

Rheology of gel networks

combining experimental, computational
and theoretical insights

Lyon, France, 21-23 June 2017

Book of abstracts



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Instructions for connecting the Wifi network: invites

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AIM OF THE WORKSHOP

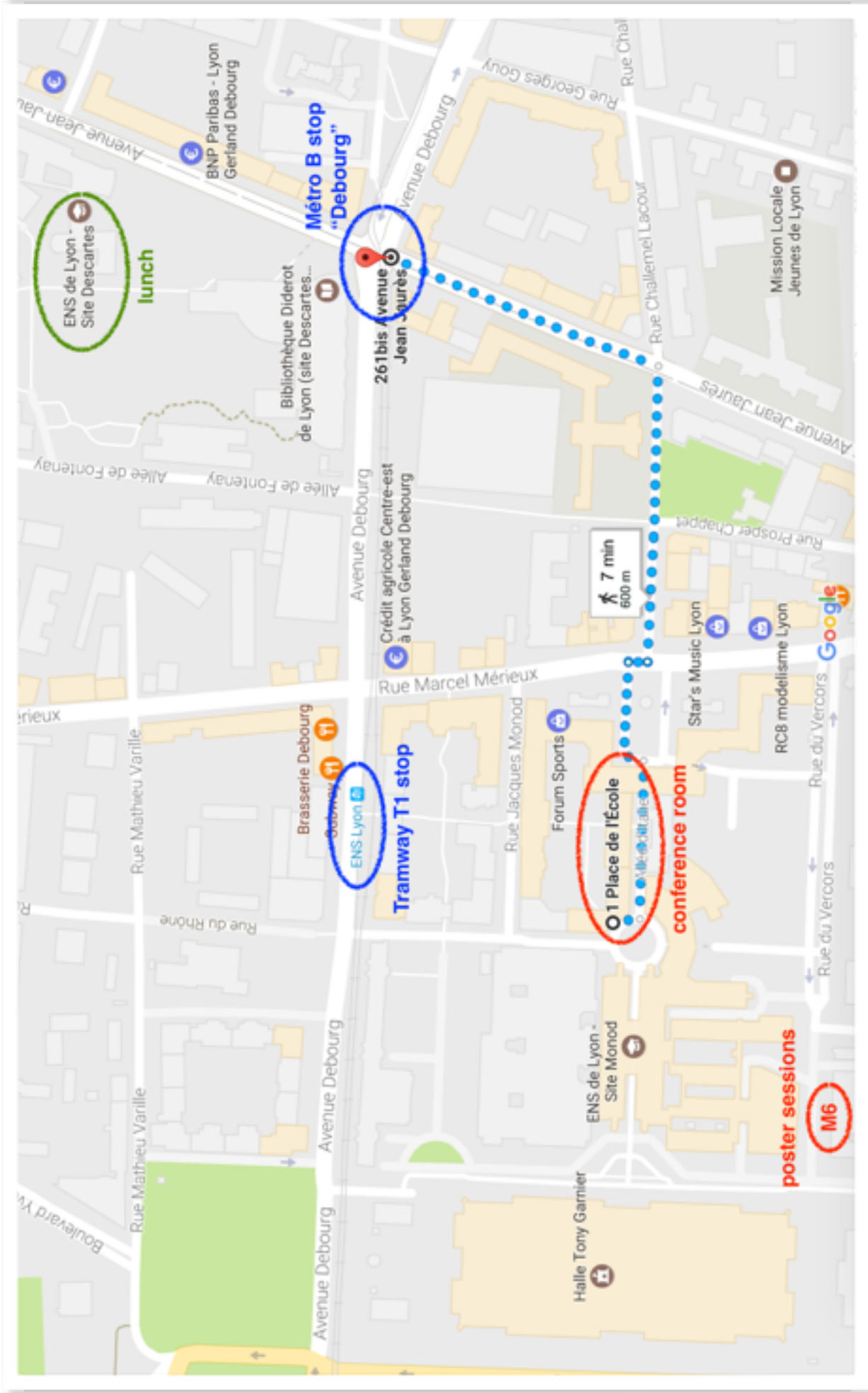
The idea of this workshop is to bring together international experts in the field of the dynamics of gel networks, to discuss recent progress and insight from computational, theoretical and experimental approaches. This field is very young especially concerning modeling aspects, due to the computational challenges related to the complex molecular structures which are crucial, in many cases, for relaxation dynamics and mechanical responses on large scales.

In the recent years, however, the computer power and new parallel coding techniques like GPGPU or large scale MPI programming techniques has allowed for significant progress in accessing reasonable time and length scales to address questions that were difficult to tackle before. Also on the experimental side, new approaches combining different techniques (e.g. various types of spectroscopy and rheology) allow for an investigation on a more mesoscopic scale of the complex dynamics, being able to probe scales that can be modeled within, for example, MD simulations. In addition, recent theoretical developments now address specifically the non-linear response of soft materials, providing new concepts and ideas to be tested in experiments and simulations. There seems to be a unique opportunity, at this point, in combining such efforts to develop a new understanding of gels, closely related to their technological applications.

INVITED SPEAKERS

- R. Angelini
- J.-L. Barrat
- T. Baumberger
- D. Blair
- M. Bouzid
- M. Caggioni
- R. Castañeda-Priego
- P. Chaudhuri
- L. Cipelletti
- C. Creton
- T. Divoux
- G. Foffi
- L. Hsiao
- R. Leheny
- G. Luengo
- X. Mao
- G. McKinley
- C. Osuji
- G. Petekidis
- F. Puosi
- L. Ramos
- J. Swan
- J. Van der Gucht
- J. Vermant
- R. Zia

Map of the conference place



Fête de la Musique

From Wikipedia, the free encyclopedia

Fête de la Musique (Festival of Music)

The *Fête de la Musique*, also known as **Music Day**, **Make Music Day** or **World Music Day**, is an annual music celebration taking place on 21 June. The concept of an all-day musical celebration on the days of the solstice, was originated by the French Minister of Culture, Jack Lang. The festival later became celebrated in 120 countries around the world.



History

In October 1981, Maurice Fleuret became Director of Music and Dance at Minister of Culture Jack Lang's request, and applied his reflections to the musical practice and its evolution: "the music everywhere and the concert nowhere". When he discovered, in a 1982 study on the cultural habits of the French, that five million people, one child out of two, played a musical instrument, he began to dream of a way to bring people out on the streets. It first took place in 1982 in Paris as the Fête de la Musique. Ever since, the festival has become an international phenomenon, celebrated on the same day in more than 700 cities in 120 countries, including China, India, Germany, Italy, Greece, Russia, Australia, Peru, Brazil, Ecuador, Mexico, Canada, the United States, and Japan.

Fête de la Musique's purpose is to promote music in two ways:

- Amateur and professional musicians are encouraged to perform in the streets, under the slogan "*Faites de la musique*" ("make music", a homophone of *Fête de la Musique*).
- Many free concerts are organized, making all genres of music accessible to the public. Two of the caveats to being sanctioned by the official Fête de la Musique organization in Paris are that all concerts must be free to the public, and all performers donate their time for free. This is true of most participating cities, now, as well.

Fête de la Musique in LYON 2017:

<http://www.lyon.fr/page/fete-de-la-musique.html>

<https://www.evous.fr/Fete-de-la-Musique-a-Lyon-concerts-programme,1189718.html>

How to get to the conference dinner



Conference dinner

The conference dinner will take place at 8pm on thursday at the restaurant "La Gargotte".

"La Gargotte" is located in the historic city center at 15 rue Royale. It is close to the "Hotel de Ville Louis Pradel" stop on the Métro A line (8 min walk, see map below).

To get there **from ENS**, take the Tramway T1 at "ENS Lyon" (direction IUT Feyssine) to "Perrache" and change there for Métro A (direction Vaux-en-Velin La Soie) and get off at "Hotel de Ville Louis Pradel".

To get there **from the Séjour & Affaires and Appart'City hotels** in Gerland, take the Métro B at "Place Jean Jaurès" (direction Charpennes) and either change at "Charpennes" for Métro A (direction Perrache) and get off at "Hotel de Ville Louis Pradel".

In both cases, allow about 35 minutes to get to the restaurant.

**Oral contributions
Abstracts**

(in order of the schedule)

Aging dynamics and spontaneous glass-glass transition in a colloidal clay

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Soft materials have long been the subject of intense research, thanks to their unusual and unexpected behaviours, they offer the possibility to observe new phases and states besides the ones commonly experienced in atomic or molecular systems. Most of these materials are out of thermodynamical equilibrium and present a continuous evolution of the mechanical and dynamical properties (aging). Measuring the time evolution of the dynamic structure factor is the most direct way to access microscopic information on aging. It allows extracting the characteristic times of the system by fitting the decay of the intensity correlation functions through the Kohlrausch-Williams-Watts expression $f(Q, t) \sim \exp[-(t/\tau)^\beta]$ where τ is an “effective” relaxation time and β measures the distribution of relaxation times (associated with simple exponential decays). Most commonly, the different relaxation times present in glassy materials lead to a stretching of the correlation functions and an exponent $\beta < 1$ which is referred as “stretched behavior”. On the contrary, an exponent $\beta > 1$ (compressed behavior) is associated to an anomalous dynamics recognized as a novel salient feature of disordered arrested materials among these, colloidal clays. Here we study the aging dynamics of a colloidal clay and we show that a stretched behavior ($\beta < 1$) is always found for spontaneously aged samples and a compressed exponent ($\beta > 1$) appears only when the system is rejuvenated by the application of a shear field after a critical aging time [1, 2] and in both cases the relaxation times scale as Q^{-1} [2, 3]. These differences are also reflected in the correlation lengths of spontaneously aged and rejuvenated samples [4]. Moreover through a combination of X-ray Photon Correlation Spectroscopy, Small Angle X-ray Scattering (SAXS), dilution experiments, rheological measurements and Monte Carlo (MC) simulations we found the existence of two different behaviours below and above t_c in the dynamical properties of the system indicating a spontaneous glass-glass transition taking place during aging [1]. Two different glassy states are distinguished with evolving waiting time: a first one, occurring at the arrest transition (after a waiting of the order of hours), is dominated by long range screened Coulombic repulsion (Wigner glass) and a second one, previously unreported and stabilized by orientational attractions between clay platelets (Disconnected House of Cards (DHOC) glass) is found at much longer waiting times (of the order of days). The present system offers therefore an overview of various dynamical be-

haviours previously observed in different systems and the possibility to pass from one to the other choosing ad hoc the time parameter [5]. Finally these findings may have relevance for applications where a fine con-

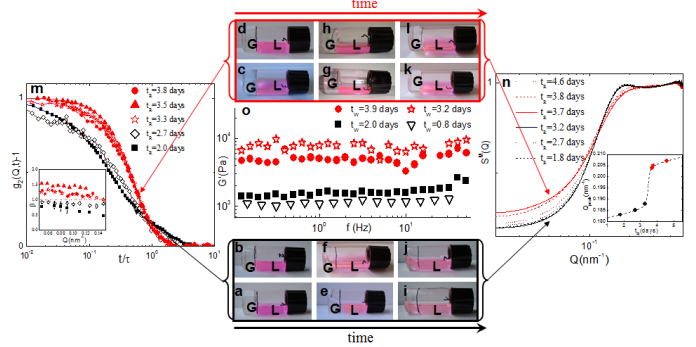


FIG. 1. (a-l) Photographic time sequence of a dilution experiment for Laponite suspensions. (m) XPCS intensity autocorrelation functions for rejuvenated aqueous Laponite suspensions at different rejuvenation times t_R . In the inset, the β exponent is shown as a function of Q . (n) Static structure factor for rejuvenated aqueous Laponite suspensions at different rejuvenation times t_R . In the inset, the peak position as a function of the rejuvenation time t_R shows a transition between two different structures. (o) Frequency dependence of the elastic modulus G' at different waiting times t_w .

trol of the local order and/or long term stability of amorphous materials are required.

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Notes

Aging, stiffening and softening of gel networks

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Disordered elastic solids of soft condensed matter like proteins, colloids or polymers are ubiquitous in nature and important for modern technologies. They can form even at very low solid volume fraction via aggregation into a variety of complex and often poorly connected gel networks [1, 2]. In most cases, the interaction energies and the size of the aggregating units make these structures quite sensitive to thermal fluctuations, with a rich relaxation dynamics [3–14], associated to spontaneous local reorganizations often referred to as "micro-collapses". Investigating how such different dynamical processes emerge at rest and how they depend on the material microstructure remains a challenge.

We have used 3D numerical simulations of model solids [15] to show that, the relaxation dynamics underlying the aging change dramatically if enthalpic stresses, frozen-in upon solidification are significantly larger than Brownian stresses [16]. The timescales governing stress relaxation respectively through thermal fluctuations and elastic recovery are key: when thermal fluctuations are weak with respect to enthalpic stress heterogeneities, the stress can partially relax through elastically driven fluctuations. Such fluctuations are intermittent, because of strong spatio-temporal correlations that persist well beyond the timescale of experiments or simulations, and the elasticity built into the solid structure controls microscopic displacements, leading to the faster than exponential dynamics reported in experiments and hypothesized by recent theories [17]. Thermal fluctuations, instead, disrupt the spatial distributions of local stresses and their persistence in time, favoring a gradual loss of correlations and a slow evolution of the material properties.

In addition to affecting the time evolution of the material properties at rest, these processes interplay with an imposed mechanical load or deformation [18–22] and hence may be crucial for the mechanical response of this class of solids. We show how tuning the structural connectivity and the local internal stresses controls the non-linear mechanical response under shear deformations. Our model gels exhibit strong localization of tensile stresses that may be released through the breaking of bonds, leading to a strain softening and/or strain hardening. Our findings help to rationalize the non-linear behavior highlighted in various

experimental observations [2, 23].

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Notes

Slow relaxations and aging of gelatin gels

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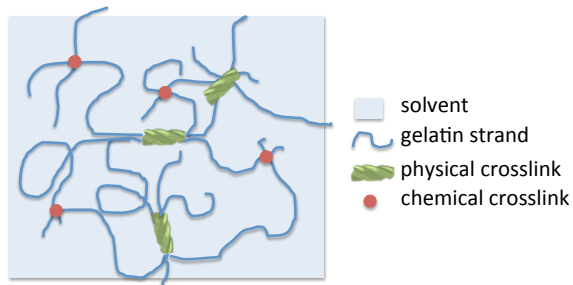


FIG. 1. Gelatin gels can be formed by standard thermoreversible gelation upon cooling and/or by forming covalent bonds. Tailored hybrid gels containing both “physical” and “chemical” crosslinks makes it possible to study e.g. the effect of the restriction of the parameter space accessible to the structural rearrangements responsible for slow aging and stress relaxations.

Gelatin gels, the archetype of thermoreversible hydrogels, are obtained by partial renaturation of the native collagen triple helices upon cooling. These act as extended crosslinks for the polypeptidic coils to form an elastic polymer network. The resulting gels exhibit the slow dynamical behavior characteristic of soft glassy materials : slow logarithmic aging of the shear modulus and stress relaxations à la Kohlrausch.

Gelatin gels can be termed experimental model systems in view of the versatile physico-chemical and mechanical toolbox available (cf. Fig.1), which makes it possible to probe the relaxation dynamics in the complex energy landscape at various time and length scales, both in the linear and extremely non-linear (fracture) response regimes.

I will review the salient features of this slow dynamics with emphasis on intriguing issues which remain open for further theoretical and computational investigations.

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Notes

Ultra-long-range dynamic correlations during aging of gels

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Gels are ubiquitous in our daily life and understanding the mechanisms via which they form remains a challenging task, specially in the context of designing such materials with specific mechanical response. A common method to form gels is via a nonequilibrium route, during which a homogeneous fluid is thermally quenched into a phase coexistence region. Such a quench process generates bicontinuous structures and when the dense phase forms an amorphous solid, the phase separation is kinetically hindered leading to the formation of a gel.

The aging dynamics during the formation of such a non-equilibrium gel has been investigated in diverse experiments and the observations differ qualitatively from those in liquids and glasses. The most striking feature is the finding that time correlation functions are described by compressed exponential relaxations, to which has also been associated the existence of long-ranged spatial correlations in the dynamics. A microscopic understanding of such *anomalous* behaviour is still missing.

Using large-scale computer simulations, we explore the aging dynamics in a microscopic model for gels, following a thermal quench into the phase coexistence region. We find that gelation resulting via an arrested phase separation process is accompanied by the *anomalous* dynamical signatures as reported in experiments, viz. occurrence of superdiffusive particle motion and correspondingly compressed exponential

relaxation of time correlation functions (left panel of Fig.1). Further, via a spatio-temporal analysis of the dynamics, we demonstrate that intermittent heterogeneities produce spatial correlations over extremely large length scales; see right panel of Fig.1.

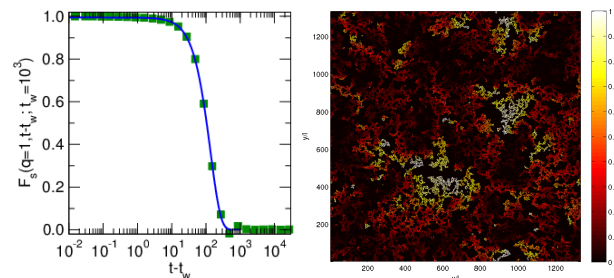


FIG. 1. (Left) Self-intermediate scattering function, measured for wave-vector $q = 1$, corresponding to an age $t_w = 10^3$ of the gel, following a thermal quench. The straight line shows that the data can be fitted with a compressed exponential. (Right) Spatial map of mobility, during the aging process relative to the same age, demonstrating that the size of mobile/immobile domains extends over large length-scales.

Thus, our study provides a microscopic insight into the spontaneous aging processes observed experimentally in gels and other similar soft materials.

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[1] P. Chaudhuri, and L. Berthier, *arXiv:1605.09770*.

Notes

Coherent x-ray studies of the microscopic dynamics underlying the phase behavior and nonlinear rheology of gel-forming nanocolloidal suspensions

Robert Leheny,^{1,*} Michael Rogers,² Kui Chen,¹ Martine Bertrand,² Tyler Shendruk,³ Suresh Narayanan,⁴ Subramanian Ramakrishnan,⁵ and James Harden²

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⁴*Argonne National Laboratory*

⁵*Florida State University*

This talk will describe two related projects exploring the properties of gels formed from nanometer-scale colloids. The first involves the phase behavior and microstructural dynamics of concentrated binary mixtures of spherical colloids with a size ratio near two and with a tunable, intrinsic short-range attraction [1]. In the absence of the attraction, the suspensions behave as well mixed, hard-sphere liquids. For sufficiently strong attraction, the suspensions undergo a gel transition. However, the fluid-gel boundary does not follow an ideal mixing law, but rather the gel state is stable at weaker interparticle attraction in the mixtures than in the corresponding monodisperse suspensions. X-ray photon correlation spectroscopy measurements reveal that gel formation in the mixtures coincides with dynamic arrest of the smaller colloids while the larger colloids remain mobile. Complementary molecular dynamics simulations indicate the arrest results from microphase separation that is caused by a subtle interplay of entropic and enthalpic effects and that drives the smaller particles to form gel nuclei in the vicinity of the larger colloids.

