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Computer Simulation Study of the Wetting Behavior and Line Tensions of Nanometer Size Particulates at a Liquid-Vapor Interface

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We study the behavior of nanometer size particulates at a liquid-vapor interface by means of molecular dynamics simulations. We propose a methodology for computing the line tension using computer simulations, and present new data for the wetting of particulates at a planar liquid-vapor interface, as a function of particulate size. For the sizes considered in this work the line tension is negative and influences the wetting behavior of particulates at the liquid-vapor interface. [S0031-9007(98)05956-0]

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Young's equation [1] provides a simple description of wetting and drying transitions in terms of the surface tensions of the different interfaces. However, the line tension, a property characteristic of three phase equilibrium, is known to have a considerable influence on the wetting transition of some systems, and therefore it has to be considered as a correction in a more general treatment [2,3]. Indeed, it has been shown theoretically [4,5] that a large line tension may induce a wetting transition (in this Letter we take the term "wetting transition" to refer to both continuous and discontinuous changes in wetting state). We note that the available experimental data for line tensions [6–11] show a wide range of possible values and that, although theoretical studies have considered various aspects of the line tension problem [12–17], as far as the authors are aware, there have been no molecular simulation estimates of the line tension.

In this Letter we consider the wetting transition undergone by a spherical particulate of nanometer size at a planar liquid-vapor interface. We introduce a new methodology for computing the line tension within a molecular simulation, and present new data for the wetting of particulates at interfaces. These studies are aimed at improving our understanding of the underlying physics of wetting as well as a variety of complex phenomena in which colloidal particles are present at interfaces. For instance, the effect of particulates on the breaking of emulsions and foams depends on their ability to enter the interface [11], i.e., on the feasibility of the wetting transition which in turn may depend on the line tension. Nanometer size particulates (e.g., calcium carbonate stabilized by surfactant) are used as fuel additives in the petrochemical industry [18].

The location of a spherical particulate (p) in a liquid (l)-vapor (v) interface can be described in terms of the contact angle θ that it makes with the surface (cf. Fig. 1). From thermodynamic analysis [4,5] it is known that this angle changes with the line tension, and eventually for some value of the line tension, it can drop discontinuously to zero (at least for particles where the variation of surface and line tensions with curvature can be neglected). This point, characterized by the equality of the free energies of the particulate both at the liquid phase and at the interface, determines the wetting transition. The free energy of the particulate in the planar surface with respect to the planar liquid-vapor interface can be expressed as [5]

$$F^s = 2\pi R^2 \left[\gamma_{pl}(1 + \cos\theta) + \gamma_{pv}(1 - \cos\theta) - 0.5\gamma_{lv}\sin^2\theta + \frac{\tau\sin\theta}{R} \right], \tag{1}$$

where $\gamma_{\alpha\beta}$ represents the surface tension of the interface between phases α and β, and τ is the line tension and is defined as the excess free energy per unit length associated with the three phase line. In Fig. 1, h represents the depth of immersion of the particulate in the liquid, and, as we will see below, its determination allows the computation of the contact angle directly from a computer simulation. It is apparent from expression (1) that knowledge of the free energy, surface tensions, and contact angle makes possible the computation of the line tension. In what follows we will use this equation to compute the line tension of our system as a function of the particulate size.

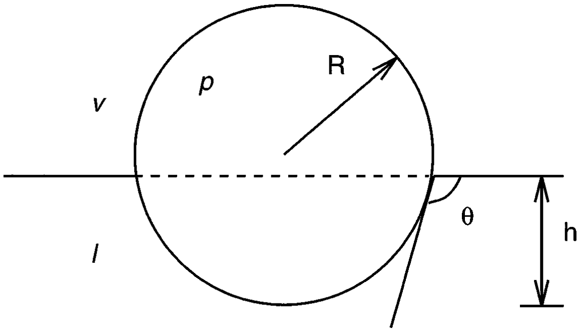

FIG. 1. Illustration of a particulate at the liquid-vapor interface. For definitions see text.

