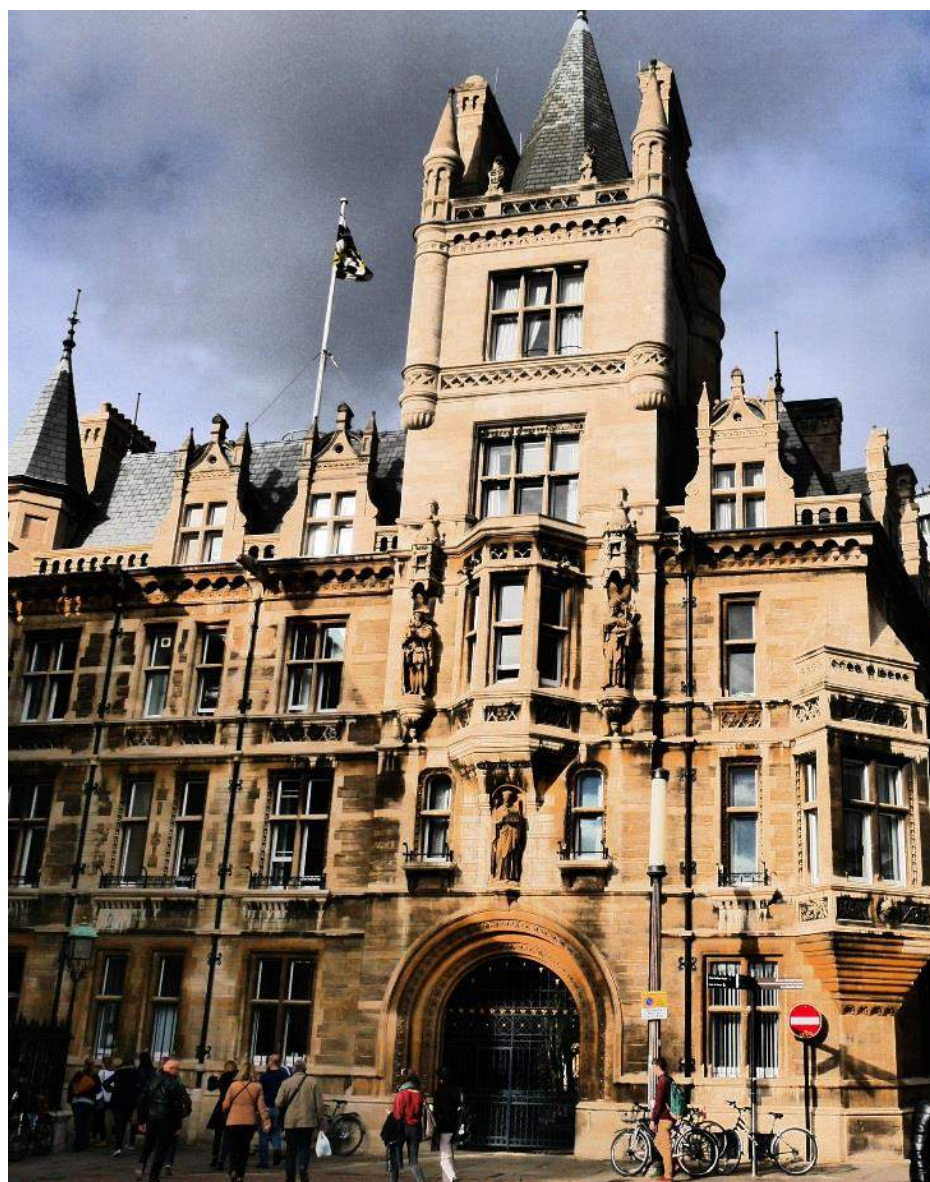# ARRESTED GELS

DYNAMICS, STRUCTURE & APPLICATIONS

CAMBRIDGE: 23 TO 25 MARCH 2015

CONFERENCE BOOK

RSC/SCI Colloids Group

The Organising Committee of Arrested Gels is indebted to the generous support of our sponsors and exhibitors

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Welcome to Arrested Gels 2015

Dear Participant,

It is with great pleasure that we welcome you to our Arrested Gels conference. Gels are fascinating systems whether you study them for research or design complex formulations, and the intention of this conference is to bring these two sides together with the aspiration that new ideas, new solutions to existing problems, new inspirations and new challenges with new questions to answer will emerge.

On the macroscopic scale the properties of gels can be measured without excessive difficulty yet these properties are governed by the microscopic and mesoscopic scale microstructure and dynamics which are less well understood and more complex to study. Understanding these will allow more advanced 'gel' formulations to be designed not from an empirical approach but rather from a more scientific understanding of how the various elements fit together and importantly how to engineer the desired microstructure and bulk properties. To achieve this requires a diverse collection of theorists, physicists, chemists, engineers, experimentalists, formulation scientists and industrialists from many parts of the world and we encourage you to take this opportunity to use the rich diversity here to learn and explore new ideas.

Cambridge has a special 'atmosphere' for creativity and intellectual exchange and for this reason we have chosen to hold the meeting here. Please take this opportunity provided to you to explore and adsorb some of this rich history and atmosphere.

We are greatly indebted to the generosity of our sponsors and exhibitors, who through their support have notably made this meeting more accessible to all participants and especially students.

We wish you a most stimulating, fascinating and inspiring conference.

Malcolm Faers, Paul Bartlett, Paddy Royall & Alex Routh.

The RSC/SCI Joint Colloids Group

In 1958 Sir Eric Rideal, a Past President of the SCI, founded the Colloid and Surface Chemistry Group to support the growing importance of colloids and surface chemistry in industry. Subsequently, in 1971 Ron Ottewill, Geoff Parfitt and Dennis Haydon with the support of Sir Eric created the Colloid and Interface Science Group within the Faraday Society, one of the RSC forerunner societies. This was in response to the increasing number of colloid centres being formed in academic institutions.

Since 2002 the two groups have worked jointly forming the "Joint Colloids Group" in order to provide a coherent focus for the UK colloid and interface science community, both in academia and industry. The Colloids Group organises various scientific events ranging from one day meetings to its multiday international meeting, UK Colloids 2014. The group also manages three awards, the McBain Medal, the Thomas Graham Lecture and the Rideal Lecture for early, mid and later career contributions to colloid and interface science.

For further details including our other events please see our website:
www.colloidsgroup.org.uk.

RSC/SCI Colloids Group

Invited Speakers

Dr Ludovic Berthier | CNRS & Université Montpellier 2

Ludovic Berthier received his Ph. D. in theoretical physics in 2001 at the Ecole Normale Supérieure in Lyon, France. He was a Marie Curie Postdoctoral Fellow at the Department of Theoretical Physics at Oxford University until 2003. In 2004 he was appointed as a CNRS researcher at the Laboratoire Charles Coulomb at University of Montpellier, France. In 2007, he was a visiting scientist at the James Franck Institute of the University of Chicago, US. He works on the statistical mechanics of disordered materials, non-equilibrium systems, and soft matter.

Prof Daniel Bonn | University of Amsterdam

Daniel Bonn is director of the Institute of Physics of the University of Amsterdam, where over 200 researchers work. He is also group leader of the 'Soft Matter' Group, which totals about 30 people, including 4 permanent scientific staff. He is currently supervisor of 15 doctoral students and in his career accompanied to date 26 successful PhD students. Before coming to Amsterdam recently, he was a CNRS research director at the Laboratoire de Physique Statistique of the Ecole Normale Supérieure in Paris, where he led the 'complex fluids' group. He published more than 200 papers on wetting phenomena, complex fluids, hydrodynamics, mechanics and the statistical mechanics of glasses of which several in Nature, Science and Physical Review Letters (59x); he was invited more than 40 times as a speaker at international conferences In the past five years.

Prof Luca Cipelletti | CNRS & Université Montpellier 2

Luca Cipelletti received his PhD in Physics in 1997 from Universita' degli Studi di Milano, working with M. Giglio on small angle light scattering from colloidal systems. He spent the following 2.5 years as a postdoc with D. Weitz at University of Pennsylvania and Harvard University. Since 2000, he is a faculty member of University of Montpellier, where he was promoted full professor in 2003. He was awarded membership of the Institut Universitaire de France in 2004. In 2008, he spent a sabbatical as a visiting scientist at the Center for Soft Matter Research (NY University) with D. Pine. He is an experimentalist developing original light scattering methods to investigate the dynamics of glassy and jammed soft matter.

Dr William Frith | Unilever

Dr William Frith is a physical scientist specialising in foods and personal care product technology. He's been working in industrial R&D since 1986, after completing his PhD Dr Frith joined ICI in Runcorn, UK and spent seven years there. In 1993 he joined Unilever R&D at Colworth, and has been there ever since.

People call him a Rheologist, but he sees himself as more of a general physical scientist, and has experience across a broad range of topics including

- Reactivity in powder mixtures.
- Pigment structure and scattering in coatings.
- Computer simulation of particle packing.
- Optical tweezers for micro-rheology applications.
- Rheology of suspensions, emulsions, polymer solutions and gels.
- Formation and properties of sheared gels.
- Formation, stability and rheology of particle stabilised emulsions.
- Self-assembly and gel formation of functionalised peptides and amino acids.

Prof Peter Schurtenberger | Lund University

Peter Schurtenberger is currently a Professor in Physical Chemistry at the Division of Physical Chemistry at Lund University. His research interests focus on soft matter physics, nanotechnology, biophysics, materials sciences, on the characterization of soft matter with light, X-ray and neutron scattering, and on the development of new instruments for this task.

Schurtenberger received his PhD from the Swiss Federal Institute of Technology (ETH) in Zurich. He then worked as a postdoc and research fellow at Lund University, Sweden, MIT and Harvard University Medical School. From 1987 – 1999 he was a senior researcher at the Department of Materials of ETHZ. In 1999 he was appointed as the chair in experimental soft matter physics at the University of Fribourg. In 2006 he founded the Fribourg Center for Nanomaterials. In 2008 he became the first director of the newly founded Adolphe Merkle Institute for Pure and Applied Nanoscience, and received a chair in Experimental Physics and Nanoscience. He moved to Lund University at the end of 2010.

He received among other honors and awards the Latsis Prize of the ETHZ in 1993, the Rhodia Prize of the European Colloid and Interface Society in 2007, and an ERC Advanced Grant in 2013. He has been elected as a member of the Royal Swedish Academy of Sciences in 2014, and is a Fellow of the Royal Society of Chemistry. He is co-founder and board member of the start-up company LS Instruments. He has published 234 scientific articles and book chapters, and has an h-index of 50.

Prof Hajime Tanaka | University of Tokyo

Hajime Tanaka obtained his bachelor's, Masters', and Ph. D. degrees from the Department of Applied Physics, the University of Tokyo, Japan, (1977, 1979, and 1982). He is currently Professor at the Department of Fundamental Engineering, the Institute of Industrial Science, the University of Tokyo. After getting his Ph.D, he became Assistant Professor at the Department of Applied Physics, the University of Tokyo, and moved to the current institution in 1989. He was also appointed as Adjunct Professor, Tohoku University WPI, Advanced Institute for Materials Research (WPI-AIMR) from 2012. He was a visiting scientist at AT&T Bell Laboratories 1987, and at Cavendish Laboratory, the University of Cambridge and Ecole Normale Superior at Paris in 1997. He has worked on a wide range of problems related to soft matter physics and liquid matter physics both experimentally and theoretically. He has been intrigued by the general behavior of a system having spatio-temporally hierarchical structures and the commonality between soft matter and liquid matter in that respect. More specifically, he has been interested in pattern formation and nonlinear rheology of soft matter, physics of water, liquid-liquid transition, glass transition, and crystallization. He has published some 250 papers in refereed Journals.

Awards for research have included the Award of the Society of Polymer Science, Japan (1997), Humboldt Research Award (Alexander von Humboldt Foundation, Germany) (2006), and The Liquid Crystal Society, Top Paper Award (2010). He became a Fellow of Institute of Physics in 2007. He has served on the editorial boards of several scientific journals including Journal of Physics: Condensed Matter, Molecular Physics, and Soft Matter.

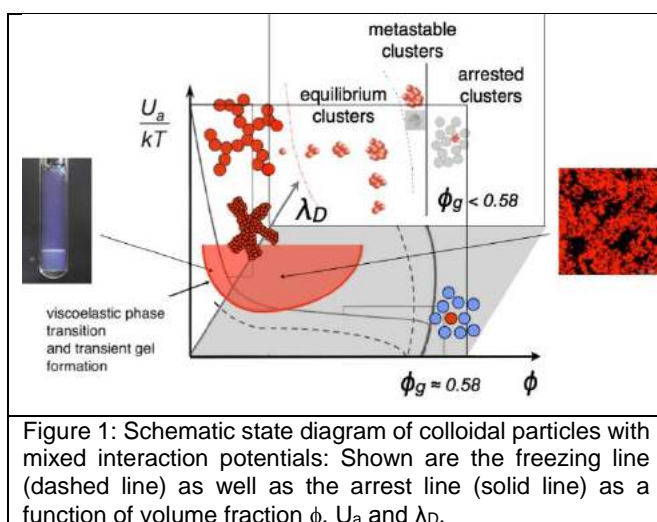# Abstracts for Oral Presentations

Colloidal gels with tailored properties – from transient networks to arrested spinodal decomposition structures

Peter Schurtenberger

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Fluid-solid transitions such as dynamical arrest, jamming or gelation frequently encountered in colloidal suspensions have been at the center of experimental and theoretical activities during the last few years. Numerous studies have demonstrated the presence of solid-like structures such as particle gels or colloidal glasses under conditions where either repulsive or attractive interactions dominate. Particularly interesting are also systems with mixed potentials, i.e. with a combination of a short-range attraction and a long-range soft repulsion.

Our current understanding of the phenomenon of dynamical arrest in systems with mixed potentials as a function of the strength of the attractive part and of the range of the soft repulsive part of the interparticle interaction potential is schematically summarized in Figure 1. Three cases are particularly highlighted: (1) attractive particles with a short range attraction of strength U_a, where a metastable liquid-liquid phase separation occurs in addition to the commonly found liquid, crystalline and glassy or gel states; (2) purely repulsive systems with a hard sphere repulsion and a screened Coulomb repulsion with screening length λ_D; and (3) particles with mixed potentials where the range of the soft repulsion is significantly larger than the attraction, and where one also finds an equilibrium cluster phase and a cluster glass.

Figure 1: Schematic state diagram of colloidal particles with mixed interaction potentials: Shown are the freezing line (dashed line) as well as the arrest line (solid line) as a function of volume fraction ϕ, U_a and λ_D.

We will discuss how we can tailor the effective interparticle potential in order to create colloidal gels with vastly differing structural and mechanical properties. Systems chosen will be colloidal particles with a tuneable interaction potential such as thermoresponsive microgels or proteins. We will also focus on mixed systems, where the attraction is due to the presence of a non-adsorbing polymer that induces a depletion interaction. Finally, we will also present hard or soft sphere colloids with added block copolymers, where the polymer can be used to create different types of arrested systems ranging from binary glasses to temporary networks, and thus allows us to fabricate gels with dramatically different mechanical properties.

A considerable emphasis will also be given to the suite of techniques that allows us to investigate the structural and dynamic properties of colloidal fluids and gels in a non-invasive and time resolved manner. We will show how to use a combination of real and reciprocal space techniques such as confocal laser scanning microscopy, dynamic and static light scattering, and small-angle neutron and x-ray scattering as well as micro- and macrorheological measurements. As colloidal gels are often highly turbid, I will in particular present light scattering techniques that are either capable to suppress multiple scattering such as 3D cross correlation dynamic light scattering, or use it such as diffusing wave spectroscopy.

Structural signatures of percolation and arrested phase separation in colloidal gels
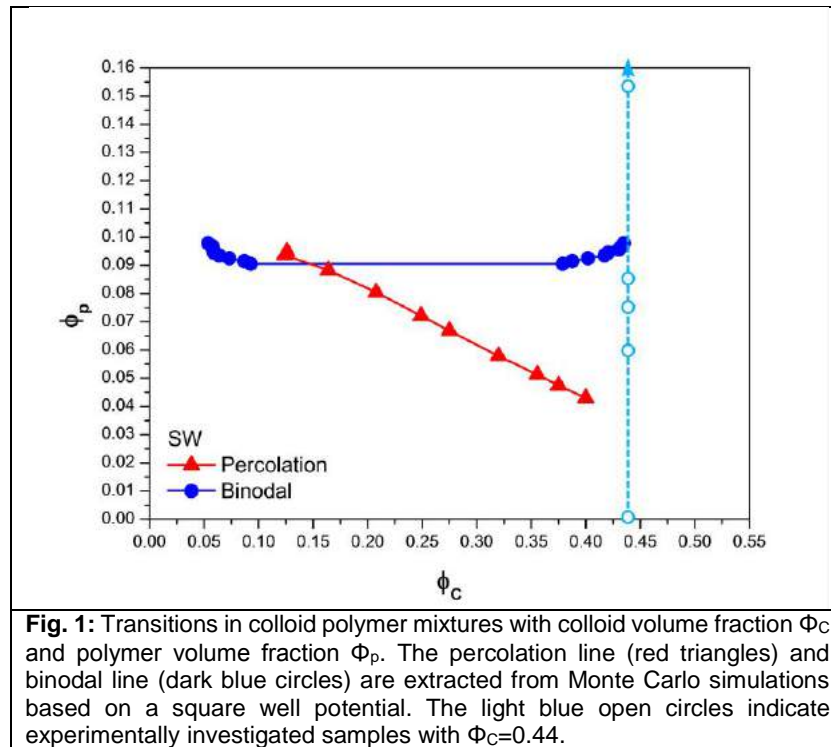
R. F. Capellmann [a], N. E. Valadez Pérez [b], M. Kohl [a], M. Schmiedeberg [a], S. U. Egelhaaf [a], M. Laurati [a] and R. Castañeda-Priego [b]

[a] *Heinrich Heine University, Düsseldorf, Germany*
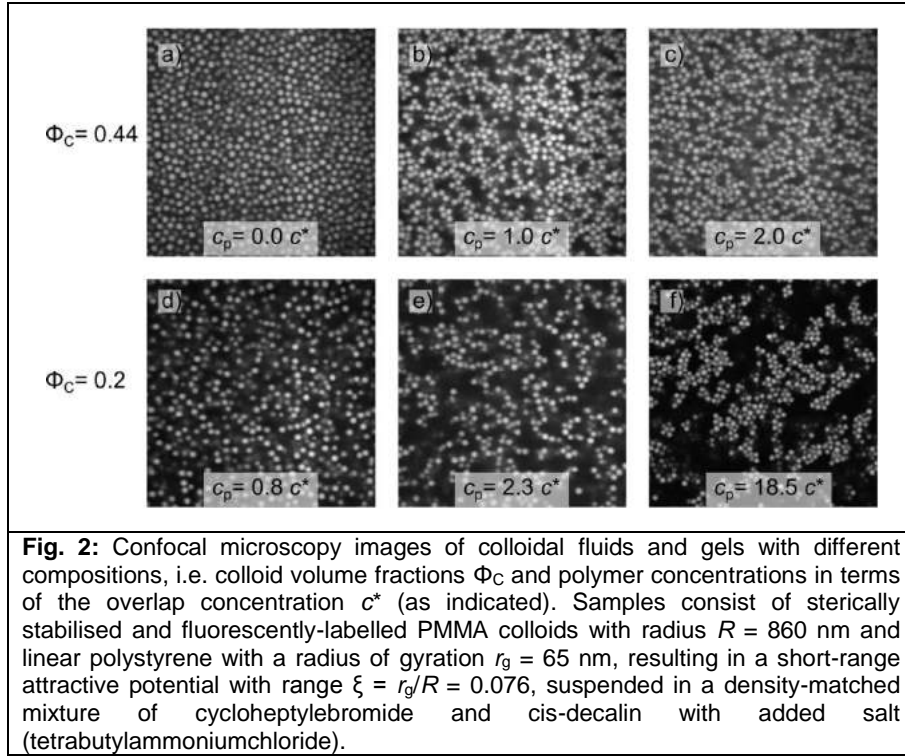[b] *University of Guanajuato, Leon, Mexico*

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Gels form in mixtures of hard-sphere colloids and linear polymer chains, in which the polymers induce a short-range depletion attraction between the colloids. Depending on the colloid volume fraction Φ_C and the polymer concentration and size, which control the depth and range of the attractive interaction potential, gel formation is induced by different mechanisms [1, 2]. We investigate gels using confocal microscopy and simulations, and characterize the gel structure by the radial, $g(r)$, and angular, $g(\theta)$, distribution functions, and the bond distribution $P(n_b)$. Two series with $\Phi_C = 0.2$ and 0.44, respectively, and increasing polymer concentration are investigated.

Fig. 1: Transitions in colloid polymer mixtures with colloid volume fraction Φ_C and polymer volume fraction Φ_p. The percolation line (red triangles) and binodal line (dark blue circles) are extracted from Monte Carlo simulations based on a square well potential. The light blue open circles indicate experimentally investigated samples with $\Phi_C=0.44$.

In the Monte Carlo simulations a square-well potential, the Asakura-Oosawa potential and a potential obtained from the inversion of the experimentally measured radial distribution functions, respectively, are used to describe the effective interactions between the colloids in order to estimate the transition lines in the suspension. Depending on the sample composition, i.e. the colloid volume fraction Φ_C and the volume fraction of the polymers Φ_p, the simulations predict different transitions (Fig. 1). For low Φ_C and Φ_p, a fluid or a cluster fluid exists, while the clusters percolate to form a space spanning network, i.e. a gel, if the sample is located above the percolation line (red triangles). Further increasing the polymer concentration, a binodal line is encountered (dark blue circles), above which the sample undergoes spinodal decomposition into a gas and a liquid. If the liquid crosses the percolation line during this process, the phase separation is arrested and a gel forms. [1, 2]

Fig. 2: Confocal microscopy images of colloidal fluids and gels with different compositions, i.e. colloid volume fractions Φ_C and polymer concentrations in terms of the overlap concentration c^* (as indicated). Samples consist of sterically stabilised and fluorescently-labelled PMMA colloids with radius R = 860 nm and linear polystyrene with a radius of gyration r_g = 65 nm, resulting in a short-range attractive potential with range $\xi = r_g/R$ = 0.076, suspended in a density-matched mixture of cycloheptylebromide and cis-decalin with added salt (tetrabutylammoniumchloride).

These predictions are compared to experimental results obtained by confocal microscopy (Fig. 2). At Φ_C = 0.44 and without any polymers, i.e. a polymer concentration in units of the overlap concentration c^* of c_p = 0.0 c^*, the experimental sample exhibits a fluid state (Fig. 2) which is also reflected in the radial, angular and bond distributions (Fig. 3, 4). For larger c_p, inside the percolation region according to simulations, changes in the radial, $g(r)$, and angular, $g(\theta)$, distribution functions, as well as the bond distribution $P(n_b)$, are observed; the first peak and the following minimum in $g(r)$ are sharper and followed by a broad double peak, typical for trimer structures. Also in the angular distribution, the first peak at 60° is narrower, followed by an increased probability between 80° and 120°. The bond distribution shows a lower probability for larger bond numbers. These all consistently indicate gelation.
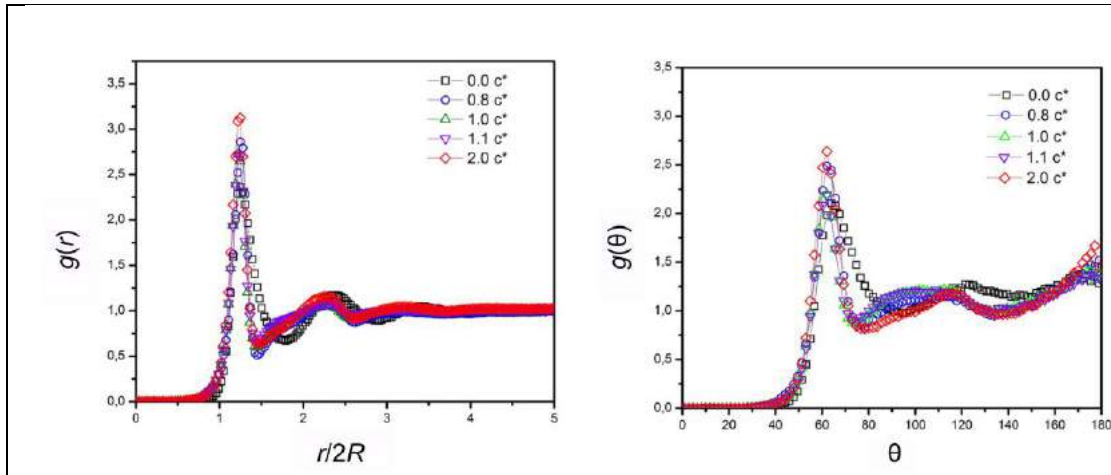

Fig. 3: Radial distribution function $g(r)$ (left) and angular distribution function $g(\theta)$ (right) for a colloid volume fraction Φ_C = 0.44 and different polymer concentrations (as indicated).

Further increasing the attraction, according to the simulations to the region between the percolation and the binodal line, no significant changes in the radial and angular distribution functions are observed. Instead, the maximum of the bond distribution moves to 3 bonds per particle.

10

For even larger polymer concentrations, corresponding to the region beyond the binodal line, the split second peak in the $g(r)$ function disappears. Furthermore, in the angular distribution the broad distribution changes to an increased probability at 120° and 180°. There is hence a structural change between the gels formed through arrested spinodal decomposition and percolation, respectively. Interestingly, this difference is not captured by the bond distribution, which shows only minor changes.

In summary, with increasing attraction the radial, angular and

Fig. 4: Distribution of the number of bonds $P(n_b)$ for a colloid volume fraction Φ_C = 0.44 and different polymer concentrations (as indicated).

bond distributions change when crossing the percolation line, that is upon gelation, and again the radial and angular, but not the bond distribution at the binodal line. Thus the distribution functions represent a structural signature that distinguishes the gels formed through percolation and arrested spinodal decomposition, respectively.
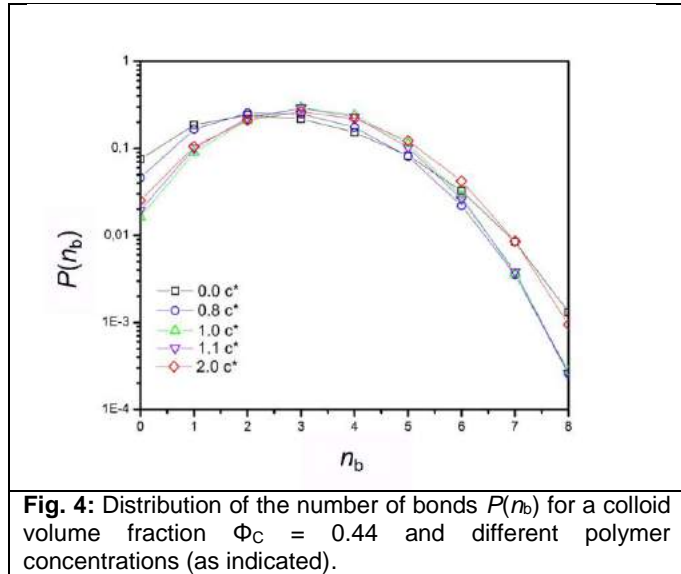
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Tuning colloidal interactions by controlling the solvent properties: beyond critical Casimir forces

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It is known that effective forces can deeply modify the phase diagram of colloidal particles. This happens, for instance, in the presence of depletion forces, i.e. effective forces that originate from the presence of a co-solute (polymers, surfactants) in the suspension. Beside short-range depletion, also long-range effective interactions can be exploited for controlling the behaviour of a colloidal solution. The most famous example is that of the critical Casimir force[1], which arises when two colloids are immersed in a solvent close to its critical point. In such a case, the confinement of the density critical fluctuations between the colloids surfaces give rise to a long-range force[2-5], that can be controlled through a tiny variation of the temperature close to the critical point.

In analogy with critical phenomena, Clusters close to the gelation play the same role as thermal critical fluctuations, both being described by scale-free distributions, whose first moment shows a power-law behavior at the transition point~[6].

