Wetting State of a Crystal-Fluid System of Hard Spheres

David J. Courtemanche and Frank van Swol
Department of Chemical Engineering, University of Illinois, Urbana, Illinois 61801

(Received 27 April 1992)

We report on a molecular-dynamics study of the wetting state of a system of hard spheres near a planar hard wall. A direct simulation at the melting point of a two-phase system between two walls develops all the way from complete wetting by fluid via a partial wetting state to a final arrangement of complete wetting by crystal. This implies that a hard-sphere fluid closely approaching coexistence from below should spontaneously crystallize at a smooth hard wall, contrary to existing beliefs.

PACS numbers: 61.20.Ja, 64.70.Dv, 68.10.Cr, 68.45.Gd

The last decade has seen a large increase in activity in the traditional areas of wetting, adhesion, and heterogeneous nucleation. To a large extent the renewed efforts were stimulated by the work of Cahn [1], who first argued the existence of a wetting transition in fluid-fluid systems on the basis of an elegant scaling argument. Researchers have focused on the order of the wetting transition, looked for prewetting lines, and investigated the role of the interaction ranges and the role of fluctuations. A comprehensive review has been published by Dietrich [2]. Much of the focus has been on fluid-fluid systems near substrates or in contact with a noncritical spectator phase. Wetting studies involving the crystal phase are much smaller in number [2]. Of these most have focused on surface melting of single crystals and on adsorbed crystalline layers which constitutes an example of the approach of complete wetting along the sublimation curve. However, a few experimental studies have addressed wetting of He phases near the melting line [2], the topic of this Letter. Extending recent advances in describing fluid-fluid wetting phenomena (which have primarily been made with the use of density functional theory) is hindered by the difficulty of describing the symmetry and rapid spatial variations of density for the crystal and the crystal-fluid interface. Similarly, simulation of liquid-crystal coexistence is found to be more challenging than fluid-fluid coexistence. In this Letter we will present what we believe to be the first thorough simulation of wetting at coexistence by crystal on a substrate. We find that even a perfectly smooth wall can be wetted by crystal. This implies the existence of spontaneous heterogeneous nucleation when saturation is approached from below, a phenomenon which is often referred to as prefreezing. Prefreezing is sometimes observed when dense colloidal suspensions nucleate near smooth container walls. Our simulations closely mimic this case because the length scales of roughness on the container walls is such that the walls appear smooth to the large colloidal particles. Our results appear to be contrary to all previous speculations based on earlier simulation attempts [3-5]. We shall discuss these contradictions below.

The molecular-dynamics (MD) simulations [6] were performed on a system of $N=2100$ hard spheres. The initial calculations were started from a perfect fcc crystal configuration with the (111) planes in the x-y plane. By partially stretching the crystal we induced melting in part of the system producing a final box of dimensions $L_x=5.537818\sigma$, $L_y=9.591777\sigma$, and $L_z=40.234751\sigma$ (where σ is the hard-sphere diameter) and hence an overall density of $\rho\sigma^3=0.98261$, within the coexistence region. Two-phase simulations involving nonisotropic phases such as crystals are substantially more complicated than fluid-fluid simulations in that the in-plane dimensions (x and y in our case) combined with periodic boundary conditions (PBC) imply a unique density of the unstrained crystal. In other words, unlike the fluid phase the crystal phase can only adjust its coexistence density by changing the interlayer spacing in the direction perpendicular to the interface. This typically leads to a nonzero stress and strain in the solid phase. Thus the two-phase simulations really require very accurate *a priori* knowledge of the crystal density at coexistence. For the hard-sphere system we are in the fortunate position that this value is known more accurately than for any other system. The bulk phase diagram is shown in Fig. 1. Our initial guess for the solid density is that of Hoover and Ree [7], $\rho_s\sigma^3=1.0409$. This density is consistent with the fcc solid free energy calculated by Frenkel and

