

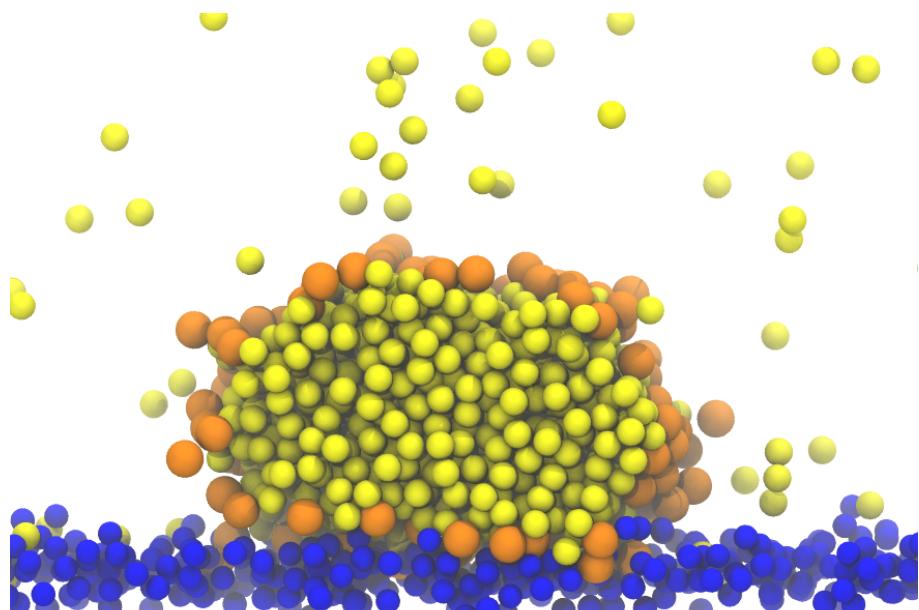
Project Description

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SPP 2171: Dynamic wetting of flexible, adaptive and switchable surfaces

Intrinsic analysis of dynamic wetting on soft surfaces



Summary

Surface phenomena are remarkable because they are dominated by extreme forces localised right at the interfaces, in a spatial domain that usually involves few (1-3) molecular layers. In case of fluids or soft materials, however, thermally activated surface capillary waves corrugate the interface on larger scales, frustrating the attempt to investigate its structure and dynamics at molecular resolution through conventional analyses of atomistic simulation trajectories. Intrinsic analysis approaches, instead, by undoing the smearing effect of capillary waves have been used with success in recent years to analyse the structure of liquid/vapour and liquid/liquid interfaces. In this project, we propose to generalise these approaches to ternary systems and apply them to liquid droplets on soft substrates, to obtain a clearer picture of the molecular structure and dynamics close to the contact line at thermodynamic equilibrium, and, during the process of de-pinning. In our proposed approach, we will study both a simplified model of droplet/soft substrate, and, a realistic model at atomistic resolution of a water droplet on the surface of a polyelectrolyte multilayer. The model system will enable us to span a wide range of parameters, including different type of solutes, and, therefore, to investigate trends and to compare with, and extend, available theoretical models. The water/polyelectrolyte system, on the other hand, will give us the opportunity to investigate the link between the microscopic changes at the contact line and the macroscopic effects in a quantitative way, and to compare them directly with experimental measurements. With this approach, we will bring the current picture of the properties of the moving contact line to an unprecedented resolution.

Zusammenfassung

Oberflächenphänomene sind bemerkenswert, weil sie von extremen Kräften dominiert werden, die direkt an den Grenzflächen lokalisiert sind, in einem räumlichen Bereich, der normalerweise nur wenige (1-3) molekulare Schichten umfasst. Im Fall von Fluiden oder weichen Materialien wölben jedoch thermisch aktivierte Oberflächenkapillarwellen die Grenzfläche in größeren Maßstäben, was den Versuch bereitstellt, ihre Struktur und Dynamik mit molekularer Auflösung durch herkömmliche Analysen atomistischer Simulationstrajektorien zu untersuchen. Stattdessen wurden in den letzten Jahren erfolgreich intrinsische Analyseansätze eingesetzt, um ohne die störende Schmierwirkung von Kapillarwellen die Struktur von Fluid-Fluid- und Fluid-Gas-Grenzflächen zu analysieren. In diesem Projekt wird vorgeschlagen, diese Ansätze für ternäre Systeme zu verallgemeinern und auf flüssige Tröpfchen auf weichen Substraten anzuwenden, um so ein klareres Bild der molekularen Struktur und Dynamik nahe der Kontaktlinie im thermodynamischen Gleichgewicht und während des Loslösens des Tropfens (*depinning*) zu erhalten. In unserem vorgeschlagenen Ansatz werden wir sowohl ein vereinfachtes Modell eines Tropfens auf weichem Substrat als auch ein realistisches Modell atomistischer Auflösung eines Wassertropfens auf der Oberfläche einer Polyelektrolyt-Mehrfachschicht untersuchen. Das Modellsystem wird es uns ermöglichen, einen breiten Parameterbereich zu erfassen, einschließlich unterschiedlicher Arten von gelösten Stoffen, und somit Trends zu untersuchen, mit verfügbaren theoretischen Modellen zu vergleichen und diese Modelle zu erweitern. Das Wasser-Polyelektrolytsystem wird uns andererseits die Möglichkeit geben, Zusammenhänge zwischen mikroskopischen Veränderungen an der Kontaktlinie und den resultierenden makroskopischen Effekten quantitativ zu untersuchen und direkt mit experimentellen Messungen zu vergleichen. Mit diesem Ansatz werden wir das aktuelle Bild der Eigenschaften beweglicher Kontaktlinien zu einer bisher unerreichten Auflösung befördern.

