AAPG2024	**DYNAMO**	JCJC
Coordinated by :	Marion GRZELKA	48 months
CES 06 Polymères, composites, physico-chimie de la matière molle		

Wetting dynamics of polymeric liquids at nanoscale

I. Pre-proposal's context, positioning and objective(s)

Project's objectives and research hypotheses

The DYNAMO project aims at understanding how the wetting dynamics of polymeric liquids is correlated to the nanometric roughness, present on all usual surfaces. Through a multidisciplinary approach combining physics and surface chemistry, I propose systematic model experiments that allow a multiscale visualization and characterization of the spreading of a polymer drop. The goal is to compare and model the energy dissipation mechanisms (viscous, viscoelastic, frictional…) competing between nanometric roughness (topographic or chemical) and the propagation of a nanometric film, so-called precursor film, spreading ahead of the macroscopic drop.

Position of the project in relation to the state of the art

Dynamic wetting, which corresponds to the spreading of a liquid over a solid surface, is a phenomenon of great importance in many industrial fields, such as painting, antibacterial coatings and immersion lithography. Over the centuries, wetting has been the subject of extensive research due to its omnipresence in our daily lives. Thanks to recent technological advances enabling us to better control the micro- and nano-texturing of solid surfaces, new wetting behaviors, such as self-cleaning superhydrophobic surfaces, have been discovered in recent years. However, the recent emergence of these new nanoscale wetting behaviors, and innovations in micro- and nanofluidic technologies, call for a better fundamental understanding of this **multiscale phenomenon**, in order to correctly capture macro- and microscopic wetting properties, from the **millimetric size of a drop to nanoscale liquid/substrate interaction**[1].

Indeed, **energy dissipation mechanisms at the contact line are still largely unknown**. On atomically flat, chemically homogeneous surfaces, it has been shown that a film, known as the **precursor film**, precedes the macroscopic drop (Fig. 1a). The presence of this film was predicted theoretically[2], as it was necessary for the dissipation of stress divergence at the contact line, but was difficult to observe experimentally due to its small thickness (<100 nm). The conditions necessary for its emergence and its spreading dynamics remain unknown on these model surfaces, and even unknown on real, rough and heterogeneous surfaces[3].

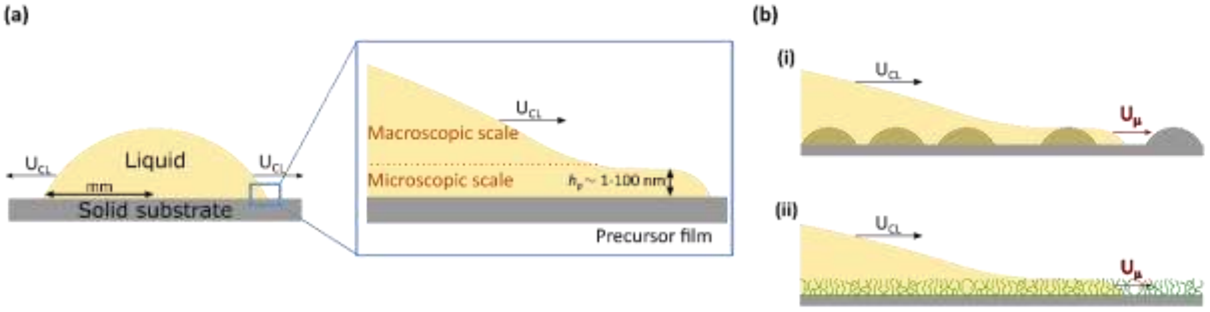

Figure 1: (a) Illustration of a liquid drop spreading with a velocity U_{CL} on a flat solid substrate. Close to the moving contact line, viscous dissipation occurs from the macro- to the micro- scopic scale. Ahead of the macroscopic drop, a thin film, called precursor film, spreads. (b) Additional energy dissipation is induced (i) by roughness and (ii) by polymer coatings. I aim to understand how these extra dissipations compete with the viscous dissipation in a precursor film.

