



Workshop on «Transport & diffusion in soft matter », 29th May 2019, Reims

Program

9h30-10h: welcome

10h-10h10: presentation of the workshop

10h10-11h: Keynote by **Gerhard Nagele**, Forschungszentrum Juelich GmbH

11h-11h15: **Jean-Baptiste Salmon** (LOF, Bordeaux) "Confined drying of a charged colloidal dispersion"

11h15-11h30: Coffee break

11h30-11h45: **Pierre Illien** (PHENIX, Paris) "Phoresis and enhanced diffusion compete in enzyme chemotaxis"

11h45-12h: **Patrick Guenoun** (LIONS, Saclay) "Diffusion of polymers in concentrated solutions for applications to phase separation"

12h-12h15: **Virginie Hugouvieux** (IATE, Montpellier) « Structure and dynamics of a polymer-nanoparticle composite »

12h15-14h: Lunch

14h-14h15: **Bloen Metzger** (IUSTI, Marseille) "Mixing in sheared particulate suspensions"

14h15-14h30: **Bruno Isenmann**, (ILM, Lyon) "Viscosity and self-diffusion coefficient measurements of water and supercooled aqueous solutions"

14h30-14h45: **Gabriel Paës**, (FARE, Reims), "Investigating diffusion of macromolecules in lignocellulose"

14h45-15h: Coffee break

15h-15h15: **Philippe Coussot** (LN, Champs sur marne) "Capillary impregnation controlled by adsorption and diffusion of water in model woods (hydrogels)"

15h15-15-30: **Gaëlle Rondepierre** (ESPCI, Paris) "Influence of surfactants on the statics and dynamics of the wetting of oil on a solid in water"

15h30-15h45: **Claire Schune** (ESPCI, Paris) "Precursor films dynamics of polymer melts"

16h-16h30: closing discussion

Practical information

Venue

CREA (Centre de Recherche en Environnement et Agronomie)

2 , esplanade Roland Garros, 51100 Reims. Free parkings available

How to come by public transport

From "Reims Centre" train station in the centre of Reims, take the bus line number 6, direction "Croix Blandin - Parc Expositions", stop at "Parc Expositions", then walk for 5 min. For more information please visit www.citura.fr (Reims public transport)

ABSTRACTS

Confined drying of a charged colloidal dispersion

A. Bouchaudy, C. Lousert, J.-B. Salmon

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We studied the drying of a charged colloidal dispersion in droplets confined between two circular plates [1-2]. More precisely, we combined this technique with in-situ measurements of concentration fields using Raman micro-spectroscopy, of flow patterns using particle tracking, and of drying-induced mechanical stresses using a precision scale, to probe the roles of (i) colloidal interactions, (ii) buoyancy-driven flows, and (iii) the liquid to solid transition, on the collective diffusion of the dispersion.

[1] *Drying dynamics of a charged colloidal dispersion in a confined drop*. C. Lousert, A. Bouchaudy, and J.B. Salmon. *Phys. Rev. Fluids* **1**, 84201 (2016)

[2] *Drying-induced stresses before solidification in colloidal dispersions: in situ measurements*. A. Bouchaudy, and J.B. Salmon, *Soft Matter* **15**, 2768 (2019)

Phoresis and Enhanced Diffusion Compete in Enzyme Chemotaxis

P. Illien

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Chemotaxis of enzymes in response to gradients in the concentration of their substrate has been widely reported in recent experiments, but a basic understanding of the process is still lacking. Here, we develop a microscopic theory for chemotaxis that is valid for enzymes and other small molecules. Our theory includes both nonspecific interactions between enzyme and substrate as well as complex formation through specific binding between the enzyme and the substrate. We find that two distinct mechanisms contribute to enzyme chemotaxis: a diffusiophoretic mechanism due to the nonspecific interactions and a new type of mechanism due to binding-induced changes in the diffusion coefficient of the enzyme. For a typical enzyme, attractive phoresis and binding-induced enhanced diffusion will compete against each other. We find that phoresis dominates above a critical substrate concentration, whereas binding-induced enhanced diffusion dominates for low substrate concentration. Our results resolve an apparent contradiction regarding the direction of chemotaxis observed in experiments and, in general, clarify the relation between the enhanced diffusion and the chemotaxis of enzymes.