1 State of the art and preliminary work

1.1 State of the Art

Classical wetting theory can be summarised by its two central results: (a) the Young-Dupré equation[1], which explains the dependence of the contact angle of a droplet on a smooth solid substrate in terms of surface free energies and, (b) Neumann's balance equation[2] relating the components of the surface stress to the interface normals at the contact line between three fluids. The wetting properties of **soft surfaces cannot be described by either** of these two paradigms, because of the deformation induced in the soft substrate by the presence of the interface between the two fluid phases. The series of physical mechanisms determining the behaviour of droplets on soft substrates goes collectively under the name of **elastocapillarity**. At the microscopic level, this involves the complex interplay between molecular forces acting at the liquid-liquid interface with the deformable substrate, the effect of which are captured by quantity γ/aY , the ratio between the surface stress γ , molecular size a and Young modulus Y [3, 4]. Viscous dissipation, on the other hand, is the main quantity that comes into play when a droplet is set in motion[5]. Noticeably, similar properties to those of soft surfaces, like anisotropic and strain-dependent stress, are found also in complex fluid interfaces, when, for example, surfactants or particles are present[6]. The physics of the moving contact line, even at a solid substrate, is characterized by a scale bridge from the hydrodynamic level down to the molecular one, due to the inherent dissipation singularity[7]. The presence of **a deformable substrate introduces a more complicated picture of the contact line motion**, including dissipation through viscoelastic breaking[8, 9] for which only recently some theoretical frameworks started being proposed[10, 11]. **A microscopic picture** at the molecular level of the mechanisms involved in the motion of the contact line of simple fluids on soft substrates, or of complex fluids, **is currently missing**.

In order to investigate wetting in soft surfaces at the molecular level, **it is necessary to resolve** the structure and the dynamics of the interfaces **down to the size of a single molecule**. While this detail is in principle provided by atomistic molecular dynamics simulations, traditional analysis approaches suffer from severe shortcomings in this context. In fact, **the contact line is corrugated by capillary fluctuations** generated by all of the components. Already in the simple case of a liquid/vapour interface, the thermal capillary waves make the usual approach of computing histograms of the properties of interest as a function of an external, macroscopic coordinate, less useful as one would hope, as **the fluctuation amplitude are usually larger than the molecular size**[12]. The strong anisotropy that fluids are displaying at the interface is usually decaying to zero moving towards the bulk depending on the range of the intermolecular correlations. For a liquid like water, in absence of dissolved charges, this corresponds to about three molecular layers, with most of the total anisotropy being concentrated in the first one[13]. **Several computational approaches have been developed** in the course of the last decade to **remove the smearing effect of capillary waves**, but, to the best of the applicant's knowledge, **these methods** have always been applied to the case of liquid/vapour or liquid/liquid interfaces, and **never been applied to the moving contact line problem**, most likely because these approaches were developed mainly within the physical-chemistry community.

The properties of complex interfaces and soft wetting systems, however, are not only dictated by the short-range intermolecular forces. Counterions released from the substrate are forming the so-called Stern layer[14], followed by a more diffuse layer characterised at mean field level by the Gouy-Chapman length for desalinated solutions or, in presence of salt, by the Debye length (see

Fig. 1), which is of the order of one nanometer at physiological conditions. The phase diagrams of systems with dissolved ions can be very rich, and even without reaching the strong coupling limit[15], fascinating effects due to correlations of multivalent ions can be observed already in the bulk, including like-charge attraction[16] or mobility reversal in colloid electrophoresis[17, 18]. The effect of electrical inhomogeneities has a broad impact on the out-of-equilibrium dynamical properties of the contact line in several respects, and has led to the discovery of new physical phenomena emerging due to the matching of the electrical characteristic lenght scale with the geometrical hydrodynamical ones, such as concentration polarization effects [19, 20], electrokinetic instabilities [21], limiting and overlimiting currents[22], induced-charge electrokinetic phenomena[23], emergence of negative pressure [24] and permselectivity [25, 26]. Within the class of soft substrates, polyelectrolyte multilayers represent a versatile type of thin film, which is prepared using the so-called layer-by-layer technique[27], consisting in alternating the deposition of polycations and polyanions on a substrate. The self-assembled nature of polyelectrolyte multilayers and the degree of control that can be reached in building them and in tayloring the layer properties make them excellent candidates for building new materials, and attracted much attention in the surface and colloidal science community, also because of the possibility of incorporating functional materials[28] and for possible biomedical applications[29]. Polyelectrolyte multilayers display also a rich landscape of wetting properties[30, 31], that make them suitable for a wide range of applications, from the creation of stable superhydrophobic coatings[32], to highly efficient oil-water separation filters[33].

Another factor that influences dramatically the fluid flow is the presence of slip at the liquid-substrate interface. As already mentioned, a finite slip at the interface is a necessary condition to regularise the viscous singularity present at the contact line of the two phases[7], and due to recent technological advancements in micro- and nanofluidics, the problem of hydrodynamic boundary conditions has been the focus of a renewed attention [34–37]. From the computational point of view, several approaches have been employed to study problems related to the contact line, starting with macroscopic/mesoscopic methods including multicomponent Lattice Boltzmann[38] and volume of fluid approaches[39] to microscopic methods based on non-equilibrium molecular dynamics [40]. These approaches have shown the ability to discover a rich phenomenology, some example of which are represented by the dependence of the droplet evaporation on the contact line curvature[41], the possibility to tailor slippage[42] and the complex effects arising from substrate deformability[43]. Several computer simulation investigating the microscopic structure have addressed the problem of static wetting on soft substrates, including the analysis of the transition from Neumann to Young behaviour[44], the breakdown of continuum theory[45], or, the properties of polymeric droplets[46].

