Systematic Improvement of Classical Nucleation Theory

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We reconsider the applicability of classical nucleation theory (CNT) to the calculation of the free energy of solid cluster formation in a liquid and its use to the evaluation of interface free energies from nucleation barriers. Using two different freezing transitions (hard spheres and NaCl) as test cases, we first observe that the interface-free-energy estimates based on CNT are generally in error. As successive refinements of nucleation-barrier theory, we consider corrections due to a nonsharp solid-liquid interface and to a nonspherical cluster shape. Extensive calculations for the Ising model show that corrections due to a nonsharp and thermally fluctuating interface account for the barrier shape with excellent accuracy. The experimental solid nucleation rates that are measured in colloids are better accounted for by these non-CNT terms, whose effect appears to be crucial in the interpretation of data and in the extraction of the interface tension from them.

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The decay of metastable states, such as the solidification of a supercooled liquid, takes place through the nucleation and growth of some small-sized droplet within the system [1]. The initial stage of the phase transformation is usually described within the time-honored classical nucleation theory (CNT) [2–4], where the droplet is envisaged as a sphere of, say, bulk solid, separated from the liquid by a sharp interface, giving rise to a free-energy penalty proportional to the interface area and a total Gibbs-free-energy activation barrier

$$\Delta G(n) = -|\Delta\mu| n + A n^{2/3}, \tag{1}$$

where n is the number of particles in the solid cluster, $\Delta\mu < 0$ is the chemical potential difference between solid and liquid, $A = (36\pi)^{1/3}\rho_s^{-2/3}\sigma$ with ρ_s the bulk-solid number density and σ the specific surface free energy (surface tension) of the planar interface, all anisotropies being neglected at this stage. The droplet grows if it exceeds a critical size n^* corresponding to the maximum $\Delta G(n)$ ($\equiv \Delta G^*$). CNT is routinely used to estimate the nucleation rate $I = I_0 e^{-\beta\Delta G^*}$, where $\beta = 1/(k_B T)$ is the inverse temperature and I_0 a kinetic prefactor that varies slowly with T. Clearly, this connection between I and σ [4] relies on several severe approximations. First of all the choice of an appropriate reaction coordinate, here the droplet size n, an issue largely discussed and criticized in the literature [5–8]. Moreover, I_0 is notoriously influenced by genuinely nonequilibrium effects and various expressions resulting from a more detailed consideration of the nucleation kinetics are known since a long time [9–11].

In this Letter, we do not address the issue of the validity of CNT for predicting the nucleation rate but rather consider an even more fundamental question, namely, the efficacy of CNT in describing the dependence of the interface free energy of the solid cluster on its size. Our starting point is to show that the profiles of $\Delta G(n)$ obtained by numerical simulation of nucleation clusters in a variety of systems are not consistent with Eq. (1). We then explore corrections, some already present in the literature, some novel. It emerges that the numerical profiles can be accurately reproduced by assuming a diffuse and thermally fluctuating solid-liquid interface. Finally, we show how this finding is of direct use to interpret nucleation rates and correctly extract interface free energies from them, a result that should be of considerable interest to experimentalists.

We begin by displaying in Fig. 1 existing accurate simulation data for $\Delta G(n)$ of a solid cluster nucleating inside a bulk liquid, available for hard spheres [12] and for the Fumi-Tosi model of NaCl [13]. In each case, we superpose a CNT least-squares fit to Eq. (1) for comparison. It is clear that CNT is not generally adequate to describe $\Delta G(n)$. The deviations are systematic and of different sign at low and large n. The fit quality does not improve by restricting data to large clusters only, indicating that even in the barrier region the cluster free energy does not obey Eq. (1). To shed light on this failure of CNT, we relax the approximations leading to Eq. (1) one at a time. Eventually, we shall get a more general expression for the free-energy cost of a n-particle cluster for large n, which turns out to have the Dillmann-Meier [14] form

$$\Delta G = 4\pi R^2 \tilde{\sigma}\left(1 - \frac{2\tilde{\delta}}{R} + \frac{\tilde{\epsilon}}{R^2}\right) - \frac{4}{3}\pi R^3 \rho_s |\Delta\mu| + C \ln\frac{R}{a}, \tag{2}$$

with $R = [3n/(4\pi\rho_s)]^{1/3}$ and a a microscopic length, and where $\tilde{\sigma}$, $\tilde{\delta}$, $\tilde{\epsilon}$, and C are theory-dependent parameters.