Reference: "Phoresis and Enhanced Diffusion Compete in Enzyme Chemotaxis", J. Agudo-Canalejo, P. Illien, R. Golestanian, *Nano Lett.* **18**, 2711 (2018)

Diffusion of polymers in concentrated solutions for applications to phase separation

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For modeling phase separation (PS) of concentrated polymer solutions, such as for describing the fabrication of membranes by introduction of a non-solvent or by inducing a temperature change, one needs an adequate description of polymer mobility, or equivalently collective diffusion. However several theoretical models were proposed in literature in the last 40 years without always reaching a clear consensus. Here we report on a test of such different models in the framework of 2D phase-field calculations of PS without hydrodynamics for polymer solutions. It is concluded that the dependence of mobility with concentration is crucial but that the choice of the model is not so critical as far as PS is concerned. This situation could change when hydrodynamics is taken into account.

Structure and dynamics of a polymer-nanoparticle composite

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Understanding the motion of nanoparticles in polymer solutions and melts is a problem of broad importance, with applications to many different fields, such as material science, biophysics, and medicine. If the nanoparticles are larger than the polymer's radius of gyration, their structure and dynamics can be well described in terms of effective pair potentials. However, much remains to be understood in the so-called “protein limit”, where the size of the nanoparticles becomes comparable to or smaller than that of the polymers. Moreover, most of the previous studies considering this size range have only focused on the dilute nanoparticle regime, which is easier to handle since inter-nanoparticle interaction can be neglected and the properties of the polymer solution or melt are expected to be unchanged.

Using molecular dynamics simulations, we study the structural and dynamic properties of a semidilute polymer solution containing well dispersed spherical nanoparticles of size smaller than the polymer's radius of gyration. We consider various nanoparticle diameters and a broad range of nanoparticle volume fractions, up to values for which the inter-nanoparticle interaction becomes important. We find that the polymers slow down when the nanoparticle concentration is increased (see Fig. 1, right), in qualitative agreement with the confinement parameter theory [1], according to which polymers slow down because they have to squeeze through “bottlenecks” created by the presence of the nanoparticles. We observe, however, that a purely geometric confinement parameter is not able to capture the dynamics of the polymers at lower temperature: we introduce therefore a (temperature dependent) dynamic confinement parameter, which allows to describe data at different temperatures using a single master curve.

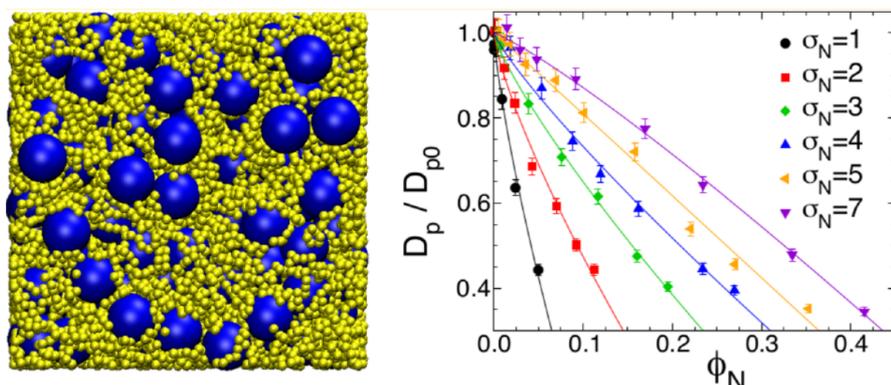


Figure 1: Left: Snapshot of a system

containing NPs of diameter $\sigma_N = 4$ (yellow spheres: monomers; blue spheres: NPs). Right: Reduced diffusion coefficient of the centers of mass (CM) of the chains D_p / D_{p0} as a function of NP volume fraction, where $D_{p0} = D_p (\Phi_N = 0)$.

