



Department of Research Evaluation

RESEARCH UNIT SELF-ASSESSMENT DOCUMENT

—
2023-2024 EVALUATION CAMPAIGN
GROUP D

September 2022



1- GENERAL INFORMATION FOR THE CURRENT CONTRACT

1 Unit Identification

Unit name:

Sciences et Ingénierie de la Matière Molle

Soft Matter Science and Engineering

Acronym: SIMM

Label and number: UMR 7615

Main scientific field:

Soft Matter

Scientific panels (in the Hcéres classification) by descending order of importance:

Panel 1

ST4: Chemistry

Panel 2

ST2: Physics

Panel 3

Panel 4

Choose one.

Executive team:

Etienne Barthel

Director

Guylaine Ducouret

Vice-director, in charge of lab management

Jean-Baptiste d'Espinose

Vice-director, in charge of scientific matters

List of the research unit's supervisory institutions and bodies:

ESPCI Paris PSL

(hosting institution)

CNRS

Sorbonne Université

Doctoral schools of affiliation:

Physics and Chemistry of Materials

multi-disciplinary and inter-disciplinary approaches in Materials Sciences - ED 397

2 Presentation of the unit

History, location of the unit:

SIMM as such has been created in 2014 and results from the earlier fusion of two polymer laboratories with complementary expertises in glassy polymers and in soft matter physical chemistry. The laboratory is hosted by ESPCI and located on the campus rue Vauquelin (Paris 5e), but inherited from its history, it is split over two distinct locations some distance across the same building. This situation will soon be overcome with the new premises (fall 2023).

Structure of the unit

With a relatively small size (19 researchers and professors & 10 technical staff including 3 research engineers), the workforce is predominantly CNRS (9 researchers, 9 technical staff) then Sorbonne Université (6 professors) and ESPCI Paris PSL (4 professors, 1 technical staff). The laboratory also hosts a *laboratoire commun* with the company Total.

Scientific orientations of the unit:

Our scientific area is the **chemical engineering and material sciences of soft solids and complex fluids**, with a **broad spectrum** spanning **materials chemistry, physical chemistry, mechanics all the way to physicist's approaches**. In terms of properties, we target especially **transport, flow, rheology and deformation**. Our research is organized around three major scientific areas:

- **functional assembly** (CAID): assembly, self-assembly and disassembly of soft matter – supramolecular architecture of solids and complex liquids, using macromolecules, colloids and emulsions;
- **soft polymer networks** (SPN): multiscale mechanics of soft solids – structure and dissipation mechanisms of strongly deformable solids;
- **out of equilibrium soft matter** (MMHE) - surfaces and interfaces, their structure and properties and their roles in the structure and the stability of supramolecular architecture and macroscopic properties.

Teams, platforms, shared services, etc.:

Because of the strong interconnections between these different scientific areas, many SIMM members work across their boundaries. Therefore, **this report focuses on the scientific areas** rather than on the teams. Also, we routinely use and maintain a large portfolio of **shared characterisation apparatus**. About 15 of them are made available to lab members (and to external users under defined conditions) through three experimental platforms:

- a. Thermal and chromatographic analysis of polymers (M. Hanafi, AI CNRS)
- b. Forces at all scales (B. Bresson, IR CNRS)
- c. Rheology (G. Ducouret / L. Jorgensen, IR CNRS)

3 Scientific subjects and their implications

It is convenient to define soft matter as **deformable condensed matter**. In fact, even if we are also interested in other properties like optical properties (3.1.A, 3.1.B), the **mechanical properties** (elastic, viscoplastic or viscous flow), i.e. resistance to deformation, are central to our work (sic passim). This **material deformability** is made possible through a few **defining features**:

a) **Weak interactions** within the structure play a prominent role, either short range **weak chemical bonds** (3.1) or **longer range interactions** (e.g. van der Waals between surfaces (cf 3.2.B) or electrostatics).

b) **Supramolecular structures**, at various length scales, from 10 nm to 100 μm . Controlling the assembly (3.1.A & B, 3.2.A & 3.3) and disassembly (3.1.C) of these structures is a challenge. Nature exhibits highly hierarchical structures with outstanding properties (eg - wood or bone for mechanics, organ vascularization for transport - 3.1.A) but has powerful tools (beyond our reach) to make them in a very controlled way. Composition heterogeneities (blends (3.2.B), gels (3.1.A, 3.2.A), phase separation (3.1.B, 3.3.B & C), dispersions (3.2.C) are different paths to structure matter at different length scales and design the architectures of **disordered materials** (3.3).

c) **Surfaces and interfaces** play a role because deformation can imply changes in surface area and an associated change in energy, which may become significant because the bulk energy contribution is weak (3.1.B). Surfaces and interfaces often themselves have a (macro)molecular structure (through adsorption or segregation of chemical entities or particules at the interface - 3.2.B) and will undergo dissipation etc... In addition, they are boundary conditions for transport phenomena including the transport of momentum (which generates stress - 3.2.A).

With these three characteristics in mind, and to illustrate our scientific strategy, we have chosen a number of **examples of our recent research results on the formation and deformation of soft matter**. Our research aims at **fundamental understanding** of the deformation of soft matter, through a large range of experimental systems. Beyond their fundamental interest, these topics are **relevant for many technological problems** dealing with the formulation and shaping of a wide spectrum of materials: the corresponding technological issues are also mentioned throughout.

For readability, we have grouped these examples under three categories: *Functional assembly*; *Interfaces and dynamics*; and *Multiscale mechanics*; but as the afterword will show, other readings along transverse directions are equally possible, which also define the specificities of our research.

Note about references: references to **our papers** published **within the reference period (2017-2022)** are shown as **[FirstAuthor Year]** and listed in a separate file. References to **other papers** are shown as **(FirstAuthor Year)** and listed in the text, at the end of each section.

3.1 FUNCTIONAL ASSEMBLY

The orchestration of specific interactions at the molecular level, to design and control assemblies at the supra(macro)molecular scale, is one of the cornerstones of soft matter regardless of the properties sought, whether strength (3.1.A, 3.1.B), deformation (3.1.B), adhesion (3.1.B), shaping (dispensing, e.g. injection, and consolidation, or the converse – dissociation and flow - 3.1.A, B and C). It applies equally to macromolecules (3.1.A, 3.1.B) or colloids (liquid or solid - 3.1.C), either in bulk (3.1.A, B and C) or at interfaces (3.1.B and C). On this topic, our research activity has been oriented towards

- a) designing systems where interactions can be controlled by the environment – this includes the use of controlled changes of environment (ie stimuli - evaporation 3.1.A, pH, salt concentration, temperature - 3.1.A, B, C) to trigger the targeted structure/property;
- b) materials and formulations based on biopolymers and biomimetic approaches for biomedical applications.

The 3 following sub-themes illustrate these orientations.

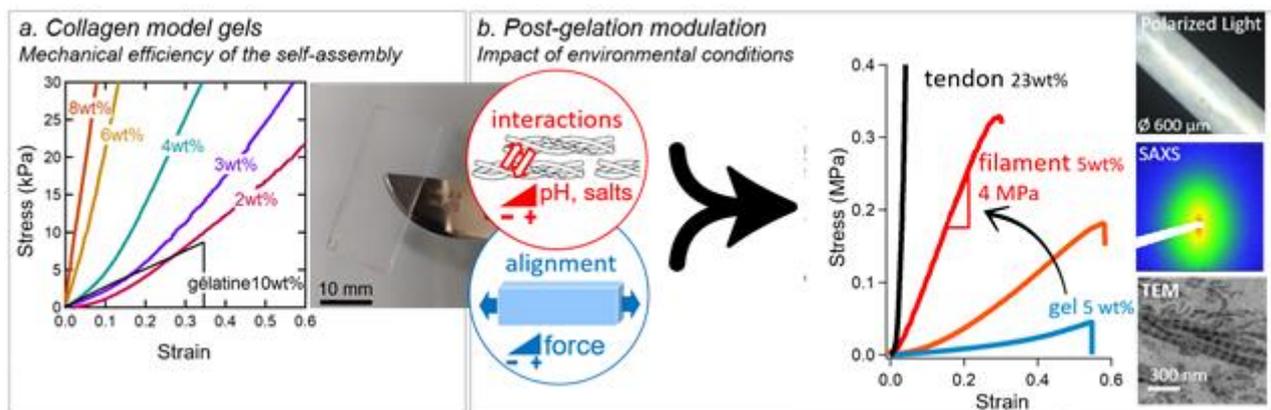
3.1.A - Gel strengthening

A. Marcellan, N. Pantoustier

Because polymer gels are usually networks sparsely crosslinked with strong covalent bonds, designing *tough* gels with only *weak* bonds may seem paradoxical. Yet, self-assembly by noncovalent interactions in aqueous media is a universal feature in living matter (Lehn 2002) and biological constructions give rise to remarkably efficient architectures, such as the orthogonal “plywood” structure (Bouligand 2008). They can also result in fascinating mechanical properties: materials with elastic moduli in the MPa-GPa range can be obtained with hydration levels of about 70 wt% (Fratzl, Misof et al. 1998). The highly selective recognition processes *at the molecular level* characteristic of supramolecular chemistry also generates a great diversity of structures and properties *at higher hierarchical levels* – and with one single basic building block - cell recognition signals, permanent remodeling and self-healing of organs, or regulation of controllable mechanical properties. Here, we tried to harness the supramolecular assembly of collagen, the main building block and component of vertebrate connective tissues.

Main results. In recent works, collagen-based gels have often displayed morphologies and properties that deeply differ from biological tissues (Antoine, Vlachos et al. 2014). Colleagues at Laboratoire de Chimie de la Matière Condensée Paris (LCMCP) have proposed a novel method of assembly, based on spray drying. We have studied the interesting mechanical properties of the collagen resulting from the fast evaporation rate [Lama 2020, Salameh 2020, Camman 2023]. We have also been working to develop model systems to better understand the structure/dynamics and mechanical performance relationships. Collagen gels were synthesized in the lab from rat tail tendon extraction

and purification. Collagen concentrations ranging from 2 to 10 %wt. were investigated with the aim to screen the phase diagram [Lama 2021]. The gelation process - fibrillogenesis - arises from the non-covalent self-assembly of collagen molecules into staggered lateral and head-to-tail arrangement, resulting in the formation a 3D-percolating network of cross-striated fibrils. Figure 1a illustrates the extreme efficiency of this supramolecular assembly on the mechanical response, by comparing the tensile response of collagen and gelatin gels. Indeed, in the case of gelatin, the irreversible denaturation of the native collagen triple helix into a more random coiled structure suppresses the self-assembly into hierarchical fibrillar structures. For the same concentration and almost the same composition, without any addition of chemical cross-links, the collagen gels exhibited stiffnesses an order of magnitude greater than those of gelatin.



Fine tuning of supramolecular interactions for advanced mechanical responses.

a. Fibrillogenesis (i.e. sol-gel transition) arises from the non-covalent self-assembly of collagen molecules into staggered lateral and head-to-tail arrangement. The effect of collagen concentration was investigated in a preliminary study (Ph.D. Lama 2019). *In vitro* collagen gels demonstrated remarkable mechanical responses.

b. Recently we demonstrated that post-gelation, playing with environmental conditions (chemistry and mechanics) can offer an added value to unravel the intricate effects of polymer dynamics and structure (Ph.D. Brun 2023). Structure and its dynamics was investigated by *in situ* WAXD/SAXS (Soleil, coll. F. Boué and J. Perez,) polarized light optical microscopy, environmental SEM and TEM.

Currently, we focus on using environmental parameters (pH and salts) to improve the collagen structure *after the gelation has occurred*. We demonstrate that the swelling conditions fine tune the supramolecular interactions (in both amplitude and dynamics) and results in a large scale remodeling of the structure including fibril diameter and correlation length. We find that the stiffness of the gels is not directly related to collagen concentration or diameter of the fibrils but rather to the quality of the supramolecular arrangement. Mechanical conditioning (relaxation under traction) was also found to result in a large-scale anisotropy and improve mechanical performance. After optimization, and

with 95wt% water, without any chemical cross-links, our collagen filaments can reach a modulus of 4 MPa modulus, about twice the value expected for an unfilled rubber.

References

- Bouligand, Y. (2008). "Liquid crystals and biological morphogenesis: Ancient and new questions." *Comptes Rendus Chimie* 11(3): 281-296.
- Fratzl, P., K. Misof, I. Zizak, G. Rapp, H. Amenitsch and S. Bernstorff (1998). "Fibrillar Structure and Mechanical Properties of Collagen." *Journal of Structural Biology* 122(1): 119-122.

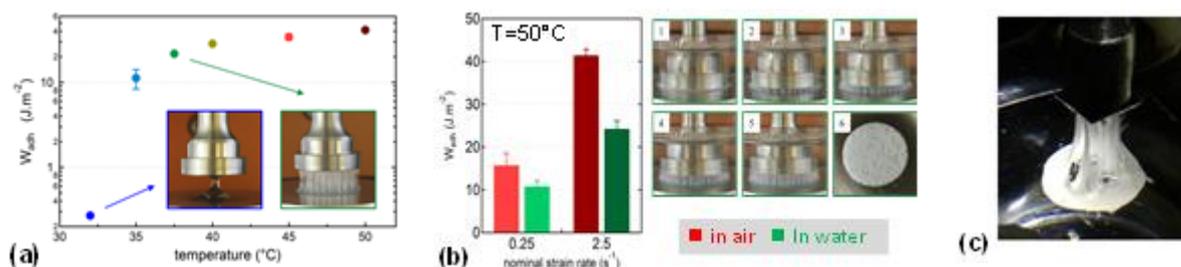
3.1.B – Macromolecular assembly in solution and at surfaces

D. Hourdet, C. Creton, Y. Tran

In solution - In line with our previous works on thermoassociating polymers, that have been devoted to a wide range of industrial applications (drilling fluids, paper manufacture, glass fibering, cosmetics...), our recent developments have more particularly focused on the chemical coupling of environmental sensors (responsive LCST polymer chains) and biomacromolecules (alginates and hyaluronans) and their use in biomedical applications. Their sol/gel transition, triggered by temperature and/or ionic strength in the human body, has been used to design injectable hydrogels with controlled release properties. Indeed, as the liquid formulations gel spontaneously under physiological conditions, they can be easily injected and slow down the diffusion of small molecules or drugs in the organism once in the gel state [Guo 2018; Barbier 2023]. Injecting and releasing living cells is also a challenge as demonstrated by our present work in the field of animal reproduction, in collaboration with IMV technologies.