Putting forward such analogy it is possible to demonstrate that long-range forces between two colloids can occur also close to gelation [7].
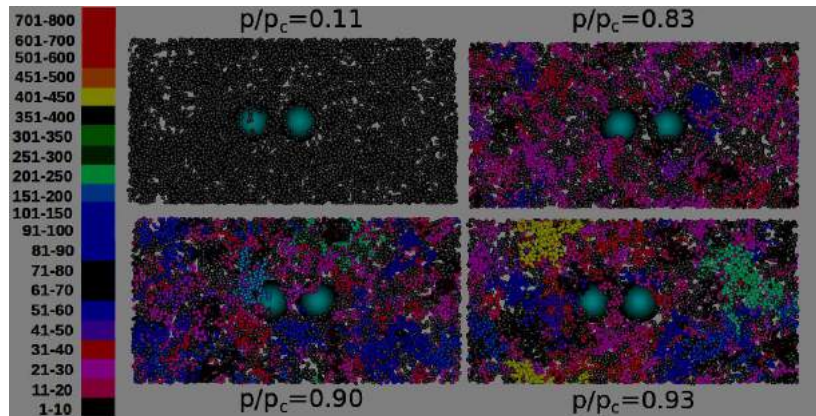
Clustering of the sol close to percolation: Snapshots of the system for different distances from the gelation point (p is the bonding probability and p_c is its critical value at the percolation transition), Each snapshot shows the two colloids immersed in the sol of clusters on approaching the percolation treshold. Clusters of different sizes are represented in a different color (see legend).

We demonstrate this by showing results from Monte Carlo simulations of two colloidal particles immersed in a sol clustering irreversibly to form a chemical gel (See Figure). For each cluster distribution we numerically evaluate the effective potential between the colloidal particles and we show that it becomes attractive and long-ranged on approaching the sol percolation transition. Our results provide the geometric analogue of the critical Casimir force, since the measured long-range effective potential results from the confinement of the cluster-size fluctuations between the surface of the two colloids. Since we use irreversible clusters to generate such effective interaction, we discuss the effect of the cluster lifetime on the effective potential. Indeed we show that in the case of irreversible clusters (i.e. clusters with infinite lifetime) the range of the potential is controlled by the connectivity length of the system, while for clusters with variable, but finite, lifetime the resulting effective potential has a much shorter range which is controlled by the range of the radial distribution function, which offers a measure of the effective size (dressed by thermal correlations) of the monomer. We also discuss a theoretical description based on a polydisperse Asakura-Oosawa model which captures the divergence of the interaction range. The good agreement between theory and numerical simulations shows that the mechanism controlling the long-range effective interaction close to percolation can be assimilated to a depletion effect.

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Colloidal gels, glasses and attractive glasses

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Suspensions of various colloids can be strongly visco-elastic, even at very low particle concentrations. The formation of a gels (evidenced by the existence of a fractal network), and glass formation has been invoked in explaining the visco-elasticity. We study the structure, dynamics and rheology of these systems using confocal microscopy and light scattering.

For Laponite suspension, the formation of a gel, evidenced by the existence of a fractal network, has been invoked in explaining the visco-elasticity. We study the structure and viscosity of Laponite using static light scattering. Contrary to previous observations, we find no evidence of a fractal-like organization of the colloidal particles. The interpretation of our results is that Laponite solutions form colloidal glasses, rather than gels. The phase diagram shows even a third, distinct phase that we call attractive glass. We then study the aging dynamics of this colloidal glass. By shear-melting the glass, we can perform a quench into the liquid (sol) phase and follow the dynamics of glass formation in time, using dynamic light scattering to measure the diffusion of the colloidal particles. The results can be described in terms of a cage-diffusion process. For short aging times, the dominant dynamical process is the escape of the particles from dynamic 'cages' formed by neighboring particles. However, at long times the cages stiffen; the particles cannot escape anymore, and the system becomes strongly non-ergodic. The shear melting is shown to reverse this process, and consequently allows to 'rejuvenate' the glass.

We also study the aging dynamics of colloidal glasses and gels. For hard-sphere colloids but also in general, the nature of the glass transition is one of the most important unsolved problems. The difference between glasses and liquids is believed to be caused by very large free energy barriers for particle rearrangements; however, so far it has not been possible to confirm this experimentally. We provide the first quantitative determination of the free energy for an aging hard sphere colloidal glass. The determination of the free energy allows for a number of new insights in the glass transition, notably the quantification of the strong spatial and temporal heterogeneity in the free energy. A study of the local minima of the free energy reveals that the observed variations are directly related to the rearrangements of the particles. Our main finding is that the probability of particle rearrangements shows a power law dependence on the free energy changes associated with the rearrangements similar to the Gutenberg-Richter law in seismology.

References:

Direct Measurement of the Free Energy of Aging Hard Sphere Colloidal Glasses

Phys. Rev. Lett. **110**, 258301 (2013)

Rojman Zargar, Bernard Nienhuis, Peter Schall, and Daniel Bonn

Dynamical heterogeneity in aging colloidal glasses of Laponite

S Jabbari-Farouji, R Zargar, GH Wegdam, D Bonn

Soft Matter 8 (20), 5507-5512 (2012)

Arrested States in a Colloidal Clay: Dynamics and Structure

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Recent advances in the study of soft materials have led in the last decades to a deeper knowledge of equilibrium and non equilibrium states and to the discovery of new phases besides the ones commonly experienced in atomic or molecular systems. The tunability of colloidal effective interactions offers the possibility to observe unusual phase diagrams including reentrant or empty liquid regimes, and multiple arrested states, such as gels and glassy states. To investigate the formation of these states, colloidal clays have emerged as suitable candidates, among them aqueous Laponite suspensions are prototype systems that exhibit a rich phase diagram. When dispersed in water Laponite ages, passing with waiting time t_w from a liquid towards different arrested states which depend on Laponite weight concentration, C_w as shown in Fig.1

[1]. The combination of several techniques as Dynamic Light Scattering (DLS), dilution experiments, X-Ray Photon Correlation Spectroscopy (XPCS), Small Angle X-ray Scattering (SAXS), rheometry and Monte Carlo (MC) simulations has allowed us to probe in detail the structure and dynamics of this system. At very low concentration ($C_w < 1.0\%$) a gel state is obtained after a few months from preparation: this lasts a few years and eventually separates into clay rich and clay poor phases (Fig.1 a, d). An equilibrium gel is instead obtained at $1.0\% \leq C_w < 2.0\%$ (Fig.1 b,e). The macroscopic behaviours in these two regions are shown in Fig.2 where a photograph of different concentration samples about three years after their preparation is reported. The height of the colloid rich part (indicated by the dashed lines) increases progressively with C_w, filling up the whole sample when $C_w \sim 1.0\%$. This value thus marks the threshold of the phase-separation region. In contrast, higher-
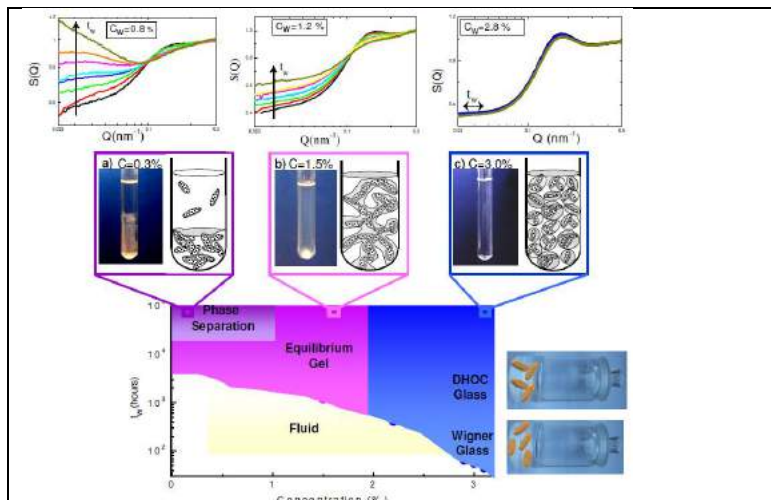

Fig.1: Phase diagram of diluted Laponite suspensions, in the waiting-time versus-concentration plane. Lower panel, Symbols correspond to experimental *t*w values required to observe non-ergodic behaviour by DLS. For long g times, three ent regions are i d, whose represe macroscopic our, a pictorial mi pic view and static structure factors are reported in a–c and d-f respectively. a, Phase-separated sample with colloid-poor (upper part) and colloid-rich (lower part) regions for $C_w<1.0\%$. b, Equilibrium gel for $1.0<C_w <2.0\%$, characterized by a spanning network of T-bonded discs. c,Wigner glass, expected for $2.0\leq C_w\leq3.0\%$ where disconnected platelets are stabilized in a glass structure by the electrostatic repulsion, progressively hampering the formation of T bonds. d-e, Static structure factor in the phase separation region (d) in the equilibrium gel (e) and in the Wigner glass (f). g, Pictorial microscopic view of the Wigner and DHOC glasses.

concentration samples (C_w >1.0%) do not show any phase separation and maintain their arrested and transparent character at all times (see the C_w =1.2% sample in Fig. 2). At higher concentrations in the range 2.0% ≤ C_w ≤ 3.0% (Fig.1 c, f) the sample arrests in a few hours as a Wigner glass dominated by long-range screened Coulombic repulsion as found through dilution experiments which allowed us to distinguish this disconnected glassy state, which melts upon addition of water, from the low concentration gel state, which does not melt. [2]. Furthermore at C_w = 3.0% two different glassy states are distinguished with evolving waiting time. At first the system arrests, after a waiting time of t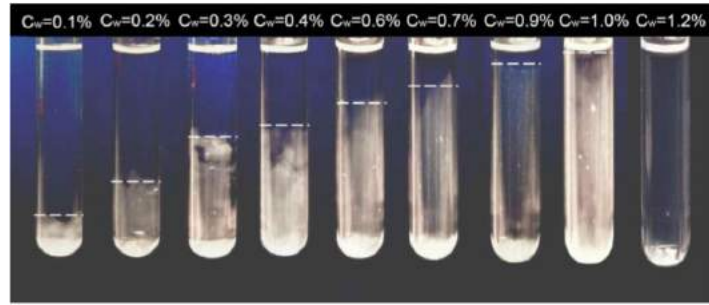he order of hours, into a Wigner glass however, at much longer waiting time, of the order of days, a second glass, is found. This is stabilized by orientational attractions between clay platelets and is referred as Disconnected House of Cards (DHOC) glass [3]. Such complex behaviours are ascribed to the anisotropy both in shape and in charge distribution of Laponite particles and to the competition

Fig.2: Photographs of samples in the concentration range 0.1 < C_w < 1.2% at very long waiting times (about 30.000 h). All samples with C_w < 1.0% show clear evidence of two coexisting phases.

between attractive and repulsive interactions. These findings shows that a careful choice of the density may provide materials that are extremely stable in the long term, because they are formed continuously from the liquid state, but finally reaching-through a very slow dynamics-their equilibrium configuration and may have implications for applications where a fine control of the local order and/or long term stability of amorphous materials are required.

Edge and Face Surface Modifications and their Effects on the Structural and Viscoelastic Behaviour of Aqueous Montmorillonite Platelet Suspensions

William J. Ganley,[a] Jeroen S. van Duijneveldt [a]

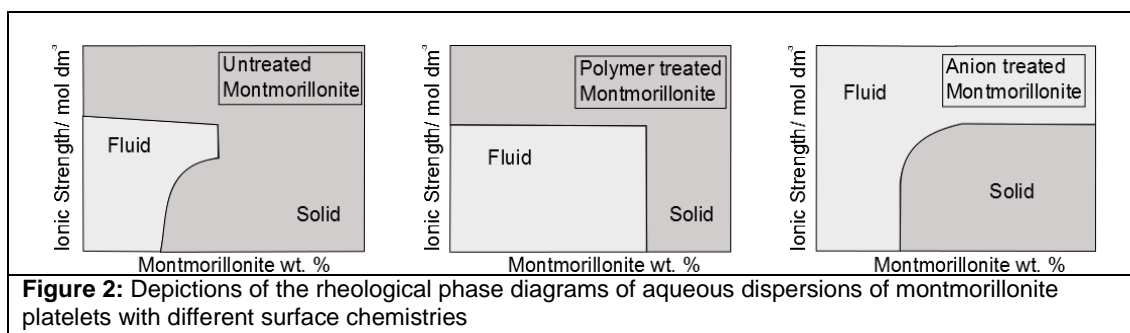[a] School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

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Clay minerals can be dispersed into liquids to form suspensions of high aspect ratio, nanometric colloidal particles which present a wealth of phase behaviour ranging from fluids to delicate liquid crystalline phases and low volume fraction glassy or gelled states. The typical dimensions of a montmorillonite platelet is shown in figure 1.

Figure 1: The scale of a single montmorillonite platelet detailing the edge and face surfaces
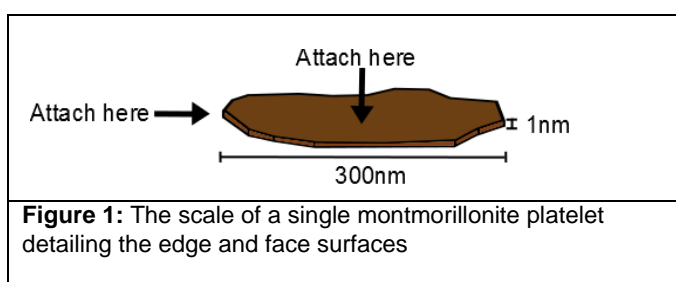
Such systems are ubiquitous in industrial formulation science as a means of controlling the flow properties of liquids and soft solids, stabilising emulsions and providing additional microstructure to composite materials and have potential uses as model systems for the study of flow in non-spherical particle suspensions. To date the phase behaviour of these systems has been characterised in depth as a function of weight fraction and ionic strength[1], however industrial systems are rarely so straightforward.

Here we present an extension to current work on these highly anisotropic systems by taking two molecules that adsorb to different faces of the platelet surface and characterising their effects on rheology and structure at a range of length scales. We find that these molecules alter behaviour in different regions of the rheological phase diagrams illustrated in figure 2. The weight fraction required for a solid-fluid transition in the glassy regime is increased by the adsorption of an amine terminated amphiphilic polymer to the particle face and in the gelled regime it is increased by adsorption of multivalent pyrophosphate anions to the particle edges.

Figure 2: Depictions of the rheological phase diagrams of aqueous dispersions of montmorillonite platelets with different surface chemistries

Structural signatures in the fluid phase accompanying these differences are only found at

length scales above a micron where colloidal clusters and elongated assemblies are observed in small angle light scattering. Such clusters are common in systems with competing attractive and repulsive interactions such as synthetic polymer-colloid mixtures[2] and natural protein[3] and clay suspensions[4].

The balance the competing interactions is tipped by adsorbing molecules which change or introduce different particle interactions. This alters the morphology of the resultant cluster structures which in turn has drastic effects on the rheology of the suspensions as the dynamics of the whole system is dependent on the mobility of these largest units.

The two adsorbing molecules studied here do not interact with each other and act in different regions of the phase diagram hence have the potential to control rheology across a large range of ionic strengths. This type of dual functionalisation can therefore be used to build systems with both specific functions and wide ranging stability windows. Examples could include drilling fluids composed of shale inhibiting polymers and platelets that do not flocculate at high ionic strength or Pickering emulsions with high particle loading at the interface and additional sites to perform further chemistry.

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Microscopic dynamics of colloidal gels: from spontaneous anomalous relaxations to stress-induced creep and failure.

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In this talk, I'll discuss various kinds of dynamics observed in colloidal gels. I'll first review earlier work on the spontaneous dynamics of strongly aggregated gels. These gels exhibit ultraslow relaxations associated with an unexpected ballistic displacement of the particles. A similar behaviour has been observed in many out-of-equilibrium soft materials (concentrated emulsions, surfactant phases, colloidal polycrystals...) and even in metallic glasses. It has been attributed to the relaxation of internal stress [1] built-in at the fluid to solid transition: recent work on colloidal [2] and actin [3] gels where scattering methods are mixed with imaging techniques supports this view.
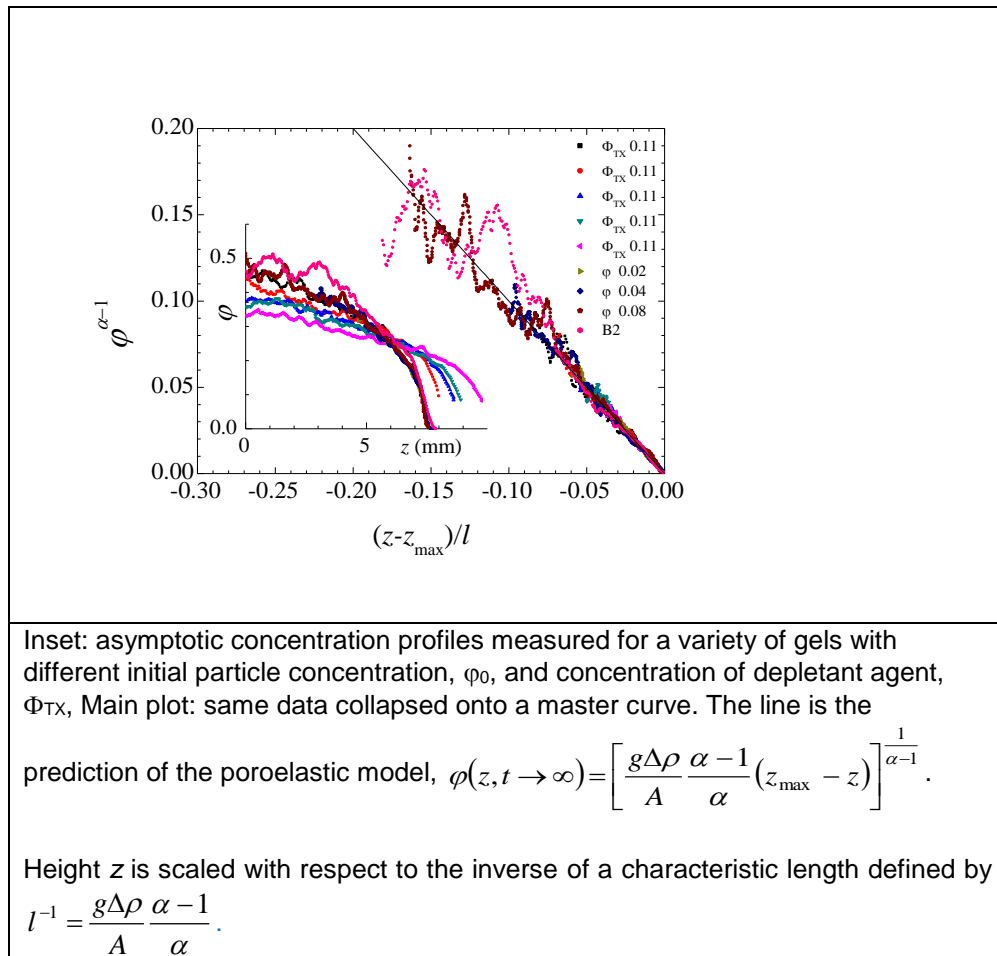
I'll then discuss the behaviour of colloidal gels under gravitational stress. We have studied both the macroscopic behaviour and the microscopic dynamics of a gel composed of particles interacting through the depletion force. We use Photon Correlation Imaging, a technique that combines imaging and scattering, in order to obtain the particle concentration, sedimentation velocity, and microscopic dynamics with both temporal and spatial (i.e. as a function of height, z, in the gel sample) resolution. We find that the temporal evolution of the total height of the gel, of the concentration profiles, $\varphi(z)$, and of the velocity profiles, $v(z)$, can be accounted for by a simple "poro-elasitic" model, combining viscous dissipation due to the flow of the solvent through the gel pores and the (non-linear) elastic response of the gel to gravitational stress.

Unlike in previous works where only the total height evolution was experimentally measurable, our detailed measurements of $\varphi(z)$ and $v(z)$ allow us to determine precisely the volume fraction dependence of the gel elasticity and porosity. Moreover, we find that the macroscopic deformation of the gel is directly related to its microscopic dynamics, since the relaxation time of the intermediate structure factor scales as the inverse macroscopic strain rate over more than 2 decades [4].

The findings of the gel studied in [4] are quite general. Indeed, in [5] we have studied the evolution of the concentration profile for gels prepared at various particle volume fractions and interaction strength. We find that for all these gels the poroelastic model accounts well for the temporal evolution of the concentration profile. Moreover, the asymptotic concentration profiles measured for $t \to \infty$, when mechanical equilibrium is reached, exhibit remarkable scaling properties, as shown in fig. 1. This scaling is due to the particularly simple volume fraction dependence of the compressive stress of then gels, which we find to scale as $\sigma(\varphi) = A\varphi^{\alpha}$, with α ~3.5-4.1 depending on the gel composition.

Finally, I'll touch upon ongoing experimental efforts aiming at understanding the microscopic rearrangements in a colloidal gel submitted to a shear stress. It has been shown [6] that for imposed stress close to but lower than the dynamical yield stress, the gels slowly creeps during an induction time that may last thousands of seconds, until it suddenly and catastrophically yields. This behaviour is strongly reminiscent of the delayed collapse often observed in gravitationally stressed gels. By performing simultaneous rheology and light scattering and microscopy experiments, we hope to reach a microscopic view of the rearrangements leading to such material failure.

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Inset: asymptotic concentration profiles measured for a variety of gels with different initial particle concentration, φ_0, and concentration of depletant agent, Φ_{TX}, Main plot: same data collapsed onto a master curve. The line is the

prediction of the poroelastic model, $\varphi(z, t \rightarrow \infty) = \left[\dfrac{g\Delta\rho}{A} \dfrac{\alpha - 1}{\alpha} (z_{max} - z) \right]^{\frac{1}{\alpha - 1}}$.

Height z is scaled with respect to the inverse of a characteristic length defined by

$l^{-1} = \dfrac{g\Delta\rho}{A} \dfrac{\alpha - 1}{\alpha}$.

A micro-mechanical study of coarsening and rheology of colloidal gels: cage building, cage hopping, and Smoluchowski's ratchet

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Overview: We present a study of the evolving structure, particle dynamics, and time-dependent rheology of a reversible colloidal gel as it evolves with age, via a combination of theoretical and simulation studies. In particular, we focus on the particle-scale dynamics that drive structural coarsening and age-related changes in linear response behavior. When colloids in suspension attract one another, the attractions can lead to phase separation into particle-rich and particle-poor regions separated by a single interface. However, this transition is sometimes interrupted. For certain particle concentrations and interparticle potentials, the same attractions that promote phase separation also inhibit it, dramatically slowing separation and 'freezing in' a non-equilibrium particle microstructure. The result is a network of bonded particles that forms a space-spanning gel. If attractions are on the order of a few kT, such arrested gelation can lead to non-fractal bi-continuous morphologies. In these so-called reversible gels, thermal kicks from the solvent are strong enough to dislodge particles from the network, but these quickly form new bonds, restructuring the gel over time. But, because particle diffusion is dramatically slowed by attractions, the march toward equilibrium is frustrated. While previous studies have examined evolution of length scales and dynamics such as decorrelation times or heterogeneity, important questions were left open, such as how the particle-rich regions are structured (liquid-like, glassy, crystalline), how restructuring takes place (via bulk diffusion, surface migration, coalescence of large structures), and the impact of the evolution on rheology. We have conducted dynamic simulation studies to elucidate the post-gelation evolution of a system of 750,000 Brownian spheres interacting via a hard-sphere repulsion and short- range attractions of order kT , as would be generated by a polymer depletant, for example. We find that the network strands comprise an immobile interior formed by an attractive glass, enclosed by a liquid-like surface along which the diffusive migration of particles drives coarsening. We show that coarsening is a three-step process of cage forming, cage hopping, and cage trapping, with particles migrating into ever-deeper energy wells in a mechanism analogous to Smoluchowski's ratchet. The linear-response rheology reveals elastic and viscous moduli that scale with the square-root of the frequency at high frequency, similar to the perfectly viscoelastic behavior of non-hydrodynamically interacting, purely repulsive dispersions. However, even with weak reversible bonds, gel response is elastic over all frequencies, with a quantitative offset between elastic and viscous moduli that owes its origin to the hindrance of diffusion by particle attractions. Propagation of this elasticity via the network gives rise to age-stiffening as the gel coarsens. Inspired by the tandem evolution of length scale and elasticity, we rescale the age-dependent moduli on network length scale at each age which, when carried out, collapses each modulus for all gel ages onto a single universal curve. We put forth a theoretical model inspired by the Rouse dynamics and, from it, obtain an analytical expression that captures the effects of (finite) structural aging on rheology: the moduli are linear in the network size, suggesting that linear mechanical response can be determined at any age by measurement of dominant network length scale—or vice versa.

Background: Colloidal suspensions span a rich range of states—from dispersed to condensed, mobile to arrested, with liquid-like to solid-like behavior. In a colloidal suspension where particles experience attractive forces, the particle attractions can lead to phase separation—analogous to the phase transition of steam to liquid water—into particle-
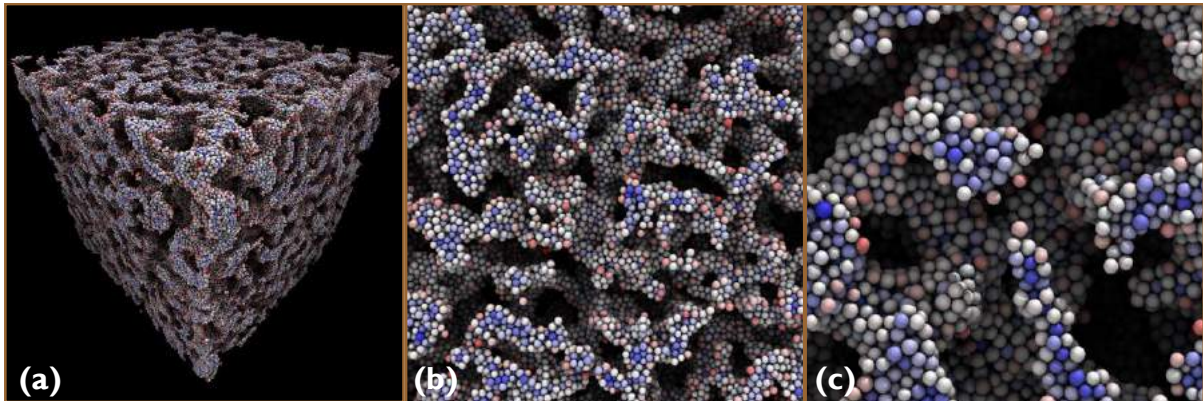
Figure 1 Snapshots of gel simulation. (a) One periodic cell. (b) 2x magnification. (c) 4x magnification. Number of contacts per particle indicated by color, ranging from red (few contacts) to blue (many contacts). Gel strands spanning the boundary of the periodic cell shown in section view, revealing high-contact number interior particles. From Zia et al.,[1] with permission from the Journal of Rheology.

rich and particle-poor regions separated by a single interface.[2-9] But this separation is sometimes interrupted before full separation occurs: at certain particle concentrations and interparticle potentials, the same attractions between particles that promote phase separation also inhibit it, leading to kinetic arrest of the phase separation and the subsequent formation of a space-spanning network—a gel.[9-12] In some cases the network morphology is fractal, while in others it is heterogeneous and bicontinuous. The formation of such gels is formally described by their position beneath a binodal (and perhaps a spinodal) in a phase diagram.[3,4] For the sake of brevity here we touch only briefly on this rich topic; a thorough review may be found in Zaccarelli.[9] Fractals gels form by diffusion-limited aggregation and are favored in dilute systems with particle attractions $U/kT \gg 1$, where U is the potential energy of attraction, k is Boltzmanns constant and T the absolute temperature.[10] The bonds in such strong gels are essentially permanent. However, when attractions between particles are on the order of just a few kT, e.g. as arises in the presence of a polymer depletant, the kinetic arrest of the phase separation can lead to a non-fractal bi-continuous morphology, a so-called reversible colloidal gel.[9,12] In such gels bonds continue to break and reform due to thermal fluctuations, allowing ongoing aging and restructuring of the gel. Because thermal particle motion is dramatically slowed by inter-particle attractions however, such gels may never reach equilibrium because the thermal rearrangements required to do so are weak and difficult. Macroscopically, reversible bonds lead to rich mechanical phenomenology: colloidal gels may yield and flow when forced, but with a higher viscosity than their dispersed-particle counterpart. When flow is stopped, the gel network reforms and elastic behavior returns, a highly desirable property for e.g. injectable delivery. While both (strong) fractal and (weak) colloidal gels are kinetically arrested, one key difference between the two is that the frequency of thermal rearrangements in fractal gels is vanishingly small—they do not evolve with time after gelation—whereas weak gels continue to experience particle rearrangements toward full phase separation. While the formation routes of gels is a rich space, we focus on post-gelation only behavior of reversible colloidal gels.