Within this landscape of fundamental investigations and applications involving wetting on soft substrates, it emerges that **an approach is currently missing**, which can **resolve the microscopic structure by undoing the statistical smearing of capillary fluctuations** at the contact line to link it to the dynamic wetting properties.

1.2 Preliminary Work

The applicant has a long-standing experience in developing and applying advanced methods for the calculation of **intrinsic properties of liquid interfaces**, which lie at the core of the present proposal. The generalised method for identifying interfacial molecules in **arbitrary geometries**, developed by the applicant in 2013[48], has been devised precisely to **compute the interfacial layers in complex geometrical contexts**, such as those involved by wetting on soft substrates. In the course of the last 5 years, we studied the interfacial layers of several liquids, showing that the first molecular layer of the liquid phase has markedly different properties from the subsequent layers, including structural and thermodynamical ones[13, 49, 50], but also transport properties like the tangential and normal diffusion coefficients and the corresponding velocity autocorrelation functions[51]. In addition, in our previous works we developed a strategy to handle the case of **partial miscibility**[52], which we know to be a **relevant issue in the case of polyelectrolyte multilayers** (*vide infra*) and it is expected to be present also in simpler model systems. Recently, we developed a **python package for the interfacial analysis** of molecular systems (pytim), which collects several algorithms for phase and surface identification in a coherent framework[47]. This will allow to easily script the required analysis tools, which will be smoothly integrated in the pytim package, making them also available for future investigations, as well as for the larger scientific community.

Previous work of the applicant has also shown how critical the softness of the interaction is, even in case of liquid solid wetting, to the determination of slip properties[54, 55]. For what concerns the **target systems**, preliminary simulations of simple liquid droplets on model substrates (WP1) have been already successfully run (see Fig.4, while **equilibrated structures of the polyelectrolyte multilayers** (WP2) have been already produced by the applicant and coworkers during the past years. In particular, we simulated explicitly the deposition protocol of poly(styrene sulfonate)/poly(diallyldimethylammonium) (PSS/PDADMA) multilayers, investigating the structural and dynamical properties of bilayers[56, 57] and quadrilaterals[53, 58], allowing to obtain a **realistic model** at atomistic detail of the multilayer structure, which includes also hydration water strongly bound to the polyanions and polycations.

In this sense, the **large majority of the prerequisites** for carrying out this project, in terms of analysis tools and system configurations, are already present, guaranteeing that the project will kick-start quickly and smoothly.

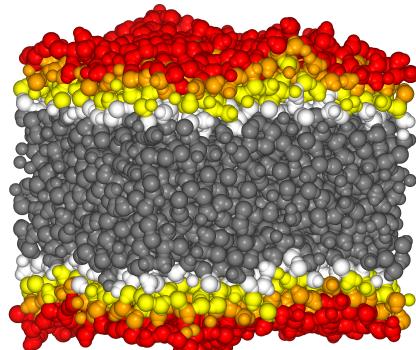


Fig. 1: Example of the surface layers of the water/vapour interface (oxygen atoms shown) identified with pytim[47]

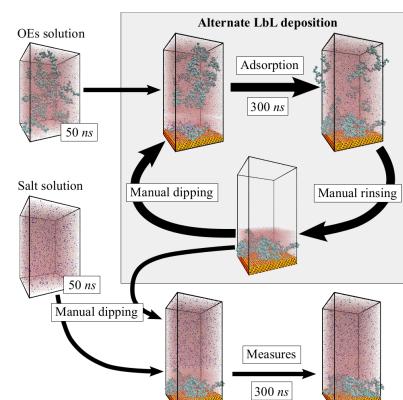


Fig. 2: Schematics of the simulated layer-by-layer deposition of PSS/PDADMA used to generate the bilayer and quadrilateral structures[53]

1.2.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

1.2.1.1 Intrinsic interfaces, Slip properties

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- Segà, M., Fábián, B. and Jedlovszky, P., 2015. Layer-by-layer and intrinsic analysis of molecular and thermodynamic properties across soft interfaces. *J. Chem. Phys.*, 143(11), p.114709.[49]
- Segà, M., Sbragaglia, M., Biferale, L. and Succi, S., 2013. Regularization of the slip length divergence in water nanoflows by inhomogeneities at the Angstrom scale. *Soft Matter*, 9(35), pp.8526-8531.[54]
- Segà, M., Sbragaglia, M., Biferale, L. and Succi, S., 2015. The importance of chemical potential in the determination of water slip in nanochannels. *Eur. Phys. J. E*, 38(11), p.127.[55]
- Segà, M., 2016. The role of a small-scale cutoff in determining molecular layers at fluid interfaces. *Phys. Chem. Chem. Phys.*, 18(33), pp.23354-23357.[59]
- Segà, M., Hantal, G., Fábián, B. and Jedlovszky, P., 2018, Pytim: A python package for the interfacial analysis of molecular simulations. *J. Comput. Chem.* 2018, *published online* DOI:10.1002/jcc.25384[47]

1.2.1.2 Polyelectrolyte Multilayers

- Qiao, B., Segà, M. and Holm, C., 2011. An atomistic study of a poly (styrene sulfonate)/poly (diallyldimethylammonium) bilayer: the role of surface properties and charge reversal. *Phys. Chem. Chem. Phys.*, 13(36), pp.16336-16342.[56]
- Qiao, B.F., Segà, M. and Holm, C., 2012. Properties of water in the interfacial region of a polyelectrolyte bilayer adsorbed onto a substrate studied by computer simulations. *Phys. Chem. Chem. Phys.*, 14(32), pp.11425-11432.[57]
- Micciulla, S., Sánchez, P.A., Smiatek, J., Qiao, B., Segà, M., Laschewsky, A., Holm, C. and Von Klitzing, R., 2014. Layer-by-layer formation of oligoelectrolyte multilayers: a combined experimental and computational study. *Soft Mater.*, 12(sup1), pp.S14-S21.[58]
- Sánchez, P.A., Smiatek, J., Qiao, B., Segà, M. and Holm, C., 2016. Atomistic Simulation of Oligoelectrolyte Multilayers Growth. In *High Performance Computing in Science and Engineering' 15* (pp. 215-228). Springer, Cham.[53]

2 Objectives and work programme

2.1 Anticipated total duration of the project

The project is planned to start on 01.10.2019 and will have a total duration of 36 months.

