-ramp at a well-defined moment during gelation. The first stress block induces most of the final strain and alignment, however sequential increases in stress cause a dramatic increase of the modulus. Coarse grained molecular dynamics simulations of a gel model system suggest that the microscopic mechanism of inducing high stiffness could be very generic and is controlled by the rigidity percolation transition. Thus, we not only show that the true non-linear capabilities of biomaterials are tenfold higher than previously assessed, but also provide insight into in vivo structure formation of collagen and potential other (bio-)polymers.

Numerical study of the deformation and fracture of multiple polymer networks

Magali Le Goff

Network-forming polymeric materials are ubiquitous, from industrial products (tires, food, cosmetics,...) to living organisms (cytoskeleton, extracellular matrix,...). These materials often possess remarkable properties, such as high toughness, compliance, light weight or optical transparency. Understanding the mechanical properties of multiple network materials at the molecular scale is essential to improve the quality of these new macromolecular architectures. In this talk I will present a study based on coarse-grained numerical simulations of polymer networks to address the question how they deform and fracture under external loads. We investigate the mechanical response as well as the damage dynamics in these systems by comparing single and double networks.The double networks are characterized by a first istotropically pre-streched network that is close to failure coupled to a second floppy network that only breaks at later stages. We show that depending on the preparation protocol we can control the ductility of the double network that depends on the volume fraction of the second network. Within these simulations we have direct access to the local damage that we can correlate to the macroscopic failure behaviour. We show that in the single network bond breaking events are strongly correlated in space and lead to more brittle failure of the network, whereas in double networks the bond breaking events are more delocalised promoting the ductile failure behaviour of double networks.

Tuesday

Hydrogels of Carboxymethylcellulose

__Thibaut Divoux__

In this talk, we offer a comprehensive description of a model hydrophobic physical gel obtained by acidification of carboxymethylcellulose (CMC), a water-soluble derivative of cellulose broadly used in numerous applications ranging from food packaging to biomedical engineering. Linear viscoelastic properties measured at various pH and CMC contents allow us to build a sol-gel phase diagram and show that CMC gels exhibit broad power-law viscoelastic spectra that can be rescaled onto a master curve following a time-composition superposition principle. These results demonstrate the microstructural self-similarity of CMC gels and inspire a simple model based on hydrophobic interchain association that accounts for the sol-gel boundary over the entire range of CMC content under study. Neutron scattering experiments further confirm this picture and suggest that CMC gels comprise a fibrous network cross-linked by aggregates, while low-field NMR measurements offer an original signature of the gelation from the solvent perspective. Finally, we discuss the shear-induced yielding transition in CMC gels through Large Amplitude Oscillatory Shear experiments, including intracycle analysis, which offer additional insights on CMC gels microstructure. Altogether, these results open avenues for the precise manipulation and control of CMC-based hydrogels.

Triggering the pressure response of metallic glasses through the ergodicity of the compressed state

__Beatrice Ruta__

Understanding the atomic structural changes and dynamics induced by thermo-mechanical treatments in metallic glasses is a challenging task, whose knowledge is fundamental to assure desired properties during applications. By developing and combining in-situ high pressure x-ray photon correlation spectroscopy measurements with high energy synchrotron diffraction and fast scanning calorimetry, we show how the level of ergodicity reached by the material during hot hydrostatic compression determines the degree of relaxation or rejuvenation reached by the system after the treatment. The resulting compressed glasses correspond to polyamorphic states with different thermal, structural and dynamical properties, which persist even once the system is re-heated in the equilibrium liquid. Furthermore, a complex devitrification mechanism is observed under high pressure which contrasts with the common wisdom of an equilibrium recovery controlled solely by the structural α-relaxation, in agreement with recent results obtained in other families of glasses.

Discrete-to-continuum models for elastic response of crosslinked protein networks subject to localized and bulk deformations

Jakub Köry

Crosslinked networks of proteins are ubiquitous in living systems, as they form scaffolding structures of tunable strength and elasticity, thus conferring mechanical stability on both cells and tissues. Existing models of protein network mechanics fall into two categories: discrete (microscale) models enable inclusion of detailed biophysics but are typically computationally challenging due to the large number of discrete elements and their interactions, while continuum (macroscale) models are easier to solve but the manner in which microscale parameters and processes manifest themselves at the macroscale is usually unclear. Mathematical modelling efforts involving more rational and rigorous mathematical methods to systematically bridge between these two approaches are still largely missing. One such method is discrete-to-continuum asymptotics where, assuming that two separate length scales exist, one can rationally upscale force balance equations based on Taylor expansions to form a continuum system of governing equations, inferring the corresponding macroscopic stress tensor and strain energy density. In this talk, we develop and utilize such multiscale mechanical frameworks in two simple settings involving intra- and extra-cellular spaces: the mechanics of eukaryotic cell cytoplasm during intra-cellular transport, considered primarily due to deformations of the cytoskeleton (a network of crosslinked filamentous proteins) and that of human cornea when loaded with intraocular pressure under healthy and diseased conditions. We disregard complex biorheological aspects involving visco-elastic, poro-elastic and plastic effects, thus focussing solely on the network elasticity. As the first application of this methodology, we estimate forces exerted on a small circular object when transported through a simple cytoskeletal network. The discrete model involves an initially regular (square) array of pre-stretched protein filaments (e.g. actin, vimentin) which exhibit resistance to enthalpic stretching, joined at crosslinks to form a planar network. To mimic inertialess motion of the object, we impose a quasi-static displacement of a set of crosslinks localized to the centre of the domain and solve for the remaining nodes through a local force balance. Assuming that the inter-filament distance is much shorter than the size of the cell we construct the continuum model via discrete-to-continuum upscaling. We solve both models numerically, calculate net force exerted on the object at a fixed displacement and infer force-displacement curves which show good quantitative agreement across the parameter space. The force-displacement curves have weak dependence on the pulling angle (with respect to the initial filament orientation). The net force acting on the object increases with increasing pre-stress and larger objects. Furthermore, we linearize the continuum model to construct analytical approximations for the stress and strain fields in the neighbourhood of the moving object, and explicitly compute the net force required to generate a given deformation as a function of key parameters, such as the object and mesh sizes, the pulling angle and the network pre-stress. We conclude this part by presenting preliminary findings from ongoing work where we study localized deformations in disordered networks composed of randomly positioned long fibers and short crosslinks located at their intersection. Then, we consider mechanical behaviour of a planar slice of human corneal tissue, in equilibrium under the (macroscale) action of intraocular pressure. The discrete model considers a regular (two-dimensional) network of structural elements mimicking a discrete number of collagen lamellae connected by proteoglycan crosslinks. Since the thickness of each collagen lamella is small compared to the corneal thickness, we upscale the discrete force balance into a continuum system. For physiological value of the intraocular pressure, we demonstrate that the predictions of the discrete model converge to those of the continuum model. We use the computationally efficient continuum model to simulate the progression of the degenerative disease known as keratoconus, characterized by a large bulging of the cornea. We assign a spatial distribution of damage (i.e., reduction of the stiffness) to the mechanical properties of the structural elements and predict the resulting macroscopic shape of the cornea, showing that a large reduction in the element stiffness results in substantial corneal thinning and a significant increase in the curvature of both the anterior and posterior surfaces. Future work will incorporate nonlinear effects in polymer elasticity, dynamic aspects of cell rheology and through-thickness variations in mechanical properties of the cornea. Acknowledgements: This research was funded by EPSRC grant EP/S030875/1, supervised by Profs. Peter Stewart, Nick Hill and Xiaoyu Luo and done in collaboration with Profs. Anna Pandolfi (Politecnico di Milano; cornea) and Ming Guo (MIT; disordered networks). We also thank Prof. Roger Kamm (MIT) for valuable discussions.