Also the nanoparticles slow down when their concentration is increased, with the magnitude of the slowing down depending in a non-trivial way on their size. Surprisingly, if the concentration of the nanoparticles is increased past the range in which the nanoparticle dispersion is good, the diffusivities of both polymers and nanoparticles reach a minimum and then start to increase [2].

[1] Choi *et al.*, ACS Macro Lett. 2013, **2**, 485–490

[2] Sorichetti *et al.*, Macromolecules 2018, **51**, 5375–5391

Mixing in sheared particulate suspensions

B. Metzger

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The question addressed is how the presence of rigid particles in a viscous shear flow accelerates mixing. High-resolution PIV measurements of the fluid phase were performed to reconstruct the stretching histories of material lines of the interstitial fluid. We found that the nature of the stretching law changes drastically from linear, in absence of particles, to exponential in the presence of particles. The mean and the standard-deviation of the material line elongations are found to grow exponentially in time and the distribution of elongations converges to a log-normal. A multiplicative stretching model, based on the distribution of local shear-rates and on their persistence time, is derived. This model which quantitatively captures the experimental stretching laws provides a complete description of the flow kinematics. Predictions of the mixing times are then inferred showing that the presence of particles accelerates mixing at large Péclet numbers. The wide distribution of stretching rates results in heterogeneous mixing and hence, broadly distributed mixing times.



Figure 1: Mixing of a drop of dye in a sheared particulate suspension.

Ref: Stretching and mixing in sheared particulate suspensions (2017) JFM 812, 611-635.

Viscosity and self-diffusion coefficient measurements of water and supercooled aqueous solutions

B. Issenmann, L. P. Singh, A. Dehaoui, R. Berthelard and F. Caupin

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Water is a familiar and yet misunderstood liquid. It has many anomalies, among which the effect of pressure on transport coefficients is particularly interesting: at room temperature, an increase in pressure induces a decrease in viscosity and an increase in the molecules' self-diffusion coefficient. When the pressure is high enough, this effect reverses and the water behaves like a normal liquid again.

Until now, viscosity measurements in supercooled water have been very scarce. We will present here viscosity measurements by two different methods: using a Poiseuille flow[1], as well as studying the diffusion of colloids suspended in water by differential dynamic microscopy[2]. We were able to observe an amplification of the anomaly on the viscosity during cooling: at 244K, the viscosity is almost halved when applying a pressure of 2000 bar.

To observe what happens at temperatures where supercooled water is too unstable to study, a solute can be added to the water to lower the nucleation temperature. A particularly interesting solution is glycerol, analogies between water-glycerol and pure water solutions having been observed. Therefore, we also measured the viscosity and self-diffusion coefficient in diluted glycerol solutions.

[1] L. P. Singh, B. Issenmann, F. Caupin. Proc. Natl. Acad. Sci. USA **114**, 4312 (2017)

[2] A. Dehaoui, B. Issenmann, F. Caupin, Proc. Natl. Acad. Sci. USA **112**, 12020 (2015)

Investigating diffusion of macromolecules in lignocellulose

Gabriel Paës

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In the context of global warming, renewable sources of carbon are essential to consider, that is why transformation of plant biomass into chemicals, materials and fuels has become an important topic of research. Due to its natural chemical and structural complexity, lignocellulose which makes plant cell walls cannot be converted efficiently through enzymatic reactions. One important issue is that nano-scale pores and non-specific interactions prevent enzymes from reaching their substrate, leading to an increase of the process cost. Understanding diffusion of enzymes in such complex polymer assemblies is thus a challenge which needs to be addressed to optimize lignocellulose transformation. This presentation will detail main results obtained in the frame of the ANR-funded *Lignopro* project dedicated to the analysis of progression of macromolecules in plant cell walls and how complementary microscopy and spectroscopy techniques have been devised in model and real lignocellulosic matrices.