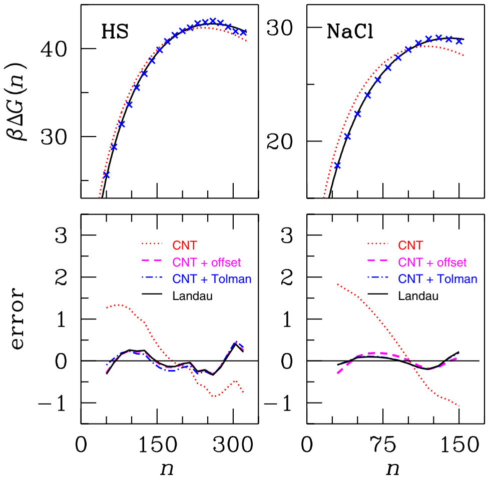

FIG. 1 (color online). Gibbs-free-energy cost $\Delta G(n)$ of an n cluster in units of k_BT. Left: hard spheres at a packing fraction of 0.5207, from [12]; right: NaCl at $T = 825$ K, from [13]. Top panels: blue crosses, MC data (selection of data points); red dotted line, CNT best fit; black solid line, Landau-theory best fit. In all fits, data for $n \lesssim n^*/5$ are ignored. Bottom panels: deviation of the fitting curves from the data. CNT [$\tilde{\delta} = \tilde{\epsilon} = C = 0$ in Eq. (2)]; CNT + offset ($\tilde{\delta} = C = 0$); CNT + Tolman ($\tilde{\epsilon} = C = 0$); Landau ($C = 0$). Values for σ from CNT are the following: hard spheres, $\beta\sigma d^2 = 0.724$ (sphere diameter d); NaCl (cubic nucleus), $\sigma = 79.75\ \mathrm{erg/cm^2}$. In hard spheres, the optimal $\beta\tilde{\sigma}d^2$ is 0.737 for Landau theory (with $\tilde{\delta} = -0.017d$ and $\tilde{\epsilon} = -0.332d^2$), 0.741 for CNT + offset (with $4\pi\beta\tilde{\sigma}\,\tilde{\epsilon} = -2.599$), and 0.761 for CNT + Tolman (with $\tilde{\delta} = 0.086d$). In NaCl (cubic nucleus), the optimal $\tilde{\sigma}$ is 88.87 $\mathrm{erg/cm^2}$ for Landau theory (with $\tilde{\delta} = 0.716$ Å and $\tilde{\epsilon} = 0.471$ Å^2), 83.74 $\mathrm{erg/cm^2}$ for CNT + offset (with $6\beta\tilde{\sigma}\,\tilde{\epsilon} = -3.833$), and 88.53 $\mathrm{erg/cm^2}$ for CNT + Tolman (with $\tilde{\delta} = 0.675$ Å). Note the large improvement over CNT obtained with just one more fitting parameter and how similar is the quality of the fit based on CNT + offset to the Landau fit.

The assumption in (2) is that of a spherical cluster shape—a different shape, that would be determined by free-energy anisotropy, would slightly change the value of $\tilde{\sigma}$ but not the physical discussion that follows. The first modification to CNT we consider is dropping the sharp-interface approximation [15]. Within Landau theory, the free-energy cost of the critical droplet is the unstable stationary point of a functional, e.g.,

$$\mathcal{G}[\phi] = \int d^3x\left\{\frac{c}{2}(\nabla\phi)^2 + \frac{\kappa}{2}(\nabla^2\phi)^2 + g(\phi(\mathbf{x}))\right\}. \quad (3)$$