Underwater adhesives - Associative properties can also be harnessed to obtain underwater adhesion, which is the focus of many recent developments motivated by potential biomedical applications. Underwater adhesion is technically challenging, because the performance of most adhesives is compromised by the presence of water, which eventually leads to bond failure. Although most literature on underwater adhesives has focused on strong covalent chemistries, soft materials based on weak molecular interactions are really promising substitutes due to their low toxicity. Controlled and responsive adhesion in aqueous medium is obtained by triggering specific interactions in situ under temperature, pH or ionic strength control. In a first series of investigations, we have used electrostatic interactions between a macroscopic anionic gel and a cationic hydrogel thin film and vice versa and tested them in a specific mechanical setup for the evaluation of underwater adhesion [Macron 2018; Cedano-Serrano 2019]. Our latest studies have focused on natural polymers (gelatin, agarose and carrageenan). Impact of the patterning of hydrogel thin films by photolithography has also been evaluated: patterning greatly improves adhesiveness by draining the water film from the interface. More recently, within the framework of the European network BioSmartTrainee, we have characterized the effect of large deformations on confined systems using mixtures of homopolymers or graft copolymers coupling electrostatic interactions and/or thermosensitive associations. In close collaboration with the group of M. Kamperman (University of Wageningen), we have shown that in these biomimetic systems, each specific interaction contributes or interferes with the adhesive

properties, in particular through the deformability of the physical gels formed. Thus, the use of thermosensitive polymers makes it possible to generate adhesion at body temperature. Polyelectrolyte complexes can be used as well, playing with the ionic strength (Figure 1) [Dompé 2019 a,b; Dompé 2020 a,b,c; Vahdati 2020 a,b,c].



Work of adhesion of injectable solution of thermoresponsive graft copolymer (8 wt% in water) during probe tack test with extensive fibrillation while debonding at high temperature (a) in air and (b) in water. (c) A soft PSA-like physical hydrogel based on electrostatic interactions showing extensive fibrillation in 0.1 M NaCl.

At surfaces - Besides bulk properties, we have developed organized and structured assemblies on substrates through a platform of nano- and micro-structures of grafted hydrogels thin films (Chollet 2016). We use the synthesis strategy called CLAG (Cross-Linking And Grafting) developed in the SIMM laboratory which consists in simultaneously cross-linking and grafting the preformed and functionalized polymer chains by click chemistry (thiol-ene). The covalent grafting on substrates and the chemical cross-linking between chains ensure chemical and mechanical stability against environmental changes such as swelling, stimulation, temperature, pH and ionic strength [Martwong 2021]. This approach is very flexible and can be generalized to many inorganic substrates (oxide and metal) and to many polymers. It is possible to create hydrogel structures with thicknesses ranging from a few nanometers to ten microns with custom planar patterns designed by photolithography. Fine architectures of nano- and micro-structured polymer-polymer and polymer-inorganic multilayers can thus be tailored.

We propose a new generation of actuatable one- and two-dimensional photonic crystals by exploiting the platform of grafted nano- and micro-hydrogel structures [D'Eramo 2018]. The thermo-responsive properties of hydrogels allow to spectrally modulate photonic crystals. We have obtained Bragg mirrors with high spectral modulation using a multilayer architecture by alternating periodically (thermo)responsive hydrogel layers and continuous inorganic layers with high refractive index. New types of two-dimensional photonic crystals have also been designed by activating (thermally or mechanically) a regular array of hydrogel micro-dots in the lateral plane to modulate the light diffraction properties.

Reference

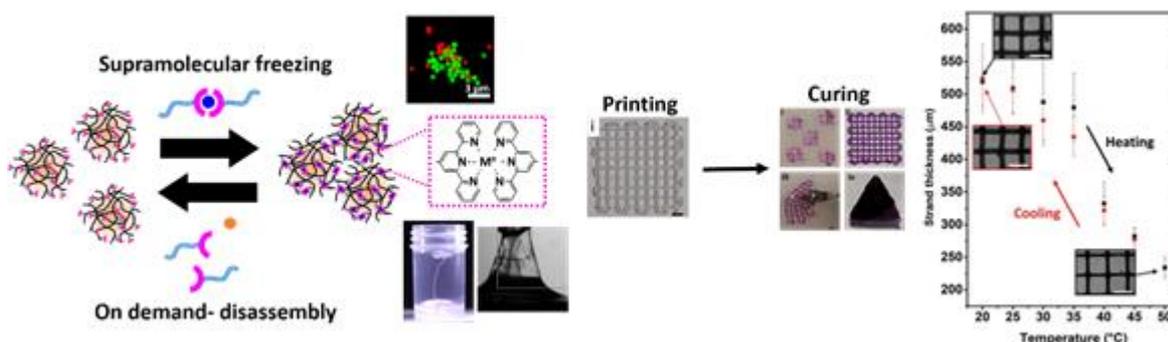
B Chollet, M Li, E Martwong, B Bresson, C Fretigny, P Tabeling, Y Tran, Multiscale surface-attached hydrogel thin films with tailored architecture, ACS Applied Materials & Interfaces 8, 11729, 2016.

3.1.C – 3D colloidal assembly and interface design

N. Sanson, P. Perrin, C. Monteux

Precise control over associative entities is a key concept for 3D colloidal assembly/de-assembly or for dynamic control of 2D interfacial dynamics.

For 3D assembly, research has recently been oriented towards **deformable and versatile colloids named microgels** which are colloidal polymer crosslinked networks dispersed in a solvent (often water). Their chemical nature, which can be adapted on-demand to introduce specific functionalities, and their soft hairy structure, allowing them to come into contact without irreversible aggregation, make microgels outstanding candidates to form colloidal assemblies (Plamper 2017). **The versatility of microgel particles as building blocks can be further enhanced with supramolecular chemistry**, enabling the design of selective or reversible colloidal assemblies.



Supramolecular Engineering of Microgels. (from left to right) Chemical design of metallo-supramolecular microgels as building blocks. Fine tuning of the attractive and repulsive potentials between microgels combined with supramolecular links allow the elaboration of 1D and 2D materials. A supramolecular microgels dispersion with desired rheological properties can be also used as a 3D printing ink.

With such a combination of soft particles and supramolecular chemistry, we have created new stimuli-responsive materials [Es Sayed 2019, Es Sayed 2020 a]. We have first designed the building blocks from terpyridine-functionalized PNiPAM microgels. We have then shown that we can « freeze » macro-assemblies such as macrogels or aggregates of microgels with the help of **metallo-supramolecular links** involving the metal coordination complex. The physicochemical parameters (microgel volume fraction, ionic strength, metal cations, and depletant molecules) have been screened to define **rules for the supramolecular assembly of microgels**. Subsequently, this work was extended and the supramolecular microgels were tested as a 3D printable ink. It is **cured post-printing by metal cations** for long-term stabilization. Through their thermal sensitivity, the microgels can be put into shape in a reversible (and cyclable) manner, and the printing resolution has been enhanced. The supramolecular cross-linking also provides a **mechanism for de-assembly on demand** [Es Sayed 2022].

Turning to interfaces, with a similar supramolecular chemistry, we have developed an advanced class of **microgel emulsifiers** containing stimutable metallo-supramolecular microgels instead of frozen covalent cross-links. [Es Sayed 2020 b] Indeed, oil-in-water emulsions stabilized with these microgels can then be **destabilized on demand by the cleavage of the supramolecular links**. These supramolecular cross-linked microgels should help to understand the mechanisms involved in microgel-stabilized emulsions, an ongoing debate. This opportunity arises from the possibility to “switch on/off” the cross-links for a thorough control of the supramolecular complexes opening, leading to a precise adjustment of the microgel deformability in situ.

A similar strategy for stabilization/destabilization can be applied to liquid systems. Here, **oil droplets** were **encapsulated by assembling polymers directly at liquid interfaces** using **hydrogen bonds** [Dupre de Baubigny 2017, 2021]. With these non-covalent interactions, we were still able to stabilize emulsions over months and **destabilize them on demand by pH variations**, which decrease the interaction strength. For the stability, an important aspect is the **mechanical properties of the capsules**, which we were able to measure using **microfluidic chips**, deforming the capsules in well controlled **elongational flows** [Tregouet 2018, 2019].

Reference

F. A. Plamper, W. Richtering, *Acc. Chem. Res.* 2017, 50, 131.

3.2 INTERFACES AND DYNAMICS

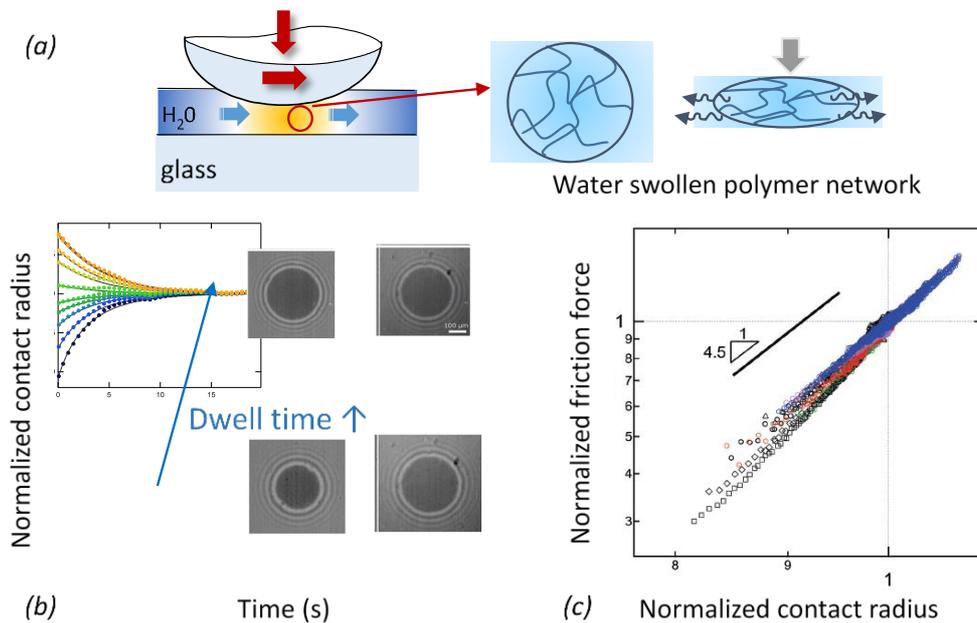
Rich interfaces (often due to surfactants, polymers or particle segregation at the interface) have complex structures which drive non trivial dynamics (3.2.B & C). Combined with diffusion, transport and deformation phenomena, these interface dynamics result in an endless variety of effects, especially for systems with reduced dimensionalities (films 3.2.A & B), and must be harnessed to build architected materials from colloidal systems (3.2.C).

3.2.A - Gel interfaces - Friction and poroelastic transport of thin hydrogel films

A. Chateauinois, Y. Tran, E. Verneuil - Collaboration with Saint Gobain Research (SGR) and with Chung-Yuen Hui (Cornell Univ.)

Friction of water-swollen hydrogels involves a complex and poorly understood interplay between elasto-hydrodynamic lubrication, molecular interactions at the contact interface and stress-induced transport phenomena within the gel network. In situations where thin hydrogel films are confined between rigid substrates, transport phenomena during sliding have a strong impact as a result of mechanical confinement. For example, when a spherical glass sphere is pressed on a hydrogel thin film, the swollen network releases water and the resulting contact depends on the elastic properties of the polymer network and on the contact loading conditions (Fig a). The drainage of water out of the contact zone is characterized by the so-called poroelastic time, which also depends on the network permeability (Delavoipière 2016).

If now the sphere slides on the hydrogel film, we have shown that the poroelastic flow entirely sets the contact size. For that purpose, we have used well-controlled model hydrogel films synthesized using click-chemistry (cf 3.1.B) and dedicated friction experiments allowing contact visualization. Both the friction force and contact shape were found to be controlled by a Peclet number, Pe , defined as the ratio of poroelastic time to a contact time. When $Pe < 1$, the equilibrium circular contact achieved under static normal indentation remains unchanged during sliding. Conversely, for $Pe > 1$, a pore pressure imbalance between the leading and trailing edges of the contact results in a lift force which induces a decrease in contact size and consequently a decrease in the friction force. These observations were modeled within a thin-film approximation which allows a quantitative prediction of the contact shape [Delavoipière 2018 a, b].



Sliding of a spherical glass sphere on a thin hydrogel film (μm -thick). (b) During the onset of sliding, the contact size varies due to water transfers in the gel film under the contact. Depending on the dwell time, the onset of sliding causes either an incoming or an expelling flux and the contact size either decreases or increases. (c) The time variations of the friction force during the transient follow a power law variation with contact radius allowing to collapse all the data on a single master curve.

They were extended to the transient regime corresponding to the onset of sliding during which both the contact radius and the friction force adjust to the movement as a consequence of poroelastic flow (fig b). We also showed that the friction force is set by the contact area through a power law (fig. c) [Ciapa 2020].

This work pertains to many practical applications such as the development of anti-mist coatings or lubricating coatings for bio-medical devices.

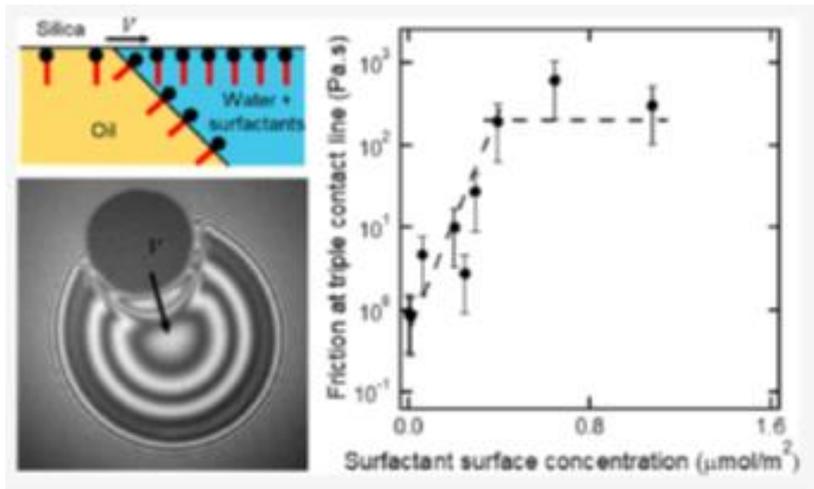
Reference

J. Delavoipière, Y. Tran, E. Verneuil and A. Chateauminois, Poroelastic indentation of mechanically confined hydrogel layers, Soft Matter 12 (2016) 8049-8058

3.2.B – Stability of thin liquid films

E. Verneuil, L. Talini, C. Frétiigny, F. Lequeux

Thin liquid films - beyond hydrodynamics - have their dynamics controlled both by Van der Waal interactions and by solutal and thermal Marangoni effects. In the laboratory, and in particular in the *laboratoire commun* with Totalenergies, the Physicochemistry of Complex Interfaces (PIC) laboratory, we focus on understanding the role of physical chemistry on the macroscopic properties of wetting and stability of liquid films either in foams or in emulsions.

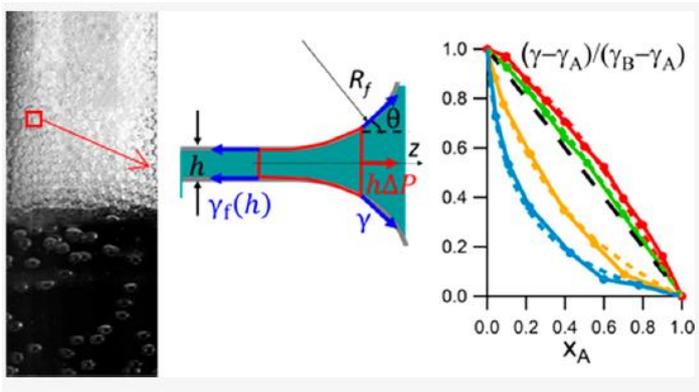


Wetting Dynamics in real systems - In textbooks, the wetting dynamics is predicted theoretically as depending on the viscous dissipation near the

contact line. In practice, the famous Cox-Voinov law rarely applies. We have shown that the presence of surfactants, for a triple oil/water/silica line, generates enormous line friction [Rondepierre 2021]. Furthermore, we have also shown that the geometry itself can influence the existence of a liquid film left by stalling of the moving contact line [Hayoun 2022]. Finally, the only situation for which the Cox Voinov rule is observed is the situation for which precursor films exist. We have shown that on clean silica, liquid polymers all propagate with precursor films, either in full wetting or in (pseudo)partial wetting. Specifically, we have observed that the dynamics of subnanometer polymer films follow Rouse-like dynamics [Schune 2019, Schune 2020].