The second part of the talk will describe coherent x-ray experiments on (monodisperse) nanocolloidal gels subjected to *in situ* shear, which provide information about the spatial character of nanometer-scale particle rearrangements associated with nonlinear rheology and yielding of the gels and the dynamical recovery of the gels following cessation of shear [2]. One focus will be on gels subjected to *in situ* oscillatory strain, which causes periodic echoes in the x-ray speckle pattern, thereby creating peaks in the intensity autocorrelation function. An example is shown in the Figure. The peak amplitudes become attenuated above a threshold strain, signaling the onset of irreversible particle rearrangements. The gels display strain softening well below the threshold, indicating a range of strains at which deformations are nonlinear but reversible. The peak amplitudes decay exponentially with the number of shear cycles above the threshold strain, demonstrating that all regions in the sample are equally susceptible to yielding and surprisingly that the probability of a region yielding is independent of previous shear history. The wave-vector dependence of the decay rate reveals a power-law distribution in the size of rearranging regions, suggesting a nonequilibrium critical transition at yielding. Another focus will be recent

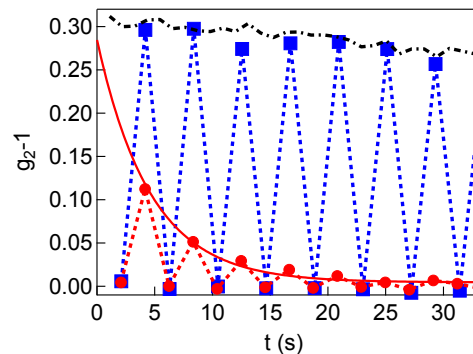


FIG. 1. Shear echoes in the XPCS intensity autocorrelation function measured on a concentrated nanocolloidal gel during application of oscillatory strain with amplitudes $\gamma = 4\%$ (blue squares) and 12% (red circles) at $q = 0.18 \text{ nm}^{-1}$. The oscillation period was 4.14 s . The dashed red and blue lines are guides to the eye. The echoes peak at $\gamma = 4\%$ decay at the same rate as the intensity autocorrelation of the quiescent gel (dash-dotted black line), indicating that shear plays no role in decorrelation for this strain amplitude. The peaks at $\gamma = 12\%$ decay rapidly with the number of cycles of shear separating x-ray images, revealing significant irreversible rearrangement in the gel. The solid red line is the result of a fit of an exponential decay to the echo peaks at $\gamma = 12\%$.

studies of gels formed from the synthetic clay Lapointe that are undergoing aging. Here, we observe that the aging can be transiently reversed (i.e., “rejuvenated”) or accelerated (i.e., “over-aged”) by shear of the appropriate frequency and amplitude.

We acknowledge support from the NSF (CBET-1336166), and the NSERC Discovery and RTI programs. RL also thanks the X-ray Sciences Division Visitor Program at Argonne National Laboratory. Use of the APS was supported by DOE BES under Contract No. DE-AC02-06CH11357.

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Notes

Elastoplastic models of relaxation, deformation and creep in disordered materials

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In this talk I will review a description of deformation in disordered materials based on the notion that this deformation is based on a combination of local irreversible events (often described as "shear transformations") that interact through elastic interactions, leading to a complex collective behavior. A number of features observed in the rheology and relaxation of gels and emulsions can be understood from the study of simple lattice models that incorporate this scenario, either within a numerical implementation or in a simplified mean field version. I will discuss in particular:

- The relation between elastic interactions and compressed exponential relaxation [1].
- Factors that lead to permanent strain localisation and fracture [2–4].
- The statistics of stress drops at very low strain

rates [5].

- The description of creep behavior using a simplified mean field description [6].

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 - [5] C. Liu, E.E. Ferrero, F. Puosi, J-L. Barrat, K. Martens, Phys. Rev. Lett. **116**, 058303 (2016)
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Notes

Failure precursors in the dynamics of a colloidal gel under creep

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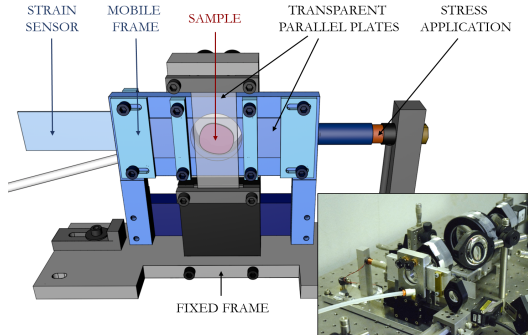


FIG. 1.

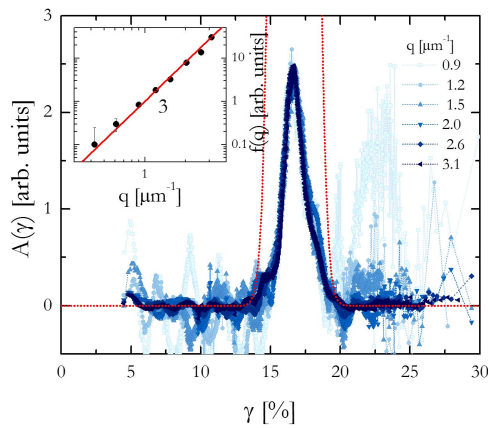


FIG. 2.

We study the microscopic dynamics of a model fractal colloidal gel under load by coupling a small angle light scattering apparatus to a custom stress-controlled shear cell [1], shown in Fig. 1. We find that

the creep consists of three regimes. After an instantaneous elastic jump, a power law (primary) creep, well described by linear viscoelasticity, is found to last several hours. In this regime, non-affine microscopic dynamics are observed, but these non-affine dynamics are fully reversible. Upon deviation from linear viscoelasticity, a sharp acceleration of the non-affine dynamics is observed, localized in time. In this regime, the non-affine dynamics are irreversible: they lead to permanent changes in the gel that weaken the network. Remarkably, these faster rearrangements precede the macroscopic failure of the gel by thousands of seconds: they thus are ‘dynamic precursors’ of failure. Data collected at several scattering vectors q can be collapsed onto a master curve, proportional to the amount A of microscopic rearrangements per unit volume and unit strain deformation (fig. 2). Remarkably, the dynamics in these regime exhibit an unusual q^{-3} scaling of the relaxation time (inset of fig. 2). A exhibits a non-monotonic behavior: after a burst of plastic rearrangements lasting thousands of seconds, the gel dynamics slow down again, until the material suddenly fails.

We would like to acknowledge many inspiring discussions with D. Vlassopoulos and T. Divoux. We thank G. Prévot and J.-M. Fromental for help in instrumentation. This work is supported by the French ANR (FAPRES, ANR-14-CE32-0005-01).

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 [1] S. Aime *et al.*, *A stress-controlled shear cell for small-angle light scattering and microscopy*, *Rev. Sci. Instrum.* **87**, 123907 (2016)

Notes

Creep, failure and shear banding in a phase separating system

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In the last decades the understanding of the steady state flow of disordered matter has greatly improved. The current physical picture is based on the idea of local shear transformations that induce long-range elastic deformations in the system leading to complex correlations of the yielding regions. The steady state is not reached instantaneously and, depending on the applied force, transient regimes, preceding the material failure, can last for very long time. This is the case of creep experiments: for an applied stress close to the yield stress, one usually observes an extremely slow increase of the strain which can eventually lead to the material failure, in the form of homogeneous flow, shear banding or ductile/fragile fracture. This behavior before failure is rather generic and in particular sublinear creep has been reported in several systems, such as dense colloidal suspension and gels [1]. Yet, the microscopic scenario from the very first stage of the creep up to the onset of flow is still an open issue.

In this work, we use large-scale MD simulations to investigate the mechanical response of a simple glass-forming system under the effect of an external stress. At sufficiently low density, a deep quench leads to a system with a gel-like bicontinuous structure that is fully arrested in the limit where thermal fluctuations are negligible [2]. Here, as the applied shear stress increases, the system response changes from creep deformation, with power-law dependence on time, to macroscopic failure; for intermediate stress values reentrant solid-like behavior is reported (see Fig. 1). While this scenario is stable with respect to the choice of temperature T and density ρ , the creep exponent is not universal as its specific value depends on T , ρ and the applied stress. In particular a deeper quench results in a change from power-law to logarithmic creep. Further, steady flow is observed only for larger densities, approaching the dense regime, in which the gas phase occupies disconnected bubbles inside the dense one. Heterogeneous flow takes place in

the form of a shear band localized in a small region close to the cavity.

Our approach, based on microscopic simulations, allow the study of creep dynamics and failure at the atomic level, overcoming the limitations of the experiments on this subject. We show that macroscopic creep is connected to particles inability to diffuse: the large part of the system is virtually arrested whereas few mobile particles constitute sparse cluster located at the interfaces between dense and gas phases. Fi-

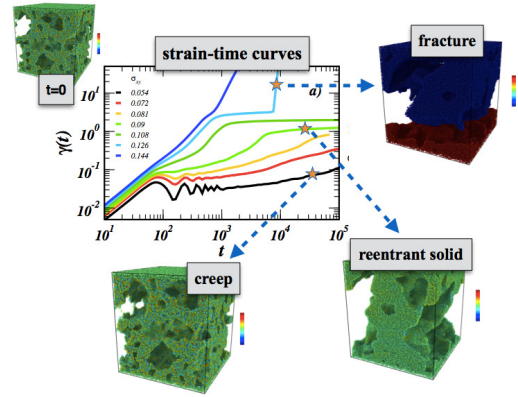


FIG. 1. Main panel: response of the systems to applied shear stress, as described by the time evolution of the shear strain. Depending on the stress value, different behaviors are observed, ranging from creep deformation to resolidification or fracture. Typical particle configurations are shown.

nally, focusing on microscopy dynamics, we investigate the possibility to predict the onset of macroscopic failure.

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Notes

Gravitational Collapse of Colloidal Gels

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We investigate the phenomenon of gravitational collapse in colloidal gels via dynamic simulation in moderately concentrated gels formed via arrested phase separation. In such gels, rupture and re-formation of bonds of strength $O(kT)$ permits ongoing structural rearrangements that lead to temporal evolution — aging — of gel structure and rheology [1]. The reversible nature of the bonds also allows the gel to transition from solid-like behavior to liquid-like behavior and back to solid-like behavior when forcing is removed. But such gels have also been reported to be susceptible to sudden and catastrophic collapse of the entire structural network, during which the gel sediments into a dense layer, eliminating any intended functionality of the network scaffold. Although the phenomenon is well studied in the experimental literature, the microscopic mechanism underlying the collapse is not understood [2–17].

To study this behavior, we conduct large-scale dynamic simulation to model the structural and rheological evolution of a gel subjected to a range of strengths of gravitational stress. The model comprises 750,000 Brownian particles interacting via a hard-core repulsion and short-range attractive interactions that lead to formation of a gel; the gel is evolved quiescently over time, whereby its structure and rheology evolve via diffusive particle migration [1]. A range of attraction strengths and gel ages are studied. Particle positions and network stress are monitored throughout simulation, along with bulk strain of the gel.

We find that the bulk deformation of the gel agrees with experimentally reported behavior [3, 9, 14]: Three temporal regimes emerge: macroscopic slow, pre-collapse evolution; collapse and rapid sedimentation; and long-time compaction, each of which is connected to distinct phases of structural and rheological evolution. The detailed microstructural evolution during this process is reported, along with the dependence of the delay time and speed with attraction strength and magnitude of the applied stress relative to Brownian forces. The influence of the interplay between Brownian motion, attractive forces, osmotic pressure, and gravitational forces on collapse and subsequent restructuring is elucidated, and a connection to phase behavior is made.

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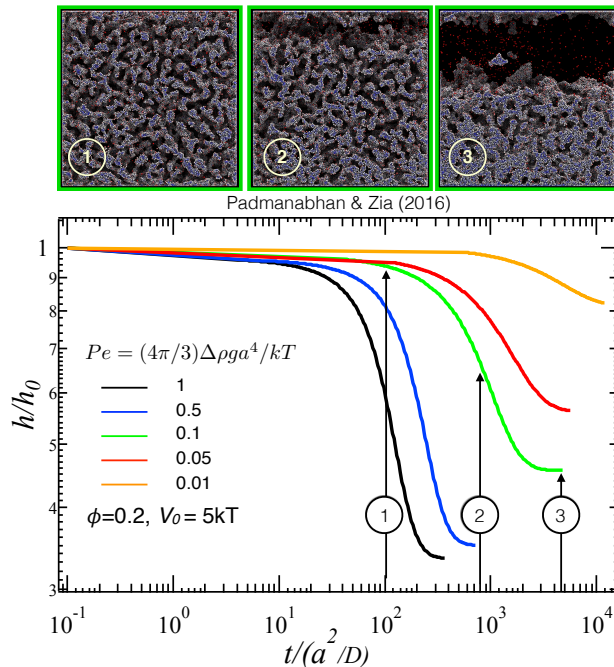


FIG. 1. Top row: Snapshots from dynamic simulation of gravitational collapse. Plot: Gel height over time.

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Notes

Precursors to failure in a gel forming system

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Detecting precursors of failure in gels subjected to mechanical load is an interdisciplinary challenge with important applications in numerous fields including material science, medicine, engineering and geology, as well as food science and cosmetic.

It is well known that gels behave in a viscoelastic way, flowing like a viscous liquid or deforming like a solid according to the forces applied, but the mechanisms underlying the macroscopic failure in soft materials under load remain unclear. It has been shown that gels can be fragile [1] and local deformation and structural rearrangements may trigger catastrophic macroscopic failure. Hence, the detection of any dynamical precursor of failure would ensure a control of the conditions leading the material to fail. Despite the importance of the topic, little is known on the local dynamics [2–4], before the occurrence of such catastrophic events.

Dynamical light scattering experiments on PDMS samples by the group of L. Cipelletti in Montpellier have shown that it is possible to observe a change in local dynamical features well before the macroscopic failure (to be published).

To detect precursors of failure at an atomistic level that are not easily accessible by experiments we chose to carry out atomistic molecular dynamic simulations. In particular, to gain insight in the microscopic dynamical precursors that lead to the macroscopic failure this work discusses the response of a gel model [5] to tensile strain step cycles. Each cycle consists of a strain step plus a subsequent long relaxation stage. Despite the idealized model system used for our investigations, the simulations are able to reproduce the dynamical change before failure, observed by experiments, suggesting this to be a very generic scenario. Within the simulations we are able to probe the reasons for this dynamical change at the molecular scale. We rationalize the experimentally

observed precursors by studying in our simulations the broken bond statistics during the relaxation stages and the long range elastic consequences of individual bond breaking events. In this study we show that a powerful combination of experiments and simulations allows to make successful temporal and spatial predictions of macroscopic failure.

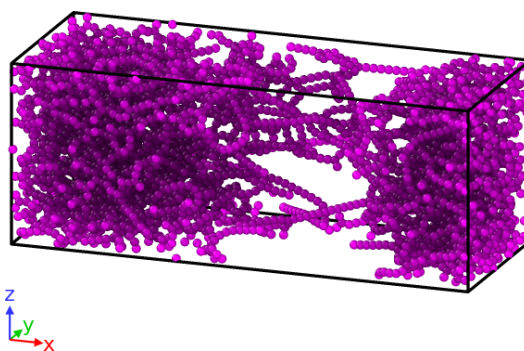


FIG. 1. Simulation snapshot of the gel system after several tensile step deformations leading to failure.

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Notes

Rigidity percolation, floppy modes, and frequency dependent shear modulus of colloidal gels

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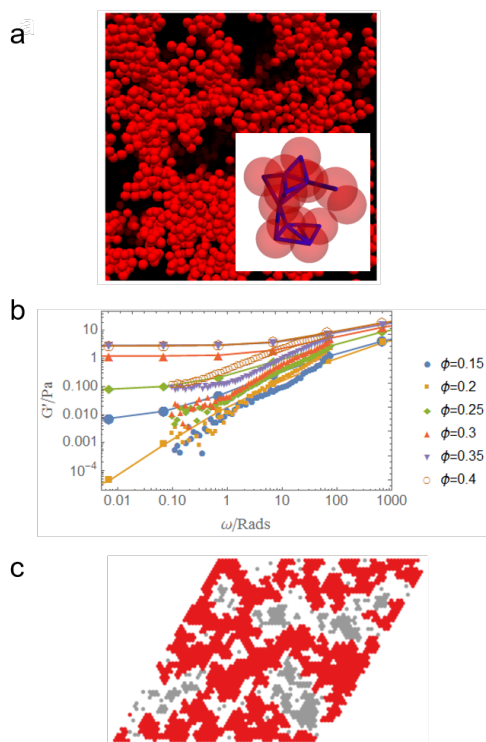


FIG. 1. (a) Reconstructed 3D image of colloidal gel particles and bonds, from confocal image analysis. (b) Agreement between experimental (scattered data points) and simulation results (connected data points) of colloidal gel shear modulus as a function of frequency. (c) Numerical simulation of correlated site rigidity percolation (red: percolating rigid cluster, gray: floppy clusters).

Colloidal particles subject to short-range attractive depletion interactions form gels: self-organized, disordered networks with marginal solidity. In this talk, we mainly focus on mechanical stability of colloidal gels.

The notion of mechanical stability traces back to J. C. Maxwell, who relates the number of floppy modes in a system to the difference between the numbers of

degrees of freedom and constraints. In Maxwell's theory, mechanical stability is equivalent to the vanishing of floppy modes, which simplifies to the equation $\langle z \rangle = 2d$ for simple systems with point-like particles and central-force constraints (where z is the particle coordination number and d is the spatial dimension).

We will first discuss our recent project taking real 3D configurations of colloidal particles from confocal microscopy (Fig. 1a), and numerically study their mechanical properties. We find that, interestingly, for the samples we studied with volume fraction within (15%, 40%), the coordination number is significantly below $2d$. However, these samples still exhibit finite shear modulus. We performed a computational study of the mode structure of these samples, and obtained good agreement with experimental shear modulus at varying frequency [1].

We will then discuss our theoretical study on the formation of these dilute structures with mechanical stability. Our theoretical model is based on site rigidity percolation with positional correlation between the particles that mimics the short range attraction. We obtained a phase diagram for this simple model that resembles the phase diagram of colloidal gels. We have also analyzed the criticality of the rigidity transition in this model, and found that it belongs to the same universality class as uncorrelated rigidity percolation, albeit with shifted transition point, indicating lower critical volume fraction for stronger correlation [2].

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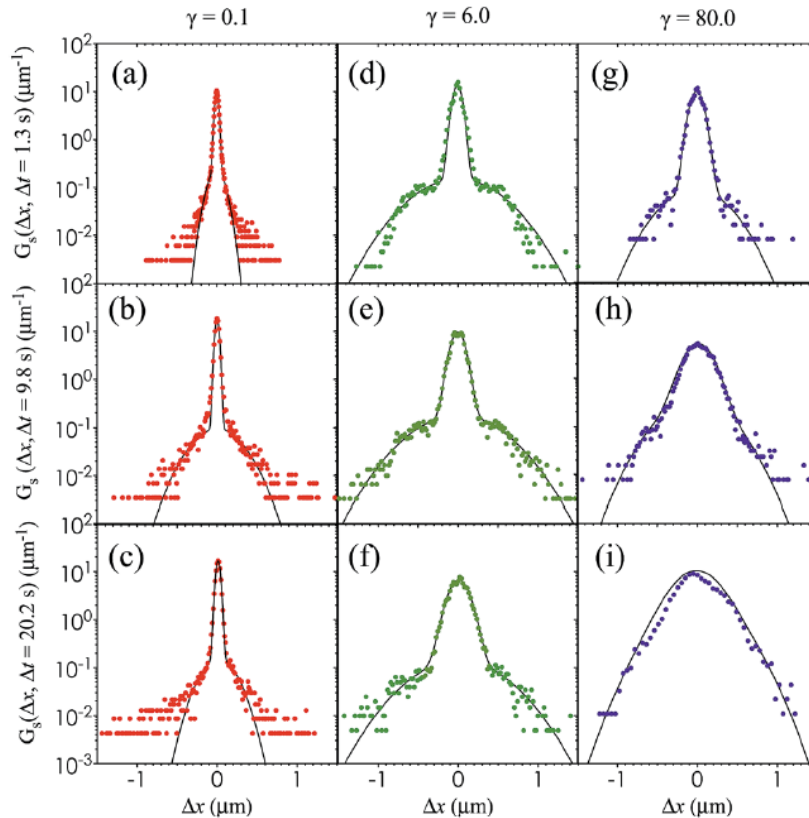
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Structural and dynamical heterogeneities in colloidal gel rheology

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Michael J. Solomon (University of Michigan, Department of Chemical Engineering)

Colloidal gels are known to exhibit complex structural and dynamical changes when sheared, particularly when the applied flow is strong enough to cause rupture. Such systems of colloids interacting through short range attractive forces are good models of associating species, such as associating polymers. Here, we investigate the effect of structural rigidity and dynamical heterogeneity on the nonlinear elasticity of colloidal gels that have undergone yielding. These gels are comprised of fluorescent, sterically stabilized poly(methyl methacrylate) colloids that are suspended at intermediate volume fractions in refractive index and density matched solvents. Non-adsorbing polystyrene is added to induce gelation with weak, short-ranged attraction. Our work shows that the nonlinear elasticity in sheared gels can be attributed to the stress-bearing capability imparted by rigid, slow-diffusing clusters that persist after the flow ceases. In addition, we observe a decrease in the subdiffusive motion of the particles as the applied strain increases. This deformation introduces a bimodal distribution in the van Hove self-correlation function, suggesting the existence of a fast and slow subpopulation of colloids within sheared gels. We show that the predictive power of microscopic theories that connect elasticity to localization length can be improved by considering only this slow subpopulation.