Capillary impregnation controlled by adsorption and diffusion of water in model woods (hydrogels)

P. Coussot

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Liquid transfers in wood or plant-like materials are at the origin of life but also raise various practical problems, as they affect the mechanical behavior or durability of the material. We focus on the soaking mechanisms (longitudinal) in a hardwood sample placed in contact with a water bath. The structure of this type of wood consists mainly of long open vessels with a diameter of about 100 microns. Unexpectedly, the liquid ascent is about 1000 times slower than expected from a balance between viscous and capillary effects (Washburn model) [1-2].

From MRI and synchrotron observations we show that this effect results from the adsorption and diffusion of bound water in the solid matrix of the wood, which controls the wettability of the walls.

In order to better understand this effect, we have reproduced it by using hydrogel samples as a model wood, pierced by a channel of a few hundred microns. It is then observed that the capillary rise is very rapid when the hydrogel is previously saturated with water. On the contrary, this rise is slowed down by a factor of about 10,000 if the hydrogel has previously been partially dehydrated (which allows it to adsorb part of the liquid during imbibition). In particular, we observe that the contact angle of the liquid in the channel is very close to 90° when the hydrogel is partially saturated. Finally, it is shown that the liquid ascends into the channel only when enough water has been adsorbed into the hydrogel, and diffuses vertically beyond the liquid-air interface into the channel. There is in fact a coupling between the two mechanisms, and as a first approximation, the phenomenon can be well described by diffusion equations with moving boundaries, which show that the dynamics of the phenomenon, equivalent to the propagation of a solidification front in a liquid, is mainly controlled by diffusion in hydrogel.

[1] M. Zhou, S. Caré, A. King, D. Courtier-Murias, S. Rodts, G. Gerber, P. Aïmediou, M. Bonnet, M. Bornert, P. Coussot, Liquid uptake governed by water adsorption in hygroscopic plant-like materials, submitted (2019)

[2] M. Zhou, S. Caré, D. Courtier-Murias, P. Faure, S. Rodts, P. Coussot, Magnetic resonance imaging evidences of the impact of water sorption on hardwood capillary imbibition dynamics, *Wood Science and Technology*, 52, 929-955 (2018)

Influence of surfactants on the statics and dynamics of the wetting of oil on a solid in water

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The wetting of oil on a solid substrate in water is of interest to the petroleum industry and particularly if surfactants are added to the system. In the literature, the role of surfactants on the static wetting behaviour of liquids onto a solid substrate has been intensively studied in the past, in the frame of flotation of solid particles at air/water interfaces. At equilibrium, the adsorption of the surfactants to the solids strongly depends on concentration. As it increases, the arrangement of the surfactants on the surface goes through successive steps (monolayer, bilayer) which modifies the wetting properties of the substrate [1].

Regarding the dynamics of wetting, the role of these different possible phases is less understood. It has been shown that some surfactants can improve the spreading of oil on solids, but this phenomenon depends on many parameters and no theory has been developed yet [2]. More precisely, the transfers of the surfactants to and within the solid/liquid and liquid/liquid interfaces and their competition for adsorption require further investigations.

In this framework, we focus on the case of an oil droplet immersed in water and driven towards a glass substrate. Our objective is to characterize the mechanisms of the dynamic processes occurring when a water film, squeezed between oil and a solid, is destabilized and yields to the wetting of the oil phase onto the solid, in the presence of surfactants.

To achieve this goal, the experimental framework is the following: a dodecane droplet is immersed into a water/surfactants solution at concentrations varying from pure water to several times the critical micellar concentration. The droplet is then driven towards a silica surface, initially trapping and then draining an aqueous film, possibly followed by the wetting of oil on silica. The whole process is imaged using a high-speed camera and the water film thicknesses are measured by an interferometry technique [3].

