Irreducible Finite-Size Effects in the Surface Free Energy of NaCl Crystals from Crystal-Nucleation Data

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In this Letter we report a simulation study in which we compare the solid-liquid interfacial free energy of NaCl at coexistence, γ_{LS}, with the value that follows from the height of the homogeneous nucleation barrier. The two estimates differ by more than 100%. Smaller discrepancies are found for γ_{LS} of hard-sphere and of Lennard-Jones particles. We consider a variety of possible causes for this discrepancy and conclude that it is due to a finite-size effect that cannot be corrected for by any simple thermodynamic procedure. By taking into account the finite-size effects of γ_{LS} obtained in real nucleation experiments, we obtain quantitative agreement between γ_{LS} estimated in the simulations and derived from the experiments. Our finding suggests that most published solid-liquid surface free energies derived from nucleation experiments will have to be revised.

The study of homogeneous crystal nucleation is of interest because it provides information about the pathway by which crystalline order emerges from the disordered parent phase. However, such experiments are also of considerable practical importance, as they are used to estimate the magnitude of the solid-liquid interfacial free energy. Classical nucleation theory (CNT), see, e.g., [1], provides the route by which experimental nucleation rates are related to surface free energies. CNT relates the number of crystal nuclei that form per second per cubic meter (denoted by R) to ΔG_{crit}, the height of the free-energy barrier that has to be crossed to nucleate a crystal: $R = \kappa e^{-\Delta G_{\text{crit}}/k_B T}$. Here κ is a kinetic prefactor, T is the absolute temperature, and k_B is Boltzmann's constant. CNT predicts the following expression for the height of the nucleation barrier: $\Delta G_{\text{crit}} = c\frac{\gamma_{LS}^3}{\rho_S^2|\Delta\mu|^2}$, where γ_{LS} is the liquid-solid surface free energy per unit area, $\Delta\mu$ is the difference in chemical potential between the solid and the supercooled liquid, and ρ_S is the number density of the crystalline phase. c is a constant that depends on the shape of the cluster, e.g., $c = 16\pi/3$ for a spherical crystal nucleus. As the nucleation rate depends exponentially on ΔG_{crit}, the rate is a very sensitive function of the surface free-energy density γ_{LS}. A crucial assumption underlying CNT is that the bulk and surface properties of a small crystal nucleus are the same as those of a macroscopic crystal. However, it has been long realized that this assumption is questionable, as a critical crystal nucleus often contains only a few hundred molecules. Indeed, in his review on crystal nucleation, Kelton writes, "While the precise meaning of [γ_{LS}] is uncertain, it constitutes a parameter that can be

determined for each element and profitably used to make predictions of the nucleation behavior." In other words, the γ_{LS} determined from nucleation experiments can be used only to predict the outcome of other nucleation experiments, thus severely limiting the predictive value of CNT. More microscopic theories such as density-functional theory (DFT) [2,3], the Cahn-Hilliard approach (CH) [4], or the phase-field formalism (PF) [5] can and have been used to improve upon CNT. Yet, the question remains whether the widely used CNT can be reformulated in such a way that it correctly describes the properties of small clusters while at the same time reproducing the correct, macroscopic surface free energy.

Increasingly accurate simulation techniques allow us to probe both the free energy of small nuclei and the surface free energies of planar crystal-liquid interfaces. A case in point is the system NaCl in contact with its melt. Reference [6] reported the surface free energy of a NaCl [100] interface in contact with the coexisting liquid phase: $\gamma_{LS} \approx 36 \pm 6 \text{ mJ m}^{-2}$. The effective surface free energy that follows from the NaCl crystal-nucleation barrier at 800 K was reported in Ref. [7]: $\gamma_{LS} = 80 \pm 1 \text{ mJ m}^{-2}$ (assuming that the nucleus has a cubic shape). In addition, nucleation experiments at 905 K [8] provide an experimental estimate of $\gamma_{LS} \approx 68 \text{ mJ m}^{-2}$.

Another example of a large difference between γ_{LS} derived from the nucleation barrier and from coexistence data comes from hard-sphere colloids: a comparison of simulations at coexistence [9] and in the supersaturated regime [10] indicate that the value of γ_{LS} estimated on the basis of the nucleation barrier is some 30% larger than the value for a planar interface at coexistence. A similar dis-

crepancy [$\mathcal{O}(20\%)$] exists between the surface free energy for the planar interface and the crystal nucleus of the [truncated and (force-)shifted] Lennard-Jones potential [11–13]. It is clearly of considerable interest to understand the origin of the discrepancy between the nucleation data and the results for γ_{LS} at coexistence, as this might facilitate the interpretation and analysis of experimental nucleation data.