Notes

Are rigidity and directed percolations the precursors of colloidal gelation?

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One major goal in condensed matter is identifying the physical mechanisms that lead to arrested states of matter, especially gels and glasses. The complex nature and microscopic details of each particular system are relevant. However, from both scientific and technological viewpoints, a general, consistent and unified definition is of paramount importance. Through Monte Carlo computer simulations of states identified in experiments, we demonstrate that dynamical arrest in adhesive hard-sphere (AHS) dispersions is the result of rigidity percolation with coordination number, $\langle n_b \rangle = 2.4$. This corresponds to an established mechanism leading to mechanical transitions in network-forming materials. Thus, our findings connect the concept of critical gel formation in colloidal suspensions with short-range attractive interactions to the universal concept of rigidity percolation. Furthermore, with states recently explored in confocal microscopy experiments of colloid-polymer mixtures at intermediate colloidal volume fractions and in computer simulations, we corroborate that directed percolation can be identified as the equilibrium pre-transition towards the formation of gels in colloidal dispersions with competing interactions.

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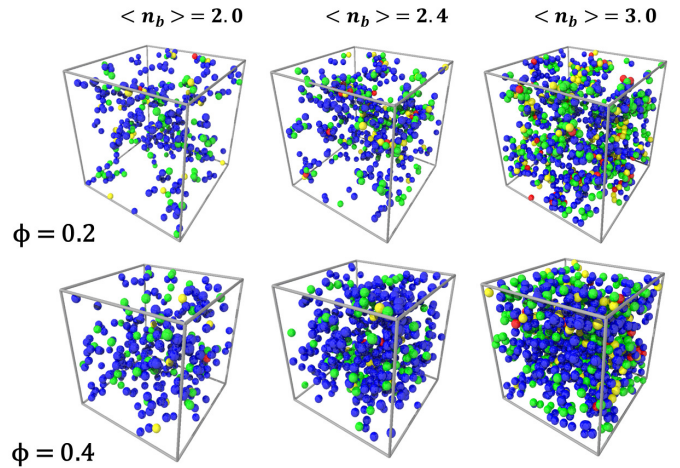


FIG. 1. Snapshots of the AHS system at two different volume fractions for three different iso-coordination number curves: $\langle n_b \rangle = 2$ (left), $\langle n_b \rangle = 2.4$ (middle) and $\langle n_b \rangle = 3$ (right). Particles with 4 (blue), 5 (green), 6 (yellow) and 7 or more (red) bonds are only displayed, which would correspond to rigid regions.

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Notes

Pre-Fracture Softening in Intermediate Filament Networks

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The cytoskeleton is impressively versatile, manifesting the ability to either stiffen[1] or soften[2] in different stress regimes. A major challenge in cell mechanics has been to identify the mechanical and structural origin of this behaviour.

Of the various predominant cytoskeletal components, intermediate filaments are of particular interest as they have a complex hierarchical structure spanning multiple length scales from the alpha-helical secondary structure of monomers, to rope-like filaments and fully crosslinked networks. Each stage of this structural hierarchy contributes a different mechanism of stress response. While much has been revealed from single filament[3] and simulation studies[4] a comprehensive understanding requires us to consider the structural hierarchies beyond the single filament level. Our motivation is to disentangle the different structural and mechanical regimes of intermediate filaments through probing the rheology of minimal intermediate filament networks using a range of applied stresses.

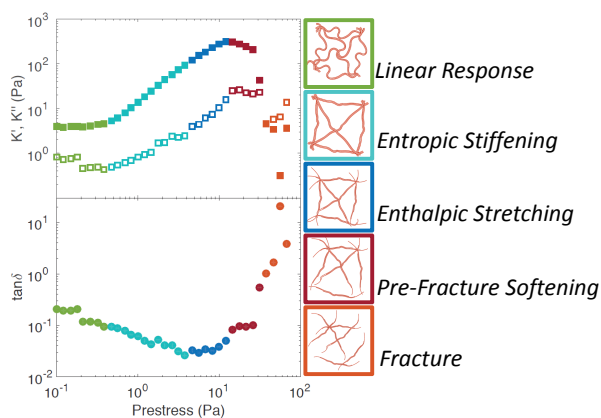


FIG. 1. Non-linear rheological response of Vimentin Intermediate Filament networks. By increasing the stress incrementally, a range of different mechanical regimes are revealed.

Transiently crosslinked intermediate filaments networks are probed with a prestress rheology protocol[5] to increase mechanical load, with long increments of

constant stress, allowing the cytoskeletal network to creep and reach a steady state between each subsequent stress step. This not only allows us to access higher applied stress and strain regimes than have previously been reported but also allows network remodelling to be measured from the viscoelastic creep and analysed using a nonlinear generalisation of the Kelvin-Voigt model.

Our approach reveals a rich diversity of mechanical responses over different force regimes, arising from the structural hierarchy within the network (Fig. 1). Filaments exhibit entropic stiffening at low forces and enthalpic backbone stretching at intermediate forces. Significantly, we reveal a regime of pre-fracture softening regime, not previously observed. From the creep response we directly link this softening to network remodelling and compare different crosslinking agents to infer that the remodelling is driven by crosslinker unbinding, leading to loss of network connectivity. This provides intriguing new insights into how intermediate filaments contribute to the cells ability to store and dissipate applied mechanical loads.

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Notes

Droplets in emulsion gels: from fillers to networks

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Because of their ability to strongly adsorb at oil/water interfaces and to stabilise oil droplets by steric and electrostatic repulsion, water-soluble proteins are widely used as efficient emulsifiers. At low pH, proteins can aggregate and also form gels, either of protein molecules in solution or of protein-covered droplets.

The soft materials formed from protein-stabilised emulsions are referred to as emulsion gels [1], however, this designation is not precise enough to reflect the variety of composition of these materials. It is thus important to take into account the ratio between adsorbed and suspended proteins in solution before gelation, as during emulsification not all the proteins in solution adsorb at the interface. If the ratio is low, *i.e.* most of the protein is suspended, the system can be seen as a matrix of protein gel with the oil droplets acting as fillers, as in polymeric materials [2]. At a higher ratio the emulsion gel is more of a composite formed of both a protein and a droplet network [3].

Our objective is to study in detail the protein-stabilised emulsion gels considering the full range of their composition. A first step is to characterise separately the gelation of purified suspensions of protein-stabilised droplets, and of suspensions of pure proteins. These components are then combined, resulting in emulsion gels of well-characterised compositions, thus allowing a rigorous approach to these systems.

We use sodium caseinate as a case-study for the protein because of its outstanding properties as a surface-active agent and stabiliser, and because of its well-known ability to form gels [4]. Sodium caseinate-stabilised emulsions are produced using a high-pressure homogeniser, the resulting droplet size is close to the size of naturally occurring caseinate assemblies, *i.e.* 100-200 nm.

We combine rheological and microscopic approaches to characterise the behaviour of the gels, in order to develop our understanding of how the separate networks of droplets and proteins develop and contribute to the overall properties.

We find on Figure 1 that droplet networks exhibit a higher storage modulus than protein networks at an equivalent volume fraction. In both cases, their storage modulus varies according to a power law as a function of the volume fraction ϕ ,

$$G'_{t_{gel}+2500s}(\phi) = G'_0 \phi^\alpha. \quad (1)$$

We find that for protein-stabilised droplet gels the exponent is $\alpha_{droplet} = 3.20 \pm 0.09$ and the prefactor is $\log(G'_{0,droplet}) = 4.51 \pm 0.07$ while for protein gels $\alpha_{protein} = 3.19 \pm 0.15$ and $\log(G'_{0,protein}) = 3.78 \pm 0.10$.

The value for the exponent is consistent with those found in the literature for colloidal gels, either thermo-reversible systems, where $\alpha = 3.0 \pm 0.5$ [5] or weak fractal networks, where $\alpha = 3.9$ [6]. Mixtures have an intermediate behaviour, and their storage modulus depends significantly on their composition, described by the ratio $\chi_{protein}$ defined as:

$$\chi_{protein} = \frac{\phi_{protein}}{\phi_{protein} + \phi_{droplet}}. \quad (2)$$

They tend to be closer in terms of elasticity to a droplet gel if they are mainly composed of droplets, and vice-versa if they are mainly composed of proteins.

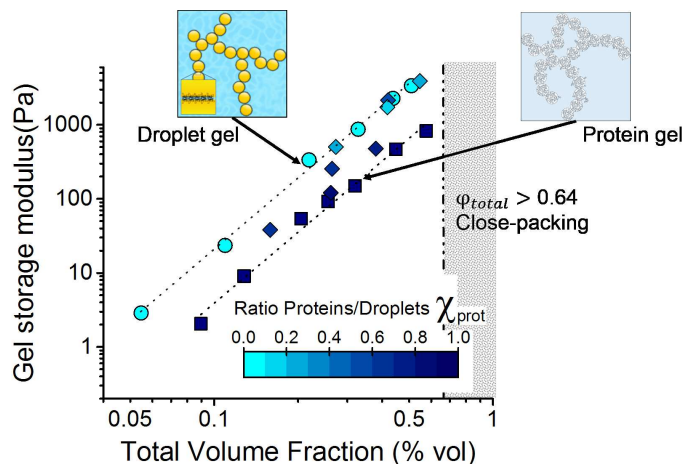


FIG. 1. Storage moduli of gels composed of: only protein-coated droplets (\bullet), only proteins (\blacksquare), and a mixture of proteins and droplets (\diamond , the colour indicates the value of $\chi_{protein}$ defined in Eq. (2)) as a function of the total volume fraction.

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Notes

Elasticity and yielding of calcite paste: scaling laws in a dense colloidal suspension

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We address the mechanical characterization of calcite paste as a model system to investigate the relation between microstructure and macroscopic behavior of colloidal suspensions. The ultimate goal is to achieve a control of the elastic and yielding properties of calcite which will prove valuable in several domains, from paper coating to paint manufacture and eventually in the comprehension and control of the mechanical properties of carbonate rocks. Rheological measurements have been performed on calcite suspensions for a wide range of particle concentrations. The calcite paste exhibits a typical colloidal gel behavior, with an elastic regime and a clear yield strain above which it enters a plastic regime. The yield strain shows a minimum when increasing the solid concentration, connected to a change of the power law scaling of the storage modulus. In the framework of the classical fractal elasticity model for colloidal suspensions of Shih et al.[1], we interpret this behavior as a switch with the concentration from the strong-link regime to the weak-link regime, which had never been observed so far in one well-defined system without external or chemical forcing.

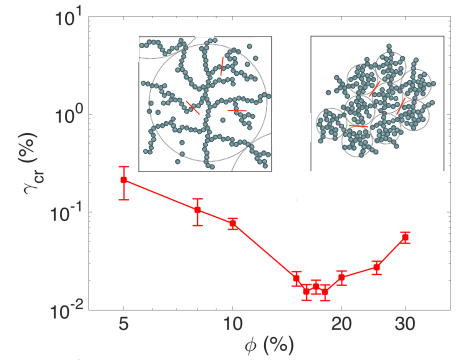


FIG. 1. Yield strain of calcite suspensions exhibits a minimum versus concentration, a major prediction of colloidal-gel theory, never verified so far.

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Notes

Optimal Fourier Transforms for Probing Oscillatory Rheology of Networks

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Numerous approaches have been proposed for time-resolved oscillatory rheometric protocols that can provide both time- and frequency-resolved measurements on an aging, curing or crosslinking gel system. Previous approaches include multiwave superposition techniques, random/white noise sequences, short-time Fourier transforms and repeated step strain pulses. Here we revisit a common audio signal processing sequence known as the exponential chirp, which offers a number of benefits including (i) a frequency-independent strain amplitude and (ii) a continuously-varying phase. This chirp sequence enables the linear viscoelastic properties of a ‘mutating’ (or time-evolving) gel to be rapidly determined over several decades in frequency in $\sim 30 - 100$ s and has been claimed to be an optimal Fourier transform sequence [1, 2]. However, closer investigation of high-resolution calibration data on a model polymer network shows that regardless of choice of the time-frequency bandwidth parameter, measurement precision can be severely compromised at the highest and lowest frequencies by ‘leakage’ of material information into side-lobes of the chirp power spectrum. Taking inspiration from the audio sequences used by bats in echolocation [3], we illustrate how these inaccuracies can be resolved through convolution of the chirp sequence with a carefully-chosen windowing function or envelope. The resulting Optimized Windowed Chirp (or OWCh) function provided to the rheometer consists of an exponential chirp multiplied with a Tukey window with window width parameter r and has the form shown in Figure 1:

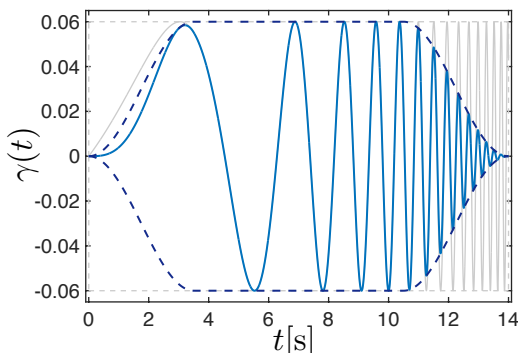


FIG. 1. An Optimized Windowed Chirp (OWCh) function of constant imposed strain amplitude containing frequency information from $0.3 \leq \omega \leq 30$ rad/s.

The optimized waveform/window function can be

readily encoded in Matlab and then used to drive the motor of an ARES controlled-strain rheometer. Fast Fourier transformation of the input strain $\tilde{\gamma}(\omega)$ and measured stress response $\tilde{\sigma}(\omega)$ allows direct computation of the linear viscoelastic modulus across a spectrum of frequencies as $G^*(\omega) = \tilde{\sigma}(\omega)/\tilde{\gamma}(\omega)$ in an acquisition time of order $T \simeq 2\pi/\omega_{\min}$.

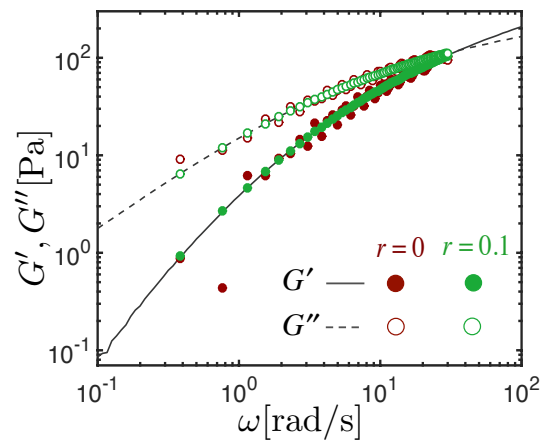


FIG. 2. Use of Optimized Windowed Chirp (OWCh) functions with window width r to extract the linear viscoelastic spectrum of an entangled viscoelastic PIB polymer solution.

Numerical computations and experimental measurements show that the error magnitude can, in fact, be reduced exponentially with window width r through correct selection of the window function, combined with implementation of careful signal conditioning protocols. We present experimental measurements on a semi-dilute entangled polymer solution (cf. Fig. 2), a worm-like micellar fluid and a time-evolving cross-linked biopolymer gel, to show that this approach can indeed rapidly and accurately extract the entire linear viscoelastic spectrum of a time-evolving complex material in less than 15 s, the time typically required to obtain the complex modulus at a single low frequency.

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Notes

Dynamic and rheological signatures of repulsive and attractive colloidal glasses during yielding.

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The structural changes and microscopic dynamics and their relation to the mechanical response of frustrated colloidal systems such as glasses and gels is the subject of intense ongoing research aiming in unraveling the fundamental underlying mechanisms responsible for their shear induced solid to liquid transition. Here we present some key ingredients linking microscopic and macroscopic response of repulsive (hard-sphere) and attractive glasses during nonlinear rheology and yielding deduced from a combined experimental and computer simulation study [1, 2, 3].

We mainly focus on the way such systems yield under the application of steady or oscillatory shear via start-up shear tests and large amplitude oscillatory shear, as well as on the mechanisms of structural reformation and related stress relaxation after shear cessation. We discuss the phenomenology of two-step yielding, widely observed experimentally and the underlying mechanisms and relevant length- and time-scales that cause such behavior, contrast it with findings from Brownian Dynamics (BD) simulations and discuss the role of hydrodynamic interactions (HI). Both experiments and BD simulations show two peaks in stress versus strain during start-up shear tests with good qualitative agreement suggesting that HI are not crucially important at such highly concentrated systems. Structural analysis obtained from BD simulations confirms that the first yield is related to the breaking of the structure at the length scales smaller than attraction range while the second yield point is a direct consequence of maximum anisotropy in the pair distribution function related with the cage deformation.

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Notes

Glasses and (bi)-gel under (Oscillatory) deformation

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The presentation will be divided in two parts. In the first part, I will discuss the unusual scenario that emerges when a glass former undergoes oscillatory deformation. There will be indication for a dynamic transition [1] as well as unusual memory effects [2]. In the second part, I will introduce some doubly percolating networks (bigels) that results from an arrested demixing [3] and I will discuss some preliminary results on their peculiar mechanical behavior [4]. I acknowledge the very fruitful collaboration with all the co-authors that appear in the referenced papers,

without them this work would have not been possible

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Notes

Gel drops and beads under extreme deformations

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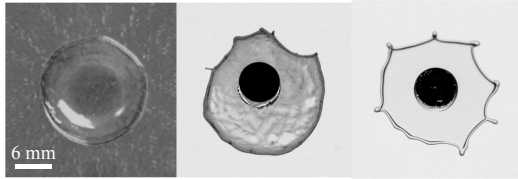


FIG. 1. Images of a soft elastic drop (left), a viscoelastic gel drop (middle) and a viscous drop (right) impacting a solid surface covered with liquid nitrogen (left) and a small solid target (middle and right). Images are taken at the maximal expansion of the sheets. The scale is the same for the three images.

Impact experiments are conducted to investigate the behavior of gels under very large deformation.

We are interested the dynamics of thin sheets freely expanding in air, which are produced by impacting a drop or bead onto a small solid target or onto a cushion of liquid nitrogen, in order to suppress any dissipation process. To disentangle the role of capillary, viscous and elastic forces in the dynamics of the sheets, a large variety of materials is investigated, whose rheological characteristics are tuned over many orders of magnitude: viscous liquids, and permanent and transient gels. The reversible gels are self-assembled viscoelastic Maxwell fluids characterized by an elastic modulus, G_0 , a relaxation time, τ , and a zero-shear viscosity, $\eta_0 = G_0\tau$. The permanent gels are cross-linked polymer networks with an elastic modulus as low as 10 Pa. For transient gels, when τ is shorter than the typical lifetime of the sheet (~ 10 ms), the dynamics of the sheet is similar to that of Newtonian viscous liquids with equal zero-shear viscosity. In that case, the maximal expansion of the sheet, d_{\max} , decreases with η_0 and can be quantitatively accounted for by a model based on the viscous dissipation on the small solid target. On the other hand, when τ is longer than the typical lifetime of the sheet, the behavior drastically differs. The sheet expansion is strongly enhanced as compared to that of viscous samples with comparable zero-shear viscosity, but is heterogeneous

with the occurrence of cracks, revealing the elastic nature of the viscoelastic fluid. By contrast, the sheets produced by the impact of ultrasoft solid beads can expand significantly but never break.