Experimental studies indicate that colloidal gels coarsen over time, where network strands grow thicker and the colloid-poor voids grow larger[13-15]. For example, fluorescent confocal microscopy experiments have revealed continuous evolution over all length scales.[15-17] Theoretical perspectives of aging inspired by Kramers escape-time theory[14,18,19] or transient network theory[11] are consistent with these observations. However, an alternative picture has emerged in the last decade: some experimental studies indicate that while coarsening occurs in gels with long-range attractions, aging is brief and finite in those with short-ranged attractions. It has been asserted that the latter arrest completely shortly after gelation[9,15,20]. We will show that short-ranged colloidal gels do indeed coarsen over long times after gelation, with pronounced effects on dynamics and rheology.

If gels do coarsen over time, the next question is "how do they evolve?" Proposed models, primarily inspired by molecular coarsening theories, include bulk diffusion, migration along the surface of the network, and advective flow of the condensed phase [see e.g.[13,15,17]]. Others model coarsening as a systematic disconnection and/or coalescence of strands[16,21–23]. For example, D'Arjuzon and co-workers[21] conducted dynamic simulation of 1, 000 hard spheres interacting via short-range attractions over 5,000 diffusive times, a2/D (where a is the particle size, D = kT/6πηa is the bare diffusion coefficient and η is the solvent viscosity), from which they conclude that individual particle migration plays a negligible role in structural rearrangement, justified by visual inspection of simulation video renderings. The authors instead assert that restructuring occurs via large-scale rearrangements where entire strands break, diffuse, and coalesce. Previous experimental studies that support this view can also be found [see, e.g. Verhaegh et al.[16]]. However, it is contradicted by simulations conducted by[24] on a gel of 1, 000 hard spheres with short-range attractions. Their study revealed two dynamical populations of particles—fast and slow—suggesting that individual particle motion may be important. Experimental studies confirm this finding; for example, Solomon and co-workers conducted detailed microscopy studies and identified fast and slow particle dynamics which were independent of structural heterogeneity in the gel[25,26]. While formative in the study of particle motion in gels, however, neither of these two investigations studied aging.

One macroscopic signature of reversible colloidal gels is mechanical properties that seem to evolve with age. Several studies have suggested that gels should stiffen with age in tandem with structural coarsening[23,27,28]. Guo et al.[29] conducted X-ray scattering and rheological studies of thermoreversible gels with short-ranged attractions that evolve rheologically over time and connected rheology to particle dynamics. Citing mode coupling theory developed by Schweizer and Yatsenko[30], they identified a so-called "localization length" to define particle caging that increasingly restricted particle mobility over time. This suggests that changes in particle mobility with gel aging may correlate with an evolving elastic modulus.

The goal of this study is to elucidate the micro-scale dynamics of coarsening and its effects on gel rheology. To do so, we studied via large-scale dynamic simulation and theoretical analysis the structural and rheological evolution of a reversible colloidal gel with hard-sphere repulsion and short-range attractions, with a detailed accounting of particle configurations, particle dynamics and linear-response rheology. Two attraction strengths are studied. We find that the network comprises interconnected strands with glassy interiors of approximate volume fraction $0.62 \leq \varphi \leq 0.64$, where the surface of the strands are liquid-like and mobile. We show that colloidal gels with attractions of order kT do indeed age and that coarsening takes place primarily via migration of individual particles along the surface of the network. Coarsening occurs in a three-step process: particles travel rapidly along the network surface until they become bonded to neighbors (cage building); they then migrate from cage to cage along the surface (cage hopping); and finally, particles become buried within network strands (cage trapping). This transfer of particles from more-mobile to less- mobile populations is stochastic but with a mean drift to higher contact-number populations which we view as a beautiful example of Smoluchowski's ratchet[31].

We find that the rate of coarsening cannot be described by pair-bond kinetics i.e. via a simple Kramers escape-time model, nor the familiar asymptotic predictions set by molecular coarsening theories. Our model for transport processes in colloidal gels combines features of both glassy and liquid-like systems, but with a novel exchange process between particle populations on the surface and in the solvent, a "micro-condensation / evaporation" process and a "micro-freeze / melt" process between the surface particles and the solid phase in the interior of the gel strands.

Gel rheology evolves with structural coarsening and changes in particle mobility. The high-frequency elastic and viscous moduli both scale with the square-root of the frequency as in colloidal dispersions in the absence of hydrodynamics[32,33] but the two are offset owing to the

hindrance of diffusive (viscous) motion by particle attractions. The gel is elastic over all frequencies studied, and this dominance grows with age: the gel age-stiffens. We show that this linear response is set by relaxations at the dominant network length scale, and put forth a scaling argument that collapses the moduli for gels of any age onto a single curve. A theoretical model inspired by the Rouse dynamics is advanced, leading to a simple analytical expression that captures this universal scaling behavior, suggesting that linear mechanical response can be determined at any age by measurement of dominant network length scale— or vice versa.

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Connecting structure and mechanics in arrested spinodal-decomposition protein gels

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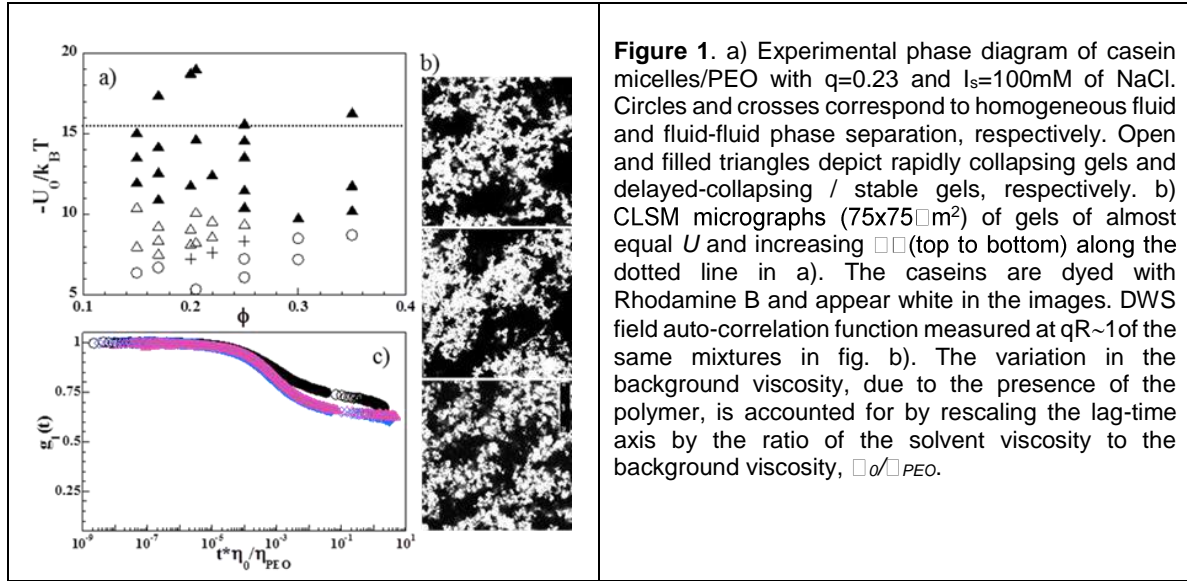
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Investigations of disordered solid-like states in colloidal suspensions have shown that dynamical arrest is strongly dependent on the colloidal volume fraction, ϕ and the strength, *U*, and nature of interactions.[1, 2] Solid-like structures such as colloidal glasses or particle gels form under either attractive or repulsive interactions.[2-4] For short-range attraction, it is well established now that gelation at high *U* and very low ϕ is driven by the diffusion-limited cluster aggregation (DLCA) of fractal clusters of colloidal particles,[5, 6] while at high ϕ colloids arrest to form a glass.[7] The mechanism of gel formation at low and intermediate ϕ is much less consensual.[2] Several mechanisms were proposed including mode-coupling theory (MCT) attractive glass,[8] cluster MCT,[9] viscoelastic phase-separation[10] and arrested spinodal-decomposition.[11-14] The latter has been shown to lead to the formation of amorphous protein networks with elastic properties that depend remarkably strongly on changes in ϕ.[15] It could thus offer a mechanism that would allow us to design protein-based food gels with tailored mechanical and structural properties.

We show that casein micelles at intermediate ϕ and medium-range depletion attraction indeed show a fluid to gel transition as a result of an arrested spinodal decomposition. We find that the elastic properties of arrested casein gels exhibit a strong dependence on ϕ and that they show a remarkable scaling behaviour with the localisation length, based on naïve mode coupling theory.[16] This quantitative connection between the microscopic motion and the macroscopic elasticity of arrested spinodal decomposition gels indicates that it is rather the local structure than the long-range correlation length that dictates the mechanical properties of depletion gels.
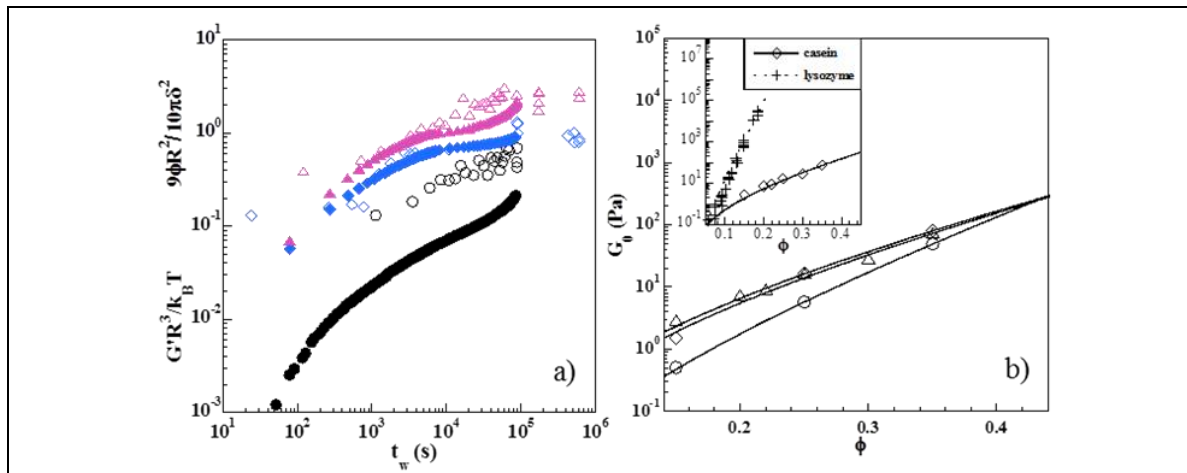
The protein and polymer used are casein micelles (R=70 nm and PI~0.43) and poly(ethylene oxide) (PEO: R_g=15.9nm, c^*=1.37wt%), respectively. Casein and PEO solutions were prepared and purified in mill-Q water with 100mM NaCl to screen electrostatic repulsions. Structural, dynamical and mechanical properties of casein-PEO mixtures were determined using confocal laser scanning microscopy (CLSM), diffusive wave spectroscopy (DWS) and rheology, respectively.

Casein micelles interacting via PEO-induced depletion show a rich phase diagram, fig 1.a, characterized mainly by a transition from a homogeneous ergodic fluid of clusters at low c/c^* to a non-equilibrium nonergodic gel at higher c/c^* and/or ϕ. The gelation proceeds directly from the homogeneous fluid phase at $\phi \geq \phi_c$, in contrast to lower ϕ where more complex phase behaviour is observed. Indeed, at $\phi \leq 0.25$ and immediately above the homogeneous fluid boundary the system undergoes a fluid-fluid phase-separation. Upon slightly increasing the attraction, the system phase-separates into a fluid and a gel. At even higher attraction, the system gels immediately after mixing.

The appearance of space-spanning networks, fig. 1b, is accompanied by nonergodic microscopic dynamics where an only partially-decaying $g_1(t)$ with a nearly time-independent plateau value is recorded, fig. 1c. The plateau value increases with age indicating a subdiffusive restricted motion of casein micelles within the gel network, characterized by a plateau in the mean square displacement, δ^2, called localization length.

Figure 1. a) Experimental phase diagram of casein micelles/PEO with q=0.23 and I_s=100mM of NaCl. Circles and crosses correspond to homogeneous fluid and fluid-fluid phase separation, respectively. Open and filled triangles depict rapidly collapsing gels and delayed-collapsing / stable gels, respectively. b) CLSM micrographs (75x75 m²) of gels of almost equal U and increasing (top to bottom) along the dotted line in a). The caseins are dyed with Rhodamine B and appear white in the images. DWS field auto-correlation function measured at qR~1of the same mixtures in fig. b). The variation in the background viscosity, due to the presence of the polymer, is accounted for by rescaling the lag-time axis by the ratio of the solvent viscosity to the background viscosity, $_0/_{PEO}$.

Macroscopically, the elasticity of casein-PEO gels increases over a relatively long period of time. The temporal evolution of G' is very similar to that of short-range attraction colloidal gels; namely thermo-reversible silica gels.[17, 18] charge-stabilised particle gels[19, 20] and arrested SD protein gels.[21] The temporal evolution of casein-PEO gels rigidity (fig. 2a) can be divided into three stages: a short latency period in which the mixture is fluid, followed by an exponential increase of G' indicating gel formation. At longer times, G' continues increasing but slowly (weak power law). The presence of three regimes was observed in thermo-reversible silica gels [18, 22], and the crossover from an exponential to a weak power law growth ascribed to a separation in the formation of the gel at short times and its aging at longer times.[18] Subsequently, the elastic modulus G_0 of the gels is determined and shows a surprising exponential growth with , fig. 2b, as opposed to the typical power-law dependence usually found for depletion gels.[16, 23, 24]

Figure 2. a) Elastic moduli of casein-PEO gels of "equal" attraction strength (U~15.5±0.5 k_BT) increase as a function of time elapsed after pre-shear. Triangles denote casein at = 0.35 and PEO at c/c^* = 0.71, diamonds casein at = 0.25 and PEO at c/c^* = 1.02 and circles casein at = 0.15 and PEO at c/c^* = 1.31. Full symbols represent normalized G' and open symbols represent normalized localisation length δ². b) Low-frequency elastic modulus G_0 as a function of casein for depletion gels at different polymer concentrations (c/c^*): 1.02 (circles), 1.31 (diamonds), 1.82 (triangles). The solid lines are exponential fits of the data with exponents decreasing from 14.7 to 9.2 with increasing c/c^*. The inset shows G_0 versus for the casein with deepest quench compared to data on lysozyme gels from Gibaud *et al.*[15]

In a recent paper on arrested spinodal-decomposition lysozyme gels, Gibaud *et al.* found that their elasticity increases exponentially with $\square\square$[15] This unusual strong dependence, reminiscent of porous media, was attributed to the large difference between the particle and strand size.[15] Compared to our results, lysozyme gels are stronger and their pore-geometry prefactor is 2.5-4 times larger. These differences are likely to be due to the higher size ratio between strand thickness and particle size of lysozyme gels ($\sim 10^3$ for lysozyme versus $\sim$ 20-50 for casein-PEO).[15]

One important issue in arrested spinodal-decomposition gels is the connection between the gel structure and its bulk mechanical properties. In casein-PEO gels, the structure arrests within minutes of mixing cessation while the elasticity increases continuously before reaching a "steady state", fig. 2a. Concomitant with the increase in gel elasticity, the localisation length decays with time, suggesting that the macroscopic stiffening of the gel is accompanied by growing restriction of the motion of casein micelles. Using a relation derived by Schweizer *et al.* based on naïve MCT for short-range attraction gels, $\frac{G'R^3}{k_BT} = \frac{9\phi R^2}{10\pi\delta^2}$, a good scaling behaviour is found for the localization length and the elastic modulus.[16] This quantitative connection between microscopic motion and macroscopic elasticity of arrested spinodal-decomposition gels indicates that it is rather the local structure than the long-range correlation length that dictates the mechanical properties of depletion gels.

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Universal phase diagram for the formation and collapse of colloidal gels

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Gelation in systems of particle with labile, short-range interparticle attractive bonds is now believed to be due to arrested spinodal decomposition. When the system phase separates into a colloid rich and a polymer rich phase the colloid rich phase hits the glass transition line and arrests. Colloidal gels so formed are prone to collapse suddenly after a long time of apparent stability. The origin of this phenomenon, sometimes known as 'delayed sedimentation', is still incompletely understood. The effect of particle size and polydispersity - important in all practical applications - have not been systematically explored; neither is gelation at high volume fractions or the nature of the particle dynamics leading ultimately to gel collapse understood. We explore these issues by combining computer simulations with experiments on a system where a short-range attraction is induced by the depletion mechanism.

We find that data from two quite different experimental systems can be described in terms of a single, universal out-of-equilibrium phase diagram modified by gravity (and thus particle size) and sample shape. At low colloid volume fractions the gels are very week and start collapsing before they are fully formed, at intermediate volume fractions the gels are stable for some time before they suddenly collapse quickly, at high volume fractions the gels are also stable but their ultimate collapse is postponed longer and much slower.

Images of a phase separating, sample. The time t is given in minutes after homogenisation.
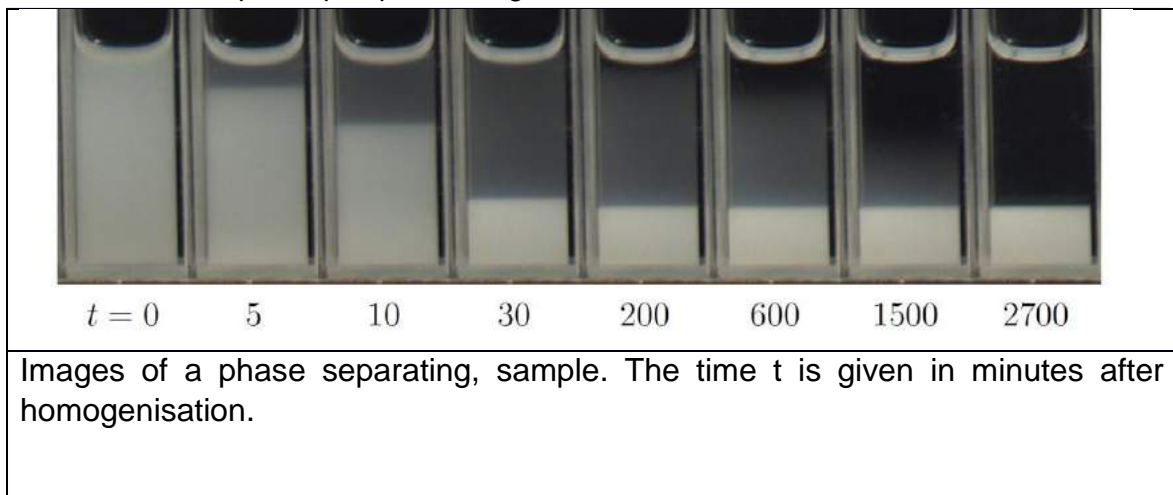
Multiple Light Scattering to characterize emulsions with polymers

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Polymers are widely used in the industry as a tool to increase the stability. Depending on their concentration, they can act as depletion agents or gel agent. The stability of these systems is driven by the polymers and the structure of the network of droplets and can lead to collapse of the emulsions.

In this work, Multiple Light Scattering device is used to monitor the behaviour of w/o emulsions stabilized with polymers. The heart of the optical scanning analyser is a detection head, which moves up and down along a flat-bottomed cylindrical glass cell (see figure). The detection head is composed of a pulsed near infrared light source (wavelenght = 880 nm) and two synchronous detectors. The transmission detector (at 180°) receives the light, which goes through the sample, while the backscattering detector (at 45°) receives the light scattered backward by the sample. The detection head scans the entire height of the sample, acquiring transmission and backscattering data every 40 μm.
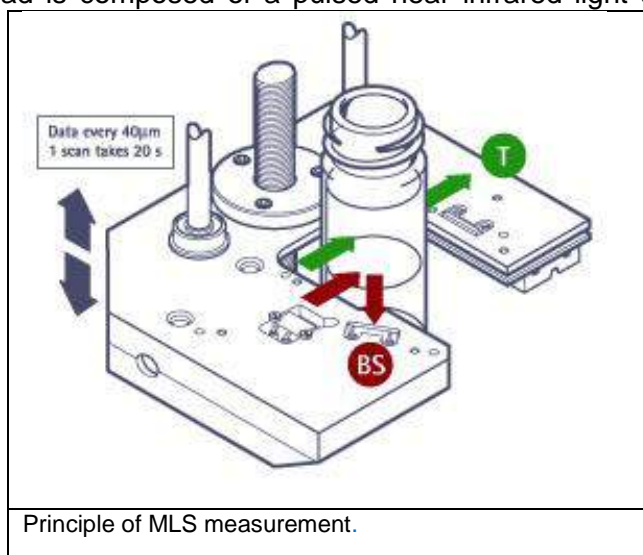
Principle of MLS measurement.

We propose a description of the behaviour of o/w emulsions stabilized with different polysaccharides, we will show the advantages of using Multiple Light Scattering (MLS) to monitor their stability and propose a method to predict stability of these emulsions thanks to their size evolution in the first days after preparation.

Self assembly of small molecules and the formation of arrested gels.

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Arrested gels are receiving considerable attention in the literature currently, principally in the form of those arising from colloidal aggregation processes. However, at least two other types of aggregation form arrested gels. Certain classes of biopolymers (for instance agar, carrageenan or albumin) have long been known to form such gels. More recently, the self-assembly of small molecules into ordered supramolecular structures, such as fibrils, have received attention, and clearly also form arrested gels.

In this talk I will consider a particular class of self-assembling small molecules (Fmoc-amino acids) that form arrested gels, but may also form other classes of materials, such as entangled solutions of worm-like micelles. It is also conceivable that these materials form hierarchically arrested states, in that the fibrillar structures formed are often meta-stable, but the gels formed from these structures may also be separately arrested through aggregation of the fibrils. The influence of molecular structure on the self-assembly processes, the microstructures formed and properties of the resulting gels will be discussed.

The yield stress of cohesive suspensions can be rate-dependent. (or, "an unlikely model system").

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There are many reasons to be interested in the constitutive rheology of colloidal suspensions, including the need to develop better engineering models of industrial processes, be they large or micro-scale. Colloidally unstable systems, i.e. aggregated or cohesive systems are of overwhelming importance in that context, stable systems being rare in technology and the environment. Of particular interest is the phenomenon of yielding, which is known to be subtle [e.g. 1-3]. In the favourable cases yield can be packaged into a lumped engineering parameter, the yield stress, although this simple parameterisation fails more generally, there being examples of systems where almost any value can be obtained, depending upon how one attempts to measure the yield stress [e.g. 3,4]. One should not be too surprised perhaps, since the yield stress is no more than a convenient fiction, given that stress can only be its own invariant, trivially, in one stress or strain dimension. Hence, underlying the yield stress there has always to be another criterion, or set of criteria governing the solid-to-liquid transition. At the simplest level one might look to stored strain energy, this being consistent with Von Mises invariant. Precisely how the true yield criterion is met in a particular test or loading protocol is then going to depend upon the viscoelasticity of the material sub-yield, and in general a combination of (CR) and controlled stress (CS) rheometry will be needed in order to develop a complete picture [e.g. 1-4].

Work on a somewhat unlikely model system will be reported, namely, a suspension of 4.5μm dia. $CaCO_3$ particles in water, coagulated at the IEP. "Unlikely", because the particle size is at the top of the colloidal range, except that this turns out to be a significant advantage in some respects. We have found this system to show just about every feature of yielding reported hitherto, together with some significant new facets.

In flow start-up experiments using step shear-rate, the stress-time curves could be scaled with shear-rate to yield curves of stress versus strain at different rates, just as could those for flocculated PMMA dispersions [3,5]. Transitions were seen at two characteristic strains, firstly, softening above a strain similar in magnitude to the scaled interparticle separation of the bonded particles (the "bond strain") and later a peak at a strain near unity. This type of behaviour has been reported before, notably by Petekidis et al. [3,5], who worked on weakly-flocculated sub-micron PMMA particles, except that they saw the peak stress increase with shear-rate only, whereas we see decrease at first. Koumakis & Petekidis [5] have suggested that this should happen, but at very high Pe; their prediction would suggest Pe ~ 10^5 or more for our system, whereas we see the decrease at low Pe <1. (Curve A in fig.1)

The initial decrease in peak stress with shear-rate has a profound effect on the flow curves, which are highly non-monotonic (curve B in fig. 1). It also causes the suspension depicted in fig. 1, with a peak stress of ca. 200 Pa, and a 'yield stress' of ~ 75 to ~ 100 Pa, depending upon how it is measured, to show an extrapolated or Herschel-Bulkley yield stress of ~zero.
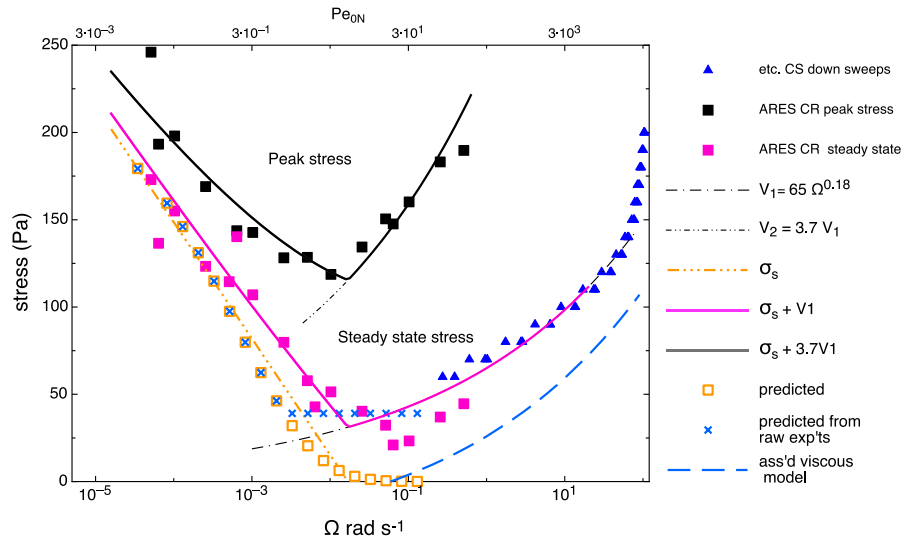
Fig.1 A plot of stress versus angular velocity (bottom) and Pe (top) for 40%v/v Omyacarb $CaCO_3$. The steady-state curve can be decomposed by fitting into a power-law viscous part (V1) and a strain-rate thinning solid-phase part (σ_s). Data taken from ref. 4.

It is helpful to separate the stress into two parts, a solid-phase part, which, were it not to be variable, one would call 'the yield stress', and a viscous part. In step-strain-rate testing, the solid phase part was found to strain-soften above the bond strain, but in a Pe-dependent way. At low Pe the softening was weak and the solid stress reaches a plateau at the "cage strain" ~1 [cf. 3], whereas at higher Pe the softening became strong enough to eliminate the cage strain peak. The viscous stress was found to peak at the 'cage-strain' too and this accounted for the rise in peak stress with strain-rate seen at higher strain-rates.

The strain softening extended over more than three decades in strain and it could be characterised in terms of a softening exponent (fig. 2). The exponent appears to be both Pe and volume-fraction dependent, notionally, although the latter dependence is thought to be an artefact attributable to the viscous stress growth [7].

One way to describe our findings in broad terms is to say that the yield strain drops from cage strain to the bond strain as Pe approaches unity. The limited data currently available suggest that the same thing happens when the volume-fraction is reduced below 0.25 [5-7]. If so, then the apparent yield strain is both strain-rate and concentration dependent.

Although Koumakis & Petekidis [5] measured their step strain-rate transients over a similar Pe range, they did not report seeing rate-dependent softening. Nor, from their figure 12, did they see non-monotonic flow curves, prompting the question "why not?" A different balance between the solid-phase and viscous stresses is one possibility. That they saw the peak stress rise with shear-rate suggests that the viscous stress growth always dominated the solid-phase stress in their system even at strains ~1. If so, then that in turn could mean perhaps that the two stress components scale differently particle-size etc., although that remains to be seen.

