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A molecular dynamics study of the force between planar substrates due to capillary bridges

Jorge H. Saavedra [a], Roberto E. Rozas [b], Pedro G. Toledo [a,*]

[a] Chemical Engineering Department and Surface Analysis Laboratory (ASIF), University of Concepción, PO Box 160-C, Correo 3, Concepción, Chile
[b] Institut für Theoretische Physik der Weichen Materie, Heinrich Heine-Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

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ABSTRACT

Molecular dynamics simulations are used to study capillary liquid bridges between two planar substrates and the origin, strength and range of the resulting force between them. Pairwise interactions are described by the Lennard–Jones potential. Surface wettability is tuned by varying the fluid–substrate well depth interaction parameter. The force between the substrates due to a bridge of liquid is estimated by different methods including non-equilibrium simulations of moving substrates connected by liquid bridges and macroscopic balance of forces. The latter involves knowledge of liquid–vapor interfacial free energy, curvature radii, radius of wetted area and contact angle at the triple-phase contact line. All these physical quantities are estimated from equilibrium simulations. The force is attractive when the substrates are solvophilic or moderately solvophobic; and thus for cavities surrounded by the same liquid the force is attractive even when the substrates are moderately solvophilic. Two threshold values for the fluid–substrate potential interaction parameter can be identified; one for which the effective interaction between substrates due to liquid bridges changes from repulsive to attractive and another for which the capillary bridge becomes mechanically unstable and breaks into droplets.

1. Introduction

Molecular simulations have been used to study the behavior of fluids confined between substrates and also the wetting behavior of liquid drops and nuclei on solid substrates but not, to the best of our knowledge, the nature and range of the resulting force between the surfaces for different wettability conditions. The wetting of the liquid phase, droplets or bridges, is set by the strength of the interaction between particles in the fluid and in the substrate. Strong fluid–solid interactions lead to lower contact angles, measured through the liquid phase, and thus to higher wettability.

Molecular dynamics was used early by Koplik et al. [1] to study microscopic aspects of slow viscous flows past a solid wall, where both fluid and wall have molecular structure. They also simulated an immiscible two-fluid system and were able to vary the interaction between the fluids and the wall. A static meniscus was observed whose contact angle agrees with estimates from the Young equation and, when motion occurs, advancing and receding contact angles were observed. Although solid–fluid interaction was not explored thoroughly, partial results indicate that contact angle, measured through the wetting phase, decreases as the interaction increases. Later, Busic et al. [2] studied by molecular dynamics simulations the extensional rheology of Newtonian and non-Newtonian fluid bridges between two substrates. The evolution of the liquid filament profile and the forces exerted on the end-plates obtained from the simulations, and also the internal dynamics of the fluid and the molecular configurations, were in good agreement with experimental data and with results from macroscopic numerical calculations. Koplik and Banavar [3] presented molecular dynamics simulations of filaments of a non-Newtonian liquid stretched under uniaxial deformation to the point of breaking. They observed non-uniform extensions leading to highly uneven shapes and alternating stretched and unstretched regions of liquid. Bucior et al. [4] used non-equilibrium molecular dynamics to investigate the kinetics aspects of the evaporation of liquid bridges confined between walls for different wetting conditions to elucidate the effect of the capillary inhomogeneity on this process.

Concerning simulation studies of the three-phase contact of equilibrated liquid droplets/bridges with substrates two main approaches are commonly used to determine the contact angle from simulations; in one method the liquid or droplet is prepared and the angle is obtained from averaged density profiles, in the other, the Young equation is used to estimate the angle and the involved interfacial free energies γ_{AB} are determined separately. Both methods have been also used in combination to test the consistency of the

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* Corresponding author. Fax: + 56 41 2247491.
E-mail address: petoledo@udec.cl (P.G. Toledo).

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results. Maruyama et al. [5] used molecular dynamics simulations to study a Lennard–Jones liquid droplet on a solid substrate made of particles pinned to fcc lattice points by harmonic springs and applied the same methodology to study droplets of water on platinum fcc substrates [6]. They found that the contact angle depends on the crystalline orientation of the substrate being larger for fcc(100), intermediate for fcc(111) and lower for fcc(110). Shi and Dir [7] obtained contact angles from density profiles of a Lennard–Jones liquid droplet on a Lennard–Jones substrate at different temperatures and wetting conditions and also studied the effect of temperature over the contact angle of water over platinum. The role of the substrate–fluid interaction strength and substrate topographies was investigated by Leroy and Müller-Plathe [8] using molecular dynamics simulations. The contact angles were directly determined from density profiles, the solid–liquid and liquid–vapor interfacial free energies were respectively determined from thermodynamic integration method and from the anisotropy of the pressure tensor at the interface. The simulation results showed that the contribution of the solid–vapor interfacial free energy in the Young equation is small when the solid–liquid interaction is weak. Semiromi and Azimian [9] studied the effect of temperature and solid–fluid interaction on the wetting of a Lennard–Jones system. A common result of these works is the lowering of the contact angle as the solid–fluid interaction parameter increases. An alternative approach was applied by Grzelak and Errington [10] to determine contact angle, solid–vapor and solid–liquid interfacial tensions. The method is based on biased grand canonical Monte Carlo simulation which provides the dependence of the interfacial free energy on density (for a description of the method see also [11–13]). Their results show good agreement with those obtained from the mechanical definition of interfacial tension. Das and Binder [14] used Monte Carlo simulations to investigate a immiscible binary Lennard–Jones fluid between walls, a system where bridges rich in one of the components are formed. They evaluated contact angles and interfacial free energies separately for different wall-fluid interaction strengths and showed that the Young's equation applies at the nanoscale.

