VOLUME 91, NUMBER 1 PHYSICAL REVIEW LETTERS week ending 4 JULY 2003

Line Tension Controls Wall-Induced Crystal Nucleation in Hard-Sphere Colloids

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(Received 3 March 2003; published 2 July 2003)

We report on a numerical study of the effect of a smooth, hard wall on the crystallization of hard-sphere colloids. We find that the presence of the wall drastically lowers the barrier for crystal nucleation, but it does not eliminate it. Crystal nucleation becomes noticeable at pressures that are some 5% above the coexistence value. The first particles to crystallize on the wall form a (111) plane. Initially, this crystallite grows laterally, rather than in the third dimension. The free energy of the critical crystal nucleus on the wall is about 2 orders of magnitudes lower than in the bulk. Analysis of the numerical data indicates that, at coexistence, the (111) plane is at the threshold of wetting the wall. The nucleation barrier is dominated by line tension.

DOI: 10.1103/PhysRevLett.91.015703 PACS numbers: 64.70.Dv

If ice could only form through homogeneous nucleation, the freezing of water would be a rare phenomenon in countries with moderate climates. This illustrates the fact that external factors, such as the presence of a surface or a seed crystal, are of great practical importance for the rate of crystal nucleation. In this Letter, we present a direct numerical study of the effect of an external surface on the rate of crystal nucleation. The system that we study is a colloidal suspension of monodisperse, hard spheres. This is probably the simplest system that can freeze. At low colloid concentrations, the suspension is in a fluid state, but when the colloids occupy more than 49.4% of the total volume, the solid state becomes more stable [1]. For bulk suspensions, the kinetics of this freezing transition have been studied extensively, both experimentally [2–4] and in computer simulations [5,6]. However, much less is known about the effect of the presence of a flat surface on the crystallization kinetics. Depending on the nature of the surface, it may have different effects on the freezing transition. One possibility is that the crystal phase "wets" the surface: in that case, one or more crystalline layers form at the surface, before the bulk freezing transition. Alternatively, the crystal may partially wet the wall, in which case crystal nucleation from a supersaturated solution takes place at the wall, rather than in the bulk. The effect of a surface on crystallization has been studied experimentally in mixtures of binary hard spheres [7,8] and colloid-polymer mixtures [9–11]. In both systems surface crystallization was found to take place before bulk fluid-solid coexistence. In the systems studied in Refs. [7–11], depletion forces favor the accumulation of the larger component on the wall, and this should facilitate surface crystallization [12]. Heni and Löwen [13] performed simulations of hard spheres in contact with a patterned substrate. These simulations indicated that surface freezing already sets in 29% below the coexistence pressure. But for the important case of pure hard-sphere systems confined by flat walls, it is not *a priori* clear if bulk freezing will be preceded by surface crystallization. Yet, we are not aware of any systematic, experimental studies of surface crystallization in pure hard-sphere systems. Courtemanche and van Swol [14] reported a numerical study of a (rather small) one-component hard-sphere system, confined between two plane hard walls. These simulations suggested that surface crystallization occurred at a pressure some 3% below the coexistence value.

In this Letter we investigate how the pathway for hard-sphere crystallization is influenced by the presence of a smooth wall. In our simulations, we study a system of colloidal hard spheres between two planar hard walls. The distance between the walls was chosen sufficiently large to avoid direct interaction between the ordering at either wall. Before we present the simulation results, we briefly discuss the effect of a wall on crystal nucleation in the context of classical nucleation theory (CNT). In CNT, the free energy of a crystal nucleus that forms in the supersaturated liquid is described by two competing terms. The first is a bulk term, $n\Delta\mu$, that describes the gain in free energy if n particles transform from the liquid to the solid state. Here $\Delta\mu = \mu_s - \mu_l$ is the difference in chemical potential between the two phases. This term is opposed by the free energy needed to create a liquid/solid interface $A\gamma$, where A is the surface area and γ the liquid/solid interfacial free-energy density. Turnbull [15] extended CNT to the case of heterogeneous nucleation of a crystal that forms on a plane substrate. The difference with the homogeneous case is that there are now two interfaces present. The Gibbs free energy of a crystal containing n particles is given by