Emergent Mechanics of Equilibrium and Out-of-equilibrium Dynamic Networks

Franck Vernerey

A large majority of soft biological materials are made of molecular networks with changing topology, allowing to accommodate growth, remodeling, and self-healing over time. Such behaviors can now be replicated in man-made polymers through the synthesis of networks whose chains are connected by weak molecular bonds, which under thermal fluctuations can permanently associate and dissociate. In contrast to their elastic counterparts, these networks therefore exhibit a myriad of new physics (flow, elastic deformation, self-healing, programmability, actuation, ...) that can be controlled by the nature of the constituents, their topology as well as bond dynamics. With these opportunities come challenges, related to a steep increase in the design space, but also a hindered ability to fully comprehend the complex spatio-temporal response of these materials. This talk will discuss how we can use tools in statistical mechanics and the dynamics of complex systems to address these shortcomings. In the first part of the talk, we discuss a statistical mechanics framework that enables us to understand the trajectories of these networks as they are subjected to external loading or to the work of internal processes. We will pay particular attention to the link between bond dynamics and the complex emerging response of the network, including nonlinear rheology, yield stress behavior, damage, and self-healing. We will also discuss how the concept of detailed balance can be used to draw a clear distinction between thermally driven and active (out-of-equilibrium) networks. In the second part of the talk, we will shift our focus to active networks, whose bond dynamics is not ensured by thermal fluctuations. For this, we take the example of a biological network made by Solenopsis invicta (better known as fire ants) as they form cohesive rafts to escape floods. We will see that while they recapitulate most features of thermally driven polymers, these networks differ in that they do violate detailed balance. This enables the raft to actively heal defects and exhibit treadmilling dynamics, a behavior that is reminiscent of that of the actin cytoskeleton, another albeit more complex living network. We finally show that these dynamics culminate with the network's ability to exhibit morphogenesis with the stochastic emergence and retraction of long protrusions from the raft's edge. To conclude, we discuss how a fundamental understanding of dynamic networks is crucial for elucidating the intricate mechanical characteristics of transient polymers, active living materials, and for designing decentralized, autonomous active matter, and synthetic swarms.

Anisotropic micromechanics of fibrous gels stretched illuminate the cellular microenvironment

Shahar Goren

Semiflexible fiber gels such as collagen and fibrin have unique nonlinear mechanical properties that play an important role in tissue morphogenesis, wound healing, and cancer metastasis. Optical tweezers microrheology has greatly contributed to the understanding of the mechanics of fibrous gels at the microscale, including its heterogeneity and anisotropy. However, the explicit relationship between micromechanical properties and gel deformation has been largely overlooked. We introduce a unique gel-stretching apparatus and employ it to study the relationship between microscale strain and stiffening in fibrin and collagen gels, with emphasis on the development of anisotropy in the gel. We find that gels stretched by as much as 15% stiffen dramatically both in parallel and perpendicular to the stretching axis, and that the parallel axis is 2-3 times stiffer than the transverse axis. This anisotropy modifies the force propagation in the gel, leading to enhanced propagation of mechanical signals. We also measure the stiffening and anisotropy along bands of aligned fibers created by aggregates of cancer cells, and find similar effects as in gels stretched with the tensile apparatus. Our results illustrate that the extracellular microenvironment is highly sensitive to deformation, with implications for tissue homeostasis and pathology.

When actin pushes : self-organization of active polymer networks under compression

Serge Dmitrieff

Actin gels are networks of active flexible filaments. Although individual filaments can exert modest active force (in the picoNewton range) on their environment, networks of actin can exert much larger forces (in the nanoNewton range). Here, we used a combination of analytical theory and numerical simulations to understand how the growth of actin networks depend on the imposed stress. We find that the relationship between growth speed and stress exhibits three regimes, that can be understood by simple scaling arguments.

Unconventional colloidal aggregation in chiral bacterial baths

Dan Grober

Beginning in the iron age, craftsmen used the annealing process to hone the properties of steel. Thousands of years later, we understand that injecting energy into the metal through repeated heating and cooling cycles change the structure of the steel at a mesoscopic level; these structural changes determine the material properties. My work aims to transfer the annealing concept to soft materials (gels) assembled from micrometric building blocks (colloids). Rather than temperature, we leverage energy injected by active matter (swimming bacteria) into the suspending fluid to agitate and re-organize the material structure. Our recently published experimental work [Grober et al., Nature Physics, 2023] investigates the 2D aggregation of sticky colloids into unconventional phases, controlled by the concentration of swimming E. Coli bacteria present in the suspending medium. This establishes the activity of the bacterial bath as a potent lever of control over the structure of the material. A minimal numerical model of sticky colloids aggregating in an active bath displays excellent agreement with the structures and networks observed in the experimental system. Furthermore, these simulations indicate that colloidal gels assembled in the active bath exhibit novel material properties, and these properties can be tuned by the activity of the bath. Ongoing experimental work exploits opto-genetically modified E. coli, whose speed can be tuned by the intensity of incident green light, to dynamically adjust the agitation of the surrounding media in both time and space. Pairing this experimental system with classical rheological techniques, we hope to develop and characterize a new class of novel soft materials whose mechanical properties are directed by the internal injection of energy.

Resilience-rigidity duality in colloidal gels

Safa Jamali

Colloidal gels exhibit solid-like behavior at vanishingly small fractions of solids, owing to ramified space-spanning networks that form due to particle–particle interactions. These networks give the gel its rigidity, and with stronger attractions the elasticity grows as well. The emergence of rigidity can be described through a mean field approach; nonetheless, fundamental understanding of how rigidity varies in gels of different attractions is lacking. Moreover, recovering an accurate gelation phase diagram based on the system's variables has been an extremely challenging task. Understanding the nature of colloidal clusters, and how rigidity emerges from their connections is key to controlling and designing gels with desirable properties. Here, we employ network analysis tools to interrogate and characterize the colloidal structures. We construct a particle-level network, having all the spatial coordinates of colloids with different attraction levels, and also identify polydisperse rigid fractal clusters using a Gaussian mixture model, to form a coarse-grained cluster network that distinctly shows main physical features of the colloidal gels. A simple mass-spring model then is used to recover quantitatively the elasticity of colloidal gels from these cluster networks. Interrogating the resilience of these gel networks shows that the elasticity of a gel (a dynamic property) is directly correlated to its cluster network's resilience (a static measure). Finally, we use the resilience investigations to devise [and experimentally validate] a fully resolved phase diagram for colloidal gelation, with a clear solid–liquid phase boundary using a single volume fraction of particles well beyond this phase boundary.