2.2 Objectives

The overarching theme of this project is the **relation between the molecular structure of the fluid interfaces and the the dynamical properties of their contact line**. The focal point and unique characteristic of the proposed approach is the usage of advanced **algorithms for the intrinsic interfacial analysis** of fluid interfaces, targeted at the elimination of the smearing effect induced by surface capillary waves in molecular dynamics simulations, through the identification of the interfacial molecular layers. Fig.4 shows, on the right, a pictorial representation of the current understanding, at the continuum level, of the structure of the contact line at a soft substrate. Clearly, this picture must break down at the molecular scale a , but it is exactly that scale that governs the interfacial properties themselves. **Observables computed in the conventional way**, namely, by averaging over the capillary fluctuations, even if obtained from a simulation at atomistic resolution, **cannot provide a full account of the microscopic detail**, because **the regularisation of the hydrodynamic divergence at the contact line is expected to happen at a scale smaller than the fluctuations themselves**.

The intrinsic analysis put forward in this project is expected to provide a **much more accurate description** of the physics at the microscale, than what can be reached with conventional analysis approaches.

We plan to run two classes of molecular dynamics simulations. The first is aimed at modelling the general mechanisms involved in the process of substrate deformation and interface depinning, and consists in simulating a **model system** based on a Lennard-Jones fluid droplet on a substrate characterised by a tunable degree of softness. The second approach will focus instead on reproducing the **atomistic detail** of a real-case experimental setup, namely, water droplet on polyelectrolyte multilayers.

The main questions addressed by the proposed work are the following:

- what is microscopic structure of the contact line on soft surfaces, when the effect of capillary fluctuations is removed?
- what structural rearrangement happen at molecular level in proximity of the contact line at and after the depinning process ?
- how does the velocity field behave close to the contact line?
- how are solutes such as counterions and surfactants arranged in proximity of the contact line, and how are they affected by its motion?

Besides providing answers to these specific problems, the project will also provide the generalisation of intrinsic profiles to multivariate distributions for multiphase systems, as well as the first account of intrinsic velocity profiles.

The reasons for choosing to attack the problem from two sides (model system and atomistic detail) are several, and can be summarised in the following way:

Model systems:

- allows to capture the essential elements of the problems, make general predictions;
- given the reduced computational resources requirement, we will be able to span a wide parameter space (substrate softness, presence of dissolved ions, presence of surfactants in the fluid);
- long temporal and spatial scales will be accessible
- allows qualitative comparison with experiments (**PI: Hardt**) and numerical simulations in the continuum (**PI: Reusken**) on scales not reachable by the atomistic-detail simulations.

System at atomistic-detail

- Builds on an already successful set of simulations, tested against experimental results for the properties of supported multilayers in solution.
- Allows for quantitative predictions, to be compared directly with contact angle experiments (**PI: von Klitzing**) and with lattice-based models (**PI: Holm**)
- Will be a fundamental test for the model system, indicating whether it needs to be refined
- Allows to test specifically the behaviour of water, as one of the most common used fluids

The work programme is divided in two work packages **WP1** and **WP2**, corresponding to the two following main goals of the project.

2.3 Work programme incl. proposed research methods

2.3.1 General background: Identification of the contact line and calculation of intrinsic properties

One of the **elements of novelty** in this proposal regards the **extension of the calculation of intrinsic properties** from two-phase to the case of **three-phase systems**. This generalisation is not completely straightforward, and this project will likely set the standard for this kind of analysis. The two main problems one faces by approaching an intrinsic analysis of three coexisting phases are the identification of the atoms at the contact line, and finding an appropriate way to convey the information about the local structure. We will make use of the points described here in both WP1 and WP2.

Among the algorithms suitable for the identification of interfacial atoms of curved interfaces one can find GITIM[48], the Willard-Chandler method[60] and the Connolly Surface method[61]. All of them could be used interchangeably, for the purposes of our project, and will be used in each of the WPs to test the *stability of the results against the different analysis approaches*. Here, we will focus for simplicity on GITIM only. The algorithm is based on the Delaunay triangulation of the N atomic centres in the simulation box, and on a generalisation of the concept of alpha-shapes[62], that takes into account the excluded volume of atoms. The triangulation can be performed efficiently with a computational complexity of $\mathcal{O}N \log(N)$. For each of the tetrahedra belonging