How nanometric roughness, with a characteristic size close to the precursor film thickness, influences the spreading behaviors is still an open question. Recent studies underline that nanometric roughness, either topographic (Fig. 1b (i)) or chemical (Fig. 1b (ii))[4], adds new sources of energy dissipation to the contact line, which affects the hysteresis of the contact angle.

I aim to increase our understanding of wetting dynamics on more usual surfaces, by answering the following topical questions:

1. How does **purely topographic roughness at the nanoscale** affect the spontaneous spreading dynamics of a liquid? **Can a precursor film form and propagate**? How does this formation differ from an atomically flat surface?
2. **How does a chemical nano-coating, polymer brush-type, change the spontaneous wetting dynamics**? Does **viscoelastic energy dissipation** impede the formation of a precursor film?
3. In the case of **forced wetting**, when the substrate is moving at a high velocity, is **frictional dissipation** driving the wetting dynamics on physical and chemical nanostructures?

Methodology to reach the scientific objectives of the project, detailed description of the intended method(s) including its disciplinary coverage (mono-trans-inter-disciplinary) ;

This project is divided in three work packages (WPs). The studied liquid will be a silicone oil, also known as **polydimethylsiloxane melt** (PDMS), considered an **ideal model system for controlled experiments**: it is a polymer melt at ambient temperature. It is also low volatile, very chemically stable and its surface tension γ is almost independent of the degree of polymerization and the temperature. Furthermore, a broad range of viscosity η (from 10^{-2} to 10^{-5} Pa.s) is easily accessible by varying the length of polymer chains. Then, as the wetting dynamics is possibly controlled by the characteristic speed $V_c \sim \eta/\gamma$ (as for most of the capillary phenomena in a viscous regime), a broad temporal range of dynamics can be probed.

WP1: Spontaneous wetting dynamics on topographic nanometric defects

Nanotextured surfaces will be prepared by **depositing silica nanoparticles** on silicon wafers[5]. Defect density is controlled during the liquid deposition phase (nanoparticules solution imbibition time or concentration) and defect size is controlled during the sintering step (furnace temperature and duration). These surfaces will be characterized by atomic force microscopy and X-ray reflectivity.

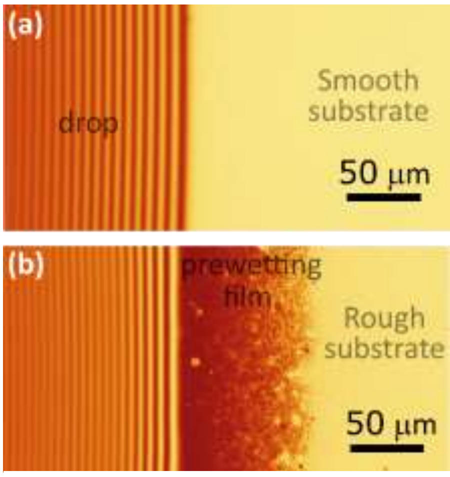

Figure 2: Optical images of a drop of silicone oil spreading on (a) a "smooth" and (b) a "nanorough" substrates. The nanoroughness of the substrate initiates the formation of a prewetting film.wich appears to be inhomogeneous.

As wetting is a multiscale phenomenon, **classical imaging techniques** will be used to probe **macroscopic scales**: fluorescence microscopy, after addition of fluorophore to the liquid, allows 1) reconstructing the thickness profile of the macroscopic drop thanks to fringes of equal thickness (Fig. 2) and 2) visualizing and quantify the film thickness after a fluorescent intensity/thickness calibration.

Preliminary experiments have revealed the importance of nanometric roughness on wetting dynamics. On surfaces with nanodefects, a prewetting film thick enough ($\sim$150 nm) to be seen by optical microscopy forms and spreads (Fig. 2b), when it is not optically visible on a flat surface (Fig. 2a). These preliminary data suggest that the prewetting film formation strongly depends on defect size and/or density.