In this Letter, we report a systematic study of the finite-size effects in the surface free energy of NaCl crystals in contact with their melt. We chose this system because it shows the largest discrepancy of all examples listed above. As in Refs. [6,7,14] we use the Tosi-Fumi rigid-ion-pair interaction potential [15] to model the interionic interactions in NaCl. We note at the outset that it is imprecise to speak of *the* surface free-energy density of a small crystallite, as the value of γ_{LS} depends on the choice of the dividing surface (equimolar dividing surface, equienthalpy dividing surface, surface of tension, etc.—see Ref. [16]). For flat interfaces, the corresponding surface free energies are all the same, but this is not the case for strongly curved surfaces. The surface free energy that enters into CNT is the one associated with the surface of tension [17]. One property of the surface of tension is that it is, to lowest order, independent of the choice of the dividing surface. We use this property to determine γ_{LS} associated with the surface of tension. To facilitate the comparison with the data of Ref. [6] that refer to a flat interface at coexistence, we deduce γ_{LS} from the size dependence of the free energy of a small crystallite at coexistence. At coexistence, there is no difference in chemical potential between the liquid and the bulk solid; hence, the excess free energy of a small crystallite is entirely due to its surface.

All simulations were carried out at the coexistence temperature $T_M = (1060 \pm 10)$ K. T_M is reported in [14,18]. The melting temperature of Tosi-Fumi NaCl is close to the experimental value: $T_M^{exp} = 1074$ K [19]. As a first step, we determine the dependence of the free energy of small NaCl crystallites on the number of ions in the crystal. For this part of the calculation, we make use of umbrella sampling [20] at constant N, P, and T. These simulations yield the excess free energy of the largest crystalline cluster in the system as a function of the number of particles in that cluster. We use a geometrical criterion (see Ref. [7]) to distinguish crystalline from liquidlike particles. We can then deduce the surface free-energy density using

$$\gamma_{LS}(N) = \frac{\Delta G(N)}{C} \rho_s^{2/3} N^{-2/3}, \qquad (1)$$

where N denotes the number of crystalline particles and C is a geometrical constant that has a value of 6 for a cubic nucleus and $(36\pi)^{1/3}$ for a sphere. Although there are strong fluctuations in the shape of a small NaCl crystallite in contact with its melt, its average shape is fairly cubic (see Fig. 1). Of course, we need not assume *a priori* that the

cluster is cubic: we can use the average cluster shape from Fig. 1 to perform a Wulff construction (see, e.g., [21]) that yields the variation of the surface free energy with orientation. Assuming that the surface free energy of the [100] equals the macroscopic value, we can then compute the average γ_{LS} of the cluster. Leaving apart the question whether a Wulff construction is at all meaningful for clusters containing $\mathcal{O}(10^2)$ particles, we note that this procedure yields $\langle\gamma_{LS}\rangle \approx 40$ mJ m^{-2}, which is within 10% of the value expected for a perfect cube. In what follows, we therefore assume that small NaCl crystals have the same cubic morphology as macroscopic crystals. From Fig. 2, we cannot yet deduce the surface free energy because there is no *a priori* reason to assume that the surface of this geometrical cluster has any thermodynamic meaning. We know, however, that in the thermodynamic limit, the ratio of N_g to N, the "thermodynamic" number of atoms in the crystal, should approach 1. We therefore make the ansatz $N = (N_g^{1/3} + a)^3$, where a is an adjustable parameter that remains to be determined. To find the number of atoms within the surface of tension, we choose a value of a that minimizes the variation of γ_{LS} with the size of the cluster. This analysis leads to a value of $a \approx 0$. Figure 3 shows that, over the range of cluster sizes studied, the resulting value of γ_{LS} is indeed almost independent of N for all but the smallest clusters. More interestingly, we find that the resulting value of γ_{LS} is very close to the value $\gamma_{LS} \approx 80$ mJ m^{-2} that follows from the analysis of the nucleation barrier at 800 K [7] (see Fig. 3). Moreover, a similar analysis at 800 K leads to the same estimate of γ_{LS}. The internal consistency between the values of γ_{LS} derived from the nucleation barrier and from the surface of tension would be encouraging were it not for the fact that it does nothing to resolve the discrepancy with the value of
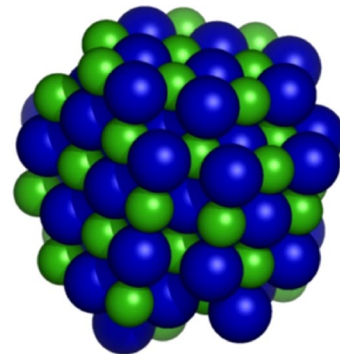

