

Abstract

A challenging topic in surface engineering is predicting the wetting properties of soft interfaces and 2D materials with different liquids. Surfaces with tailored properties find practical applications in the energy sector, including the design of materials for optronic devices, drag reduction for boats, anti-icing for aircraft wings, self-cleaning for solar and photovoltaic panels, and desalination membranes. The ability to predict and control wetting behavior in these materials will enable the development of more efficient and effective surfaces, leading to improvements in energy production, storage, consumption, and thus environmental sustainability. However, a robust and fast computational protocol suitable for predicting wettability with molecular precision is still lacking.

In this thesis, a workflow based on molecular dynamics simulations to predict the wettability of soft surfaces and 2D materials is proposed and tested against the experimental contact angle of several polar and non-polar liquids. The study cases addressed here focus on polymers as soft surfaces and on graphene as 2D material, but the proposed experimental-modeling protocols may have broader fields of application. Structural properties and surface roughness of numerical substrates have been analyzed through microscopy measurements and compared with chemically equivalent experimental samples. Then, the contact angle and interface tension were evaluated reproducing numerically the sessile droplet method, or via a thermodynamics approach, namely the free energy perturbation. The results were finally validated against standardized characterization tests, reaching a good agreement with experimental evidence, and providing insights on possible effects of roughness at the nanoscale, experimental conditions, and graphene wetting semi-transparency.

Overall, this work represents the initial steps towards an integrated multi-scale framework for predicting the wettability of more complex interfaces, which will

eventually take into account the effect of surface topology at higher scales and synergically be employed with experimental characterization techniques.

With this in mind, a coarse-grained model for water and polymers with atomistic accuracy to speed up mesoscopic simulations is proposed. Such a model will be useful to describe interfaces with characteristic dimensions typically larger than the ones exploitable with classical molecular dynamics. Indeed, atomistic simulations are constrained by the feasible computational capacity but calibrated coarse-grained (CG) models can go beyond these limits. First, three popular atomistic water models are compared with their corresponding CG models built using finite-size particles such as ellipsoids.

Similarly, the coarse-grained model of PLGA is compared with its corresponding atomistic model, where every polymer residual is described by only one bead. Differently from previous approaches, short-range interactions are accounted for with the generalized Gay-Berne potential, while electrostatics and long-range interactions are computed from virtual charges inside the ellipsoids. Such an approach leads to a quantitative agreement between the original atomistic models and their CG counterparts. Results show that a timestep up to 10 fs can be achieved to integrate the equations of motion without significant degradation of the physical observables extracted from the computed trajectories, thus unlocking a significant acceleration (up to six times with respect to the atomistic counterparts) of mesoscopic simulations at given accuracy.

Still, in the context of a multiscale framework, this study demonstrates how the outcomes derived from atomistic and mesoscopic simulations can be effectively utilized in multiphase numerical experiments that rely on finite element simulations.