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The use of Monte Carlo simulation to obtain the wetting properties of water

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Abstract

The interface potential approach is used to compute interfacial properties of a model system consisting of water at a structureless non-polar surface. Both spreading and drying versions of the method, in which one focuses on the growth of a thin liquid and vapor film from the surface, respectively, are employed. We examine the substrate strength dependence of interfacial properties, including the spreading and drying coefficients, contact angle, and liquid-vapor surface tension, at a temperature of 500 K as well as the temperature dependence of these properties for a surface of moderate strength.

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1. Introduction

Fluids routinely interact with solid substrates in industrial processes, natural phenomena, and throughout our daily experiences. Examples vary from the use of liquid detergents to clean stained fabric to the collection of rain water onto tree leaves. The interfacial properties of such systems feature prominently in the design of various devices, additives, and fabrics. In this work, we describe a general molecular simulation strategy for computing interfacial properties.

The approach that we pursue focuses on the computation and subsequent analysis of an interface potential [1, 2], which provides the surface excess free energy as a function of the thickness of a fluid film in contact with a substrate. This technique [3] provides several advantageous features. First, the approach does not require the establishment of a nanodroplet on the substrate. Therefore, one avoids formation of the three phase contact line and the potential complications that stem from this structure [4, 5]. Second, because the method is based upon the calculation of free energies, one can devise schemes that enble one to efficiently connect multiple states of interest (e.g. state points, substrate conditions). The third issue we highlight is related to the study of interfacial phenomena involving heterogeneous substrates [6, 7]. The interface potential approach focuses on a thin film, and therefore simulations can be completed with a substrate that spans just one period of a heterogeneity of interest. As a result, one is able to probe relatively large-scale heterogeneities with reasonable system sizes.

There are two versions of this general strategy that we puruse [3]: (1) a “spreading” method in which one focuses on the growth of a liquid film from a substrate in a mother vapor and (2) a “drying” method in which one focuses on the growth of a vapor film from a substrate in a mother liquid. The spreading method is designed for systems characterized by moderate to strong substrate-fluid interaction strength, whereas the drying method is designed for systems characterized by weak to moderate substrate-fluid interaction strength (e.g. fluids near superhydrophobic and superoleophobic surfaces).

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In a previous report [3] we detailed this approach and provided examples of its use to characterize the wetting properties of Lennard-Jones systems. Here, we demonstrate application of these methods to a model system consisting of water at a flat non-polar surface. In what follows, we first sketch the molecular simulation methods used to compute interfacial properties of interest. We then introduce the model and subsequently provide results that show how wetting properties evolve with temperature and the strength of the substrate-fluid interaction.

2. Methods

We begin by outlining the drying method [3]. Within this approach the interface potential provides the surface excess free energy $V_d(l)$ as a function of the thickness l of a vapor film in contact with a substrate and background liquid at temperature T and chemical potential μ. Here, we focus on wetting properties, and therefore restrict our attention to state conditions along the bulk liquid-vapor saturation line (T, μ_b). An example of V_d for a system in the partial wetting regime is provided in Figure 1. For partial wetting conditions, a global minimum emerges at low $l = l_\mathrm{liq}$ followed by a plateau region at relatively high $l = l_\mathrm{plat}$. The global minimum corresponds to a physical situation in which a liquid is in contact with the solid, and the associated free energy $V_d\left(l_\mathrm{liq}\right)$ is related to the excess free energy of a solid-liquid interface $\gamma_\mathrm{sl}A$. The plateau region is associated with a vapor film in contact with the solid and a liquid, and therefore $V_d\left(l_\mathrm{plat}\right)$ is related to the excess free energy due to a solid-vapor and liquid-vapor interface $(\gamma_\mathrm{sv} + \gamma_\mathrm{lv})A$. The drying coefficient d is defined as the difference between these two free energies, as is illustrated in Figure 1,

$$d = \gamma_\mathrm{sl} - (\gamma_\mathrm{sv} + \gamma_\mathrm{lv}) = \frac{1}{A}\left[V_d\left(l_\mathrm{liq}\right) - V_d\left(l_\mathrm{plat}\right)\right] \tag{1}$$

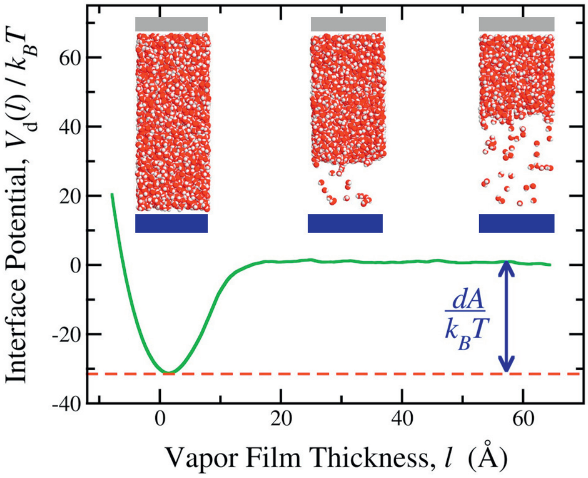

Figure 1: Drying interface potential collected at $T = 500$ K with $\epsilon_\mathrm{sf} = 3.33$ kJ/mol. Simulation cell images represent typical particle configurations at the film thickness indicated. The lower blue surface is the substrate of interest (SOI). The upper gray surface corresponds to a sticky wall.

Within the spreading method [8] the interface potential provides the surface excess free energy V_s as a function of the thickness (surface density) l of a liquid film in contact with a substrate and background vapor at temperature T and chemical potential μ_b. The general features of the spreading potential are similar to those of the drying potential. Examples of V_s for a Lennard-Jones system are found in [3, 6, 8, 9, 10]. The qualitative features that the spreading potential adopts under different wetting scenarios have been described in a number of theoretical studies [1, 2, 11]. For partial wetting conditions, a global minimum emerges at low $l = l_\mathrm{vap}$ followed by a plateau region at relatively high $l = l_\mathrm{plat}$. The global minimum corresponds to a physical situation in which a vapor is in contact with the solid, and the associated free energy $V_s\left(l_\mathrm{vap}\right)$ is related to the excess free energy of a solid-vapor interface $\gamma_\mathrm{sv}A$, where γ is the interfacial tension and A is the cross-sectional area of the interface. The plateau region is associated with a liquid film in contact with the solid and a vapor. It follows that $V_s\left(l_\mathrm{plat}\right)$ is related to the excess free energy due to a