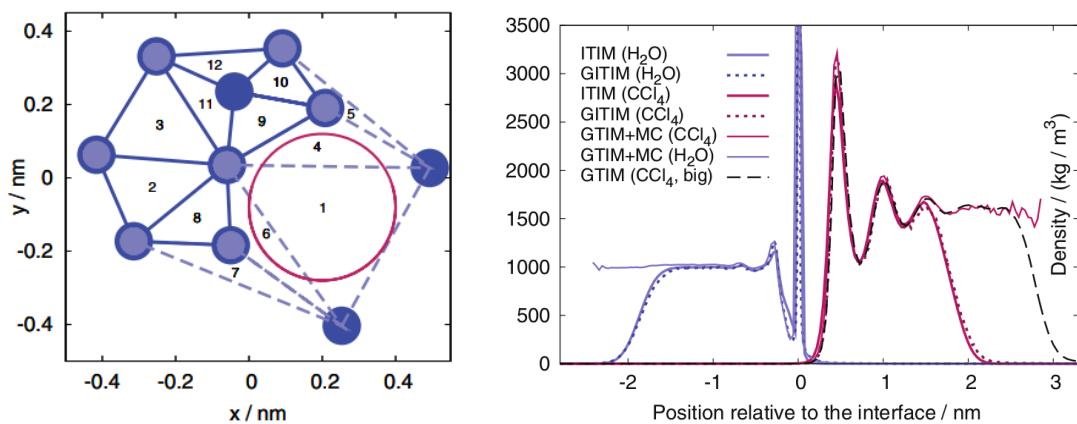


Fig. 3: 2D sketch of the triangulation and probe-sphere test involved in the GITIM algorithm for the determination of surface atoms. Right: intrinsic density profiles at the water/CCl₄ liquid interface, comparison of different algorithms, including the random sampling (MC) mentioned in the proposal for the calculation of metric factors. Taken from[48]

to the (periodic) triangulation, the algorithm checks using a geometrical condition, whether a test sphere of a predefined radius can fit within the network of the neighbouring atoms (see Fig.3) If the test sphere fits, the atoms are marked as being as belonging to the surface ones (this includes also internal pockets)

The strategy for the identification of the atoms located at the contact line **that we put forward** comprises the following steps: (1) searching for the atoms belonging to the interface of the liquid phase (see Fig. 4, right panel) using the GITIM algorithm; (2) identifying in the same manner the atoms belonging to the surface between the whole condensed phase (surface + liquid); (3) selecting those atoms which are not present in both sets (1) and (2), namely, those on the contact disc, and, finally, (4) employing a density-based filtering [52] to select the atoms at the border of the contact disc, that is to say, the atoms of the liquid phase belonging to the contact line. Of course, the same procedure can be repeated, exchanging the components, to identify the atoms of the surface, which are at the contact line.

In systems with one type of interface only, the intrinsic properties can be computed as a function of the distance from the instantaneous, local position of the interface. **In three-phase systems, this approach needs to be extended** by taking into account the **bivariate distribution of the property of interest** (density, charge, velocity,...) as a function of the (intrinsic) distances from both surfaces $\xi_1(\mathbf{r})$ (liquid-vapour) and $\xi_2(\mathbf{r})$ (liquid-substrate) In this way, the bivariate intrinsic density map would be written as

$$\rho(z_1, z_2) = \frac{1}{N J(z_1, z_2)} \sum_i \langle \delta(z_1 - \xi_1(\mathbf{r}_i), z_2 - \xi_2(\mathbf{r}_i)) \rangle,$$

where $J(z_1, z_2)$ encodes the metric factor.

Atoms at the contact line will be located at the origin of the bivariate distribution. Because the local coordinates generated using the intrinsic distances are inherently curvilinear (the geometrical shape of the interface, besides having a wedge-like structure, is continuously changing) one needs to take particular care of the metric factor. This will be accounted for by computing the histogram of the bivariate distribution of a random, uniform sampling of points in the simulation box, as it is already been done for the simpler one-dimensional distribution functions in GITIM[48]

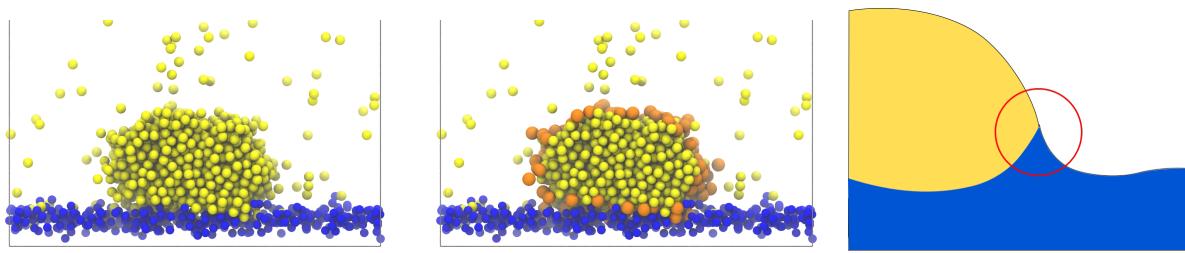


Fig. 4: Left: simulation snapshot from a preliminary test of a model droplet (yellow) on a soft surface (blue). The interaction potential is a Lennard-Jones one for all centres (with different interaction strengths, in this case yielding a slightly hydrophobic surface). The soft surface particles are tethered to the $x - y$ plane with a harmonic potential. Middle: instantaneous surface atoms, as detected by the GITIM algorithm, marked in orange. Right: pictorial view of the contact line, including deformation of the substrate.

2.3.2 WP1: Intrinsic properties of the dynamic contact line in model systems

The simulations planned in WP1 are focusing on the simplest possible model with explicit solvent that can reproduce the general properties of wetting on soft substrates. More in detail, in the model the fluid particles and the substrate particles interact through the Lennard-Jones potential,

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

with different values of the interaction strength ϵ . The surface atoms will be tethered to the $x - y$ surface using a harmonic potential, and will interact between each other either with a Lennard-Jones potential (see the preliminary setup shown in Fig4), or with harmonic links to nearest neighbours on an hexagonal lattice. In this way, the model reproduces a soft substrate that can support the liquid phase, while allowing to tune easily the static properties, such as the contact angle and the permeability of the liquid phase.

In the first step of WP1, we will characterise the relevant static properties of the system, such as, for example, contact angle, substrate deformation, structure at the contact line as a function of (a) the fluid-substrate interaction strength (b) the spring constant and (c) the droplet size, as this is a relevant control parameter in case of soft wetting. Both droplet with the shape of a spherical cap and with that of a cylindrical cap will be considered, in order to disentangle possible effects related to the contact line curvature.