The liquid phase viscosity was however much higher for the PMMA systems too. The third figure shows the effect taking the fit to the flow curve in fig.1 and increasing the viscous term by a constant factor of up 15, by way of illustration. The non-monotonic behaviour is then obscured for viscosity increases > 10 interestingly.

A fuller account of this work has been submitted to J. non-Newtonian Fluid Mechanics, preprint is available at arxiv.org/abs/1410.0179.
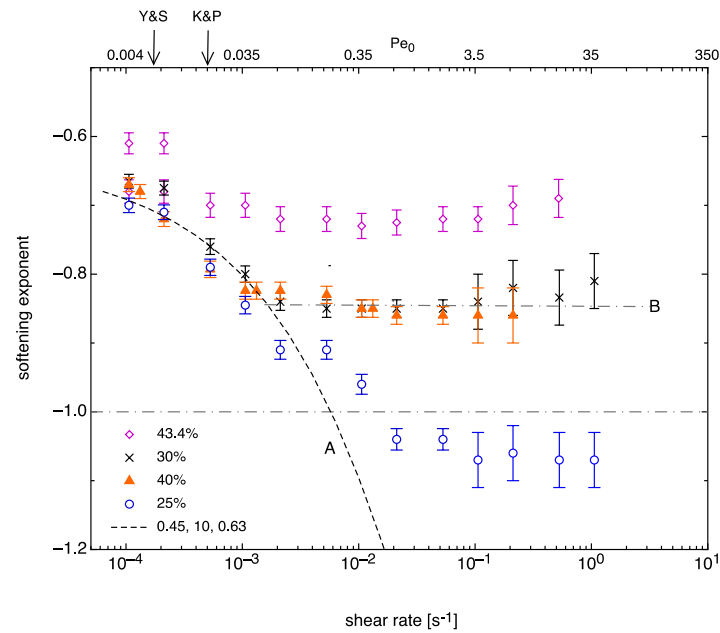
Fig. 2 Strain softening exponents for Omyacarb $CaCO_3$ at four concentrations plotted against shear rate (bottom) and Pe (top). It is thought that the true softening exponent of solid-phase stress alone follows a trend something like line A, with the apparent exponent derived from the total stress following curves more like B because of the increase in viscous stress with strain-rate.
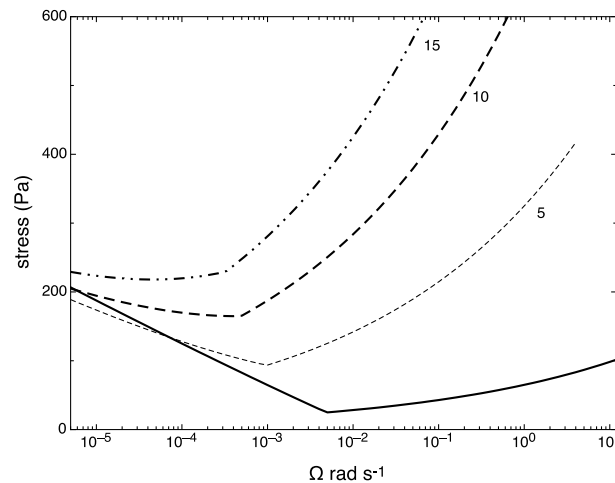

Fig. 3 shows the effect of increasing the liquid phase viscosity would have on the fit to the flow curves shown in fig.1. The viscous term has been increased by the factor shown and the solid-phase stress has been shifted down the rate axis to keep its dependence on Pe unaffected.

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Beyond friction: cohesion and interlocking in shear thickening of suspensions

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Colloidal suspensions are complex by nature. Various types of forces: hydrodynamic, Brownian, and surface forces, etc., act on particles in a suspension, affecting its microstructure and in turn its rheology. This complexity makes the modeling of suspension rheology difficult. To make progress, it is essential to have useful model systems of colloidal suspensions. Indeed, there have been significant experimental efforts; hard-sphere colloids have been developed [1], and ways to minimize inessential effects for suspension flow such as sedimentation and aggregation have been introduced [2]. Rheometers are also designed to make the situation simpler, i.e. to achieve simple shear flow as closely as possible, with the objective being to characterize the bulk rheology of samples. Unexpected boundary effects may affect the flow of suspensions, but boundary effects need to be clearly distinguished from effects stemming from bulk flow properties.
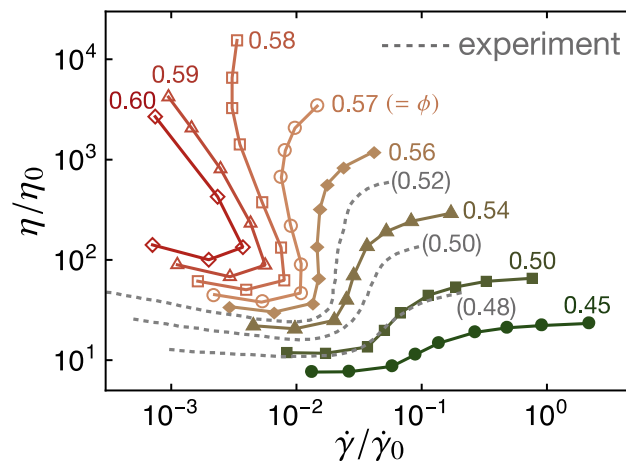
Fig.1 The viscosity as a function of the shear rate for several values of the volume fraction in our stress controlled simulation. They are compared with silica suspension data from Cwalina and Wagner [2] (dashed lines, with corresponding volume fractions in parenthesis).

We recently established a minimal model for predicting discontinuous shear thickening in suspensions [3, 4]. Systems exhibiting shear thickening are complex; an idealized suspension model that omits surface roughness, frictional contact, and repulsive forces is too simple. Such idealized models are commonly used in situations where the focus is on hydrodynamic effects, e.g., Stokesian Dynamics [5]. Frictional contact, in particular, is critical in our model, because it influences the jamming points of suspensions. The shear thickening reproduced in our simulation is truly a bulk property; no boundary effects can occur due to the periodic boundary conditions. Furthermore, a recently-introduced stress-controlled simulation methodology reveals a complete set of flow curves for steady-state shear rheology, including non-monotonic S-shaped and arched curves (see Fig.1)[6].

As shown in Fig. 1, our simulation results (plots with solid lines) are very similar to the experimental data (dashed lines) reported by Cwalina and Wagner [2]. However, our predictions differ quantitatively from other published. For example, cornstarch suspensions exhibit discontinuous shear thickening at rather lower volume fractions [7]. The gap is still an open question. It may stem from the incomplete knowledge of the actual contact forces. It seems very difficult to experimentally characterize the friction law between individual colloidal particles, however; it is not known if the actual contact force can be cast as bare "friction." To understand the sensitivity of the contact model for shear thickening, we study a more comprehensive model that includes rolling friction and attractive forces [8]. This extension allows us to investigate the impact of a cohesive force or interlocking between particles on rheology. We discuss how such different types of contact forces perform as alternatives to friction.

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Intermittent aging dynamics and logarithmic coarsening in nonequilibrium gels

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Snapshots of representative gel-like bicontinous structures formed during liquid - gas spinodal decomposition of a simple Lennard-Jones numerical model a low temperatures (from Ref [1]). Coarsening becomes logarithmically slow and characterized by an intermittent aging dynamics at low temperatures.
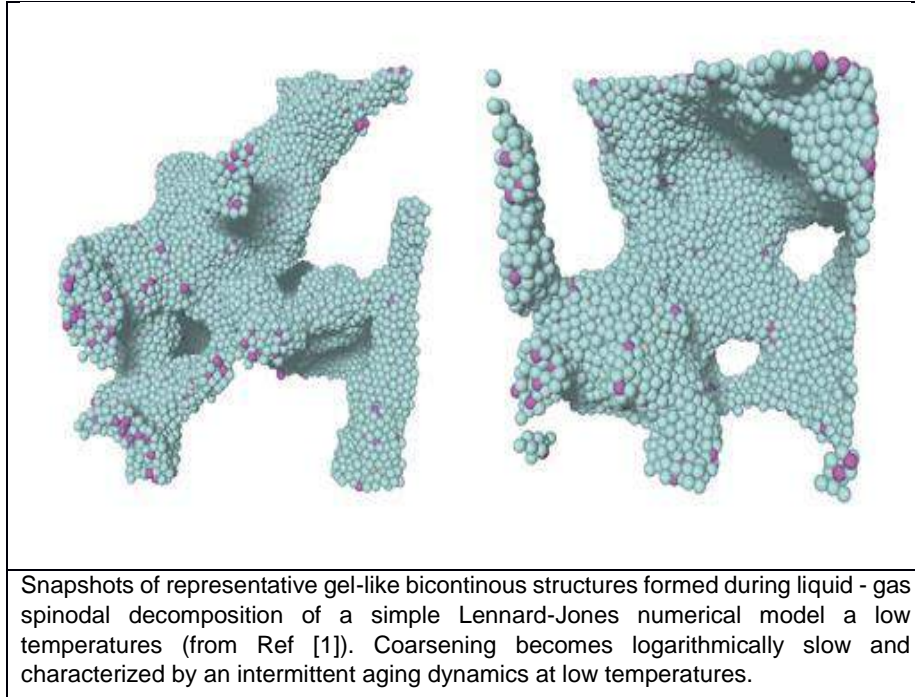
Kinetically arrested phase separation has been invoked as a possible route towards the production of arrested gels in colloidal systems. At the theoretical level, one should then understand better the generic problem of a phase separation process in the presence of a non-equilibrium, arrested phase. To address this issue, we use computer simulations to analyse the fate of the liquid - gas spinodal decomposition at low temperatures where the dense phase can get kinetically arrested in an amorphous solid phase. Upon lowering the temperature, we observe a gradual change from complete phase separation at high temperatures to non-equilibrium, gel-like structures that evolve very slowly at low temperatures. The microscopic mechanisms responsible for the coarsening strongly depend on temperature, and change from normal diffusive motion at high temperature to a strongly intermittent, heterogeneous and thermally activated dynamics at low temperature, leading to

logarithmically slow growth of the typical domain size, and anomalous time correlation functions during the aging process.

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Dynamical Simulation of Delayed Yield in Reversible Colloidal Gels

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We study the nonlinear response of a reversible colloidal gel undergoing deformation due to an applied stress via dynamic simulation, with a view toward elucidating the mechanisms of macroscopic yield at the level of particle-scale dynamics. Colloidal gels are soft solids comprising microscopic particles bonded to one another via inter-particle attractive potentials or other mechanisms. When bonds between the colloids are not strong, the gel may flow when subjected to a shear stress, and then regain solid-like behavior upon removal of the imposed stress. This facilitates their handling and makes them desirable media for pharmaceuticals, pesticides, and cosmetics [1,2]. The transition from solid-like to fluid-like behavior is a yielding process that is not necessarily instantaneous but rather may occur after a time delay [3]. The length of this delay decreases sharply as stress is increased [3–7], but the precise relationship between applied stress and time to yield is not straightforward. Recent experiments have revealed two apparently distinct regimes of time-to-yield vs. applied stress, suggesting multiple failure mechanisms [5]. The more fundamental question of whether there is a stress below which delayed yield never occurs has been debated [5,6]. To explain the dependence of the time-delay on the applied stress, theories have been advanced to link gel structure to rheology, and aim to predict the ultimate fate of a gel under an applied load [3,5]. While these theories hypothesize a competition between bond breakage and reconnection rates, no such particle-scale dynamics have been directly observed. Furthermore, it is not clear how to reconcile these theories, which envisage the gel structure as quasi-static with fluctuating bonds, with observations of large-scale, ongoing structural evolution [8,9]. An understanding of the structure and individual-particle dynamics will shed light on the mechanisms of this and other yield behaviors in reversible colloidal gels.

In the present study we utilize large-scale dynamic simulation to model structural evolution and particle transport in colloidal gels subjected to a step stress. The model comprises 750,000 Brownian particles interacting via a hard-core repulsion and short-range attractive interactions, leading to the formation of a gel, as one would obtain via depletion-flocculated colloids, for example; the gel evolved quiescently over time, whereby its structure and rheology evolved with ongoing particle migration [9]. A feedback-control method was employed so as to impart a step-shear stress to the periodically replicated gel [10]; a range of gel volume fractions, attraction strengths, and imposed stresses was studied. Detailed particle positions, trajectories, and particle-phase stress were monitored throughout simulation.

We find that the bulk deformation of the gel agrees with experimentally reported behavior [4–7] as follows. The temporal dependence of the shear rate varies qualitatively with the level of stress applied: large, medium, and small. For all levels, immediately following imposition of the applied stress, the gel deforms; however, the corresponding shear rate decreases with time with a power-law dependence that suggests a solid-like creep response [4,7]. Following this, under large stresses, the shear rate reaches a local minimum, increases, signifying yield, and finally reaches a long period of unsteady flow, where the shear rate is large and fluctuating. Under medium stresses, the shear rate also reaches a local minimum, but after significantly longer time-delays. Surprisingly, the shear rate also reaches a local maximum and then plummets. This suggests a return to solid-like behavior: a re-solidification. Under small stresses, the system does not yield: the shear rate monotonically decreases throughout the duration of the simulations.

Under both medium and large stresses, the shear rate reaches a local minimum at a strain of 2--3%, which is smaller but close in magnitude to the ratio of the bond length to the particle size (10%). A "critical strain" such as this has also been found in other soft matter systems [4]. We do not find strong evidence that the time-to-yield shows two distinct regimes [5]. It appears to follow a single regime where the time diverges at a critical stress [7,11].

Our analysis of the structural transformations and particle dynamics of stressed gels is revealing, albeit preliminary. The re-solidification under medium stresses seems to be caused by rearrangements of broken particle-rich regions into a new space-spanning network that resists the load in a process reminiscent of jamming. Finally, we investigate how particle transport occurring before the critical strain bears on whether a gel yields at the critical strain.

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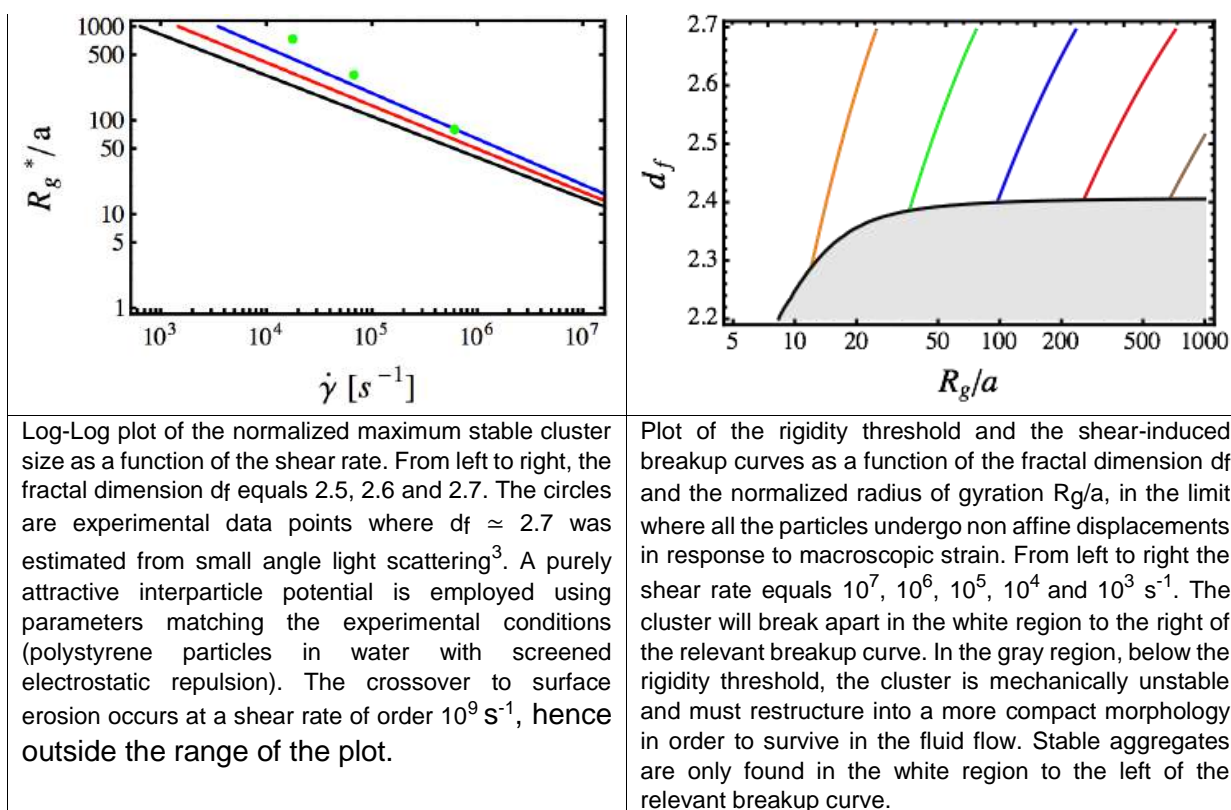
The breakup and stability of biomolecular and colloidal aggregates in a shear flow

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The theory of self-assembly of colloidal particles in shear flow is incomplete. Previous analytical approaches have failed to capture the microscopic interplay between diffusion, shear and intermolecular interactions which controls the aggregates fate in shear. In this work[1] we analytically solved the drift-diffusion equation for the breakup rate of a dimer in flow. Then applying rigidity percolation theory, we found that the lifetime of a generic cluster formed under shear is controlled by the typical lifetime of a single bond in its interior, which in turn depends on the efficiency of the stress transmitted from other bonds in the cluster. We showed that aggregate breakup is a thermally-activated process where the activation energy is controlled by the interplay between intermolecular forces and the shear drift, and where structural parameters determine whether cluster fragmentation or surface erosion prevails. In our latest work[2], we analyzed floppy modes and non affine deformations to derive a lower bound on the fractal dimension d_f below which aggregates are mechanically unstable, ie. for large aggregates $d_f \simeq 2.4$. This theoretical framework is in quantitative agreement with experiments and can be used for the population balance modeling of colloidal and protein aggregation.

Log-Log plot of the normalized maximum stable cluster size as a function of the shear rate. From left to right, the fractal dimension d_f equals 2.5, 2.6 and 2.7. The circles are experimental data points where $d_f \simeq 2.7$ was estimated from small angle light scattering[3]. A purely attractive interparticle potential is employed using parameters matching the experimental conditions (polystyrene particles in water with screened electrostatic repulsion). The crossover to surface erosion occurs at a shear rate of order 10^9 s^{-1}, hence outside the range of the plot.	Plot of the rigidity threshold and the shear-induced breakup curves as a function of the fractal dimension d_f and the normalized radius of gyration R_g/a, in the limit where all the particles undergo non affine displacements in response to macroscopic strain. From left to right the shear rate equals 10^7, 10^6, 10^5, 10^4 and 10^3 s^{-1}. The cluster will break apart in the white region to the right of the relevant breakup curve. In the gray region, below the rigidity threshold, the cluster is mechanically unstable and must restructure into a more compact morphology in order to survive in the fluid flow. Stable aggregates are only found in the white region to the left of the relevant breakup curve.

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Colloidal gelation as viscoelastic phase separation

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Colloidal gelation is often thought to be a consequence of phase separation and its dynamic arrest by an ergodic-to-nonergodic transition such as glass transition. Here we will show a crucial role of hydrodynamic interactions in gel formation, which are a consequence of the size asymmetry between colloidal particles and liquid molecules. The size asymmetry and the resulting dynamic asymmetry is the key to viscoelastic phase separation, where mechanical stress plays a crucial role in structural evolution as a result of asymmetric stress division between the two components. When the self-generated stress by attractive interactions between colloidal particles becomes weaker than the yield stress of a network, dynamic arrest takes place and a network structure is frozen. The coarsening process is primarily not a thermally activated process, but rather a process of mechanical fracture of a network. The final stabilization of a network structure is a consequence of the formation of mechanically stable local structures. We will show a several pieces of such evidence from both confocal microscopy observation and numerical simulations incorporating hydrodynamic interactions. This work was done under collaboration with Takeaki Araki and Akira Furukawa (simulations) and Paddy Royall, Mathieu Leocmach, and Hideki Tsurusawa (confocal microscopy experiments).

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Viscous coarsening and fragmentation in phase separating oxide glasses

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When a homogeneous liquid is suddenly brought into a phase coexistence region, phase domains appear by nucleation or spinodal decomposition. This early stage of phase separation is followed by a coarsening stage : domain growth driven by surface tension. The characteristic size of these domains increases as a power law of time : $\xi(t) \approx t^\alpha$ where the exponent α depends on the transport mechanism (diffusive, viscous, inertial). While phase separation has recently been mainly discussed in the context of soft matter studies, it has also early been a subject of interest in glass science[1]. Many oxide glass compositions indeed present a large domain of phase separation. Depending on the composition, the critical temperature of phase separation may lie well above the temperature of glass transition or in the supercooled regime. In the latter case the dynamics of coarsening directly competes with the viscous slowing down associated to glass transition. The control of such a dynamical arrest in the phase separation of oxide glasses has been early used to produce porous glasses of tunable nanometric-size porosity[2].

We discuss here recent in-situ X-ray tomographic experiments on a ternary oxide glass system, a barium borosilicate glass. The two phases, barium-rich and silica-rich respectively, present a high density contrast, which enables a good quality segmentation of the 3D images. The two separating phases are also characterized by a strong viscosity contrast[3]. Experiments have been performed on the beam-line ID19 at the European Synchrotron Radiation Facility (ESRF). Samples 2 mm in diameter were placed into refractory crucibles, and the glass samples were then observed during a heat treatment. The glass melt is studied at high temperatures (in the range [1000°C-1300°C]), well above the temperature of glass transition so that it is liquid. Volumes of size up to 700µmX700µmX350µm were reconstructed with a voxel of micrometric size (0.35µm to 1.1µm depending on the set-up).

As evidenced in Fig. 1 the use of 3D imaging enabled us to directly follow the domain growth. The linear character of the time dependence of the characteristic size of the domains was establihed quantitatively, in agreement with Siggia's prediction for viscous coarsening[4]. The hypothesis of dynamic scaling invariance was tested on the distribution of local slopes measured on the domains. Although this hypothesis was mainly obeyed, a slight departure from scaling invariance was observed.

Limits to dynamic scaling invariance could be attributed to an original phenomenon: the gradual fragmentation of domains of the less viscous phase. While viscous flow is at play within the percolating domain, this hydrodynamic transport mechanism is no longer present for isolated droplets. The growth of the latter thus relies on diffusion only and does not obey the viscous scaling law.

Interestingly, we could show that the distribution of isolated domains induced by fragmentation inherits from the self-similar character of the coarsening structure: a power-law distribution of droplets is obtained[3].
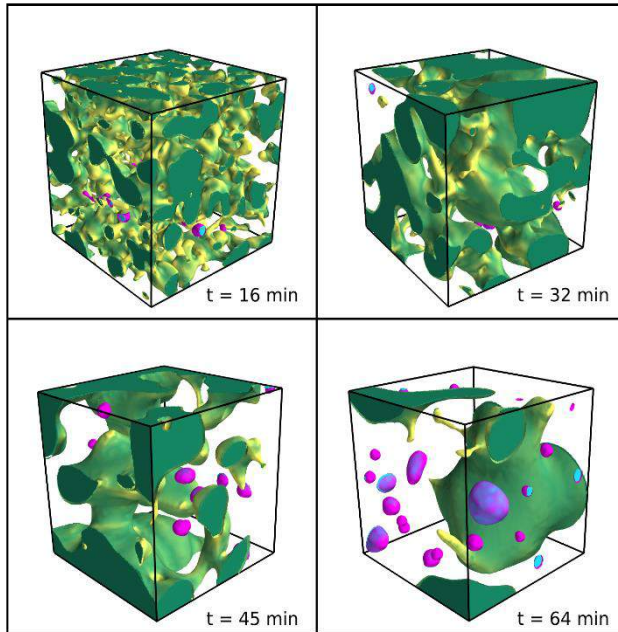

Fig. 1: X-ray tomography of a barium borosilicate glass under coarsening at 1130°C (after 16mn, 32 mn, 45mn and 64mn). The lateral size of the cube is 140µm. Only the minority (barium-rich) phase is represented. The percolating domain is represented in shades of green, following the mean local curvature. Isolated domains are represented in shades of purple.

As shown in Fig. 2, in conditions of viscous coarsening, domain growth results from series of hydrodynamic pinch-off events at small scale. However, far from the percolation threshold, the breaking of an isolated link of a cluster is unlikely to induce fragmentation (the appearance of a new isolated cluster). The fragmentation at play in our experiments should be rather related to another hydrodynamic phenomenon, end-pinching[5]. After elongation, the relaxation of droplets suspended in another fluid strongly depends on the viscosity contrast between the two fluids. Droplets of high viscosity can re-form while droplets of low viscosity break-up in two or more droplets. In the present context of phase separation, we could check that fragmentation was indeed due to the viscosity contrast. Only low viscosity domains show fragmentation[6].
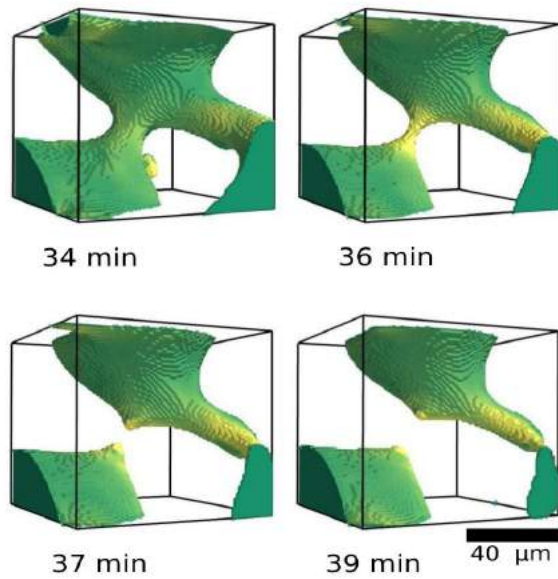
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When attractions meet repulsions: theoretical and experimental studies of phase behaviour and structure in colloids-polymer mixture

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Colloidal gels are widely applied in food products and other materials. Nowadays, many experimental data are available on exploring the structure of colloids-polymer mixtures; however, there is less information theoretically. In this work, the phase behaviour and structure of aqueous mixture of charged colloids with neutral polymers is studied theoretically, and compared with experimental measurements obtained by small-angle neutron scattering (SANS). Specially, we aim for more accurate potential of mean forces (PMF), than those obtained from screened Coloumb (electrostatics) and Asakura-Oosawa (AO) polymer approximations.

Firstly, the full Poisson-Boltzmann (PB) equation, rather than its linearized version (Screened Coulomb), has been used to calculate the long-range electrostatic repulsion. We show that this has a profound influence on the predicted shape of the electrostatic repulsion (which cannot be handled simply by rescaling the effective charge and/or the Debye length).

Secondly, the experimentally used polymer, poly(ethylene oxide) (PEO), with a radius of gyration (R_g) 4.7nm, has been modelled as explicit pearl-necklace polymers, i.e. as connected hard-sphere beads. Specially, one such bead represents either CH_2 or O , so that one monomer is modelled as three linearly connected hard-sphere beads. Each bead is assumed to have a diameter similar to a water molecule, and the bond length is adjusted so that the experimental R_g is reproduced. The polymer-induced PMF (depletion attraction) was then established by classical polymer density functional theory (DFT). This theory has been shown to be remarkably accurate, yet exceptionally fast, especially in flat (or spherical) geometries. Additionally, two different excluded volume approximations were considered: generalized Flory dimer (GFD) treatment and the thermodynamic perturbation theory (TPTD1).

Monte Carlo simulations (using the established PMF) are then utilized to obtain the structure factor curves, which can be directly compared with SANS measurements. Since the particles are much larger than the polymers as well as the Debye length, the models used in this work are based on the Derjaguin Approximation, i.e. the PMF between (spherical) particles are established from flat surface (slit) models.