$$\Delta G(n) = n\Delta\mu + A_{ws}(\gamma_{ws} - \gamma_{wl}) + A_{ls}\gamma_{ls}, \qquad (1)$$

where the subscripts w, l, s refer, respectively, to the wall, the liquid, and the solid. Note that in this formulation the contribution to $\Delta G(n)$ due to the line tension is neglected. More seriously, the dependence of the interfacial free energy on the surface orientation is ignored. With those assumptions, the shape that minimizes $\Delta G(n)$ at fixed n, is a sphere sector, with a contact angle θ of the two phases with the wall given by $\cos(\theta) = (\gamma_{wl} - \gamma_{ws})/\gamma_{ls}$. The

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resulting height of the nucleation barrier is

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma_{ls}^3 f(\theta)}{(\rho_s \Delta\mu)^2}, \tag{2}$$

where ρ_s is the number density of the bulk solid and the factor $f(\theta) = [2 + \cos(\theta)][1 - \cos(\theta)]^2/4$. The only difference with the expression for the homogeneous case is the factor $f(\theta)$. Depending on the values for the interfacial free-energy densities, we distinguish three different cases. The first case corresponds to the situation where $\gamma_{ws} > \gamma_{wl} + \gamma_{sl}$. Under these conditions the crystal will not form on the substrate, because this would increase its free energy, and nucleation will take place in the bulk. A second scenario applies when $-\gamma_{ls} < \gamma_{wl} - \gamma_{ws} < \gamma_{ls}$. Then $-1 < \cos(\theta) < 1$. This means that a crystal can lower its free energy by attaching to the wall (partial wetting). The final case is when $\cos(\theta) = 1 (\theta = 0°)$ or $\gamma_{wl} > \gamma_{ws} + \gamma_{ls}$. In that case, the solid phase prefers to form a thin layer on the wall (complete wetting) and the barrier to nucleation disappears.

For the hard-sphere system, we can speculate what scenario should apply, as all relevant surface free energies have been estimated numerically [16,17], at least at coexistence. The estimated value for the wall/liquid interfacial free-energy density at the freezing volume fraction $\eta = 0.494$ is $\gamma_{wl} = 1.99 k_B T/\sigma^2$ [16], where σ is the hard-sphere diameter and $k_B T$ the thermal energy. The values for the wall/solid interfacial free energies for different orientations (111), (110), and (100) are estimated to be $\gamma_{ws} = 1.42, 3.08, 2.01 k_B T/\sigma^2$ [16]. The values for the liquid/solid interfacial free energy for the same three orientations are $\gamma_{ls} = 0.58, 0.64, 0.62 k_B T/\sigma^2$ [17]. These numbers suggest that the (110) plane will not attach to the wall as $\gamma_{wl} + \gamma_{ls} < \gamma_{ws}$. In contrast, the (100) plane is expected to partially wet the wall. For the (111) plane, the difference between $\gamma_{ls} + \gamma_{ws}$ and γ_{wl} is estimated to be 0.01 ± 0.18, which is not significantly different from zero. Hence, the (111) plane is expected to be at, or very close to, complete wetting.

To explore the pathway for wall-induced crystallization, we performed Monte Carlo simulations in the constant normal-pressure ($NP_\perp T$) ensemble. Here N refers to the number of hard spheres in the system. The simulation box was rectangular with periodic boundary conditions in the x and y directions. In the z direction, the system is confined by two flat, hard walls at a distance L_z. $P_\perp$ is the component of the pressure tensor perpendicular to the plane wall, and T is the temperature. As our unit of length we used the hard-sphere diameter σ. T only sets the energy scale. In the following we always use reduced units. The state of the bulk hard-sphere system is completely specified by its volume fraction η. The coexistence volume fractions for the bulk fluid and solid phase are known [1]: $\eta_f = 0.494$ and $\eta_m = 0.545$. The corresponding coexistence pressure is $P_c = 11.57$. To suppress finite-size effects, we simulated a system containing $N = 13\,824$ particles. The wall area was fixed at $L_x L_y = 600.25\sigma^2$; the distance between the two walls in the z direction fluctuated but was close to 24σ, which is much larger than any correlation length in the fluid. During the simulations, we performed on average one volume move per two cycles (trial moves per particle).

