Irreducible finite-size effects in surface free energies 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, with the value that follows from the height of the homogeneous nucleation barrier. We find that the two estimates differ by more than 100\%. Similar, although smaller discrepancies are found for crystals of hard-sphere colloids and of Lennard-Jones (“argon”) particles. We consider a variety of possible causes for this discrepancy and are forced to conclude that it is due to a finite-size effect that cannot be corrected for by any simple thermodynamic procedure. Importantly, we find that the surface free energies that follow from real nucleation experiments should be subject to large finite size effects. Taking this in to account, we obtain quantitative agreement between the simulation data and the surface free energy of NaCl that follows from nucleation experiments. Our finding suggests that most published solid-liquid surface free energies derived from nucleation experiments will have to be revised.

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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. \cite{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 \( \Delta G_{\text{crit}} \), the height of the free-energy barrier that has to be crossed to nucleate a crystal: \( R = \kappa e^{-\Delta G_{\text{crit}}/k_BT} \). Here \( \kappa \) 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: \( \Delta G_{\text{crit}} = c \hat{\gamma}_{\text{LS}} \rho_S^{1/2} |\Delta \mu|^2 \), where \( \gamma_{\text{LS}} \) 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 \( \rho_S \) 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. The nucleation rate depends exponentially on \( \Delta G_{\text{crit}} \), the rate is a very sensitive function of the surface free-energy density \( \gamma_{\text{LS}} \). 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 [\( \gamma_{\text{LS}} \)] 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 \( \gamma_{\text{LS}} \) determined from nucleation experiments can only be used 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) \textsuperscript{2,3}, the Cahn-Hilliard approach (CH) \textsuperscript{4}, or the phase-field formalism (PF) \textsuperscript{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 yet, at te same time, reproduces 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. Ref. \textsuperscript{6} reported the surface free energy of a NaCl [100] interface in contact with the coexisting liquid phase: \( \gamma_{\text{LS}} \approx 36 \pm 6 \text{ mJ m}^{-2} \). The effective surface free energy that follows from the NaCl crystal-nucleation barrier at 800 K was reported in ref. \textsuperscript{7}: \( \gamma_{\text{LS}} = 80 \pm 1 \text{ mJ m}^{-2} \) (assuming that the nucleus has a cubic shape). In addition, nucleation experiments at 905K \textsuperscript{8} provide an experimental estimate of \( \gamma_{\text{LS}} \approx 68 \text{ mJ m}^{-2} \).

Another example of a large difference between \( \gamma_{\text{LS}} \) determined from the nucleation barrier and from coexistence data comes from hard-sphere colloids: a comparison of simulations at coexistence \textsuperscript{9} and in the supersaturated regime \textsuperscript{10} indicate that the value of \( \gamma_{\text{LS}} \) estimated on the basis of the nucleation barrier is some 30\% larger than the value for a planar interface at coexistence. A similar discrepancy (\( \mathcal{O} (20\%) \)) 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 \(\gamma_{LS}\) 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 ref. \[6\-7\-14\], we use the Tosi-Fumi rigid-ion-pair interaction potential \[15\] to model the inter-ionic 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 \(\gamma_{LS}\) depends on the choice of the dividing surface (equimolar dividing surface, equi-enthalpy 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 \(\gamma_{LS}\) 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 \(\gamma_{LS}\) 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 \(T_M=(1060\pm10)\) K. \(T_M\) 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 liquid-like particles. We can then deduce the surface free-energy density using

\[
\gamma_{LS}(N) = \frac{\Delta G(N)}{C} \rho_S^{2/3} N^{-2/3},
\]

where \(N\) denotes the number of crystalline particles and \(C\) is a geometrical constant that has a value 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 figure \[1\]). Of course, we need not assume a priori that the cluster is cubic: we can use the average cluster shape from figure \[1\] 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 compute the average \(\gamma_{LS}\) of the cluster. Leaving apart the question whether a Wulff construction is at all meaningful for clusters containing \(O(10^2)\) particles, we note that this procedure yields \(\gamma_{LS} \approx 40\) mJ m\(^{-2}\), which is within 10% of the value expected for a perfect cube. In what follows, we will therefore assume that small NaCl crystals have the same cubic morphology as macroscopic crystals. From Figure \[2\] 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 $\gamma_{LS}$ with the size of the cluster. This analysis leads to a value of $a \approx 0$. Figure 3 shows that, over range of cluster sizes studied, the resulting value of $\gamma_{LS}$ is very close to the value $\gamma_{LS} \approx 80 \text{ mJ m}^{-2}$ that follows from the analysis of the nucleation barrier at $800 \text{K}$ [7] (see figure 3). Moreover, a similar analysis at 800 K, leads to the same estimate of $\gamma_{LS}$. The internal consistency between the values of $\gamma_{LS}$ 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 36 mJ m$^{-2}$ found for a flat interface. Choosing another conventional dividing surface (e.g. the equimolar or the equi-enthalpy surface) only makes matters worse: in both cases we find a negative value of $\gamma_{LS}$ that is indeed almost independent of $N$ for all but the smallest clusters. More interestingly, 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-corrected value of $\gamma_{LS}$ that is not 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 $T = 0K$, 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:

$$\epsilon = \epsilon_B \ell^3 + 6\epsilon_S \ell^2 + 12\epsilon_E \ell + 8\epsilon_C$$  \hspace{1cm} (2)$$

where $\epsilon$ is the total internal energy per particle, $\epsilon_B$, the energy per particle in a bulk crystal, $\epsilon_S$ the energy of a particle belonging to the surface, $\epsilon_E$ the energy of a particle belonging to an edge, $\epsilon_C$ the energy of a particle belonging to a corner of the cube, and $\ell$ is the number of atoms per edge. Computing this energy for a crystal of 64, 216 and 512 atoms [26], we find that $\epsilon_E/\epsilon_S = 0.22$ and $\epsilon_C/\epsilon_S = 1.2$. 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 at even obvious how to define the various terms in that case, as not only the magnitude but even the sign of $\epsilon_E$ and $\epsilon_C$ 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 $\gamma_{LS}$ of small crystallites is due to a finite-size effect that is not easily accounted for by 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 paper, 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 ($T = 905K$), the critical nucleus is expected to contain $O(6 \times 10^5)$ 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

![Interfacial free energy as a function of N computed at the surface of tension, assuming a cubic cluster with $a=0$](image)

FIG. 3: Interfacial free energy as a function of $N$ computed at the surface of tension, assuming a cubic cluster with $a=0$ by $\gamma_{LS}$.
1/R_c ∼ Δμ, we assume that the variation in γ_{LS} is of the form: γ_{LS}(Δμ) = γ_{LS}^{ex} + bΔμ. We can determine b from the simulation data of refs [3, 2]. Inserting the value Δμ = 0.3kT at T=905K, we predict that under the condition of the nucleation experiments of ref. [3], the effective value of γ_{LS} should be 67 mJ m^{-2}, in almost embarrassing agreement with the experimental data (γ_{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 Δμ-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 us 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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