Generic elasticity of thermal, under-constrained systems

Matthias Merkel

At zero-temperature, the rigidity of many amorphous systems can be determined by constraint counting, which compares the number of degrees of freedom of a system to the number of constraints. For instance, under-constrained systems are typically floppy. Examples are polymer networks and vertex models for biological tissues. However, these under-constrained systems can be rigidified by the application of external strain, and we recently developed a generic analytical theory for predicting the elastic material properties of such systems in the athermal (i.e. zero-temperature) limit. Here, we extend this theory to the finite-temperature regime close to the athermal transition point, where we show that all under-constrained systems behave in the same generic way. For instance, in the limit of infinitely stiff springs, where elasticity is purely entropic, isotropic tension t and shear modulus G scale with temperature T and isotropic strain e as $\sim T/|e|$. Furthermore, we show that for finite spring stiffness, entropic and energetic rigidity interact like two springs in series. This also provides a simple explanation for the previously only numerically observed scaling $t \sim G \sim T^{(1/2)}$ at $e = 0$. Our work unifies the physics of systems as diverse as polymer fibers & networks, membranes, and vertex models for biological tissues.

Wednesday

Fracture of double networks: insights from coarse-grained simulations

Justin Tauber, Simone Dussi, **Jasper van der Gucht**

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In the last 20 years we have seen the emergence of a new class of polymer materials that consist of two interpenetrating polymer networks. This has led to the development of ultra-tough double network hydrogel networks [1] and elastomers [2] with a strength that far exceeds that of the individual networks. While tentative explanations for the observed toughening have been proposed, it remains unclear how the mechanical interplay between the two interlocked networks governs stress localization, crack nucleation and propagation.

Here, I will present coarse-grained simulation results at various length scales to address this question. First, I will show how the double network structure fine-tunes the non-linear mechanics of composites [3]. Then, I will discuss how the relative stiffness and pre-stretch of the two networks tunes the distribution of stress in the network and can lead to a transition from brittle fracture to ductile failure with large diffuse damage [4,5]. I will then compare this to experimental results.
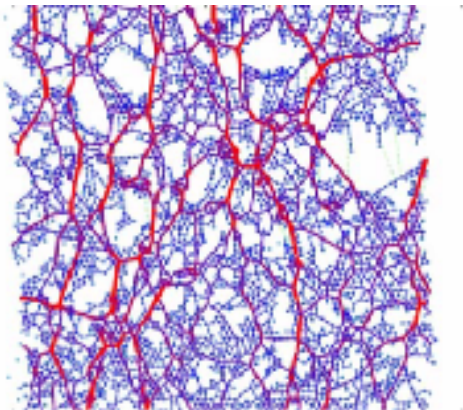
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Colloidal gels made with rough particles: Effects of non-central forces on gel rheology.

Jan Vermant

Florence Müller, Lucio Isa, Jan Vermant

When attractive interactions are introduced between particles, network structures can form, leading to macroscopic elastic gels. Surface heterogeneities (chemical or physical) have been shown to significantly impact the percolation threshold of colloidal gels as well as their rheological properties, first using simulations [1]. To elucidate the effects of particle roughness on gel properties, we prepared thermoreversible gels made from rough or smooth silica particles using a reliable click-like-chemistry-based surface grafting technique. Rheological and optical characterization revealed that rough particle gels exhibit enhanced toughness and self-healing properties. In the ralk we will also discuss the effect of surface roughness by discriminating between central and the non-central forces between primary particles on colloidal gels at low volume fractions. To this end, we performed single-particle atomic force microscopy (AFM) experiments (often called colloidal probe AFM, CP-AFM), where the same particles that were used to form the gels are now studied. Although not providing an integral view on the effects of non-central forces yet, the results demostrate the sgnificant effects of non central forces.

Shear-induced gelation of non-Brownian breakable particle suspension in polymer solution

Jacques Blin

An aggregate is a particle composed of several primary unbreakable particles held together by cohesive forces. Suspensions of such aggregates in a Newtonian liquid display standard rheological features, e.g., a shear-thinning response for increasing shear rates, with the key difference that aggregates undergo an irreversible structural degradation beyond a critical stress. Such a dramatic degradation is currently used in several applications, among which targeted drug delivery is the most popular. Here, we study the rheological properties of non-Brownian aggregates composed of fumed silica colloids and suspended in a high molecular weight polyacrylamide solution. We show that these suspensions display a shear-thickening response, and remarkably tunable viscoelastic properties selected by shear history. Indeed, under low shear rates, below the onset of shear-thickening, the suspension's elastic properties are reinforced with accumulated strain and the suspension may even form a gel. Such shear-induced gelation is fully reversible, and the gel can be disrupted when applying larger shear rates right above the onset of shear-thickening. Moreover, the linear viscoelastic spectrum of the gel obeys a remarkable shear-connectivity superposition principle, which allows us to build a master curve capturing the linear viscoelastic properties of the sample following various shear histories. Finally, we demonstrate that such phenomenology remains valid, as long as the maximum stress experienced by the suspension remains below the critical stress associated with the structural degradation of the aggregates. Indeed, once the aggregates are broken, the suspension displays a mainly shear-thinning response over the entire range of shear rates explored.

Strain-stiffening of elastic networks

Edan Lerner

Disordered elastic networks provide a framework for describing a wide variety of physical systems, ranging from amorphous solids, through polymeric fibrous materials to confluent cell tissues. In many cases, such networks feature two widely separated rigidity scales and are nearly floppy, yet they undergo a dramatic stiffening transition when driven to sufficiently large strains. In my contribution I will present a complete scaling theory of the critical strain-stiffened state in terms of the small ratio between the rigidity scales, which is conceptualized in the framework of a singular perturbation theory. The critical state features quartic anharmonicity, from which a set of nonlinear scaling relations is derived. Scaling predictions for the macroscopic elastic modulus beyond the critical state are derived as well, revealing a previously unidentified characteristic strain scale. I will then compare the predictions of the theory to a broad range of available numerical data on biopolymer network models, and discuss future research questions.

Yielding of gel and fibrous network materials

Suzanne Fielding

This talk will report the results of recent simulations aimed at understanding the yielding behaviour of gel like and fibrous network materials. It will focus on two different classes of model: (i) mesoscopic elastoplastic models, and (ii) more microscopic but still simplified network models. In each class of model, permanent breakage of local elements is incorporated. Results will be presented for yielding behaviour in different rheological protocols, with the aim of identifying commonalities in yielding mechanisms between them. Particular focus will be placed on the way in which sporadic events that pre-cursor final material failure then spatially cooperate to result in failure.