It appears that, depending on their spontaneous curvature and their concentration, cationic surfactants form structures that lead to different equilibrium situations. In the case of the wetting of oil, we show that the wetting speed varies from four orders of magnitude depending on the surfactants and their concentrations (see Figure). The different transport phenomena at the contact line are investigated in order to understand the main process that governs its motion.

[1] Haidara et al, J. Adhesion Sci. Technol., Vol,13, No 12., 1999; [2] T. Stoebe et al, Langmuir, Vol. 13, N o . 26, 1997 72 79 ; [3] Bluteau et al, Soft Matter, 2017, 13, 1384

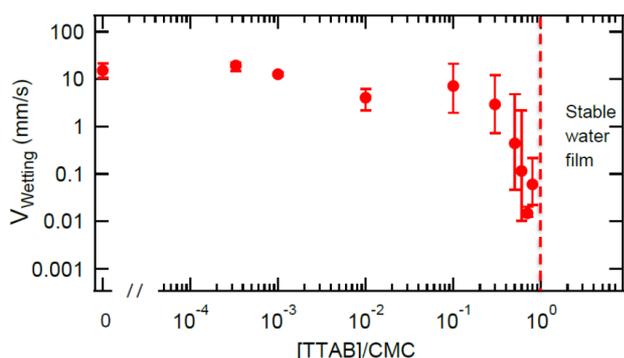


Figure: Evolution of the wetting speed of oil on silica in water as a function of the concentration for TTAB

Precursor films dynamics of polymer melts

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Wetting of liquids on high energy solids where the spreading parameter is positive is expected to lead to nanometer-thick precursor films spreading out of the macroscopic liquid body. In this film, Van der Waals interactions induce either disjoining or conjoining Derjaguin pressure that respectively tend to separate the film interfaces or bring them together. We report for the first time systematic observations of high polarizability polymer melts droplets on silica in pseudo-partial wetting situation. At equilibrium, the droplet coexists with a precursor film, in which the Derjaguin pressure is conjoining. By ellipsometry, we evidence the unique structure and dynamics of these precursor films compared to total wetting films. The thickness profiles with space and time of pseudo-partial wetting films are observed to be diffusive and the molecules form a quasi two-dimensional gas. The diffusion coefficient, specific to each polymer, is found to be independent of the chain density, which demonstrates that the polymer chains diffuse independently. This behavior differs significantly from the case of total wetting, where the diffusion coefficient is found to depend on the polymer thickness. We anticipate that measuring the structure and dynamics of precursor films of polymer melts in pseudo-partial wetting configuration will allow to characterize the dynamics of isolated chains on surfaces.

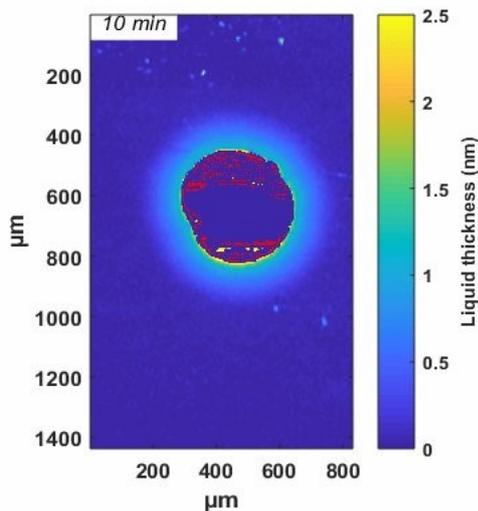


Figure 1: Thickness map of a polybutadiene droplet surrounded by its precursor film, observed by microscopic ellipsometry.

[1] Popescu, M. N.; Oshanin, G.; Dietrich, S.; Cazabat, A. M., Precursor films in wetting phenomena. *Journal of Physics Condensed Matter* 2012, 24, 1-51.

[2] Brochard-Wyart, F.; di Meglio, J. M.; Quéré, D.; de Gennes, P. G., Spreading of non volatile liquids in a continuum picture. *Langmuir* 1991, 7, 335-338.