In order to model the system represented in Fig. 1 we have chosen a potential model based on the Lennard-Jones/spline (LJ/s) [19]

$$U_{ij}(r,s) = \begin{cases} 4\epsilon_{ij}\left[\left(\frac{\sigma_f}{r-s}\right)^{12} - \left(\frac{\sigma_f}{r-s}\right)^{6}\right], & \text{if } 0 < r - s < r_{s,ij}\,, \\ a_{ij}(r - s - r_{c,ij})^2 + b_{ij}(r - s - r_{c,ij})^3, & \text{if } r_{s,ij} < r - s < r_{c,ij}\,, \\ 0, & \text{if } r_{c,ij} < r - s\,. \end{cases} \tag{2}$$

Here r is the distance between particles, σ_f the diameter of the species (hereafter referred to as the fluid) which forms the liquid-vapor interface, ϵ_{ij} represents the potential depth for interactions between species i and j, and $s = (\sigma_p - \sigma_f)/2$, where $\sigma_p = 2R$ is the size of the particulate. The remaining variables are given as follows: $r_{s,ij} = (26/7)^{1/6}\sigma_f$, $r_{c,ij} = (67/48)r_{s,ij}$, $a_{ij} = -(24\,192/3211)\,(\epsilon_{ij}/r_{s,ij}^2)$, and $b_{ij} = -(387\,072/61\,009)\,(\epsilon_{ij}/r_{s,ij}^3)$. The potential defined by Eq. (2) has a finite range, thus removing truncation effects on the surface tension [20]. In addition, the range of the interactions between the particulate and the fluid particles is independent of the size of the particulate, even for an infinite radius (i.e., where the particulate represents a planar wall).

The liquid-vapor interface has been simulated at an intermediate temperature, $T^* = k_B T/\epsilon_{ff} = 0.75$ (with respect to the critical temperature T_c of the LJ/s potential, $T_c/T \approx 1.21$), to ensure that the surface tension of the system is large enough. Since the line tension is related to the surface tension [1] this should also ensure a significant line tension. In addition, at this temperature, the vapor density is high enough to allow vapor simulations with a reasonable number of particles N. Molecular dynamics simulations of the liquid-vapor interface were performed in the canonical ensemble [21], with a time step $\delta t^* = 0.005$, and typical samples ranged from $N = 4000$ to $N = 23\,352$ particles filling a volume V. These simulations were conducted in a prismatic simulation box with length in the ratio $\{x, y, z\} = (3, 1, 1)$, where x was the coordinate normal to the interface. The coexistence densities obtained in this way were $\rho^* = N\sigma_f^3/V = 0.675 \pm 0.003$ and 0.046 ± 0.001 for the liquid and vapor, respectively, at a pressure $P^* = 0.026 \pm 0.007$. The surface tension for this state was obtained from the integral over the interface of the difference between the normal and tangential components of the pressure tensor. The result for the surface tension is $\gamma_{lv}^* = \gamma_{lv}\sigma_f^2/\epsilon_{ff} = 0.165 \pm 0.009$. In order to simulate the particulate at the interface a value must be assigned to ϵ_{fp}. It is known that changes in the depth of the potential well can drive a wetting-drying transition [22–24]. Therefore we have computed for a given particulate size the value of ϵ_{fp} which turns out in a partially wet partially dry regime, i.e., a contact angle near 90° (see below for an explanation of the method to compute the contact angle). A value of $\epsilon_{fp}/\epsilon_{ff} = 1.25$ for a particulate with size $\sigma_p = 5.0\sigma_j$ was obtained and was employed in subsequent simulations.

The computation of the line tension [see Eq. (1)] requires the particulate-liquid, γ_{pl}^*, and particulate-vapor, γ_{pv}^*, surface tensions at the saturation conditions. To compute the surface tension we consider the work done on the system to reversibly and isothermally inflate/deflate the spherical particulate by an amount dR. The free energy associated with this process is given by

$$dF = (8\pi R\gamma)dR + (4\pi R^2 P_{\text{out}})dR\,, \tag{3}$$

where P_{out} is the fluid pressure against which the particulate does work. In expression (3) we have considered that the radius of the surface of tension is equal to the radius of the particulate R. Provided the change in free energy referred to above is small ($< k_B T$), it can be calculated in the canonical ensemble as follows [25]:

$$dF \equiv \Delta F = -k_B T \ln\langle \exp(-\beta\Delta U)\rangle_0\,, \tag{4}$$

where $\beta = 1/k_B T$, and $\Delta U = U_1 - U_0$, where U_1 and U_0 are the potential energies of the "perturbed," i.e., $R = R \pm \Delta R$ and "reference" ($\Delta R = 0$), states. The subindex "0" in expression (4) denotes the average is taken over the reference state. Values of ΔR were in the range $\Delta R = 0.0025\sigma_f - 0.025\sigma_f$, and were chosen as a function of the particulate size. The simulations to compute the surface tensions were performed using molecular dynamics in the canonical ensemble of a system composed of the particulate and the fluid at the liquid-vapor coexistence pressure, $P^* = 0.026$. The overall density of the particulate-fluid system was adjusted slightly for each particulate such that the *fluid* densities (obtained from the particulate-fluid radial distribution function at large separations) were close to the fluid coexistence density. This adjustment gave a system pressure equal, within statistical error, to the liquid-vapor coexistence pressure. For the largest particulate studied in this work, $\sigma_p = 10\sigma_f$, we employed around 40 000 particles.