The particle charge, which in principle is an unknown parameter, was fitted by comparing the structure factor from MC simulation with SANS results in polymer-free colloids dispersion. A few examples of predicted and measured structure factors, in solutions of charged polystyrene particles with added PEO in 50mM salt, are given in Figure 1. Gelation occurs (at this salt concentration) when the polymer concentration is 8.53g/l. The agreement between theoretical predictions and experimental measurements is quite reasonable. Interestingly enough, almost as good agreements can be obtained with much cruder models, resulting in very different PMF. In other words, $S(q)$ seems to be a very crude tool to explore/verify interactions in a given system.

The salt-depended phase behaviour and other polymer concentration of the colloids-polymer mixture have also been studied.
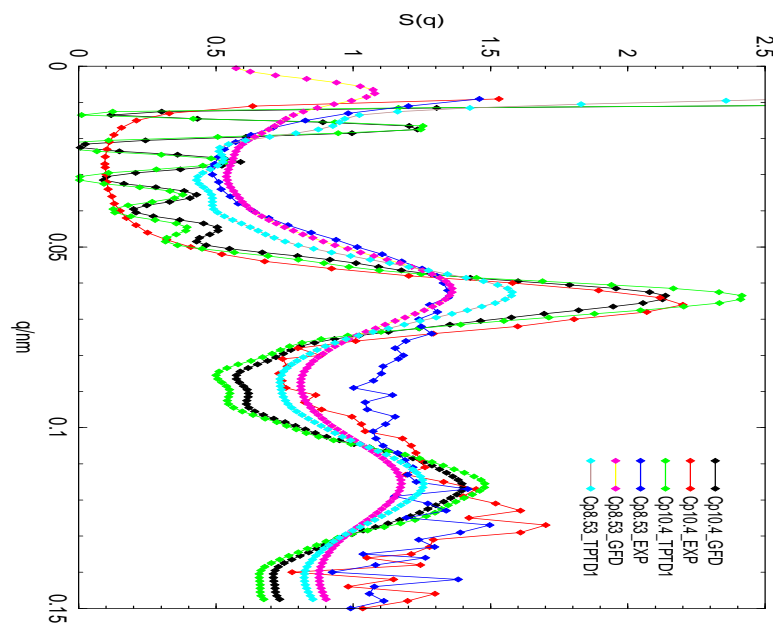

Figure 1. SANS measurements and theoretical calculations of structure factors in colloids-polymer mixture with different polymer concentration in 50mM salt solution.

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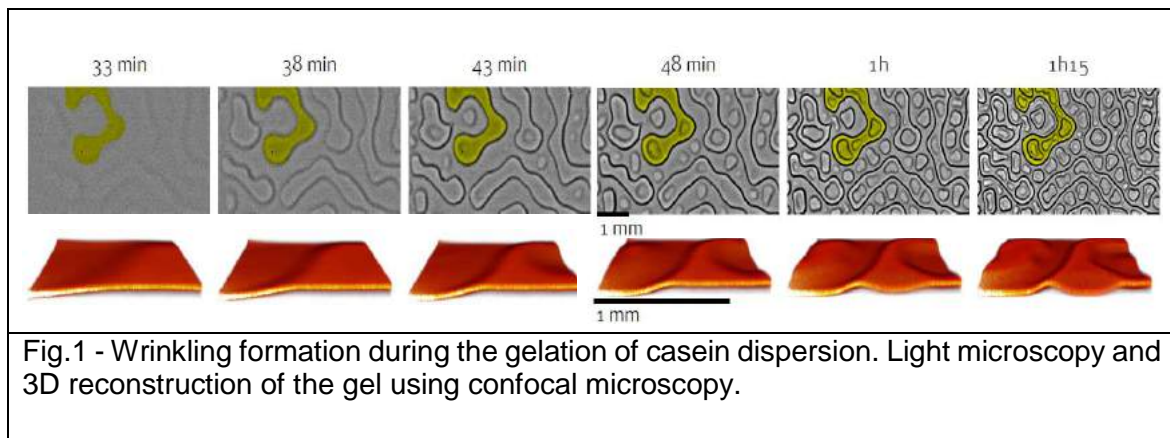
Wrinkling gels

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The slow acidification of milk proteins such as casein is well known to result in the formation of gels – this is indeed one of the key steps to make cheese or yogurt. Here, we slowly acidify a casein dispersion confined in a slit geometry. We observe the formation of a gel that wrinkles in cascade when casein adhesion to the slit wall is turned off (Fig. 1). Using a combination of rheology, light microscopy and confocal microscopy, we demonstrate that, during the acidification, the gels shrink and swell creating constrains that induce Darcy and Poiseuille flows and wrinkles the gel. Tuning the slit geometry and the properties of the dispersion allows us to size and organize the wrinkles. Such phenomena relates to daily life problems such as wrinkles encountered while putting up wall paper but could also be of interest to texture food or nest cells.

Fig.1 - Wrinkling formation during the gelation of casein dispersion. Light microscopy and 3D reconstruction of the gel using confocal microscopy.

Tough Polyacrylamide-Polyvinylpyrrolidone Arrested Hydrogels Formed by Thermal and/or pH Triggered Gelation

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Upstream oil and gas operations often utilize settable polymeric gels to seal downhole fissures while drilling or to block water contact zones during well production. Many of these gel chemistries consist of polyacrylamide co-polymers crosslinked with transition metal ions such as chromium (III), aluminium (III), titanium (IV) or zirconium (IV). The crosslinking process is presumed to consist of a complexation between metal ions and carboxylate groups from hydrolysed amide groups on the polymer. To allow delivery from surface, gels are initially pumped as polymer solutions with delayed crosslinking achieved by competing ligands. Once gelled, the polymeric materials create elastic, semi-rigid structures with moduli in excess of 100 Pa. Final gel properties can be adjusted by changes in polymer molecular weight, as well as concentrations of polymer and crosslinker [1, 2].
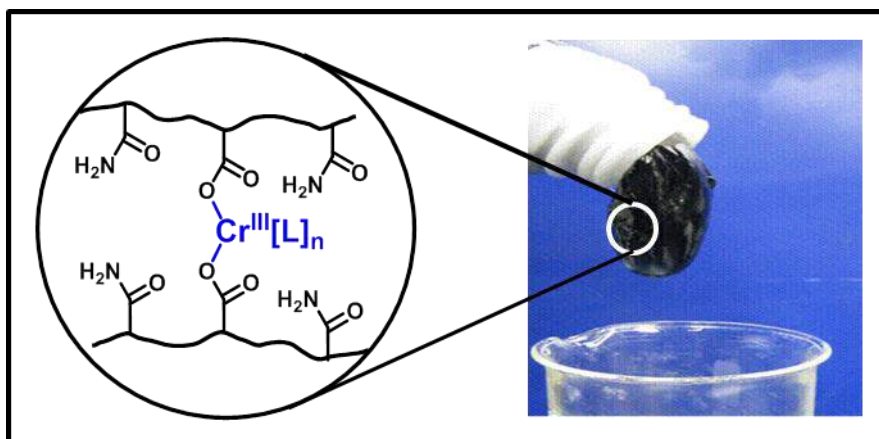
Figure. 1. Chemistry of a metal crosslinked gel of partially hydrolysed polyacrylamide.

Although these metal crosslinked gels create adequate sealing structures in laboratory conditions, downhole success can be undermined by poor control over gel set-time and high sensitivity to adventitious mixing with reservoir brines and hydrocarbons prior to crosslinking. Also, some metal crosslinking chemistries are not acceptable in offshore applications due to environmental concern. In addition, the systems that utilize the carboxylate groups as crosslinking sites are incompatible with cement, which frequently is used in tandem with gel pills for water shutoff applications. These limitations motivate a continued interest in arrested gels with more control over gelation kinetics, more tolerance to contamination, and access to enhanced rheology or adhesion.

In this work we present the synthesis and characterization of tough, elastic, and highly adhesive hydrogels obtained from mixtures of partially-hydrolised polyacrylamide (PHPA) and polyvinylpyrrolidone (PVP). Gelation can be induced by increasing either the pH or the temperature of the polymer mixture.
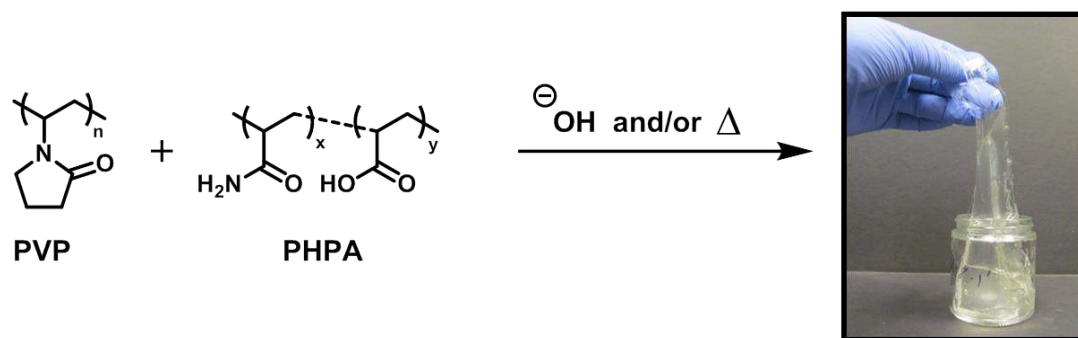

Figure 2. Formation of PVP-PHPA gel upon exposure to elevated temperature or added base.

Using oscillatory rheology, we studied the influence of the pH and temperature on the kinetics of setting and the rheological properties of the gels. The results indicate that both pH and temperature have strong influence on gelation time. However, the rheology of the final gels was found to be similar regardless of the initial gelling conditions. Comparative experiments with non-hydrolised polyacrylamide (PAM) and polyacrylic acid (PAA) indicate that the amide groups are required for gelation, and our results suggest that a transamidation process between ring-opened PVP and the amide groups in PHPA contributes to the gel formation.
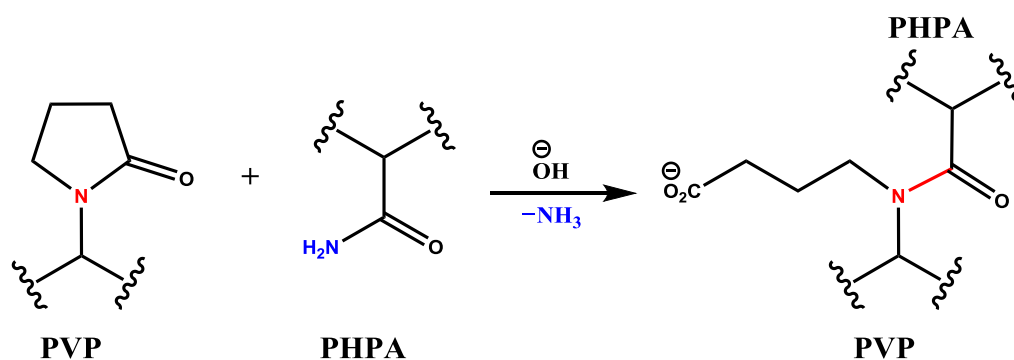
Figure 3. Proposed covalent crosslinking in PVP-PHPA gels.

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Mechanistic details of energy storage in protein gels during mechanical deformation

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The fracture and macroscopic breakdown properties of gels can be explained by the energy balance in the materials. When energy is exerted on viscoelastic materials such as food gels by mechanical deformation, part of the energy applied will dissipate by various processes. The energy that does not dissipate is referred to as the "recoverable energy". The recoverable energy has been related to certain mouthfeel attributes of the gels such as the crumbly perception. However, to be able to tailor crumbly perception, physical properties of food gels that relate to crumbliness, such as the extent of recoverable energy, have to be understood. Fine-stranded networks are known to have a higher ability to elastically store energy than coarse-stranded network. The ability to store energy in this case can be related to the coarseness of the gel, defined as inhomogeneity of gel networks in relation to the thickness of the strands that spans the networks, or to morphological differences caused by changes in the porosity of the networks, which are shown to be related to the amount of energy that is dissipated via serum flow of the entrapped liquid during deformation.

In this work, a range of protein gels were created from different protein sources (ovalbumin, pea, whey) under defined conditions (ionic strength, pH, and protein concentration), that differ in network morphology as analyzed with confocal and electron microscopy and the large deformation properties of these gels were evaluated. Changes in various structural aspects of the networks such as the mesh size, strand thickness, strand stiffness, and the viscosity of the serum phase, were shown to influence the contribution of energy dissipated via various modes and this had a concomitant effect on the recoverable energy. These findings suggest that for reformulation of protein-based products by employing other protein sources a focus on the ability of the networks to elastically store energy is important as this can be used as a tool to engineer the texture attributes of food materials.

Arrested Hybrid Gels made of DNA-functionalized Gold Nanoparticles and fd-Viruses

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We have demonstrated that colloidal particles functionalized with the right DNA can be made to form inter-percolating arrested phases, termed bigels, which have the potential for many interesting applications. [1,2] Recently we have extended our binary gel system to mixtures of gold nanoclusters functionalized with single-stranded (ss) DNA such that they can only bind to filamentous fd-viruses functionalized with the complementary ssDNA. Here I will present how these gels form and discuss the aggregation and aging dynamics. [3] In particular different nanocolloid-to-rod ratios will be discusses, both in light of the fact that the rods have the ability to undergo an isotropic-to-nematic phase transition, and as model systems of cross-linked networks of semiflexible rods.

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Native fibroin solutions: silk feedstocks as temporally arrested gels.

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Much has been written about the impressive mechanical properties of silk fibres – especially the major ampullate (i.e. dragline and scaffold) fibres from orb weaving spiders [1, 2]. Perhaps even more remarkable, though, is the ability of the various silk-producing animals to rapidly convert an aqueous protein feedstock solution into a solid fibre, rapidly and at ambient conditions, using minimal energy and without recourse to harsh process chemicals [2, 3]. This process occurs within specialised organs (silk glands) inside the animal.   Under normal spinning conditions, this phase transition is brought about by shear and extensional flow, as the silk proteins travel down the gland, which induces alignment and conversion of the highly repetitive amino-acid sequences from random coil to β-sheet conformations. Moreover, after spinning, the fibre remains solid and does not redissolve, unless acted upon by rather harsh, chaotropic solvents.

Clearly, premature gelation of the feedstock causing blockages prior to spinning would be problematic for the animal; hence, a certain degree of feedstock stability is required. Conversely, though, too large an energy barrier to gelation would at best be inefficient and selected against through evolution and at worst prevent fibre formation entirely.

These facts suggest that a delicately balanced thermodynamic landscape must exist between the native fibroin solution (precursor) and the fibre (product). In this respect, the fibroin solution can be regarded as a temporally arrested system – stable, but poised to gel when required.

In order to investigate this process, we have used the native fibroin solution from the domesticated silkworm (*Bombyx mori*) as a model system. This is more easily available than equivalent feedstocks from spiders, wild silkworms or other animals and, although different silk types are based on somewhat
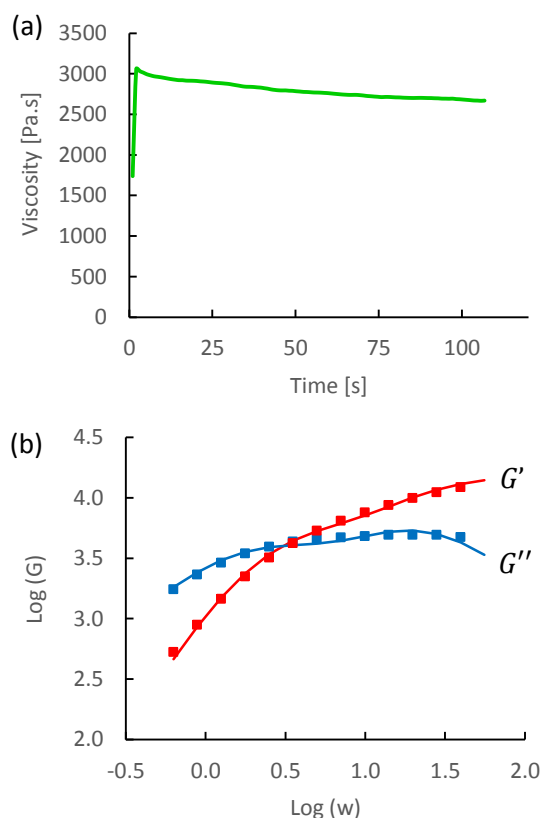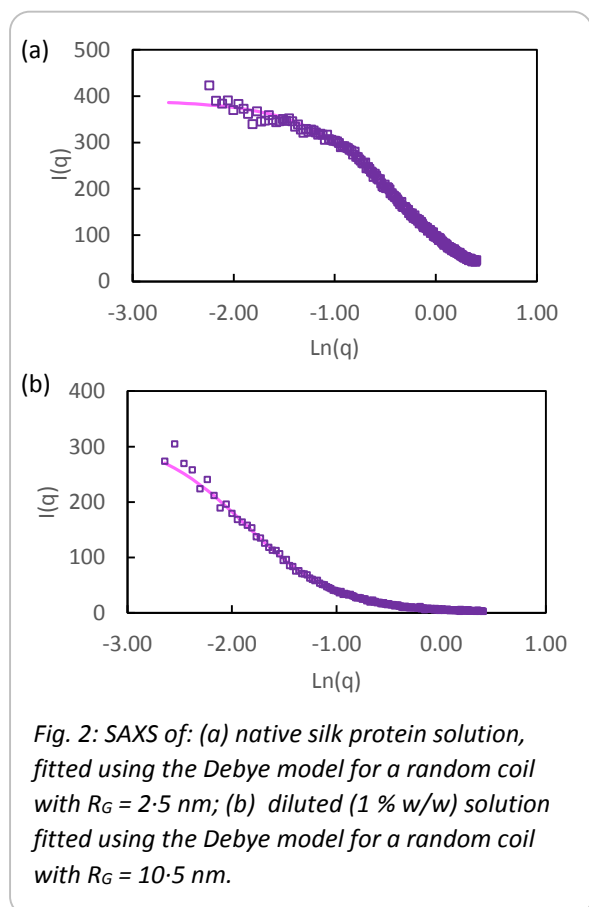

Fig. 1: Rheological data for a typical native silk feedstock solution (ca. 25 % w/w protein concentration): (a) apparent shear viscosity, measured at $\dot{\gamma} = 1\ s^{-1}$ over 100 s; (b) oscillatory measurements (continuous lines represent the best fit to the data using a binary Maxwell model).

different proteins, there are common themes of molecular architecture and clear similarities in the overall spinning process.

Rheology provides a useful method for studying polymer solutions [4, 5]. Examples of shear and oscillatory measurements on a typical native fibroin solution are shown in Figure 1. Analysis of the data using the Maxwell model for viscoelasticity and the Rouse theory [6] has provided information on effective molecular weight (M) and average molecular weight between entanglements (M_e) for the species present. Although the data shows significant sample-to-sample differences, consistent with measurements on a naturally variable biological system, the consensus (from over 100 analyses) suggests $M \approx 250 – 300$ kDa and $M_e \approx 60 – 90$ kDa, equivalent to roughly 3 to 5 entanglements per chain.

Fig. 2: SAXS of: (a) native silk protein solution, fitted using the Debye model for a random coil with R_G = 2·5 nm; (b) diluted (1 % w/w) solution fitted using the Debye model for a random coil with R_G = 10·5 nm.

This seems a surprisingly small amount of entanglement for such large molecules, but may indicate that the protein chains in the native feedstock solution adopt a rather dense tertiary structure. This could be due to the balance between sequences of hydrophilic and hydrophobic amino-acids, intramolecular hydrogen bonding and disulphide bridges between cysteine residues.

Further information concerning the structure of the native fibroin solution can be gained using small-angle X-ray or neutron scattering (SAXS or SANS). SAXS patterns appeared relatively featureless, with the intensity decreasing progressively towards higher angles; nevertheless, the data fitted the Debye model (for random polymer coils) very well, as shown in Figure 2.

The best fit for the native protein solution (Fig. 2a) was achieved with R_G = 2·5 nm. This must be viewed with caution, though, as the chains are expected to be interpenetrated. Hence, this is an effective R_G, perhaps associated with density variations between the centre of the polymer coils and the (interpenetrating) periphery.
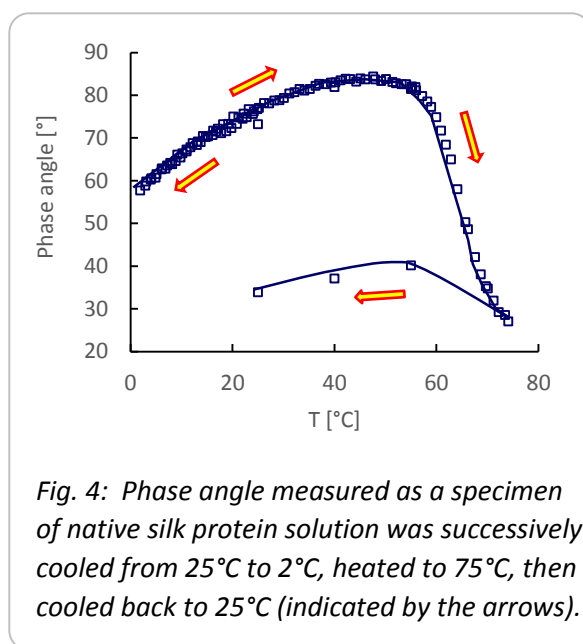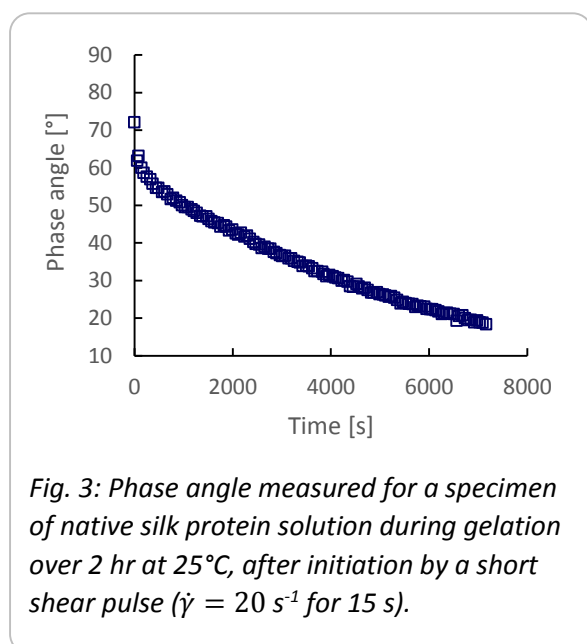
The extent of chain overlap can be reduced by dilution. Hence, a more reasonable value of R_G = 10·5 nm for the native protein molecules was obtained from the diluted solution (Fig. 2b). This value agreed well with previously published results from SANS [7]. Moreover, based on the average contour length and formula weight of an amino-acid, this value of R_G corresponded to $M \approx 269$ kDa, which agreed with expectations and the estimate from rheology. (Note: while the main fibroin chains are expected to have M around 400 kDa, the mean value in the native protein solution is expected to be lower, due to smaller proteins that are also present.)

Preliminary results on shear-initiated gelation are shown in Figure 3. A relatively short period of high shear ($\dot{\gamma} = 20$ s^{-1} for 15 s, at 25°C) was used to initiate the gelation process, which was subsequently monitored by oscillatory measurements (at 0·1 Hz). Although the native protein solution appeared to be still in a liquid-like state immediately after the initiation ($G' < G''$,

phase angle $\delta > 45°$), a progressive decrease in δ occurred over time with conversion to a gel state ($G' > G''$, $\delta < 45°$) beyond about 28 min.

Silk protein solutions can also undergo thermal gelation, as demonstrated in Figure 4. Starting from 25°C, the physical properties of the solution changed as the temperature was first lowered (to 2°C) then heated, as indicated by the changes in phase angle. Nevertheless, it was found that the solution remained in the liquid state ($\delta > 45°$) up to around 60°C. Gelation occurred rapidly above that temperature, as indicated by the steep decrease in δ.

This process showed some superficial similarities to lower critical solution temperature (LCST) behaviour [8] and may have a common underlying explanation in terms of the balance between a (favourable) enthalpy of solvation and (unfavourable) entropy of solution. In stark contrast to typical LCST behaviour, however, the silk protein gel did not return to the liquid state as the temperature was lowered, as indicated by the lower branch of the plot in Figure 4.

Fig. 3: Phase angle measured for a specimen of native silk protein solution during gelation over 2 hr at 25°C, after initiation by a short shear pulse ($\dot{\gamma} = 20$ s^{-1} for 15 s).

Fig. 4: Phase angle measured as a specimen of native silk protein solution was successively cooled from 25°C to 2°C, heated to 75°C, then cooled back to 25°C (indicated by the arrows).

Although the science underlying natural silk fibre spinning has received much attention, there still seems to be much to learn. This is a key aspect of our work. Moreover, we suggest that a good understanding of the physical chemistry involved in converting the (liquid) feedstock to the (solid) fibre would tell us much concerning protein folding and stability, with possible benefits in fields as diverse as food science and the biochemistry of disease.

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Clay nanoparticle based gels as injectable stem cell microenvironments for regenerative medicine

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Regenerative medicine seeks to harness the tissue forming potential of stem cells to replace tissue lost or damaged through injury and disease. A central component of this strategy is the 3D matrix which serves to deliver and maintain at the site of damage an extracellular niche conducive for stem cell-mediated tissue regeneration. Important to this function is the ability to retain, in space and time the necessary bioactive molecules involved in the growth and differentiation of stem and progenitor populations.

Polymeric hydrogels have been extensively explored in this regard. However, while the high water content (>90%) of hydrogels facilitates diffusion of nutrients and contributes to the biocompatibility of the material their characteristically open hydrophilic polymer networks typically result in the rapid release of incorporated proteins necessitating elaborate modifications for extended protein retention.

Clays have been widely used for modified drug delivery approaches. Typically, clay particles are dispersed in drug solutions, recovered as a solid phase upon equilibration and dried to allow delivery of the drug-clay complex in tablet form. Alternatively clay particle aggregations in saline slurries or polymer-clay nanocomposites have also been developed with the aim of modified drug release.

We have explored the potential to harness the sorptive capacity of clay nanoparticles for tissue regeneration through electrolyte-induced formation of gel capsules from pristine clay particles with the aim of developing chemically defined niches for stem-cell mediated regeneration.[1,2]

Flocculation of clay particles in electrolyte solutions significantly enhances the sorptive capacity of clay and facilitates the entrapment of active molecules.[3] Pre-dispersed nano-suspensions of the synthetic hectorite, Laponite displayed high and broad-spectrum affinity for proteins in saline solution (including cell culture media) following drop-wise addition and resultant gelation. Negligible release of either albumin (66.4 kDa, PI, 4.7) or lysozyme (14.4 kDa, PI, 11) from the clay gel capsules was observed and, furthermore, clay–gel capsule formation induced active uptake of the two proteins from the media via sorption to the gel capsule surface.

The utility of this approach to generate niches for tissue regeneration was demonstrated both with the matrix molecules fibronectin and type I collagen, the angiogenic vascular endothelial growth factor (VEGF) and osteogenic Bone Morphogenic Protein 2 (BMP2). Addition of fibronectin and type I collagen into clay gel films stabilized the tubule formation of cultured endothelial cells, co-encapsulation of fibronectin into clay gel capsules enhanced the chondrogenic differentiation of mesenchymal stem cells, and induction of blood vessel growth and ectopic bone formation through the clay gel encapsulation of VEGF and BMP2 respectively.

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Effects of Added Silica Nanoparticles on Smectite Clay Gels

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Smectite clay minerals are layered aluminosilicate compounds consisting of two tetrahedral layers sandwiching one octahedral layer.The whole structure bears a negative layer charge compensated by interlayer exchangeable cations. An important property of smectite clay minerals is their ability to form yield stress materials when dispersed in water at very low concentrations (1vol% or even less)[1].This feature is used extensively in various industrial applications (drilling fluids, cosmetics, etc.). In this talk we will discuss the rheology modification of smectite clay gels by adding small amounts of silica nanoparticles[2]. Depending on the nature of the nanoparticle and the concentration regime, this can result in either gel enhancement or gel breaking.

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Rheological Characterisation of Non-Equilibrium Highly Yielding Synthetic Layered Silicate (SLS) Colloidal Gels.