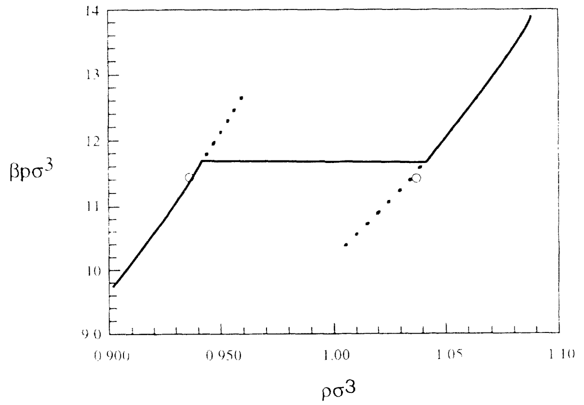

FIG. 1. Bulk phase diagram for hard spheres. The solid line indicates the equation of state. The broken lines indicate the metastable crystal and fluid states. The circles indicate the densities and pressures used in this study.

Ladd [8]. The above choice led to a coexistence pressure $\beta p_N\sigma^3=11.4$ (where β is the inverse of Boltzmann's constant times absolute temperature); see Fig. 2. We note that 11.4 is below the pressure of the bulk solid which is 11.7. This indicates that our crystal must be slightly expanded, and that our guess of $\rho\sigma^3=1.0409$ is slightly too high [9]. Therefore, the results presented here refer to a system that has, by our choice of L_x and L_y, been constrained to produce coexistence between isotropic fluid and a slightly strained crystal. Although one would prefer that the pressure difference between the two-phase and single-phase simulations be within the accuracy to which the pressure can be measured [9], we stress that for studying the wetting state it is only necessary that we preserve self-consistency. In particular, the coexistence properties for this system are those determined by the direct simulation and are not those determined from the equations of state describing fluid and zero-strain crystal. This is particularly relevant when assessing the degree of undersaturation that would characterize prewetting or prefreezing (see below).

The bulk two-phase system was allowed to equilibrate for 29×10^6 collisions. This proved to be a long enough simulation to observe equilibrium fluctuations in the number of crystal layers. The normal pressure, $\beta p_N\sigma^3$, of the system demonstrated a marked correlation with these events. When the number of crystal layers decreased (melting event), the pressure rose. A freezing event led to a drop in pressure. We will concentrate on describing the key results of our simulations, namely, the spontaneous development of a state of complete wetting by crystal. Sikkenk *et al.* [10] have shown that it follows from comparing the total surface free energies that in the *NVT* ensemble complete wetting implies a symmetric density profile with the crystal phase covering both walls and the fluid phase occupying the center of the box. Complete wetting by fluid leads to the inverse profile with crystal occupying the center region. Partial wetting means an asymmetric profile; fluid will occupy one half of the box and crystal the other half and only one crystal-fluid interface will be present. In particular, let γ_1 denote the total surface free energy of the system that shows complete wetting by crystal. Similarly, let γ_2 and γ_3 denote the total surface free energy for partial and complete wetting by fluid systems, respectively. Further, let γ_{WF} denote the surface free energy of a wall-fluid interface, γ_{WC} that of a wall-crystal interface, and γ_{CF} that of a crystal-fluid interface. We have $\gamma_1=2\gamma_{WC}+2\gamma_{CF}$, $\gamma_2=\gamma_{WC}+\gamma_{CF}+\gamma_{WF}$, and $\gamma_3=2\gamma_{WF}+2\gamma_{CF}$. The equilibrium state corresponds to the state of lowest surface free energy. Stability of partial wetting versus complete wetting by crystal follows from comparing γ_1 and γ_2. Partial wetting requires $\gamma_2<\gamma_1$. This corresponds to $\gamma_{WC}+\gamma_{CF}+\gamma_{WF}<2\gamma_{WC}+2\gamma_{CF}$ or $\cos(\theta)=(\gamma_{WF}-\gamma_{WC})/\gamma_{CF}<1$, in accordance with the standard thermodynamic definition of the contact angle [10]. One might have expected to see partial wetting manifested as truncated crystals which leave each wall in contact with both crystal and fluid phases just as in a physical experiment. However, in a simulation that employs two identical walls and PBC in the transverse directions a lower free energy will result if one wall is covered by crystal and the other by fluid, producing an asymmetric profile. The origin of the asymmetry lies in the fact that three-phase contact regions are then avoided. This eliminates positive contributions to the free energy that originate from line tensions and curvature.