Here $c, \kappa > 0$, $\phi(\mathbf{x})$ is the "crystallinity" order parameter (OP) that distinguishes the solid ($\phi > 0$) from the liquid ($\phi = 0$), and $g(\phi)$ is the Landau free energy per unit volume of the homogeneous system. Below melting, $T < T_m$, g shows, besides the liquid minimum $g(0) = 0$, a second and deeper solid minimum. Right at T_m, we assume $g(\phi) = c_{20}\phi^2(1 - \phi/\phi_{s0})^2(1 + \tau\phi/\phi_{s0})$ with $c_{20} > 0$ and $\tau > -1$ [16], where ϕ_{s0} is the value of ϕ in the bulk solid at coexistence, and where a nonzero value of τ creates an asymmetry between the liquid and the solid minimum. We also assume that, slightly below T_m and at fixed pressure, g acquires a linear dependence on $\Delta T = T - T_m$ only through its ϕ^2 term, which becomes $c_2\phi^2$ with $c_2 = c_{20} + c'_{20}\Delta T$. With this standard setup, the free energy of a cluster of radius R is $\mathcal{G}[\phi_R]$, where $\phi_R(r)$ is the spherically symmetric OP profile of the cluster. Assuming, as in [17], that for small supersaturation and large R, $\phi_R(r)$ may be approximated with $\phi_0(r - R)$, where $\phi_0(z)$ is the OP profile for a planar interface centered at $z = 0$, the cluster free energy takes precisely the form (2), with $C = 0$, $\rho_s\Delta\mu = c'_{20}\phi_{s0}^2\Delta T$, and $\tilde{\sigma}$, $\tilde{\delta}$, $\tilde{\epsilon}$ all linear functions of ΔT, expressed in terms of c, κ, and $\phi_0(z)$ [18]. At coexistence and to first order in the deviations from the ϕ^4 theory (viz. $\kappa = \tau = 0$), we have for $\tilde{\sigma}(T_m) \equiv \sigma$, etc.

$$\begin{aligned}\sigma &= \frac{c\phi_{s0}^2}{3\ell}\left(1 + \frac{1}{4}\tau + \frac{2}{5}\frac{\kappa}{c\ell^2}\right),\\ \delta &= \frac{5\ell}{48}\tau, \quad \text{and} \qquad\qquad (4)\\ \epsilon &= \ell^2\left[\frac{\pi^2 - 6}{12}\left(1 - \frac{\tau}{4}\right) + \left(\frac{26}{5} - \frac{\pi^2}{3}\right)\frac{\kappa}{c\ell^2}\right],\end{aligned}$$

where $\ell = \sqrt{2c/c_{20}}$ is a measure of the interface width.

A second effect that is absent in CNT but present in nature and observed in simulations is that shapes of clusters, far from being static, fluctuate widely away from their mean shape [19,20]. To describe shape fluctuations, we employ a field theory for the Canham-Helfrich (CH) Hamiltonian, containing spontaneous-curvature and bending-energy terms in addition to surface tension. A CH interface Hamiltonian $\mathcal{H}_s$ can be derived from the free-energy functional (3) for small deviations of the interface from planarity. Denoting by Σ the generic closed-surface profile and by $\hat{\mathbf{n}}$ its outward normal, we obtain [18]

$$\mathcal{H}_s = \int_\Sigma dS\left(\sigma - \sigma\delta\nabla\cdot\hat{\mathbf{n}} + \frac{1}{2}\lambda(\nabla\cdot\hat{\mathbf{n}})^2\right), \quad (5)$$

where σ and δ are the same as in Landau theory and $\lambda = \kappa\phi_{s0}^2/(3\ell)$ under the same hypotheses for which Eq. (4) holds. $\Delta G(R)$ can be evaluated explicitly [18] for a quasispherical cluster [21], where only quadratic deviations from sphericity are kept. The wavelength of surface undulations is cut off at a lower limit $a = \rho_s^{-1/3}$ to account for the granularity of matter. We find that the surface free energy has a form consistent with Eq. (2), with new T-dependent parameters $\tilde{\sigma}$, $\tilde{\delta}$, and $\tilde{\epsilon}$ (whose explicit expressions are given in [18]) and with $C = -(7/3)k_BT$, which shows that small deviations around a nominally spherical cluster shape simply add a universal logarithmic correction to the mean-field functional form of ΔG. This correction is responsible for the well-known $R^{*7/3}$ term in the exponential prefactor of the nucleation rate [22].