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Synthetic layered silicate (SLS), also described as synthetic hectorites, magnesium silicates, etc., are a widely used rheology modifier. These types of synthetic clays form aqueous colloidal gels which display extreme shear thinning post yielding and high gel strength before yielding. It should be noted that we define a gel as when G'>G'' at all frequencies[1] (when the stress amplitude is within the linear viscoelastic region (LVR)). Furthermore the small particle size provides significantly improved network recovery rates and clarity when compared to natural clays. These properties have rendered them important in the formulation of such products as; metallic pigment coatings, cosmetics, toothpaste, drilling fluids and shower gels. All of these applications utilise the rheology of SLS dispersions to create such final performances of as; pigment orientation, anti-settling/creaming and optimised sagging/levelling.

To characterise the gelation properties, 3% w/w SLS dispersions in synthetic tap water were chosen as model systems and analysed through oscillatory rheology. Previous research[2,3] has often focussed on looking at SLS in deionised water – where the gelation process is slowed considerably. Under "synthetic tap water" electrolyte conditions the systems display an optimum rheological performance as repulsion between the negatively charged SLS platelets is reduced by shielding from the co-ions. This enables a more rapid generation of the edge-to-face house of cards structure causing rapid and strong gelation. It was considered that these conditions were more akin to real world conditions (albeit with higher SLS loadings than would normally be used).

The gelation properties of SLS colloidal gels were best characterised by the LVR storage modulus (G'_0), also referred to as the gel strength, and the yield stress (τ_y) as determined by an amplitude sweep, see figure 1. Where G'_0 defines the extent of the network and therefore the anti-settling/sag performance and the τ_y defines the energy required to shear melt the gel. This definition of yield stress was preferred to the traditional G'/G'' cross-over point or the onset of decrease in G' due to said metrics being either in a region of non-linear viscoelasticity or subject to user error.

Within this definition of gel strength some unique arrested gel properties of SLS dispersions became apparent. Firstly when trying to define a period of rest post sample loading, i.e. shearing, no equilibrium state was observed. Figure 2 displays the recovery of the SLS colloidal gel strength post a pre-shear of $500 s^{-1}$ for 300 seconds, wherein it can be observed that even after 3 days the LVR storage modulus continues to increase. It is hypothesised the system will increase in gel strength, albeit at an ever decreasing rate, to infinity as the thermodynamically preferred process of gelation kinetically hinders itself. Secondly it was apparent that the pre-shear conditions are critical. In figure 3 it can be observed that both the duration and rate of the pre-shear impacts the magnitude of the gel strength measured after a constant equilibration period. This means that there is minimum shear energy required to complete the shear melting of SLS colloidal gels and that above that energy agglomerates of SLS particles can continue to exist independent of the shear duration. Shukla and Joshi[4] using oscillatory shear to generate extreme shear profiles couldn't identify a zero energy melt stage – it may be impossible to reach this condition with current rheometers. Finally after controlling the pre-shear and equilibration it was observed that the gel strength was also dependent upon the rest time (number of days resting post preparation) of the SLS gel, see figure 4. This is a result of the pre-shear conditions not taking the gel to

the minimum energy state and that the gelation process continues indefinitely, such that the shear melting stage results in increasingly structured melts with increasing rest time (i.e. increasingly structured pre-melt gels). These effects have also been reported by Shahin and Joshi[5].

In conclusion the arrested nature of SLS colloidal gels means that they never reach an equilibrium condition. This means that rheological analysis of their structure is always compromised by said structure continually evolving. To ensure that reliable measurements are made care needs to be taken in controlling; shear melting during sample loading, post-melting equilibration and rest time during which the sample can generate its initial inherent structure.
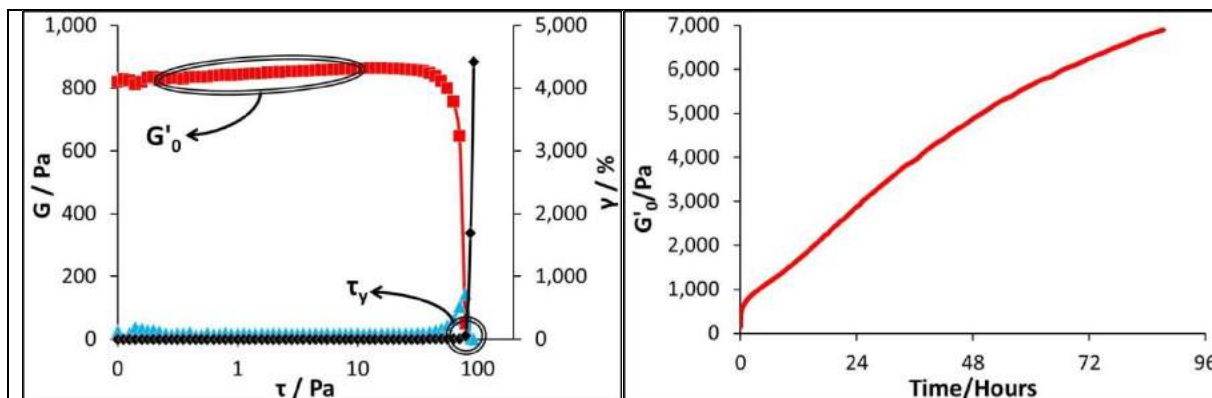
Figure 1; Oscillatory amplitude sweep of 3% w/w SLS dispersion in synthetic tap water. Storage modulus (red), loss modulus (blue) and oscillatory strain (black – 2nd axis) are plotted against oscillatory stress. The gel strength and yield stress are clearly indicated. Collected on a TA HR2 rheometer using a 60mm 1° cone and plate geometry at 1 Hz after a pre-shear of 500s^{-1} for 60s^{-1} and an equilibration of 10mins under ambient conditions.	Figure 2; Gel strength of a 3% w/w SLS dispersion as a function of time post shear-melting. Collected on a TA HR2 rheometer using a DIN Concentric Cylinder geometry at 1 Hz and 1-2Pa after a pre-shear of 500s^{-1} for 60s^{-1} under ambient conditions..
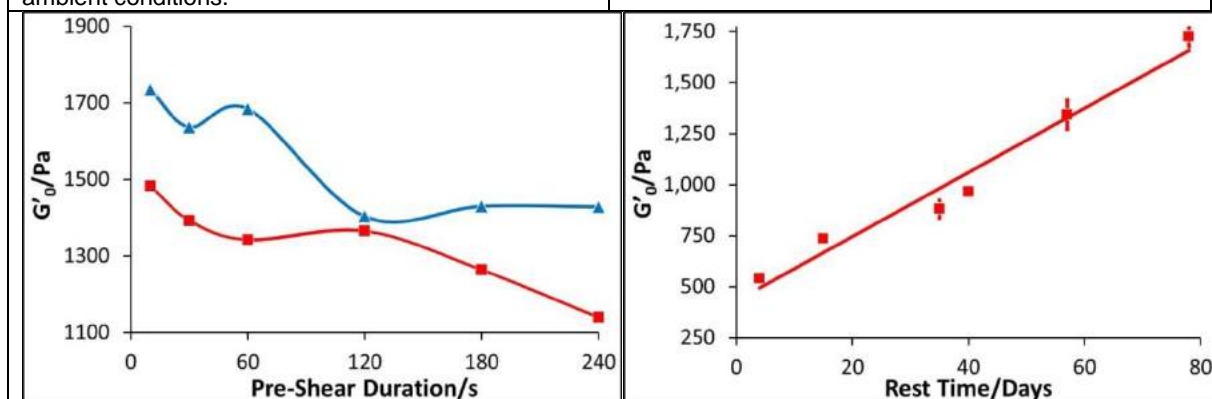
Figure 3; Gel strength of a 3% w/w SLS dispersion as a function of pre-shear duration at pre-shear rates of 500s^{-1} (red) and 100s^{-1} (blue). Collected on a TA HR2 rheometer using a 60mm 1° cone and plate geometry at 1 Hz and 1Pa with an equilibration of 10mins under ambient conditions.	Figure 4; Gel strength of a 3% w/w SLS dispersion as a function of rest time. Collected on a TA HR2 rheometer using a 60mm 1° cone and plate geometry at 1 Hz and 1Pa with a pre-shear of 500s^{-1} for 60 seconds and an equilibration of 10mins under ambient conditions. Errors are quoted to two standard deviations of 3 measurements.

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Metastable supramolecular micellar solution correlations with final hydrogel properties

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We are interested in preparing hydrogels by the self-assembly of small molecules. The understanding of the phenomena behind this self-assembly is of paramount importance if we wish to build multi-functional materials and devices. These materials have the potential to be easily manufactured, biocompatible, and reusable and can contain as much as 99.9 wt% water. Additionally, these self-assembled gels have a strong resemblance to other systems seen in nature (e.g. extracellular matrix, microtubule (inner cell environment) and amyloid diseases (uncontrolled fiber aggregate formation). We have recently come to realize the importance of the self-assembly process in determining mechanical properties of low molecular weight hydrogels (LMWG) [1, 2, 3, 4, 5].

We have devised a new pH triggered method of self-assembly using the acidification from the liquid-air interface with CO_2 (method 1) or in a two-step process, with the additional use of hydrolysis of glucono-delta-lactone as proton donor to the solution to lower the pH (method 2). These new methods (Figure 1) allow us to not only make significantly different materials in terms of mechanical properties and microscopic interactions with the same structural component, but also allow us to study an intermediate stage of self-assembly, where the pH of the solution is equal to the pK_a of the LMWG [2].

We understand that the self-assembly in confinements [3] and interfaces [4] allows us to form elastic films of peptides coating the interface. These interface-focused assembly

Figure 1 – CO_2 gas-phase pH-switch gelation of BrNapAV by method 1 (A, B, C) and by method 2 (D, E, and F).

processes modify the mechanical properties of the solution. This is visible through a reduced evaporation, delayed collapse of small liquid droplets of solution [3] and trapping air bubbles in the liquid phase [4].

Furthermore, we have found it is possible to magnetically align the micellar solutions preceding the hydrogels [5]. Additionally, it is possible to self-assemble these LMWG using either the pH-switch method or by adding a suitable salt such as $CaCl_2$ to keep the alignment on hydrogel formation (modifying the self-assembly pathway, but maintaining the magnetic alignment).

We are currently investigating the molecular, microstructural and macroscopic transformations and the corresponding macroscopic effects in order to establish self-assembly principles to build more complex supramolecular materials. In order to further understand these assemblies, we have determined the phase diagram of specific micellar solutions at high pH. We have then triggered gelation and attempted to correlate the phases and transformations with the final metastable hydrogel properties. Our current work uses the rheological, scattering, microscopy and ionic measurements to characterise the micellar phases, which include liquid crystalline phases, worm-like micellar phases and spherical aggregate phases (Figure 2), and evaluate if the colloidal phases are connected with the hydrogel properties. Interestingly, the thermodynamic and kinetic interplay in the network formation results in different mechanical properties when temperature and aging (time-evolution) effects are considered.
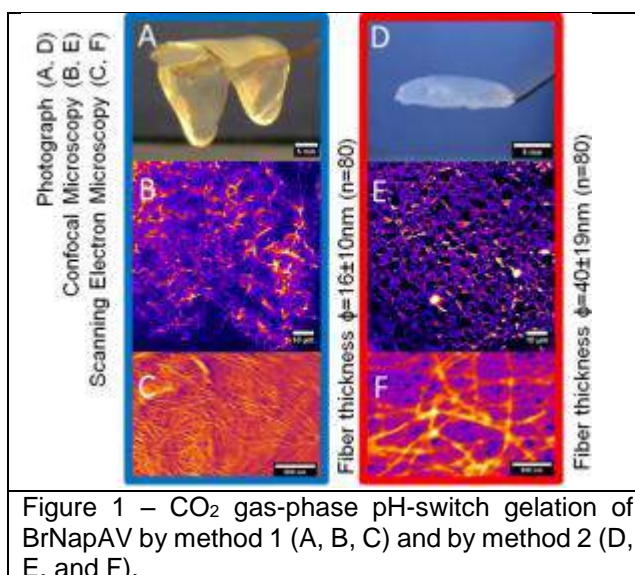
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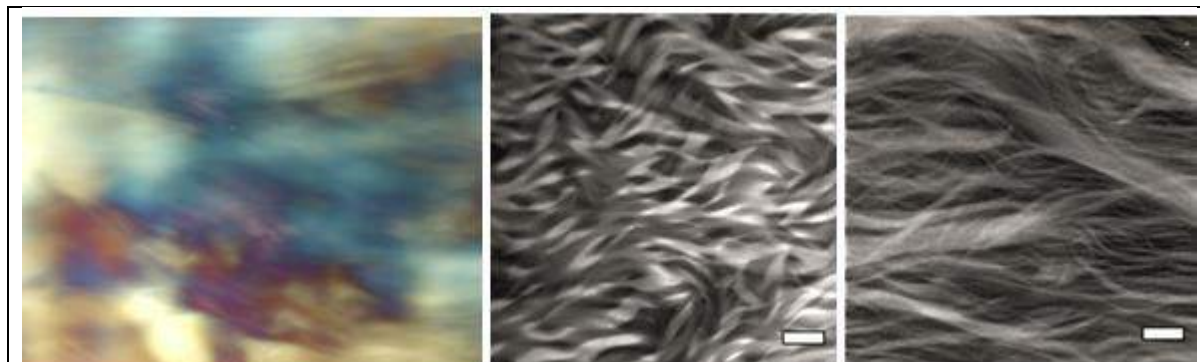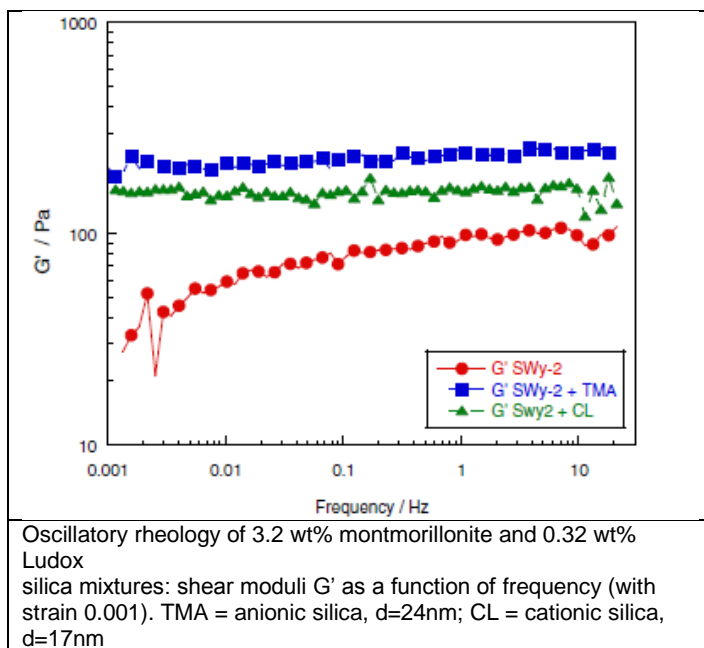
Figure 2 – Solution of 2NapFF liquid-crystalline phase with optical microscopy 20x magnification (cross-polarizers) (left), Confocal microscopy of 2NapFF solution in liquid crystalline phase (middle) and salt-switched assembled hydrogel (right) stained with Nile Blue (scale bar: 50 um).

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Oscillatory rheology of 3.2 wt% montmorillonite and 0.32 wt% Ludox
silica mixtures: shear moduli G' as a function of frequency (with strain 0.001). TMA = anionic silica, d=24nm; CL = cationic silica, d=17nm

Abstracts for Poster Presentations

Dynamics and structure: a study of arrest in a non-aqueous colloidal system

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Overbased detergents are a class of engine oil additive which have been routinely used since the 1940s [1]. Included in the lubricant to prevent deposit formation and to neutralise acids, they promote engine cleanliness, fuel efficiency and extend the life-time of the engine. The additive consists of colloidal metal carbonate nanoparticles (typically 1 – 10 nm in diameter) stabilised by an adsorbed surfactant layer. With the increased use of bio-diesel, an increase in the volume of polar liquids (such as water and acetic acid) contaminating the lubricant has been observed. It is known that water hinders the efficacy of overbased detergents [2]; however, the interactions of the polar species and additive are not fully understood.

Previous work in the group has been undertaken to study the effect of water on sulfonate surfactant based systems. Using FT-IR, small angle neutron scattering and dynamic light scattering, it was shown that water forms a layer around the core of the overbased detergent particles [3]. Whilst they remained suspended in the solvent, other studies have shown that their acid neutralising capability decreased.

Upon the addition of water to solutions of a particular salicylate overbased detergent in n-dodecane, gelling occurs over a period of weeks. The dynamics of gelling and mechanical properties of the gel have been found to vary depending on the volume fraction of particles and the volume of water added. The arrest is hypothesised to be due to a bridging space spanning structure, induced by the formation of aggregates of surfactant.

Fig. 1. Normalised intensity correlation functions of one gelling sample over 5 weeks (taken using dynamic light scattering.
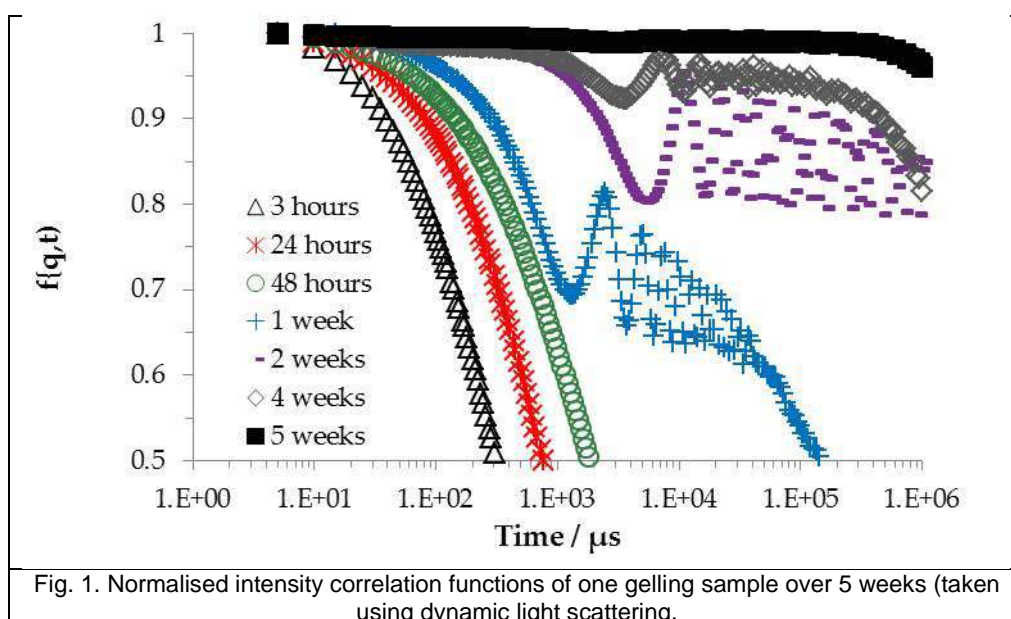
This system has been studied by dynamic light scattering (see fig. 1) and small angle neutron scattering. The gels have been characterised using controlled stress rheology and thermogravimetric analysis; results have shown different compositions and rheological properties at different sample heights. Varying the particle volume fraction, volume fraction of contaminant, free surfactant concentration and length of the *n*-alkane solvent chain have all been found to have an impact on the dynamics of the arrest.

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Formulating Complex Products Containing Sodium Carboxymetyl Cellulose (Na CMC)

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Food, pharmaceutical, personal and home care products stem from complex formulations containing multiple types of components such as salts, emulsifiers, solid particles, flavour/fragrance oils and gelling or thickening agents. Typically, the active ingredients allow the product to fulfil its purpose while others are incorporated to manage the product structure, its taste or its shelf-life. A general challenge in formulating such complex systems is to understand the interactions between all the components and their effects on the efficiency and the stability of the product over its full shelf-life.

The aim of this study is to investigate the interactions between one widely used thickener and some standard components of complex formulations of such products. The behaviour of thickener solutions at different concentrations is studied before other system components of interest are added. The selected thickening agent is Sodium Carboxymethyl Cellulose (Na CMC) which is a water-soluble negatively charged linear polymer derived from cellulose. It is well known that its behaviour in water is very complex and a function of several parameters including the characteristics of the polymer itself (i.e. molecular weight, degree of substitution), its dissolution within the aqueous phase (i.e. comprising type of mixing and addition order of the system components) and its concentration. Rheology and Dynamic Light Scattering (DLS) techniques are used here to explore some of the variables above in studying the properties of simple Na CMC solutions. The poster presents some preliminary results of this study.

Delayed collapse of concentrated dispersions flocculated in a secondary minimum.

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It is possible to arrange for the controlled secondary minimum flocculation of colloidal particles by deliberately choosing stabiliser moieties that are too short to attenuate the VdW force entirely. This trick has been used in aqueous media by us [1,7] and by Bergstrom in a non-aqueous medium [2], to obtain interparticle potential well-depths of magnitude 5 kT upwards.

It has been argued from the scaling of delay times that, whereas the delayed collapse of such systems is undoubtedly an activated process, it depends upon the activated diffusion of particles in environments that are significantly less concentrated that the average [1]. The interface between particulate and medium is one such environment and hence that could be taken as a hint that interfacial diffusion might be important. Furthermore, the delay and collapse time scaling reported by Teece et al. [3] can be interpreted in this way [4]. The most compelling case for the importance surface diffusion is however made by the recent work of Zia et al. [5] who used large-scale LAMMPS simulations to study coarsening in detail.

Because monodisperse non-ionic surfactants are very difficult to make and hard to source, only one chain-length was used in the current work ($C_{12}E_6$), together with three particle sizes, as shown in the table nearby; the well-depth and particle size being proportional: the fourth column to be explained below.

Delay times were measured as a function of volume-fraction, both under normal gravity and in a swing-out centrifuge at 1.5 and 7 'g'. The storage modulus G' measured at ca. 200 Hz and a strain ~ 1ppm by means of wave-propagation will be reported too. The latter is plotted in fig. 1. The moduli vary like $\varphi^{3.9}$, the exponent being similar to that seen for strong (coagulated) PSL gels, although the magnitude

PS latex	Particle radius a (nm)	Well depth U/kT	Delay time ratio
SJP8	490	- 6.4	1
SJP10	710	-10.8	0.88
SJP11	960	-13.7	0.63

is ca. 500 times smaller, as is shown in the appended figure on p.3. G' appears to be independent of particle size, the scatter not withstanding, which is surprising at first sight, since scaling on kTU/a^3 ~ a^{-2} might have been expected. The latter fails to recognise though that the network strands might be rope like rather than thread like, whereby Zia et al. [5] suggest an additional proportionality to the characteristic strand thickness L/a. Interpreted in these terms the data in fig. 1 imply L/a ~ a^{-2}, which could also be L/a ~ a^{-1}/U for the present SM case (cf. the table above).

The delay times are plotted in fig. 2. They scale like $\varphi^{2.8}/g$, where g is the dimensionless acceleration (normal gravity = 1). They are found to be nearly, but not quite, independent of particle size too. The average ratio of times obtained from fits to each size separately is shown in the fourth column of the table above.
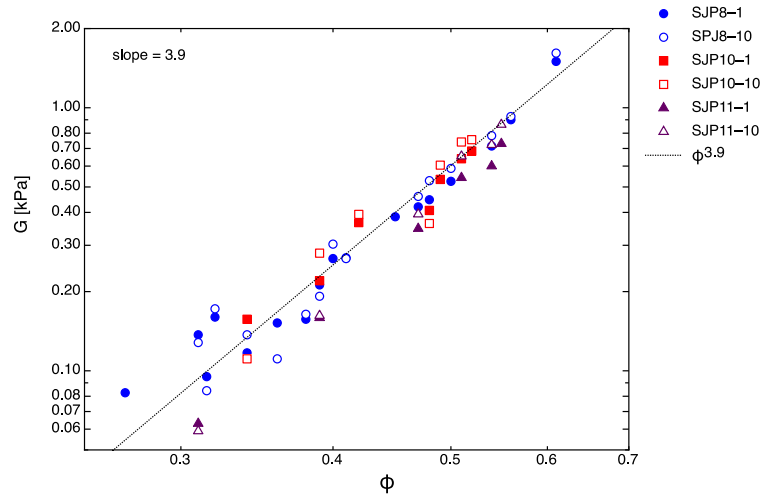

Fig. 1 G' versus volume-fraction for the three latices.

The inverse linear dependence on g might again be thought surprising, given that collapse is an activated process, since then tilting of the energy landscape by the body force might have been expected to give an exponential increase in rate and indeed this feature puzzled us for some time.

Induction time scaled by mean acceleration versus volume fraction for SJP8,10 &11
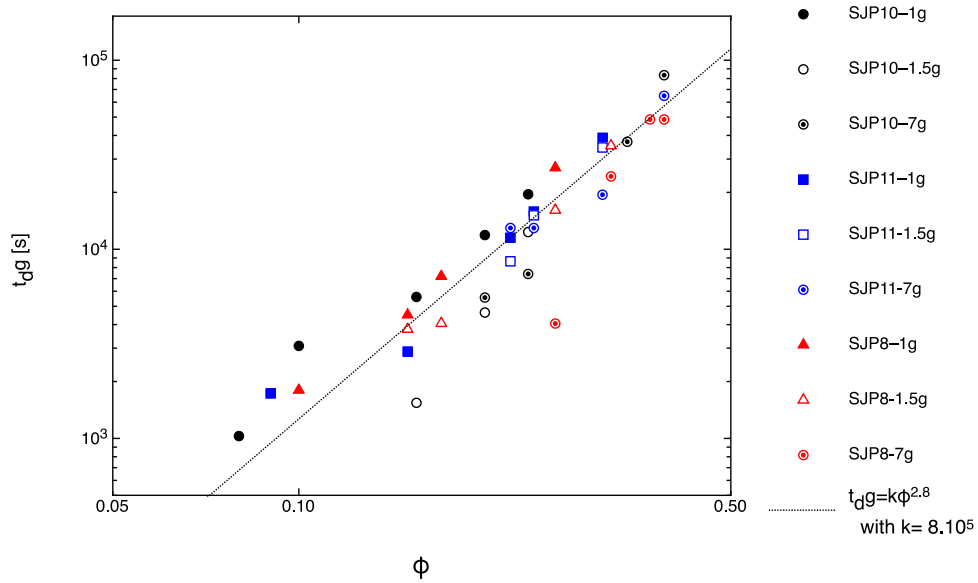
Fig. 2 scaled delay times versus concentration: the times have be multiplied by g and divided by the factors given in the RH column of the table.

Interfacial diffusion and the presence of a fluid interfacial region [5] could however account for this perhaps, with gravity driven flow superposed on the interfacial diffusion and enabled near the interface. By such means particles might be transported to the bottom of the gel by means of gravity imposing a bias or drift on the interfacial diffusion. One problem with this scenario is that it would not appear to explain the Rayleigh-Taylor instability seen in very weak gels [6]. The parameter space over which delayed collapse occurs is huge however [1] and hence it cannot be assumed necessarily that the mode and mechanism of collapse are the same across the parameter space, a general scaling of delay and collapse times not withstanding

[1]. Furthermore, there has to be a return upward flow in the pores, hence transport of particles upwards by erosion cannot be precluded in marginally rigid gels, as can not local variations, given that the particle and fluid flows need only be opposite and balanced net.

It is ca. 30 years since the phenomenon of delayed collapse was first recognised as a physical effect [7], as opposed to, say, being a result of colloidal or chemical instability, yet it still remains rather poorly understood. It was mentioned above that the parameter space (of well-depth, particle size, particle concentration, etc.) for collapse is huge. It is thus almost inevitable that it has only been explored sparsely, with volume-fraction as a neglected variable; this being the case for the zero-shear viscosity too [8]: the effects of particle size and volume-fraction in particular would benefit from further systematic exploration. The effect of centrifugal acceleration looks to be worth exploring further too.

The three separate plots underlying fig. 2 can be found at [4].

Malcolm Faers is thank for helpful discussions; in particular for pointing out that transport of eroded particles upwards by backflow could contribute to destabilisation.