Conformal invariance of rigidity percolation

Nina Javerzat

Rigidity percolation is a simple and generic framework to understand the solidification of amorphous matter, by focusing on the subnetworks responsible for the overall solidity --the rigid clusters. I will explain that, although amorphous matter does not display any structural symmetry (no long range order), an important symmetry emerges at the onset of rigidity percolation: conformal invariance. I will explain indeed how we can show that rigid clusters are statistically conformally invariant, and how we can use this symmetry to predict universal behaviour. Based on Phys. Rev. Lett. 130, 268201 (2023) and arXiv:2301.07614

Systematic modification of functionality in disordered elastic networks through free energy surface tailoring

Dan Mendels

A combined machine learning–physics–based approach is explored for molecular and materials engineering. Specifically, collective variables, akin to those used in enhanced sampled simulations, are constructed using a machine learning model trained on data gathered from a single system. Through the constructed collective variables, it becomes possible to identify critical molecular interactions in the considered system, the modulation of which enables a systematic tailoring of the system's free energy landscape. To explore the efficacy of the proposed approach, we use it to engineer allosteric regulation and uniaxial strain fluctuations in a complex disordered elastic network. Its successful application in these two cases provides insights regarding how functionality is governed in systems characterized by extensive connectivity and points to its potential for design of complex molecular systems.

Controlling the properties of colloidal gels by shear history

George Petekidis
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Attractive colloids form out-of-equilibrium states such as colloidal gels and attractive glasses which often exhibit strong thixotropy. Their mechanical properties are affected by pre-shear history and show a time evolution after nonlinear steady or oscillatory shear tests due to shear induced structural changes and subsequent restructuring after shear cessation. Both in model and industrial systems such preshear protocols can be used to tailor the structure and mechanical properties by driving the system in different metastable states, possibly, not accessible via a thermodynamic route.

Here we present a series of experiments (combining rheometry and confocal microscopy) and computer simulations on colloidal gels of varying interactions and volume fractions utilizing both model colloid-polymer gels as well as more complex systems of industrial interest. We use steady and oscillatory pre-shear with varying shear rate and strain amplitude respectively and follow microstructural changes introduced by such flow history and how they can be used to tune the linear and nonlinear mechanical properties of the gel. These studies demonstrate the potential of shear and flow history to manipulate a broad range of metastable soft matter systems.

Thursday

Elasticity from transient filament contacts in branched actin

Olivia du Roure & Martin Lenz

The biologically crucial elasticity of actin networks is usually understood as an interplay between the bending and stretching of its filaments. This point of view however fails when applied to the weakly coordinated branched actin networks found at the leading edge of the cell. Through experiments and theory, we show that their elasticity crucially involves reversible contacts between their filaments. These contacts can in turn be controlled through filament entanglement during network growth to regulate the final properties of the network. These properties could be key to understanding how moving cells dynamically adapt their cytoskeleton to their environment.

Active deformation, force transmission and mechanical interaction in elastic biopolymer networks

Abhinav Kumar

Myosin motors produce mechanical forces in cells by contracting a disordered actin network. These forces drive various cellular processes such as shape change, cell division and locomotion. Moreover, the combined action of multiple myosin motors leads to macroscopic contraction of actin gel which occurs as a network of crosslinked elastic fibers. These fibers can undergo multiple deformation modes such as stretching, bending, and buckling leading to a long-range and heterogeneous transmission of forces through the elastic network. To investigate the force transmission and interaction between myosin motors through an underlying actin network, and to investigate motor driven macroscopic contraction, we model a percolated fiber lattice network, where fibers are represented as linear elastic elements that can bend, buckle and stretch. The contractile activity of myosin motors is represented by force dipoles, with both isotropic and anisotropic components possible in principle. We quantify how forces propagate through the network from a single anisotropic force dipole by analyzing clusters of nodes connected by highly strained bonds, as well as through the decay rate of strain energy with distance from a force dipole. We show how inter-dipole interaction depends on the dipoles' mutual separation and orientation. The resulting elastic interaction energy may mediate a configurational force between multiple distant dipoles, directing their self-organization into ordered configurations. This provides a potential pathway for active mechanical force-driven structural order in elastic biopolymer networks. Furthermore, to investigate network contractions seen in actin gels, we characterize the strain distribution and normal forces at the boundaries of the network for different configurations of isotropic dipoles. We find that networks with stiffer-to-bend fibers show more force chains as well as higher normal forces at the boundaries, a measure of macroscopic network contraction. Thus, bending-dominated fiber networks under internal forces behaves differently from conventional elastic materials under external compression. These results may be compared to in vitro actomyosin network contraction, where the bending rigidity of actin bundles is varied by changing the concentration of bundling crosslinkers like fascin.

Mechanical relaxation of DNA networks and metabolically active nuclei

Paul Janmey

The cell nucleus is generally considered to be the stiffest organelle in the cell, with a Young's modulus on the order of 1-10 kPa. But cell motility through 3D matrices with elastic moduli less than 1 kPa deform the nucleus to large strains capable of breaking the nuclear lamina, and lipid droplets in a hepatocyte exerting 100 Pa stresses on them also deform the nucleus. Metabolically active nuclei were produced from live cells by a centrifugation process that enucleates the cell. This process leaves behind a cytoplast and produces a nucleus that is wrapped by a plasma membrane and a thin layer of cytosol (a karyoplast), but no discernible cytoskeleton, endoplasmic reticulum, ribosomes or other large organelles[1,2]. Enucleation is more efficient from vimentin null fibroblasts compared to normal fibroblasts with a perinuclear vimentin cage, but the isolated nuclei are indistinguishable. Force-indentation curves are consistent with an elastic object with an apparent Young's modulus of 5 to 8 kilopascal, but retraction curves show that most of the work of compression is dissipated. Disrupting ATP production with glycolysis inhibitors stiffness the nucleus and eliminates dissipation. These results suggest that in metabolically intact nuclei, deformation is largely an active process that can be triggered by relatively modest forces that depend on internal and external mechanical stresses. Nuclear stiffness depends strongly on the elastic modulus of the substrate on which the cells are cultured, and nuclei are sensitive to changes in osmotic pressure of the surrounding medium, softening when they swell and stiffening when compressed. This method of isolating metabolically active karyoplasts can be done within 20 minutes and enables a range of studies of how cell perturbations, such as loss of intermediate filaments or linkers of the nuclear membrane to the cytoskeleton, impact the mechanical properties of the nucleus.