Starting with an equilibrated two-phase configuration we replaced the PBC condition in the z direction by a pair of hard walls in the fluid region. Thus, after an initial equilibration to adjust to the local perturbations of the inserted walls we have an initial arrangement of complete wetting by fluid. This state is shown in Figs. 3(a) and 3(b) where we depict an instantaneous configuration.

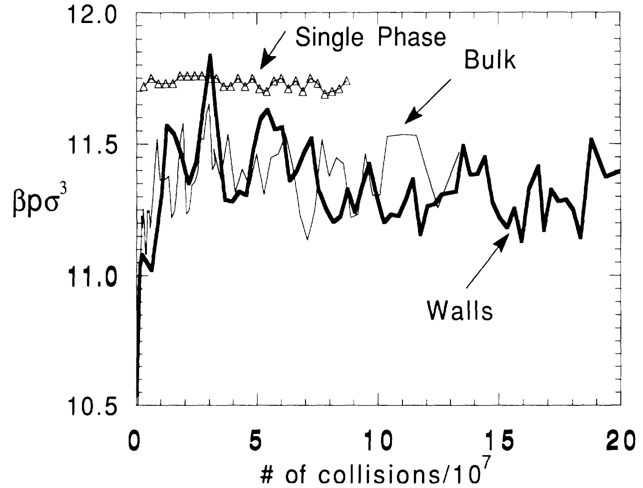

FIG. 2. Normal component of the pressure tensor vs time.

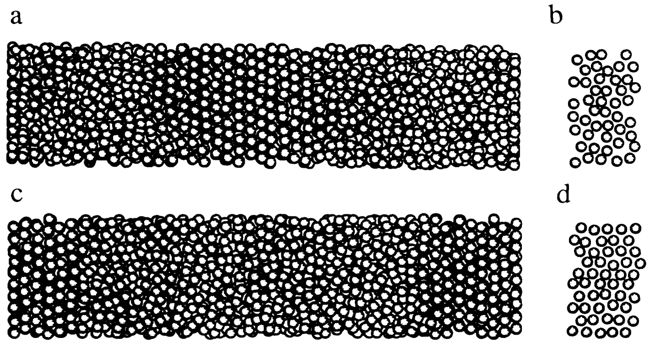

FIG. 3. (a) System in a typical state of complete wetting by fluid. (b) End view of wall layer for wetting by fluid. (c) System in its final state of complete wetting by crystal. (d) End view of wall layer for complete wetting by crystal. The initial state of this simulation is that indicated by (a) and (b). The final, equilibrium state is that shown by (c) and (d).

Figure 3(b) shows the arrangement of the layer closest to the right-hand side wall. The simulation was then continued for a total of 10^8 collisions or a total time of $5000(m\sigma^2/kT)^{1/2}$. This corresponds to approximately 4.4×10^{-9} s for a simple fluid such as argon. As the simulation proceeded we witnessed the expected fluctuations in the density profile that corresponded to layers melting and freezing at the crystal-fluid interface. The refreezing would occur on either side of the crystal and hence the center-of-mass crystal phase wandered.

After a substantial time had elapsed ($\cong 4\times 10^7$ collisions) the system displayed a very large increase in the normal pressure due to a number of layers melting (see Fig. 2). This increase in pressure reflects the free-energy barrier that separates the wetting states. The system subsequently recrystallized at the left-hand wall. Initially two perfect hexagonally packed layers were formed while the p_N dropped dramatically.

