Supplementary material for paper:

Wetting behaviour of nematic nanodroplets on planar surfaces and their contact angles anisotropy

Davide Vanzo, Matteo Ricci, Roberto Berardi and Claudio Zannoni
Department of Industrial Chemistry *"Toso Montanari"*,
University of Bologna, viale Risorgimento 4, 40136 Bologna, IT

The composite crystalline surface was set up by taking two contiguous (001) fcc layers of LJ particles (at distance 0.794 σ_0 units) and adding an underlying effective surface potential whose origin was displaced 1.3 σ_0 units from the plane defined by the centres of mass of the lowest LJ layer (see Figure 2–B). This displacement was found to better approximate for the tails of the interactions. As a final check we also run a few test MD simulations with either the explicit or the composite surface models to verify that the properties of a LJ fluid wetting them would be the same within the range of thermal fluctuations, which indeed was the case.

To determine an optimal parameterisation for the effective surface potential U_{eff} we have performed a preliminary MD simulation, 2×10^5 time steps long, of a LJ fluid at dimensionless density $\rho^* = 0.65$, and temperature $T^* = 1$, wetting a XY periodic (001) fcc LJ crystal slab with a 5.556 σ_0 thickness, corresponding to eight (001) fcc monolayers. We computed, with stride 100 time steps, the average histogram of the interaction energy values between each LJ fluid particle and the surface centres of the fcc LJ crystal. The histogram was sampled with respect to discrete bins measuring the distance z between a fluid LJ particle and the surface (*i.e.* the plane defined by the centres of mass of the topmost layer of crystal particles). To improve the sampling accuracy for larger centre–centre separations we used (specifically to this simulation) a 5 σ_0 cutoff for the LJ interactions. The resulting energy profile was used to determine, by a non–linear least–squares minimisation based on the Nelder–Mead simplex algorithm [1], the four dimensionless a, b, m, and n parameters of the following modified LJ potential

$$U_{\text{eff}}(z) = \varepsilon_{\text{LJ}} \left[a \left(\frac{\sigma_{\text{LJ}}}{z} \right)^n - b \left(\frac{\sigma_{\text{LJ}}}{z} \right)^m \right]. \qquad \text{(S1)}$$

The optimal dimensionless parameters we have found are $a = 50.81$, $b = 50.62$, $n = 6.24$, and $m = 5.43$. A plot of the corresponding energy profile is provided in Figure S1.

To quantify the extent of the dynamical shape fluctuations of the equilibrated sessile droplets we have also computed the average of the (absolute value of the) deviations of the instantaneous particle density maps from the average values of Figure 5. These results are plotted in Figure S2. We see that the regions with large changes in particle density actually have a thickness of a few σ_0 units, comparable to that of the nematic–vapour interface [2] (not shown here for clarity).

[1] J. A. Nelder and R. Mead, *Comput. J.*, 1965, **7**, 308–313.

[2] D. Vanzo, M. Ricci, R. Berardi and C. Zannoni, *Soft Matter*, 2012, **8**, 11790–11800.

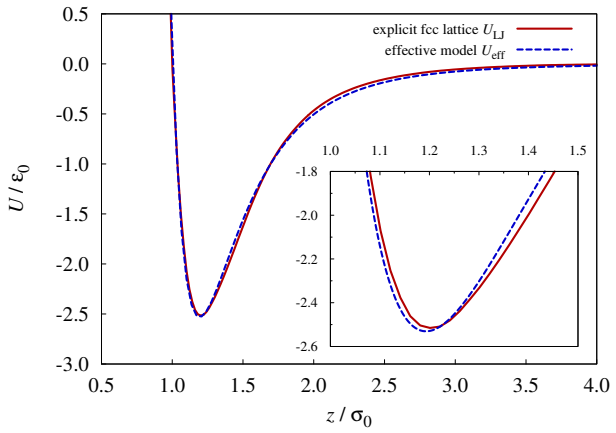

Fig. S1 Comparison between the explicit potential for a LJ particle with distance z from a planar (001) eight layers thick fcc LJ lattice (solid red curve), and the effective potential of Equation S1 (dashed blue curve) with parameters $a = 50.81$, $b = 50.62$, $n = 6.24$, and $m = 5.43$. In the distance range $z = 1$–4 σ_0 the mean square deviation between the energy values of the two curves is less than 5%.

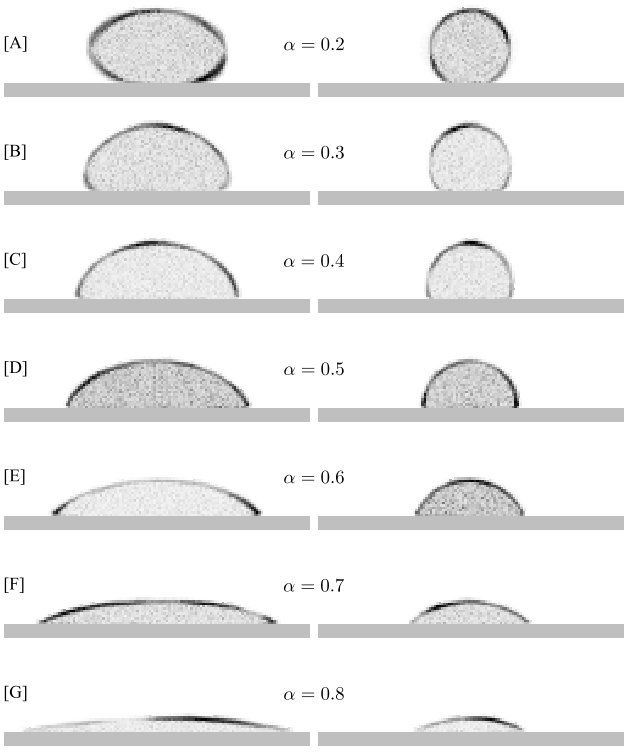

Fig. S2 Maps of the average (absolute value) fluctuations of particle densities from the average populations of Figure 5.