We will proceed with a study of the static contact angle, investigating the size-dependence of the contact angles θ_1 and θ_2 , with vapour and substrate, respectively, devoting particular attention at the difference between the case of spherical cap droplets with cylindrical cap droplets. In the case of solid surface wetting, the generalised Young equation that links θ to the contact base radius R_B of a spherical cap droplet and to the liquid-vapour surface tension γ_{LV} reads

$$\cos \theta = \cos \theta_\infty - \frac{\tau}{\gamma_{LV} R_B},$$

where $\cos(\theta_\infty)$ is the macroscopic contact angle, as opposed to a size-independent contact angle in case of a cylindrical cap droplet.

In case of soft substrates, an approximate expression by Cao and Dobrynin[44] can be used to express the two contact angles to the droplet base radius and to the substrate shear modulus G_S

$$\gamma_L \sin \theta_1 / \sin \theta_2 = \gamma_{SL} + \frac{28}{15\pi} G_S R_B.$$

The size-dependent contact angles must, however, depend in this case both on the presence of an equivalent line tension contribution, as well as on the substrate deformation induced by the Laplace pressure of the curved droplet surface (an expression for cylindrical cap droplets was derived by Hui and Jagota[63]). Comparison of the simulation results obtained with the cylindrical and spherical cap droplets are expected to show differences that will enable us to understand better the different role of surface and line curvature on the wetting properties.

In the second step, we will apply a body force to the droplet, investigating the deformations induced in droplet and substrate, both in term of the contact angle, as well as in the microscopic structure of the surface layers, especially at the contact line. By using the intrinsic analysis methods described above, we will be able to both **follow the event of depinning on a frame by frame basis** thanks to the instantaneous identification of contact line atoms, and to obtain a **detailed averaged picture** by calculating bivariate intrinsic density maps (for the cylindrical cap drops). This will enable us to characterise the structural and dynamical modifications happening at the contact line during the process. These analysis will be again performed on a set of simulation with varying interaction parameters and sizes as described in the first step, and will be also compared with available theoretical models[10, 11].

In the final setup of WP1, we will study **the influence of different solutes** to the static and dynamic properties of the contact line. First, we will study the influence of counterions in solution, which will be modelled by adding dissociable groups on the soft substrate. We will concentrate on the intrinsic structure of ions at the liquid/vapour, liquid/substrate interfaces and at the contact line, again reporting the bivariate correlation function as a function of the intrinsic distances from the liquid/vapour and liquid/substrate interfaces. This system has a particular relevance, as it will test the general prediction of this simple type of modelling against the atomistic simulation results of the PSS/PDADMA polyelectrolyte system described in WP2, as well as against the **experimental measurements of PI von Klitzing** and the **lattice-based modelling of PI Holm**. Next, we will simulate a system with three components, replacing the substrate with a second, immiscible liquid, and will **add to the system simple surfactant molecules**, modelled as dumbbells with amphiphilic character. Depending on the strength of the interparticle interaction, we will be able to model systems with different surface excess of surfactants, and study their distribution and migration within the moving droplet, as well as in and out of the liquid/liquid interface. These data will be used to investigate the dependence of the dynamic wetting properties on the intrinsic bivariate distribution of surfactants, as well as dynamical effects on the distribution of the surfactants themselves as a function of the external forcing term. The results will serve as an **input for the models developed by PIs Hardt/Reusken** for the dynamic wetting of liquid infused surfaces. **Preliminary simulations** (see Fig. 4) have already shown the feasibility of the basic modelling approach, and, of the analysis strategy. Regarding the computational resources required, the small preliminary setup presented here (2000 atoms) reaches thermodynamic equilibrium within ten minutes of calculation on a single-core machine. Scaling to much larger systems is not expected to be problematic, also envisaging the use of log-linear scaling mesh-based electrostatic calculations, as described below, and exploiting the parallelism of ESPResSo.

Technical details: To perform the simulations we will employ ESPResSo[64], a parallel simulation package for soft matter systems, of which the applicant is a developer. The feasibility of the model has been already tested on a small system (see Fig.4). Given the use of short-range potentials for the dispersion forces, and mesh-based Ewald methods for the electrostatic interaction, the simulations can be performed on parallel machines with, according to the per-

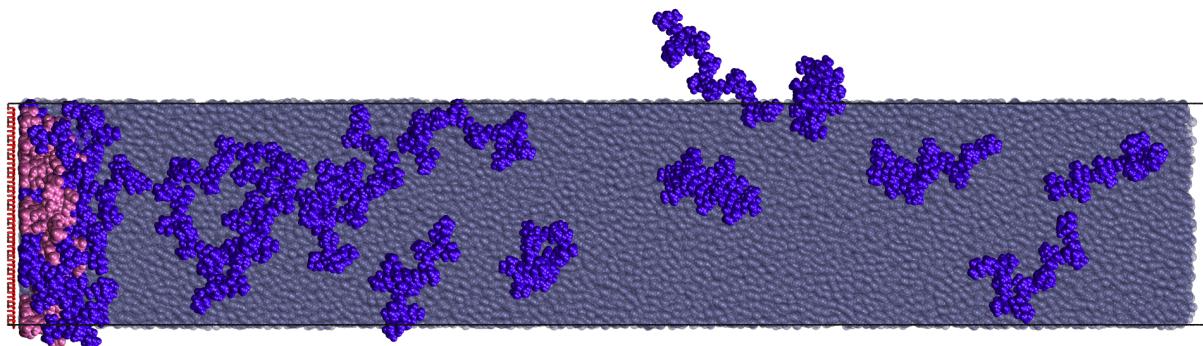


Fig. 5: Snapshot from the simulated deposition process (at atomistic detail) of a layer of PDADMA (blue) on a layer of PSS (mauve) supported on an hydroxylated substrate. After rinsing the non-adsorbed PDADMA, the remaining PSS/PDADMA bilayer is stable and ready to test the wetting properties of water[56]

sonal experience of the applicant, excellent scaling performances. The software used for the identification of surface molecules is Pytim[47] (<http://github.com/Marcello-Sega/pytim/>), a high-performance python package developed by the applicant, that allows to script easily complex surface analysis procedures.

