Viscoelastic wetting: normal stress effects

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Preference: TALK & S4 - Gels, polymers, foams and rheology at/with interfaces

Keywords (5 max): viscoelasticity, contact-line motion, polymer solutions, dip-coating, drop impact

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Abstract: The motion of a contact line is classically described by the Cox-Voinov theory, linking the macroscopically contact angle to the contact line speed and the microscopic wetting angle. Here, we investigate how viscoelasticity, specifically via the normal stress effect, modifies the wetting dynamics. Using the thin film equation for the second-order fluid, it is found that the normal stress effect is dominant at small scales yet can significantly affect macroscopic motion. We show that the effect can be incorporated in the Cox-Voinov theory through an apparent microscopic angle, which differs from the true microscopic angle. The theory is applied to two classical wetting problems. First, viscoelastic effects slow down the retraction of a drop, which justifies the polymer-induced suppression of rebound observed experimentally after drop impact (Fig. 1(a)). Secondly, we extend the model to large angle, deriving a viscoelastic generalized lubrication theory, which is used to investigate dip coating (Fig. 1(b)). The critical receding speed for liquid entrainment decreases with increasing normal stress.

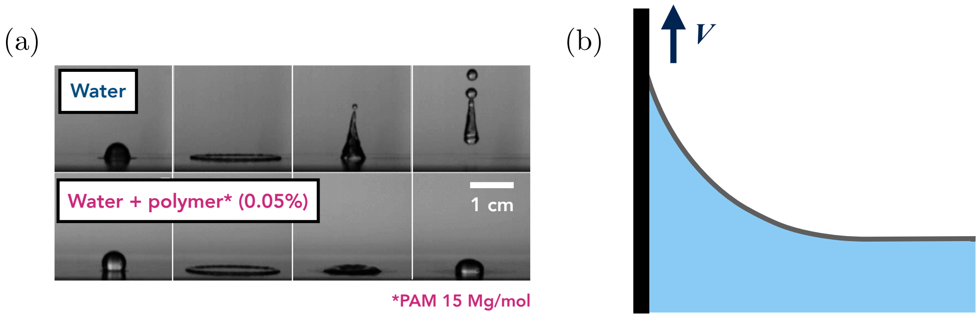

Figure 1: (a) Polymer-induced suppression of the rebound of a drop impacting a hydrophobic surface (adapted from Bartolo et al. 2007 PRL **99**). (b) Schematic of dip coating.

Structural and mechanical analysis of collagen gels

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Preference: TALK

Keywords: collagen network, gel, microstructre, simulations

Abstract: The complex interaction between cancer cells and their microenvironment plays an essential role in tumor progression and metastasis. Collagen appears as a key structural component of the extracellular matrix (ECM) that interacts and influences cells and their behavior, including migration. Understanding the link between the microstructure and the mechanical properties of the collagen fibrous gels would be a major step toward comprehending cancer cell interplay with the matrix. We experimentally investigate the influence of different physico-chemical parameters such as temperature, collagen concentration and pH on the gel structure. From confocal microscopy, we infer several structural descriptors to characterize the gels morphology, through the pore size distribution, the fiber thickness and volume fraction. This catalogue of gels microstructure is rationalized through coarse-grained molecular dynamics simulations of a model gel system that incorporate simple but enough ingredient to capture several structural features of collagen networks formation.

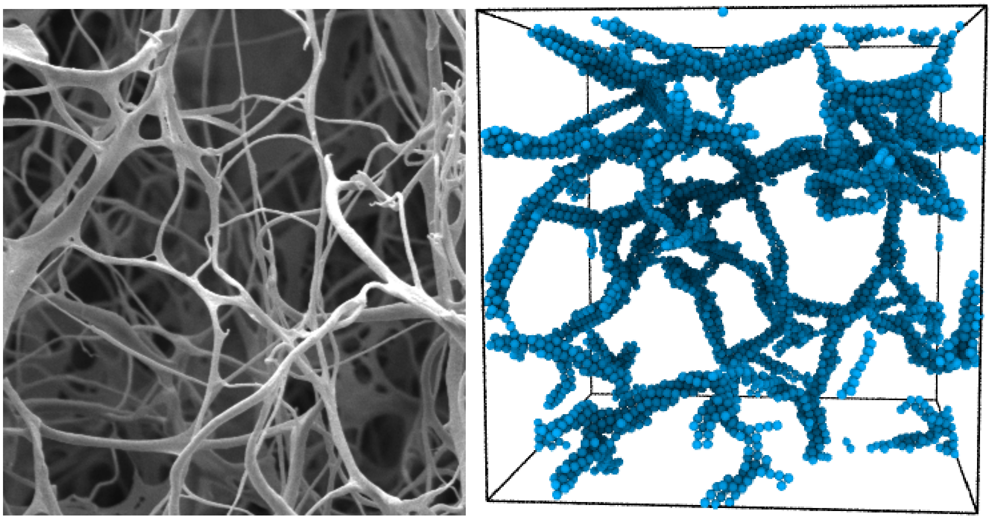

Figure 1: (left) A SEM image of collagen gel at concentration 2 mg/ml (right) A typical network structure from a simulated system at 2 % particle volume fraction.

Inhomogeneous capillary flows of granular suspensions

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Preference: TALK preferred, poster possible.
Keywords (5 max): Granular suspensions, Capillary Flows, Droplet pinch-off, Liquid atomization

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Abstract (250 Words Max):

At large scales, granular suspensions flow like viscous homogeneous liquids, but at the particle scale they are granular liquids. Depending on the flow, a suspension will therefore behave like a homogeneous or a heterogeneous medium. Both dynamics can be observed during the pinch-off of suspension drops. As a drop detaches, the thickness of the liquid thread that holds it must vanish, and so the flow evolves through all the scales from the size of the drop down to zero. Experimentally, we observe a clear threshold under which the flow differs from Newtonian behavior. We derive a scaling law by comparing two mechanisms of viscous dissipation, which describes this intermediate scale. It is validated by our experiments with suspensions of spherical polystyrene beads, both in the monodisperse and polydisperse cases, and also with suspensions of rigid nylon fibers. It also matches separate experiments in which a capillary bridge of granular suspension is quickly stretched between two rods; constant upward acceleration replaces gravity, but the physics remain unchanged. This universal rescaling suggests that a least dissipation principle proves efficient in describing the suspension, at least in extensional flow.