Shear-Induced Yielding of Cellulose Nanocrystal Gels

Lise Morlet-Decarnin

Cellulose nanocrystals (CNCs) are rodlike biosourced colloidal particles used as key building blocks in a growing number of materials with innovative mechanical and optical properties. While CNCs form stable suspensions at low volume fractions in pure water, they aggregate in the presence of salt and form reversible colloidal gels with time-dependent properties. Here, we study experimentally the yielding behavior of a CNC gel in shear start-up experiments, coupling rheology and ultrasound velocimetry. These gels display a stress overshoot with a maximum whose coordinates are used to rescale stress-strain responses recorded at various shear rates. Such rescaled stress responses show that, counter-intuitively, the CNC gel yields in a more ductile way for increasing shear rates. Local measurements show that yielding first occurs at the moving wall and that, in the case of a brittle-like breakdown, the stress overshoot is followed by a strong elastic recoil, which gives way to a total wall slip regime. The same apparent brittle-to-ductile transition is observed upon decreasing the sample "age", i.e., the rest time between a rejuvenation under high shear and the start-up of shear. The above observations are interpreted as the signature of the interplay between aging and yielding. Indeed, for a given sample age and under a small applied shear rate, it takes a significant amount of time to reach the critical deformation at which the gel breaks. During this initial stage, the material response remains solid-like, and the gel elasticity builds up due to aging, which leads to the formation of a consolidated network whose rupture is more brittle-like. In order to quantify the degree of brittleness, we introduce a parameter B defined as the maximum slope past the overshoot of the stress vs strain curve in logarithmic coordinates. We show that B decreases logarithmically with the applied shear rate. We also confront our results with predictions of recent models for the scaling of the stress maximum with the applied shear rate and show significant deviations from the expected scalings.

Tuning the Underwater Adhesiveness of Antibacterial Polysaccharides Complex Coacervates

Mehdi Vahdati

Adjusting the water content and mechanical properties of polyelectrolyte complex coacervates for optimal underwater adhesion requires simultaneous control of the macromolecular design and the type and concentration of the salt used. Using synthetic or bio-inspired polymers to make coacervates often involves complicated chemistries and large variations in salt concentration. The underwater adhesiveness of simple, bio-sourced coacervates can be tuned with relatively small variations in salt concentration. Bio-sourced polymers can also impart beneficial biological activities to the final material. We made complex coacervates from charged chitosan (CHI) and hyaluronic acid (HA) with NaCl as the salt. Their water content and viscoelastic properties were investigated to identify the formulation with optimal underwater adhesion in physiological conditions. The coacervates were also studied in antibacterial and cytotoxicity experiments. As predicted by linear rheology, the CHI-HA coacervates at 0.1 and 0.2 M NaCl had the highest pull-off adhesion strengths of 44.4 and 40.3 kPa in their respective supernatants. In-situ physical hardening of the 0.2 M coacervate upon a salt switch in 0.1 M NaCl resulted in a pull-off adhesion strength of 62.9 kPa. This material maintained its adhesive properties in physiological conditions. Finally, the optimal adhesive was found to be non-cytotoxic and inherently antimicrobial through a chitosan release-killing mechanism.

Heterogeneous water structure and dynamics in the collagen microfibril crystal

Maxime Vassaux

Collagen is almost ubiquitous in animal kingdom. It is the protein of choice by Nature to design structural materials. Collagen type I is the most occurring type of collagen among the 28 co-existing collagen sequences. Collagen type I is found in tendons, bone and cornea among others in humans. Its hierarchical fibrillar structure confers to collagen its outstanding mechanical properties refined through thousands of years of evolution. The resulting, specific, amino acid structure, dictating the self-assembly of tropocollagen molecules into this intricate fibrillar architecture is widely accepted as a key ingredient of the mechanical properties of the tissues made of collagen type I. However, fibrillar collagen may rather be viewed as a composite material made of protein, macromolecules (such as glycosaminoglycans and proteoglycans) and last but not least, water. The properties of water and the fine interactions of water with the protein constituent of these nanocomposites have only received limited attention. Here, we propose to investigate in-depth water structure and dynamics confined within the microfibril crystal structure of collagen type I. We found that the properties of water are strongly dependent upon the level of hydration of the crystal. The properties of water also vary significantly along the long axis of the crystal, namely moving from the so-called gap region to the so-called overlap region. Water dynamics range from stuck, confined or frozen to bulk. The drastic change in water properties confer to water molecules a wide variety of roles within the crystal. At low hydration, water acts as a glue between protein chains; while at high hydration, water acts as a lubricant. Furthermore, anisotropic water dynamics (diffusion) may play a substantial role determining the shape of mineral crystals during the biomineralization processes involved in bone formation.

Isotropic compression of colloidal gels

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We investigate the macroscopic behavior and the microscopic rearrangements of colloidal gels upon applying an isotropic compression. The gels are formed by aggregation of nanometric silica particles confined in a millimeter-sized drop. The compression is imposed by depositing the gel drop on a super hydrophobic substrate and letting the solvent slowly evaporate. In addition to conventional video imaging, we use small-angle X-ray scattering (SAXS) and space-resolved dynamic light scattering [1] to probe the evolution of the microscopic structure and dynamics under compression.
We find that the gel volume may be reduced by up to ~70% with no macroscopic failure, in startling contrast to failure under a shear strain, which typically occurs at much lower strains. Surprisingly, the microscopic dynamics are close to the affine deformation field predicted for an elastic, homogeneous sphere, in spite of the irreversible nature of the rearrangements leading to compaction. Leveraging the SAXS data, we propose a tentative model where the gel compaction is driven by the peripheral interpenetration of the fractal cluster that form the gel.

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Dynamics of nanoparticles in polydisperse polymer networks: From free diffusion to hopping

Valerio Sorichetti

In biology, molecules, cells and organisms frequently have to move through crowded environments. Often, the crowding agents are polymer networks. Examples include the diffusion of enzymes and other proteins in the cytoplasm and in the nucleus, cell migration in the extra-cellular matrix and the diffusion of bacteria in biofilms, were the crowding agent is in large part produced by the bacteria themselves. When the size of the probe is comparable to the mesh size of the polymer network in which it is embedded, the probe becomes transiently trapped by the mesh. In order to escape from its local cage, the probe willl have to wait for a large enough thermal fluctuation that will open a gap in the local mesh and allow it to "jump" to a neighboring cage. Using molecular dynamics simulations we study the static and dynamic properties of spherical nanoparticles (NPs) embedded in a disordered and polydisperse polymer network. Purely repulsive (RNP) as well as weakly attractive (ANP) polymer-NP interactions are considered. It is found that for both types of particles the NP dynamics at intermediate and at long times is controlled by the confinement parameter C, defined as the ratio between the NP diameter and the dynamic localization length of the crosslinks. Three dynamical regimes are identified: i) For weak confinement ($C \lesssim 1$) the NPs can freely diffuse through the mesh; ii) For strong confinement ($C \gtrsim 1$) NPs proceed by means of activated hopping; iii) For extreme confinement ($C \gtrsim 3$) the mean squared displacement shows on intermediate time scales a quasi-plateau since the NPs are trapped by the mesh for very long times. Escaping from this local cage is a process that depends strongly on the local environment, thus giving rise to an extremely heterogeneous relaxation dynamics. The simulation data are compared with the two main theories for the diffusion process of NPs in gels. Both theories give a very good description of the C−dependence of the NP diffusion constant, but fail to reproduce the heterogeneous dynamics at intermediate time scales.