Figure 2 shows the final results for γ_{pl}^* and γ_{pv}^*, represented as the difference $\gamma_{pv}^* - \gamma_{pl}^*$. We remark that these values when extrapolated to a particulate of infinite size, i.e., a wall, are consistent with the surface tensions of a planar fluid-solid interface, which were obtained from the pressure tensor. The condition of partial wetting, $|\gamma_{pv} - \gamma_{pl}| < \gamma_{lv}$, is fulfilled in the entire range of particulate diameters. From our data, Young's equation, $\cos\theta = (\gamma_{pv} - \gamma_{pl})/\gamma_{lv}$, implies that increasing size pushes the particulate farther into the vapor phase. However, we should expect the line tension to play a role in determining the contact angle and the location of any

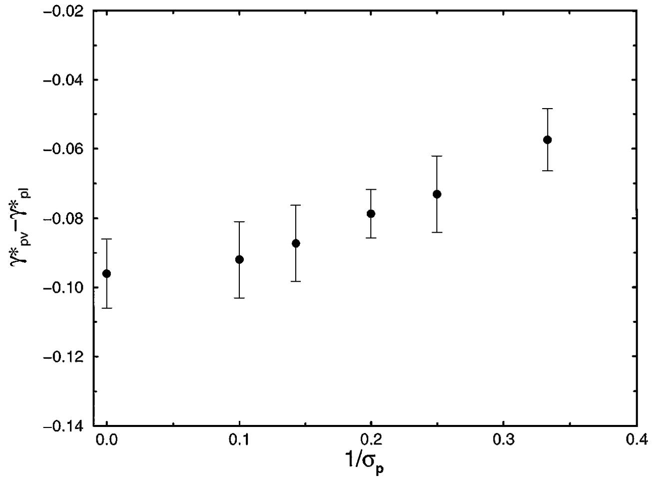

FIG. 2. Dependence of the difference of the surface tensions, $\gamma^*_{pv} - \gamma^*_{pl}$, with the particulate size for $\epsilon_{fp}/\epsilon_{ff} = 1.25$.

wetting transition. We have studied the wetting behavior as a function of the particulate size *directly* by measuring the contact angle in molecular dynamics simulations of the particulate at the interface. The simulations show that the movement of the particulate in the direction normal to the interface is constrained, and it diffuses on a well defined layer parallel to the interface. From the simulated configurations h can be calculated (see Fig. 1). Note that $h = R - d$, where d is the average distance between the particulate and the equimolar dividing surface taken at the liquid-vapor interface. A contact angle follows from $\cos\theta = h/R - 1$. These new values are plotted in Fig. 3. The contact angles obtained in this way are smaller than the values predicted by Young's equation, indicating that the line tension is acting upon the particulate in the sense that it is pushed farther into the liquid. In addition, the simulation results allow us to observe directly the wetting transition (the entry of the particulate into the liquid phase) that appears around $\sigma_p \approx 2.5\sigma_f$.

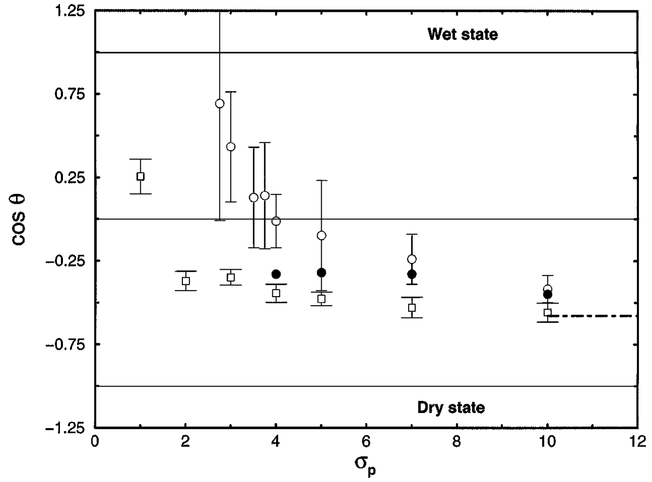

FIG. 3. Variation of the contact angle with particulate size for $\epsilon_{fp}/\epsilon_{ff} = 1.25$. Open circles represent data obtained directly from molecular dynamics simulations. Squares result from Young's equation and full circles data obtained from solution of Eqs. (5) and (6) as described in the text. The dot-dashed line represents the contact angle for the wall-fluid interface.