Furthermore, we demonstrate that the surface tension of the soft drops and beads of gel must be taken into account in order to successfully model their expansion.

Overall, we have quantitatively rationalized the spreading of sheets for viscous, viscoelastic and elastic materials by taking into account surface tension, elastic deformation and viscous dissipation.

This work was supported by the EU (Marie

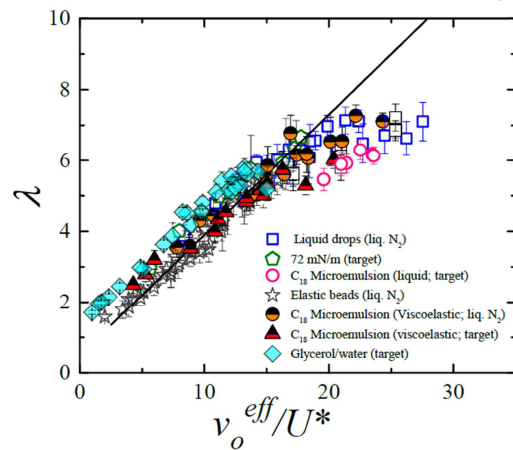


FIG. 2. Maximal spreading factor (maximal expansion of the sheet normalized by initial drop/bead size) as a function of a normalized impact velocity that takes into account the viscous dissipation on the solid target divided by a velocity of generalized elastic and capillary deformations.

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Notes

How Protein Gels Stiffen, Harden and Remember

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The material properties of solids can be strongly coupled to the magnitude of externally applied shear deformations. Yield, flow and plasticity are terms used to describe the irreversible mechanical alterations to highly deformed matter. Soft disordered solids composed of discrete elements have relatively small yield strains that is closely linked to the length scale and interaction energies of the constituents. In contrast however, many biopolymer gels can respond in ways that are distinct from their synthetic analogs. In particular, biological gels exhibit remarkable nonlinear elasticities resulting in dramatic increases in material stiffness[1]. In this talk I will discuss our results that connect the structure and mechanics for a variety of biologically derived gel networks including intra- and extra- cellular matrices and reconstituted silks [2–5]. All of these materials exhibit a highly nonlinear response that is linked to the existence of hierarchical structures and complex cross-linking. Overall, the re-

sulting nonlinear rheology is a mix of hardening, stiffening and mechano-memory effects under the application of large shear strains. I will connect these bulk viscoelastic descriptions to the microscopic behavior of the gels through real space 3-D imaging, boundary stress microscopy, and neutron scattering. If there is time, I will also discuss recent results on the mechanics of active gel networks.

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Notes

Damage accumulation and delayed failure in soft polymer networks

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We study the delayed failure of a soft polymer network in tension. Using a multiple scattering-based imaging technique we monitor the spatiotemporal accumula-

tion of damage in the network prior to macroscopic failure. We interpret our results using a discrete network model.

Notes

Experiment and modelling of the mechanical and fracture properties of dual-crosslink gels

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One of the strategies used to improve the toughness of polymer networks is the introduction of sacrificial bonds, which can break before the main bonds break. These sacrificial bonds serve a double purpose. They dissipate energy and delay crack propagation, and they redistribute forces in the main bonds avoiding too sharp stress concentrations at the tip of a crack. Simple crosslinked networks of flexible polymer chains possess great reversible elasticity but over a limited range since they are typically rather brittle. This is particularly true of hydrogels, which are highly swollen with water. Because molecular friction cannot be used in hydrogels to create energy dissipation, the dissipation relies on bond failure where a stretched elastic chain loses its strain energy as it is broken and return to its equilibrium conformation. Two classes of materials have been mainly developed to address this question: materials where the sacrificial bonds are of a similar nature as the main bonds but are overloaded due to network architecture [1, 2]. And materials where a population of weaker bonds is

introduced [3, 4]. In this talk we will present some recent results concerning the latter case, where physical reversible bonds have been introduced in an otherwise chemically crosslinked network. Our networks are swollen in water and contain a minority of strong covalent bonds and a majority of weak dynamic bonds that can break and reform. We will discuss in particular two points: How this strategy can be beneficial for fracture resistance, and in particular what is the relation between the bond dynamics and the fracture process, and how such soft solids can be modelled at the macroscopic scale.

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Notes

Nonlinear viscoelasticity and generalized failure criterion for polymer gels

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Polymer gels find ubiquitous applications in material science, from biological tissues to manufactured goods, among which food stuffs and medical products are the most widespread [1]. These materials commonly feature a porous microstructure filled with water, which results in solid-like viscoelastic mechanical properties. While soft polymer gels share common features with hard materials, including delayed failure [2, 3], crack propagation [4, 5] or work-hardening, their porous microstructure also confers upon them remarkable nonlinear viscoelastic properties. Indeed, such soft solids strongly stiffen upon increasing deformation, which stems from the inherent nonlinear elastic behavior of the polymer chains and the structure of the gel network [6, 7]. Polymer gels hence endure large strains to failure and dissipate substantial mechanical work. However, to date no quantitative link has been made between the nonlinear viscoelasticity of polymer gels and the failure that is subsequently observed as the strain-loading is increased beyond the initial stiffening regime.

Here we apply the concept of a strain damping function, traditionally used for polymeric liquids and rubber-like materials [8] to quantify the nonlinear viscoelastic response of a prototypical protein gel. The form of the damping function $h(\gamma)$ is determined through a series of stress relaxation tests performed on freshly prepared gels that allow us to probe large deformations while injecting very little energy into the gel. The damping function $h(\gamma)$ is used to construct a time-strain separable constitutive equation of K-BKZ (Kaye–Bernstein–Kearsley–Zapas) form [9, 10] that predicts the gel mechanical response to arbitrary loading histories:

$$\sigma(t) = \int_{-\infty}^t G(t-t')h(\gamma)\dot{\gamma}(t')dt' \quad (1)$$

This approach captures the strain-stiffening of the gel during start up of steady shear tests up to the appearance of a stress maximum that is accompanied by the onset of the first macroscopic crack. Moreover, in order to link the nonlinear viscoelastic response of the gel to its subsequent brittle-like rupture, we adopt the failure criterion introduced by J. Bailey, which successfully describes the rupture of much stiffer materi-

als such as glasses [11] and elastomeric-like materials [12]. This criterion assumes that the failure process is Markovian, i.e. the failure of the material results from the accumulation of local failure events that are independent [13]. The combination of the stress response predicted by the K-BKZ constitutive formulation with the Bailey criterion allows us to predict the scaling of the critical stress and strain at failure with the applied shear rate.

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Notes

Design and characterization of gel networks in consumer products

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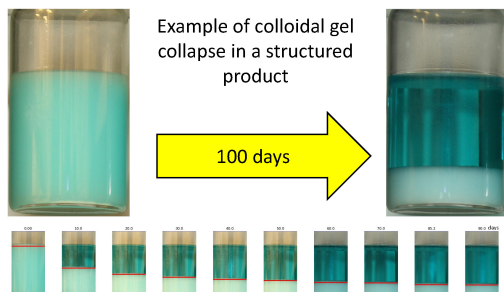


FIG. 1. The gel network initially distributed homogeneously along the vertical direction is modified by the constant gravitational stress applied on it. Mechanical failure mechanism happening over long time scale need to be avoided or at least well controlled via proper design of the colloidal scale microstructure.

In the last 20 years many consumer products evolved from simple solutions to multiphase complex fluids in which surfactants, polymers, solid particles, encapsulated materials and emulsion droplets coexist in a delicate equilibrium. Such evolution enabled the addition and fine-tuning of multiple functions but also increased the complexity of the liquid microstructure and required the development of fluid structuring strategies that are closely related to gel networks. The product formulation effort changed significantly from

independent selection of ingredients and subsequent optimization of production processes, to a much more interdependent selection of formulation and processing strategies. The motivation for such changes is not only to deliver active chemical ingredients but to also design the physical colloidal scale microstructure that makes delivery possible and efficient. Many of today's liquid detergents, for example, rely on colloidal gel or glass microstructures to provide physical stability of suspended colloidal particles to deliver benefits beyond just cleaning. The mechanical stability of the colloidal microstructure over long timescale, example provided in in Fig. 1, is an interesting problem associated with structured fluids and can be interpreted within the theoretical framework developed in the colloidal gel literature [1],[2]. In this talk, we will review some of the challenges we face in characterizing and designing the mechanical properties of liquid formulated products, with emphasis on the open questions that would certainly benefit from a strong partnership with the soft matter community.

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Notes

Predicting and assessing rupture in protein gels under oscillatory shear

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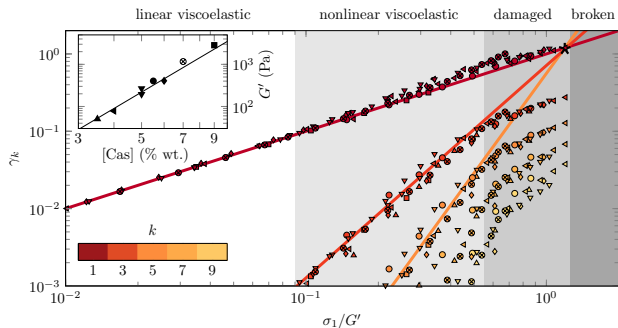


FIG. 1. Build-up of nonlinear modes γ_k of the strain response of casein gels subject to an oscillatory stress of amplitude σ_1 for various casein concentrations. Colors code for $k = 1$ to 9. The stress amplitude is normalized by the elastic modulus G' of the gel measured in the LVE regime. Solid lines show the best power-law fits of γ_k for $\sigma_1/G' < 0.5$. Background colors delimit the various regimes discussed in the text. Inset: G' as a function of $[cas]$. The symbols code for casein concentration in the main graph. The solid line is $G' \sim [cas]^4$.

Soft materials may break irreversibly upon applying sufficiently large shear oscillations, a process which physical mechanism remains largely elusive. In this work[1], we predict and access the rupture of protein gels made of sodium caseinate under an oscillatory stress.

The samples are gelled in the rheometer and subsequently submitted to an imposed oscillatory shear stress $\sigma(t) = \sigma_1 \cos(2\pi ft)$ with frequency f and amplitude σ_1 . The sample strain response $\gamma(t)$ is recorded by the rheometer. Under medium and large amplitude oscillatory stresses, $\gamma(t)$ becomes nonlinear. This results in the presence of harmonics in the Fourier series decomposition of $\gamma(t)$:

$$\gamma(t) = \sum_k \gamma_k \cos(2\pi kft + \phi_k), \quad (1)$$

where γ_k is the amplitude of the k^{th} harmonics and ϕ_k its phase with respect to $\sigma(t)$.

Upon increasing the stress amplitude σ_1 , the build-up of harmonic modes in the strain response, γ_k , can be rescaled for all gel concentrations ($[cas]$). This rescaling yields an empirical criterion to predict the rupture point way before the samples are significantly damaged, Fig. 1.

“Fatigue” experiments under stress oscillations of constant amplitude can be mapped onto the former results, which indicates that rupture is independent of the temporal pathway in which strain and damage accumulate.

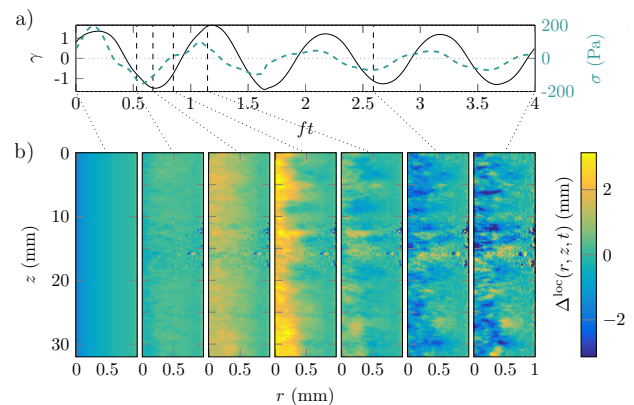


FIG. 2. Rupture of a casein gel under oscillatory shear. (a) Strain γ and stress σ as a function of ft . Note that the rheometer fails to apply a perfectly constant amplitude γ . (b) Local displacement maps $\Delta^{loc}(r, z, t)$ obtained with LORE[2] during gel breakdown.

Finally, using ultrasonic imaging, we measure the local mechanical properties of the gels before, during and after breakdown, showing that the strain field remains perfectly homogeneous up to rupture but suddenly gives way to a solid–fluid phase separation upon breakdown, Fig. 2.

We expect this work to trigger numerical modeling and theoretical efforts to explain the power-law evolution of the higher harmonic modes as well as the rupture criterion. We believe those scalings and the rupture prediction to be also relevant for biological networks and biopolymer gels made of, e.g., actin, alginate, gelatin or agar. Further experiments on these various systems are in line to check for generality. Our work also opens the way to deeper local investigations of the damage process of soft materials under oscillatory shear.

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Notes

Free-Volume Measurement and Instability in a Sheared Polymer Glass

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Deforming a polymer glass can result in flow, even at temperatures below the glass transition temperature. We show that the local free-volume changes in a sheared glass can be measured using environment-sensitive fluorescence probes dispersed in the polymer matrix. The shear-induced glass transition leads to shear localization for large strains: a region of strongly localized deformation is observed with a large free volume. This transition can be accounted for assuming that the free energy barriers in the glassy free energy landscape decrease strongly with the applied deformation. We reveal the importance of free volume and non-affine contributions to explain the inelastic behavior of a glassy system under large deformation. The

Eyring model is only valid at low strain amplitude and fails to explain the yielding behavior at large deformations. We introduce a modified Eyring model to quantitatively describe the mechanical instability and yielding of the material under shear. Furthermore, a microscopic non-affine deformation model is used to quantitatively link the measured free volume changes during the shear-induced glass transition with the observed mechanical instability and with the measured rheology. We provide a deeper understanding of the glass transition, and specifically of the roles of free volume, shear and molecular mobility in the polymer glass transition.

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Notes

Superposition Rheology and Anisotropy in Rheological Properties of Sheared Colloidal Gels

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Gelling colloidal suspensions are characterized by a solid-to-liquid transition at a given shear stress level. Moreover, they often exhibit a complex time-dependent rheological behavior known as thixotropy. The viscosity changes find their origin in the microstructure, which depends on flow history. Yet, the structural response to flow of colloidal gels differs fundamentally from most complex fluids, where flow induces orientation and stretching. Upon yielding, low to intermediate volume fraction gels break down in a spatially anisotropic way. Bonds in the velocity-velocity gradient plane break down, whereas microstructural features in other planes are less affected. The subsequent flow-induced microstructural anisotropy is characterized by generic butterfly scattering patterns or can be inferred from microscopy images. However, as yet there was no evidence for the

pertinence of this anisotropy for the rheological properties of these systems. In the present work, orthogonal superposition rheometry was used to first evaluate how the flow-induced microstructure affects the viscoelastic properties. It is shown to retain significant elasticity in the velocity-vorticity plane, even when the structure liquefies. Secondly, the shear-induced mechanical anisotropy was measured using two-dimensional small amplitude oscillatory shear, exploiting the fact that for suitable thixotropic samples the recovery after arresting the flow is relatively slow. It is hence possible to measure the anisotropy of the moduli upon cessation of flow. The mechanical anisotropy is shown to be spectacular, with the storage moduli in perpendicular directions differing by as much as two orders of magnitude.

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Notes

Large, anisotropic structures during steady shear of colloidal gels

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Breakdown of the networked microstructure in colloidal gels subjected external stresses is responsible for failure of these materials in applications essential to industry and of recent scientific interest [1]. For example, colloidal networks built from conductive carbon particles have been utilized as “flowable electrodes” in capacitive deionization processes for desalination and in flow batteries for grid scale energy storage [2]. Flow of these networks through microfluidic electrode geometries can lead to breakdown of the network and formation of vorticity aligned flocs with significantly reduced conductive properties. This instability is widely observed in suspensions of attractive particles including: carbon black and alumina powders, carbon nanotubes, silica and polystyrene spheres, among others. The origins of the instability remain mysterious in spite of its ubiquity. To date, no computational study has been able to reproduce this effect.

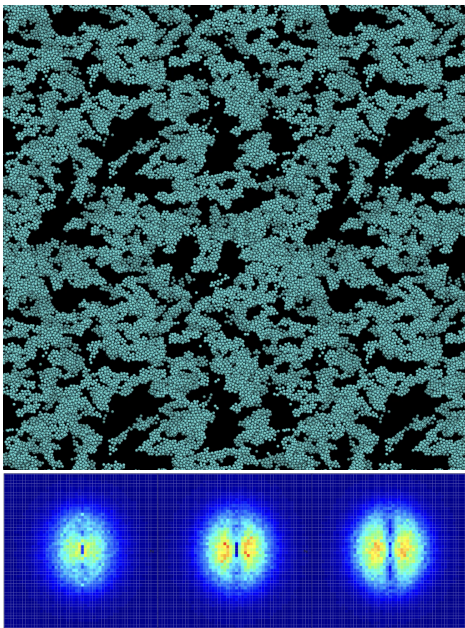


FIG. 1. (top) Snapshot of the flow-vorticity plane in a colloidal gel under shear indicating large-scale microstructural anisotropy. (bottom) Structure factors in the flow-vorticity plane with increasing shear rate applied to a colloidal gel depicting vorticity alignment.

In this talk, I discuss accelerated computational methods for modeling colloidal gels and the application of these methods to study the behavior of gels under

steady shear [3]. These methods enable rapid simulations of dispersions of hydrodynamically interacting colloids with up to 10^6 particles on a single GPU. A key feature of this new technique is the ability to generate Brownian noise satisfying the fluctuation-dissipation theorem for fractal microstructures in linear time. Hydrodynamic coupling among suspended particles is shown to be key to the development and stabilization of vorticity aligned flocs in simple shear flow. The presented simulation results are the first to correctly reproduce large-scale anisotropic structures in flowing dispersions of attractive particles (see figure 1, top) [4].

The anisotropic microstructure resulting from the applied shear flow is quantified in terms of a structure factor (see figure 1, bottom) projected onto the flow-vorticity plane, which exhibits the commonly observed “butterfly” scattering pattern reported in light, x-ray, and neutron scattering experiments. A scalar measure of the degree of anisotropy is mapped onto a dimensionless parameter measuring the strength of the shear flow relative to the most probable rupture force for the bonds between the particles. This parameter ensures dynamic similarity of the steady state across a broad range of physical parameters. The characteristic size of the vorticity aligned flocs and the non-hydrodynamic contribution to the relative viscosity of the dispersion can be similarly collapsed as a function of flow rate, particle volume fraction, and interaction parameter using the same scalar parameter. Finally, comparisons with simulations neglecting hydrodynamic flows are used to determine the hydrodynamic mechanics, which stabilizes the vorticity aligned flocs under flow.

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Notes

Flow, arrest and yielding in dense colloidal suspensions - glasses *vs.* gels

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Rheology modification in complex fluids is important for a wide range of applications including formulation of engineering fluids and consumer products. The ways in which such fluids evolve after cessation of flow and during yielding under flow have important implications for the properties and performance of the fluid in its intended application. Here we consider flow properties, dynamical arrest, and yielding in systems with repulsive and attractive interactions, i.e. systems which form soft colloidal glasses and systems which form colloidal gels, respectively. Rheological studies chart the evolution from metastable fluid-like states into arrested solid-like states as a function of time following cessation of flow for repulsively-interacting systems, or a thermal quench for thermoreversible gelation of particles with attractive interactions. We observe distinct signatures that are associated with dynamical arrest in both cases.

