

Solid–liquid interfacial free energy of small colloidal hard-sphere crystals

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(Received 27 May 2003; accepted 17 July 2003)

Using free-energy calculations on small crystalline clusters, we estimate the free-energy density γ_{SL} for the solid–liquid equimolar interface of a system of hard-sphere colloids. By studying the behavior of a crystallite at coexistence, we determine the dependence of γ_{SL} on the radius of curvature of the interface. An extrapolation to infinite radius of curvature (flat interface), yields $\gamma_{SL}(R \rightarrow \infty) = 0.616(3)$, in good agreement with recent numerical estimates. Subsequently, we consider the dependence of the interfacial free-energy density on the degree of supersaturation. Our simulations suggest that the γ_{SL} associated with the equimolar surface is fairly insensitive to changes in supersaturation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1607307]

Work is needed to create an interface between two distinct phases. The interfacial free-energy density, γ , measures the required amount of reversible work per unit of interfacial area. In the literature, most discussions of γ (for fluid–fluid interfaces: the surface tension) focus on interfaces between thermodynamically stable phases (see, e.g., Ref. 1). Yet, in many cases we need to estimate the free energy of an interface that separates two phases that are not in thermodynamic equilibrium. For example, knowledge of the interfacial free energy is required in classical nucleation theory (CNT) to predict the free energy barrier for the formation of nucleus of a new phase from a metastable parent phase. Here, and in what follows, we consider crystal nucleation, but the analysis for liquid–vapor nucleation, should be similar.

According to CNT, the Gibbs free energy of a nucleus of N solid particles in a homogeneous, supersaturated liquid is

$$\Delta G = \gamma_{SL}A - N|\Delta\mu|, \quad (1)$$

where A is the area dividing solid from liquid and $\Delta\mu = \mu_{sol} - \mu_{liq}$ is the difference in chemical potential between the two phases. If we assume that the crystal nucleus is *spherical* and *incompressible*, we can write

$$N = \frac{4}{3}\pi R^3 \rho_s, \quad (2)$$

where ρ_s is the number density of the bulk solid phase at the coexistence pressure, and R is the radius of the sphere. The CNT approximation for the free energy associated with the formation of a spherical crystal nucleus of radius R then becomes

$$\Delta G(R) = 4\pi R^2 \gamma_{SL} - \frac{4\pi}{3} R^3 \rho_s |\Delta\mu|. \quad (3)$$

We stress that Eq. (3) is an approximation of the more general form for the Gibbs free energy of a spherical crystallite.² Apart from the fact that the crystal nucleus is assumed to be incompressible, the dependence of γ_{SL} on the size of the nucleus and on the degree of supersaturation is often ig-

nored. In fact, it is not easy to disentangle the dependence of γ_{SL} on R and $\Delta\mu$. The reason is that, in experiments, information about the surface free energy of a small nucleus is obtained by fitting measured crystal nucleation rates to the corresponding CNT expression.^{3,4} However, such experiments only yield information about the value of γ_{SL} for one particular crystallite size, namely the critical nucleus. As the supersaturation is varied, the size of the critical nucleus changes. Hence, any variation in the measured value of γ_{SL} may be due either to an intrinsic variation of the surface free energy with supersaturation, or to a variation of γ_{SL} with R , the radius of the nucleus, or both. To complicate things even further, we have to define what we mean by the radius of the crystal nucleus. In what follows, we take R to be equal to R_e , the radius associated with the equimolar dividing surface, i.e., we *define* R through Eq. (2).¹ Of course, the physical properties of the (crystal) nucleus do not depend on our choice of the dividing surface.¹ In fact, it is often more convenient to choose the radius of the droplet to be equal to R_s , the radius of the “surface of tension.” However, in the present case, there is a good reason to prefer R_e over R_s . The equimolar dividing surface is defined such that, by construction, the number of particles adsorbed in the surface is zero (for a one-component system). Therefore,

$$\frac{\partial \gamma}{\partial \mu} = 0. \quad (4)$$

This suggests that, for an incompressible nucleus, the surface free-energy density does not depend on the supersaturation. If this is true, then it should be possible to superimpose the curves of γ_{SL} versus N that are determined at different supersaturations.