Clearly, the parameters in Eq. (2) are determined by the values of c and κ in (3), as well as by the form of $g(\phi)$—all system-dependent quantities that require a case-specific theory. We here aim at elucidating the relative importance of the different terms $\tilde{\delta}$, $\tilde{\epsilon}$, C implied by interface thickness and shape fluctuations. To get a quantitative measure of that, we directly fit the parameter values in (2) to the numerical results for $\Delta G(n)$ for the two systems of Fig. 1. Consistently with the assumptions underlying our mesoscopic description, each fit is made only to data points for sufficiently large n. We first include the leading $\propto \tilde{\delta} n^{1/3}$ ("Tolman" [23]) correction to CNT. As shown in Fig. 1, this improves the quality of the fit significantly. The error is reduced substantially in both systems, although not monotonically. Only a marginal improvement is obtained if both $\tilde{\delta}$ and $\tilde{\epsilon}$ are allowed in the fit. The inclusion of the logarithmic shape correction gives no further appreciable gain. Next, we attempted fitting the data by retaining just the offset ($\equiv 4\pi\tilde{\sigma}\,\tilde{\epsilon}$) in (2) beyond $\tilde{\sigma}$. Alone, the simple offset gave an improvement of about the same quality as with all terms allowed. We conclude that corrections to CNT exclusively deriving from a fluctuating cluster shape appear to be much smaller than those arising, already in Landau theory, from allowing a nonzero thickness of the interface (shape fluctuations are not anyway immaterial since they renormalize, even significantly, the Landau-theory parameters [18]). Moreover, either the Tolman correction or, alternatively, the constant offset each lead to significant fit improvement over CNT. The origin of both terms is in the finite thickness of the interface, which makes the reversible work to create a cluster systematically smaller than what would be needed for the same cluster with a sharp spherical interface.

The existing simulation data do not permit us to assess the relative importance of the two smooth-interface contributions $\tilde{\delta}$ and $\tilde{\epsilon}$ and of the logarithmic correction; more specific work is needed in order to decide that case by case. Using the 3D Ising model as a test system, we carried out extensive simulations at moderate supersaturations, computing the cluster free energy for the nucleation process of magnetization reversal by the same method as in Refs. [24–27]. We computed $\Delta G(n)$ for a number of values of the field h ($0.35, 0.40, \ldots, 0.65$, in J units) and plotted the ratio $\sigma(n)$ of the surface free energy $F_s = \Delta G(n) + |\Delta\mu| n$ to the area $(36\pi)^{1/3}(na^3)^{2/3}$ of the cluster surface as a function of the inverse radius $n^{-1/3}$ (see Fig. 2). We verified that, for all h values considered, clusters close to critical indeed contain the vast majority of up spins in the system, coherently with the physical picture at the basis of our theories. It is evident that only the joint consideration of $\tilde{\delta}$ and $\tilde{\epsilon}$ is able to reproduce the upward concavity of $\sigma(n)$ as a function of $n^{-1/3}$ in the n region ($n > 40$) where $F_s(n) \propto n^{2/3}$. A positive offset $\tilde{\epsilon} > 0$ is confirmed, as expected from Landau-theory results for ϵ and from the formula for λ in Eq. (5) [18]. In our regime of h, the logarithmic term does not change the quality of the fit; as shown in Fig. 2, this correction becomes sizeable only at values of n outside the fit range. However, inclusion of the logarithm has consequences on the optimal $\tilde{\delta}$ values, which reduce from ≈ 0.10 to ≈ 0.02 throughout the h range considered (the Tolman length δ [23] is zero for the Ising model at coexistence [17]). From this example we conclude that (a) neither $\tilde{\delta}$ nor $\tilde{\epsilon}$, both arising from the finite interface width, can generally be neglected in the description of the nucleation free-energy barrier; (b) shape fluctuations improve the description especially for small cluster sizes ($n < 80$).