For colloidal glasses, arrest occurs due to a sudden onset of elasticity. The elastic component of the shear modulus grows rapidly and quickly exceeds the viscous component of the shear modulus, with a crossover that occurs concurrent with the evolution of a maximum in the viscous modulus. Arrest is delayed by the application of stress, with the arrest time τ_a diverging beyond a critical stress σ_c that is similar in magnitude to the yield stress, i.e. $\tau_a \sim \exp[1/(\sigma - \sigma_c)]$. Notably, the temporal width of the peak in the viscous modulus of the system is a strong function of the applied stress, which signals that the stress modifies the distribution of arrest timescales in the system.

In colloidal gels, arrest proceeds via the formation of a critical gel, with a clear inversion in the frequency dependence of the loss angle, $\tan \delta$, which is not observed for the colloidal glass. The scaling exponents describing the approach to the critical state can be captured through a systematic set of time-resolved measurements, revealing strong similarities to the critical behavior of many commonly studied polymer gels. The critical gel is described completely by its relaxation modulus, $G(t) = St^{-n}$ with $S = 0.33$ and $n = 0.5$. From the frequency dependence of the rate of evolution of the critical gel we extract the dynamic critical exponent, κ , as defined in Equation 1, and the relationship between the rate of growth of the elastic and viscous moduli, given by the constant of proportionality C . As shown in Figure 1, for appropriate temperatures, the system exhibits a weak power law

dependence of the modulus growth rate on frequency, with a dynamic critical exponent $\kappa \approx 0.25$ and proportionality $C \approx 2$.

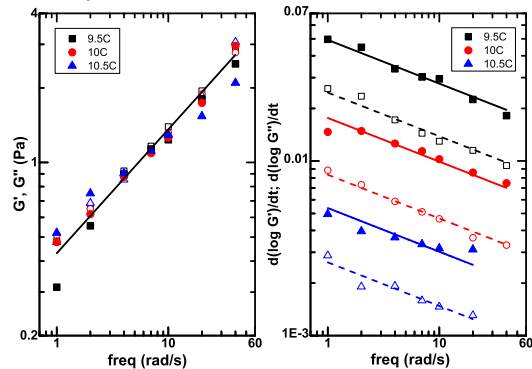


FIG. 1. Left: Elastic (G' , closed symbols) and viscous (G'' , open symbols) moduli in the near critical gel for 3 temperatures as shown. $G' \sim G'' \sim \omega^{0.5}$. A line of slope 0.5 is drawn as a guide to the eye. Right: Rate of change of the modulus as a function of frequency at the gel points for 3 temperatures as shown. Lines of slope $\kappa = 0.25$ are drawn as guides for the eye. Data conform to Equation 1 with $C \approx 2$.

$$\left(\frac{1}{G'} \frac{\partial G'}{\partial t} \right)_{t=t_g} \simeq C \left(\frac{1}{G''} \frac{\partial G''}{\partial t} \right)_{t=t_g} \sim \omega^{-\kappa} \quad (1)$$

We examine the yielding response in a model suspension as the system is deliberately tuned from a soft colloidal glass to an attractive colloidal gel by adjusting ionic strength, which modulates the electrostatic interactions of the particles. The colloidal glass is marked by rapid recovery of rheological properties following yielding, whereas the gel is subject to much longer transients and exhibits path-dependence in its rheological properties due to the sensitivity of the aggregation state to shear flow. The implications of dynamical arrest and yielding are discussed in the context of formulating complex fluids and rheology modification for various applications. A novel approach to rheology modification is discussed, based on the deliberate design of systems featuring hierarchical dynamics.

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Notes

Structured Materials for Cosmetic Applications.

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In cosmetic science a great diversity of materials are used to protect or improve the structural and sensorial properties of the cosmetic substrate (hair and skin). From shampoos to lacquers or gels, materials are used commonly used to perform a particular function (mechanical , optical, etc.).

Knowledge of the structure and nature of the cosmetic substrate is essential if we want to clearly determine the degree of improvement of its physical properties. This description will be further illustrated with a few examples of our current research efforts deciphering the physical chemical properties at the bulk and surface level and at the macro, micro and sub-microscopic scale.

For hair's surface repair we will describe the nature and properties of polymers commonly used in shampoos and conditioners. Alternatively, in the case of fiber reinforcing materials, we will focus on our recent sol-gel based strategies to allow the penetration of big macromolecular materials. Finally we will present examples of rheological behavior of gel formulations present in common products as a result of its degree of micro or nano-structuration. We expect these examples can be interesting challenges for modeling efforts in the field and help in the future better study how these materials can be effectively tuned to the consumer's advantage.

Notes

Probing the linear and nonlinear rheology of thermokinematically-trapped gels

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Many highly-structured gels commonly used in food-stuffs, bioengineering, and a wide variety of industrial applications (e.g., inks, paints and crude oils) display memory of the protocol used to achieve gelation [1–3]. As a result, their viscometric behavior, under both small and large deformations, is a function of the structural network established during gel formation, e.g. level of applied deformation and temperature history. Such systems therefore show what we refer to as *thermokinematic memory* [4]. Being able to characterize the evolution in material properties during gelation is of great importance and practical interest, although time-resolved rheometry may not always be practically feasible with available experimental techniques when the data acquisition time is greater than the characteristic timescale of mutation within the material [5].

In this paper, we consider a model thermo-reversible gel composed of a mixture of mineral oil and paraffin wax. Such a mixture is Newtonian above a critical temperature, established by the liquidus temperature at a given paraffin concentration (commonly referred to as the wax appearance temperature T_{wa}), while showing viscoelasticity as well as plastic yielding behavior below T_{wa} . The transition from a Newtonian fluid to a plastically-deformable gel, (also known as an elasto-visco-plastic (EVP) material), is due to the appearance of a loosely aggregated and percolated network of paraffin crystals with platelet-like shape (see Fig. 1 top), which interact via hydrodynamic as well as van der Waals forces. The importance of the underlying microstructure and its relationship with the resulting elasto-visco-plastic behavior observed below T_{wa} can be understood and quantified in terms of the microstructural morphology acquired during gelation as a function of both thermal and shear history [4].

Here, we present a detailed investigation of the effects that both temperature and deformation have on the linear and non-linear viscoelastic behavior measured during gelation (see Fig. 1). Using a novel experimental technique that we have developed to improve the temporal resolution of linear viscoelastic measurements, we study the evolution of the gel's complex modulus as a function of both cooling rate and shear rate. The protocol presented and developed for this particular material can be applied to study many different gel-like materials that show similar thermokinematic memory, and can be more generally adapted to investigate any time-evolving gel whose properties are changing due to either a controllable or a naturally occurring process (e.g., tunable external temperature, reaction-limited pH conditions). Finally, we present a theoretical framework that can be used to consistently describe the constitutive behavior of thermokinematic

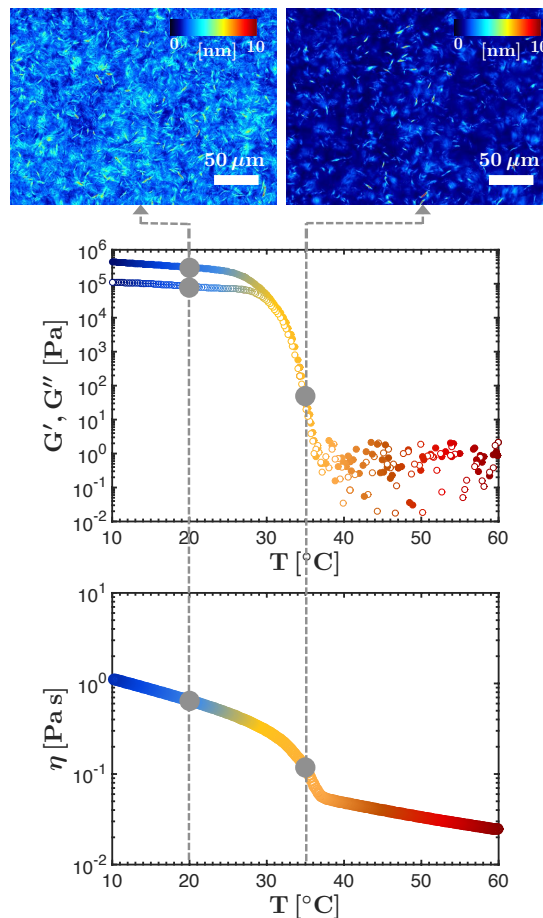


FIG. 1. From bottom to top: viscosity evolution as a function of temperature at constant cooling rate $\dot{T} = -1^\circ\text{C}/\text{min}$ and constant shear rate $\dot{\gamma} = 50\text{s}^{-1}$; evolution of viscoelastic moduli during gelation at the same constant cooling rate $\dot{T} = -1^\circ\text{C}/\text{min}$, $\omega = 1\text{rad/s}$ and $\gamma_0 = 0.1\%$; birefringence images of the gel microstructure under zero-shear conditions at different temperatures.

gels by directly accounting for both thermal and shear effects on the microstructural morphology.

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Notes

**Poster contributions
Abstracts**

(with panel numbers)

Aging and relaxation of polysaccharide physical gels

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Gel is shown as a material, made of network spanning a liquid phases, which has a solid-like behavior [1]. The quality of gel products can be changed by several factors over time; the composition, structure and properties of the gels continue to change with time in a process called aging, because the mechanism (e.g. reaction, aggregation) that leads to gelation continues long after the solution turns to a gel, causing changes in the characteristics of the initial gel.

This work attempts to provide an explanation of flow phenomenon inherent in the aging process of soft physical gels. The gel in this study is made of physical cross-linked polyelectrolyte biopolymer in water phases. A few minutes after the polymer solution gels, aging may produce shrinkage of the gel network, because the gel spontaneously releases fluid called syneresis. The difficulty to determine the origin of the aging was in the measurement of the released fluid and the interaction between the several factors that impact directly the characteristics of the gel. For instance, salt shifts the gelation temperature; however the temperature affects the elastic properties, which supports the shrinkage behaviour of the gel [2].

Although the set of combined effects yields difficulty to assess the origin of syneresis, the different methods that we have performed allow to stress the contribution of the gel's own weight pressure (P_g , weight per unit area) in the aging process. The shrinkage rate, given in the amount of released water percent, should not depend on P_g . However, it increases sharply when P_g is increased above a characteristic weight Pressure (P_y) but remains almost constant when P_g is decreased below P_y ; which suggests that, there are inherent factors other than P_g at work in the aging process. The shrinkage rate (S_r) and P_g relationship is fitted with a stretched exponential function.

$$S_r = S_1 + S_2 \cdot (1 - e^{-r}) \quad (1)$$

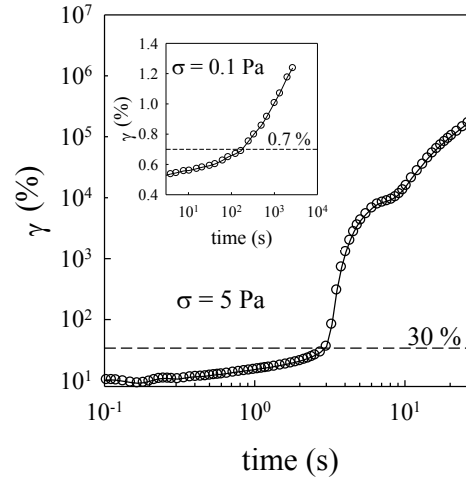


Fig.1. Creep measurement of 2 g/L kappa-carrageenan with 40 mM KCl at 40°C and 1Hz. The stress imposed for the test is 5 Pa and 0.1 Pa. The horizontal dash line indicates the strain where flow is seen.

with

$$r = (P_g / \sigma)^\beta \quad (2)$$

Where S_1 is the shrinkage without weight effects, S_2 the shrinkage induced by P_g . Beta, β is the stretched exponent and σ (Pa) is the stress from which the flow of liquid starts to decrease. The creep testing (Fig.1) has demonstrated flow (yield) of the gel at stress below P_g . Therefore, similar gels yield while syneresing [3]. It means that, a part of the aging process (syneresis) will depend on the elastic behaviour of the initial gels. However, the interplay between aging and elastic property of the gel is not yet clear.

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Structural and cooperative length scales in polymer gels

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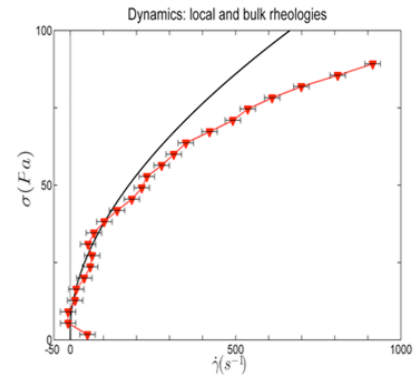
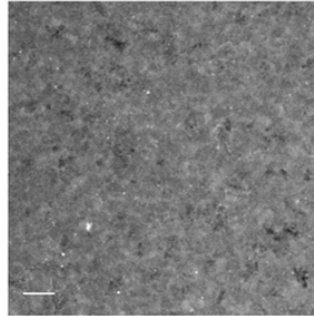
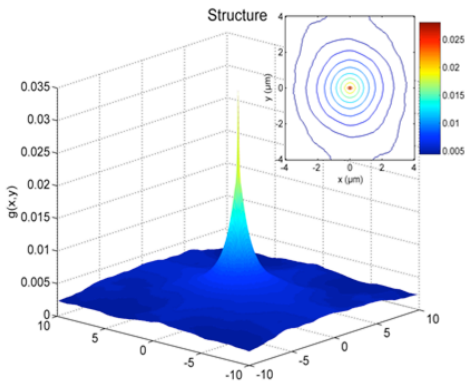
Understanding the relationship between the material structural details, the geometrical confining constraints, the local dynamical events and the global rheological response is at the aim of the present investigation on complex fluid properties. In our study, this problem is addressed on a model yield stress fluid made of highly entangled polymer gels of Carbopol which follows at the macroscopic scale the well-known Herschel-Bulkley rheological law.

First, performing local rheology measurements up to high shear rates (up to 100 s.1) and under confinement, we evidence unambiguously the breakdown of bulk rheology associated with cooperative processes under flow. Moreover, we show that these behaviors are fully captured with a unique cooperativity

length over the whole range of experimental conditions. Second, we introduce an original optical microscopy method to access structural properties of the entangled polymer gel in the direct space.

Performing image correlation spectroscopy of fluorophore-loaded gels, the characteristic size D of carbopol gels microstructure is determined as a function of preparation protocol. Combining both dynamical and structural information shows that the measured cooperative length corresponds to 2.5 times the underlying structural size D , thus providing a strong grounding to the "Shear Transformation Zones" modeling approach.

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Poster 03

Dielectric Spectroscopy of a Stretched Polymer Glass: Heterogeneous Dynamics and Plasticity

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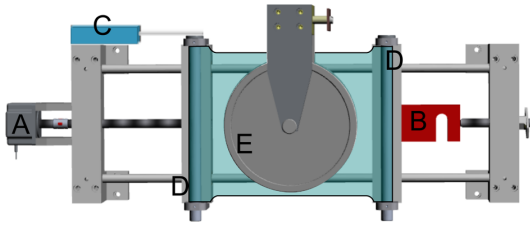


FIG. 1. Experimental setup: motor (A), load cell (B), linear transducer (C), sample fastening cylinders (D), and electrodes for dielectric measurement (E).

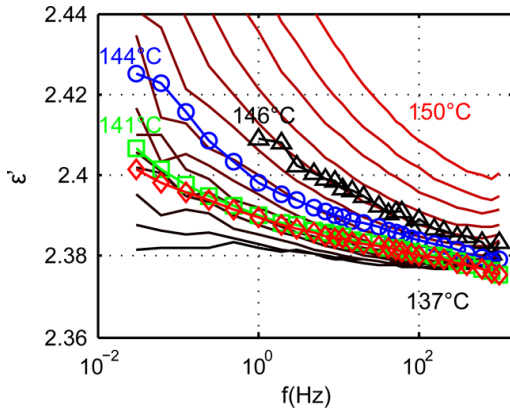


FIG. 2. Real part of the permittivity ε' measured under deformation (line with symbols) at $\lambda = 1.07$ (stretch ratio) as a function of frequency at strain rates $2.5 \cdot 10^{-3} \text{ s}^{-1}$ (black triangles), $2.5 \cdot 10^{-4} \text{ s}^{-1}$ (blue circles), $2.5 \cdot 10^{-5} \text{ s}^{-1}$ (green squares), and $2.5 \cdot 10^{-6} \text{ s}^{-1}$ (red diamonds).

We study the dielectric relaxation of polycarbonate (PC) at room temperature under imposed strain rate $\dot{\gamma}$, above the yield stress, and up to 13% strain. We find that the dielectric response of stretched PC behaves as if it was heated up at a temperature just below its glass transition temperature, $T_g \approx 423 \text{ K}$ for PC. Indeed, in the frequency range of our experiment [1] (10^{-2} and 10^3 Hz), the dielectric response of the stretched PC at room temperature superimposes to the dielectric response of PC at a temperature $T_a(\dot{\gamma}) < T_g$, which is a function of strain rate.

Specifically we observe that at T_a the dominant relaxation time $\tau_\alpha(T_a)$ of PC at rest is related to $\dot{\gamma}$ in such a way that $\tau_\alpha(T_a) \propto 1/\dot{\gamma}$ at and beyond the yield point. In our experiment, $10^{-5} \text{ s}^{-1} < \dot{\gamma} < 10^{-3} \text{ s}^{-1}$, the temperature shifts $T - g - T_a$ are of a few kelvin. The mechanical rejuvenation modifies the dielectric response at frequencies smaller than 10 Hz, whereas for higher frequencies the spectrum is only slightly modified.[2]

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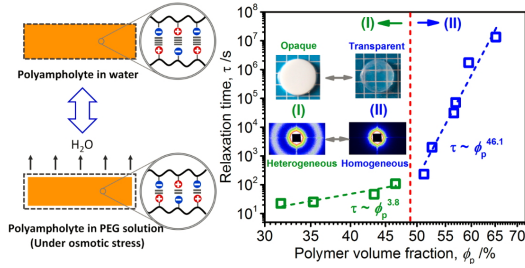


FIG. 1. Schematic of polyampholyte equilibrated in water and PEG solution. Optical images of the hydrogels at different ionic interaction, the corresponding SAXS patterns and relaxation time. ϕ_p is the polymer fraction.

Recently, we have developed a series of charge balanced polyampholytes (PA) physical hydrogels composed of randomly dispersed cationic and anionic repeat groups. This new class of hydrogel shows high toughness, self-healing ability and viscoelasticity [1, 2]. Those supramolecular physical hydrogels are deemed to possess dichotomic structure, where the strong bonds act as permanent crosslinks to impart elasticity, while the weak bonds break and reform reversibly to dissipate energy. The supramolecular structure can be tuned to change mechanical properties of PA gels over wide ranges by tuning the bond

strength and density. In this work, we systematically discuss the effects of ionic interaction on the structure and mechanical property of PA hydrogels.

The detailed synthesis method of PA hydrogels can be found in our published work [1, 2]. To change ionic interaction, the water equilibrated hydrogels were immersed into poly (ethylene glycol) (PEG) aqueous solution at room temperature for one week. The high osmotic pressure of PEG solution leads to the deswelling of the hydrogels and thus increased ionic interaction.

FIG. 1 demonstrates the effects of ionic interaction on optical, structural and rheological properties on PA hydrogels. By increasing ionic interaction, an opaque to transparent transition is observed (FIG. 1), which is due to the heterogeneous-homogeneous transition as demonstrated by SAXS. Interestingly, the opaque to transparent transition in optical property is just corresponding to the two-stage power law relaxation time in rheological behavior. Surprisingly, the relaxation time can be increased in about 6 orders by increasing the ionic interaction.

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Telechelic star polymers networks under shear

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Star polymers are interesting both for their industrial applications as well as from a scientific perspective as they constitute a bridge between colloids and polymeric chains[1]. Structurally star polymers are composed of a number of polymeric chains (called arms) which all have one end attached to a single central point. If, in addition, the outer ends of each arm are functionalized so that they can attach to each other, the star is called telechelic (TSP) (see Fig. 1 (a)).