Thin liquid film destabilization and triple line friction as a function of surface excess of surfactant.

Life and death of thin liquid films - The stability of thin liquid films controls the existence and lifetime of emulsions and foams. For emulsions with high concentrations of surfactants, we have shown that the classical picture of hole formation and expansion (Kabalnov Wennerstrom 1996) can quantitatively describe the lifetime of water/alcohol/water thin films [Dinh 2021a, Dinh2021b]. We have also modeled the dynamics of emulsion creaming and provided a quantitative relationship between the macroscopic lifetime of emulsions, and the local hole formation rate [Dinh 2020].



For asymmetric binary mixtures, that is, made of molecules of very different sizes, strong nonlinearities in surface tension can be measured, that are associated with large foam lifetimes.

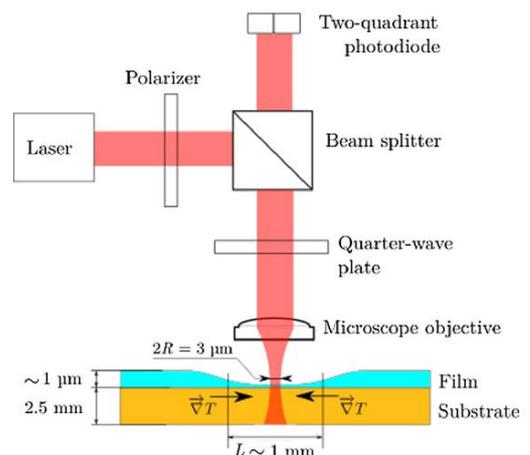
In the absence of surfactant, simple liquids do not foam. In contrast, binary mixtures of simple liquids do foam. This phenomenon was observed in the 1970s, but we give the theoretical explanation. In a binary mixture, one of the components has a lower surface tension than the other and induces a surfactant-like effect on the other [Tran 2020, Tran 2021, Tran 2022]. (see figure). This effect provides insight into the formation and lifetime of foams in oil mixtures. In addition, the mechanism of antifoams (silicone oil) for foams in oil mixtures has been identified: it requires the existence of a two-phase mixture, and the transient interfacial properties of these

mixtures have been understood [Delance 2022].

Reference

Kabalnov and H. Wenerström, *Macroemulsion stability: the oriented wedge theory revisited*, *Langmuir*, 12, 276, 1996.

Thin films on substrates - Liquid films smaller than 100 nm have mechanical properties influenced by Van der Waal interactions. However, it is very difficult to demonstrate this effect experimentally. Using Marangoni thermal effects, we have successfully generated liquid films of controlled thicknesses smaller than 100 nm on substrates and observed how Van der Waal interactions modify their fluxes and fluctuations [Clavaud 2021, Maza-Cuello 2022].



Surface fluctuations of very thin liquid films are affected by long range forces.

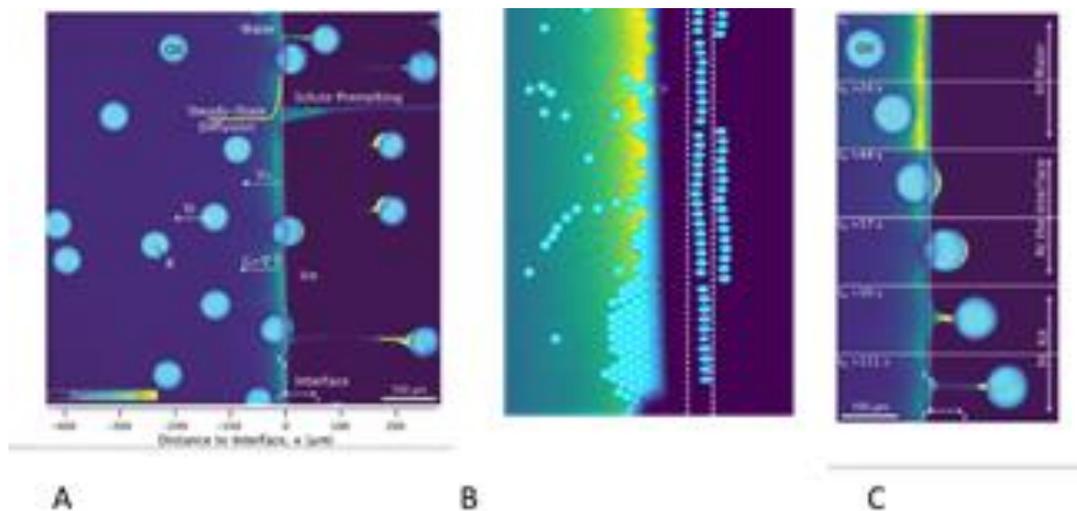
3.2.C – Material architectures and interface dynamics

C. Monteux, A. Kovalenko, N. Sanson, J.-B. d’Espinose

Material architecture at scales larger than the micron may impart various properties such as mechanical strength or, for porous materials, thermal insulation, acoustic absorption etc... To obtain the desired structures at this scale, the solidification of dispersions, foams or emulsions is an interesting

strategy. To implement it, however, the stability, shape and distribution of the fillers, bubbles or droplets must be controlled throughout the solidification process, during which phase changes, surface tension effects, transport and flow (or stress) couple in a complex manner, as shown here by three examples.

Freezing of emulsions - In collaboration with S. Deville at Institut Lumière Matière in Lyon we have studied the behaviour of droplets and bubbles during the solidification of a continuous aqueous phase (freezing) [Dedovets 2018, 2019; Tyagi, 2020, 2021, 2022]. Using fluorescent oil droplets in water with a soluble dye under a confocal microscope, we observed the interaction of the droplets with the



A. Cryoconfocal images of an ice front (dark) advancing at a controlled velocity and encountering oil droplets (in blue). The continuous phase contains a fluorescent dye (rhodamine which appears yellow) and a surfactant. B. Accumulation of oil droplets close to the front and engulfment in rows. C. Shape of an oil droplet during engulfment showing a highly concentrated film around the droplets that keeps them spherical.

ice front (Figure A). We found that the droplets are convected by the freezing front over large distances, starting to interact from a few microns distance. The interaction is mediated by the strong concentration gradient of surfactant, which is non soluble in ice, near the front. As a consequence, droplets accumulate close to the front until they get engulfed in rows or in clusters (Figure B). Besides the spatial distribution of droplets in the solid phase, we also showed that the concentration gradient controls their final shape. Indeed, the high surfactant concentration close to the ice front depresses the freezing point of the aqueous film between the droplets and the front, creating a pocket of unfrozen water surrounding the drops and enabling them to remain almost spherical during the engulfment process (Figure C).

Confined cavitation in soft porous materials - In recent years, increasing attention has been paid to soft porous elastomers, or sponges (Zhu 2017), due to their use as compressible parts in mechanical sensors and soft actuators. Moreover, these materials are expected to enable novel acoustic metamaterials [Talon 2021] and gradient lenses (Jin 2019) due to their extremely low sound speeds at ultrasound frequencies [Kovalenko 2017]. In collaboration with the Navier Laboratory, we have studied the drying of water-saturated porous polydimethylsiloxane (PDMS) elastomers with closed porosity [Nguyen 2020] in which the evaporation of water is possible only via the diffusion across PDMS (Milner 2017).

Starting from water/PDMS emulsions, we fabricated soft macroporous samples with different pore diameter distributions and average diameters ranging from 10 to 300 μm . In these materials, the drying may lead to either a collapsed state with low porosity or the cavitation and reopening of a fraction of the pores. Using optical microscopy and porosity measurements, we showed the influence of the pore diameters and interactions on the result of drying. At pore diameters lower than 30 μm , the majority of pores remain collapsed. We attribute the permanence of the collapse of most small pores to a low probability of cavitation and to the adhesion of the pore walls. Pores with diameters larger than 100 μm reopen via cavitation of the water they contain. The behavior of pores with diameters ranging from 30 to 100 μm depends on the porosity and drying temperature. We also visualize collective cavitation upon the drying of sponges initially saturated with sodium chloride solution. In this case, the cavitation in the largest pores leads to the reopening of small pores in a neighboring zone of the sample. Our results present the first experimental proof of the pore-size-dependent and cooperative nature of the response of soft sponges with closed porosity to drying.

Polymer conformation in cementitious pastes – Another example on our work tailoring materials properties through polymers at interfaces concerns cement admixtures. Modern cement and concrete all rely on the usage of copolymers (most often polycarboxylate ethers) which, by adsorption onto the cement grain, control their fluidity and yield stress by modulating steric repulsions. We have uncovered that the efficiency of these polymers depends on their conformation which is determined by the quality of the solvent, hence by the chemistry of the cement pore solution [Paillard, 2022]. This understanding is crucial as the chemistry of new low-carbon cements is radically different from ordinary Portland cement.

References

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3.3 MULTISCALE MECHANICS

Soft matter is characterised by heterogeneous, multilengthscale structures. Moreover, it is usually disordered and often amorphous, which makes it even more difficult to apprehend. However, the mechanical response is strongly coupled to the structure and mechanical properties must be understood in relation to the material structure, its dynamics and its evolution. This strategy applies both for bulk materials (3.3A) or when interfaces (or cracks) are involved (3.3B & C). In this context, we develop original experimental approaches to link macroscopic mechanical properties to material structure, its dynamics and transformations, and propose relevant models of the main phenomena (3.3A, B & C).

3.3.A – Physical mechanics of amorphous materials – plasticity and dynamics

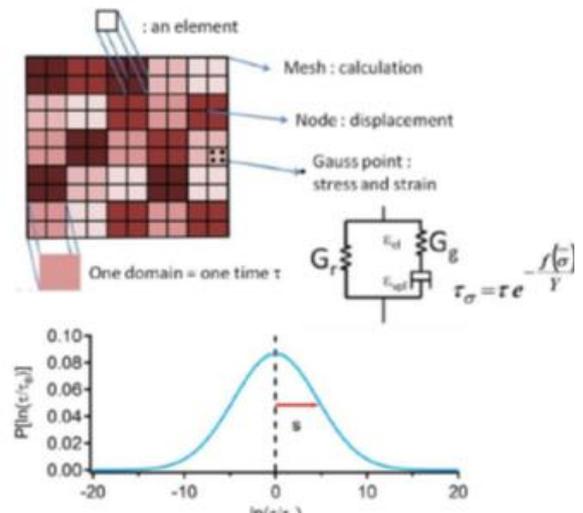
H. Montès, F. Lequeux, E. Barthel

Amorphous materials, in their glassy phase, whether polymeric or inorganic, are materials of daily use, but their mechanical properties, especially plasticity and fracture, are still not fully understood. Under stress, these materials deform by *local* plastic events: reorganization of monomers for polymers and scission recombination of chemical bonds for inorganic glasses. In the SIMM laboratory, we seek to quantify locally and macroscopically this irreversible mechanical behavior, and model it numerically to finally propose constitutive equations.

Finally, the laboratory has shown in the past years that in elastomers reinforced by inorganic particles, the dynamics of polymer chains near the surfaces were similar to those of chains in the glassy state. The understanding of this mechanism allowed the development of calculation codes (within the framework of the MINES/ESPCI/HUTCHINSON chair) and the development of predictions on the mechanical properties of reinforced elastomers

Physical mechanics of amorphous polymers near the glass transition

- For more than twenty years, the physics of amorphous materials has highlighted the existence of dynamic heterogeneities, i.e. considerable variations of the dynamic and thus mechanical properties over distances of a few nanometers. This led us to propose a mechanical approach (collaboration D. Long LPMA, Lyon and S. Cantournet CDM Mines) consisting in directly modeling



Schematic representation of the dynamic heterogeneities, their response and the distribution of characteristic times.

this mechanical heterogeneity [Montes 2019, Masurel 2017 b, Belguise 2021]. With the help of finite element simulations, we were able to show that these gradients in mechanical properties are responsible for the confinement effects observed in reinforced elastomers [Masurel 2017 a]. Moreover, we were able to show experimentally that the dynamics under stress is not multiplied by the exponential of the stress as described in the textbooks, but by the exponential of the square of the stress [Belguise 2021] in agreement with the prediction of Long et al. (PRM 2018).

Reference

D. Long, L. Conca and P. Sotta, Dynamics in glassy polymers: The Eyring model revisited, Phys. Rev. Mater. 2, 105601 (2018)

Plastic deformation in silicate glasses – mechanisms and structural origins - In spite of common wisdom, rupture in silicate glasses is not perfectly brittle. However, plasticity in silicate glasses has been a long-standing challenge because it combines two difficulties: a) it is very local in nature (microns) and b) structural changes due to plastic flow are difficult to demonstrate because the material is amorphous [Barthel 2022].

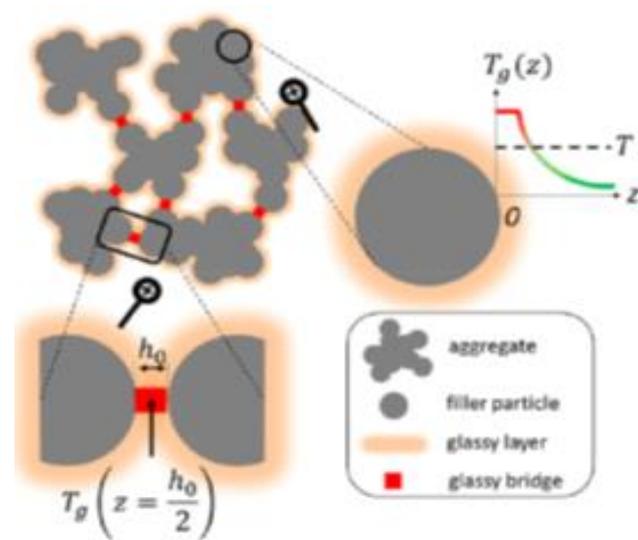
In collaboration with G. Kermouche at EMSE, G. Molnar and A. Tanguy at INSA Lyon and C. Martinet and T. Deschamps at ILM Lyon, we have investigated the plasticity of silicate glasses experimentally by dedicated micromechanics experiments (eg micropillar compression [Martinet 2020] or microRaman spectroscopy [Deschamps 2022]). The results are used to propose constitutive relations for quantitative, continuum scale description of the plastic response of silicate glasses, depending on composition and processing.

Based on this constitutive modelling, with G. Kermouche (EMSE), G. Rosales (Nippon Electric Glass – Shiga, Japan) and V. Keryvin (IRDL), we have recently challenged the accepted idea that irreversible volumetric strain (aka densification) plays a significant role to limit crack initiation in silicate glasses [Barthel 2020]. If true, our claim should open up new avenues to understand crack resistance of silicate glasses, including the high performance of the borosilicate glasses which are ubiquitous in screens for e.g. mobile phone.