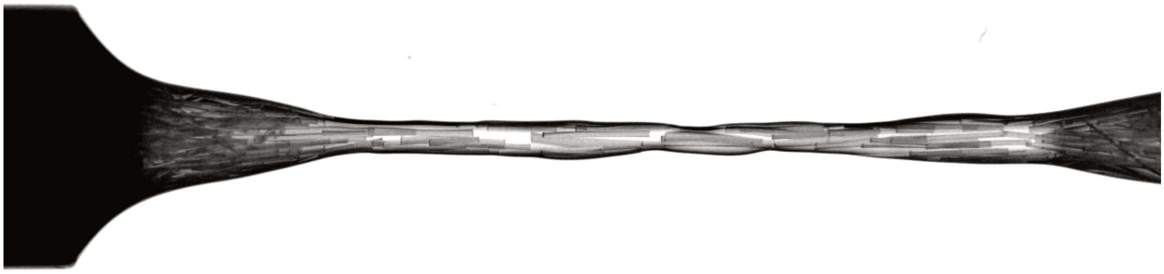

Figure 1: Detachment of a drop of suspension of rigid rods. The nozzle (left) is 2.75 mm wide; the rods are 1 mm-long and 50 μm-thick. Gravity goes from left to right.

Morphology of sheared multilayer films of polymer melts

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Preference: Talk & preferred session 4. Gels, polymers, foams and rheology at/with interfaces

Keywords (5 max): Coextruded multilayer, Polymer films, Morphology, Layer breakup

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Abstract: Coextruded multinanolayer polymer films have attracted attention due to their numerous applications, for example in gas barrier plastic films. During the multilayer coextrusion, the polymer melts experience shear and extensional flows. Here, we present a combined rheological and microscopical study of the properties of a non-compatibilized interphase of two well-known immiscible amorphous polymers: polystyrene (PS) and poly(methyl methacrylate) (PMMA). Films with 129 to 2049 layers and layer thicknes down to about 100 nm were examined in oscillatory shear at different strain amplitudes and frequencies. Starting from uniform layers, the morphology of the multilayer films is monitored up to the appearance of defects and breakup of layers. The complex viscosity time evolution and the role of the interface will be also discussed. The onset of dewetting is found to have a smooth transition as a function of time and is independent of the oscillation frequency. The large amplitude oscillation has a drastic effect on the breakup. These findings give insights into layer breakup kinetics and mechanisms.

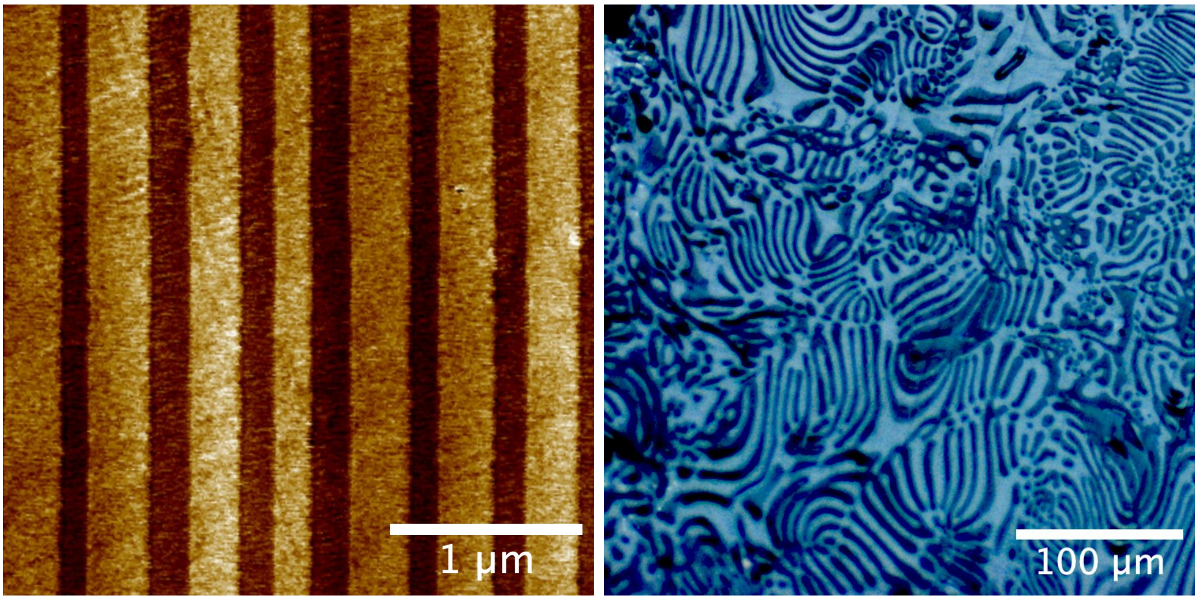

Figure 1: Microscope images of multinanolayer PS/PMMA films

Rheology of particle laden film

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Preference : TALK & S4

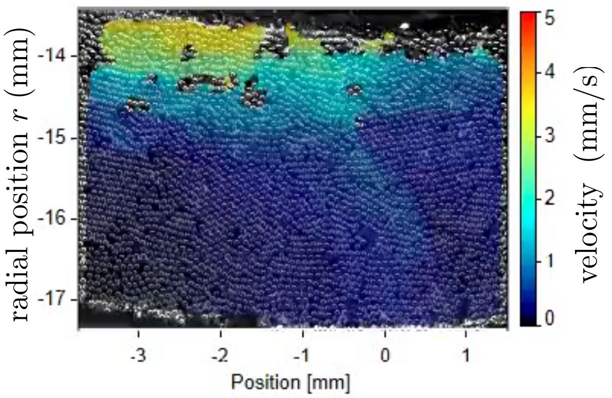
Keywords (5 max): Rheology, Granular media, soap film.