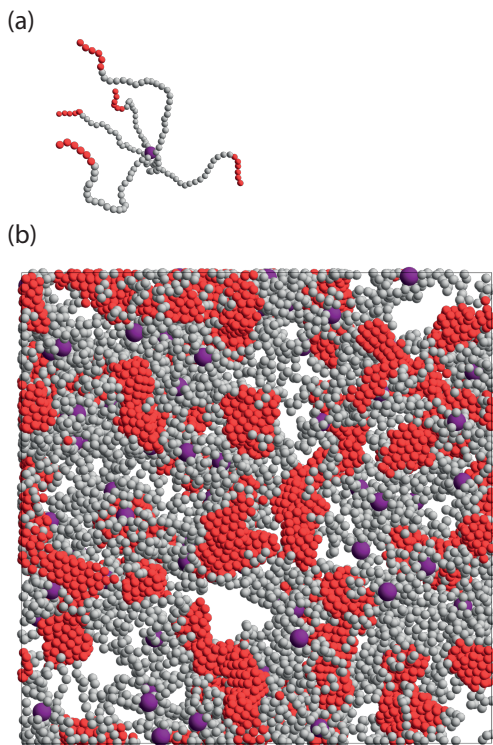


FIG. 1. (a) Snapshot of a TSP in the open star configuration (where no arms are bound together). The anchor is drawn in purple, the arms in gray with the attractive part in red. (b) Snapshot of an equilibrated network obtained from open TSPs.

In the very dilute regime the inter-star interaction is negligible and single telechelic stars can, under particular conditions, self-assemble into aggregates where the functionalized parts of multiple arms come together to form attractive patches. The number of patches depends on the characteristics of the TSPs such as the numbers of arms, the arm fraction that is functionalized, and the strength of the attractive interaction [2]. If the density is increased, the single star aggregates come together connecting via the attractive patches, forming either micelles [3] (which are spherical aggregates containing, at the core, the attractive patches bound together which are shielded by the non-interacting parts of the stars) or networks. It is also possible to assemble networks starting from TSPs in an open configuration (see Fig. 1 (b)).

Here, using Molecular Dynamics, we investigate the equilibrium properties (such as the size and shape of the attractive patches and the coordination number of stars within the gels) of network which we assemble out of either open TSPs or previously self-assembled stars. We then proceed to shear the equilibrated networks using nonequilibrium Molecular Dynamics simulations (SLLOD algorithm) [4] and track structural changes of our gels due to shear.

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Rheology of Organic Conductive inks

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Organic conductive polymers are used in flexible electronics as transparent electrodes in OLED for example. Their main interest lies in their price, their flexibility and the ease with which they can be processed. Only poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is now commercially available.

Among the alternatives to this system and that have been tested so far, the system composed of PEDOT and poly(4-styrene trifluoromethyl(bissulfonylimide)) (PEDOT:PSTFSI) (see Fig. 1) shows the best promise[1].

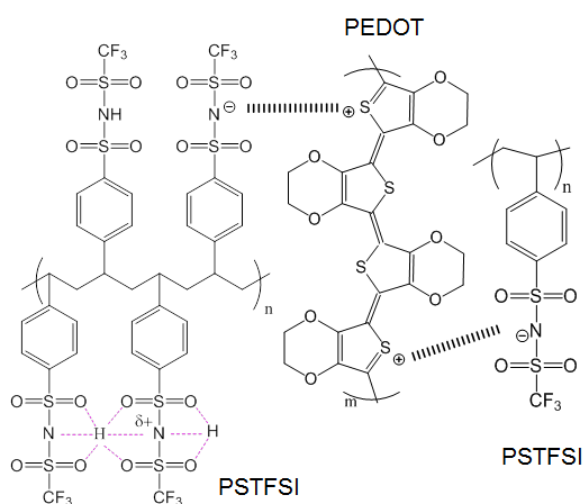


FIG. 1. Schematic of the PEDOT:PSTFSI complex[2]

Comparable results, in terms of conductivity and transmittance were obtained from these inks as compared to classical PEDOT:PSS. However, PSTFSI brings some specificities to the PEDOT inks making them of interest for further use in printed organic electronics. For instance, unlike PEDOT:PSS inks, that show viscoelastic behavior, PEDOT:PSTFSI inks present a gel phase (see Fig. 2).

From a structural point of view, we could already assess that unlike PSS, PSTFSI is more prone to develop hydrogen bonding as suggested by XPS measurements (see Fig. 3)[3].

Here, we address the main differences in rheological behaviour observed in both systems PEDOT:PSS and PEDOT:PSTFSI as a function of the formulation of these inks and with the objective to evaluate them in various printing processes.

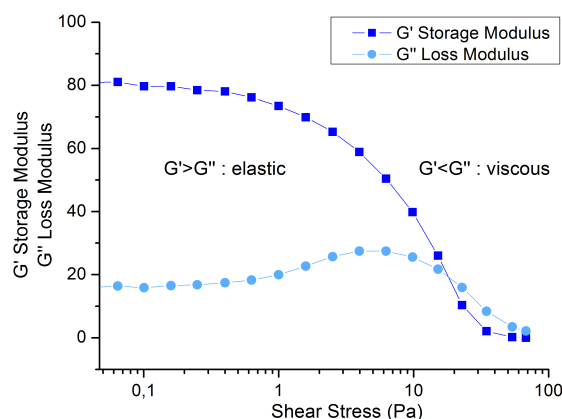


FIG. 2. Storage and loss modulus of a PEDOT:PSTFSI ink

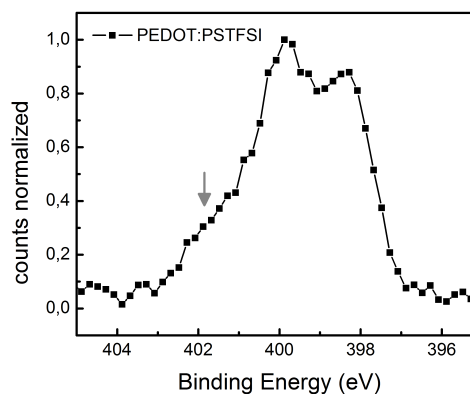


FIG. 3. XPS N1s spectrum of PEDOT:PSTFSI

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Structure and Dynamics of entangled polymers under shear flow studied by Neutron Scattering

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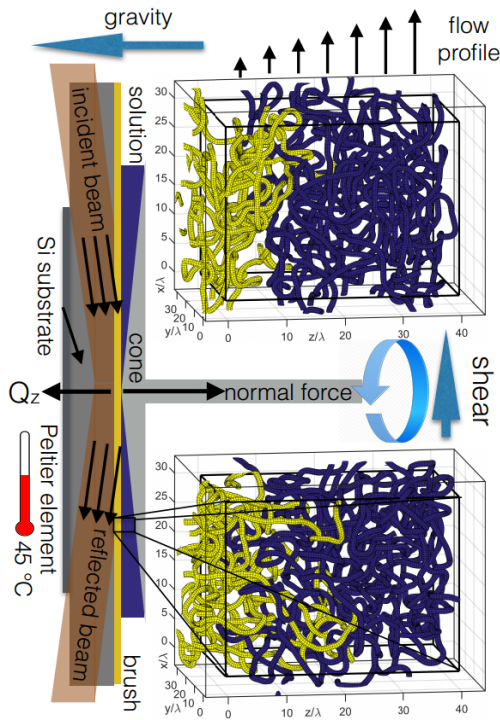


FIG. 1. Schematic representation of the *in situ* rheo-NR set-up probing a polymer brush in contact with free polymer chains.

The study of flow in soft matter is a multidisciplinary and active research area. The challenge is to relate out of equilibrium internal complex fluids structure to their macroscopic rheological response. Whether flow deformation triggers bulk material structural reorganization or subtle surface orientation is of critical importance for daily life products. Understanding and characterizing those effects is a current challenge that will improve material properties and applications.

Here we present the latest results on the combination of Neutron Scattering and rheology at the Institut Laue-Langevin, Grenoble on entangled linear polymers. Two examples will be presented: Firstly a commercially purchased rheometer with an adapted cone/plate or plate/plate geometry [1] is used in conjunction with Neutron Reflectometry (NR) to probe the structure of polystyrene (PS) brushes chemically attached to a solid surface sheared against a semi-

dilute PS solution (see Fig. 1). We report a reversible collapse of the polymer brush once the bulk solution is sheared in the non-Newtonian regime [2]. We explain the observation by the normal stress difference of the free chains exerted on the brush overwhelming any internal brush dynamics.

The second example combines our newly developed cone-plate shear device with Small Angle Neutron Scattering (SANS) and Neutron Spin Echo Spectroscopy (NSE) [3]. We sheared an entangled melt of polydimethyl-siloxane (PDMS) and report on the single chain form factor and the intermediate scattering function under shear rates extending into the non-linear regime. While the chain is not deformed at our highest shear rate ($Wi \approx 3$) as probed by SANS we observe accelerated dynamics in the vorticity direction at large length scales and long Fourier times according to the NSE results [4]. We believe these results support the idea of Convective Constraint Release (CCR) in sheared entangled polymers.

In addition, all our experimental results are compared to recently developed coarse-grained computer simulations of entangled polymers [5, 6].

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Wall slip of polymer microgels

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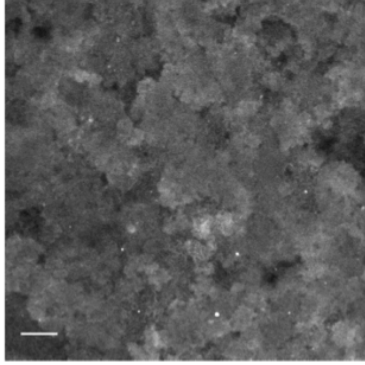


FIG. 1. Fluorescent imaging of carbopol microstructure (scale: 10 μm).

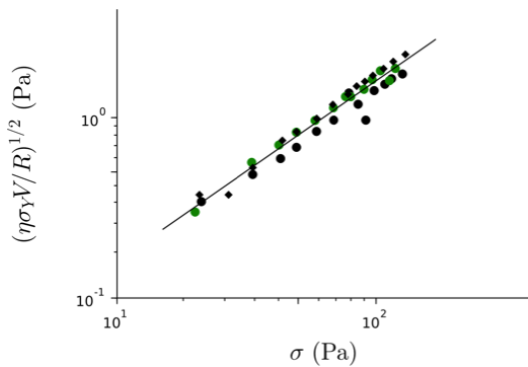


FIG. 2. Wall stress predicted by elasto-hydrodynamic model [1] from measured slip velocity v_s vs applied stress for carbopols with different yield stresses and microstructure sizes.

Jammed polymer gels like polyacrylate-based carbopol are complex yield stress fluids widely used in applications like cosmetics or oil extraction: solid-like at rest, they become liquids under a sufficient stress. Besides, their flow properties are very dependent upon wall properties, as they can exhibit significant slip, especially under confinement like in porous rocks or in microfluidic channels. We will present wall slip measurements performed on carbopol in glass microfluidic devices, coupled to fluorescent imaging of the polymer structure (Fig. 1).

At large polymer concentration, we show that the stress-velocity relation and its dependence upon yield stress and polymer microstructure size are well predicted by the elasto-hydrodynamic model developed by Meeker et al. [1] for soft spheres (Fig. 2), despite the entanglement of polymers in carbopol. At lower concentrations, a different friction regime is evidenced, as in other yield stress fluids [2]. Finally, we discuss unsteady effects at the wall and the influence of flow history in this experimental configuration.

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A colloidal gel is an important non-ergodic state of matter, which can have elasticity and fluidity at the same time. Colloidal gels are known to be formed by phase separation accompanying dynamical arrest of a colloid-rich phase due to glass transition [1–5]. However there has been little work on how rigidity emerges from such a phase separation. In the present work, we study how fluid mechanics influences the phase separation and how phase separation gives rise to rigidity. Using a novel experimental protocol initiating phase separation, we successfully follow by confocal microscopy observation the entire process of gelation from the very beginning with a single-particle resolution and reveal the roles of hydrodynamics and mechanics in gelation, for the first time.

The presence of a liquid component should play crucial roles in the formation of a network structure and its time evolution, since it gives a constraint from the conservation of fluid momentum, which is known to affect the kinetic pathway of non-equilibrium phenomena [6]. We show that hydrodynamic interactions between colloids mediated by a liquid component are the key to formation of a percolated network structure in a dilute system. Furthermore, the network formed by this mechanism is inevitably in a high energy state and under self-generated mechanical tension due to its connectivity. From the bond breaking rate we measure this internal mechanical tension and correlate its decay with the coarsening of the network. A measure of stress heterogeneity displays clear experimental evidence that network coarsening proceeds by sequentially repeating stress-driven mechanical fracture of a network strand. This demonstrates that the kinetic pathway toward a gel is selected not by a thermodynamics factor but by mechanical factors.

Hsiao *et al.* [7] have proposed from large amplitude rheological experiments that a gel load-bearing ability was linked to the abundance of locally isostatic (6 neighbours or more per particles) clusters. van Doorn *et al.* [8] have recently demonstrated that highly coordinated particles can be linked to slow dynamics. Here, with our new protocol we can go further and monitor the emergence of rigidity as gelation proceeds. We measure G' and G'' the elastic and viscous parts of the shear modulus by two-point microrheology. We are able to relate the onset of rigidity neither to simple network percolation, nor to the number of isostatic particles, but rather to the percolation of isostaticity. These findings provide an experimental basis for understanding the mechanics of gels at the microscopic

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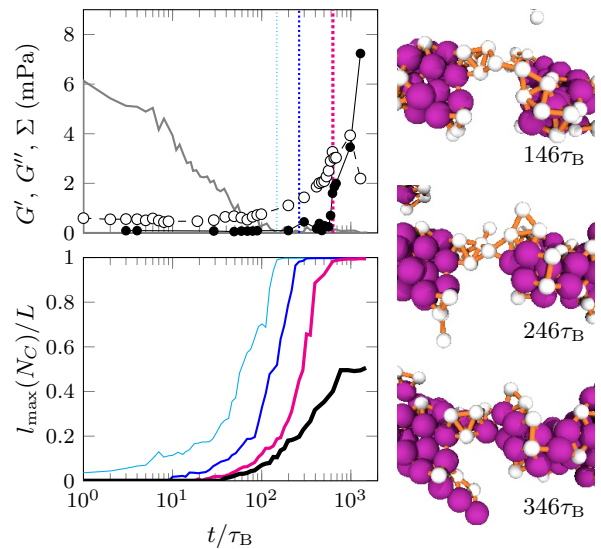


FIG. 1. **Percolation of isostaticity.** $\phi = 8\%$, $c_p = 1.5$ g/l. **Top:** Mechanics Internal stress Σ is drawn as thick gray curve. Elastic (G') and viscous (G'') shear moduli at high frequency ($f = 0.1\tau_B^{-1}$), are drawn respectively as filled and open circles. **Bottom:** Size of the largest cluster of particles having 2 (cyan), 4 (blue), 6 (magenta) and 7 (black) neighbours. Respective percolation is reported as a vertical line on top. **Right:** Reconstruction from experimental coordinates of the connection process between two isostatic clusters. Isostatic particles are drawn to scale in purple. Other particles are drawn half size in white. Links are drawn in orange.

Athermal creep dynamics of yield-stress fluids

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We develop an elasto-plastic description for the transient dynamics prior to steady flow of athermally yielding materials including foams, emulsions, physical gels, or granular media. In spite of the irrelevance of thermal fluctuations, the creep dynamics of such systems will depend on the preparation process and on the subsequent waiting period, during which slow athermal processes such as coarsening or compaction can alter the initial level or relaxation. In experiments the creep test implemented after a specific preparation protocol which results in a well defined initial state ensuring reproducibility of the results.

We focus our study on the influence of initial conditions on the creep behavior, addressing the two specific phenomena: (i) The strain rate response to a stress larger than the yield stress, which is strongly non linear and exhibits an "s-shaped" curve for $\dot{\gamma}(t)$ [2–4]. (ii) The dependence of the fluidization time scale τ_f on the difference between the applied stress and the yield stress $\Delta\sigma = \sigma - \sigma_y$.

Our description of the creep dynamics is directly derived from the Hébraud-Lequeux model [1] dealing with the time evolution of the distribution of stress values σ , $\mathcal{P}(\sigma, t)$, on a typical mesoscopic region. A modification is introduced for carrying out a stress control protocol. In this formulation, the initial condition $\mathcal{P}(\sigma, t = 0)$ fully determines the creep behavior. We consider distributions with zero mean, that will be instantaneously shifted by the desired value of the applied stress σ^{ext} at the onset of the creep experiment. The dispersion of $\mathcal{P}(\sigma, t = 0)$ characterized by its standard deviation s_d is generally expected to be inversely related with the level of relaxation prior to a creep test. We study the creep behavior of athermal amorphous materials starting from different initial levels of relaxation.

In spite of its simplicity, the model is able to reproduce the s-shaped response of the shear rate after imposing a step stress, in qualitative agreement with experimental observations [2, 4], shown in the Fig. 1. We quantify the slowing down in the creep regime with a power law $\dot{\gamma} \sim t^{-\mu}$ and find that the exponent μ lies in the same numeric range as reported in experiments [3]. The exponent is however not universal, and depends on the applied stress and the level of initial relaxation. We distinguished the different underlying mechanisms for the two time scales τ_m (minimum

strain rate) and τ_f (fluidization). τ_m is determined by the first plastic activations and depends sensitively on the initial distribution of internal stresses $\mathcal{P}(\sigma, t = 0)$. τ_f characterizes the loss of memory with respect to this initial distribution. We rationalized our results for the fluidization time τ_f by introducing a static yield stress σ_y^S that increases with initial relaxation. The behavior of τ_f can then be described by a power law $\tau_f \sim (\sigma^{\text{ext}} - \sigma_y^S)^{-\beta_s}$, where β_s increases with decreasing initial aging, and has again values comparable to those reported in experiments.

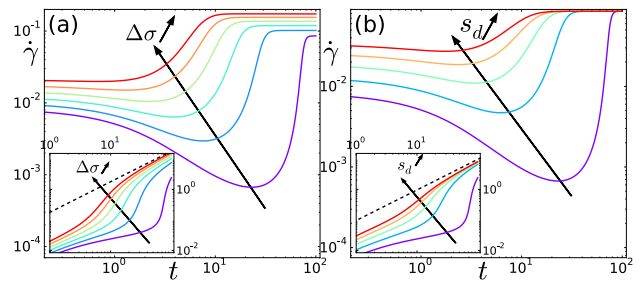


FIG. 1. *Creep curves* Main figures: the strain rate time series $\dot{\gamma}(t)$. Insets: the corresponding strain time series $\gamma(t)$ with respect to the main figures. Dashed line linear in time serves as a guide for the eye. (a) The creep behavior for different applied stresses for a fixed initial aging level $s_d = 0.28$. From the bottom to the top, $\Delta\sigma = 0.18, 0.2, \dots, 0.28$. (b) The creep behavior for a fixed applied stresses $\Delta\sigma = 0.18$ for different initial aging levels. From the bottom to the top, $s_d = 0.28, 0.3, \dots, 0.36$.

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Emergent properties of composite F-actin and intermediate filaments networks: Theoretical model and validation

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The synthetic biopolymeric gels demands great interest as bio-material to mimic many biological scaffolding structures. These can contribute to a better understanding of cytoskeleton like structural building blocks and soft nanotechnology. In particular the study of semiflexible F-actin and vimentin intermediate filaments (IF) both form complex networks, and are key regulators of cellular stiffness. While the mechanics of F-actin networks or IF have been characterised, the interaction between this two networks is largely unknown. Experimental studies using large deformations rheology show that copolymerisation of F-actin and IF can produce composite networks either stronger or weaker than pure F-actin networks [1].

We verify these effects theoretically developing a model into the framework of nonlinear continuum mechanics, in which we define a free energy functional considering the role of the entropic-elastic for semiflexible networks with weak crosslinks [2,3] plus an energetic term to describe the interaction parameter which allows the coupling among the two networks.