In addition, we perform specific molecular dynamics (MD) simulations to emulate the mechanical response of silicate glasses. These MD results further feed the constitutive descriptions [Molnar 2017] but also complement the micromechanics results and highlight possible mechanisms of plasticity and their relation to specific glass structures. As an example, a comparison of microRaman results with MD predictions have evidenced a dependence of the structure of plastically deformed amorphous silica upon loading path [Martinet 2020]. Even more intriguingly, we have evidenced anelasticity phenomena (ie a memory effect) in hydrostatically densified soda lime silica glass, and related the phenomenon to an homogenisation of the structure upon volumetric plastic deformation [Deschamps 2022].

Physical mechanics of reinforced elastomers

Reinforced elastomers are elastomeric matrices containing high concentrations of very rigid inorganic particles. In their condition of use (most soft polymeric materials) the matrix is in the rubbery phase, but in the vicinity of the surface of these particles, the polymer can be considered as glassy. We have shown that the mechanics of reinforced elastomers is governed by the mechanics of the polymer confined between adjacent particles [Montes 2022]. This confined polymer can form glassy bridges that are sensitive to temperature and stress [Masurel 2017]. We have developed tools to simulate the mechanics of these systems [Colombo 2020] and we have demonstrated for the first time a pressure-temperature equivalence law experimentally confirmed on an industrial sample [Champagne 2021].



Formation, geometry and properties of glassy bridges across fillers in reinforced elastomers.

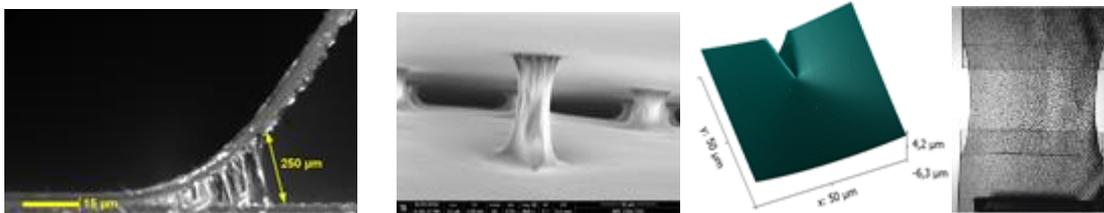
3.3.B – Rupture, interfaces and instabilities in soft dissipative materials

T. Narita, C. Creton, M. Ciccotti, E. Barthel, B. Bresson, A. Chateauminois & C. Frétygn

Fracture properties of tough hydrogels with dynamic crosslinks –As already mentioned in 3.1.A, conventional chemically crosslinked hydrogels are brittle due to the lack of dissipative mechanisms. The discovery of tough double network hydrogels by J.P. Gong has spurred many ideas and investigations. Yet the detailed molecular mechanisms of toughening, often due to structural and dynamic heterogeneities, remain poorly known. In order to investigate one such toughening mechanism, we introduced controlled dynamic crosslinks, which can reversibly break and heal. In order to optimize the number and lifetime of the dynamic crosslinks for improved fracture resistance and for better design of network architecture, we have synthesized two model dynamic hydrogels, based on dynamic covalent bonds or metal-ligand coordination bonds. A small amount of permanent crosslinks prevents terminal flow. By tuning either the bond lifetime through chemistry or the deformation rate through the loading, we have investigated the mechanical properties of these dynamic hydrogels under small and large deformations as well as their fracture behavior in a wide range of time scales. We found that the deformation rate can be normalized by the bond life time to obtain a Weissenberg number which varies over 8 decades over which the fracture energy exhibits a universal behavior. We found a transition from brittle to ductile behavior with decreasing Weissenberg number at a Weissenberg number of the order of 10^{-2} [Debertrand 2021, Zhao 2022].

Towards predictive modelling of toughness - Traditional fracture mechanics relies on the separation between a small region of failure (the crack tip, where the energy needed to separate the surfaces defines the fracture energy) and a well defined stress field coupling this region to the outer boundaries of the sample where the loads are applied. This « simple » situation is lost when dealing with soft and dissipative materials such as soft viscoelastic polymers, hydrogels, food or biological tissues because the regions affected by large strains and bulk dissipation are no longer ‘small’ compared to typical sample dimensions. This makes it difficult to compare toughness measurements carried out with different sample geometries, and it becomes even questionable whether a fracture energy can be unambiguously defined (Creton and Ciccotti, 2016).

In the last five years we have implemented an original approach to overcome these problems. We have developed novel experimental tools to measure both mechanical stress/strain fields during fracture propagation tests and the spatial organization of damage mechanisms at both intermediate (meso) scale and molecular scale. These methods are combined with multi scale mechanical models that aim at describing the energy flow and energy losses from the macroscopic scale (sample loading) to the microscopic scale (molecular bond breaking). The richness of the multidisciplinary expertise at SIMM is a major asset to combine the different descriptions required by the different scales, such as mechanics, large strain rheology, micromechanical modeling, polymer physics and surface chemistry.



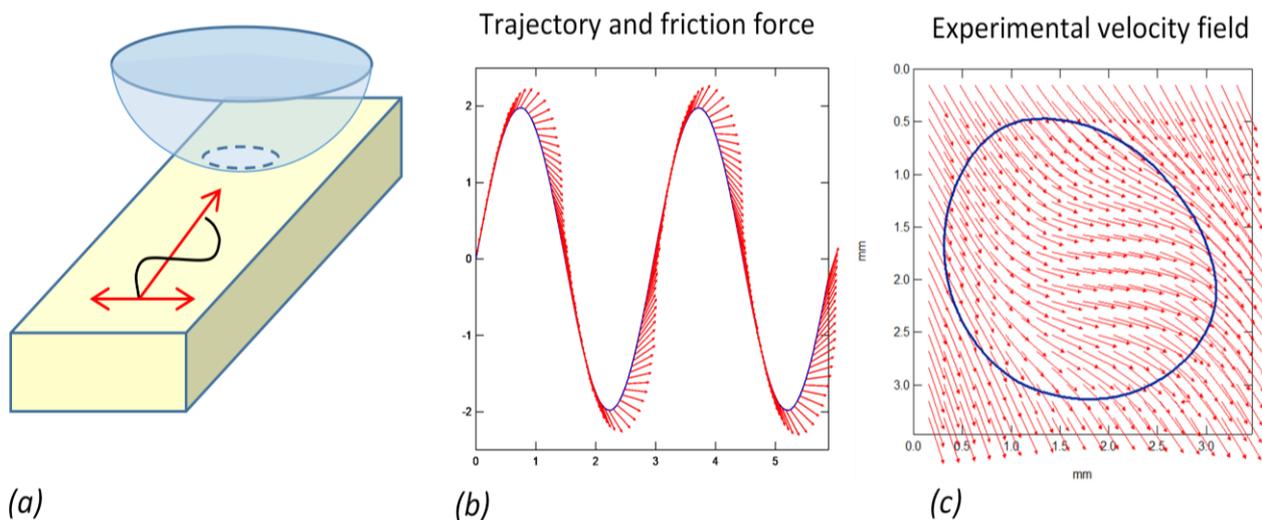
a) side view of the peeling of a pressure-sensitive-adhesive tape [Villey, 2017]. B) SEM image of the detachment of a viscoelastic fibril. c) AFM image of the propagation of a crack in an epoxy resin [George, 2018] d) delamination of a soft viscoelastic layer from glass [Elzière, 2017]

In order to test the generality of this approach we have targeted a series of different materials, by choosing both model materials and advanced technical materials provided by industrial partners, including pressure sensitive adhesives [Villey 2017, Chopin 2018], glassy polymers [George 2018, Nziakou 2020], filled and unfilled elastomers and polymer blends [Elzière 2017, 2019; Fourton 2020]. Moreover, we targeted different kinds of tests and applications which cover a wide range of fracture mechanics, such as peeling, shear joints, probe-tack for adhesion tests [Hui 2018, Liu 2019, Pandey 2020], notched tensile tests and pure shear samples for cohesive fracture tests under monotonic or cyclical loading (fatigue) [Scetta 2021a, b & c, Sanoja 2021].

Reference

Creton, C. and M. Ciccotti (2016). "Fracture and Adhesion of Soft Materials: A Review." *Reports on Progress in Physics* **79**(4): 046601.

Memory effects in friction - Collaboration Fabien Amiot (FEMTO Besançon) and Hutchinson - Transient frictional regimes have long been recognized to involve complex history effects which remains essentially described within the framework of phenomenological models such as the so-called state-and-rate model developed by Rice and Ruina (1983). In order to address the underlying physical mechanisms, we carry out dedicated friction experiments where the contact interface is perturbed by non rectilinear sliding trajectories. As an example, controlled transient friction is achieved by imposing a sinus wave motion to a spherical glass probe in contact with a plane rubber substrate, while measuring the two components of the friction force within the contact plane (Fig. a). We find that the friction force is not tangent to the trajectory (Fig. b) as a result of finite size effects which induce a non-uniform distribution of the sliding velocity within the contact interface (Fig. c). These observations are accounted for by a friction model which takes into account heterogeneous displacements within the contact area [Fazio 2021].



(a) Contact between a rubber substrate and a spherical glass probe under sinus wave motions. (b) Red arrows: Orientation of the friction force along the imposed trajectory (blue line) (c) Red arrows: Sliding velocity field measured within and around the contact. Blue line: contact edge.

The description of sliding non-uniformities at the contact scale thus provides a physical substance to the memory effects embedded in the state-and-rate friction model. This is thought to pave the way to a more physical description of several engineering problems, for which dynamic friction phenomena are involved.

Reference

Rice, J.R., Ruina, A.L., 1983. Stability of steady frictional slipping. *J.Appl.Mech.*50, 343–349.

3.3.C - Towards the molecular scale – original multiscale approaches to fracture

T. Narita, C. Creton, M. Ciccotti, J. Comtet & A. Marcellan

In parallel to the meso/macro approach (3.3.B) which tries to unify tests carried out with the same material but different geometries, we develop alternative approaches targeted at understanding and comparing fracture mechanisms of soft polymer networks at the molecular level.

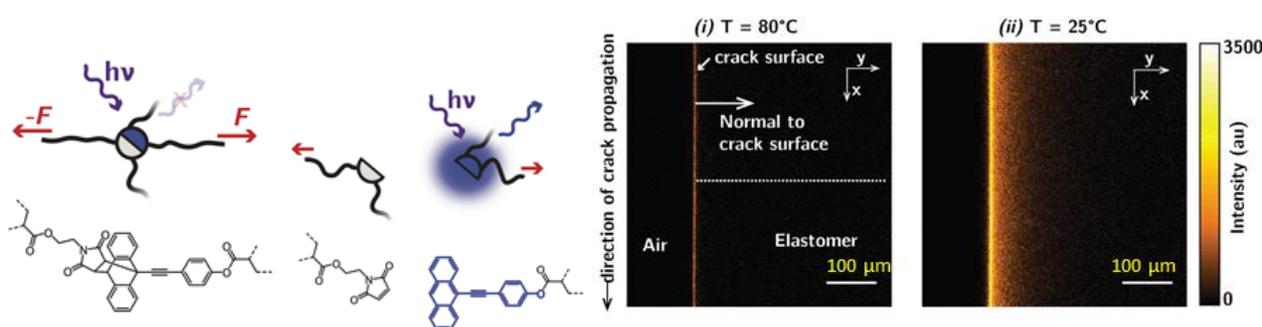
Observation of local dynamics near crack tip of soft solids –In the fracture process of soft solids, localized structural and mechanical changes occur near the crack tip well before a macroscopic failure is detected as crack propagation. The investigation of these local events of “fracture precursors” can help us to understand fracture mechanisms and to develop tools able to predict the occurrence of catastrophic fracture before it actually happens. We developed characterization protocols with multiple speckle diffusing-wave spectroscopy (MSDWS), which is a variation of dynamic light scattering, to map the deformation rate with excellent time and strain rate resolution. We measure the decorrelation profile of multiply scattered light intensity from the probes in the materials. Two other optical techniques were complementarily used: (1) confocal microscopy to map the local damage detected by mechanophore molecules (see below) and (2) digital image correlation to map the displacement field. We applied MSDWS to measure the transient change in deformation rate heterogeneity before crack propagation and other macroscopic transitions. We characterized the fracture behavior in a model commercial brittle silicone elastomer. We detected the acceleration of dynamics (thus damage accumulation) around the crack tip at relatively long time scales (~ 10 min) before the onset of a detectable crack propagation. This is a new optical technique in the context of fracture: it allows in-situ observation of the local events and can be used in real time in a non-destructive way to estimate life time or prevent failure [Ju 2022].

Multiscale approach to fracture through mechanochemistry The cornerstone of this research project, focus of the ERC Advanced grant awarded to C. Creton in 2015, are novel chemistry tools to detect spatially resolved molecular forces and molecular damage in soft materials with molecules called mechanophores. These molecules report an optical signal in response to a mechanical force. When these molecules are suitably incorporated in a soft network they can become fluorescent or change absorption wavelength when the force on a specific chemical bond exceeds a threshold or when the bond breaks [Chen, 2021 review].

Two types of molecules were used for different purposes: using non scissile mechanophores (spyropyran), we investigated and quantified how to map stresses inside materials in multiple network elastomers [Chen 2020], how stresses are transferred from one network to the other [Chen 2021-1] and were also able to investigate the load history of the molecules inside the network [Chen 2021-2].

In parallel, using scissile mechanophores that become fluorescent when the weak bond breaks, we carried out systematic experiments of fracture on single edge notched elastomer samples, loaded in tension [Slotman 2020]. We showed that in simple networks, the extent of bond scission occurring

close to the crack plane during the propagation was greatly dependent on both strain rate and temperature and closely correlated with linear viscoelastic dissipation occurring far from the tip of the crack. Then we demonstrated that the mechanisms of sacrificial bond scission in multiple network elastomers, first demonstrated at room temperature by Ducrot et al. (2014) was active at temperatures much higher than T_g where viscoelastic dissipation becomes negligible in simple networks [Slootman 2022].



Diels-Alder adduct of PI-extended anthracene in the intact form and broken form and fluorescence detection at the fracture surface characterized by confocal microscopy at 80°C (very localized) and 25°C (much more delocalized) in simple networks.

The same mechanophore tool was also used to investigate molecular damage occurring close to the crack tip during fatigue crack growth. Results showed that the low amplitude cycles cause an increasingly localized damage and slow propagation, while a more delocalized damage occurs for higher cycle amplitudes, disproving the idea that the crack advances when a critical level of damage is reached [Sanoja 2021]. Comparing two materials with identical moduli but different strain hardening behaviors, we were able to show that the best structure to optimize fatigue resistance was different from the best structure for fracture toughness.

A last study was carried out in collaboration with Sylvie Castagnet of Poitiers on the damage caused by explosive decompression of hydrogen gas in elastomers. The labeling of elastomers with mechanophores revealed that the cavities observed during the decompression are actually inflated penny-shaped cracks and post-mortem observation by confocal microscopy showed unambiguously that chemical bond scission follows a fracture plane as opposed to a spherical shape [Morelle 2021].