Creep and failure prediction in paper

Tero Maekinen

Paper is a quasi-2D fiber network of cellulose fibers. The creep behavior of paper is known to follow a similar master curve [1] as gel networks [2]: after a power law decrease of the strain rate in the primary creep regime [3], a strain rate minimum is achieved in the secondary creep regime at a specific (geometry dependent) percentage of the sample lifetime. After that, in the tertiary creep regime, a power-law acceleration of the strain rate is seen. This onset of the acceleration towards failure is accompanied by strain localization [4], leading to eventual crack formation, and can be used as a failure precursor [5]. Using digital image correlation methods this localization can be seen by eye or alternatively one can employ various detection methods [6, 7] to try to achieve reliable failure predictions. We present recent results related to the strain localization in tertiary creep [4], sample lifetime predictions [6], as well as on the effect of imposing hierarchical patterns on the paper sheets [8].

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Friday

Thermodynamically driven auxeticity in polymer networks

Andrea Ninarello

Auxetic materials expand or contract perpendicularly when stretched or compressed by uniaxial strain. Hence, they are characterized by a negative Poisson's ratio ν. Common pathways to auxeticity consist in conveniently designing or tailoring the system geometry [1][2]. The lowest bound for the mechanical stability of solids is reached when the amount of deformation in response to the applied force is equal to the imposed one ($\nu = -1$), here referred to as hyper-auxeticity. In this work [3], we numerically show that cross-linked polymer networks under tension display hyper-auxetic behavior at given cross-linker concentrations. At this point, the nearby mechanical instability triggers the onset of a critical-like transition between two states of different densities. We will discuss the analogies and differences of this criticality with respect to the gas-liquid phase separation, the polymer coil-globule transition, and the gel volume phase transition. The present results not only provide a theoretical playground for both materials engineering and critical phenomena, but also, as our model is able to faithfully describe real-world hydrogels, they can be readily tested in laboratory experiments.

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Elasticity of fractal colloidal gels: structural signatures

Stefano Aime

Colloidal gels are soft viscoelastic solids formed by aggregating colloidal particles in a solvent. Their elasticity arises from the formation of a percolated network of particles, whose structural and mechanical properties depend on the aggregation conditions as well as on particle size and concentration. The study of the microscopic origin of linear and nonlinear rheology of colloidal gels has been object of intense research effort in the last decades, leading to a variety of models predicting how the gel elasticity should scale with particle volume fraction.
In this work, we focus on a particular class of colloidal gels, formed by colloidal particles interacting through a very strong attractive potential and characterized by a fractal microstructure and a power-law linear rheology. By combining structural and rheological characterization, we show that, surprisingly, our gels cannot be described by well-established models based on the assumption that the gel elasticity arises from that of individual fractal clusters.
Instead, we show that the gel elasticity can be described by considering the contribution of contacts between clusters, as in dense packings of rigid objects. We discuss the generality of this model by introducing larger-scale heterogeneities in the gel network, and following the evolution of their linear rheology

Capillary stress and structural relaxation in moist granular materials

Katerina Ioannidou

Capillary effects, such as imbibition drying cycles, impact the mechanics of granular systems over time. A multiscale poromechanics framework was applied to cement paste, which is the most common building material, experiencing broad humidity variations over the lifetime of infrastructure. First, the liquid density distribution at intermediate to high relative humidity is obtained using a lattice gas density functional method together with a realistic nano-granular model of cement hydrates. The calculated adsorption/desorption isotherms and pore size distributions are discussed and compare well with nitrogen and water experiments. The standard method for pore size distribution determination from desorption data is evaluated. Second, the integration of the Korteweg liquid stress field around each cement hydrate particle provided the capillary forces at the nanoscale. The cement mesoscale structure was relaxed under the action of the capillary forces. Local irreversible deformations of the cement nano-grains assembly were identified due to liquid–solid interactions. The spatial correlations of the non-affine displacements extend to a few tens of nanometers. Third, the Love–Weber method provided the homogenized liquid stress at the micrometer scale. The homogenization length coincided with the spatial correlation length of non-affine displacements. Our results on the solid response to capillary stress field suggest that the micrometer-scale texture is not affected by mild drying, while nanoscale irreversible deformations still occur. These results pave the way for understanding capillary phenomena induced stresses in heterogeneous porous media ranging from construction materials to hydrogels and living systems.

How nature employs plastic crystallinity for light harvesting: approaching new boundaries for physical modellers

Agur Sevink

Chlorosomes are large antennae complexes found in Green Sulfur Bacteria that capture and transport photon energy with near 100% quantum efficiency. Being composed of pigments only, such antennae offer a possibility for studying how this important property is encoded in the assembly structure and in its dynamic disorder, and why the coupling between electronic, atomistic and molecular degrees of freedom gives rise to such great efficiency without the help of any proteins. Computational investigations have shown that a rotational degree of freedom of pigments within a quasi-crystalline structure provides the structure the unique mechanical properties associated with plastic crystalline materials, namely a Young's modulus that is determined by the chiral packing of the pigments in the tubular stacks and renders the assembly soft enough to be stable within the natural environment of a membrane. We note that such chirality is also present in other biological structures, e.g. protein filaments, and thus may have a generic mechanical function. In addition, we have coupled the classical description for a thermalised system to a quantum description for the excitonic properties to extract what makes this unique material so efficient in the transport of excitonic energy.

Logarithmic aging via scale-free thermal avalanches of instabilities

Dor Shohat

Understanding the ever-slowing aging dynamics of disordered materials remains a long-standing challenge. Yet, they are not very hard to observe. Take, for example, a thin plastic sheet and crumple it into a ball. It might not be immediately evident, but this seemingly mundane object exhibits many of the nonequilibrium behaviors akin to disordered systems, including memory formation, intermittent responses and crackling, and logarithmic aging dynamics in their compaction under an external load, spanning a huge range of timescales. This macroscopic tabletop experiment provides unique insight to how disordered solids age under external loading [1]. Combining experiments and simulations of a minimal model, we show that during logarithmic compaction the system dwells at a marginally stable state, where it can stay for long but finite times. These quiescent dwell times are interrupted intermittently by localized instabilities which facilitate each other to form scale-free 'thermal' avalanches. Using the statistics of these events we reconstruct the energy landscape and build a scaling description of its evolution over time. This reveals that aging arises from a growing energy gap in the excitation spectrum. Finally, we confirm the scaling description with a thermal elastoplastic model of amorphous solids.