Abstract : Particle laden interfaces are ubiquitous in industry (e.g. oil recovery, filtration processes, armored droplets used as microreactors, or concrete foams) where the interface stabilization effect must be controlled. Recent studies [1,2] have shown that mechanical properties of particle-laden films differ from those of single particle laden interface, though the origin of the differences remains unclear. We study experimentally the rheology of a macroscopic particle-laden soap film constituted of polystyrene spheres trapped in a single film made of a tetradecyl trimethyl ammonium bromide (TTAB) and glycerol aqueous mixture of the same density as the particles. The particles are larger than the typical film thickness, they cross both interfaces and capillarity gives rise to attractive interactions between the particles. To study the strain-stress relation of such particle laden film, it is first stretched in an annular rheometer cell and sheared at imposed velocity, measuring the stress. The strain-stress results are compared with local shear rate measured through image correlation. We show that, at dense particle volume fraction, the granular film exhibits a complex visco-plastic behavior which is influenced by interfacial parameters such as surface tension and surface viscosity of the carrying fluid. To account for the non-local rheology of the particle laden soap film, we confront the particle velocity fields to kinetic theory extended to dense granular media [3]. In a second configuration the extensional viscosity of the particle laden film was studied. The film was stretched between a ring and a particle raft.

[1] N. Taccoen, F. Lequeux, D. Z. Gunes, and C. N. Baroud, Physical Review X 6, 011010 (2016).

[2] Y. Timounay, O. Pitois, and F. Rouyer, Physical Review Letters 118, 228001 (2017).

[3] W. Losert, L. Bocquet, T. C. Lubensky, and J. P. Gollub, Phys. Rev. Lett. 85, 1428 (2000).



Lattice Boltzmann modeling of flowing foams: capturing shear thinning, yield stress, and viscoelasticity

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Preference: TALK & S4: Gels, polymers, foams and rheology at/with interfaces

Keywords: Foams, Highly Concentrated Suspensions, Lattice Boltzmann, Viscoelasticity, Yield Stress

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Abstract: We modified a classical two-phase lattice Boltzmann scheme with a Shan-Chen type inter-species repulsion force by adding a repulsion between droplets of the same species. This allows to create a stable emulsion. By increasing the dispersed phase fraction, it is possible to model highly concentrated suspensions and foams. The main advantage of this approach is that both the drops and the films that separate the drops are hydrodynamically resolved allowing the study of phenomena such as drainage or the flows occurring in the films during a T1-transformation. The flows in the foam are induce by adding a gravitational force parallel to the walls and the slip at the walls is prevented by adding wetting properties reflecting location of the bubbles and the films. Velocity profiles and mean flows allow to put in evidence the expected rheological properties of dry foams like shear thinning, yield stress and viscoelasticity.

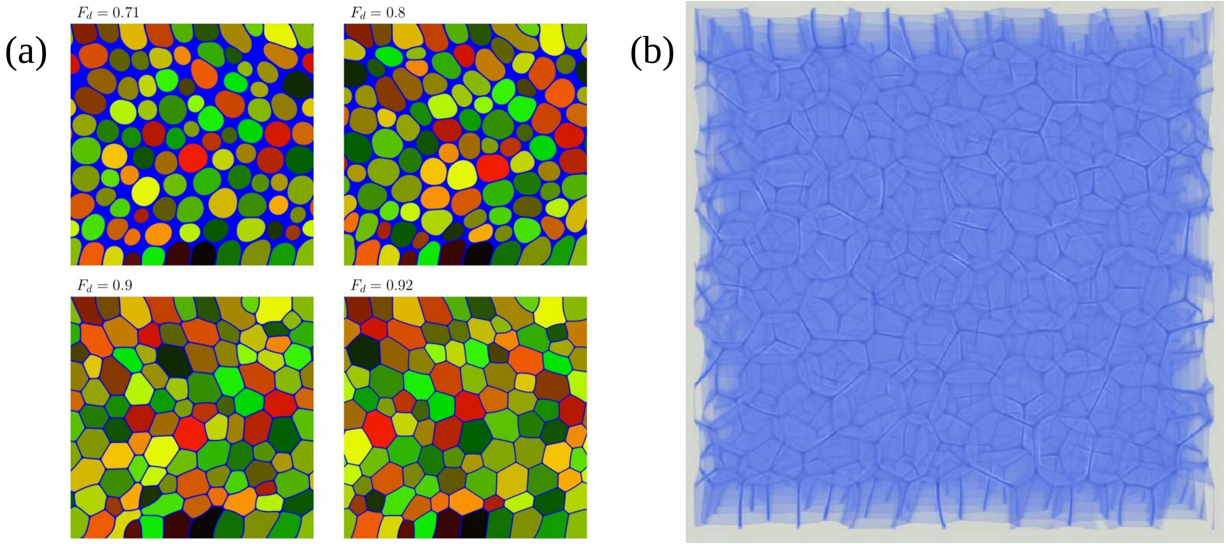

Figure 1: Typical exemples of flowing foams modelled by a two phase lattice Boltzmann scheme: (a) 2D simulations with increasing fractions of the dispersed phase F_d and (b) a 3D simulation.

How Viscoelasticity Controls Instabilities and Pattern Formation in a Confined Flow?