Reference

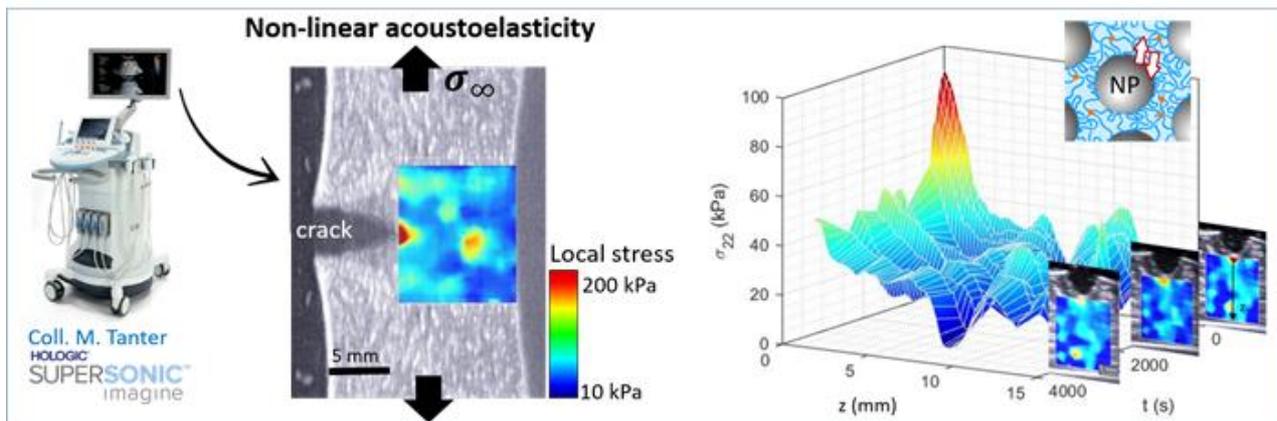
Ducrot, E., Y. Chen, M. Bulters, R. P. Sijbesma and C. Creton (2014). "Toughening Elastomers with Sacrificial Bonds and Watching them Break." *Science* **344**(6180): 186-189.

Development of ultrafast ultrasound (US) imaging for real time mapping of crack mechanisms–

Ultrasound (US) imaging has been commonly used as a qualitative method for the assessment of tissue stiffness for medical diagnosis. In that context, shear wave elastography has recently been developed in the laboratory Physique pour la Médecine (Inserm U1273, ESPCI Paris, PSL University, CNRS UMR 8063) for *in vivo* tissue stiffness imaging. Hence, elastic modulus mapping can provide

clinicians with quantitative data to detect breast cancer, for example. A preliminary study has pioneered the relevance of US elastography for a quantitative viscoelasticity assessment in nanocomposite gels at rest (Genisson, Marcellan et al. 2014). Recently, we took a step further by developing the US imaging elastography technique for imaging the stress state of gels under large stretch.

Based on non-linear acoustoelasticity theory (Destrade and Ogden 2010), we have developed the analysis to experimentally assess the local stress gradient, especially around the crack tip where large dissipative processes take place (Le Blay 2021). We worked on well-controlled, purely elastic poly(*N,N*-Dimethylacrylamide) (PDMA) gels, which were compared to viscoelastic gels filled with silica nanoparticles (NP). With non-linear US imaging, we evidenced a process zone (few mm) around the crack tip where large (quantified) stress relaxation processes operate thanks to the presence



Gel fracture mechanisms in nanocomposite gels probed by UltraSound (US) elastography imaging. Using US elastography for gel fracture is not straightforward: under stress, the shear wave propagation becomes much more complex. Theoretical works on nonlinear acoustoelasticity have never been conducted experimentally. Here, we demonstrate the promise of the method as a new tool to study macromolecular mechanisms involved in gels fracture.

of NP. The stress field imaging demonstrated the shielding effect of NP. Surprisingly, no strong difference in stress relaxation processes (same characteristic time) was observed locally at the crack tip and macroscopically. Finally, at long timescales, full relaxation of the physical network occurs, including at the crack tip, i.e. the stress fields for nanocomposite and unfilled gels are perfectly analogous. Hence, the remarkable fracture toughening effect of NP only operates within the characteristic timescale of stress relaxation.

This work opens new perspectives for the study of macromolecular mechanisms involved in gels fracture. Thus, the promise of the method relies on: 1/ ultrafast imaging of the gel and local probing of viscoelastic properties around the crack (i.e., at framerate/frequency bandwidth being 5,000 Hz that is relevant for rapid crack propagation) and 2/ being non-invasive, a stress mapping at the crack tip in the bulk of the specimen (not only at the gel surface). With a time resolution of tens of milliseconds, the spatial resolution of the mapping for gels is typically around 50 - 100 μm .

References

Destrade, M. and R. W. Ogden (2010). "On the third- and fourth-order constants of incompressible isotropic elasticity." The Journal of the Acoustical Society of America 128(6): 3334-3343.

Gennisson, J.-L., A. Marcellan, A. Dizeux and M. Tanter (2014). "Rheology Over Five Orders of Magnitude in Model Hydrogels: Agreement Between Strain-Controlled Rheometry, Transient Elastography, and Supersonic Shear Wave Imaging." Ieee Transactions on Ultrasonics Ferroelectrics and Frequency Control 61(6): 946-954.

Le Blay, H., T. Deffieux, M. Tanter and A. Marcellan (2021). Development of non-invasive shear wave elastography to assess the mechanical and fracture behavior of tough model gels. APS March Meeting Abstracts.

3.4 OVERVIEW

3.4.A – Interfaces

As suggested by the previous examples, our research is characterized by a **multiscale approach** - assembly (3.1.A & B, 3.3.C) or deassembly (3.1.C) is understood from molecular level interactions and supramolecular structure but primarily probed at the macroscopic scale. For exemple, when studying adhesion rupture (3.3.B), bulk fracture (3.3.C) or dewetting (3.2.B), we pay attention to the full coupling from the macroscopic far field down to the molecular rupture zone and we try to take all relevant processes into account at the relevant length scales. In many cases, the length scale issue is complex because of the coupling between a number of phenomena – transport, phase change, surface tension, flow – all with possibly different lengthscales (3.1.B, 3.2.B, 3.2.C, 3.3.B). In this respect, surfaces are an additional element of complexity: indeed, surface design is central to many systems (3.1.B, 3.2.A, 3.3.B) while interfaces are key in several material architectures (3.1.B, 3.2.C). Analogous to bulks, interfaces also have their own structures (eg decorated by molecules or particles 3.1.C) with associated dissipative processes (3.2.B) through surfactants, precursor films or composition gradients. Finally, their dynamics and stability is also affected by long range interactions (3.2.B).

Directly associated with lengthscale is timescale: through molecular engineering (3.1.B, 3.1.C, 3.3.B & C) or system engineering (and especially confinement - 3.2.A, B & C, 3.3.B), we can also tune the time scales. Smart adaptation of material time scales can be harnessed through temperature (glass

transition or consolubility (NIPAM)) but also other stimuli (pH, salts - 3.1.A, B & C). Such a control is crucial for designed material architecture as best exemplified by the issue of 3D printing (3.1.C). However, besides the mere switching between solid and liquid (3.1.C), our soft matter systems are often characterized by an ambivalent response, their solid or liquid character depending upon time and length scales. For example, surface tension imparts elasticity to a liquid front (3.2.B), a poroelastic material has some degree of liquid flow (3.2.A) while a pressure sensitive adhesive is a highly viscous solid (3.3.B). As a result, to master such complex flow properties, there is a need to better describe the associated material (viscoelastic (3.3.B & C), non-newtonian viscous, viscoplastic (3.3.A)). Because the material has a low elastic modulus, large strains are incurred, which further complexify the problem through geometrical non linearities (adhesion 3.3 and 3.2.B). Fundamental understanding then requires physics-inspired modeling, trying to identify the key ingredients in an attempt to reproduce the overall trends without including the full details (3.2.A & B, 3.3.A & B).

3.4.B – Competences

Following our scientific strategy, we rely on chemistry to perform molecular modification to adapt preexisting molecules to the required type of associativity and tune the properties of surfactants, gels or elastomers, made of acrylates, acrylamides, siloxanes, etc... Recently, natural molecules (polysaccharides) have been increasingly used (3.1.B). Other objects such as microgels or small particles (cement, algae) are also used. In keeping with this expertise in material assembly, we maintain a consistent range of equipment for the characterization of molecule structure (GPC, DLS) material composition (COT, ATG, spectrometers) or thermodynamic properties. Some of these pieces of equipment form the thermal and chromatographic analysis platform headed by M. Hanafi (AI CNRS). Non linear mechanical response and dissipative properties are measured through the rheology platform (9 rheometers - G. Ducouret, IRHC CNRS, to be succeeded by L. Jorgensen) for more liquid like materials or through the multiscale force measurement platform (from pN to kN - 7 instruments - B. Bresson IR CNRS).

In many cases, the mechanical or flow configuration of interest cannot be obtained in standard characterisation devices. For this reason, we rely on numerous dedicated experimental set ups developed in house and based on cameras and sensors. The ESPCI mechanical fabrication workshop (see below) is central for helping with the design and fabrication of these set ups. With these systems, we can measure macroscopic response in ad hoc conditions but also record flow or strain maps through standard (imaging, DIC) or more original (acoustic impedance, mechanophores (3.3.C), Raman spectroscopy (3.3.A)) local probes.

4 Activity profile

Activities (Distribute 100 points on these 7 items)	
Contribution to innovative teaching based on research (University Research Schools - EUR, structuring training through research - SFRI, etc.)	15
Research administration (responsibility for steering research (VP, Institute Management, Scientific Director, etc.), participation in evaluation systems (CNU, CoNRS, CSS, etc.), responsibility for IdEx, project management (ANR, Horizon Europe, ERC, CPER State-Region contract, France 2030, etc.), editorial responsibilities in national or international journals or collections.	25
Research dissemination (sharing knowledge with the general public, scientific outreach, interface between science/society)	5
Research and research supervision (involvement in supervision at doctoral level and post-doctoral level)	35
Technical expertise (for national and regional public authorities, businesses, international bodies (UN, FAO, WHO, etc.))	5
Valorisation, transfer, innovation	15

5 Research environment

Beyond our hosting institution and supervisory bodies, and our involvement in their instances (A. Marcellan – member of comité national CNRS; C. Creton, VP Research ESPCI Paris PSL), we are actively involved in transverse initiatives focusing either on research or teaching. When the **Institut Carnot IPGG Microfluïque** (Chimie ParisTech PSL, ESPCI Paris PSL, ENS) has expanded its perimeter in 2020, SIMM has been actively involved in the definition of the new scientific and technological areas and has become a member/contributor. SIMM now has a representative in the executive board and is actively involved in the development of the Institut through various projects. SIMM has also contributed to setting up the **DIM MaTerRE** (5 year Ile de France initiative – materials for environment and energy) and is an active member of the executive board. It is also a member of the DIM PAMIR (patrimonial materials), participating in several projects.

SIMM is involved in the **build-up of PSL University** through participation in the organisation of the graduate programs of chemistry and of engineering, and through the transverse action **Soft Matter Days** and of **Sorbonne Université** through participation in the Institut des Matériaux iMat. With the LPEM, SIMM (J-B. d’Espinose) is in charge of a PSL solid-state NMR platform dedicated to the study of magnetic and soft matter.

SIMM has a *laboratoire commun* with TotalEnergies.

SIMM has active members in the boards of several **scientific societies** : Groupement Français des Polymères, Groupement Français de Rhéologie, Société Française de Mécanique (mécanique des matériaux – MécaMat). The role of scientific societies has been made more visible within the lab through lab-wide enrolment instead of individual applications.

6 Consideration of the recommendations in the previous report

In this section, the *text in italics* summarizes the recommendations from the detailed HCERES report on the unit.

Reference

HCERES document D2019-EV-0753429V-DER-PUR190015801-022302-RD.pdf ☺

Note : the relatively detailed answers provided below overlap to some extent with the elements provided for the self-evaluation (ch. 3). No attempt has been made to avoid repetitions so that the two sections hold independently.

Keep the high level of publications in terms of quantity and quality

- Number (2012-2016: 210 – 2017-2022: 241) – published in the high end journals of the respective disciplines such as Langmuir, Macromolecules, Soft Matter, Cement and Concrete Research, Physical Review Letters, Physical Review Fluids, Journal of Mechanics and Physics of Solids... but also on occasions in more generalist higher impact factor journals and in particular Physical Review X, Proceedings of the National Academy of Sciences, Angewandte Chemie, Science Advances.

The initiatives taken by the unit to promote the recognition of its youngest researchers and teacher-researchers, encouraged by the previous expert committee, must be further developed.

- The older leaders of research axes have been replaced in 2019 by a younger generation (N. Sanson, Y. Tran & E. Verneuil) - see all lab communications (web site, organisation chart)
- The younger generation (our X generation) is actively involved in teaching or organisational responsibilities (A. Marcellan UE SU, Y. Tran PG chime PSL, ED 397 academic counsel, E. Verneuil Chaire Total, C. Monteux PG Ingénierie PSL & Soft Matter Days PSL), scientific societies (Y. Tran GFP, A. Marcellan Mecamat, T. Narita GFR) and national (A. Marcelan CNRS national committee, C. Monteux ANR review committee) or international (C. Monteux SoftComp Network of Excellence) instances.

The great difficulty in obtaining promotions for the members of the unit, linked to the local context of the ESPCI and UPMC supervisory bodies, constitutes a risk of loss of momentum and evaporation of the unit's research strength.

- As of 2017, the situation was:
 - ESPCI: 2 maîtres de conférences, both with habilitation (HDR) and 2 professors;
 - SU (was UPMC) : 4 maîtres de conférences (2 HDR), 2 professors.

Of the 4 maîtres de conférences with HDR, half of them now hold A category positions, one having been promoted to ESPCI professor (J.-B. d'Espinose) and one having left to take a research director (DR CNRS) position (L. Talini – UMR 125 CNRS/Saint-Gobain – INP sec. 5). For the global vitality of research and the liveliness of researchers, we think that some degree of mobility between

labs is beneficial, under all its forms, national and international, including for promotion and that an attractive lab should be in a state of dynamic equilibrium. Of course, excessive mobility may also trigger instabilities, and we hope that the *repyramidage* ongoing at both ESPCI and SU can help in easing out the difficult promotion bottleneck.

In addition to this risk, the low number of new recruits could lead, in the long term, to an insufficient renewal of the unit's research staff if it continues.

- Since 2017 we have welcome 4 young recruits: Artem Kovalenko (2018 – CR CNRS), Jean Comtet (2021 – CR CNRS), Loren Jorgensen (2022 – IR CNRS) and Théo Merland (2022 – MdC SU). A more aggressive lobbying will be needed to hire the next ESPCI maître de conférence after Y. Tran (2001). Attracting senior researchers should also be set as a priority, the latest being E. Barthel (2014) and M. Ciccotti (2011), setting aside Annie Colin (2015) who departed to CBI-ESPCI in 2016.

Industrial contracts represent half of the laboratory's funding (except for the ERC) and a third of the funding for thesis grants. This is certainly a strength but also a potential risk insofar as the objectives and time constraints linked to industrial issues may be out of step with the continuity and time required for academic research.