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Stress-Stress Correlations Reveal Force Chains in Gels

Fabiola Diaz Ruiz

We investigate the spatial correlations of microscopic stresses in soft particulate gels using 2D and 3D numerical simulations. We use a recently developed theoretical framework predicting the analytical form of stress–stress correlations in amorphous assemblies of athermal grains that acquire rigidity under an external load. These correlations exhibit a pinch-point singularity in Fourier space. This leads to long-range correlations and strong anisotropy in real space, which are at the origin of force-chains in granular solids. Our analysis of the model particulate gels at low particle volume fractions demonstrates that stress–stress correlations in these soft materials have characteristics very similar to those in granular solids and can be used to identify force chains. We show that the stress–stress correlations can distinguish floppy from rigid gel networks and that the intensity patterns reflect changes in shear moduli and network topology, due to the emergence of rigid structures during solidification.

Poster

Shear induced ordering and phase separation of colloidal gels under oscillatory shear

__Vasiliki Chrysoulaki__

Combined rheology and confocal microscopy is used together with molecular dynamics simulations to probe microstructural changes in attractive colloidal gels under oscillatory shear. The system under study is a depletion gel of (nearly) monodisperse Poly-methyl methacrylate (PMMA) particles at large volume fraction (44%). The attractive interactions are simulated using a Morse potential (harmonic oscillator with cutoff). We find that when such colloidal gels are sheared dynamically (i.e. applying oscillatory shear) they show a drop in their modulus (G) which depends on the applied strain amplitude.

Heat capacity of a Tournament

__Faezeh Khodabandehlou__

Let a randomly oriented complete graph G_N (tournament) decide the transition rates of a random walker for hopping over an edge, biased in the direction of orientation. Because of the many loops, time-reversal symmetry is violated. Yet, as the number of vertices $N\uparrow \infty$ grows large, and for typical tournaments (where the in-degree fluctuates around $N/2$), detailed balance emerges for the induced process on the in-degrees of visited vertices. In other words, the process of the consecutive in-degrees becomes Markovian and reversible. The stationary distribution behaves like a paramagnet in a small magnetic field. We provide arguments but proofs are lacking still.

Measuring the Coarsening Dynamics of Transient Ferrogranular Networks - Is There a New Candidate for Viscoelastic Phase Separation?

Ali Lakkis

Measuring the Coarsening Dynamics of Transient Ferrogranular Networks - Is There a New Candidate for Viscoelastic Phase Separation? Authors: Ali Lakkis, Matthias Biersack, Oksana Bilous, Pedro A. Sanchez, Sofia Kantorovich and Reinhard Richter. We are exploring in experiments the aggregation process in a shaken granular mixture of glass and magnetized steel beads, filled in a horizontal vessel. After the shaking amplitude is suddenly decreased, the magnetized beads form a transient network that coarsens in time into compact clusters, resembling a viscoelastic phase separation [1], where attached beads represent the slow phase[2]. To shed more light on the nature of the transition one would like to control the mobility of the different constituents prone to phase separation, "yet opportunities to manipulate it are surprisingly subtle and complex" [3]. Therefore we quantify how a homogeneous magnetic field $B_{\bot}$ oriented in vertical direction impedes the emergence and growth of the networks [4]. Moreover we investigate how an increased volume fraction ϕ of the granulate accelerates the coarsening. We explore the coarsening dynamics in the $(\phi,B_{\bot})$-control parameter space, and observe that low filling fractions are more susceptible to an increase of $B_{\bot}$ than high ones [5]. Our experimental results are compared with those of numerical simulations [4,6].

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Slimming down through frustration

Martin Lenz

In many disease, proteins aggregate into fibers. Why? One could think of molecular reasons, but here we try something more general. We propose that when particles with complex shapes aggregate, geometrical frustration builds up and fibers generically appear. Such a rule could be very useful in designing artificial self-assembling systems.

Glassy Dynamics & Ultraslow Gelation of Cellulose Nanocrystals Dispersions

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Cellulose nanocrystals (CNCs) are rodlike biosourced colloidal particles used as key building blocks in a growing number of materials with innovative mechanical or optical properties. While CNCs form stable suspensions at low volume fractions in pure water, they aggregate in the presence of salt and form colloidal gels with time-dependent properties.

Here, we study the impact of salt concentration on the slow aging dynamics of CNC gels following the cessation of a high-shear flow that fully fluidizes the sample. We show that the higher the salt content, the faster the recovery of elasticity upon flow cessation. Most remarkably, the elastic modulus G' obeys a time-composition superposition principle: the temporal evolution of G' can be rescaled onto a universal sigmoidal master curve spanning 13 orders of magnitude in time for a wide range of salt concentrations. Such a rescaling is obtained through a time-shift factor that follows a steep power-law decay with increasing salt concentration, until it saturates at large salt content. These findings are robust to changes in the type of salt and in the CNC content. We further show that both linear and nonlinear rheological properties of CNC gels of various compositions, including, e.g., the frequency-dependence of viscoelastic spectra and the yield strain, can be rescaled based on the sample age along the general master curve.

Our results provide strong evidence for universality in the aging dynamics of CNC gels, and call for microstructural investigations during recovery as well as theoretical modelling of time-composition superposition in rodlike colloids.

Shear Induced Tuning of Mechanical Properties and Ionic Conductivity of Composite Polymer Electrolytes

Athanasios Machas

Composite polymer electrolytes have been shown to be promising candidates to enhance the poor mechanical properties of conventional polymer electrolytes. Many inorganic particles have been tested in order to induce percolation inside the composite electrolyte and provide mechanical stability. Even though the effect of the addition of inorganic particles on the ionic conductivity has been previously studied, little attention has been given to the effect of the morphology of the network itself. In this work, composites are synthesized using low molecular weight poly(ethylene) glycol (Mr=500 g/mol), hydrophobic fumed silica and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), a system known to have shear history effects. Rheology is used to induce structural changes to the network formed by the fumed silica, through steady and oscillatory preshear. We combine this with a custom-made Rheo-Electrochemical Impedance Spectroscopy setup to measure the conductivity of the composite electrolyte in-situ, and thus, correlate the conductive pathways of the ions with the microstructure. We find that the inorganic particles enhance ionic conductivity due to the interaction of the ions with the oxygen atoms on the fumed silica and that conductivity is independent of the applied preshear, even though the storage modulus of the gel created varies almost an order of magnitude.