The number of layers then quickly grew to about 5. At this stage the center-region crystal fully disintegrated, leaving a partial wetting state with crystal on the left and fluid on the right-hand side of the box (see Fig. 4). During the continuation of the simulation we again observed normal pressure fluctuations that closely correlated with the melting and freezing of crystal layers at the crystal-fluid interface. Eventually, after approximately 7×10^7 collisions we witnessed a second transition now at the right-hand side wall where the fluid suddenly crystallized, forming about 2 layers. The number of layers on the left-hand wall continued to fluctuate. The layers would then reform at either wall. Eventually an equilibrium was reached where each wall had approximately 5 layers. The final configuration is shown in Figs. 3(c) and 3(d).

This final configuration implies that complete wetting by crystal corresponds to an absolute minimum in the surface free energy and we conclude that $\gamma_{WF} = \gamma_{WC} + \gamma_{CF}$, or equivalently $\cos(\theta) = 1$. As mentioned in the introduction, Cahn [1] has shown that complete wetting will lead to spontaneous nucleation of the new phase (crystal in the present case) precluding the possibility of supersaturation. Just below saturation one expects to see a thin layer of the incipient phase the thickness of which will diverge as saturation is approached more closely. The latter path of approach may or may not cross a prewetting line or, more appropriately for a hard-sphere system, a prewetting point. Our system shows at least five layers on either wall. Hence we do not expect to be able to measure the deviation in chemical potential, or equivalently in pressure or bulk liquid density, from the saturation point [11]; see Fig. 2. However, we have performed some simulations with fluctuating walls to control the pressure [12]. Our preliminary results indicate that the number of crystal layers is reduced to 3–4 by lowering the pressure to $\beta p_N \sigma^3 = 11.3$. Lowering the pressure to $\beta p_N \sigma^3 = 11.2$ caused all the layers to melt. We conclude that we can also observe states below the saturation pressure that are consistent with prefreezing.

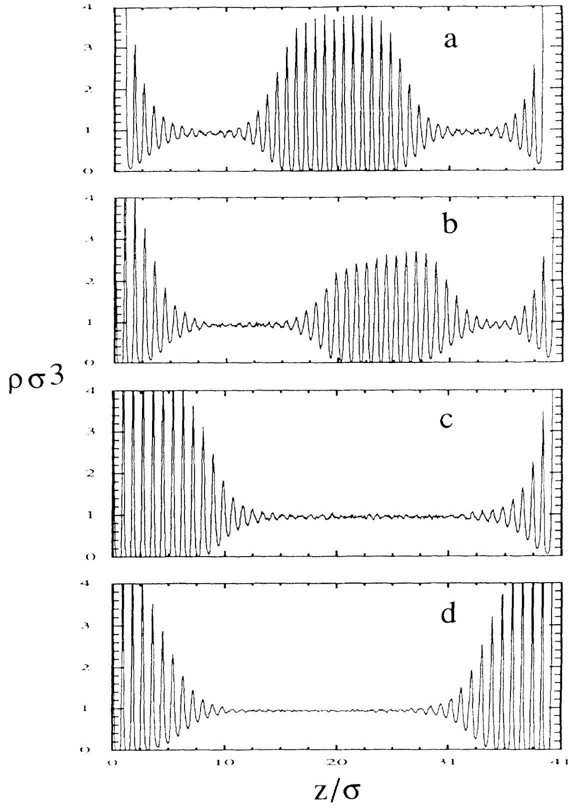

FIG. 4. Density profiles of system. (a) 23×10^6 collisions; the system is still in its initial state of complete wetting by fluid. (b) 38×10^6 collisions; at this point a portion of the crystal has melted and reformed at the left wall. (c) 53×10^6 collisions; the crystal in the center region has totally melted and the system is in a state of partial wetting; i.e., the left wall is wet by crystal while the right is wet by fluid. (d) 206×10^6 collisions; the final equilibrium state of complete wetting by crystal.