In order to compute the line tension through Eq. (1) we need the free energy of the particulate at the surface. The absolute value for this quantity is not easy to compute, but the free energy difference between two states can be obtained by resorting to the methodology employed above to get γ_{pl} and γ_{pv}. We consider the expression

$$\begin{aligned} dF = \{&4\pi R[\gamma_{pl}(1+\cos\theta) + \gamma_{pv}(1-\cos\theta) \\ &- 0.5\gamma_{lv}\sin^2\theta] + (2\pi\tau\sin\theta)\}dR \\ &+ (4\pi R^2 P_{\text{out}})\,dR\,, \end{aligned} \qquad (5)$$

where the first term in curly brackets is the force due to the surface tension and line tension against which the particulate does work. Again P_{out} is the external pressure due to the fluid, i.e., the saturation pressure. $dF \equiv \Delta F$ was computed using the perturbation method described above. The ΔR values employed in this case were in the range $0.005-0.025\sigma_f$. In Table I we report results for the line tension as a function of the particulate size. The negative values obtained are in agreement with the smaller contact angles measured in the simulation as compared with the Young's equation results.

The procedure outlined above allows an estimate of the line tension, but it requires as input the contact angles which have large uncertainties as compared with the other variables present in expression (1). However, noting that the equilibrium value for the contact angle θ is that which minimizes the free energy, and assuming that γ and τ do not depend on the contact angle, we get the additional expression

$$\gamma_{pv} - \gamma_{pl} - \gamma_{lv}\cos\theta + \frac{\tau\cos\theta}{R\sin\theta} = 0\,, \qquad (6)$$

which represents a correction to Young's equation. Then from (5) and (6) both the line tension and the contact angle can be estimated. The results for the line tension and contact angles obtained in this way agree down to $\sigma_p = 5\sigma_f$ with those reported above (see Table I and Fig. 3). The small differences between this new

TABLE I. Results for the line tension, $\tau^* = \tau\sigma_f/\epsilon_{ff}$, and contact angle as a function of particulate size. $\epsilon_{fp}/\epsilon_{ff} = 1.25$.

σ_p/σ_f	$\tau^{*\,a}$	$\cos\theta^{\,b}$	$\tau^{*\,c}$	$\cos\theta^{\,c}$
4.0	−0.2	−0.01 ± 0.16	−0.1	−0.33
5.0	−0.2	−0.10 ± 0.33	−0.2	−0.32
7.0	−0.4	−0.24 ± 0.15	−0.3	−0.33
10.0	−0.2	−0.42 ± 0.08	−0.2	−0.45

[a] From Eq. (5).
[b] Direct measurement from molecular dynamics simulations.
[c] From Eqs. (5) and (6).

computation and the direct observation of contact angles indicate that Eq. (6) is accurate for the larger systems considered in this work. As a whole we can conclude from our data that the line tension is not a function of particulate size.

It remains to compare our results for the magnitude of the line tension with experimental data. Taking the values $\sigma_f = 3.4$ Å and $\epsilon_{ff}/k_B = 166$ K [26] as representative of argon, we obtain a line tension of $\approx 10^{-12}$ N, as compared with experimental data for particulates of nanometer size $\approx 10^{-11}$ N [27], or theoretical estimates of the line tension $|\tau| \approx 10^{-10}$ N [1]. Nevertheless, an exact comparison with experiment is not straightforward, given that the line tension is expected to show a dependence on the surface tension of the liquid-vapor interface, which in our case is small $\gamma \approx 0.003$ N/m as compared with the values observed in air/water interfaces $\gamma = 0.072$ N/m [11].

There are several questions which deserve further study, such as the influence of the range and strength of the potential on the wetting transition and the contact angle and their relationship to experimental systems. Of particular interest is the importance of specific surface interactions and of internal structure for the wetting properties of colloidal particles. These questions will be addressed in forthcoming publications.

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