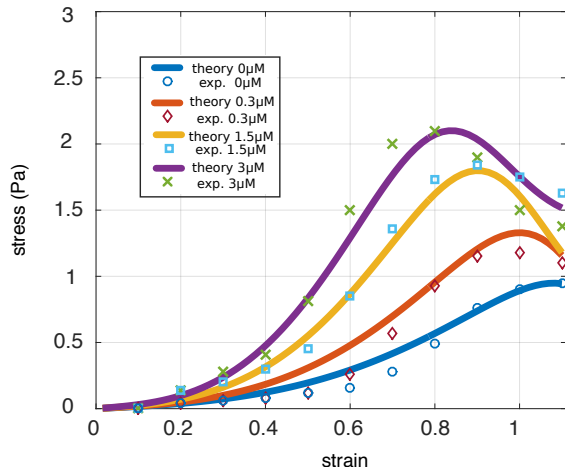


FIG. 1. in the figure can be observed the comparison between experiments and model predictions for large deformations experiments for composite networks of F-actin with different levels of concentration of intermediate filaments.

Here we consider that the increment in the concentration of IF promotes an increment of the physical crosslinks over the F-actin bundles reducing the contour length (Lc) and the degree of fluctuations of the actin. As the Lc is reduced the ratio r/Lc tend to one and the composite network manifest a rise in the stress. But, as the IF filaments are very flexible the increment in the density of physical crosslinks due to the interaction with F-actin will not produce a relevant change over the stress sustained by the network. Therefore in order to simplify the model we neglect the effect over the physical crosslinks over the IF and only focus on the role of physical crosslinks over the F-actin. Also, the rise of the internal stress is propagated towards the chemical crosslinks lowering the characteristic strain λ_0 (yielding point).

Finally we validate the theoretical model with measurements performed on large deformations rheological experiments with different concentrations of actin and vimentin performed by Jensen et al [1]

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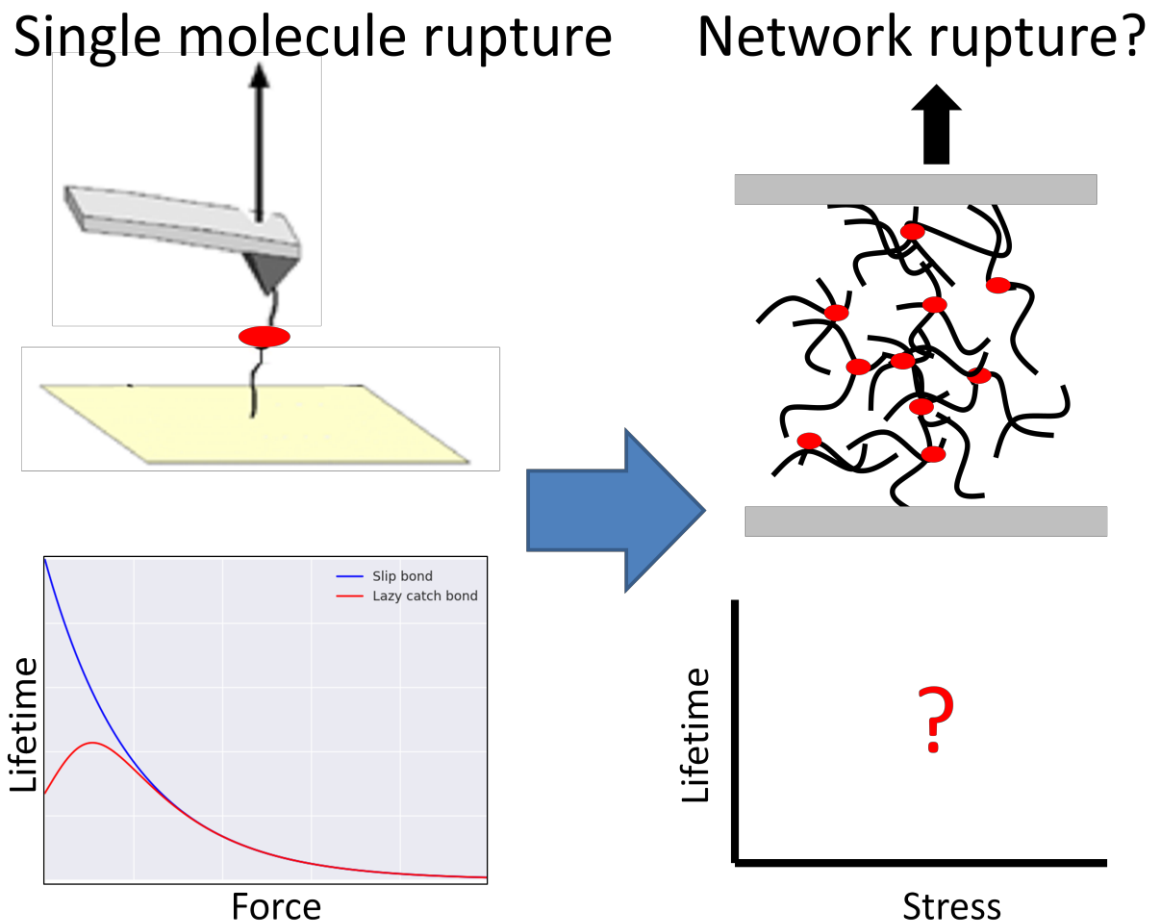
Weaker bonds, stronger networks? Biology's counter-intuitive strategy against material failure

Yuval Mulla, Gijsje Koendernink

Imagine you pull on two molecules bound to each other. Intuitively you would expect the lifetime of the bond to decrease. This is usually true in synthetic materials, but not always in biology. Recently molecular bonds have been found where lifetime increases for limited force. This is named catch (opposed to slip) bond behavior, and can be conceptually compared to a Chinese finger trap.

I will explain how these bonds behave the way they do. Moreover I'll focus on the bulk material properties of a network connected by many catch bonds. Through a combination of experiment and statistical thermodynamics we found surprising emergent behavior, which causes weaker bonds to result in stronger networks.

I'll shortly discuss the potential application for smart materials of catch bonds and address the possible biomedical relevance of this physical effect.



Viscoelastic properties of two coarse-grained models of cis-polyisoprene with and without pressure correction

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We investigate viscoelastic properties of two coarse-grained (CG) models of a cis-polyisoprene melt by means of molecular dynamics simulation. The chains are composed of 24 monomers, well below the entanglement molecular weight.

CG models are made according to the structure-based systematic coarse-graining scheme [1]. The mapping rule used here is shown in fig. 1 where two types of CG beads are defined. As the reference system, we adopt an united atom model [2] at temperature 393 [K] and pressure 1.0 [bar].

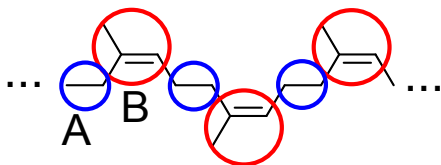


FIG. 1. Mapping rule for the two CG beads, A and B, for cis-polyisoprene.

Non-bonded interactions between two CG models are obtained applying the iterative Boltzmann inversion method with and without pressure correction, respectively [3, 4]. It is well known that the pressure of a CG model without pressure correction is much higher than that of the reference atomistic model at the same temperature and the same density. Conversely, in the pressure corrected model the compressibility usually deviates from that of the atomistic model. In fact, this trade-off relationship is confirmed in our CG models. Since pressure is a component of stress tensor, it is interesting to see whether the off-diagonal components of the stress tensor are affected by pressure correction.

In order to compare the viscoelastic properties, the time scale of the CG models are rescaled by a single factor which is determined so that the relaxation time of the first normal mode of the chains matches that of the atomistic model. It is noted that the Kuhn lengths of the two CG models are almost the same as that of the atomistic model.

In fig. 2, we show the stress relaxation function $G(t)$ obtained by Green-Kubo relation described as

$$G(t) = \frac{V}{k_B T} \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle, \quad (1)$$

where σ_{xy} is the xy component of the stress tensor at equilibrium with Boltzmann constant k_B , temperature T and the system size V . It is found that the two CG models show the same long time decay and agree well with the stress relaxation function of the atomistic model. This time scale corresponds to the segmental relaxation time of the beads. We will also discuss the viscosity under steady shear and the temperature dependence of the normal mode relaxation time.

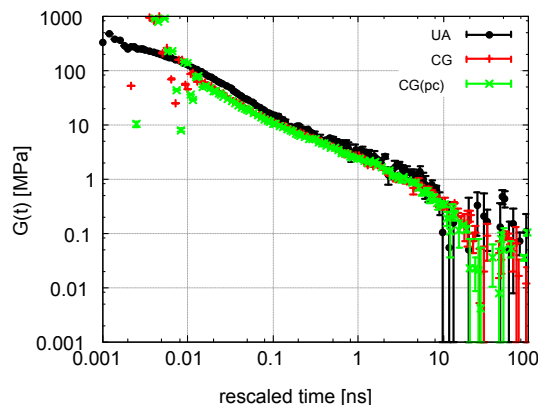


FIG. 2. The stress relaxation functions evaluated by Green-Kubo relation. The black dots are the result of the united atom model. Red plus and green cross represent the results of the CG models without and with pressure correction, respectively.

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Non-uniform flow during start-up shear

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We investigated start-up experiments of concentrated hard-sphere suspensions around the glass transition. Rheo-confocal experiments were carried out to elucidate single-particle structure and dynamics.

Figure 1A shows the rheological response after the application of a constant shear rate. After an initial linear regime, the response becomes non-linear and can, depending on, e.g., Peclet number and volume fraction, show an overshoot. After yielding, a fluid-like steady state is observed. Simultaneously, the mean squared displacement (MSD) in the vorticity direction $\Delta y^2(\tau)$ is measured (Fig. 1B). In the linear regime $\Delta y^2(\tau)$ shows a plateau at low τ which progressively increases with time and, around the stress overshoot, reaches a slope of 2 indicating super-diffusion. At higher strains the system exhibits a fluid-like response, with the slope of $\Delta y^2(\tau)$ becoming about 1 indicating a diffusive process. These observations agree with previous experimental and simulation results [1, 2].

For systems with flow instabilities, the steady state can be transient and extend beyond 10,000% strain

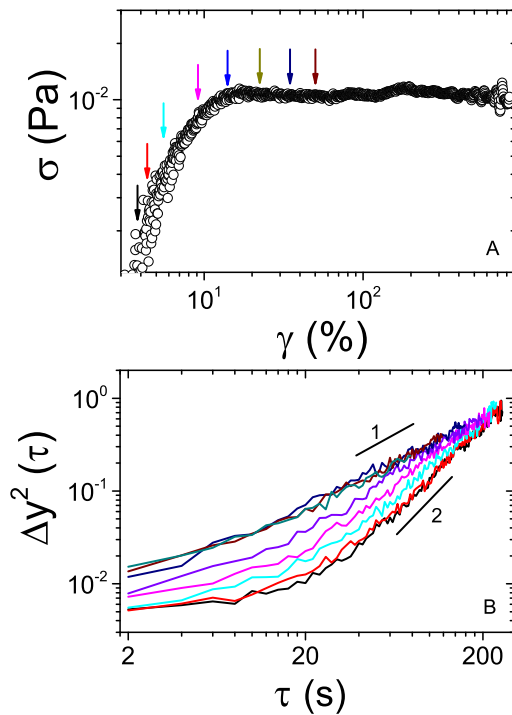


FIG. 1. (A) Shear stress σ as a function of strain γ and (B) MSD $\Delta y^2(\tau)$ in the vorticity direction as a function of delay time for different waiting times (as indicated by the arrow of the same colour). Volume fraction $\phi = 0.57$ and shear rate $\dot{\gamma} = 0.0025$ corresponding to a Peclet number $Pe_0 = 0.017$.

[3]. We observe a transient non-linear velocity profile. Figure 2 shows the deviation from a linear velocity profile, Δu , as a function of the relative position z/H . At low strains the shear profile is close to that expected for a Newtonian fluid ($\Delta u \approx 0$). As the strain is increased, the velocity profile increasingly deviates (becomes faster) and reaches a maximum deviation at about 20% strain, i.e. close to the overshoot. The deviation decreases as the strain is further increased, and at high strains the velocity profile is even smaller (slower) compared to the shear profile at $\gamma \approx 0$. Hence, we observe a transient, time-dependent velocity profile and thus a non-uniform flow. It occurs even at low ϕ and Pe , revealing the complexity of such systems, even in regimes of Pe and ϕ where stable uniform flow is eventually expected at very long times [4].

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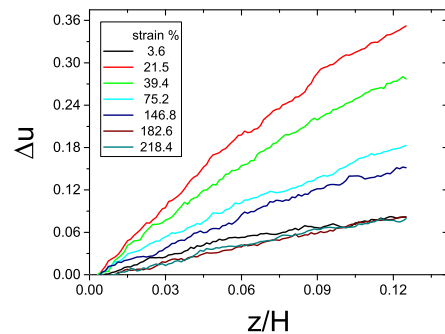


FIG. 2. Deviation from a linear velocity profile, Δu , as a function of the relative height z/H for different strains, with Δu the difference between the observed and, based on a linear profile, expected Newtonian velocity.

Differential Variance Analysis of soft glassy materials: a direct method to quantify and visualize structural relaxation and dynamic heterogeneities

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Sluggish relaxation accompanied by dynamic heterogeneity (DH) is the hallmark of soft materials close to structural arrest, such as gels [1], glasses [2], cell tissues [3] and many complex formulated products. Such a feature is crucial to understand and tailor the rheology of these systems, but its experimental characterization still remains a complicated task, handled by few specialized groups, since it requires to resolve the dynamics in space and time and estimate deviations from the average behavior.

Single particle tracking can be exploited only when particles are clearly resolved by the microscope and, even in this case, quantitative measurements of DHs suffers major limitations and may be not statistically meaningful. Dynamic Light Scattering (DLS) techniques are probably the most robust quantitative methods [2], but do not provide any direct visualization of DHs. Simultaneous visualization and quantitative measurements require instead more sophisticated techniques that combine features of both DLS and imaging [4]. Differential Dynamic Microscopic [5] is an elegant and promising technique but currently limited to monitor the structural relaxation and not DHs.

Considering that soft glassy materials are common in technological applications and biological systems, it appears clearly that an easy way to fully characterize complex fluids with dynamic heterogeneity is highly desirable. In this talk, we will introduce the Differential Variance Analysis (DVA), a novel method that dramatically simplifies this experimental task, since it is straightforward and directly applicable to digital videos of a sample, without tracking the single particle positions [6]. First, we will illustrate the DVA strategy drawing on video microscopy of dense hard sphere colloidal suspensions: the method focuses on the differential frames, obtained subtracting images at different lag-times. The dynamic order parameter and the dynamic susceptibility, shown in 1 a and b, are simply obtained from the real space variance of differential frames and its fluctuations, respectively. Moreover, direct visualization of dynamic heterogeneities naturally appears in the differential frames, when the lag-time is set to the one corresponding to the maximum dynamic susceptibility (see Inset of 1b). In particular, we will present a framework for visualizing DHs, not only as spatial correlations, but also as ensemble fluctuations.

In the last part of the talk, we will show that DVA can be exploited to characterize a wide variety of soft materials, including colloidal gels and complex formu-

lated products. To this aim, new results on different systems [7] will be discussed.

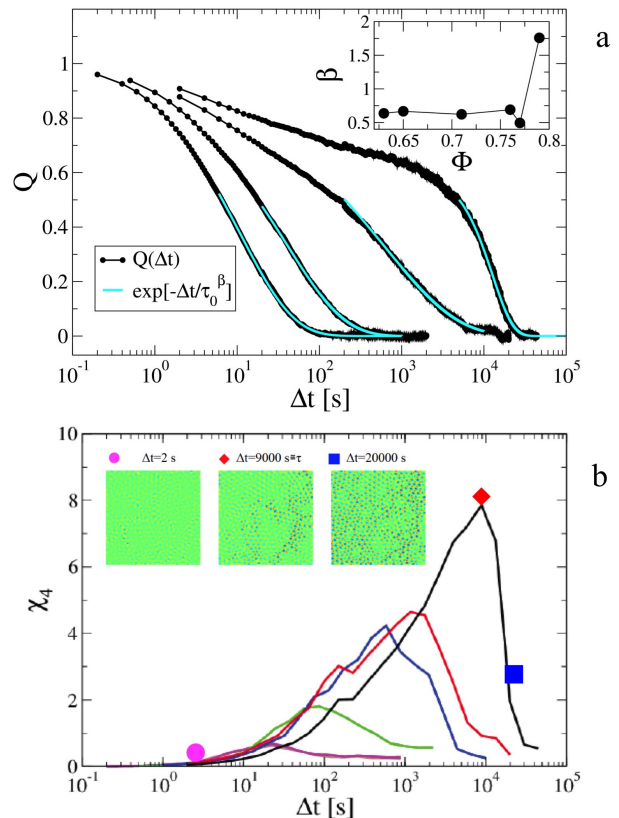


FIG. 1. For colloidal suspensions at volume fraction, Φ , increasing from left to right, (a) DVA dynamic order parameter, $Q(\Delta t)$. The solid lines are fits, Ae^{-t/τ_0^β} , to the late decay of $Q(\Delta t)$, with the value of β indicating a crossover from stretched to a compressed exponentials as Φ increases (Inset). (b) DVA dynamic susceptibility, $\chi_4(\Delta t)$. Inset: for the largest investigated volume fraction, sequence of differential frames at increasing lag-times, Δt . Symbols highlight the values of χ_4 at the lag-times reported in the sequence.

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Fatigue of a colloidal gel under Large Amplitude Oscillation Stress

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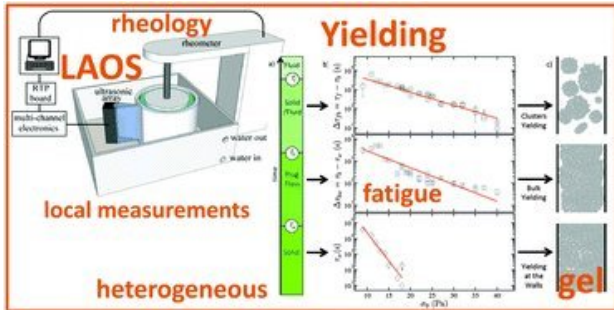


FIG. 1. Experimental setup and scaling of the characteristic yielding times as a function of the amplitude of the applied oscillatory stress.

Fatigue refers to changes in material properties caused by repeatedly applied loads. It has been widely studied in metals but little has been done in soft materials such as colloidal gels. Colloidal gels like many viscoelastic solids such as foams or emulsions flow when sheared above a critical stress, the yield stress. This shear-induced fluidization is involved in virtually any application of colloidal gels and measuring correctly the yield stress is essential to ensure the safe and proper use of the material. Here, we first evidence the spatiotemporal complexity of the yielding behavior of a colloidal gel by combining standard rheology

and ultrasonic imaging to probe the local displacement within the gel during large-amplitude oscillatory stress (LAOS) experiments, Fig. 1 [1, 2]. The yielding mechanism in colloidal gels can be separated in three phases: a fatigue period where the soft material remains solid, a phase where the material becomes highly heterogeneous and displays solid/fluid coexistence and finally a phase where the flow is homogeneous [3]. Scaling and modeling of the characteristic times shows that the yielding process is dominated by fatigue and is essentially an activated process.

Figure: Experimental setup and scaling of the characteristic yielding times as a function of the amplitude of the applied oscillatory stress.