In the present paper, we analyze the shape of the free-energy barrier for crystal nucleation of a system of hard colloids at various degrees of supersaturation. We computed $\Delta G(N)$, the Gibbs free energy of a crystal nucleus containing N particles, as a function of N , using the techniques described in Ref. 5. From Eq. (1) it follows that we can define the surface free energy $\Delta\Gamma(N)$ of a cluster of size N as

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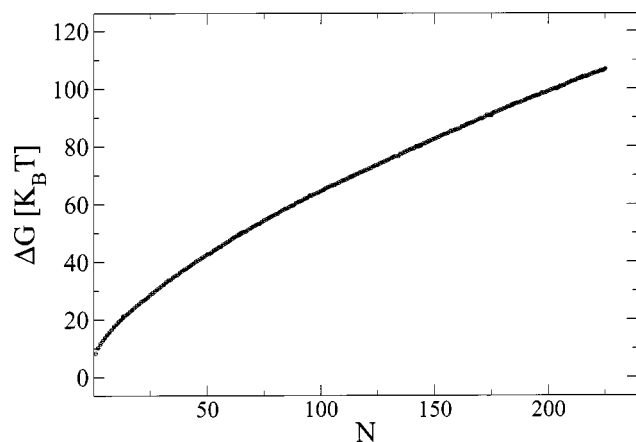


FIG. 1. Crystal nucleation barrier (ΔG) as a function of the number of particles in the nucleus (N) for a hard-sphere colloids at coexistence $P = 11.56[K_B T/\sigma^3]$.

$$\Delta \Gamma \equiv \Delta G - N \Delta \mu. \quad (5)$$

Using Eq. (2), we can then express the interfacial free-energy density γ_{SL} as⁶

$$\gamma_{SL} = \frac{\Delta \Gamma}{(4\pi)^{1/3}} \left(\frac{\rho_s}{3} \right)^{2/3} N^{-2/3}. \quad (6)$$

Before computing the surface free energy of a crystal nucleus in a supersaturated solution, we studied the free energy of a crystallite in a liquid at coexistence. Under those conditions, the free energy is exclusively due to surface terms. We computed ΔG for clusters containing up to $N = 220$ solid particles.

Figures 1 and 2 illustrate the result of these calculations. Specifically, Fig. 1 depicts the nucleation barrier itself, and Fig. 2 shows how γ_{SL} depends on the nucleus size. Curvature corrections can be incorporated into the theory by assuming the functional form

$$\gamma_{SL}(R) = \gamma_\infty + \frac{\gamma_1}{R} + \frac{\gamma_2}{R^2} \quad (7)$$

or equivalently

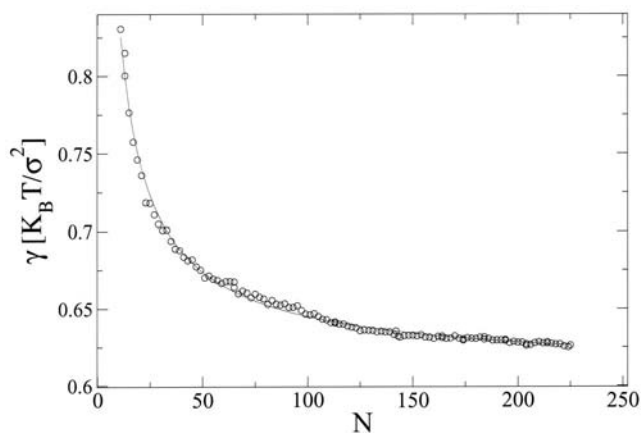


FIG. 2. Interfacial free energy density (γ_{SL}) vs crystal nucleus size (N) as obtained from Eq. (6).