FIG. 1 (color online). Average shape of a NaCl crystallite consisting of 140 solidlike particles. As the shape of such a small cluster fluctuates, we obtain the average shape by superimposing a large number of instantaneous configurations of the same mass, fixing their center of mass, and the orientation of the crystal axes. We average over all 48 symmetry-related orientations. The surface is defined as the set of points where the average density equals the average of the solid and liquid densities. Only the crystalline particles inside this surface are shown.
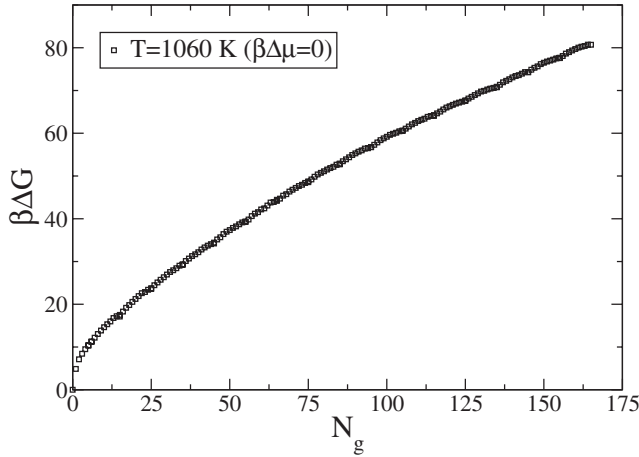
FIG. 2. Free-energy barriers ($\beta\Delta G$) as a function of N_g at coexistence T_M. The error bars in $\beta\Delta G$ are comparable to the size of the symbols.

36 mJ m^{-2} found for a flat interface. Choosing another conventional dividing surface (e.g., the equimolar or the equienthalpy surface) [22] only makes matters worse: in both cases we find a negative value of a that results in an even larger value of γ_{LS} that is, moreover, strongly cluster-size dependent. Hence, we conclude that the discrepancy between the properties of a small crystal and a flat interface cannot be corrected for by choosing a better definition of the location of the solid-liquid interface.

The above discussion suggests that the conventional version of CNT cannot account for the observed discrepancy between the surface free energy of a flat interface and that of a small crystallite. However, even within a thermodynamic approach, one can introduce corrections to classical nucleation theory that would change the apparent value of the surface free energy. One such correction takes into account that the crystal nucleus is compressible and that the surface free energy depends on the density of the crystal. To estimate the magnitude of this effect, we extend
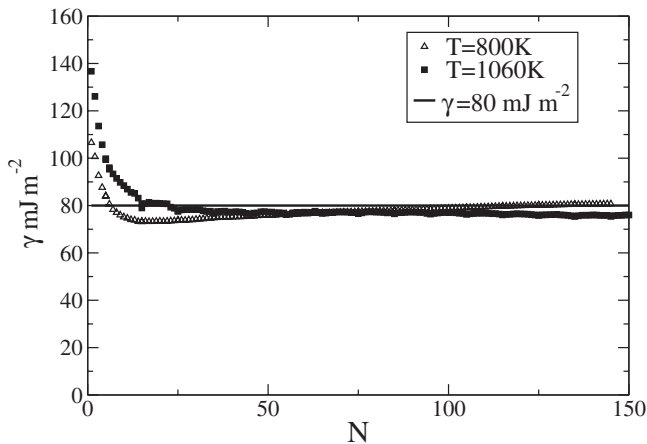

FIG. 3. Interfacial free energy as a function of N computed at the surface of tension, assuming a cubic cluster with $a = 0$.

the analysis of Mullins [17] to obtain

$$r \approx \frac{\{\gamma_{LS}(\rho_s)/\gamma_{LS}[\rho_s(0)]\}^3}{[1 - \Delta\mu\rho_s/(2B) - \frac{1}{2}B\epsilon^2/(\rho_s\Delta\mu)]^2},$$

where r is the ratio between the barrier height in the case of compressible nuclei (with density ρ_s), compared to that for incompressible clusters [with density $\rho_s(0)$]. B denotes the bulk modulus of the crystal and ϵ the elastic strain, compared to that of a solid at the same chemical potential as that of the parent liquid. From our simulations, we find that the density at the center of the crystal nucleus is some 6% lower than the reference value. Even with this rather extreme estimate of the strain in the nucleus, we find a compressibility correction to the apparent value of γ_{LS} that is no more than 10%. Hence, we conclude that compressibility effects cannot account for the observed discrepancy.