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***Appendix** – comparison of the moduli of SM flocculated and coagulated polystyrene latex. Also shown is the compressive strength of the coagulated gel and, for comparison, similar data for SM flocculated alumina from [2].*
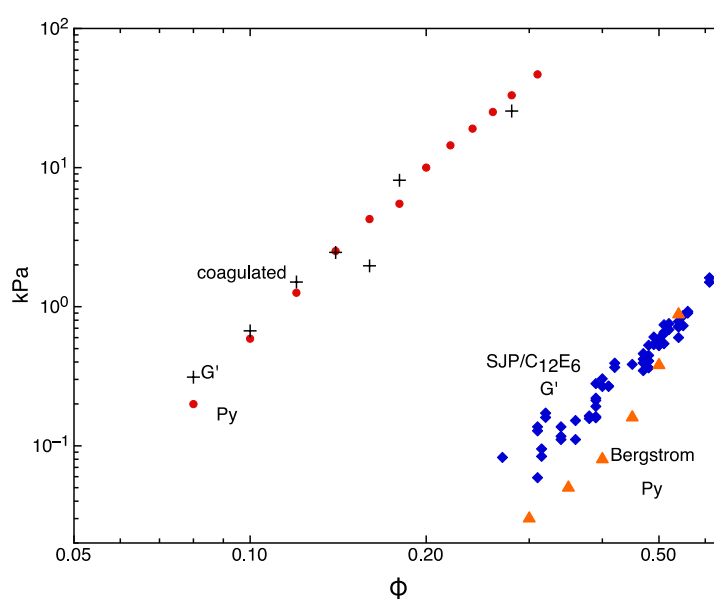
The constitutive behaviour of strong cohesive particulate gels in compression.

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Strong cohesive particulate gels undergo differential compression when they consolidate under gravity, or in a centrifuge, or when they are pressure-filtered or dried. Since the particles are sticky and a finite volumetric strain cannot sensibly be distinguished from a change in volume fraction, the volumetric Hencky strain is taken to be given by $\delta\varepsilon_H = \delta\ln\varphi$ and the bulk modulus by $K(\varphi) = dP(\varphi)/d\ln\varphi$ [1]. A simple prescription for the compressive strength P then follows, thus,

$$P(\phi) = \int_{\phi_0}^{\phi} K(x)\,d\ln(x) = \alpha \int_{\phi_0}^{\phi} G(x)\,d\ln(x) \ , \tag{1}$$

where G is the shear modulus and the order-one constant α is equal to 5/3 for the case of central forces only (by way of illustration). It follow from (1) that, strictly, $P = P(\phi, \phi_0)$ although the dependence on the starting concentration is predicted to be weak when the modulus increases rapidly with concentration, as it does in practice ($\varphi^{4.5+/-0.5}$ typically [1,6-9]), hence is usually found that $P \approx P(\phi)$, i.e., the compressive strength looks like a pseudo-material property, called the compressive yield stress by some. It is usually found also that compression is largely irreversible, which is at odds with the above prescription, from which one would expect 20% or more recoverable strain, depending upon volume fraction, given the exponent of ~4. The particles are however sticky and so a 'ratchet' [2] has invoked to explain this feature. It has been found also that above the gel-point a critical level of pressure needs to be exceeded before anything at all happens [1]; this being why $P(\phi)$ is often called the compressional yield stress. This feature certainly is at odds with the relationship above. There is however a reluctance to abandon eqn 1 nevertheless, because it does account for one very significant and widespread finding, viz. that $p \sim K \sim G \gg \sigma_y$ (away from the gel-point), where the σ_y is the shear yield stress. Cohesive particulate gels are however usually adhesive as well as cohesive and wall adhesion can explain this anomaly on laboratory scales, since then yield at the walls needs to take place [3,4].

The adhesion can be characterised by a wall shear stress σ_w[3], related to the bulk yield stress by,

$$\sigma_w \le \sigma_y \equiv \gamma_c G \tag{2}$$

where, γ_c is the apparent yield strain, defined as the ratio of yield stress to linear modulus. This definition adds nothing as such, but it provides a very convenient way of parameterizing adhesive strength [4,5,10].

Wall adhesive effects are expected to be unimportant when $\dfrac{20L\gamma_c G(\phi)}{3wp(\phi)} \ll 1$ [3,5],

where w and L are the horizontal width and vertical length of the sample, but significant otherwise. It is also easy to show from eqns 1 and 2 above that they are *always* expected to be important when and where the volume-fraction is very close to either, the starting concentration, ϕ_0, or the gel-point ϕ_g, whichever the greater, almost regardless of the value of γ_c.
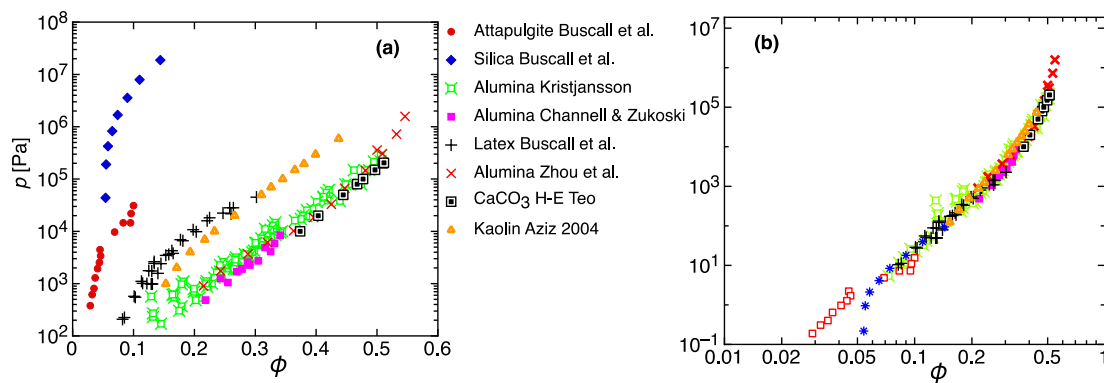
Fig. 1 Plots, semi-log and log, of compressive strength versus volume-fraction for a range of mineral suspensions and PSL [6-9]. In fig. (b) *the data in* (a) *have been scaled by shifting data on the ordinate.*

Fig. 1a shows a compilation of compressive strength data for some coagulated systems, including extensive data for colloidal alumina from 2 different labs and 4 different workers. Most of the suspensions depicted in fig.1 comprise either spheroidal or tuberoidal particles. The particle size range covered is enormous (from 4.5 µm $CaCO_3$ down to 26 nm SiO_2), although data for fine kaolin (lozenges) and attapulgite (long needles) is shown too. The data are scaled on the ordinate in fig. 1b. A master curve results. The only significant departure from the master curve is for SiO_2, which shows an obvious gel-point. The SiO_2 gels were however very strong by virtue of their small particles size (26 nm dia.) and it was only with this material that the methods used (centrifugation or pressure filtration) could measure near the gel-point. The gel-point of the colloidal alumina could well be similar to that of the silica though, as it looks to be 0.05 or less; see also fig. 2 which shows shear yield stress data for the colloidal alumina.

Fit= k $\phi^{3.0}$ (0.64-ϕ)$^{-1.8}$ with k = 2.4 kPa.
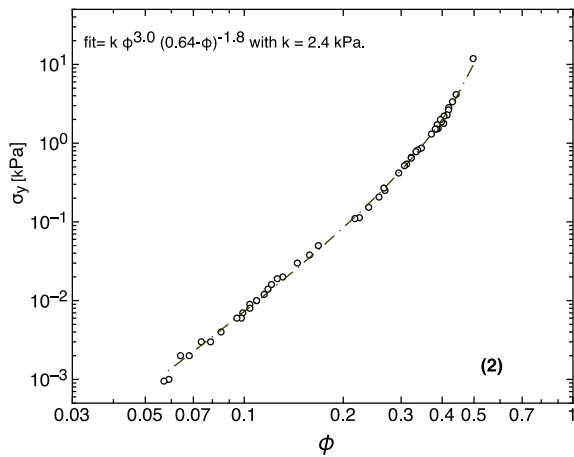
The concentration dependence of the shear yield stress is weaker than that of the compressive in the power-law region. The power-law of 3.0 is typical for shear, whereas the shear storage modulus is found to show a power of > 4 [1,6-9]. This tells us that the apparent critical strain defined by the RHS of eqn 2 increases with concentration. If eqns 1 is correct then, it should be possible to predict the compressive strength from the shear using eqns 1 and 2. The blue and red lines in

Fig. 3, show the results.

Fig. 2 Plot of shear yield stress versus volume-fraction for AKP-30 Alumina, fitted as shown.

The blue line was obtained by supposing that the apparent critical shear strain is constant (and 0.005), which we know it is not, and the red line by assuming that it is proportional to φ. The agreement between the red line experimental data is excellent for φ <0.4. Above that it is not, although there are good reasons why there might be a difference there, which space does not permit discussing here, except to say that neglect of the osmotic pressure of the particles is one aspect. The agreement below φ <0.4 is however most gratifying.

Direct experimental evidence in favour of the model encoded in eqns 1 and 2 is shown in the fig. 4, where the experimental ratio of shear to compressive strength is plotted against φ, together with the experimental uncertainty. The curves imply that the ratio starts at unity and decays rapidly with increasing volume fraction. This is exactly what eqns 1 and 2 predict must happen by embodying the idea that particulate gels are strain-hardening in compression and 'short' in shear, as they do. It alone is powerful evidence that eqns 1 and 2, simple though they are, capture most of the action. It should be noted though that the compressional data for alumina have not been corrected for wall adhesion, which must contaminate them to some extent at the lowest concentrations [10], doing so however could only make the rise towards one at low concentration even steeper, if anything, reinforcing the point. These corrections will however be made in due course and in time for the poster presentation.
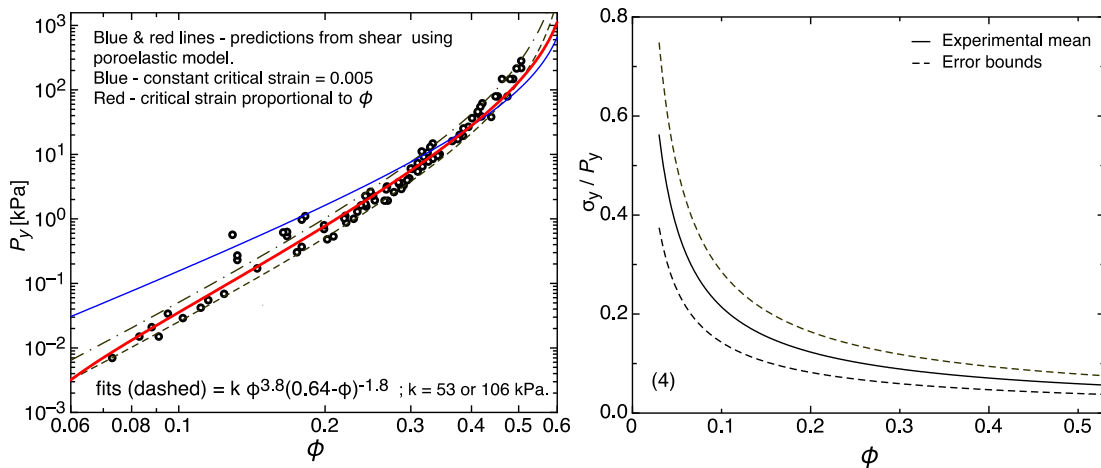

Fig. 3 - Compressional stress for AKP-30 Alumina, fitted as shown and compared with predictions made from the data in fig. 2 using eqns 1 and 2 (see text). Fig. 4 – plot of shear to compressional strength ratio obtained from the fits shown in figs 2 and 3.

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Conclusion: The scalings for spherical particles shown here strongly favour the simple constitutive behaviour encoded in eqns 1 and 2. The fact that both particle size [9] and now shape can be scaled together in fig. 1a is remarkable. That this simplest of models cannot account for irreversibility, without hand-waving, nor for critical or yield-like behaviour, are concerns. Wall adhesion may however suffice to alleviate these [3-5,10]. It certainly looks as if it can in principle, but whether it does or not quantitatively is another matter, although work aimed at finding out is in progress. Supplementary material can be found at the end of a version posted at arXiv:1410.5280.

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Ageing and Delayed Collapse of Arrested Colloidal Gels by Vane Rheometry and Confocal Microscopy – Why do Some Colloidal Gels Suddenly Collapse?

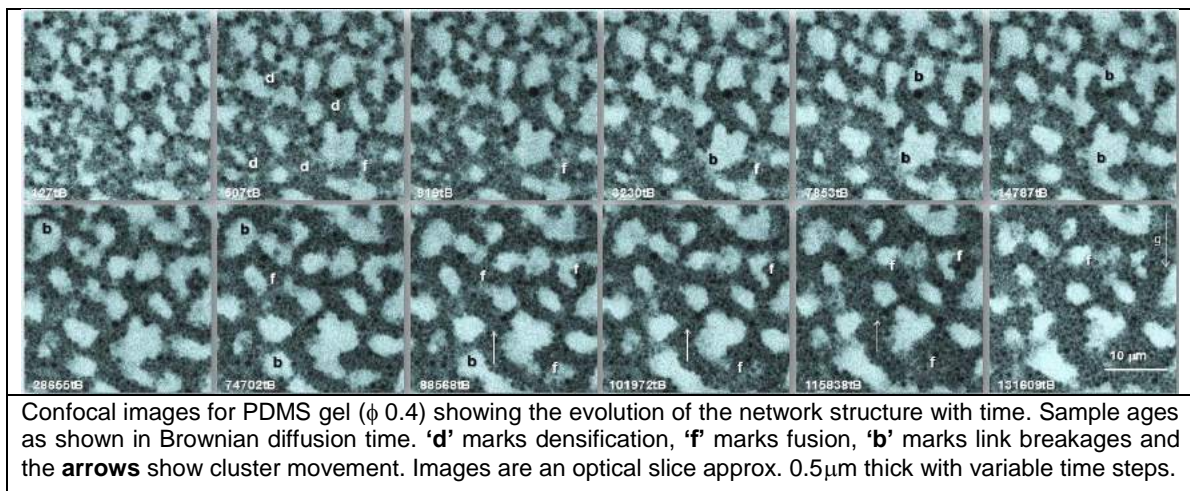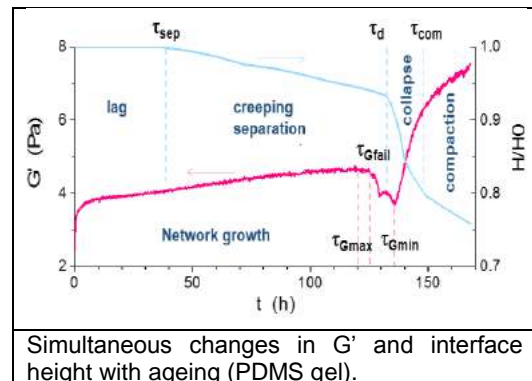M. A. Faers,[a] I Zhang,[b] C. P. Royall,[b] and P. Bartlett [b]

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The phenomenon of delayed collapse in colloidal gels, where an apparently stable colloidal gel unexpectedly separates even after long periods of stability, is a fascinating observation that is both of scientific interest and industrial relevance, and a detailed understanding of both the process and when it will or will not occur is not currently available.

To better understand this process, vane rheology measurements with a specially designed low height vane in transparent sample tubes and simultaneous time-lapse phase separation observations of weak colloidal gels that exhibited delayed collapse were performed. These were complimented with corresponding confocal microscopy observations of the microstructure specifically in the vertical plane. The experimental system was a special index matched PDMS emulsion with a medium-long range attraction induced by non-adsorbing HEC ($Rg/R=0.45$, $\Delta\rho$ 0.14 g cm^{-3}).

Increasing levels of HEC resulted in weak gels with a strength proportional to the HEC level that aged with time, corresponding to an increase in G' rheologically and an increase in the coarseness of the network microscopically. After ageing, collapse of the networks was observed as the rate of interface height change sharply increased for intermediate levels of HEC. This was seen as a sharp drop in G' and microscopically as a sharp increase in the velocity of phase separation of the network and a marked decrease in the network connectivity.

Simultaneous changes in G' and interface height with ageing (PDMS gel).

Confocal images for PDMS gel (ϕ 0.4) showing the evolution of the network structure with time. Sample ages as shown in Brownian diffusion time. **'d'** marks densification, **'f'** marks fusion, **'b'** marks link breakages and the **arrows** show cluster movement. Images are an optical slice approx. 0.5μm thick with variable time steps.

At the point of collapse there was a clear correlation between G' and the sharp change in interface height, starting first with a decrease in G' followed by the interface height. At higher levels of HEC no collapse was observed even after several weeks and ageing of the network continued without any observable end.

Analysis of the network microstructure in terms of connectors and clusters showed a decrease in both the number of connectors and clusters with time but without any correlation with the point of collapse, with collapse occurring while the network connectivity was still relatively high, showing that collapse was not due to loss of connectivity of the network. Reducing the density difference increased the delay time but interestingly did not alter the rate of increase in G' implying that the two processes are independent and that collapse is stress driven while the network ageing is not.

The increase in the mechanical strength of the gel network up to the point of collapse is an interesting finding giving new insights which imply that collapse occurs not from loss of connectivity but from stresses acting within the network that also increased with age.

Gel point determination thanks to microrheology

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This work presents a new technique of passive microrheology for the study of the microstructure viscoelastic properties and the gel point transition for polymers and hydrogels. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from the thermal energy, that is to say the Brownian motion.

Our technique is based on Diffusing Wave Spectroscopy. It consists of Dynamic Light Scattering (DLS) extended to an opaque media. The determination of the Mean Square Displacement (MSD) curve enables to characterize completely the viscoelastic properties of a sample. The technique allows to measure particles displacement in a spatial range between 0.1 and 100 nm and a time scale between 10^{-3} and 10^{5} seconds.

Biopolymers have been introduced to a large scale of formulation not only in the food sector. Their unique properties in stabilization, structuration as well as texturation made them to one of the most used components. Especially the gel formation capacity is of outmost interest.

This work presents a rescaling data processing known in rheology as time curing superposition [1-4], to determine precisely the gel point transition and gel strength parameters according to the Winter-Chabon-Criterion. Results will show the determination of the gel point versus time for carrageenan, gel point versus concentration for xanthan polymer, cross-linker concentration effect on the gel point.

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The Delayed Collapse Mechanism in Colloid-Polymer Gels

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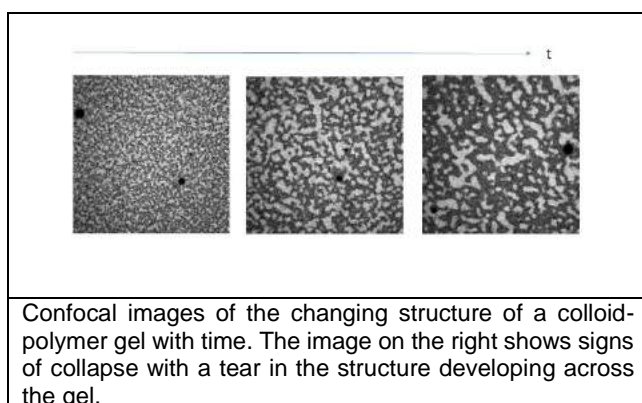
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The collapse of colloid-polymer gels formed by the depletion interaction has been studied for many years, due to its importance in soft matter in general and its application in commercial formulations such as those used in agriculture, paints and inks. The delayed collapse mechanism, which occurs in gels with intermediate attractions, consists of a delay stage where the gel remains stable followed by a rapid collapse of the network and sedimentation. The gel structure during the delay is not static[1], but gradually restructures because the interaction energy between gel particles is of the order of thermal energy. Whilst some theoretical models linking gel composition to delay time have been presented, predicting and controlling the delay time is not yet possible.

Here we present a review of recently published and unpublished work using vane rheology and confocal microscopy on silicone oil gels in aqueous solvent, with various biopolymers added as the thickener. The type of biopolymer added and the concentration controlled the structural length scale of the gel and the rate of restructuring respectively, as would be expected from previous studies. We also intend to perform research on the effect of gravitational forces on collapse. Studies using magnetic particles to apply a force acting against creaming suggest that this increases the delay time[2], but this study was limited in scope, so we expanded on it by doping our gels with silica particles of higher density than the solvent, with the intention of density matching the gel.

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Confocal images of the changing structure of a colloid-polymer gel with time. The image on the right shows signs of collapse with a tear in the structure developing across the gel.

Influence of the thermal history of agar sols on mechanical properties of gels

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Agar is a hydrophilic colloid present in numerous manufactured goods and involved in applications that ranges from food engineering where agar is used as a gelling agent [1] to biotechnology where agar gels commonly serve as growth media for microorganisms and as porous scaffold in tissue engineering [2,3]. Agar is a mixture of agaropectin, a charged sulfated carbohydrate polymer and agarose, a neutral polysaccharide. Insoluble in cold water, agar becomes soluble in boiling water and, once cooled down below 40°C, forms a thermo-reversible gel that does not melt below 80°C. The gelation process involves a competition between a spinodal demixing process and the association of agarose molecules in double helices [4-7]. This process leads to a fibrous network structure which properties are strongly influenced by the agarose concentration, the quenching rate and the final temperature [8-10].

The present work deals with the impact of the holding time of agar sol on the agar gel mechanical properties. Agar solutions are prepared by dispersing agar powder (1.5% wt.) in distilled water. The mixture is brought to a boil and later maintained at 80°C during 5 days. Samples are taken from the solution at different times ranging from 1 hour up to 5 days, and then used to prepare gels which mechanical and structural properties are characterized as follows.
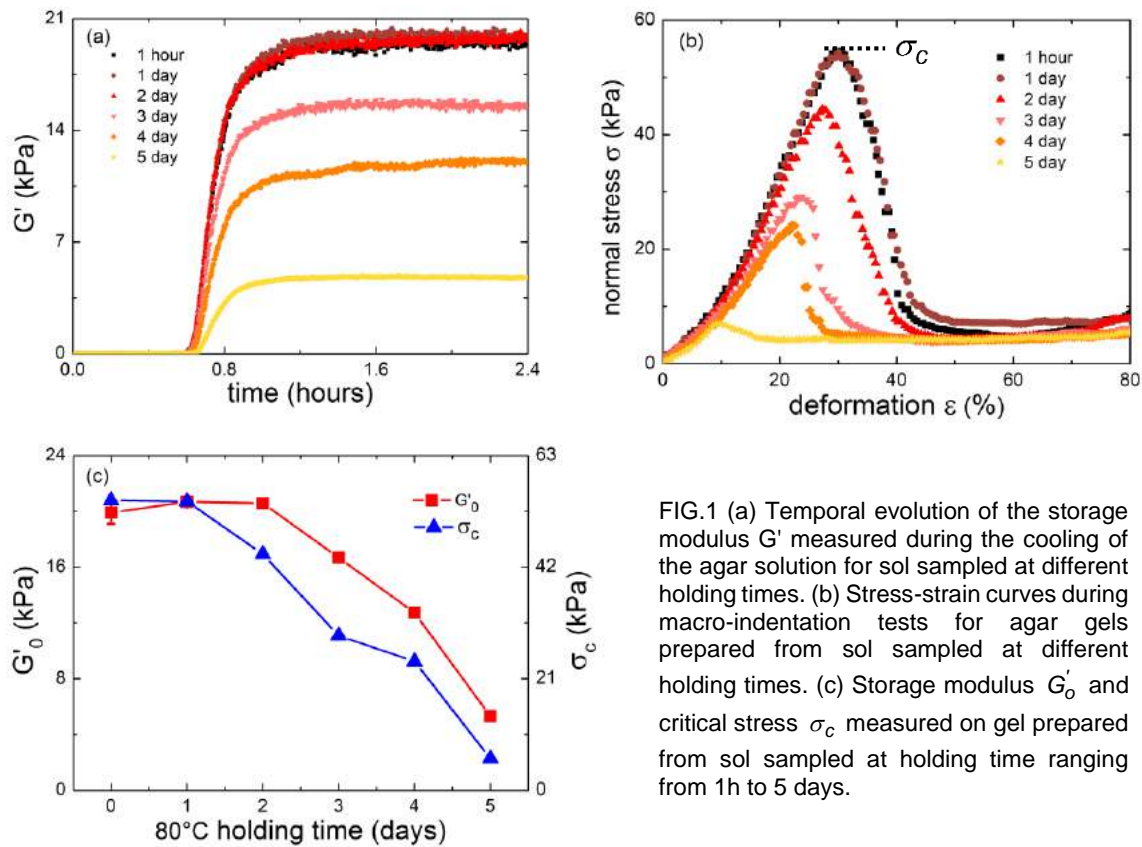

FIG.1 (a) Temporal evolution of the storage modulus G' measured during the cooling of the agar solution for sol sampled at different holding times. (b) Stress-strain curves during macro-indentation tests for agar gels prepared from sol sampled at different holding times. (c) Storage modulus G'_o and critical stress σ_c measured on gel prepared from sol sampled at holding time ranging from 1h to 5 days.

Hot sol samples are placed in the pre-heated gap of a plate-plate cell mounted on a stress-controlled rheometer. A decreasing ramp of temperature of 1°C/min cools down the sample from 80 to 20°C, while small amplitude oscillatory shear allows us to monitor the gel formation. Compensation of the gap size variation due to the temperature change and normal force cancelling by adjustment allow us to circumvent any issue due to gel contraction during its formation. As a key result, we observe that the gel elastic modulus is a decreasing function of the holding time at 80°C [Fig. 1(a)&(c)]. To further quantify the impact of the thermal history, sol samples taken at different holding times are casted in a glass plate and left to cool down at room temperature to form gel cylinders of 4mm thick. Macro-indentation experiments performed under large strain confirm that the older the sol, i.e. the longer the holding time, the weaker and the more ductile is the gel [Fig.1(b)]. This result suggests that the gel microstructure is strongly affected by the sol thermal history. To confirm this hypothesis, scanning electron microscopy (Cryo-SEM) is performed on gels prepared from sol samples taken at different holding times. Gels prepared from samples taken at increasing holding times exhibit a microstructure of increasing porosity (Fig.2), which accounts for the ductile behavior of the gels. The slow formation of stable structures in the agar solution held at least two days at 80°C likely explains the coarser microstructure of gels prepared from such older agar solutions.
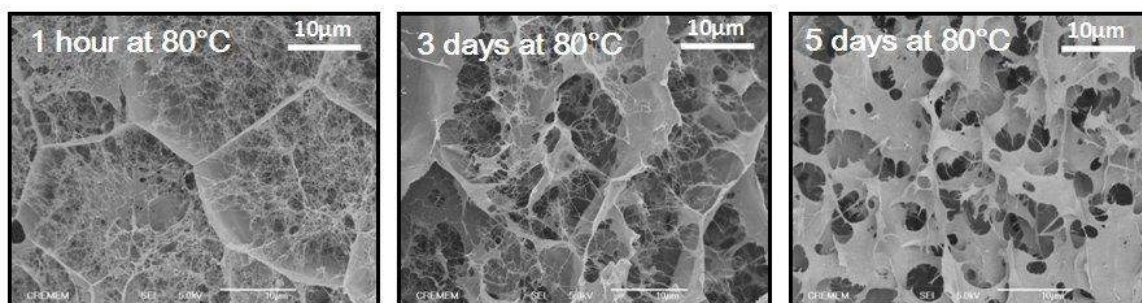

FIG.2 From left to right, Cryo-SEM images of agar gels formed after holding the aqueous agar sol at 80°C during 1 hour, 3 days and 5 days respectively.

In conclusion, the mechanical properties of agar gels strongly depend upon the thermal history of the agar solution. Holding the agar solution at a high temperature (80°C) during a few days promotes the formation of clusters in the sol that lead to gels with a coarser network and weaker mechanical properties.