A finer characterization of the structure of the prewetting film, with a thickness of less than 100 nm, will be obtained using **X-ray reflectivity** (XRR). This technique is among the only techniques that allow characterizing dynamic properties at the **molecular scale** on rough surfaces. Indeed, as ellipsometric measurements rely on the change of polarization upon reflection, its use on substrate presenting nanometric roughness can lead to severe experimental bias. The in-situ impregnation of the nanoroughness by the precursor film will be followed with **grazing incidence small-angle scattering technique (GISAS)**[6]. **The complementarity of these optical and X-ray surface scattering measurements is essential to understand the energy dissipation mechanisms at the contact line from the nanometric to the millimetric scale**.

WP2: Spontaneous wetting dynamics on chemical nano-coated surfaces

Polymer grafted layers are typical examples of **adaptive substrates**: they change their physicochemical properties (e.g., wettability, topography) during the spreading of a liquid, leading to a **coupling between liquid wetting hydrodynamics and substrate dynamics.** Theory and numerical simulations[7] predict different wetting behaviors depending on the grafting density Σ and the degree of polymerization of the free chains P. I will fill the lack of experimental data and build a (Σ, P) diagram for wetting, working with **PDMS grafted chains wetted by PDMS melts**. The conformation of the grafted layer covered by the PDMS films will be measured by **neutron reflectivity**. Using **the contrast variation method**, I will differentiate the hydrogenated grafted chains from the deuterated free chains, allowing measuring the interpenetration between grafted and free chains[8]. This technique is among the only one to predict if the grafted layer indeed "adapt" its conformation during the spreading.

Then, I will focus on the case of complete wetting, i.e., when the free chains do not fully penetrate the anchored ones (Fig. 3). Using the same tools as in WP1 (microscopy and XRR), I aim to understand if a precursor film forms and spreads on the grafted chains and how the latter influence the formation of the film (**viscoelastic deformation**?).

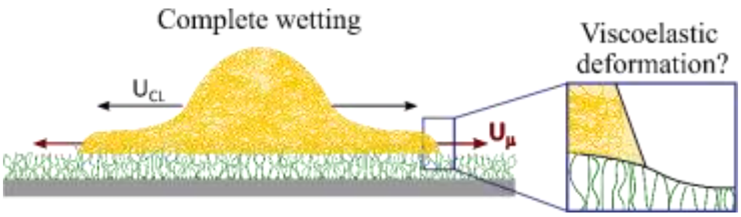

Figure 3: Illustration of complete wetting of a polymeric drop (yellow) on a polymer grafted layer (green). The existence of a precursor film on this adaptive substrate remains open, like the one of the viscoelastic deformation of the anchored chains.

WP3: Forced wetting on topographic nanometric defects and polymer brushes

Most industrial wetting processes correspond to forced wetting: an external force is applied to move the solid/liquid interface beyond equilibrium. It is then crucial to **measure the friction forces** to understand the different energy dissipation mechanisms depending on the substrate velocity. Using micropipette cantilevers, I will build a **droplet tribometer** to measure this friction force F down to tens of nN (Fig. 4). With an inverted microscope, the advancing and receding contact angle will be monitored. This setup was proven robust on flat surfaces[9] but remains to be used on topographic nanometric defects and polymer brushes such as the one studied in WP1 and WP2.

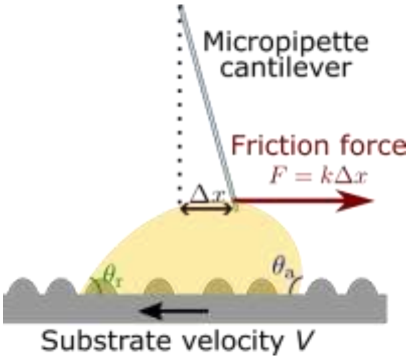

Figure 4: Illustration of the droplet tribometer. The friction force F will be measured for different substrate velocity on nanometric defects and polymer brushes.