Here we use molecular dynamics simulations of nanoscopic capillary liquid bridges between planar substrates to determine the resulting force between the substrates. The wettability is tuned by varying the solid–fluid interaction parameter. The force between the substrates is estimated from different methods; (i) from a macroscopic force balance, where the physical quantities involved are determined from equilibrium simulations (ii) by applying second Newton's law to moving substrates connected by liquid bridges, and (iii) from the integration of the normal pressure radial profile of equilibrated liquid bridges.

2. Methods

Molecular dynamics simulations of liquid capillary bridges connecting two substrates are performed. Equations of motion are solved with the velocity Verlet algorithm [15] and particle interactions are modeled with the 12-6 Lennard–Jones potential [16] truncated and shifted at a cut-off distance of 2.5 σ_{ij} with i and j denoting particles in the fluid (f) or in the substrate (s). The following reduced units are used; for length $L^* = L/\sigma_f$, time $t^* = (t/\sigma_f)(\epsilon_f/m_f)^{1/2}$, mass $m^* = m/m_f$ and temperature $T^* = k_B T/\epsilon_f$. The interaction parameters for particles in the fluid are $\sigma_f^* = 1$ and $\epsilon_f^* = 1$, for particles in the substrate $\sigma_s^* = 1$ and $\epsilon_s^* = 10$, and for the substrate–fluid particle interaction $\sigma_{sf}^* = 1$ and variable well depth ϵ_{sf}^* in order to attain different wetting conditions. The particle masses are $m_f^* = 1$ and $m_s^* = 10$. The integration time step is $t^* = 0.0023$.

2.1. Preparation of a capillary bridge

The substrate and the fluid are prepared in independent simulations and then put in contact. An fcc crystalline substrate of 4 atom layers thickness and initial lateral lengths $L_x^* = L_y^* = 30$ is relaxed in an *NPT* simulation at $T^* = 0.68$ and $P^* = 0$ (condition for which the fcc phase is stable). Then two copies of the equilibrated substrates are disposed in a simulation box at a distance D^* along the direction perpendicular to the substrate surface z. The crystalline orientation of the surface is fcc(100). The positions of the particles in the first external layer are fixed in both substrates and the system is equilibrated in an *NVT* simulation. A liquid is prepared in an *NVT* simulation in a box of lengths $L_x^* \times L_y^* \times (D^* - 2)$ using periodic boundaries in all directions. In the next step the liquid is disposed in the volume between the substrates and the system is equilibrated in *NVT* simulation over $2 \cdot 10^5$ time steps. Finally, in order to create a bridge, the particles in the liquid outside a cylinder of radius R^* are removed. The remaining number of particles in the bridge are $N = 941$ and its nominal dimensions are $R^* = 5.9$ and $D^* = 10.8$ (see Fig. 1a). The resulting system is equilibrated in an *NVT* simulation during 10^6 time steps. The temperature is kept constant with a Berendsen thermostat with a relaxation time $\tau^* = 0.46$.

2.2. Preparation of a liquid droplet

Simulations of a liquid droplet over a single substrate are used to asses the contact angle given T^* and ϵ_{sf}^* for comparison with results from simulation of a bridge with the same Lennard Jones potential and parameters. A substrate of 8 layers and initial lateral lengths $L_x^* = L_y^* = 30$ is prepared in an *NPT* simulation at $T^* = 0.68$ and $P^* = 0$. As for bridges the fcc(100) surface crystalline orientation is considered. The droplet is obtained from an independent simulation and then is located over the substrate along the z-axis. First, a system made of 500 particles at $T^* = 1.30$ and liquid density is equilibrated inside a periodic cubic simulation box. Later, the box is expanded to obtain a liquid droplet. After $2 \cdot 10^6$ time steps a liquid droplet in equilibrium with its vapor is obtained. Particles that belong to the droplet are identified according to the Stillinger criterion [17] for a threshold radius of 1.5. The droplet and its vapor are then displaced so that the lowest particle belonging to the droplet is located right at the bottom of the simulation box. Vapor particles below this limit appear at the top of the box by virtue of a periodic boundary at the bottom of the box. Then, the drop is aligned over the substrate with a gap of σ_f^* to avoid particle overlapping but enough to guarantee interaction between the

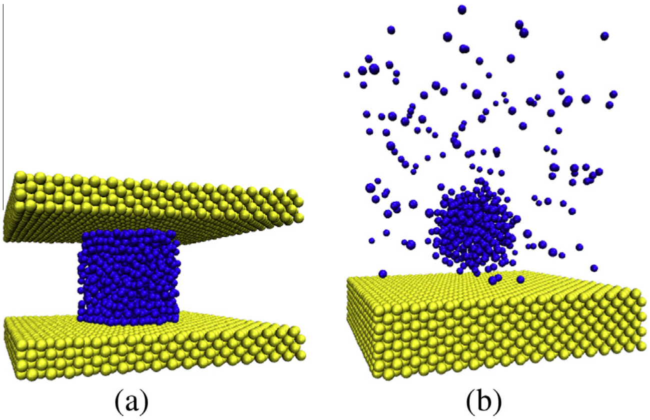

Fig. 1. Snapshots of initial configurations for simulations of (a) a liquid bridge between two planar substrates and (b) a liquid droplet over a flat substrate.