Previous work by Cape [4] and Toxvaerd [3] would appear to indicate that spontaneous nucleation does *not* occur for soft spheres at a smooth wall or even for Lennard-Jones fluid at a commensurately structured wall. However, both of these studies were flawed in that neither of them was at or close to coexistence. Cape's *NVT* system of soft spheres started off at the coexistence density for the fluid phase but, due to the large adsorption and the limited number of particles, moved away from coexistence upon introduction of the walls. Toxvaerd studied the effect of the presence of wall structure on the ordering of the fluid. He determined that its effect did not extend far into the fluid. His system was also too far removed from coexistence and thus he saw no nucleation even in the presence of wall structure that would be quite favorable to heterogeneous nucleation. A common thread among these works is the failure to work at coexistence. Groot, Elwenspoek, and Bennema [5] have argued that the layer adjacent to the wall could be considered a separate, effectively two-dimensional (2D) phase which would freeze at the 2D freezing point. These authors claim the absence of prefreezing based on the behavior of the effective 2D density as a function of bulk 3D density. They showed that in order to reach the 2D freezing density, a bulk density very close to the 3D freezing density is required. Therefore they concluded that homogeneous nucleation preempts the 2D freezing required for heterogeneous nucleation. Our results clearly indicate that the concept of a separate phase at the wall cannot be a useful approach for the prediction of prefreezing. Indeed, when prefreezing is viewed as a wetting phenomenon, it is clear that one needs to be concerned with the entire interfacial region between the bulk fluid and the substrate.

A simulation was also undertaken where the walls were structured as opposed to the smooth wall simulation just described. The structure of the wall was that of a (111) layer of crystal at the coexistence density. The system followed the same path, but at a much faster rate. The first layer of crystal formed after only 3.5×10^6 collisions and the symmetric configuration was reached after only 18.5×10^6 collisions. Future work involves perturbing the structure of the wall to find the necessary structural conditions for partial wetting and complete wetting by fluid.

[1] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[2] S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 1.

[3] S. Toxvaerd, Faraday Symp. Chem. Soc. **16**, 159 (1981).

[4] J. N. Cape, J. Chem. Soc. Faraday Trans. 2 **78**, 317 (1982).

[5] R. D. Groot, M. Elwenspoek, and P. Bennema, J. Cryst. Growth **79**, 817 (1986).

[6] J. R. Henderson and F. van Swol, Mol. Phys. **51**, 991 (1984).

[7] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).

[8] D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3118 (1984).

[9] Preliminary comparisons of simulations of two-phase systems with single-phase simulations at the same crystal density indicate that $\rho_s\sigma^3=1.035\pm0.002$ will lead to a strain-free crystal coexisting with fluid at $\beta p_N\sigma^3\sim11.4$.

[10] J. H. Sikkenk *et al.*, Phys. Rev. Lett. **59**, 98 (1987); J. H. Sikkenk *et al.*, J. Stat. Phys. **52**, 23 (1988).

[11] But it may be possible to make such a measurement by carefully reducing the thickness simply through stretching the system in the z direction.

[12] M. Lupkowski and F. van Swol, J. Chem. Phys. **93**, 737 (1990).

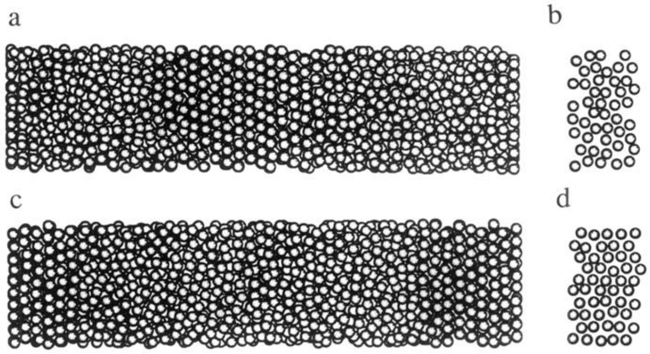

FIG. 3. (a) System in a typical state of complete wetting by fluid. (b) End view of wall layer for wetting by fluid. (c) System in its final state of complete wetting by crystal. (d) End view of wall layer for complete wetting by crystal. The initial state of this simulation is that indicated by (a) and (b). The final, equilibrium state is that shown by (c) and (d).