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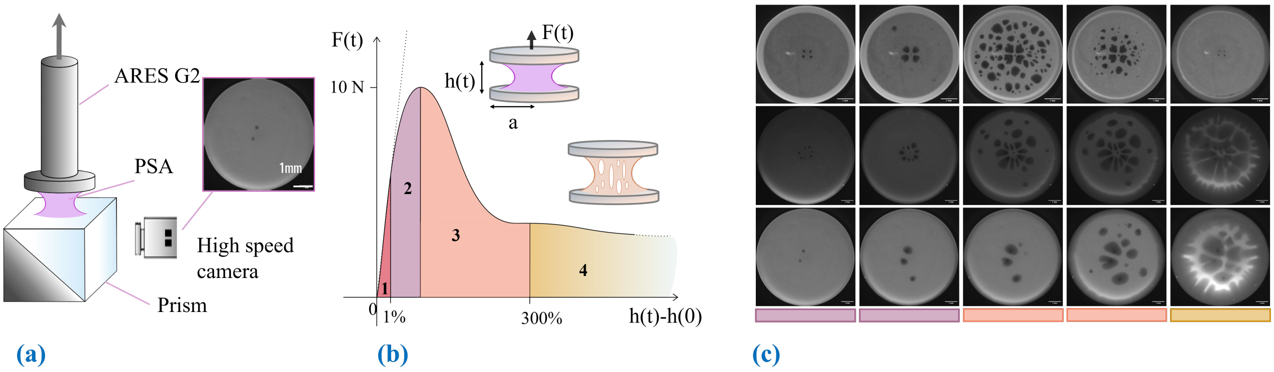
Preference: Talk in *Gels, polymers, foams and rheology at/with interfaces* session

Keywords : Viscoelasticity, Instabilities, Adhesvies, Rheo-Optics.

Pressure-sensitive adhesives (PSAs) are viscoelastic liquids composed of slightly crosslinked entangled polymer chains. They exhibit a rubbery plateau modulus G of 10^5 to 10^6 Pa and a relaxation time spectrum of $\theta = 10^{-4}$ to 10^{-1} s, their viscosity being $\eta = G\theta$. They are commonly used in medical plasters. The tack test is an industry-standard method to measure the work of adhesion in PSAs (Fig1a), that ranges from 10^2 to 10^4 J/m^2, which is typically 10 to 100 times their interfacial energy with most solid substrates. Tack test consists in measuring the force required to debond a thin cylindrical PSA layer (radius a, height $h(0)$) at a defined speed (Fig1b). Typically, in the early stage of the test (zone 1), the PSA elastic response induces a force that scales like $F \propto Ga^2\epsilon_{zz}\frac{(a/h)^2}{1+3(1-2\nu)(a/h)^2}$ where ϵ_{zz} is the vertical extension (NB: $\epsilon_{rz} = \epsilon_{zz}a/h$) and ν the Poisson ratio. The final stage (zone 4) involves the extension of fibrils, leading to $F \propto \eta\frac{\dot{h}}{h}a^2\phi$, where ϕ represents the surface fraction of fibrils. Between these stages, energy is dissipated through the formation of cavities, their growth, the movement of their contact lines and their merging. These processes remain poorly understood. We experimentally investigate each process by varying their respective characteristic time through control of velocity, aspect ratio a/h, and temperature. This approach aims to elucidate the coupling between these dissipation mechanisms and leads to possible control of the formed adhesion patterns.



(a) (b) (c)

Figure 1: (a) Tack test. (b) Force vs displacement curve. (c) Direct observation of cavities during the debonding of a PSA. Each line is a tack test respectively with an aspect ratio of $30; 80; 80$ and a surface velocity of $10mm/s; 10mm/s; 15mm/s$.

General Stress Decomposition as a powerful tool to characterize complex interfaces

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Preference: TALK S4

Keywords (5 max): Interfacial dilational rheology, complex interfaces, General Stress Decomposition, polyelectrolyte multilayers

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Abstract: The dilational response of complex interfaces exhibit often non-linear features even in the linear regime of deformation. It is therefore difficult to characterize. Here we use "General Stress Decomposition" (GSD) to analyze the pressure-deformation relations of bubbles covered by polyelectrolyte multilayers, which undergo a liquid-solid transition after four layers. Originally developed for large amplitude oscillatory shear rheology, GSD was only recently applied to oscillatory dilatational interfacial rheology.[2-4] It uses symmetry arguments to decompose the total effective interfacial stress γ_{eff} (Fig. 1a) into four contributions τ_i (Fig. 1b-e), such that $\gamma_{eff} - \gamma_0 = \tau_1 + \tau_2 + \tau_3 + \tau_4$. Here γ_0 is the γ_{eff} value in the absence of deformation, τ_1 and τ_2 are the purely elastic and viscous stresses, resp., and τ_3, τ_4 include the non-linearities introduced by the equation of state of the interface. For small deformations, τ_1 and τ_2 exhibit a linear response and are directly related to the elastic and viscous moduli (Fig. 1b-c), even though a strong non-linear behavior, associated with τ_3 and τ_4 (Fig. 1d-e), is clearly visible in the total stress-strain curve (Fig. 1a). Thus, GSD allows a clean analysis of the dilational response of complex interfaces, including highly non-linear signals, arising here after the liquid-solid transition of the viscoelastic interface. Our results are validated with Bubble Shape Elastometry and Capillary Meniscus Dynamometry. We also show that the method can be applied to other systems, for example, to follow chemical reactions at interfaces.

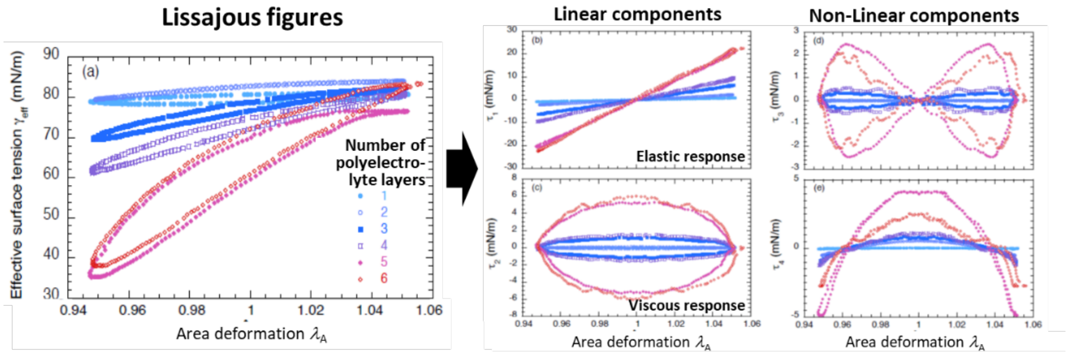

Figure 1: GSD of the stress-strain response of a bubble covered by an increasing number of polyelectrolyte layers and undergoing sinusoidal area variations in the linear deformation regime.