2.3.3 WP2: Intrinsic properties of the dynamic contact line of water on PSS/PDADMA

The second work package is dedicated to the simulation of a real-case system at atomistic detail. The target system is a PSS/PDADMA/Water system, where the polyelectrolyte layers PSS and PDADMA are acting as the soft surface on which a sessile water droplet is laid. In the last years the applicant and PI C. Holm have performed investigation of the PSS/PDADMA multilayer by means of atomistic simulations, supporting and interpreting experimental results of PI von Klitzing.

Our approach did put forward the explicit simulation of the process of deposition in solution of the alternated layers of polyanions and polycations. As a results, we have generated an extensive database of equilibrated trajectories of PSS/PDADMA bilayers and quadrilayers. Fig. 5 shows a simulation snapshot close to the terminal phase of the second round of deposition, where a layer of PDADMA has already adsorbed on the surface of PSS supported by an hydroxylated surface (visible on the left of the picture). The extensive simulations allowed us to reproduce the structure of the adsorbed layers, avoiding unrealistic bias that an ad-hoc layer placement would have introduced. Having at hand the relaxed structures of a bilayer and a quadrilayer allows us to start WP2 directly with the investigation of the properties of a water droplet deposited on the soft substrate, and to concentrate our efforts on the physics of the wetting.

The initial droplet will be obtained by removing regions of water from one of the pre-equilibrated configurations, in order to obtain droplet of different sizes both as spherical and as cylindrical caps. This will be exploited to study both the size-dependency of the wetting properties, as well as the influence of a macroscopically curved contact line. The proper relaxation of the system will be monitored by following the time evolution of different markers, including total and electrostatic energy, as well as the distribution of ions within the water droplet and in the

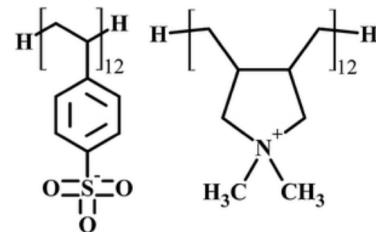


Fig. 6: The chemical formula of the PSS (left) and PDADMA (right) 12-mers used in the simulations.

multilayer. Following the same approach used in the first two steps of WP1, we will first study the static contact angle and the bivariate intrinsic density maps for different droplet sizes and topologies (cylindrical cap, spherical cap). In the second step, we will add a body force to the water molecules, and we will investigate the dependence on the advancing and receding contact angles on the control parameters, as well as changes induced in the microscopic structure, and the characteristics of the hydrodynamic velocity field, through the analysis of the intrinsic density maps. The information gathered by means of the atomistic simulations will be used (a) to check which fundamental ingredients of the model systems are necessary to reproduce the results at atomistic level (b) interpret and supplement the **experimental measurements of PI von Klitzing** on the same systems.

Technical details:

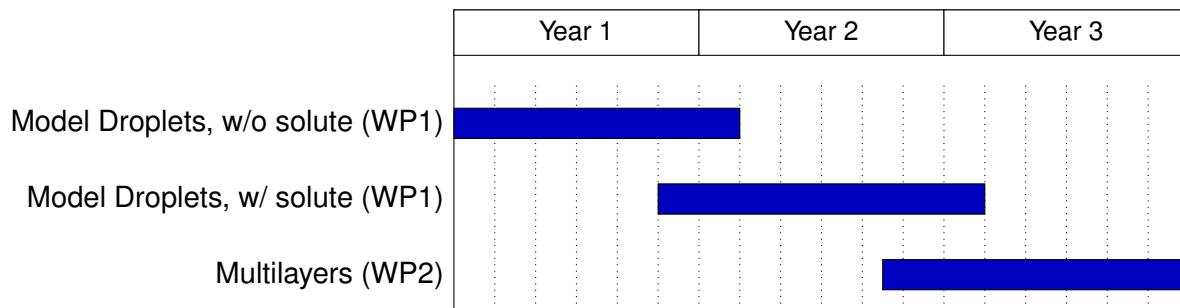
The PSS and PDADMA molecules are modelled using the OPLS-AA force field, while the model used for water molecules is the SPC/E one. The silica substrate on which the polyelectrolyte is adsorbed is modelled atomistically as four layers of silicate structure with cross sectional area of about $13\text{ nm} \times 12\text{ nm}$. The substrate surface has been hydroxylated at 75% (3 in four oxygen atoms replaced with a hydroxyl group). Because of the ionic nature of PSS/PDADMA, and because of the presence of a confining surface, the simulation has to use the appropriate numerical approaches the calculation of the electrostatic interaction. In particular we will use the Particle Mesh Ewald [65] method in its smooth variant [66], applying the Yeh-Berkowitz correction [67] to remove the contribution to the forces from periodic images in the direction normal to the surface. The atomistic simulations will be performed using the GROMACS molecular dynamics simulation package[68]. Depending on the size of the droplet, we plan to run simulations in the range from 100k to 1M atoms. Preliminary benchmark on quad-core Intel Core-i7 nodes equipped with one Quadro K2200 graphic card show performances of 0.7 ns/day/node.