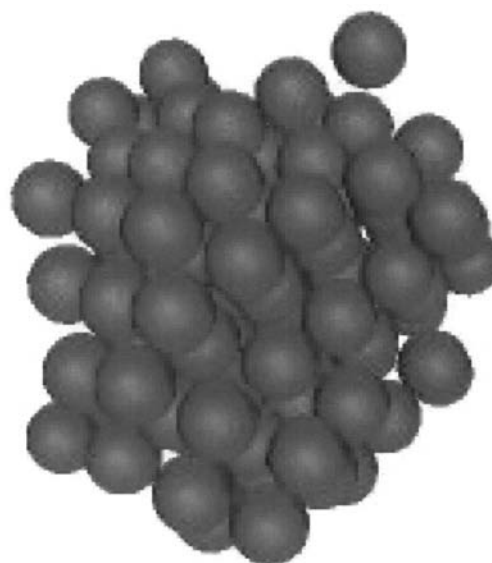


FIG. 3. Snapshot of a typical thermalized crystalline cluster made of ~ 100 solid particles.

$$\gamma_{SL}(N) = \gamma_\infty + \frac{a}{N^{1/3}} + \frac{b}{N^{2/3}}. \quad (8)$$

We stress that small crystalline clusters fluctuate wildly (see, e.g., Fig. 3). But this does not exclude the use of Eq. (8), as long as the average shape of the particle does not depend on its size. In the present simulations, we find that, on average, the crystal nuclei are spherical (a similar structure has also been observed in a Lennard-Jones system⁷). Yet, to give a simple, intuitive interpretation of Eq. (8), it is convenient to consider a faceted crystallite. In that case, the $1/R$ term in the surface free-energy density is associated with the presence of edges between different crystal faces. The $1/R^2$ term is associated with the presence of the (fixed number of) vertices where three facets meet. Fluctuations in the cluster shape will lead to quantitative changes in the edge and vertex free energy, but qualitatively, the terms remain similar.

Fitting the numerical data in Fig. 2 with Eq. (8) we obtain $\gamma_\infty = 0.616(3)$, $a = -0.18(3)$ and $b = 1.48(4)$. We note that γ_∞ is in good agreement with recent numerical estimates.⁸ It is interesting to notice that for clusters of a few hundred particles, the $1/R^2$ term is larger than the $1/R$ correction. This indicates that “vertex” effects dominate, at least for small clusters.

Next, we consider the dependence of $\gamma_{SL}(N)$ on supersaturation. In Ref. 5, we reported nucleation barriers for different supersaturations: $\Delta \mu = -0.34$, $\Delta \mu = -0.44$, and $\Delta \mu = -0.54$.

In this case, we should use Eq. (5) to deduce the surface free energy from the computed nucleation barrier. However, this procedure requires some care. The reason is that, in the simulations, we use a geometric criterion (see Refs. 5 and 9) to identify the particles that belong to the crystal nucleus. However, the number of crystalline particles thus determined need not be equal to the number of particles that belong to the cluster in the thermodynamic sense. This is not important