[1] W. Yu, P. Wang, C. Zhou, *J. Rheol.*, 2009, 53, 215–238.
[2] B. A. Noskov, A. G. Bykov, *Russ. Chem. Rev.*, 2015, 84,634–652.
[3] A. de Groot, J. Yang, L. M. Sagis, *J. Colloid Interf. Sci.*, 2023, 638, 569–581.
[4] S. Pivard, L. Jacomine, F.S. Kratz, C. Foussat, J.-P. Lamps, M. Legros, F. Boulmedais, J. Kierfeld, F. Schosseler, W. Drenckhan, *Soft Matter*, 2024, 20, 1347–1360.

Stress redistribution in flowing liquid foam

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Preference : TALK

Keywords : 3D foam, T1 event, stress redistribution.

Abstract : It is challenging to capture the structure evolution of 3D flowing liquid foams, such as the bubble deformation and plastic rearrangements. Lately, X-ray tomographic microscopy appeared as one of the useful probes to visualize the deformation and displacement fields of bubbles flowing around an obstacle [1] and through a constriction [2]. For the first time, we present a multiscale description of liquid foam subjected to a rheometric flow inside the rheometer and simultaneously 3D imaged. The foams were produced by a microfluidic setup and placed inside a plate-plate rheometer. The liquid fraction, bubble mean diameter and rheometer gap were systematically varied, respectively between 5-30 %, 50-200 µm, and 0.375-3 mm. While measuring the macroscopic torque, high-resolution tomograms were recorded every 3 s for 9 min. Each experiment consisted of three phases: elastic loading, elastoplastic plateau, and relaxation after shear cessation. We developed a 3D quantification toolbox (FoamQuant) to reconstruct the individual bubbles geometry, and to extract their individual displacements, full stress tensors and structural rearrangements (T1s). We validate our local stress measure with our macroscopic torque measurement, and unravel the way T1 plastic events redistribute the local stress in their surroundings, combining a quadrupolar response in the plane of bubble swapping with nontrivial 3D effects. This paves the way to better understand the elastoplastic behavior of foams, and more generally of amorphous materials.

[1] C. Raufaste, et al., EPL 111, 38004 (2015).
[2] F. Schott, et al., Soft Matter 19(7) (2023).

Stirring liquids of unequal viscosities: why won't it mix?

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Preference: Poster & session 4

Keywords (5 max): mixing, laminar chaotic flows, viscous flows

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Abstract (250 Words Max): The description of mixing under various flow conditions is fundamental to many industrial and scientific problems. By examining the case of an isolated blob of viscosity $\lambda\eta$ deformed in a bath of viscosity η, it has recently been shown that in a simple shear flow configuration, a large viscosity ratio triggers a rolling kinematic transition, yielding much longer mixing times. Here, we study this case in the configuration of a chaotic, laminar flow. For this purpose, we developed an experimental setup and protocol capable of inducing custom controlled 2D chaotic flows. The results confirm a change in mixing times and allow to propose a model predicting how the blob mixing time depends on the viscosity ratio and Péclet number.

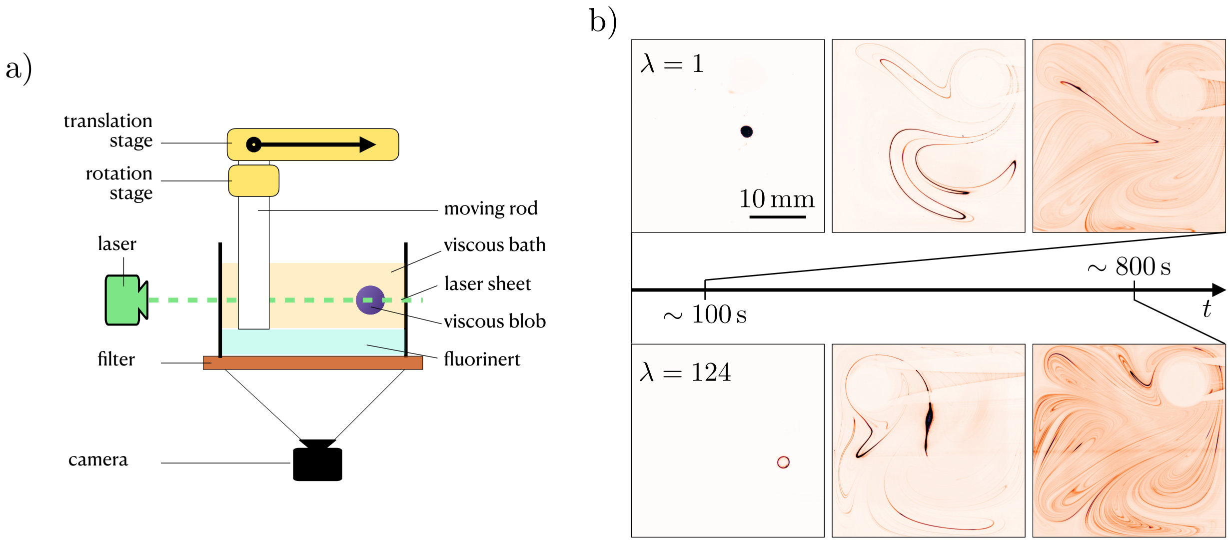

Figure 1: a) schematics side view of the experimental setup to produce a chaotic laminar flow. b) different snapshots illustrating the mixing process of (top) a blob as viscous as the bath $\lambda = 1$, and (bottom) a blob $\lambda = 124$ times more viscous than the surrounding bath.