The simplest way to detect if a crystal phase wets the surface is to measure the density profile of the particles between the two walls. In Fig. 1(a) we show the observed density profile at the end of a simulation performed at a pressure just above bulk freezing (excess pressure $\Delta P \equiv P_\perp - P_c = 0.53$). If crystallization at the wall had taken place, this would cause a pronounced dip between the first and the second peak in Fig. 1(a). No such behavior was observed, even at pressures well above P_c.

The situation changes when the excess pressure is increased to $\Delta P = 0.63$. The liquid starts to crystallize, as can be seen from the density profile shown in Fig. 1(b). These results indicate that supersaturation is needed to induce crystallization. Yet, the degree of supersaturation needed to induce nucleation is very small compared to that typical for bulk systems. In fact, in simulations of homogeneous systems of comparable size, the rate of crystal nucleation during a simulation of similar length is negligible up to excess pressures that are an order of magnitude larger [$\Delta P \approx 5.4$ ($\eta \approx 0.53$)]. In order to identify the early stages of crystal nucleation, we used a local bond-order analysis [5] to distinguish between particles with a liquidlike and a solidlike local environment. The result of this analysis is shown in Fig. 2, which shows a snapshot of the particles closest to the wall at $\Delta P = 0.53$. The dark particles have a liquidlike environment and the light particles have a solidlike environment. Only a few small crystalline clusters can be identified. These

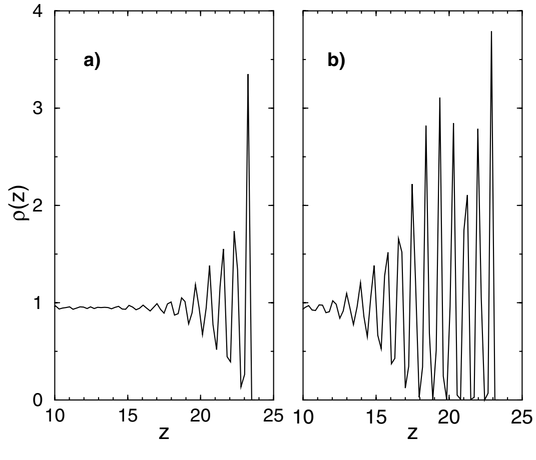

FIG. 1. (a) Density profile along the z direction for a hard-sphere system between the two plane walls at an excess pressure $\Delta P = 0.53$. The corresponding bulk volume fraction is $\eta = 0.4966$. Simulation length: 2×10^6 cycles. (b) As in (a) but at an excess pressure $\Delta P = 0.63$.

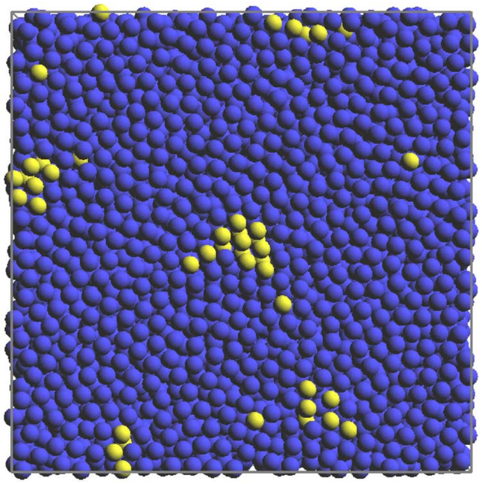

FIG. 2 (color online). Snapshot of a configuration which shows the particles at the wall. A local bond-order analysis was used to distinguish between particles with a liquidlike (dark particles) and a solidlike (light particles) environment. The snapshot is taken from a simulation at pressure $P_\perp = 12.1$.