Liquid-liquid phase separation and gelling driven by charge heterogeneity

Daniele Notarmuzi

Recently synthesized colloids engineered with differently charged surface regions [1] as well as proteins and viral capsids [2] have in common a reduced bonding valence and a complex interaction pattern dominated by like-charge attraction as well as opposite-charge repulsion. The bonding valence is known to affect the condensation of the liquid phase [3] and the anisotropic nature of the interactions is often associated to a rich assembly behavior, leading to a wide range of ordered and disordered structures [4]. While the two aspects – bonding valence and particle charge heterogeneity – are often investigated separately, we want to understand what their combined effect is on the phase diagram. We numerically address this question in a systematic fashion by taking advantage of a relatively simple coarse-grained model grounded into a robust mean-field approach [5]. With this model at hand, we investigate how the charged patterns on the particle surface, the net particle charge and the screening conditions of the solvent where particles diffuse affect the critical point, the percolation line and binodal line. Our aim is to unveil the effect of the non-trivial interplay between attractive and repulsive directional interactions on the condensation of the liquid and of the gel phase phase. [1] Small 16, 2000442 (2020); Journal of Colloid and Interface Science 583, 222 (2021); Colloids and Surfaces A: Physicochemical and Engineering Aspects 648, 129344 (2022); J. Phys.: Condens. Matter 35 174003 (2023) [2] J. Phys. Chem. B 119, 2, 503 (2015); Biophysical Journal 113, 1454 (2017); AAPS Open 8, 3 (2022) [3] Phys. Rev. Lett. 97, 168301 (2006); Soft Matter 8 1313 (2012); PNAS 117, 13238 (2020) [4] Current Opinion in Colloid & Interface Science 22, 73 (2016); Phys. Chem. Chem. Phys., 19, 19847 (2017) [5] Current Opinion in Colloid & Interface Science, 30, 18 (2017) [6] Eur Biophys J 48, 3, 285–295 (2019) [7] Biophysical Journal, 113, 7, (2017)

Pinch and roll of polymer drop moving over slippery lubricated surface

Matteo Pierno

The motion of a drop on a solid surface attracts a lot of attention for its implications on microfluidics and wetting [1]. On a tilted surface, this motion is the result of a balance between the downplane component of the drop weight and the viscous resistance, plus a capillary force related to the non-uniformity of the perimeter of the contact angle along the drop [2]. On slippery lubricated surfaces a suitable low surface tension lubricating liquid is trapped inside a surface texture [3]. This allows drops of an immiscible fluid to float on the lubricant layer with low friction, even for highly viscous solutions that otherwise would hardly move on solid surfaces [4]. We report the gravity-induced motion of small viscoelastic drops deposited on inclined lubricated surfaces. Viscoelastic fluids made of polyacrylamide (PAA) and xanthan gum exhibit shear thinning and, more importantly, a significant first normal stress difference N1. Remarkably, despite the homogeneity of the surface and fluids, drops of sufficiently high N1 move down the tilted plane with an oscillating instantaneous speed whose frequency is found to be directly proportional to the average speed and inversely to the drop volume, collapsing on a master curve if the drop boundary is accounted. The oscillatory motion is promoted by the dynamics of the polymer network through a kind of novel Weissenberg effect promoted by the polymer network, triggering the formation of a bulge that starts a rolling motion [5].
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Delayed material failure after straining in elastic networks

Sam Walker

After imposing a rapid "step" shear strain on an amorphous material, we might expect a gradual smooth stress relaxation, or even a rapid abrupt material failure if the yield strain is exceeded [1, 2]. In simulations performed in this work, we employ a simple network model of an amorphous gel-like or fibrous material with thermally activated strand failure. We find that sudden catastrophic material failure can instead be delayed to ultra-long timescales after strain imposition. This delayed failure manifests as rapid system-spanning fractures, accompanied by an abrupt stress drop. We propose a failure mechanism in our network model, associated with bonds that have strains just below their breaking threshold. These bonds break on delayed timescales due to thermal activation, which causes subsequent avalanche-like fracturing of surrounding bonds and results in material failure. We demonstrate a steep increase in failure time around the strain stiffening "critical point"" [2], with decreasing temperature and with imposed step strain amplitude. This research directly supports a phenomenon predicted theoretically in mesoscopic and continuum constitutive models, of highly delayed shear banding instabilities in amorphous materials [3]. We hope that this work will stimulate experimental efforts to demonstrate this interesting phenomenon.

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Understanding fluctuations in complex flows: Fluctuations in the Maxwell stress

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Thermal fluctuations allow the interpretation of scattering techniques [1] or microrheological experiments [2]. Furthermore, many models of complex materials such as bead-springs [3] are based on fluctuations at a microscopic scale. Yet, these applications are limited to thermodynamic equilibrium. For flows, our knowledge is restricted to Newtonian materials, where fluctuating hydrodynamics uses locally uncorrelated fluxes. This corresponds to a local-equilibrium application of the Landau and Lipshitz Ansatz [4] and hence of the fluctuation dissipation theorem (FDT) [1]. Thus, the noise is Gaussian. Here, we present some novel insights into fluctuations in flowing complex materials. We illustrates the limits of the classical Gaussian approximation and show, how in the context of a local field theory the most fundamental viscoelastic model, the Upper Convected Maxwell (UCM) [5], exhibits different fluctuations depending on the underlying microscopic dynamics. Both the Temporary Network Model (TNM) and the Dumbell Model (DM), which constitute model systems for two groups of microscopic models, reproduce the Maxwellian behavior [6, 3]. Till now, literature pointed out the equality of the two models with respect to stress evolution [7, 8, 6]. In this work, we quantify differ- ences when taking into account fluctuations and suggest techniques to measure them. With a novel formulation of the FDT [9] we point out that at the length scale of one strand in a network system, a Gaussian noise as in fluctuating hydrodynamic is doomed to fail. These findings shall alert the rheologist - fluctuations in networks are fundamentally different than in Newtonian fluids. Thanks to Prof. Öttinger for his guidance and support of the project.

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Rheological study of 3D fractal gels over a range of gelation parameters

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Gels represent intriguing materials with distinctive properties arising from their interconnected networks. Their dual nature, exhibiting solid-like and fluid-like characteristics, enables them valuable across diverse applications, spanning industrial processes and biomedical engineering. The Gel Point (GP), signifying the transition from a sol to a gel, is a critical parameter in numerous gel applications. Precise prediction and comprehension of the gel point are imperative for effective control and optimization of gel properties. In our investigation of gelation, we employ a three-dimensional model from previous research [1], offering a robust framework for exploring the intricate interactions among polymer chains and the formation of the gel network. Our gel-forming approach integrates a comprehensive model, defining diverse input parameters such as volume fractions, gelling rates, surface tension, and gel strengths. This method adeptly models various gelation mechanisms, capturing the dynamics of three pivotal gelation phases: pre-gelling, gel point, and post-gelling, accommodating different gelation rates. To enhance our understanding, we utilize the Small-Amplitude Oscillatory Shear (SAOS) to study the linear response rheology of our gels and their fractal dimension as supplementary predictive indicators. Our findings illustrate that gel elasticity is an intricate feature influenced not only by bond strength but also by factors like type of interconnectivity and gel form. Moreover, we emphasize that rheology alone may not offer comprehensive details about the gel's underlying microstructure. In contrast, combining rheology with fractal analysis provides essential insights into the gel network's structure. This understanding allows for tailored adjustments to the gel structure, achieving desired qualities for specific biological applications, such as tissue engineering and drug administration.

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