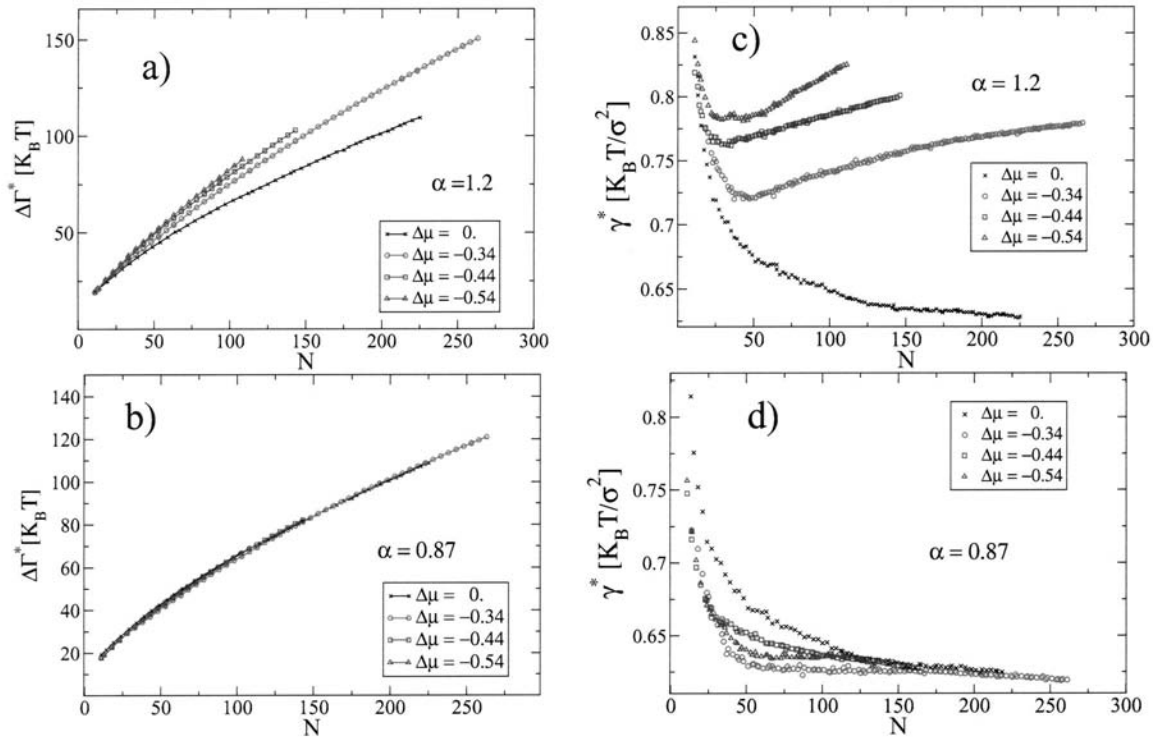


FIG. 4. $\Delta\Gamma^*$ and the relative γ_{SL}^* as a function of nucleus size for two different values of the corrective parameter α .

for the calculation of nucleation rates, as these are independent of the precise definition of crystallinity. It is also not important for the computation of γ_{SL} for the critical nucleus as, in this case, we can express γ_{SL} in terms of the barrier height and the Laplace pressure.¹⁰ However, for arbitrary cluster sizes, the computation of γ_{SL} does depend on the definition of N . In principle, the definition of the “thermodynamic” N is straightforward: it is simply the coefficient of $\Delta\mu$ in Eq. (1). Once this term has been subtracted from $\Delta G(N)$, the remainder can no longer contain terms of order N and the estimated value of $\gamma_{SL}(N)$ should be independent of N for large clusters.¹¹ However, if we assume that the geometric and thermodynamic definitions of N are equivalent, then we find that, for large N , the apparent γ_{SL} depends noticeably on N . In what follows, we make the assumption that the thermodynamic cluster size (N_T) is proportional to the geometrical cluster size (N_g):¹²

$$N_T \approx \alpha N_g, \tag{9}$$

where the constant α is to be adjusted to make $\gamma_{SL}(N_T)$ independent of N_T , for large N_T . Then our expression for the surface free energy becomes

$$\Delta\Gamma^* = \Delta G - N\alpha\Delta\mu. \tag{10}$$

The corresponding interfacial free-energy density is

$$\gamma_{SL}^* = \frac{\Delta\Gamma^*}{4\pi R^2}. \tag{11}$$

Figure 4 shows $\Delta\Gamma^*$ and γ_{SL}^* as a function of the nucleus size at different supersaturations for two different choices of α .

As can be seen from Fig. 4, small variations in α have a pronounced effect on the effective surface free energy. Visual inspection shows that a choice of α near 0.87 effectively eliminates any linear dependence of the surface free energy density γ_{SL}^* on N .

We note that the accuracy of our analysis is limited by the statistical errors in the computed free energy barriers ($\sim 1K_B T$). Moreover, our simulations were limited to relatively small clusters. Hence, we cannot probe the truly asymptotic large- N behavior. Surprisingly, for $\alpha \approx 0.87$ all the corrected surface free energies $\Delta\Gamma^*(N)$ seem to overlap [Fig. 4(b)]. No such collapse is observed if we choose, for instance, $\alpha = 1.2$ [see Fig. 4(a)]. This finding suggests that, at least in the large N limit, the surface free energy hardly depends on the degree of supersaturation. We stress that this result is not *a priori* obvious because we made no assumption about the surface free-energy densities. In fact, even a slight inconsistency in the analysis of the data—for instance, by making the assumption that the solid is incompressible in Eq. (1), but not in Eq. (2)—results in a failure of the $\gamma_{SL}^*(N)$ curves to collapse.