This is certainly a strength but also a potential risk insofar as the objectives and time constraints linked to industrial issues may be out of step with the continuity and time required for academic research. The valorisation, through patents or licences, of the new systems developed (with or without industrial participation) is a point to be considered in order to reinforce the visibility (and possibly the resources) of the unit, given its strong innovation potential.

- In connection to industrial interactions, our strategy is not to solve technical problems but to develop fundamental research on some phenomena involved in (mainly) processes or (less frequently) product properties. We mostly adopt simplified, model systems amenable to fundamental research but still relevant to applications. If this strategy can be applied, which requires a clear consensus between partners at the inception of the project, the timescale is not an issue and publications can result. However, the rate of publication may be reduced compared to more standard laboratory policies because our PhD students have less incentive to write publications which are simply not needed to go to industry. The impact of our research on the *industrial potential* (national and beyond) is *high* but the *potential for innovation* is in fact *low* as shown e.g. by the small number of patents we are involved in.

The unit must take care to reduce the heterogeneity in the number of publications of doctoral students and in particular to ensure that each student completes his or her thesis with at least one publication, as recommended by the doctoral school.

- There is still quite a bit of heterogeneity in this respect (see previous answer). Nevertheless, this point has improved as an increasing number of PhD students now write their thesis in part or in full as a collection of articles, which notably increases the publication rate.

The long-term sustainability of the quality of the unit's fundamental research must be accompanied by a policy of recruiting researchers and teacher-researchers who are up to the task. In this respect,

the multidisciplinary and the applied nature of a significant part of the research can be considered as risks in terms of visibility with regard to the academic communities that represent the unit's potential recruitment pool.

Due to the multidisciplinary nature of the research carried out in the unit (physical chemistry, physics, mechanics), it is sometimes difficult to communicate with the academic communities concerned which, moreover, belong to two different Comue (Sorbonne University and PSL); this may constitute a risk in terms of human and financial resources.

- Yes, this opportunity to foster original and fruitful research directions also bears risks. It can be alleviated by increasing and targeting our participations in GDRs (SLAMM, ISM, Dumbio, SoPhy) as well as international conferences or networks (SoftComp), scholarly societies and research consortium (ANR, ITN). Moreover, our recent experience shows that attracting talented postdocs (A. Kovalenko, L. Jorgensen, J. Comtet) facilitates recruitment.

The renovation of the buildings, which is due to start in 2018 and will last at least three years, with the unit being dispersed over five different locations, represents a real risk of difficulty for the life and scientific production of the laboratory.

- Fortunately, this threat has disappeared due to a change in the planning of the building phases and we are right now “simply” bracing up for one single move into our final abode...

The risks related to intellectual property should not be underestimated given the high level of industrial interactions of the unit. Valorisation through patents or licences is a point not to be neglected, and potentially achievable in view of the unit's approach.

- See previous comment on innovation potential.

2- PORTFOLIO INTRODUCTION

To illustrate the scope of our research, this portfolio of documents showcases our lab's activities and their context. The documents included are

- 1) Paper 1 - Mussault C., Guo H., Sanson N., Hourdet D., Marcellan A., Effect of responsive graft length on mechanical toughening and transparency in microphase-separated hydrogels, *Soft Matter* (2019) 134
- 2) Paper 2 – Fazio V., Acito V., Amiot F., Frétigny C. and Chateauminois A., Memory effects in friction: the role of sliding heterogeneities, *Proc Roy Soc. A* (2021) 477:20210559
- 3) Paper 3 - De Soete F., Passade-Boupat N., Talini L., Lequeux F., Verneuil E., Stability of particle laden interfaces of drops flowing through a pore, *Physical Review Fluids* (2022) 7, 104002
- 4) Paper 4 - Gomes P. A., d’Espinose de Lacaillerie J.-B., Lartiges B., Maliet M., Molinier V., Passade-Boupat N., Sanson N. Microalgae as Soft Permeable Particles *Langmuir* (2022) 38, 46, 14044–14052

- 5) 2020-001 Note préparation comité de pilotage PIC.pdf - A note illustrating the aims and actions of the « laboratoire commun » PIC between SIMM and the company Total headed by F. Lequeux (in French).
- 6) PSL-Soft_matter_days.docx – a summary of the transverse Soft Matter workshops co-organised yearly at ESPCI (and now at PSL level) by C. Monteux– with links to the programs of past editions.
- 7) E-M6_boules_de_Noël.avi - 13/12/2021 – TV program on Christmas balls with Flora-Maud Le Menn (PhD student) on the relation between the material the ball is made of (glass or polymer) and its brittleness and with Gilles Garnaud (ESPCI research technical staff) on the metallization of the balls.
- 8) International Summer School on Soft Matter Schedule with chairs.pdf – The summer school « Soft materials: from macromolecular building block's to soft matter physics and mechanics of solids » was organised in 2022 by C. Creton, G. Ducouret and A. Kovalenko – videos of the lectures can be found here :
https://iesc.universita.corsica/article.php?id_site=46&id_menu=0&id_rub=819&id_cat=417&id_art=5888&lang=fr

Our research on soft matter encompasses a wide range of materials, including macromolecular and colloidal systems, and the remarkable physical properties they exhibit under deformation or flow. Paper 1 illustrates the material chemistry side, involving polymer modification for dynamic control of mechanical properties through molecular interaction design and control. Paper 2 focuses on solid interface dynamics, coupled with elasticity. Local heterogeneities emerge which are modelled semi-analytically. Paper 3 investigates how armoured drops (Pickering) flow through constrictions, how this complex process couples liquid interface physics and thin solid film mechanics. Finally, Paper 4 illustrates the type of insight well that established results in more traditional disciplines can bring to rapidly emerging areas such as the colloidal interactions of microalgae, pertinent for understanding their life-cycles as well as for harnessing photosynthesis for fuel applications.

Our research has strong relevance for many industrial processes, and we have numerous interactions with industrial partners. These connections take a particular form through the "laboratoire commun" with Total, on the working of which doc. 5 provides a glimpse. We are also committed to innovative teaching based on research: with half of our staff as university professors and all researchers doing teaching, we support the present evolutions of our two universities (SU and PSL) through initiatives such as the yearly Soft Matter days at PSL (doc. 6). More widely, our research is largely carried out within more or less formal international networks, and this is illustrated by the program of the international summer school on soft matter deformation and rheology recently organised by some of us in Cargese (doc. 7). Finally, we are committed to research dissemination and scientific outreach, with the aim to share our knowledge with the general public and bridge the gap between science and society. Topics such as associative chemistry and rheology can be easily demonstrated to visitors or the general public with tabletop experiments. Other experiments such as fracture or surface modification are better explained in the context of science outreach TV programs (doc. 8) to share our scientific interests with a wider audience.

3- SELF-ASSESSMENT DOCUMENT

Evaluation area 1: Profile, Resources and Organisation of the Unit

Standard 1. The unit has set itself relevant scientific objectives.

SIMM aims at developing the fundamental understanding of soft matter from their constituents to their properties. Our research draws on material chemistry, physical chemistry, mechanics and physics. The materials at stake are mainly polymers, colloids and liquids, and their interfaces. These competences fall within the realm of the section 11 (5) of CNRS and 33 (28) of the CNU, and belong to a long tradition on soft matter at ESPCI Paris PSL. The relevance of these topics for industrial processes entails strong links with industrial partners, mostly large groups involved in materials intensive technologies.

Standard 2. The unit has resources adapted to its activity profile and research environment and mobilizes them.

Beyond endowments, the contractual resources amount to ca 0.8 M€/year on average, out of which about 0.4 M€ for the salaries of post-docs and of a few of the PhD students (e.g. ANR funded) and 0.4 M€ for supplies, equipment and travel expenses. The endowment contribution to common laboratory expenses amount to about 0.2 M€ yearly including maintenance costs amounting to ca 60 k€. Investments in equipment vary but typically range between 0.2 M€ to 0.3 M€ yearly. Our policy is to co-finance equipments from 1) endowments 2) contractual resources 3) subsidies (specific investment from the supervisory authorities, subsidies from the Ile-de-France region (Sesame, DIM) or from the Carnot IPGG microfluidique). In terms of equipment the strategy is to maintain an array of recent, high level and efficient apparatus since the budgetary pressure applies more to manpower than to equipment. At present, this strategy starts to conflict with environmental constraints which suggest that equipment has a large carbon (and others) footprint.

In view of the contractual activity of the laboratory, the human resources for administration (finances, human resources, missions) is a point of serious concern. The administrative staff should be two full time positions. However, due to the problems deriving from the allocation of half-time positions, partial contribution to hiring these persons through contractual resources and variable involvements of the supervisory bodies in administrative support, it has not been possible to maintain a stable operation of two persons full time in the last two years. Despite the full commitment of the administrator in charge, Fabienne Decuq, this situation hampers smooth administration of the laboratory on a daily bases and is a serious threat to operation continuity.

Standard 3. The unit's functioning complies with the rules and directives defined by its supervisors on human resources management, safety, environment, ethical protocols and data as well as scientific heritage protection.

Gender equality – although the gender ratio is about 1 female against 2 males (denoted 1/2) for the permanent staff, *i.e.* reasonably balanced globally (8/14 for researchers and IR, 2/5 for technicians and engineers and 1/2 for the executive team), it is more favourable for students (14/9). For the permanent staff however, the figures degrade notably further along the career path and there is a significantly larger number of male scientists among A-rank scientists (ESPCI and SU professors and CNRS research directors): there the figure drops to 2/9, against a balanced figure amongst junior staff (4/4). The promotion of researchers is mostly in the hands of their employers but we try to support each individual in his/her carrier development irrespective of gender. For example, we have kept a gender balance in the appointments (e. g. 1 male and 1 female for vice directors, 1 male and 2 females when renewing team leaders).

Concerning engineers and technician careers, the figures of female personnel are low so that it is difficult to draw reliable statistics. However, on a case by case basis, the recently arrived TCS (Fabienne Decuq) has been promoted to AI within two years and anticipating the forthcoming retirement of Guylaine Ducouret (IRHC), we have recruited a female agent, Loren Jorgensen (IR2).

Safety – the safety in the laboratory, especially in connection with the chemistry activity is a point of deep concern. Support from both the ESPCI and CNRS safety officers is adequate and to standards. They readily provide help and counselling to the laboratory AP (safety animator – Freddy Martin) and head. However, the safety culture within the laboratory is clearly still at a low ebb. Although some progress seems to have been registered, problems, dangerous situations, incidents are insufficiently reported in the online safety register. Reporting an incident is still considered by many as an act of betrayal of their colleagues, with the false impression that reporting incidents strains our relation with the ESPCI technical staff and management. The positive vision that working from an exhaustive list of the problems which have emerged and examining them with a constructive mindset and in good faith with all the people involved is the best (only) way to limit the number of more serious situations which will emerge later is unfortunately still far out of sight.

Psycho-social risks – on the purely organisational side, following the evolution of workplace practices, the official information from the supervisory bodies has been posted on the intranet. On the more practical side, we observe a gradual evolution towards more openness about the quality of interpersonal relations within the laboratory.

Data preservation – the lab's IT platform is managed by a CNRS engineer (Armand Hakopian - AI). This platform is composed of 120 user stations (laptops or desktops) as well as 70 stations controlling experimental devices (mainly under Windows). There are 4 servers for the unit, either for general purpose (2) or for dedicated experiments or calculations (2). The general purpose servers are configured to host back-up for the user's computers. Large data back-up are stored on individual hard-disks. All the new computers are encrypted. The funds devoted to our information systems are

approximately 30 k€ per year. The computers are renewed at a rate of (5 years)⁻¹ on average, except for experiments, where the turnover is much slower. Care is taken that the experiments computers are renewed before obsolescence threatens the viability of the associated set up.

Environmental risks – they are mostly linked to the possibility of chemical rejections in the Paris sewer systems. This must be avoided through the use of the chemicals disposal circuit run by ESPCI. Of the few rejections reported so far by ESPCI in the recent years, we have checked that there is no reason to suspect they come from our activities.

Business continuity plan – it has perforce been better defined since 2020 (!) through the recourse to home working. Its other major component is connected to preventive maintenance of a few sensitive experimental devices through the laboratory technical staff which obtain special permissions to enter the premises during lockdowns (never thought I could one day write such a sentence).

Synthetic self-evaluation

The laboratory operates in reasonable conditions. Presently, budgetary resources are globally not a major concern and we do not identify any major shortcoming in our working patterns. The one major threat is the chronic understaffing of the administrative office. Improvement in our safety culture is needed as well.

Evaluation area 2. Attractiveness

Standard 1. The unit has an attractive scientific reputation and contributes to the construction of the European research area.

Membership (and active participation!) to instances in the several communities relevant for the laboratory activities is encouraged. The general benefit derived from participations to committees, research groups etc... is emphasized (visibility, advanced information, lobbying). This is a general long term return both for the individual (cf comments on careers above) and the laboratory over a significant time investment. However, beyond expression of their deep gratitude, the laboratory executives have minimum opportunities to mark their appreciation: for example, a higher ranking in the lab selection for PhD scholarship (bourse de thèse) has been given to the project of a professor, in recognition of the 5 years she spent as a member of the CNRS commission, an extremely strenuous task.

However, the significant involvement of the lab members in all sorts of committees is primarily due to the selflessness and impetus of each individual, whom we thank warmly for their involvement. A list of the various capacities filled by laboratory members is given in the appended data file (tab 5). They concern the local scale (Programmes gradués = transverse actions at PSL, recruitment committees, Ecole Doctorale, Dean of Research of ESPCI) national scale (in four scientific societies for Polymers, Rheology, Mechanics & Adhesion; CNRS national committee, university recruitment committees, CNRS recruitment committees (ITA), HCERES evaluation panels, ANR committees) and international scale (ERC panel and Scientific Chair of the Dutch Polymer Institute).

Part of the attractiveness is the international status of our research. In this respect, SIMM has been the leading French partner in the International laboratory “Global Station for Soft Matter” led by the University of Hokkaido (2016-2021) and has co-organized a summer school in Sapporo in the summer of 2017. Our international footprint is also reflected in the 65 publications (about 1 in 4) which result from one or more international collaborations, with co-authors from the USA (21 cumulated occurrences), the Netherlands, Japan (10), Switzerland (9), Italy (8), Belgium (7), China (6), Russia (6), Germany (3), Australia, Austria, Canada, Korea, Spain & UK (1).

Standard 2. The unit is attractive for the quality of its staff hosting policy.

For **new personnel**, we strive to offer a fast and efficient “basic needs response” upon arrival of non-permanent staff and longer time visitors through the advanced preparation of: access pass, office space, computer, administrative registration, lab visit, primary safety instruction. The handling of lab space especially in the rather crowded chemistry labs is sometimes slightly more chaotic. We hope progress is registered once all laboratory rooms in the new premises have been assigned a person-in-charge.

A complete overhaul of the **intranet** has been carried in 2019 so that the most frequently needed **information on the laboratory operation** is now easily accessible online for perusal and for reference by lab members. This is particularly useful in a multi-institution entity like SIMM. Presently, this intranet is only in French, and because of the significant mass of information and the technicality of this information, translation into English is not a completely insignificant amount of work...