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Distribution of residual stresses in glass-forming systems

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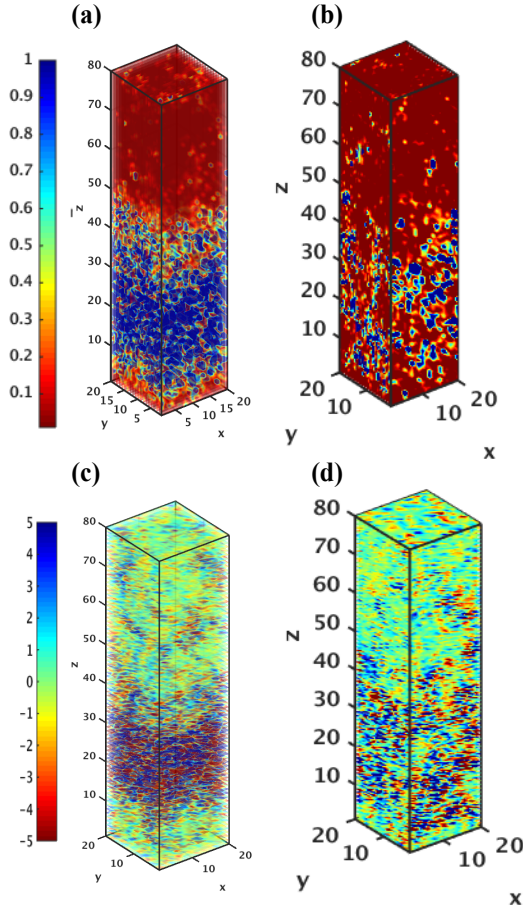


FIG. 1. (a). MSD map at $\dot{\gamma}t = 1.0$. (b). MSD map during stress relaxation at time $t = 5000$. The time origin for MSD calculation is taken at the time of shear cessation. (c) Strain map at time of shear switch off (d) Strain map at time $t = 5000$ after the shear switch off.

When a sheared glass is allowed to relax after switching off the shear, stresses do not fully relax to zero instead finite amount of stresses remain in the glass [1]. In this new glass state with residual stresses, the spatial distribution of the residual stresses is still a matter of investigation particularly when the sheared system has shear bands, i.e. the strain is localized

in space in the form of a band-like structure. Also, the effect of different shear rates, with which the initial glass is deformed, and the effect of the amount of strain present in the initial deformed glass on the residual stress distribution is poorly understood.

In the present work, we study the relaxation of stresses in a sheared model glass former using the molecular dynamics simulations[2]. We first deform the glass by shearing it with a constant strain rate. We, then, switch off the shear at different strains and allow the glass to relax. We obtain a new glass state with residual stress. The amount of residual stress in the system depends on the initial stress before the shear cessation which is consistent with previous observations [1]. To look at the dynamical heterogeneities during the shear and after the shear cessation, we plot spatially resolved mean square displacement (MSD) of particles. The MSD map at strain $\dot{\gamma}t = 1.0$ (Fig. 1(a)) shows that highly mobile regions form a shear band. We switch off the shear at this strain and allow the system to relax. Fig.1(b) shows the MSD map during the stress relaxation. The time origin for MSD calculation during stress relaxation is taken at the time of the shear cessation. It is clear from fig.1(b) that the highly mobile regions remain localized in the regions where shear band was present before the shear switch off (Fig. 1(a)). Spatially resolved map of non-affine strain (shown in Fig. 1 (c) and (d)) also shows the localization of residual strain in the region where shear band was present.

We also examine changes in the mechanical properties of the undeformed and deformed glass by calculating respective Poisson's ratios. We do not find any significant change in the Poisson's ratios of the deformed and undeformed glass which is in contrast to previous finding [3].

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Bulk Energy Dissipation Mechanism for the Fracture of Tough and Self-Healing Hydrogels

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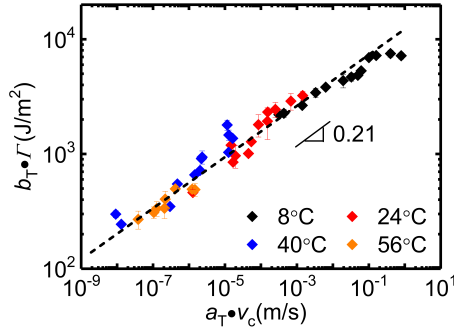


FIG. 1. The constructed master curves of tearing energy Γ against crack velocity V_c .

Recently, many tough and self-healing hydrogels have been developed based on physical bonds as reversible sacrificial bonds. As breaking and reforming of physical bonds are time-dependent, these hydrogels are viscoelastic and the deformation rate and temperature pronouncedly influence their fracture behavior. Using a polyampholyte hydrogel as a model system [1],

we observed that the time-temperature superposition principle is obeyed not only for the small strain rheology, but also for the large strain hysteresis energy dissipation and the fracture energy below a certain temperature. The three processes possess the same shift factors that obey the equation of Williams, Landel, and Ferry (WLF) time-temperature equivalence. The fracture energy Γ scales with the crack velocity V_c over a wide velocity range as, $\Gamma \sim V_c^\alpha$ ($\alpha = 0.21$), as shown in FIG. 1. The exponent α of the power law is well-related to the exponent κ of the relaxation modulus $G(t) \sim t^{-\kappa}$ ($\kappa = 0.26$), obeying the prediction $\alpha = \kappa / (1 + \kappa)$ from classic viscoelasticity theory. These results show that the fracture energy of the polyampholyte gel is dominated by the bulk viscoelastic energy dissipated around the crack tip [2]. This investigation gives an insight into designing tough and self-healing hydrogels and predicting their fracture behaviors from their dynamic mechanical spectrum.

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Interplay of coarsening, aging and stress hardening impacting the creep behavior of a colloidal gel

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We explore the dynamical and mechanical characteristics of an evolving gel, aiming to assess how the gel evolution impacts the creep response of the system. Our gel is formed by inducing the aggregation of thermosensitive colloids by a variation in temperature. We find experimental evidence that the long time evolution of this gel is due to two distinct processes: a coarsening process that involves the incorporation of mobile particles into the network structure and an aging process that triggers intermittent rearrangement events. While coarsening is the main pro-

cess governing the evolution of the elastic properties of the gel, aging is the process determining structural relaxation. The combination of both processes in addition to stress hardening governs the creep behavior of the gel, a creep behavior that is determined by three distinct contributions: an instantaneous elastic, a delayed elastic and a loss contribution. The systematic investigation of these contributions in recovery experiments provides evidence that losses and delayed elastic storage have a common origin, both being due to intermittent local structural relaxation events.

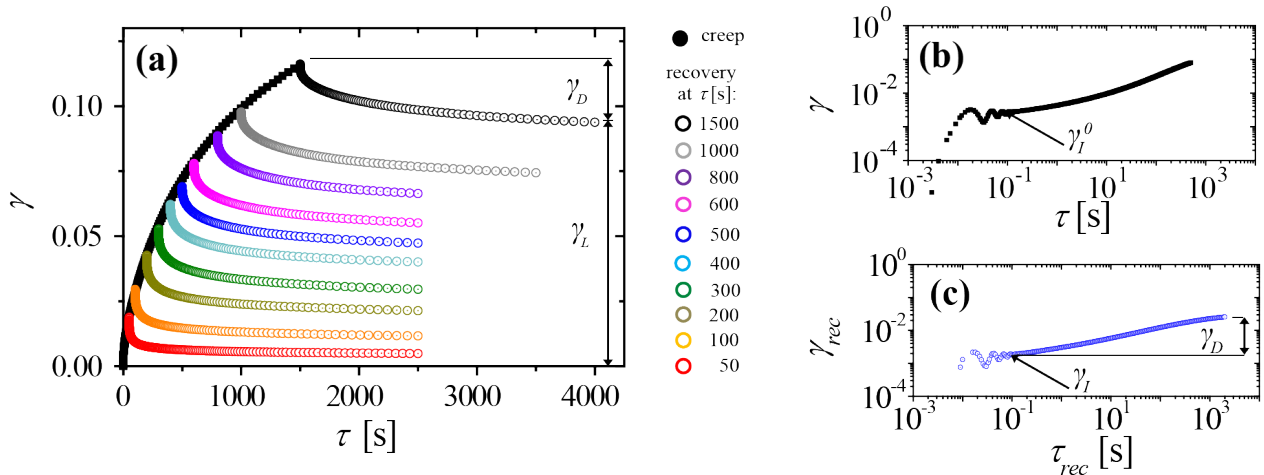


FIG. 1. (a) Systematic investigation of recoverable strain after applying a stress over different time lags. (b) Creep experiment in log-log representation. (c) Recovery test started at $\tau = 500s$, where the recovered strain is defined as $\gamma_{rec} = (\gamma^* - \gamma)$ with γ^* the maximum strain reached at the end of the creep experiment and $\tau_{rec} = 0$ at the moment the stress is set to zero. This experimental approach allows us to deconvolute the creep response into three distinct contributions: a lost strain γ_L , an instantaneous elastic strain γ_I and a time-delayed elastic strain γ_D .

On the normal modes of weak colloidal gels

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The rheological and structural properties of colloidal gels make them highly desirable for many technological applications[1]. Since the normal modes of soft materials and their associated DOS may be directly related to their linear viscoelastic response, recent work has used simulations of microstructural dynamics and relaxation to predict mechanical properties of gels[2]. Such work neglects the role of hydrodynamic coupling of the suspended particles. Contrary to atomic systems, where the phonon dispersion curve is entirely determined by particle mass and inter-particle potentials, in colloidal systems dissipative interactions mediated by the suspending fluid must be considered [3]. The complexity of modeling many-bodied hydrodynamic interactions in large systems has encouraged their neglect in work to date. However, as was recently shown, neglecting long-ranged dissipative coupling in discrete element modeling of gelling systems leads to predictions of structure and dynamics that are at odds with experimental observations[4, 5]. Indeed, since the modes of relaxation are modulated by the hydrodynamic interactions between particles, the fluid mechanics within a gel must be central to the linear viscoelastic moduli they exhibit when deformed macroscopically. Several experiments have found that models neglecting hydrodynamic coupling fail to reproduce measured dynamics and friction coefficients[6].

We investigate the normal modes and relaxation rates of weak colloidal gels in computations employing different models of the hydrodynamic interactions between colloids. The eigenspectrum is computed for freely draining, Rotne-Prager-Yamakawa and Accelerated Stokesian Dynamics approximations of the hydrodynamic mobility in a normal mode analysis of a harmonic network representing the gel. The spatial structure of the normal modes suggests that measures of collectivity and energy dissipation in the gels are fundamentally altered by long-ranged hydrodynamic interactions, while hydrodynamic lubrication affects only the relaxation rates of short wavelength modes. Models accounting for long-ranged hydrodynamic interactions exhibit a microscopic relaxation rate for each normal mode, λ that scales as $\lambda \sim l^{-2}$, where l is the spatial correlation length of the mode. For the freely draining approximation, $\lambda \sim l^\gamma$, where γ varies between 3 and 2 with increasing ϕ . A simple phenomenological model of the internal elastic response to normal mode fluctuations is developed, which shows that long-ranged hydrodynamic interactions play a central role in the viscoelasticity of the gel network.

Analogous to the Zimm model in polymer physics[7],

our results indicate that long-ranged hydrodynamic interactions play a crucial role in determining the microscopic dynamics and macroscopic properties of weak colloidal gels. With increasing volume fraction, hydrodynamic screening occurs, the majority of particles are multiply bonded, and the gel dynamics are less sensitive to the hydrodynamic model. Dynamic simulations show that the stress decay as measured by the time-dependent shear modulus matches the normal mode predictions and the phenomenological model. A computational model neglecting hydrodynamic interactions will yield erroneous estimates of $G(t)$ and other related viscoelastic and mechanical properties.

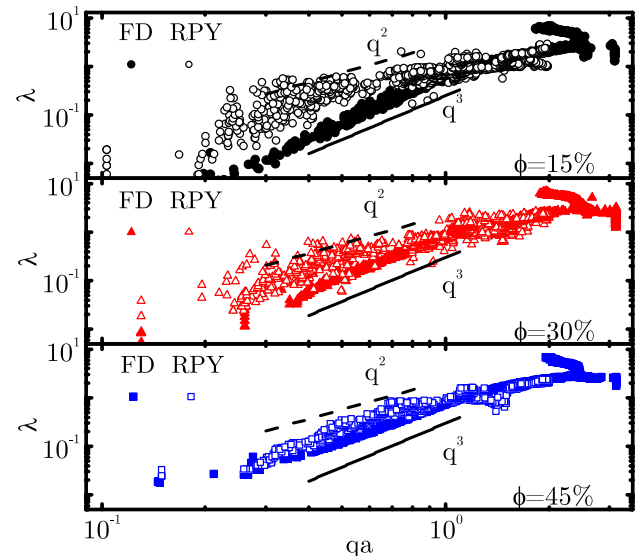


FIG. 1. Relaxation rate λ as a function of the corresponding characteristic wavelength $q = l^{-1}$ of energy dissipation for all volume fractions ϕ computed using both the freely draining (FD) and Rotne-Prager-Yamakawa (RPY) approximation for the hydrodynamic mobility.

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The rheological property of a material is well represented by the macroscopic flow curve, which shows the dependence of shear stress on the applied shear rate. Solids, including granular media, colloidal glasses, foams, emulsions etc., that flow only when the stress is larger than some critical value are called yield stress materials [1]. A simple yield stress material has a monotonic flow curve. But there exists another class of materials, sometimes referred to as viscosity bifurcating yield stress fluids, which can show non-monotonic flow curves (see Fig 1), where one finds phenomena like permanent shear banding [2].

The reasons for the transition from a monotonic to non-monotonic flow curve is inconclusive and yet to be well understood [3]. In a recent experimental work based on a dry granular system [7], it was observed that it is possible to influence the flow behaviour of the system by introducing an additional perturbation in terms of vibration. Also it was shown that, depending on the vibrational amplitude, it is possible to probe the flow curves in terms of critical dynamics associated with a dynamical phase transition at finite shear rates. Similar changes in the flow behaviour have been observed in the epithelial tissue dynamics [8], where instead of an external perturbation, it was found that an additional noise, due to local activity of individual cells fluidises the system and hence influencing the rheological property.

In this work we present a study, involving meso-scale and molecular simulations, which aims at understanding the interplay between the nature of perturbation and the flow properties. The mesoscale simulations used in this work, are based on the elasto-plastic model which has been extensively studied and describes quite well the rheology of yield stress materials exhibiting non-monotonic flow curve [4, 5]. We add to this model vibration induced plastic events that are adding up to the shear induced plastic transformations and calculate the corresponding flow behaviour.

We find that by tuning the time scale associated with vibrational induced plastic activity a fluidization process sets in, influencing the flow behaviour of yield stress material. At a critical value of this vibrational time scale we produce a crossover from a monotonic to non-monotonic flow curve. The current set of results in the stress controlled simulations in the vicinity of the corresponding saddle point, shows an increase in the strain rate fluctuations similar to approaching an equilibrium critical point [7].

The corresponding molecular dynamics simulations are performed in 3D on a dense suspension of repulsive soft particles, which shows the rheological features of a simple yield stress material, including the

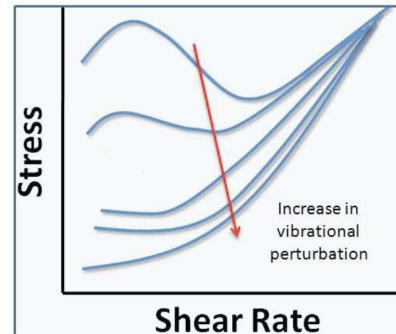


FIG. 1. Schematic flow curve showing the steady state stress as a function of shear rate for dense solids. With the increase vibrational perturbation the system fluidises influencing the macroscopic flow curve.

existence of a long persisting transient shear band [6]. In addition to shear deformation imposed at a chosen shear rate, we introduce vibrational oscillations in the vorticity direction. Tuning the amplitude and frequency of the imposed vibrations, we find that, also in molecular simulations the increase in vibrational energy leads to the fluidization of the yield stress material. We further find that the vibrations can influence the persistence time of the transient shear banding phenomenon. These promising results gives us an opportunity to map the vibrational time scales introduced within the mesoscale model with the vibration induced/enhanced plastic rearrangements in the microscopic simulations and hence shed light on the fluidization processes which governs the low shear rate regime of the flow curve.

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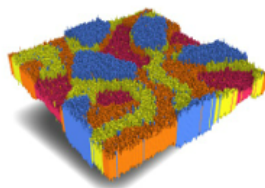
Supporting institutions



L'ORÉAL

GDR PHENIX

Faculté  des Sciences et Technologies



I(SM)²
INSTITUTE FOR SOFT MATTER
SYNTHESIS AND METROLOGY



GEORGETOWN UNIVERSITY

Rheology of gel networks: combining experimental, computational and theoretical insights

21-23 June 2017, Centre Blaise Pascal, Lyon

Wednesday	Thursday	Friday
<p>08:30 - 08:50 Registration and welcome coffee</p> <p>08:50 - 09:00 Welcome</p> <p>Session 1 Aging and relaxation</p> <p>09:00 - 09:30 R. Angelini</p> <p>09:30 - 10:00 M. Bouzid</p> <p>10:00 - 10:30 T. Baumberger</p> <p>10:30 - 11:00 Coffee break</p> <p>11:00 - 11:30 P. Chaudhuri</p> <p>11:30 - 12:00 R. Leheny</p> <p>12:00 - 12:30 Discussion (chair L. Cipolletti & B. Ruta)</p> <p>12:30 - 14:00 Lunch</p> <p>Session 2 Creep and precursors to failure</p> <p>14:00 - 14:30 J.-L. Barrat</p> <p>14:30 - 15:00 L. Cipolletti</p> <p>15:00 - 15:30 F. Puosi</p> <p>15:30 - 16:00 Coffee break</p> <p>16:00 - 16:30 R. Zia</p> <p>16:30 - 16:50 R. Cabrioli</p> <p>16:50 - 17:30 Discussion (chair: L. Ramos & K. Martens)</p> <p>17:30 - 19:30 Poster session & Apero</p>	<p>Session 3 Onset of rigidity and elasticity</p> <p>09:00 - 09:30 X. Mao</p> <p>09:30 - 10:00 L. Hsiao</p> <p>10:00 - 10:30 R. Castaneda Priego</p> <p>10:30 - 11:00 Coffee break</p> <p>11:00 - 11:20 A. Aufderhorst</p> <p>11:20 - 11:40 M. Rouillet</p> <p>11:40 - 12:00 T. Liberto</p> <p>12:00 - 12:30 Discussion (chair G. Foffi & E. Del Gado)</p> <p>12:30 - 14:00 Lunch</p> <p>Session 4 Gel rheology</p> <p>14:00 - 14:30 G. McKinley</p> <p>14:30 - 15:00 G. Petekidis</p> <p>15:00 - 15:30 G. Foffi</p> <p>15:30 - 17:00 Poster session & Coffee break</p> <p>17:00 - 17:30 L. Ramos</p> <p>17:30 - 18:00 D. Blair</p> <p>18:00 - 18:30 Discussion (chair J.L. Barrat & S. Manneville)</p> <p>20:00 Conference Dinner</p>	<p>Session 5 Design and control of mechanical instabilities</p> <p>09:00 - 09:30 J. Van der Gucht</p> <p>09:30 - 10:00 C. Creton</p> <p>10:00 - 10:30 T. Divoux</p> <p>10:30 - 11:00 Coffee break</p> <p>11:00 - 11:30 M. Caggioni</p> <p>11:30 - 11:50 T. Gibaud</p> <p>11:50 - 12:10 M. Habibi</p> <p>12:10 - 12:30 Discussion (chair J. Vermant & V. Trappe)</p> <p>12:30 - 14:00 Lunch</p> <p>Session 6 Structuring and flow-induced anisotropies</p> <p>14:00 - 14:30 J. Vermant</p> <p>14:30 - 15:00 J. Swan</p> <p>15:00 - 15:30 C. Osuji</p> <p>15:30 - 16:00 Coffee break</p> <p>16:00 - 16:30 G. Luengo</p> <p>16:30 - 16:50 M. Geri</p> <p>16:50 - 17:20 Discussion (chair E. Del Gado & B. Ruta)</p> <p>17:20 - 17:30 Concluding remarks (all organizers)</p>