Surface Free Energy Characterization of Soft Materials through Computational Experiments

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Introduction:

The surface free energy of soft coatings determines the adhesion, friction, and wettability response of solid surfaces in several applications of engineering and biomedical interest. However, the multiscale nature of these phenomena limits a bottom-up prediction of the resulting surface properties.

Theoretical background:

In this work we use molecular dynamics (MD) simulations performed in LAMMPS to characterize the surface and solid-fluid interface of low-surface-free-energy coatings and materials. In particular, the **free energy perturbation (FEP) [1,2]** approach is first used to evaluate the **work of adhesion (Wad)** between polymer surfaces and fluids; then, the **Young-Dupré** equation is adopted to compute the ideal **contact angle (ϑ).**

$$Wad = \frac{1}{A}\int_{\sqrt{\varepsilon_B}}^{\sqrt{\varepsilon_A}} \langle \frac{\partial U_s}{\partial \sqrt{\varepsilon}} \rangle_{NVT} \, d\sqrt{\varepsilon} \qquad \boldsymbol{FEP}$$

$$\vartheta = arcos\left(\frac{W_{ad}}{\gamma_l} - 1\right) \boldsymbol{Young - Dupre}$$

References:

[1] Leroy et al. J. Phys. Chem. C. (2015). doi:10.1021/acs.jpcc.5b10267.

[2] Rajan et al. Nano Lett. 2019, 19, 1539−1551

[3] Cardellini et al. *Coupling Molecular Dynamics (MD) simulations and contact angle experiments for the characterization of low free energy surfaces: the case study of Perfluoro-Decyl-Acrylate (PFDA) coated silicon.* Submitted to Materials & Design

Study cases:

We focus the attention on **hydrophilic** and **hydrophobic** polymeric coatings. In detail, we study the wettability of **Polylactic-glycol acid (PLGA)** and **Perfluoro Decyl Acrylate (PFDA)** modelled with the OPLS-AA force-field. In the case of PLGA coatings we build an amorphous system with polymer chains of 90 repetition units, while in the case of PFDA coatings we also investigate the effects of different percentages of **fluorinated alkanes (CFx)** in contact with water.

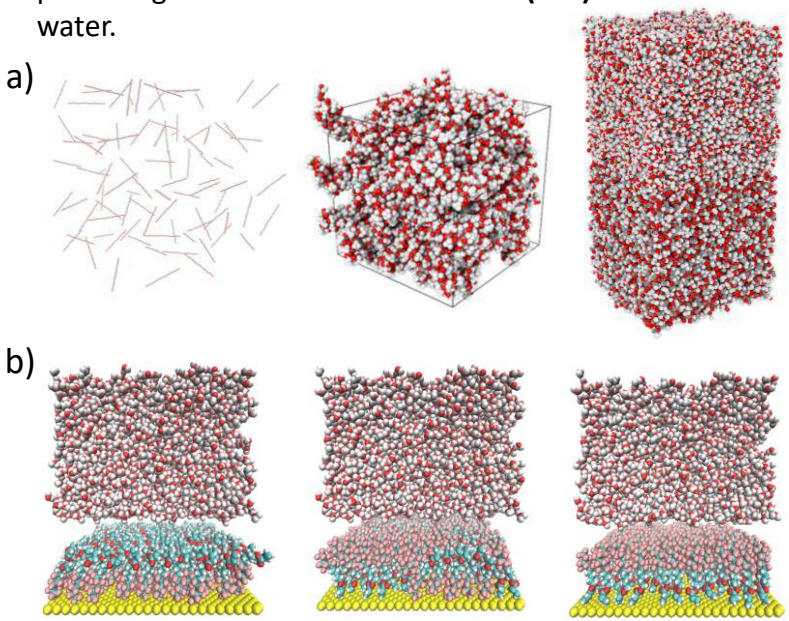

Figure 1: MD snapshots of the systems studied. a) Construction of PLGA amorphous system and coupling with water. b) PFDA coatings with different percentages of CFx

Results and conclusions:

The results in terms of surface tension (γ_l), work of adhesion (W_{ad}) and contact angle (ϑ) are compared with the experimental data provided by the project partners.

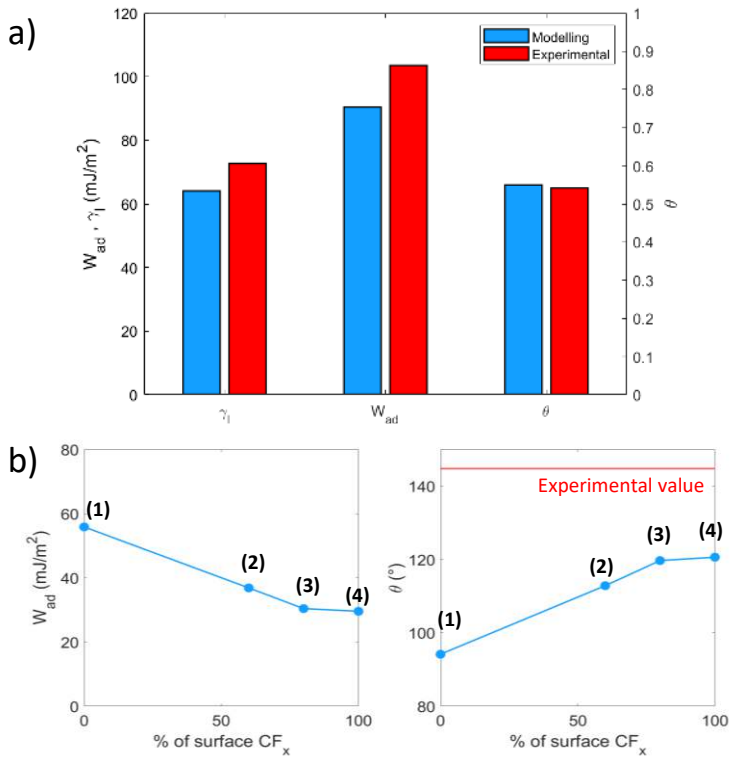

Figure 2: Wad and ϑ of the system studied. a) The simulated contact angle of PLGA is good agreement with the experimental result on a chemically equivalent sample. b) The models 3 and 4 (chemically equivalents to the experimental sample) reproduce a lower contact angle if compared with the experimental results, which are affected by surface roughness effects

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