2.4 Data handling

The main methodological and scientific results will be made available to the public at large by presenting them on a institutional web page dedicated to the subject and indexed by the main search engines. The code written for the project will be released under the GNU General Public License, and made available to the scientific community through widely-used code-sharing tools such as github and gitlab, as well as python package repositories PyPi and Conda-forge, to minimise barriers to knowledge transfer. Relevant data produced during the project (simulation trajectories, analysed data, presentations slides, open access publications, codes and scripts, media for outreach) will be in addition stored on the OpenAIRE servers which provide indefinite time storage and open access, a key point for supporting future developments of the project and re-usability of the acquired knowledge for research and teaching purposes. This way, the data will be made available to the scientific community and to the larger community. Youtube video clips will be used to disseminate the results of the project will be produced, addressing both experts and non-experts.

2.5 Other information

2.5.1 Project Schedule



The workload will be distributed approximately equally between the study of model droplets in absence of solutes, model droplets in presence of counterions/surfactants, and the atomistic simulations of the multilayers. The three tasks are internally coherent and require approximately the same amount of computational resources, as well as time necessary to develop the analysis tools.

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern

Does not apply

2.7 Information on scientific and financial involvement of international cooperation partners

Does not apply

2.8 Information on scientific cooperation within SPP 2171

- PI **Steffen Hardt** from TU Darmstadt will perform experiments of water droplets on silicone oil infused surfaces, in presence of surfactants. The results on the distribution and migration of surfactants as a function of the droplet speed will help cross-validating our microscopic approach. At the same time, the microscopic distributions obtained from our simulations will be used as input for the models developed by him and by PI **Arnold Reusken** from RWTH Aachen University.
- PI **Regine von Klitzing** from TU Darmstadt will perform experiments on the contact angle of sessile water droplets on polyelectrolyte multilayers. We will compare the results of our atomistic model with the experimental results, validating our simulation results against them, and providing feedback about the microscopic detail of the contact line in this specific case.
- PI **Christian Holm** from the University of Stuttgart, will study the contact line dynamics of a droplet of water using a mesoscopic approach, which is complementary to our particle-based one. The atomistic simulation results will be used to validate the parametrisation of the mesoscopic model, which, in turn, will provide important feedback on the behaviour at larger scales.

- With PI **J. Harting** from the Helmholtz-Institute Erlangen-Nürnberg, there will be exchange on simulation approaches and on the physics of soft substrates.

3 Bibliography

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4 Requested modules/funds

4.1 Basic Module

4.1.1 Funding for Staff

The project requires a researcher with training in statistical mechanics, molecular dynamics simulations, possibly with some background in physical chemistry. The researcher shall learn to work with different molecular dynamics simulation packages, plan and execute complex simulations, as well as advanced data analysis on the local cluster and on national supercomputing facilities. We apply for funding for 1 doctoral researcher position for the whole duration of the project (36 months, 75%). According to the current DFG recommendation, this amounts to a total cost of €145.125,-.

Total: €145.125,-

4.1.2 Direct Project Costs

4.1.2.1 Equipment up to EUR 10,000, Software and Consumables

We apply for funding for backup devices and one laptop for the researcher, for a total amount of €2.000,-

Total: €2.000,-

4.1.2.2 Travel

SPP Workshop (4 days), Year 1, PI+student	€1.500,-
SPP Workshop (4 days), Year 2, PI+student	€1.500,-
Advanced School (1 week), Year 1, student	€1.300,-
PhD-candidates Workshop (4 days), Year 2, student	€700,-
International Conference (5 days), Year 1, PI	€2.000,-
International Conference (5 days), Year 2, PI + student	€4.000,-
International Conference (5 days), Year 3, PI + student	€4.000,-
Total	€15.000,-

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

We plan one collaborative exchange visit during year 2 and 3 with the groups of PIs Holm, von Klitzing, and Hardt/Reusken, for a duration of 3 days each, for the PI and the researcher (total 36 days - 6 trips/person) for a total of €5.300,-

Total: €5.300,-

4.1.2.4 Other

None

4.1.2.5 Publications

We expect that our research will result in at least three articles that will be published in international, peer-reviewed Q1 journals. In order to cover part of the costs for guaranteeing open-access, we request €750/year.

Total: €2.250,-

4.1.3 Instrumentation

None

5 Project requirements

5.1 Employment status information

PD Dr. Marcello Sega is Group Leader at the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11) / Research Centre Jülich, on a temporary contract until 1. July 2020. The institute has confirmed (see attachment "Arbeitsplatzzusage") to continue the employment until the end of the duration of the present project, if approved.

5.2 First-time proposal data

Does not apply

5.3 Composition of the project group

The applicant is a researcher in the field of biophysics and soft matter since more than 10 years, and has developed and applied many computational approaches in the framework of particle-based and lattice-based simulation methods. A software developer (M. Zellhöfer) will be available to help with the code development, optimisation, and data organization. Further, Master and Bachelor students will participate in the project with related sub-projects.

5.4 Cooperation with other researchers

5.4.1 Researchers with whom you have agreed to cooperate on this project

5.4.2 Researchers with whom you have collaborated scientifically within the past three years

C. Dellago, G. Hantal, S. Kantorovich, C. Schröder (Vienna, Austria) P. Jedlovszky, G. Horvai, A. Imre (Eger, Budapest, Hungary) S. Succi, M. Sbragaglia, L. Biferale, C.A. Amadei, G. Falcucci (Rome, Italy) V.P. Voloshin, N.N. Medvedev (Novosibirsk, Russia) C. Vecitis (Harvard, USA) C. Holm (Stuttgart, Germany) J. Smiatek (Münster, Germany)

5.5 Scientific equipment

The simulations will be carried out on the compute cluster at the Helmholtz Institute Erlangen-Nürnberg. A proposal to request for computing time at the supercomputing facilities of the Research Center in Jülich (JURECA and JUWELS) is currently being prepared.

5.6 Project-relevant cooperation with commercial enterprises

None

5.7 Project-relevant participation in commercial enterprises

None