Hydrogels composites pour adsorption sélective

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Preference : TALK

Keywords (5 max): hydrogels, nanocharges, composites, adsorption

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Abstract : Le développement de matériaux composites stimulables et une meilleure connaissance de la relation entre propriétés et structure sont essentiels pour leurs nombreuses applications. Nous avons ainsi synthétisé des nanocharges plaquettaires d'oxyde de graphène que nous avons introduites dans des hydrogels réticulés pour optimiser l'élaboration d'hydrogels composites. Des mesures de microscopie électronique et spectroscopie photoélectronique à rayons X ont permis de caractériser la morphologie et la structure chimique des nanocharges d'oxyde de graphène et des composites. Les propriétés rhéologiques, de gonflement et d'adsorption de colorant ont été étudiées en fonction des concentrations initiales de polymère et d'oxyde de graphène. Nous avons montré que l'augmentation la plus importante des propriétés viscoélastiques et d'adsorption, dont les données expérimentales ont été analysées avec un modèle cinétique d'ordre 1, est obtenue avec l'augmentation de la concentration d'oxyde de graphene (Figure1). Une corrélation entre les propriétés de gonflement, d'adsorption, de viscoélasticité et de structure des composites est proposée.

Y. Lei, I. Boucenna, V. Thévenet, D. Dragoe, A. Ponton ACS Applied Polymer Material (2021)
Y. Lei, I. Boucenna, V. Thévenet, E. Paineau, A. Ponton, Langmuir (2024)

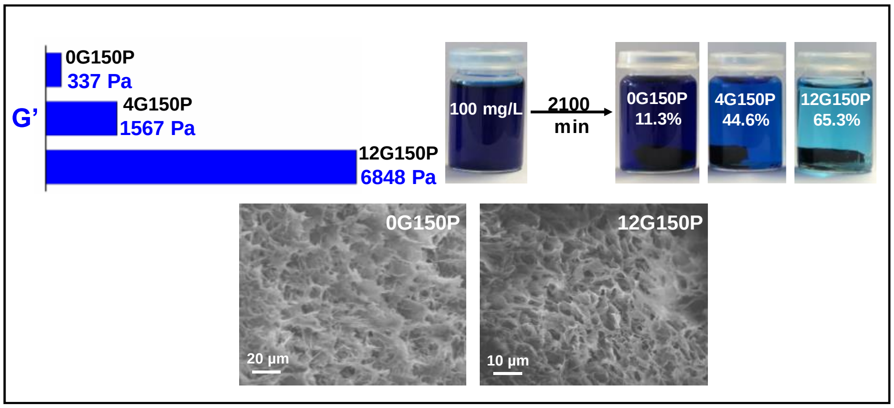

Figure 1. Augmentation des propriétés élastiques et d'adsorption de colorant cationique (bleu de méthylène) dans des composites de structure poreuse observée en microscopie électronique

Impact of interfaces properties on flotation efficiency- comparison of homopolymer and associative polymer

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Preference : TALK & S4

Keywords (5 max):interfacial rheology, tensiometry, viscoelasticity, spreading, flotation

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Abstract: Flotation is a very efficient water treatment technology. It is commonly applied to remove hydrocarbons droplets from effluents. It relies on the attachment of bubbles on oily droplets. Due to this adhesion, droplets are alleviated and separate faster from water. Many studies focused on the influence of bulk rheology on the overall process [1,2]. Here we paid attention to the impact of interfacial properties. By using an homopolymer and an associative one, we could investigate systems having the same volume rheology but different interfacial ones. L/L and L/G interfacial rheological measurements were carried out with a double wall ring at 25°C on a rotational rheometer. Oscillatory tests were performed in linear regime. The homopolymer is a classical HPAM while the associative polymer is a HPAM that comprises lateral hydrophobic moieties. Both macromolecules can be present in petroleum effluents resulting from EOR operations and it is important to understand their effect on flotation [3]. Results confirmed that the associative polymer confers stronger viscoelasticity to L/L and L/G interfaces than HPAM. As a result, oil droplets can be well covered by the associative polymer, protecting them from coalescence and spreading with gas bubbles, thus reducing flotation efficiency. Lab flotation experiments clearly confirmed these trends. Tensiometry measurements were also carried out to further investigate the adsorption of the polymers. The thermodynamic entrance and spreading coefficients can be calculated. They are consistent with spreading observations which extent is again more limited with the associative polymer and limits flotation efficiency [4]. These results demonstrate that local surface phenomena can affect macroscopic processes and that a multi scale approach can be fruitful.

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[1] H. Chakibi , I. Hénaut, A. Salonen, D. Langevin and J-F. Argillier, 'Role of bubble-drop interactions and salt addition in flotation', Energy & Fuels, 2018, 32, 4049-4056

[2] M. Piccioli, S V Aanese, H. Zhao, M. Dudek and G. Oye, 'Gas flotation of petroleum produced water: a review on status, fundamental aspects and perspectives, Energy & Fuels, 2020, 34, 15579-15592

[3] S. Tian, W. Gao Y. Liu and W. Kang, 'Study on the stability of heavy crude oil-in water emulsions stabilized by two different hydrophobic amphiphilic polymers, Colloids and Surfaces A 572 (2019) 299-306

Evolution of rheological properties and microstructure of PET: effects of reprocessing and formulation

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Preference : TALK & Gels, polymers, foams and rheology at/with interfaces

Keywords (5 max): Recycling, impact modifier, processing, rheology.