Added-value in terms of scientific contribution, concerning the object, the research issue, the methodology ; added-value in terms of knowledge production

Since grazing incidence small-angle scattering technique (GISAS) has been relatively poorly used so far for kinetic studies, WP1 will help to develop new routines to fit such GISAS data. Moreover, neutron reflectivity is the only technique with will allow to measure the interpenetration between free chains and the anchored ones, answering the question of the adaptation of the surface during wetting (WP2). Combining our understanding on viscous, viscoelastic and frictional dissipation (WP3) will pave the road to a better understanding on wetting at the nanoscale.

Ability of the project to address the research issues covered by the chosen research theme

The findings of the project will bring ***a major contribution to the insight into polymer surface and interfaces,*** which is in line with the Research Theme B.2 "Polymers, composites, chemical physics of soft matter" of the 2024 Generic Call for Proposals.

Requested resources. A total amount of **255 k€** is requested for 48 months project.

Staff expenses	Instruments and material costs	Administrative management
115 k€ (36 months PhD) + 13 k€ (1 M2 and 1 L3/M1 students)	**97 k€ (chemicals, AFM measurements, optical components, travels)**	**30 k€**

II. Partnership

Dr. Marion Grzelka, scientific coordinator of this project: I am a CEA researcher at the Léon Brillouin Laboratory (LLB) since October 2022. I have been working in the field of soft matter, with a particular interest in polymer physics at interfaces, since my PhD (defended in December 2019) at the Laboratoire de Physique des Solides d'Orsay. My research interest focus on multi-scale phenomena in polymeric systems, establishing links between nanoscale physicochemical properties and macroscopic physical phenomena (fracture, slippage, adhesion, local viscosity…). During my postdoctoral project in the University of Amsterdam, I mentored 4 PhD students on polymer physics projects. I am co-supervising *E. Mirzahossein,* a PhD candidate now entering her 4th and last year of PhD in the University of Amsterdam.

My research background in polymer fluids, surfaces preparation and characterization and optical microscopy is in perfect alignment with this proposal. Combining my expertise with that of the "Matière molle et biophysique" (MMB) group of LLB, one of the **world-leading group for neutron and X-ray experiments,** is an excellent opportunity to lead this project. In particular*, Dr. Cousin* and *Dr. Chennevière* are specialists of X-rays and neutrons reflectivity. I will benefit from the availability on a daily basis of a XEUSS X-ray reflectometer in LLB. For neutron reflectivity, experiments will be performed on the state-of the-art instruments FIGARO at Institut Laue Langevin (ILL, Grenoble) and MARIA at Heinz Maier-Leibnitz Zentrum (Munich) with long-term collaborators of the MMB group (*P. Gutfreund, A. Koutsoumpias*). I will also strongly benefit from existing collaboration with *Prof. Bonn* and *Prof. Shahidzadeh* from the University of Amsterdam, experts in hydrodynamics of wetting and flows in porous media.

By combining surface scattering techniques with friction measurements and optical microscopy, I will address long-term existing problems with a new approach meanwhile developing a new research theme at LLB. I will dedicated 90% of my working time to this project, the 10% left being devoted to help users on neutron facilities. My current experience in PhD supervision combined with the supervision of a PhD student working in the DYNAMO project will be assets to quickly pass the HDR and gain scientific autonomy. Funding this JCJC project will provide a strong foundation for my long-term research activity.

