Electronic Supplementary Material (ESI) for Soft Matter

Effect of Capillary Bridging on Janus Particle Stability at the Interface of Two Immiscible Liquids

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TECHNICAL DETAILS ON THE MOLECULAR DYNAMICS SIMULATIONS

The simulations use standard molecular dynamics (MD) techniques [1–3] and generic interactions of the Lennard-Jones form (Eq. 1) to which a linear term is added so that the force smoothly goes to zero at r_c. The $(r/\epsilon)^{-12}$ term corresponds to the hard-core repulsion, whereas the attractive $(r/\epsilon)^{-6}$ term determines the chemistry [4]. As a result, the coefficient A defines the wetting properties [5]. The specific coefficients used are depicted in Fig. 1. All calculations are done using dimensionless variables with the scaling parameters being σ (length scale), ϵ (energy scale), and m (mass of the fluid atoms) and the relevant time scale is $\tau = \sqrt{m\sigma^2/\epsilon}$. Typical numerical values are $\sigma \sim 0.3nm$, $\tau \sim 2ps$ and $\epsilon \sim 120k_B$, where k_B is Boltzmann's constant, and the temperature is measured in units of ϵ/k_B. The calculations are done using an NVT ensemble, where the temperature is fixed at $T = 1.0\epsilon/k_B$ using the Nose-Hoover thermostat and the density is set to $\rho = 0.8/\sigma^3$.

A. Fluids

Each individual fluid is a monotonic Lennard-Jones fluid characterized with a well-defined phase diagram [6] and the total number of fluid atoms in the presented simulations is 6662. The temperature and density used correspond to the liquid phase of the LJ bulk system. In order to ascertain the immiscibility of the two liquids, coefficients of $A_{ii} = 1$ and $A_{ij} = 0.5$ are chosen. The density profile of the liquid/liquid system is calculated and depicted in Fig. S1. The density gap caused by the immiscibility of the two liquids is on the order of 2.5σ, whereas the particle diameter is 6σ excluding the density gap as an origin for the particle trapping at the interface. In order to quantify the immiscibility of the two liquids, interfacial tension calculations are carried out. The interfacial tension is related to the difference between the normal and transverse components of the stress (or pressure) tensor integrated over the longitudinal direction [7]. Using the Kirkwood-Buff formulation of the tangential and normal components of the pressure tensor [8], the interfacial tension is measured to be $1.5\ \epsilon/\sigma^2$ $(21.4mN/m)$ for the set of parameters shown in Fig. 1, which is in good agreement with other MD simulations [9].

B. Walls

In order to localize the interface at the center of the simulation box, the two fluids are confined in the direction normal to the interface using two bounding walls composed of a total of 900 atoms with a mass of $m_w = 100m$, tethered to cubic lattice sites. The coefficient A for wall-fluid interactions is equal to 1. Periodic boundary conditions are applied in x and z directions. The simulation box dimensions are $L_x = L_z = 15\sigma$ (parallel to the interface) and $L_y = 34\sigma$ (normal to the interface).

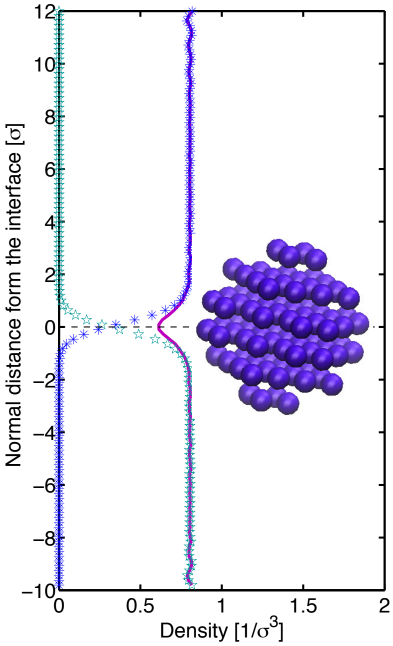

Figure S1. Density profile of the system. The coordinate y runs along the normal to the interface and the properties are averaged over the other two directions. The symbols refer to *Fluid1* ($\star$) and *Fluid2* ($*$) density profiles, while the continuous curve is the total liquid density. In order to compare the particle size (6σ) to the density gap ($\sim 2.5\sigma$), the schematic of the particle is shown to scale.

C. Particles

The particle used in this study is a spherical section of an atomic cubic lattice containing the atoms within a radius of 3σ of the center. The particle is composed of 88 atoms, roughly $2nm$ in diameter, and moves as a rigid body. Amphiphilicity is introduced by assigning different interaction coefficients to atoms in the lower and upper half of the particle in the initial configurartion. The net force and torque on the particle are computed by summing the interatomic forces between its atoms and the neighboring fluid atoms (within a cut off radius of 2.5σ), and the motion is given by Newton's and Euler's equations. Quaternion variables are used to describe the particle orientation [1]. Integrating Newton's and Euler's equations is done via a predictor-corrector algorithm using time steps of $\Delta t = 0.005\tau$.