For new **young permanent researchers**, as of 2019, they have been granted a starting package of 30 k€ cofinanced by their own institution (respectively CNRS (Jean Comtet) and SU (Théo Merland)) and by ESPCI. Moreover, the laboratory provides them with initial support for intern stipends, small equipment and consumables and if needed financial help to buy larger equipments. Support to obtain PhD scholarship is highly dependent upon the complexities of local practices and in this respect intentions have not always been followed by success. The new IR (Loren Jorgensen) will soon take charge of the rheology platform for which maintenance and investment costs are taken on lab budget.

For scientific exchanges, the laboratory can benefit from grants from ESPCI for **one-month visits by junior or senior researchers**. An average of about two to three such visits per year benefit our foreign colleagues yearly.

Scientific integrity is often a question of pressure applied in terms of quantitative evaluation of results, publication numbers etc... This pressure applied by the financing entities, evaluation entities and employers for recruitment or promotion has gradually increased over the past 20 years. There is no mechanism inside the laboratory taking into consideration such factors. For **open science**, starting around 2015, HAL has been increasingly used as a publication repository, and we now have quite a

consistent use of the tool, thanks to the unrelenting efforts of a devoted open science aficionado (Bruno Bresson) – and also to the drive from CNRS, SU and ESPCI. In the last few years, we have managed to overcome the persistent problem of multiple SIMM identifiers/affiliations etc... to consolidate the publications under a single HAL lab identity. As a result, the publication list appended to this document has been generated automatically. In 2021, an **electronic lab book** (eLabFTW) has been selected by the IT engineer (A. Hakopian), after thorough benchmarking, for use in the lab. Although the choice was good (this very same electronic notebook application has later also been selected by the CNRS specialist committee) its use is for now “very limited” in our daily operation. For the future availability of data (Open access), we follow the ANR guidelines, but the implementation is still mostly erratic and ineffective.

Standard 3. The unit is attractive because of the recognition gained through its success in competitive calls for projects.

At the local scale, DIM and Sesame Ile de France projects are mainly used for equipments (6 projects accepted between 2020-2022 – co-financed with endowment and ANR/EU/industrial contracts, see below), and DIM and Carnot projects for contributions to post-doc hiring.

PhDs (59 over the reference period ie **10/year**) are usually financed through **Ecole doctorale 397** (15 over the reference period i.e. **2/year**) and, along with post-docs (ca 6 ongoing post-doc contracts) by **other french public organisms or agencies** (9 ie **1.5/year** through ANR, CNRS, ADEME, Minist. Aff. Etr., Labex), by EU contracts (6 ie **1/year** through ITN, ERC, COFUND), **CSC or other foreign gov. agencies** (6 ie **1/year**) or **industrial projects** (CIFRE 22 ie **3.5/year** – non-CIFRE 2). For some reason, the number of PhD students, which had grown steadily over the last ten years, has fluctuated widely over the last few years round the value of 10/year. Researchers are actively answering calls for proposals and/or requested to participate as partners at national level (accepted ANR projects: 2017 2 projects/2 project leaders | 2018 1/0 | 2019 1/1 | 2020 2/1 | 2021 4/1 | 2022 1/0). At European level, the laboratory has substantially benefitted from 2 ITN and 1 ERC project (2015-2021 – C. Creton) and one ERC-POC project (2020-2023) and from the COFUND project headed by ESPCI. There is one EU project starting in 2023 (ITN) and 2 submissions in the making (J. Comtet ERC & C. Monteux ITN).

Standard 4. The unit is attractive for the quality of its major equipment and technological skills.

In keeping with the emphasis on macromolecular modification and material elaboration, the lab houses about 30 common characterization equipments which are available for use by any lab members (chromatography (2 setups), rheology (9), tensile testing (5), dynamical mechanical analysis, thermal analysis (2), light diffusion, particle size/sedimentation (2), composition analysis/spectroscopy (5), tensiometers (2), ellipsometer, profilometer, atomic force microscope, nanoindenter). This pool of measurement devices must be maintained and also renewed periodically.

In the recent years we have invested around 200 to 300 k€ yearly for the rejuvenation and improvement of our measurement capabilities. We have a three-fold mode of financing with very roughly 1/3 endowment 1/3 public subsidies (mostly Ile de France region (DIM or SESAME) but also CNRS FEI or SU) 1/3 own resources (lab researchers contracts: public ANR, ERC or private CIFRE, others).

The rheology equipment, headed for the last 20 years by Guylaine Ducouret has been the support of extensive collaborations with external labs (LAMS, PHENIX, C2RMF, LCMCP) and also material evaluation for startups. Following her retirement, the rheology platform will be headed by Loren Jorgensen as of the summer 2023.

In the recent years, we started to implement a similar structuration of our advanced characterisation capabilities with two other platforms headed by engineers for:

- thermal and chromatographic analysis of polymers (M. Hanafi AI CNRS)
- multiscale force measurements (B. Bresson IR CNRS)

In the last two years, the platforms have occasionally received requests from outside entities (mainly startups) to perform characterization runs. If the platform leader decides we have the competence and capacity to answer the request, proper contracting is enforced depending on the nature of the request. The platform structure helps bring coherence and visibility to the activities and competences of the support staff.

SIMM is also significantly involved in other experimental platforms at ESPCI level:

- ESPCI SEM platform, run by B. Bresson (IR CNRS);
- ESPCI workshop for mechanical fabrication, headed by L. Olanier (IE CNRS). Administratively hosted by SIMM, it is shared over three ESPCI laboratories (SIMM, Gulliver, LPEM) but also serves all the other laboratories within ESPCI upon request. Plans are underway to expand the platform to PSL level and scale up the resources accordingly, especially through the Carnot IPGG;
- ESPCI Solid-state NMR spectrometer – currently scaling up as a variable field platform for PSL opened to Ile de France partners (Un. Gustave Eiffel, SU) through a Sesame allocation from the region.

Synthetic self-evaluation

SIMM enjoys a good interconnection with the local and national research community, under a diversity of components. It is reasonably apt at hosting its permanent and non permanent staff. It registers a good success rate at national level (ANR) contracts and for industrial contracts. Reasonable success with EU programs give an experience which should be capitalized upon more widely.

Evaluation area 3. Scientific production

Standard 1. The scientific production of the unit meets quality criteria.

Over the reference period, we have published 241 refereed papers in journals from a rather wide scientific spectrum from physics to chemistry, through polymer sciences and mechanics. The full list is included in the evaluation file. The following list, which covers 155 of our papers, has been compiled as a representative cross-section of our production and delineates our publication pattern. It includes a few more prestigious and/or high impact factor journals (an assessment which depends largely upon the scientific area) but mostly reference journals in the various fields of soft matter research, to which we contribute regularly:

- ACS Nano (2 papers over the reference period), Acta Materialia (2)
- Advanced Materials (3), Angewandte Chemie (4)
- Carbon (2), Cement and Concrete Research (8)
- Journal of Rheology (4), Journal of the Mechanics and Physics of Solids (3)
- Langmuir (21), Macromolecules (17), Mechanics of Materials (4)
- Nature Communications (1), Physical Chemistry Chemical Physics (2)
- Phys. Rev. B (1), Phys. Rev. E (4), Phys. Rev. Fluids (5)
- Phys. Rev. Lett. (6), Phys. Rev. Mat. (2), Phys. Rev. X (1)
- Polymer (4), Polymer Chemistry (2), Polymers (4)
- PNAS (8)
- Science (2), Science Advances (6), Scientific Reports (6)
- Small (1), Soft Matter (30).

The quality of the journals in which we publish our research throughout our activity spectrum suggests that we carry out original and high level research and that we are able to turn our results into insightful publications.

Standard 2. Scientific production is proportionate to the research potential of the unit and shared out between its personnel.

Publication practices vary among fields and also among scientists. All the scientists publish regularly at rates which range between reasonable to very good depending upon the individuals. Due to the absence of recruitment of junior staff between 2008 and 2018, and given the time needed to establish a new activity, it is difficult to analyse specifically the publication rates for younger staff. Among our long-time support engineers, the 2 IRs are co-authors of numerous publications and the AI in charge of the chromatography and thermal analysis platform is co-author of 10 publications. The other technical staff have activities less directly connected to research projects and are not typically co-authors of publications.

Standard 3. The scientific production of the unit respects the principles of scientific integrity, ethics and open science. It complies with the applicable guidelines in this field.

As to traceability of the data, each new member is given an official CNRS lab book. For the rest of the process, we leave it to the individual responsibility of each researchers to ensure the scientific integrity of their work. Usually, standard data management practices are limited to backing up the most important data. More advanced practices aiming at letting the data eventually become available are gradually being implemented at the request of the financing agency. There is no established practice in this respect, however. Finally, as already mentioned, an electronic lab book has been tested but has not found widespread use to date. All publications are made available through HAL.

There is a growing concern among some of the staff about 1) the impact of our research on the environment/resources 2) the relevance of our research for environmental and energy issues. Organised discussions have started under the impetus and guidance of our two sustainable development correspondants, Alba Marcellan and Loren Jorgensen.

Synthetic self-evaluation

The nature, quality and quantity of publications is of good standard.

Evaluation area 4. Contribution of Research Activities to Society

Standard 1. The unit stands out by the quality and quantity of its non-academic interactions.

Due to the nature of our scientific know-how, and also the personal inclination of a number of scientists in the laboratory, we nurture long standing, active and mutually fruitful interactions with a number of industrial partners. These partners are mainly major, French or France-based industrial groups working in middle tech, mass production areas (mainly Total through the *laboratoire commun* PIC, Saint-Gobain, Michelin) because of the relevance of the unit's expertise for their technologies and especially their fabrication processes. In a few instances, the industrial partner is a foreign company (DSM (Holland), 3M (USA), BASF (Germany), Nippon Electric Glass (Japan)). More recently, joint projects with startup companies have also been set up (IMV, Kapsra, Guatec). By far the most frequent vector for these joint projects with industry are PhD projects under a CIFRE with collaboration agreement framework. As a result, the major portion of the contractual budget with industry is devoted to the salaries of non-permanent personnel, PhD student and post-docs, for about 0.8 M€ yearly, amounting for about 1/3 of this workforce. Ideally, the company's interest in for the research projects is a better grasp of the fundamental science behind their technology. In a limited number of cases, however, we have found that a suitably academic research theme is more difficult to find, especially in the case of startups.

Standard 2. The unit develops products for the cultural, economic and social world.

We do not usually develop products. In relation to economic activities, a few of the unit's scientists also act as expert counselors for companies in their fields of expertise.

However, as already stated, we develop fundamental scientific research in areas relevant for technological processes, which benefits our industrial partner through an increased understanding of the scientific background of their technologies.

Standard 3. The team shares its knowledge with the general public and takes part in debates in society.

A few of the unit members regularly organize or participate in outreach actions, mainly Café des Sciences & Fête de la science. On a few occasions (ca 3), lab visits have also been organised for secondary school students from underprivileged areas, at ESPCI's request. Altogether, the number of outreach actions is about 3-5 yearly. Note that the scientific areas covered by the unit activities (transformations of matter with flow, wetting, phase changes...) lend themselves to a number of simple, robust experiments idoneous to demonstrate foundational soft matter phenomena such as glass transition, gelation, Marangoni effect etc... to the layman. In an unformal way, we are presently developing a set of standard such demonstrators which would be available to all to enliven lab visits and adapt the presentation to the scientific background of the audience. However, at SIMM, this facet of the scientific work is nurtured by a few devoted individuals and the tradition is precarious.

Synthetic self-evaluation

SIMM has a strong involvement in the technological spheres of the society. It also maintains a limited number of outreach activities.

4- UNIT TRAJECTORY

SCIENTIFIC PROJECTION

As usual, there is a good deal of continuity between the status report detailed in section 1.3 and the projection sketched here. Two main features are expected to provide inflections. The first feature is the recently recruited young researchers, A. Kovalenko, J. Comtet and T. Merland. Their previous experiences in other laboratories, their own ideas and goals obviously bear on the scientific trajectory of the laboratory (sec. I.i, I.iii, I.ii, I.iii). The second feature is the recent and general focus on environmental issues, which impact our research through many channels: the researchers' own curiosity and interests, the scientific challenges of the moment, the technological and societal demands, which more or less explicitly pervade the following three themes.

I ENGINEERING BIOPOLYMER NETWORKS

Jean-Baptiste d'Espinose, Dominique Hourdet, Alba Marcellan, Théo Merland, Cécile Monteux, Nadège Pantoustier, Patrick Perrin, Nicolas Sanson, Yvette Tran

In a global context of preservation of resources and production of materials with low environmental impact, fine engineering of biopolymer networks open tracks for the rational and efficient design of high performance materials for health and environment. In particular, biosourcing and biodegradation still need more work from the community.

At SIMM lab, we feel the need to gain expertise on the polymerization of monomers from renewable resources as well as a concern to build skills on biodegradable polymers. We target several types of systems and in particular:

- Biodegradable hydrogels made from biosourced high molecular weights polymers (as collagen, chitosan, alginate, starch, cellulose, etc.) that make it difficult to control and tune their architectures.
- Handling variability and heterogeneity of biopolymer systems using strategies based on model systems, fine engineering, assemblies, cross-linking of biosourced molecular and macromolecular systems, with special emphasis on reversibility and interface engineering.

(i) Biosourced gels with reversible cross-linkings

[NP, AM]

We aim to develop fully bio-sourced and biodegradable hydrogels based on an acrylate analog: itaconic acid (extracted from *Aspergillus terreus* fungi) as polymer hydrophilic network reinforced by stereocomplex (SC) crystallization between hydrophobic polymers, i.e. Poly-D-lactide and Poly-L-lactide. We will work at reinforcing the hydrogels by playing with the strength of polyester hydrophobic interaction in water as a secondary physical crosslinking junctions. Degradability (and its conditions) will also have to be properly quantified. Using the concept of reversible sacrificial bond that we have developed in model synthetic gels and our recent experience in the design of model fibrillary collagen gels, we plan now to focus on fracture processes and self-healing capabilities by adjusting the dynamics of supramolecular interactions via pH and ionic strength.

[YT, TM, DH]

Molecular interactions can be finely imprinted within macromolecular architectures to develop responsive assemblies with dramatic transitions in swelling, viscoelastic and/or adhesive properties. In the context of animal insemination, biopolymers offer a versatile and bio-friendly platform for designing macromolecular architectures capable of responding to various issues related to the survival of spermatozoa during periods of storage either in the liquid or frozen state. While reactive assemblies

are currently used in pharmaceutical applications for the controlled release of drugs, the same strategy can also be considered in the case of sperm cells to improve the fertilization process.

(ii) Biopolymers reinforced clay structures

[NP, AM, YT, JBE]

Demographical growth and climate change have recently revived the interest for earthen constructions. Modern constructive solutions are significant greenhouse gas (GHG) emitters (cement production alone amounts to 7% of all anthropogenic GHG emissions). On the contrary, earthen materials are widely available, cheap and carbon neutral or even carbon negative. For new earthen buildings, costly maintenance emerges as an issue limiting their acceptability. This project aims at furnishing proof-of-concept of polymer additives to formulate coatings for improving both the mechanical and water resistance of earthen constructions. We propose to chemically modify biosourced polymers to improve their interaction with clay and provide them with hydrogel properties. Because we aim not just at practical solutions but also at fundamental comprehension, we will exclude complex macromolecules such as tannins or lignins that are known to be promising additives but have an ill-defined structure. The approach will be built on existing knowledge of clay-reinforced petrosourced hydrogel coatings in the SIMM laboratory.