clusters form and break up spontaneously. Under the same conditions, not a single solidlike cluster formed in the bulk of the fluid. A more quantitative measure of the effect of the surface on crystal nucleation, can be obtained from a direct calculation of the crystal-nucleation barrier. The (Gibbs) free energy of a nucleus of size n is related to $P(n)$, the probability of observing such a nucleus during a spontaneous fluctuation [18]

$$\Delta G(n) = \text{const} - \ln[P(n)].$$

The frequency with which large clusters form spontaneously is very low. We therefore used umbrella sampling [19] to compute $P(n)$. The total simulation was split into a number of smaller simulations, where each simulation was restricted to sample only a narrow range of cluster sizes (see, for instance, Ref. [5]). We used $N = 13\,824$ particles and simulated 2×10^6 cycles for every window. The result for the free-energy barrier calculated at a pressure $P_\perp = 12.1$ is shown in Fig. 3 (dots). At this pressure, the estimated barrier height is $\Delta G^* = 17k_BT$ at a critical cluster size $n_c = 150$. We can compare this estimate with a prediction for the barrier height in a homogeneous system. In an earlier publication we showed that, given the correct value for the interfacial free energy, CNT describes the barrier height quite well [5]. But we also found that the interfacial free energy depends on density. As the present system is close to coexistence we use its average coexistence value $\gamma = 0.61$ [17]. We then obtain $\Delta G^*_{\text{CNT}} = 1334k_BT$ at a critical cluster size of $n_c = 52\,000$. The overall reduction of the nucleation barrier due to the plane wall is about 2 orders of magnitude, resulting in a huge [$\mathcal{O}(10^{570})$] increase in the nucleation rate. The computed nucleation rate per unit area is $\sim 10^{-9}$ (in units D_0/σ^4, where D_0 is the self-diffusion coefficient of colloids of diameter σ in a pure solvent). The implication for experiments is clearly that crystallization of suspensions of hard-sphere colloids should proceed heterogeneously, whenever a sufficiently flat surface is available.

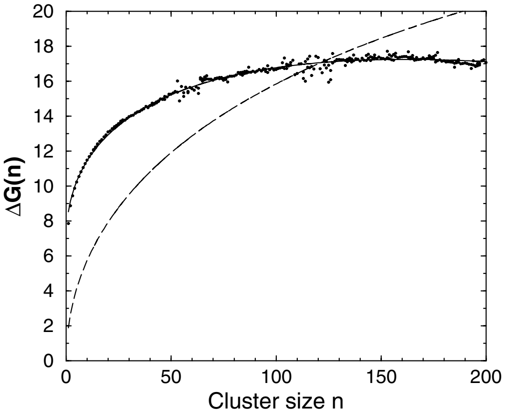

FIG. 3. Calculated nucleation barrier $\Delta G(n)$ of a crystal nucleus formed at the wall as a function of its size n (filled dots). In the figure, we show two fits to the nucleation barrier: the dashed curve assumes the published values for the surface free energies and uses a curvature-independent line tension. To obtain the drawn curve, we used γ_{wl} as a fit parameter and we assumed that the line tension was curvature dependent. If we had used the CNT expression [Eqn. (1)], there would not be a nucleation barrier at this supersaturation.

From the simulations, we can also determine the orientation and shape of the incipient crystal nucleus. Figures 4 and 5 show a snapshot of a critical nucleus containing 150 particles. From the figure, it is clear that the (111) plane attaches to the wall. Note that the critical nucleus is quite flat. Clearly, small nuclei prefer to spread

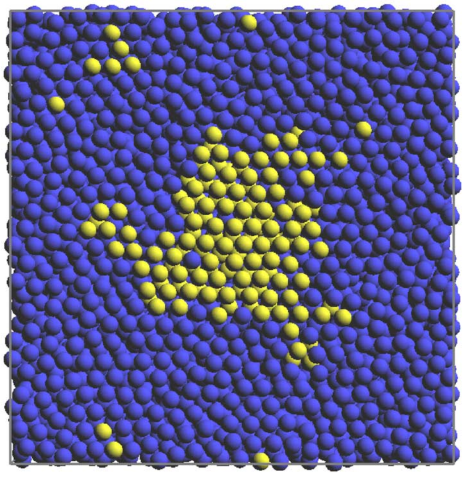

FIG. 4 (color online). Snapshot of a crystal nucleus of size $n = 150$ shown in yellow. In the figure we displayed all solid particles in the system.