Abstract : Plastic pollution is a striking example of environmental stress and recycling is one key applicable approach today. In this context, polyethylene terephthalate (PET) is in the spotlight, being one of the most recycled polymers worldwide. However, despite the effort spent on its recycling, many challenges still restrain its development. One reason for this is a lack of understanding of the structural modifications caused by successive processing steps and the effect on the final product properties, especially the impact strength. The greater challenge of formulating a polymer in a recycling scenario is another reason for the numerous drawbacks of existing solutions. This work focused on the effects of mechanical recycling and formulation on rheological and processing behavior of PET. At first, the preparation and characterization of a recycled PET (rPET) allowed pointing out the main modifications. The key point proved to be the processing of rPET itself more than its final mechanical properties, especially the impact strength. Then, the effect of an acrylic impact modifier (AIM) was studied. With optimizing compounding conditions, a core-shell structured AIM with a compatibilizer enhanced both the processing and the impact toughness. The formation of a complex network also demonstrated to have consequences on rheological behavior. A better link between the structural modifications and mechanical toughness may allow a fine tuning of the additive structure for even better results.

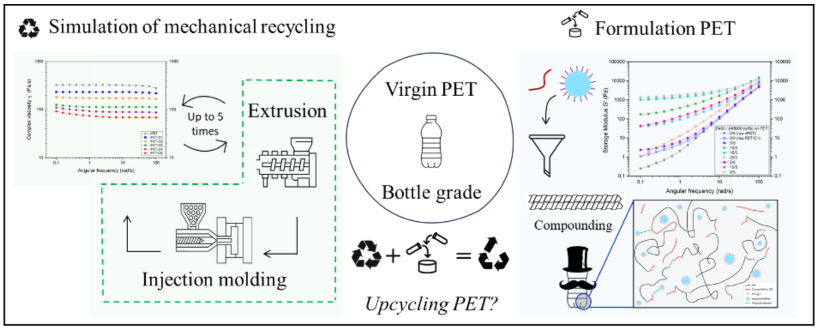

Figure 1: Schematic representation of PET's mechanical recycling and formulation with impact modifiers.

Microfluidics-Based Synthesis of Hydrogel Microparticles from Nanoemulsions Precursors for Efficient Encapsulation and Release Applications

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Preference: TALK

Keywords (5 max): Hydrogels, microparticles, nanoemulsions, microfluidics, encapsulation

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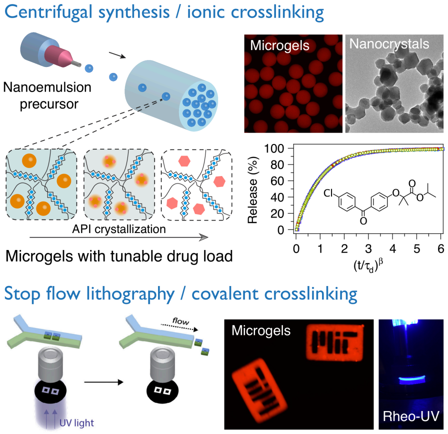
Abstract: Nanosizing of active pharmaceutical ingredients (APIs) is a key approach to improve their bioavailability, particularly in the case of water-insoluble compounds. Moreover, enabling the high load encapsulation of stable API nanocrystals is desirable for their tunable dosing in final products, as well as for further pharmaceutical formulation steps where the active compounds are often diluted with excipients or other additives. Yet, these remain challenging goals due to the lack of simple and scalable approach. Using nanoemulsion templating in microgel particles, where the droplets (dispersed phase of the emulsion) are used as hydrophobic compartments, we demonstrate that stable API nanocrystals-loaded particles can be easily synthesized up to high drug loads (> 70 %) via a scalable low-energy process. Our study shows that the drug release kinetics has a non-linear dependence on the drug load of the microgel particles, where internal packing of the nanocrystals influence their release from the microgel matrix as the drug load increases. Despite the wide range of dissolution timescales, all the dissolution profiles can be rescaled using only two adjusting parameters. The effect of particle size can also be used to tune the release rate, and significant dissolution enhancement is observed (up to 70×) compared to bulk API crystals, including at the highest drug load. Two microfluidic techniques for encapsulation, either based on alginate or diacrylate (PEGDA) chemistries, are presented.



API encapsulation via centrifugal (top) and stop flow lithography (bottom) microfluidics approaches

Modeling of chemical foaming of rubber compound and validation

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The objective of this work is to model the chemical foaming of an industrial rubber compound formulation in controlled thermal history. The chemical foaming is caused by a chemical agent (CA) decomposition with nitrogen formation. The vulcanisation system is sulphur based. Both reactions are controlled by the thermal history.

The objective is to predict the evolution of the density of the rubber along the foaming process. A simple approach consists in calculating the foam volume: $V_{foam} = V_{rubber} + V_{gas}$ during the process. The gas generation kinetics is deduced from the CA decomposition kinetics. The CA decomposition kinetics were determined from DSC data under non-isothermal conditions and fitted by the Kamal-Sourour (KS) equation. As decomposition and curing reactions are coupled, measurements were performed on the complete rubber compound formulation (Alcala, 2022). The thermal variation of the rubber volume considers its thermal dilatation with hypotheses on the effect of the curing. The gas volume is corrected for the dissolved part (Henry's law with temperature (T) and pressure (P) conditions). The perfect gas law is used to calculate the gas volume variation with T and P. This model does not consider the change of the rheological behaviour of the rubber during vulcanization. A limit condition is introduced to take into account the gel point of the rubber, limit after which the compound exhibits a solid-like behaviour and we assume that the bubble can no longer grow. The gel point was determined from rheological measurements (RPA).
The kinetic based model will be compared with a bubble growth model. The model of Amon and Denson (1984) (considering size-equivalent cells consisting of an initial bubble in a matrix shell + physical foaming) was adapted to take into account the chemical foaming, the rheological behaviour of the rubber (power law dependence) and the evolution of the viscosity due to curing up to the gel point (Castro-Macosko equation). The bubble growth model integrates physical features not considered in the kinetic based one such as the diffusion of dissolved gas to the bubble and the rheological behaviour.

Original foaming experiments were designed to measure the foaming process under simple thermomechanical conditions (constant heating rates) and to validate the models. Two types of dilatometry tests were performed: free foaming experiments (oven equipped with transparent windows to visualise the sample expansion), dilatometry tests under pressure (sample expansion in a closed mould set in a tensile testing machine allowing pressure control and displacement measurement).