D. Thermodynamic Integration Calculations

The thermodynamic integration approach (Eq. 2) is used to calculate the free energy difference during the process of nanoparticle transfer from the bulk of *Fluid1* to *Fluid2* [10, 11]. In this study the particle is initially placed in the bulk of *Fluid1* at least one particle diameter below the interface. The two liquids are equilibrated for a minimum of 500τ, while the freely rotating particle is kept fixed at its initial position. The particle is then translated at a constant velocity along the direction normal to the interface, typically over a distance of $\Delta y = 0.1\sigma$ within a time interval of $t_s = 500\tau$ ($u = 2 \times 10^{-4} \sim 1cm/\mathrm{s}$). Each translational step is followed by a relaxation step of $t_s = 500\tau$ during which the particle is held fixed in place and the force acting on the particle in the direction normal to the interface is collected. Therefore, the total translation and relaxation time per translational step is equal to $2 \times 10^5 \Delta t = 1000\tau$. This process is repeated until the particle reaches the bulk phase of *Fluid2*. During the entire process, the particle is allowed to rotate freely. In Eq. 2 where $\langle F_y \rangle_{y'}$ is the ensemble averaged force in the direction normal to the interface acting on the particle at a position y' from the interface, the time average is used as a substitute for an ensemble average in the free energy calculations assuming ergodicity [11]. The observed asymmetry in the free energy difference for the Janus particle (Fig. 4) indicates that the work required for separating the Janus particle from the interface is larger than the free energy gained by bringing the particle to the interface. Simulations with a higher translating velocity have been conducted for a Janus particle in which the total translation and relaxation time per each translation equals to 500τ. At the higher translation velocity a slightly larger asymmetry in the free energy difference is observed. The reduced asymmetry in the case of the larger characteristic time is expected, as the process should be reversible if it were to be carried out infinitely slowly. It should be noted however, that a typical time for adsorption of a freely suspended particle to the interface is less than $10^4\tau$ (determined by simulations where the particle is allowed to reach the interface via diffusion), while the characteristic time for moving the particle from the bulk of one fluid to the other in these free energy measurements is approximately $10^5\tau$ (an order of magnitude larger). Indeed, the motion of the particle in the simulations shown here is very slow compared to the natural time scale for the spontaneous process.

E. Thermostat

The energy added to the system by the work of translation has two dissipation pathways. Some of the energy is used for molecular reconfigurations and rearrangements such as the formation of the liquid shell around the Janus cap (Fig. 3. $III - e$), whereas the rest of the energy results in overall heating of the system. In a real experiment the system size is much bigger compared to a typical MD simulation and the generated heat can be readily dissipated. Contrarily, in a system as small as the one used here, heating would be significant and one needs to use a thermostat in order to dissipate the heat. Hence, the function of the Nose-Hoover thermostat in the simulations is to keep the system temperature and the resulting interfacial properties constant since heating of the system via the work done on the system during the translation may cause significant changes, for example, in the immiscibility of the two liquids.

F. Density Profiles

In order to determine whether the molecular structure of the fluids around the particle plays a role in the observed asymmetry, the density profiles of both fluids are calculated. The problem configuration is cylindrically-symmetric since nothing changes on average if the system is rotated about a vertical axis through the particle center normal to the fluid-fluid interface. As a result, calculations are done in cylindrical coordinates with the origin being at the particle's center of mass. As an example, the density profiles of *Fluid1* during the process of adsorption and desorption of the Janus particle are shown in Fig. S2.

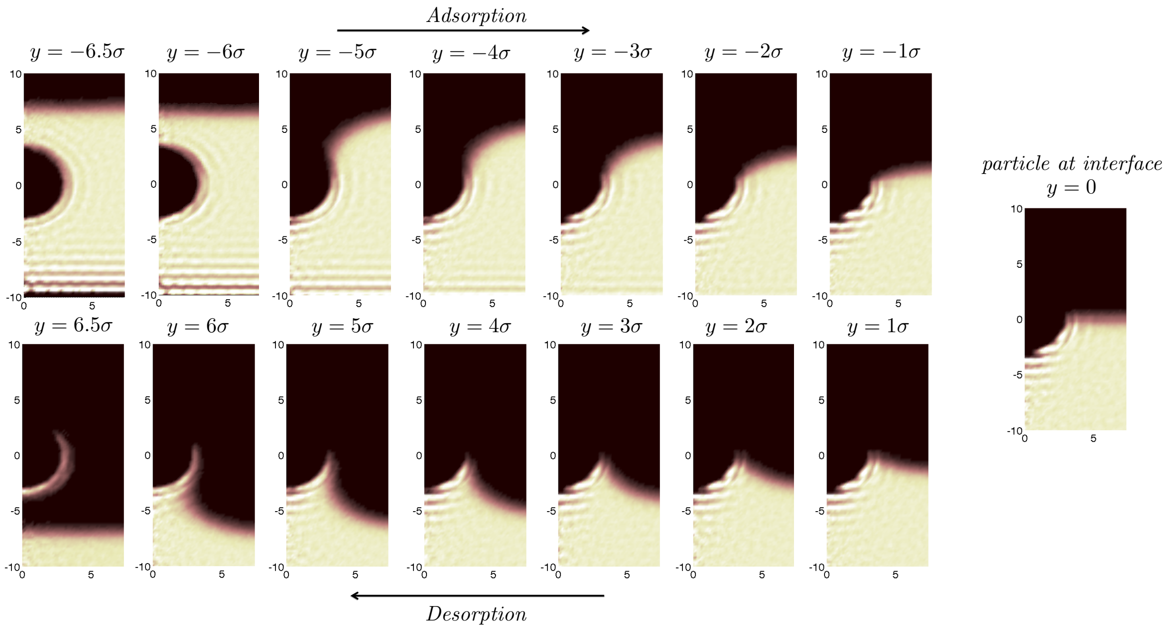

Figure S2. Density profiles of *Fluid1* as a function of $2D$ distance of a solvent atom from the axis normal to the interface passing through the particle's center of mass (horizontal axis) and height of the solvent atom from the particle's center of mass (vertical axis) at different times during the process of Janus particle adsorption to ($y < 0$) and desorption from ($y > 0$) the interface.

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