(iii) Engineering liquid-liquid interfaces and solid substrates with (bio)polymers

[PP, NP, CM, TM]

Water-in-water emulsions, which are all-aqueous emulsions obtained by the demixion of incompatible polymer mixtures, are gaining interest in the field of sustainable materials targeting applications in food science or biomedical field. They are characterized by a very low interfacial tension (100 $\mu\text{N/m}$), hence cannot be stabilized by standard surfactants. Micro- and nanoparticles can be used to stabilize W/W emulsions provided their desorption energy is high enough which requires a fine tuning of their wetting properties for the interface. We will engineer a new type of soft nanoparticles called C3M (complex coacervate core micelles) obtained by the self-assembly of biopolymers through electrostatic interactions. These biopolymers will be modified chemically to tune their affinity for the two aqueous polymer phases.

[NP, YT]

Another axis of interface engineering is the adaptability of solid substrates to biological and environmental media, through the development of nano- and micro-structures of hydrogels. These networks of cross-linked polymers grafted by covalent bonding ensure their chemical and mechanical stability on substrates against changes of the aqueous medium (ionic strength, temperature, friction, adhesion...). We propose to take up new challenges in many fields of biotechnologies where the flexibility of the physical chemistry of polymers is a real asset and still little exploited. In the

development of new microfluidic biotechnologies, LCST or UCST thermo-stimulable hydrogels are integrated as micro-cages in lab-on-a-chip for the trapping of single cells. These micro-cages allow isolation, labeling, and lysis of cells to couple sequencing and phenotype. We are also interested in the design of flexible and portable electrochemical biosensors allowing high sensitivity and selectivity of target molecules, deleterious to the environment or health. A key step in the design of an electrochemical biosensor is the immobilization on the sensing electrode of bioreceptors (aptamers, enzymes) for the molecular recognition of the target. The idea is to use the volumetric effect of the grafted hydrogel layer to considerably increase the density of the attached bioreceptors.

II MOLECULAR DYNAMICS AND TRANSPORT AT SOFT INTERFACES

Antoine Chateauminois, Jean Comtet, Jean-Baptiste d'Espinose, Cécile Monteux, Patrick Perrin, Nicolas Sanson, Yvette Tran, Emilie Verneuil

In soft matter systems, surface interactions at molecular scale control adhesion, adsorption, friction or slip at a larger scale, which in turn set the mechanical and transport properties of the whole system. For example, when rubber slides against a solid, polymer interactions contribute to dissipation through a molecular mechanism involving adsorption, elastic stretching and desorption. In colloidal suspensions, interparticulate interactions contribute to the rheological behavior, the colloidal stability or adsorption at liquid interfaces. Although molecular-scale mechanisms are at the very origin of interfacial properties with strong effects on the macroscopic behavior, they still lack a physical description. Indeed, isolating the contribution of the sole surface interactions at the single molecule level to the dynamical response of interfaces is very challenging as it often couples to transfers and to dissipation in bulk, or it involves collective effects. On the other hand, a fine control on polymer interactions at liquid interfaces would allow designing soft interfaces with a selective reactivity. In this project, the SIMM lab aims at describing and tuning the molecular-scale interactions at synthetic and biological interfaces under external forcing, and ultimately relating it to the macroscopic response, both at extended interfaces and within dispersed systems.

Our strategy relies on (i) the development of new dedicated experimental instruments specially designed to probe the interactions at the molecular scale in relation to the macroscopic behavior, (ii) the development of well controlled synthetic colloids and hydrogels for which we can control surface interactions and reactivity, and (iii) the extension of our approach to biosourced and living colloids which external surface includes biopolymers whose interactions control the suspensions dynamics and stability.

(i) Development of experimental techniques for direct correlation of the molecular parameters, surface interactions and macroscopic properties.

[AC, JC, NS, EV]

We will first consider situations involving dilute polymer interfaces in which collective effects are reduced: hydrogel friction, polymer solution flows at a wall or spreading dilute monolayers of

polymer melts. We will also consider charged solid/liquid interfaces and colloidal suspensions. To do so, several paths are offered:

- We will perform direct spatially and temporally resolved observations of the in-plane molecular dynamics under out-of-equilibrium forcing (flow, friction, electric field, confinement) by ellipsometric microscopy on dilute monolayers of polymer melts or by harvesting state-of-the-art Single Molecule Localization Microscopy techniques to track interfacial dynamics of polymer chains or ions at the single-molecule level.
- We will measure the force-velocity relationship in the low velocity limit and over several orders of magnitude in velocity in order to simultaneously probe the equilibrium and the biased out-of-equilibrium interaction potential. Several configurations will be explored: friction on macroscopic hydrogels or elastomers, friction and adhesion between colloids, nanorheology of confined electrolytes.
- Explore the concentrated limit in the mechanical response of colloidal suspensions where interparticulate interactions control the adhesion and friction at the elementary scale, and trigger the formation of aggregates and colloidal networks, the onset of an elastic and dissipative response as well as the transport properties of the solvent. Our purpose is to probe the thermal to frictional transition in these systems, the onset of adhesion and poroelasticity in order to develop a physical description that precisely accounts for the physico-chemistry of the solutions.

(ii) Micro and macro-hydrogel surfaces with controlled reactivity for the fine control of both advective-diffusive transport close to an interface and adsorption mechanisms.

[CM, PP, NS, YT]

Reactive interfaces can be obtained by adsorbing hybrid amphiphilic supramolecular microgels containing a catalyst at a liquid interface that separates two reactive phases. We will then investigate how such functionalized liquid interfaces serve as chemical reactors. Besides we will also design a new type of functionalized macroporous hydrogels, for which we can tune not only their permeability but also their reactivity with solutes. In analogy with standard polymer-based filtration membranes that are obtained by phase separation of polymer/solvent mixtures, we will use the phase separation of a mixture of cross-linking chains and free polymer chains to functionalize the pore surface.

(iii) Interactions between soft biocolloids

[CM, JBE, NS, EV]

We will use our expertise in diffuse colloidal interfaces to understand and control the formation of aggregates of biosourced colloidal systems such as microalgae or natural latexes. For microalgae, a physical description of their diffuse interface in relation to biological conditions is important for understanding the natural biological cycles of marine algae, the transfers of gas and nutrients towards their surface as well as their harvesting to capture CO₂. As a source of inspiration for industrial

processes, we aim at understanding how natural latex inside the living cells of some plants are stabilized by biopolymers such as proteins, phospholipids and fatty acids. From the physical description of the surface interactions at stake, we will gain a control on the usage properties of the natural latex through tensioactive polymers, naturally present or added to the system. This new area of research for the SIMM will be sustained by original experiments such as micropipette force sensors.

III NONLINEAR MECHANICS OF SOFT DISSIPATIVE POLYMERS

Matteo Ciccotti, Costantino Creton, Etienne Barthel, Bruno Bresson, Antoine Chateauminois, Hélène Montes, François Lequeux, Artem Kovalenko, Alba Marcellan, Tetsuharu Narita

Polymers can undergo very large strains and strong energy dissipation, which originate from physical mechanisms taking place at small scales ranging from the nanometric macromolecular networks to structural and dynamical heterogeneities at the mesoscopic level. Based on the development of innovative experimental approaches on well-defined model systems, our objective is to bridge length scales in order to provide a physical description of the very rich mechanical properties that emerge at macroscopic scales. Our strategy is divided into two main routes. On the one hand, we aim at modeling the link between dynamical or structural heterogeneities and the bulk constitutive behavior under homogenous macroscopic loading conditions. On the other hand, we will investigate how the coupling from small to large scales is perturbed by the presence of stress singularities related to propagating fronts such as in adhesion, fracture, friction and cutting.

(i) Upscaling the mechanical response of disordered heterogeneous soft solids

[TN]

The characteristic length scales relevant to the rheology of polymer solutions, the Kuhn length (persistence length) or correlation blob size, of the order of 1 – 100 nm, are well established from static scattering techniques (light, neutrons and X-ray). However, the dynamics of polymer solutions and gels has been much less investigated experimentally than the statics, since the relevant time scales are too short to be reachable by conventional rheological techniques even with different superposition methods. Innovative high-frequency rheological techniques (microrheology based on dynamic light scattering) will be used in a complementary manner to classical low-frequency rheometry in order to characterize how polymer structures of single chains and their networks affect their macroscopic dynamical responses. These high frequency techniques are particularly useful to investigate the dynamics of complex fluids and complex soft solids containing a majority of solvent where time-temperature superposition does not work.

[FL, HM, AC]

Another issue is the physics based modeling of the relationships between microstructure and mechanical properties of model semi-crystalline polymers (PEKK/PEI miscible blends or cross-linked PMMA with PEO end-functionalized chains) in weakly non-linear regimes. Such polymers

exhibit a complex microstructure with complex arrangements of lamellar crystalline stacks dispersed within inter-laminar and inter-fibrillar amorphous phases with distinct properties. Combining creep and stress relaxation responses close to T_g with X-ray investigation of the microstructure, our objective is to identify the contribution of the mechanical coupling between the different phases to the macroscopic mechanical response.

[EB]

Plasticity of glassy systems is a key to tensile strength or damage resistance. However, brittle failure often complicates the experimental analysis of these phenomena and precludes the understanding of the relation between plasticity and composition and structure. To circumvent these difficulties, a promising route is to perform mechanical experiments at small scales, from which intrinsic stress strain relations can be inferred and connected to large scale instabilities. A most interesting case of small scale effect is a craze which is almost a fracture at larger scales but involves highly stretched fibrillary structures at small scales. Similarly, in shear bands (an easier case), the strain state of the polymer inside the bands is not well characterized. Incidentally, shear bands and crazes may coexist! Based on our previous work on silicate glasses, the objective is to couple micro-mechanical experiments on micrometer-sized vitreous polymers to simulations in order to provide new insights on the development of dissipative plastic instabilities, especially shear bands in extended strain and strain rate regimes. We especially expect to elucidate how strain hardening can restrain shear in shear bands and postpone fracture through crazing instabilities.

[AK, EB]

In soft porous elastomers, the mechanical response is largely triggered by poorly understood instabilities at the cell scale. We will especially consider the non-linear regime close to structural collapse, i.e. when the pore walls come into direct contact. In this domain, the mechanical response involves a complex interplay between adhesion, geometrical disorder and both material and geometrical non linearities. Based on previous work, our approach will be based on the innovative design of well-controlled porous materials with micrometer-sized pores from emulsion or particle templating methods, which will be investigated from a combination of mechanical and optical experiments. These results will serve as a rational basis for the design of switchable foam materials with tunable optical properties achieved from the reversible collapse of pores. In another perspective, we will develop magnetic foams for soft coatings with switchable adhesion achieved either with magnetically controllable roughness or by playing with actuated heterogeneous deformation in a magnetic gradient.

(ii) Adhesion, fracture and cutting of soft dissipative materials

[MC, CC, EB, BB, AM]

Traditional fracture mechanics fails when dealing with soft and dissipative materials such as soft, sometimes viscoelastic, polymer based materials, hydrogels, food or biological tissues, especially when these materials are confined between stiffer materials such as in most composites. Since regions

affected by large strains and bulk dissipation due to the crack tip singularity are not any longer ‘small’ in front of sample size, the separability between the scale of energy dissipation, related to fracture propagation, and the scale related to the sample elastic deformation is lost. By combining multiscale modeling and original experimental techniques, we aim at extending to a wider range of materials and failure conditions our original approach that combines the description of energy losses at different scales. This multi-scale approach can then be used to recover a relationship between toughness measurements, made with different sample geometries. We consider the combination of geometrical nonlinearities, related to shape changes, and material nonlinearities, that are characterized by large strain rheology. We also focus on the modeling of damage mechanisms occurring both at the 1-100 μm mesoscale (cavitation, fibrillation, shear bands, filler/matrix debonding, filler/filler interactions, etc) and at the macromolecular network (1-50 nm) scale (chemical and physical bond breaking, dynamical bonds, disentanglement, stress transfer between multiple networks, etc).

Concerning adhesion measurements, the main new project will involve the use of micropatterned substrates in order to trigger the mesoscopic damage mechanisms in a controlled way and to test the effect of a progressive change of the material properties between a viscoelastic fluid and a soft viscoelastic solid. Moreover, the mechanisms of initiation and propagation of debonding in the shear test measurements will be investigated following the experimental strategy that was successfully used for linking peeling and probe tack measurements.

Concerning fracture measurements, the incorporation of fluorescent molecular damage probes will be further developed in order to investigate the role of molecular damage in the initiation and propagation of fractures in a larger range of model materials and loading conditions. We target mainly conventionally vulcanized elastomers, but also glassy polymers and model elastomers with dynamic bonds. Applications of damage characterization beyond mode I fracture, such as cavitation under hydrostatic tension, cutting (see below) and friction and wear will be explored with an emphasis on non-destructive testing.

Shear wave nonlinear elastography will be further developed in order to provide spatially resolved maps of strain and damage of polymer networks in the neighborhood of propagating crack tips. In-situ imaging of loaded materials and crack tips by combining optical, atomic and electron microscopes will be applied to modeling mesoscale fracture mechanisms in fiber assembly materials and biosourced glassy polymers.

Along these lines, a new promising research topic will be developed focusing on the cutting properties of soft and dissipative materials, where the large strain fracture and adhesion properties will be combined with the action of a sharp solid intruder in order to consistently link the cutting resistance with the fracture properties of materials. Moreover, the combination of geometrical and material nonlinearities in the process of cutting soft materials is the source of complex morphogenetic effects in the shape of the cut parts that will be investigated in collaboration with Ecole Normale Supérieure.

FUTURE ORGANISATION, RESOURCES AND STRATEGIC CHOICES WITH REGARDS TO OUR SCIENTIFIC AMBITIONS

In summary, the various expertises in the lab are undergoing a gradual reconfiguration around emerging themes. In terms of organization, the key considerations revolve around manpower and human resources. Instead of well defined teams, we have a more diffuse organisation which aggregates experiences around dynamic scientific challenges. In addition, four key senior researchers are expected to leave the lab in the next two to five years. In this context, there are three areas for action:

1. the career development of the intermediate (40+) generation: facilitate career consolidation by maintaining a supportive lab administration, encouraging initiatives such as responsibilities within university structures or leadership in ambitious research projects (regional initiatives, EU projects). Help build up visibility through international network;
2. the career development of the young generations (less or around 30+): ensure smooth integration of younger researchers through help to build up first projects (lab space, equipment, recruiting PhD students and post-docs, financial support) – help for project writing;
3. attract new researchers either at an early career or more advanced stage: the aim is of course to pursue the evolution of our activities and open up to new techniques or topics related to our present activities. The overall visibility of the lab activities is key for this line of action.

Within the laboratory, these developments must blend individual creativity with team work, exploiting our collective equipment and collective expertise to the best. On a wider scale, they will nurture our contribution to scientific knowledge and our involvement in the various local, national and international scientific communities through collaborations, networks and other transverse initiatives. Finally, they will foster our relations with applicative research and build up the relevance of our results for present technological challenges.