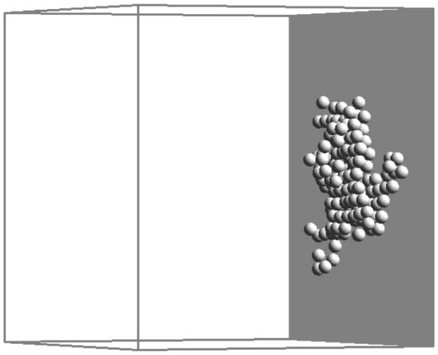

FIG. 5. Side view of the snapshot of a crystal nucleus of size $n = 150$.

on the surface rather to grow into the bulk. This is in agreement with the CNT predictions in the case where the (111) face wets the wall, either completely or very nearly so. We find that the nucleation of this surface crystallite is enough to initiate bulk crystal growth. This, together with the observations of Ref. [13], suggests that there are no appreciable barriers for the nucleation of subsequent layers [20].

When we compare the computed nucleation barrier with the predictions of classical nucleation theory [Eq. (2)], we find that this expression seriously underestimates the height of the nucleation barrier. In fact, CNT would predict that, at an excess pressure $\Delta P = 0.53$ (where $\Delta\mu = -0.05 k_B T$ [21]), the barrier to nucleation is negligible compared to $k_B T$. In order to resolve this discrepancy, we are forced to take into account the line tension, τ_{Line}, of the crystal nuclei on the wall. If we attempt to fit our numerical data to Eq. (1) plus a term due to line tension, we can indeed reproduce a nucleation barrier with the same height as found in the simulations, but the shape of the simulated barrier is reproduced rather poorly (see Fig. 3). A much better fit can be obtained by allowing γ_{wl} to vary within the bounds set by the (large) estimated error in the computed value: $1.99 \pm 0.18 k_B T/\sigma^2$. In addition, it turns out that we have to allow for a curvature correction of the line tension: $\tau_{\text{Line}} = \tau_\infty + c/R$. This fit yields $\tau_\infty = 0.43 k_B T/\sigma$, $c = 1.1 k_B T$, and $\gamma_{wl} = 2.016 k_B T/\sigma^2$. Note that with this value of γ_{wl}, the condition for complete wetting would be satisfied $\gamma_{ws} + \gamma_{sl} - \gamma_{wl} = -0.02 k_B T/\sigma^2$. This would agree with the conclusion of Ref. [14]. However, the statistical inaccuracy in this estimate is appreciable. We can compare our fitted value for τ_∞ with a naive estimate by assuming that the contribution to the free energy due to line tension is really nothing else than the surface free energy of the lateral surface of a cylinder of height 1σ. Assuming that the lateral surface free-energy density is approximately equal to $\gamma_{ls}^{(110)}$, our estimate for τ_∞ would be $\tau_\infty \approx 0.64 k_B T/\sigma$, which is within 50% of the numerical result. An estimate of the curvature correction to τ_{Line} would necessarily be even cruder.

The fact that the range of metastability becomes very narrow might provide a powerful tool for the determination of the freezing density in experiments. Using confocal microscopy, it is straightforward to detect the formation of crystallites on a flat surface. Such crystallites will be first observed under conditions where the bulk density differs less than 1% from its value at coexistence. Our simulations suggest that a stable crystalline layer first forms at the wall at a pressure that is some 2% below the coexistence pressure, but, as explained above, this estimate is subject to a large statistical uncertainty.

This work was supported by the Division of Chemical Sciences (CW) of the Netherlands organization for Scientific Research (NWO). The work of the FOM Institute is part of the research programme of FOM and is made possible by financial support from NWO. We thank Nicolas Combe, Angelo Cacciuto, Marjolein Dijkstra, and Alfons van Blaaderen for helpful suggestions.

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