Thus far, we have not considered the effect of edges and vertices on the surface free energy of a small cluster. This effect is certainly non-negligible. If, for instance, we consider a cubic NaCl crystal in vacuum at $T = 0$ K, both the line energy of the edges and the vertex energy of the corners can be determined directly. The energy of an NaCl cube can be written as $e = e_B\ell^3 + 6e_S\ell^2 + 12e_E\ell + 8e_C$, where e is the total internal energy per particle, e_B is the energy per particle in a bulk crystal, e_S is the energy of a particle belonging to the surface, e_E is the energy of a particle belonging to an edge, e_C is the energy of a particle belonging to a corner of the cube, and ℓ is the number of atoms per edge. Computing this energy for a crystal of 64, 216, and 512 atoms [23], we find that $e_E/e_S = 0.22$ and $e_C/e_s = 1.2$. The effect of these edge and vertex contributions is to increase the apparent surface energy by 13% for a crystal of 216 particles. Of course, these numbers do not apply to a hot NaCl crystal in contact with its melt, and it is not even obvious how to define the various terms in that case, as not only the magnitude but even the sign of e_E and e_C depend on the precise choice of the dividing surface. This means that, within the macroscopic framework imposed by CNT, we cannot reliably estimate the edge and corner contributions to the surface free energy.

We are therefore forced to conclude that the large apparent value of γ_{LS} of small crystallites is due to a finite-size effect that is not easily accounted for within a thermodynamic theory. Rather, the free energy of small clusters must be computed using a molecular approach, either theoretically (as in DFT [2,3], CH [4], or PF [5]) or numerically, as illustrated in the present work. In the present Letter, and in Ref. [7], we computed the free energy of relatively small clusters (up to $N = 200$). However, under the experimental conditions for crystal nucleation of NaCl ($T = 905$ K), the critical nucleus is expected to contain $\mathcal{O}(6 \times 10^2)$ particles. Calculations for larger clusters would be feasible, but expensive. We therefore make the Tolman "ansatz" that the leading correction to surface free energy is proportional to $1/R_c$, where R_c is

the radius of the critical nucleus. As $1/R_c \sim \Delta\mu$, we assume that the variation in γ_{LS} is of the form $\gamma_{LS}(\Delta\mu) = \gamma_{LS}^{coex} + b\Delta\mu$. We can determine b from the simulation data of Refs. [6,7]. Inserting the value $\Delta\mu = 0.3$ kT at $T = 905$ K, we predict that under the condition of the nucleation experiments of Ref. [8], the effective value of γ_{LS} should be 67 mJ m^{-2}, in an almost embarrassing agreement with the experimental data ($\gamma_{LS} = 68$ mJ m^{-2}). Although this good agreement is almost certainly fortuitous, it does support our conjecture that the surface free energies measured in nucleation experiments are subject to very large finite-size corrections (in this case: more than 80%). If we take this strong $\Delta\mu$ dependence of γ_{LS} seriously, it would mean that for strongly faceted crystals (although not for NaCl), the nucleation barrier could start to rise again at large supersaturations. This should be experimentally observable, as it would lead to an increase in the final crystallite size in fully crystallized samples [24]. Interestingly—but we do not know if it is really relevant—the final crystallite size in hard-sphere crystallization suddenly grows as the concentration is increased beyond a volume fraction of 58%. If the barrier is a monotonically decreasing function of the volume fraction, this should not happen.

In summary, our study of the free energy of NaCl crystallites indicates that the surface free energy is subject to large finite-size corrections that cannot be accounted for within a thermodynamic theory. Based on the small number of examples where the relevant simulation data are available (NaCl, Lennard-Jones, hard spheres), we speculate that the finite-size effects are most pronounced for strongly faceted crystals, such as NaCl. The present results support the suggestion by Kelton that the large number of published surface free energies that are based on nucleation data are of little use to predict macroscopic surface free energies. We stress that, in addition to nucleation studies, there are other, more reliable, experimental routes to determine solid-liquid surface free energies. An example is the grain-boundary groove method [25]. However, such experiments are challenging, especially for materials that have anisotropic surface free energies. Our work highlights the fact that, if nucleation studies are used to estimate solid-liquid surface free energies, the analysis cannot be based on CNT but must make use of one of the more accurate, microscopic theories for crystal nucleation that properly account for the fact that crystal nuclei are far from macroscopic.

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[22] The equimolar dividing surface is defined such that there are no surface excess particles. This means that the total number of particles in the system (N_{tot}) is equal to the sum of the number of solid and liquid particles ($N_{tot} = N_S + N_L$) and the total volume in the system is $\langle V \rangle = \langle v_L \rangle N_L + \langle v_S \rangle N_S$, where v_L and v_S are the (known) liquid and solid volumes per particle. In a simulation, we measure $\langle V \rangle$ as a function of N_g. Assuming, as before, that $N_S = (N_g^{1/3} + a)^3$, we adjust a such that we obtain the best linear relation between $\langle V \rangle$ and N_S. The analysis of the equienthalpy surface proceeds in a similar way.

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