To extract some more information on the asymptotic regime, we plotted $\gamma_{SL}^*(N)$ as a function of $N^{-1/3}$ (Fig. 5). If the N dependence of the surface free-energy density is of the form given by Eq. (8), then all curves should be parabolic. Moreover, if γ_{SL} is truly independent of $\Delta\mu$, then the curves should collapse onto a single master curve. As can be seen from Fig. 5, the collapse of the $\gamma_{SL}(N)$ curves is far from perfect. To be more precise: the curves do converge in the large N limit, but there the statistical inaccuracy in the barrier calculation makes it difficult to analyze the functional form

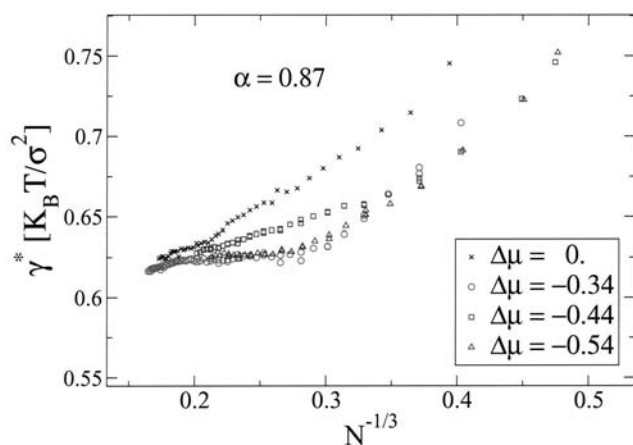


FIG. 5. $\gamma^*_{SL}(N)$ as a function of $N^{-1/3}$.

of $\gamma^*_{SL}(N)$. In contrast, for small N , clear differences between the different curves are observed. But this is in a regime where the clusters are so small (less than 30 particles) that any “thermodynamic” analysis is questionable.

Nevertheless, a general trend can be detected. Note that, at fixed $\Delta\mu$, γ_{SL} decreases with N . The dependence of γ_{SL} on supersaturation, at fixed N , is less clear. For small clusters it appears to decrease with increasing supersaturation. Yet, the simulations of Ref. 5 showed that, for the critical nucleus, γ_{SL} increases with $\Delta\mu$. The present results therefore suggest that this effect is, most likely, dominated by the increase in γ_{SL} with decreasing critical nucleus size, rather than by the intrinsic variation of γ_{SL} with $\Delta\mu$.

To summarize, we have computed the interfacial (solid/liquid) free energy of a system of hard sphere colloids using nucleation barrier calculations and classical nucleation theory. The curvature dependence and the flat interface limit of equilibrium and supersaturated solutions are extracted and

compared. Our estimate of the equilibrium interfacial free energy density is $\gamma_{SL}=0.616(3)$, in good agreement with previous numerical works. We discuss how the simulation data can be used to estimate the “thermodynamic” number of solid particles in the nucleus. Using this procedure, we find that the interfacial free energies $\Delta\Gamma(N)$ of systems at different supersaturations can be made collapse to a unique curve. Our findings suggest that, within the classical nucleation theory framework, for sufficiently large nuclei the interfacial free energy density is independent of supersaturation; however, more accurate barrier calculations and larger nuclei must be considered in order to have a more complete understanding of this last point.

D.F. thanks B. Widom for very helpful comments and suggestions. The work of the FOM Institute is part of the research program of FOM and is made possible by financial support from the Netherlands Organization for Scientific Research (NWO).

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¹⁰In this case, we do not determine the surface tension of the equimolar surface, but the one associated with the surface of tension.

¹¹Provided that the aspect ratio of the clusters does not depend on N .

¹²We also tried a different functional form for N_T , namely $N_T=N_g + \alpha N_g^{2/3}$, but obtained qualitatively the same results.