The results of the foaming tests will be presented and interpreted in relation with the timing between the CA decomposition and curing kinetics. The predictions of the two models will be compared. The role of the rheological behaviour in the foaming process will be discussed.

References:

N. Alcalá *et al.* (2022), *Polymers* 14:1101. doi :10.3390/ polym14061101
M. Amon, D. Denson (1984) *Polym. Eng. Sci.,* 24 (13), 1026-1034.

Flow Asymmetry enhanced by Viscoelasticity

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Preference: TALK (S4: Gels, polymers, foams and rheology at/with interfaces)
Keywords: Rheology, Complex Fluids, Viscoelasticity, Hydrodynamic and Elastic Instabilities

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Abstract: Planar flow of viscoelastic liquids is a well-established phenomenon be it past a confined cylinder or in other simple geometries like a T-Junction, especially since the former serves as a traditional benchmark problem in numerical studies providing crucial insights into the complex kinematics of these fluids.

The studies of note to this work are surrounding asymmetric flows where a new viscoelastic flow instability has been observed. Above a critical Weissenberg number, complex fluid flow past a confined cylinder becomes highly asymmetric developing into a preferential pathway. This has been seen experimentally and numerically in Worm-like Micelles and shear-thinning viscoelastic liquids (Haward et al. 2019, Varchanis et al. 2020).

This work explores viscoelastic planar flow but with a twist, a geometric asymmetry. In the case of viscoelastic planar flow past a confined cylinder, the cylinder is placed vertically off-centre. With the introduction of this geometric asymmetry, an intensified flow asymmetry arises at high Weissenberg numbers, but notably at much lower Wi values than reported in aforementioned works. A critical Weissenberg number is observed beyond which the flow drops almost to zero in the narrower pathway around the cylinder. A similar phenomenon is also observed in a T-junction with asymmetric branches. Most remarkably, the critical Wi is seen to be invariant with degree of asymmetry. This phenomenon is studied using 2D FVM simulations of an Oldroyd-B and White-Metzner fluids and in experiments of solutions of partially hydrolysed Polyacrylamide (HPAM), which are shear-thinning and viscoelastic, in millifluidic devices.

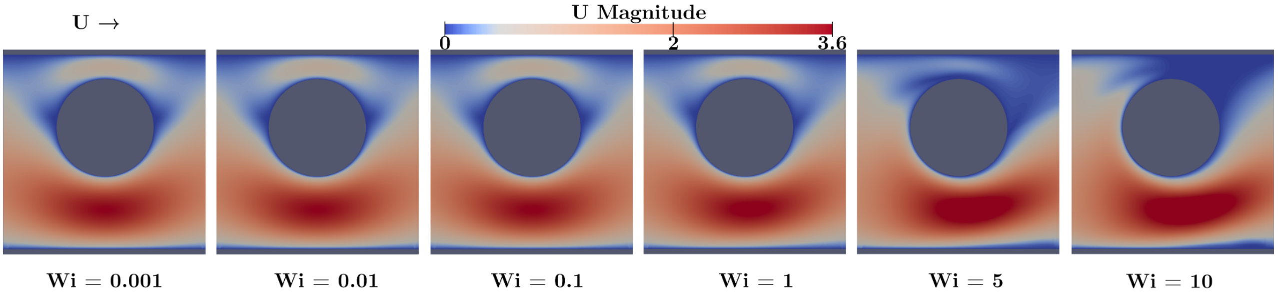

Figure 1: Velocity contours around an asymmetrically confined cylinder (from simulation)

A new way to adapt elastomers for additive manufacturing: a controlled rheologic behavior

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Preference : TALK in session "**S4/ Gels, polymers, foams and rheology at/with interfaces**"

Keywords : Elastomer, Additive Manufacturing, FDM, Viscosity, Vulcanization

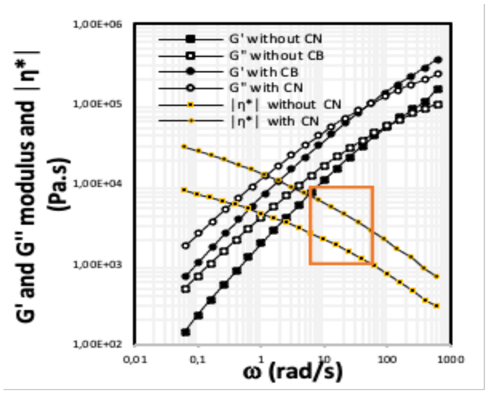

Figure 1: Targeted rheological behavior

Additive manufacturing is becoming more and more accessible. However, if we take a closer look at elastomeric materials only, they are poorly represented[1]. This work is aimed at understanding the mechanisms involved in the processing of elastomers by 3D printing, particularly the structure-property relationship, in order to adapt elastomer formulation to additive manufacturing. Controlling the rheological behavior of the formulation seems to be the main and most versatile way of adapting elastomers to the FDM process. The work we are carrying out will mainly use **E**thylene-**P**ropylene-**D**iene-**M**onomer (EPDM) elastomers and the additive manufacturing process known as ***F**used **D**eposition **M**odeling*.

The targeted rheological behavior of the formulation has to match the requirements of the FDM process, which implies a "liquid-like" behavior within the device and a "solid-like" behavior after the deposition phase. We have characterized the rheological behavior of different formulations based on elastomer blends and carbon black (CB). On the better candidate, we have explored the CB percolation threshold to reach the suitable rheological behavior. Slightly above the percolation threshold, on the one hand, "liquid-like" behavior is ensured over a range of angular frequencies at an operating temperature (120°C) with a viscosity of less than 10^4 Pa.s between 1 and 10 Hz, shown in Figure 1. On the other hand, "solid-like"

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[1] Dasgupta and Dutta, 'Printability of Elastomer as a 3D Printing Material for Additive Manufacturing', Journal of Rubber Research, **2024.**