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The role of the Hofmeister series in the gelation of colloidal silica

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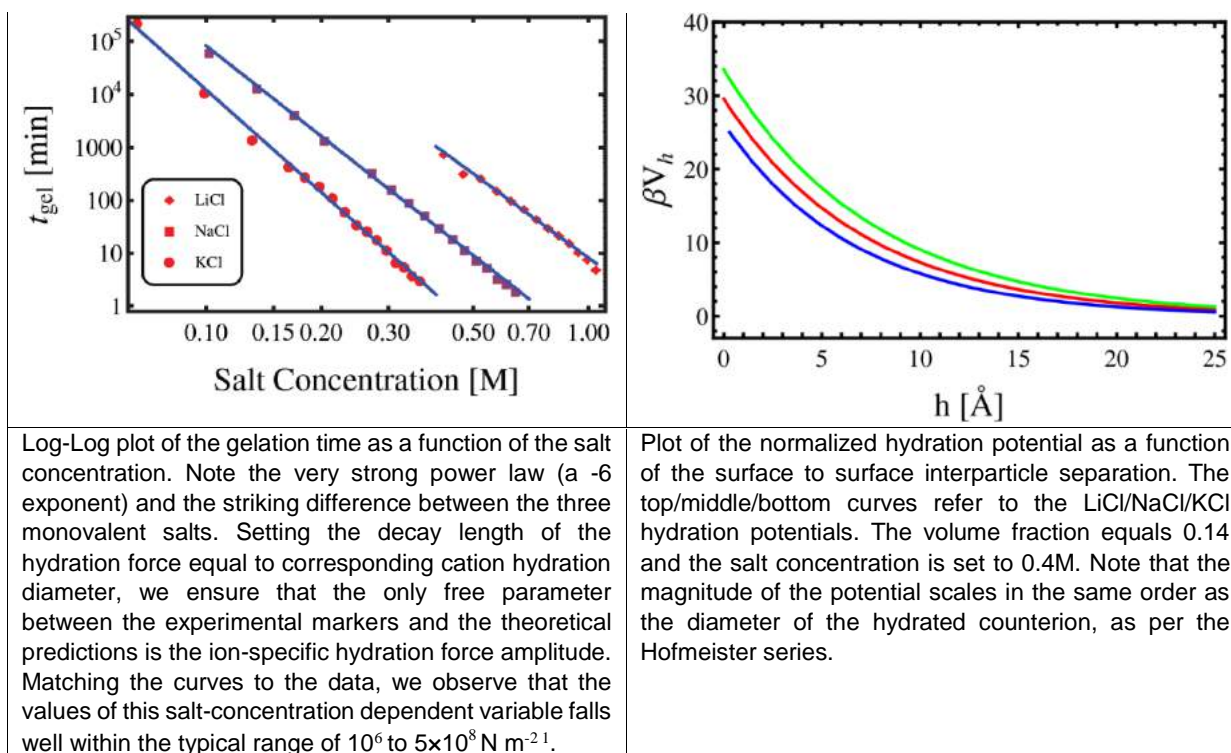
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A theory to explain the effects of ion-specificity on the gelation dynamics of silica nanoparticles is required. At high monovalent salt concentrations, we observed a correlation between the chaotropicity of the cation species and the measured gelation times. Classical DVLO theory, while immensely successful at low concentrations, cannot justify this anomaly in otherwise identical samples. This trend is consistent with the "Hofmeister series" and alludes to the presence of short-ranged surface hydration forces. In this work we treated such forces by introducing an additional exponentially-decaying, non-DVLO term. Employing recent theoretical results to connect the gelation times to the total interparticle potential, we proceeded to calibrate the magnitude of this hydration interaction. This supplementary force was found to dominate interparticle interactions at surface separations less than the hydration diameter of the cation. Its repulsion increases slightly with decreasing volume fraction, and declines at exceptionally high salt concentrations.

* These authors contributed equally to this work.

Log-Log plot of the gelation time as a function of the salt concentration. Note the very strong power law (a -6 exponent) and the striking difference between the three monovalent salts. Setting the decay length of the hydration force equal to corresponding cation hydration diameter, we ensure that the only free parameter between the experimental markers and the theoretical predictions is the ion-specific hydration force amplitude. Matching the curves to the data, we observe that the values of this salt-concentration dependent variable falls well within the typical range of 10^6 to 5×10^8 N m^{-2} [1].

Plot of the normalized hydration potential as a function of the surface to surface interparticle separation. The top/middle/bottom curves refer to the LiCl/NaCl/KCl hydration potentials. The volume fraction equals 0.14 and the salt concentration is set to 0.4M. Note that the magnitude of the potential scales in the same order as the diameter of the hydrated counterion, as per the Hofmeister series.

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Colloid-polymer interactions varied with temperature

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In this work, the interactions of a well-studied colloid-polymer mixture with the change of temperature are investigated. The effective attraction between colloids induced by the addition of non-adsorbing polymer decreased as the system is cooled approaching θ-temperature due to the decreasing radius of gyration. However, as the system is cooled the effective temperature increases, bringing about the 'melting' of colloidal gel [1]. Using the Asakura-Oosawa model for short-ranged colloidal interactions and a simple description of polymer temperature response, a quantitative description of the location of fluid-gel transition determined experimentally is feasible. Through the direct control of colloid-colloid interactions our system provides a means for direct control over the rate of self-assembly (crystallisation) and can thus explore recent numerical methods for optimizing self-assembly [2].

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Vitrification is continuous and gelation is quasi-discontinuous in sticky spheres

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Glasses and gels are the two dynamically arrested, disordered states of matter. Despite their importance, their similarities and differences remain elusive, especially at high density. We identify dynamical and structural signatures which distinguish the gel and glass transitions in a colloidal model system of hard and ``sticky'' spheres. Gelation is induced by crossing the gas-liquid phase-separation line and the resulting rapid densification of the colloid-rich phase. We find that gels can be formed at much higher densities than previously thought. Although these gels apparently look like glasses, far from being networks, the intrinsically "discontinuous" nature of the transition leads to a non-equilibrium state with distinct topological characteristics and local structures. This is markedly different from the glass transition, whose continuous nature leads to the formation of macroscopically homogeneous and locally equilibrated structures. Our findings provide a general thermodynamic, kinetic, structural, and topological basis upon which to distinguish gelation from vitrification.

1 Royall CP, Swilliams SR and Tanaka H, arXiv:1409.5469 (2014)

Fabrication and Stability of Food-grade Submicron Emulsions via Controlled Mixing in an Integrated Confined Impinging Jet Mixer

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This work presents an effective approach for low-pressure processing of emulsions as well as those requiring handling of the pressure-sensitive materials. Highly stable submicron emulsions using commercial-grade dietary oil and low-MW emulsifiers have been produced via top-down high-shear emulsification technique. Targeting submicron range, emulsions with d_{32} in a range of 20-700 nm have been produced via integration of sonication with multi-loop jet-mixing. Results have been presented to show the physiochemical effects of low-MW emulsifiers, the magnitude and duration of local turbulence and shear enhancement on the equilibrium d_{32}.

1. Introduction

Submicron emulsions (100 nm to 1 μm) are of growing interest in food and pharmaceutical industry. Their demand in specific applications is drawn by their unique large droplet surface area per unit volume, transparent to milky appearance, unique texture and the ability to encapsulate functional species within the finely-dispersed phase [1]. Though there is a good understanding on how and why emulsions form, the understanding of food-grade emulsification dynamics, process conditions is somewhat limited. Fewer acceptable ingredients for food use, the presence of pre-dissolved biosurfactants in dietary oils, oil purity levels and variations in bulk viscosity with production batches often cause product quality concerns. It is also increasingly important for emulsion-based foods to have stability during storage and disintegration upon consumption to preserve the required taste and flavor [2]. To this end, in the present work we investigate the processing of oil/water emulsions to produce food-grade emulsions smaller than 1 μm using a novel integrated confined impinging jet mixer (Figure 1). The miniature yet powerful mixer generates high micromixing and facilitates production of highly stable sub-micron emulsions (~70 kg/hour) with narrow PSD under normal pressure and temperature conditions. This effect is achieved by optimizing the emulsification process and the mixer design with multi-pass looping and integration of ultrasounics to enhance droplet breakup in the local turbulent field.

2. Experimental

Disperse phase, sunflower oil, was procured from the local supermarket and used as such while double-distilled water (conductivity ~ 1.4 μS/cm, pH = 6.8) was available locally. Water-soluble emulsifier Tween20 (Sigma-Aldrich, UK) was added to the continuous phase while polyglycerol polyricinoleate PGPR (Palsgaard, ~1000 cP) was added to the disperse phase prior to pre-emulsification step.

Pre-emulsions were prepared by dispersing sunflower oil (5 and 10 vol%) in Tween20 (1 wt%) solution at 2000 rpm for 10 minutes using a Silverson SL2T mixer. In other experiments, PGPR was added to the oil-phase at 0.5 wt%. The pre-emulsion was then fed to the mixer by the gear pumps at varying flow rates of 44 ml/min ($Re_{jet} = 10^3$) to 610 ml/min ($Re_{jet} = 13 \times 10^3$). Dye

experiments were conducted to visualize inlet jets stability. An electric sonic probe (VCX 500 from SONICS, 20 kHz and 500 W output) was later integrated into the mixer head. Sonication amplitude was varied up to 40% which was the permissible limit set up by the manufacturer. Past experiments, the samples were collected and characterized using Mastersizer2000 (Malvern Instruments, UK). Micrographs were also obtained under an optical microscope equipped with POLYVAR software but those aren't reported here.

3. Results and discussion

The experimental results are divided into three parts with each considering the effects of one operating variable on the emulsion mean droplet size (d_{32}) and its distribution. In the first part, the effect of mean hydrodynamic condition (jet Reynolds Number, $Re_{jet} = d_{jet}.V_{jet}.\rho_c/\mu_c$) is studied in the presence of water-soluble emulsifier and oil-soluble co-emulsifier. In part two, the effect of multi-pass circulation is examined. In the third part in situ sonication is integrated with jet-mixing to enhance local turbulence caused by jet-impingement with the mixer. Physical stability of the produced emulsions is also recorded over a time of several weeks.

Figure 2 (a) presents the effect of jet Reynolds Number on emulsion mean droplet size (d_{32}) in presence of Tween20 emulsifier and PGPR co-emulsifier after a single pass through the device. A decrease in mean droplet size is recorded with an increase in flow rate, indicating the influence of local hydrodynamic condition on the droplets. The droplets continue to decrease in size with increase in jet Reynolds Number and the smallest droplets are obtained at fully turbulent limit of $Re_{jet} = 13,000$. This Re corresponds to peak energy dissipation (ε_{peak}) of 3.58×10^5 W/kg estimated numerically [4] while the mean dissipation, $\varepsilon_{mean} = (2Q_{jet}.\Delta P_{mixer} + \Delta KE)/(\rho_c.V_{mixer})$ is ~9850 W/kg [4,5] across the mixing volume. Under these conditions, mean droplet size of 5 µm is obtained which is slightly greater than the turbulence microscale (Kolmogorov eddy size, $\lambda_k = (v_c^3/\varepsilon)^{1/4}$) of 3.2 µm. At low Re, droplets are expectedly larger than the Kolmogorov scale due to insufficient inertial forces to overcome turbulence dampening arising from higher disperse-phase viscosity (50x). At high Reynolds Number the resistance to droplet deformation and breakup is compensated by high shear ($\gamma = (\varepsilon/v_c)^{1/2} = 5.98 \times 10^5$ s^{-1}) in the jet impingement region of the mixing volume. Mean shear across the volume is an order smaller (9.9×10^4 s^{-1}) at Re_{jet} of 13,000. Under such conditions, Tween20 adsorption time scale is estimated to be ~10^{-7}s [5] while turbulence fluctuation life time ($t_{fluc} \sim (d_{32}/\varepsilon)^{1/3}$) is 10^{-4}s. The magnitudes of these scales indicate that droplets are way faster stabilized and interfacial tension lowered before droplets move away from each other. This is consistent with the residence time of the mixer ($t_{res} = V_{mixer}/(2Q_{jet}) = 8.4 \times 10^{-3}$ s). Also the absence of co-emulsifier (only Tween20 case) doesn't seem to have any significant effect on the mean droplet size in the fully turbulent field. This implies that while high turbulence favors droplet breakup, Tweeen20 has been equally effective in stabilizing the droplets against coalescence [6]. Expectedly similar droplets are produced at high Re as the interfacial tension for both the emulsifier and co-emulsifier is of the same order (~6 mN/m).

Figure 2 (b) shows the effect of multi-pass looping and in situ sonication on the emulsions at jet Re of 13,000 (flow = 610 ml/min). It also presents a comparison of the effect of oil-phase fraction on the emulsion droplet size in turbulent-inertial regime. We see that on being subjected to continuous shear (multi-pass) the mean droplet sizes decrease and level off to an equilibrium value. The equilibrium mean droplet size (of 2.5 µm is obtained with Tween20 at the 10th pass is roughly 2 times larger than the smallest turbulence microscale (1.3 µm); it is however very similar to the mean value of the microscale (3.2 µm) estimated from the mean energy dissipation rate. End/equilibrium droplet sizes therefore depend on the magnitude of local shear (mean: 9.9×10^4 s^{-1} and peak: 5.9×10^5 s^{-1}) as well as the timescale of the shear applied on the droplets. Droplets within the device experience shear for the residence time (t_{res}) multiplied by the number of times the emulsion passes through the mixer (multi-pass). Thus continuous shear and faster emulsifier transport to the interface at higher flow rates help

reach an equilibrium droplet size by controlling droplet coalescence. Further to this, we record a significant decrease in mean droplet size when the emulsion is exposed to ultrasonication (40% amplitude). In the new configuration, local jet mixing is coupled with in situ sonication to enhance local turbulence which helps in the further breakup of the droplets. Higher peak shear of 7.9×10^5 s^{-1} $[=(\varepsilon_{jet+sonic}/v_c)^{1/2}]$ causes the droplet size to drop further reaching an equilibrium d_{32} of 700 nm at the 11th pass. Under identical hydrodynamic conditions, the size distributions for 5% and 10% oil are found to be very similar. Similar PSDs indicate that turbulence within the mixer is sufficient to overcome the viscous-dampening arising from an increase in the oil content and the overall emulsion viscosity.

Figure 3 shows the effect of multiple passes and in situ sonication on emulsion PSD and the corresponding peaks. While a gradual shift in the mean size is observed from the 1st pass (5.2 µm) to the 10th pass (2.5 µm), a significant reduction in droplet size (700 nm) is recorded upon sonication. We are able to reach this size because the droplets continue to breakup under high local shear (turbulence enhancement with ultrasonication) for longer duration of time (multi-looping) in the new arrangement. In a turbulent shear field as in this case the droplets deform and breakup into smaller ones which are quickly stabilized by Tween20 molecules being transported to the interface sub-layer through convective mixing [6]. We can thus propose that droplet breakup is the size determining mechanism when interfacial tension and system viscosity are constant and droplet coalescence has been restricted. It is obvious that nearly one-half of the produced droplets are < 1 µm in diameter, while a tiny fraction of it is < 100 nm in size. It must be emphasized that this combined method of emulsification holds immense potential for production of nanoemulsions.

Figure 4 shows the variation in PSD on storage at room temperature. No significant shift is recorded in 5% and 10% sunflower oil samples over a time-scale of several weeks. These results present Tween20 as an effective stabilizer against droplet coalescence. There is no evidence of Oswald ripening as no secondary peaks are observed over the shelf life of 3-5 weeks.

4. Conclusions

Emulsions of mean d_{32} 700 nm have been obtained under fully turbulent (turbulent-inertial regime) and controlled shear conditions under normal pressure conditions in presence/absence of food-grade co-emulsifier. At Reynolds Number below 12,000 significantly large droplets (> 25 µm) are produced at the 1st pass in CIJM, however; above Re of 12,000 emulsion droplets of 5 µm were obtained. Formation of large droplets could be assigned to low inertial forces to overcome the resisting interfacial and viscous forces in the droplets. Slightly smaller droplets are produced with oil-soluble co-emulsifier at low Reynolds Number. This is due to additional interface stabilization induced by PGPR and lowering of coalescence due to increase in continuous phase viscosity. Higher continuous phase viscosity will likely induce slower film drainage between the colliding droplets. Thus formation of smaller droplets can be explained via two mechanisms: a) sufficiently high turbulence (not necessarily high pressure) to induce droplet breakup and b) emulsifier effectiveness to lower the interfacial tension and bring kinetic stability to the interface against coalescence.

Further, multi-pass experiments performed under turbulent flow condition show a significant size reduction. 2.5 µm droplets are obtained after the 10th pass. Longer residence time and continuous shear are found to decrease the impact of coalescence on equilibrium droplet size. Emulsifier adsorption on the interface is estimated to be very fast (10^{-7} s) and to produce droplets of the size of microscale it must be smaller than eddy lifetime and mixer residence time. Turbulence fluctuation timescale (10^{-4} s) marks the upper limit for the engagement of two droplets in a turbulent system. This is in agreement with the droplet data obtained here and elsewhere [5]. Moreover, smaller emulsions (20 nm to 700 nm) with high physical stability (3-

5 weeks) have been obtained by integrating in situ sonication with jet-induced turbulence. Smallest PSD was obtained at the highest allowable probe amplitude (40%), which gives the necessary shear intensity for droplet breakage at the micron scale. Lastly, we recognize that energy dissipation or shear intensity is the limiting variable in the absence of droplet coalescence and could be used to model process scale up. Droplet collision rate however scale with turbulence level and therefore through careful design, the residence time of droplets in a high turbulence zone must be optimized (> $t_{adsoption}$ and < t_{film}). If the droplets are not sufficiently and quickly stabilized, the droplet size would scale with this time scale. This new understanding will be useful in new rational impinging jet configurations for fabrication of nanoemulsions (< 100 nm) under normal pressure conditions.

Acknowledgements

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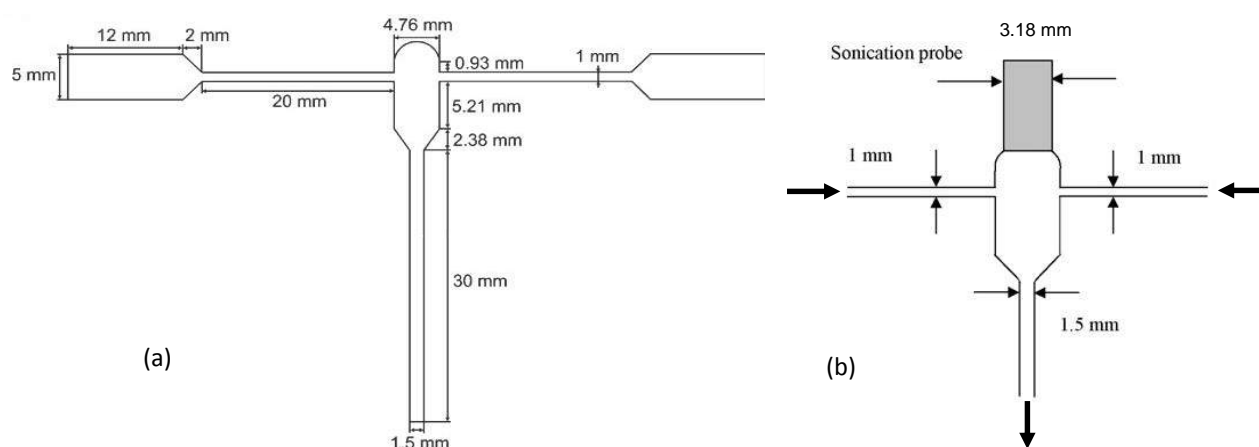
Figure 1: Schematic of the original confined impinging jet mixer and the integrated mixer geometry with 3.2 mm sonic probe. Adapted from [3].
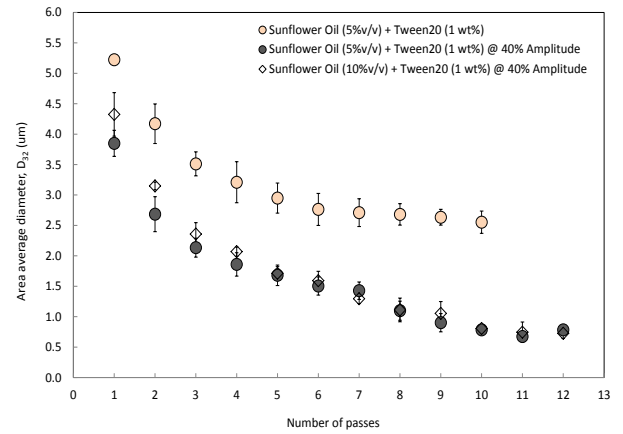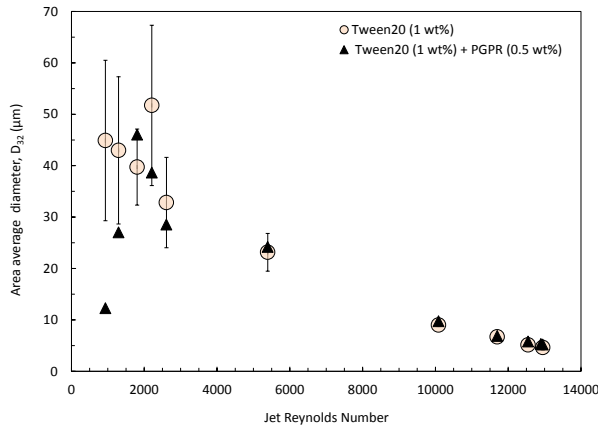
Figure 2: Effect of (a) Reynolds Number, emulsifiers and (b) multi-pass circulation, in situ sonication at highest Re of 13,000 on D_{32}
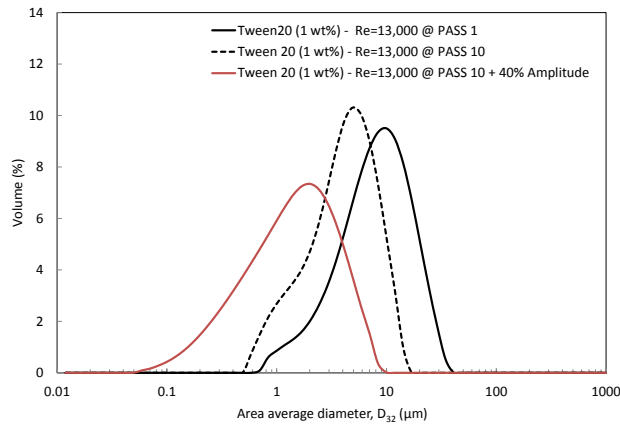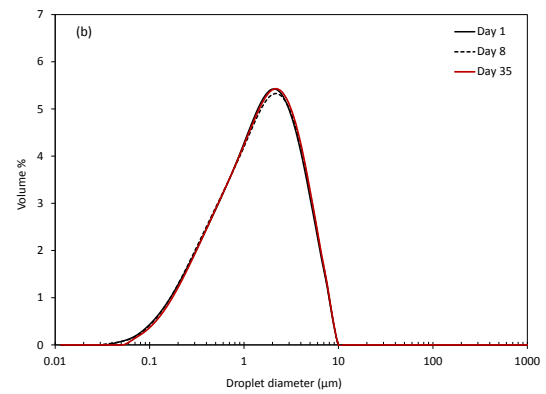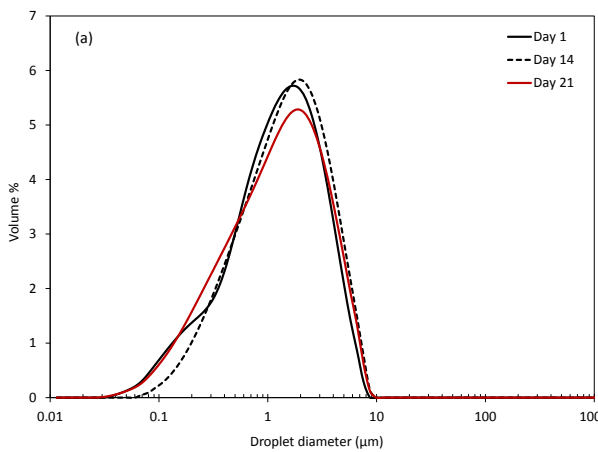

Figure 3: Effect of multi-pass circulation and in situ sonication on emulsion PSD

Figure 4: Emulsion stability of (a) 5 vol% and 10 vol% sunflower oil emulsion in presence of Tween20 (1 wt%) and jet Re of 13,000 with in situ sonication.

Rheological behaviour of a highly concentrated colloidal dispersion on different length scales

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Multi particle tracking and bulk mechanical rheometry have been used to study rheological properties of concentrated, colloidal suspensions. Using fluorescent tracer particles with particle sizes between 100 nm and 1000 nm enables MPT even in turbid systems and provides rheological information on the microscale.

Following systems have been investigated:

1. Fluid suspensions with short range repulsive interactions at $\Phi_{eff} < 0.5$, in this case perfect agreement between bulk and microrheology is found.
2. Hard sphere type crystallizing dispersions in the liquid/crystalline coexistence regime with and without added non-adsorbing polymer. A large variation in mean square displacement (MSD) of different tracer particles with slopes $\partial MSD / \partial \tau$ between 0 and 1 is found. The heterogeneity of the samples can be directly imaged based on this rheological contrast. The broadening of the coexistence region due to weak attractive depletion forces induced by added polymer is directly proven by MPT.
3. Variation of tracer particle mobility is investigated for systems approaching the colloidal glass transition.
4. The change of particle mobility and the variation of sample heterogeneity is analyzed in the so-called re-entry regime at $\Phi > \Phi_g = 0.58$ where the system transitions from glassy to fluid and from fluid to gel-like when attractive interaction controlled by non-adsorbing polymer increases from 0 to about 10 kT.

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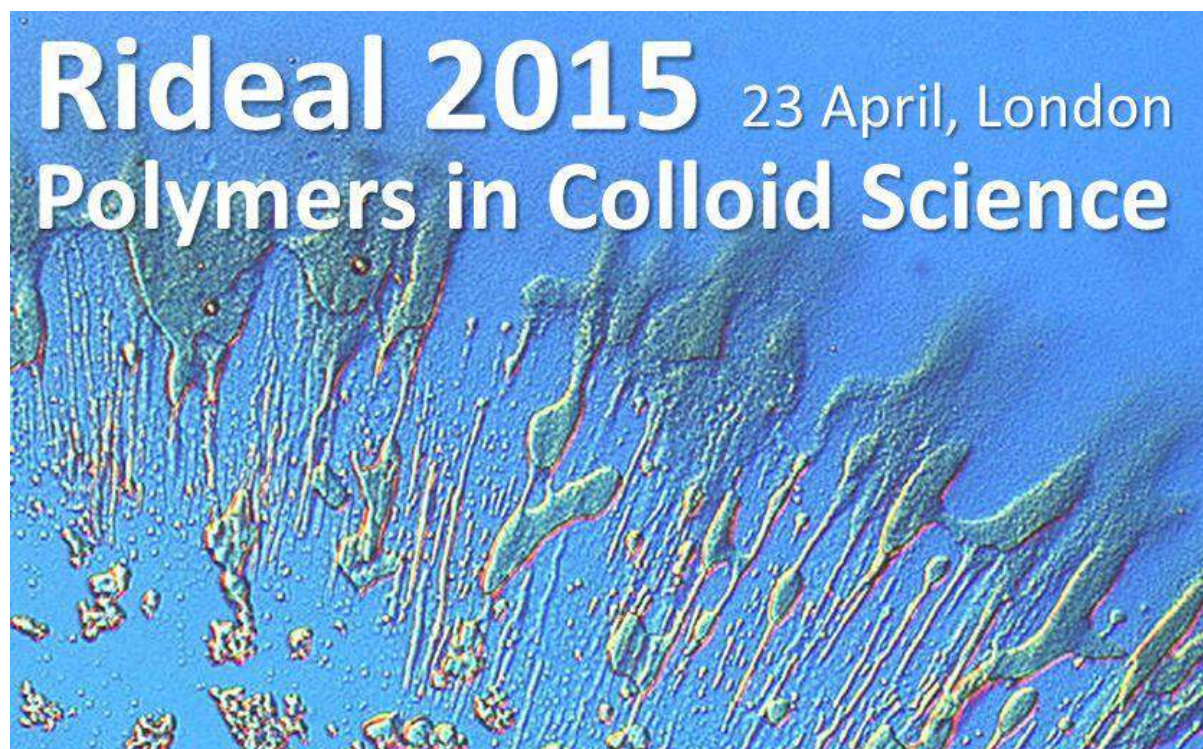
The Rideal Lecture, named after Sir Eric Rideal who was instrumental in the formation of the RSC and SCI Colloid Groups, is awarded annually in recognition of a significant and sustained contribution to colloid and interface science.

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The McBain medal is awarded annually to younger researchers who have made a meritorious contribution to colloid and interface science. The medal is named after James William McBain who postulated the presence of micelles in 1913 at the University of Bristol.

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