III. References

(1) Bonn, D.; Eggers, J.; Indekeu, J.; Meunier, J.; Rolley, E. Wetting and Spreading. *Rev. Mod. Phys.* **2009**, 81 (2), 739–805. 10.1103/RevModPhys.81.739. **(2)** Huh, C.; Scriven, L. E. Hydrodynamic Model of Steady Movement of a Solid/Liquid/Fluid Contact Line. *J. Colloid Interface Sci.* **1971**, 35 (1), 85–101. 10.1016/0021-9797(71)90188-3. **(3)** Popescu, M. N.; Oshanin, G.; Dietrich, S.; Cazabat, A.-M. Precursor Films in Wetting Phenomena. *J. Phys. Condens. Matter* **2012**, 24 (24), 243102. 10.1088/0953-8984/24/24/243102. **(4)** Lhermerout, R.; Perrin, H.; Rolley, E.; Andreotti, B.; Davitt, K. A Moving Contact Line as a Rheometer for Nanometric Interfacial Layers. *Nat. Commun.* **2016**, 7 (1), 12545. 10.1038/ncomms12545. **(5)** Lhermerout, R.; Davitt, K. Controlled Defects to Link Wetting Properties to Surface Heterogeneity. *Soft Matter* **2018**, 14 (42), 8643–8650. 10.1039/C8SM01715H. **(6)** Cousin, F.; Jestin, J.; Chaboussant, G.; Gautrot, S.; Menelle, A.; Ott, F. Probing Simultaneously the Volume and Surface Structure of Nanospheres Adsorbed at a Solid-Liquid Interface by GISANS. *Eur. Phys. J. Spec. Top.* **2009**, 167 (1), 177–183. 10.1140/epjst/e2009-00955-2. **(7)** Mensink, L. I. S.; Snoeijer, J. H.; de Beer, S. Wetting of Polymer Brushes by Polymeric Nanodroplets. *Macromolecules* **2019**, 52 (5), 2015–2020. 10.1021/acs.macromol.8b02409. **(8)** Chennevière, A.; Drockenmuller, E.; Damiron, D.; Cousin, F.; Boué, F.; Restagno, F.; Léger, L. Quantitative Analysis of Interdigitation Kinetics between a Polymer Melt and a Polymer Brush. *Macromolecules* **2013**, 46 (17), 6955–6962. 10.1021/ma4007335. **(9)** Gao, N.; Geyer, F.; Pilat, D. W.; Wooh, S.; Vollmer, D.; Butt, H.-J.; Berger, R. How Drops Start Sliding over Solid Surfaces. Nat. Phys. 2018, 14 (2), 191–196. 10.1038/nphys4305.

A successful submission does not only refer to the writing of a clear scientific document, but also to an early and consistent completion of IRIS. Please check, among other things, the following points:

☐ Is the funding instrument indicated at the top of my scientific document consistent with the one selected on the submission website?

☐ Is the scientific theme indicated at the top of my scientific document consistent with the one selected on the submission website?

The information submitted online will take precedence over that provided in the scientific document if both sources of information are inconsistent, including if they are incorrectly fulfilled or missing.

☐ Is the French/English title of my project indicated in the dedicated field? Same for the French/English summary of my project?

☐ Does the title or abstract of my project not include any information that could hinder the subsequent filling of a patent ?

☐ Does the partnership described in the scientific document comply with the partnership fulfilled online on IRIS: identity of the coordinator, the partner's scientific leaders and main people involved in the project, including foreigners in the case of a PRCI project ?

☐ In the case of a PRME project, do I have the expected 1.5 ETPR (: Full Time Research Employment)?

☐ Have I clearly indicated on the submission website my interest in co-funding, labelling by one or more competitiveness clusters, a very large research infrastructure (OSI) or a IR?*

☐ Is the online form complete at the closing date and time?

☐ Does my scientific document respect the limit of 4 pages? Is it in pdf format? Does it meet the expectations of the evaluation criteria applicable in stage 1? Have I uploaded the latest version of my scientific document on IRIS ?

No modification of the scientific document - as uploaded at the closing date and time on IRIS – will be allowed.

☐ Did I anticipate the writing of my project by approaching the FSD (Fonctionnaire Sécurité Défense) of my organisation to verify the eligibility of my project regarding the PPST (Scheme to protect the nation's scientific and technical potential, cf. §D.6 of the AAPG 2024 call text)?

☐ Are the CVs of the coordinator and the partner's scientific leaders, including foreigners in the case of the registration of a PRCI project, properly completed on IRIS at the closing date and time?

It is the responsibility of the coordinator to ensure that the CVs are correctly completed on IRIS at the closing date and time. Warning: each CV must be completed by each partner by using the same e-mail address to connect as the one used online in the field "partnership".

☐ In the case of a PRCI project: have my foreign partners taken any necessary steps with the foreign funding agency? (cf. appendices dedicated to bilateral PRCI collaborations to come on the AAPG2024 web page).