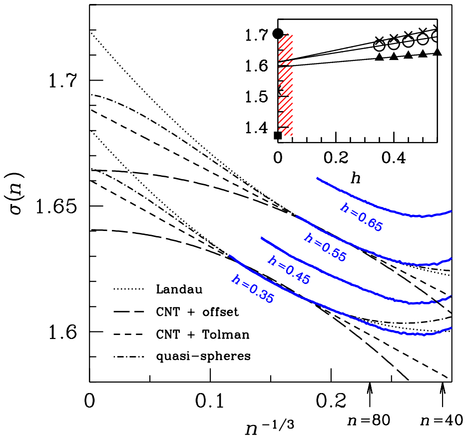

FIG. 2 (color online). The cluster interface free energy of the 3D Ising model in units of J/a^2 (a being the cubic-lattice spacing), plotted as a function of $n^{-1/3}$ for various h values. The temperature is $T = 0.6T_c$; starting at T with all spins down, the system is quenched to h. Two spins are part of the same cluster if there is an uninterrupted chain of up spins between them. The lattice consisted of 20^3 sites; for $h = 0.35$ a calculation on 25^3 sites led to practically the same $\Delta G(n)$. Three different instances of umbrella potential were considered and all led to the same $\Delta G(n)$ to within less than $0.1k_BT$ [31]. Thick blue lines, MC data for $\Delta G(n)$; black lines, least-square fits of the $n > 80$ data points for $h = 0.35$ and 0.55, based on various extensions of the CNT (see legend). Note that only the full Landau expansion captures the upward curvature of $\Delta G(n)$, and that especially the shape fluctuations capture that of smaller clusters. In the inset, different ways of extracting the interface tension σ out of finite-h values of $\sigma(\infty)$ are compared: triangles, CNT; crosses, Landau theory [$C = 0$ in Eq. (2)]; open dots, quasispheres [$C = -(7/3)k_BT$]. Linear extrapolation of data points at $h = 0$ yields $\sigma \approx 1.60$. The black dot is the value of σ calculated for the (001) interface (from Ref. [32]). The red shading indicates σ estimates from Eq. (6) for cluster shapes intermediate between cubic (lower end) and spherical (upper end). Gratifyingly, the $\tilde{\sigma}$ values extrapolate as they should to a σ_0 which is higher than that of the (001) interface, and intermediate between cubic and spherical shape—the average shape being also intermediate between the two.

Far from being academic, the existence of these corrections to CNT has a direct impact on the understanding of experiments, in particular, on the all-important extraction of the interface free energy σ from measured nucleation rates. Assuming the standard activated expression for I, σ can be extracted from the slope of $Y = \ln(I/I_0)$ as a function of $X = (T_m/\Delta T)^2$ [28]. If CNT were exact, this slope would be a constant throughout the region of liquid metastability. When the more general Eq. (2) is employed for ΔG^*, the slope depends on the distance from coexistence ΔT, as demanded by nonzero values of $\tilde{\sigma}$, $\tilde{\delta}$, $\tilde{\epsilon}$, C and their rates of variation with ΔT. Close to coexistence, one can write $Y(X)$ as a power series in ΔT:

$$\ln(I/I_0) = -\frac{\alpha T_m^2}{\Delta T^2} - \frac{\alpha' T_m}{|\Delta T|} + \mathcal{O}(1). \tag{6}$$

Here α takes the same value as in CNT, $\alpha = 16\pi\sigma^3/(3k_B T_m \rho_s^2 L_m^2)$ with L_m the latent heat of melting per particle. However, α' is not universal:

$$\alpha' = \alpha\left(1 + \frac{3\sigma' T_m}{\sigma} - \frac{3\rho_s L_m \delta}{\sigma}\right), \tag{7}$$

taking $\tilde{\sigma} = \sigma + \sigma'|\Delta T| + \ldots$ close to coexistence. For instance, for the ϕ^4 theory it turns out that $\alpha'/\alpha = 1 + 3\rho_s \ell L_m/(2\sigma) > 0$.

Because of (6), $Y(X)$ develops a concavity, which is upward if $\alpha' > 0$, as is the case, for example, in colloids (see below). The very important practical consequence is that the solid-liquid interface free energy at coexistence (σ), the key quantity which one wishes to extract from nucleation rates, is determined by the slope (α) of $Y(X)$ at asymptotically large X and not from the slope, generally different, at small X. As an example, deviations from linearity in the $Y(X)$ plot are experimentally evident in colloids, see, e.g., Refs. [29,30]. Figure 3 shows how data should be read to extract σ. Since this procedure is not to our knowledge universally followed, this suggests that at least some tabulated σ values may need a revision. Because the finite-interface corrections reduce the barrier height compared to CNT, it is to be expected that the true interface free energies are substantially smaller than believed so far.

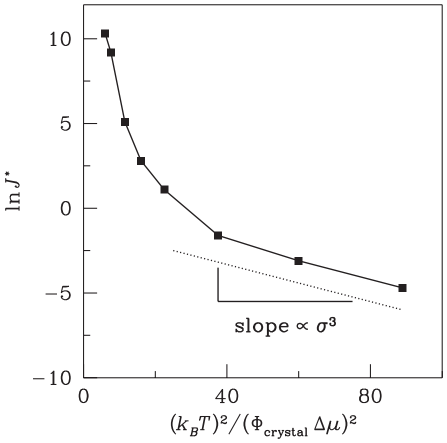

FIG. 3. Nucleation-rate data for the solidification of a colloidal fluid [Fig. 7(b) of [30]], showing $Y = \ln(I/I_0)$ as a function of a quantity akin to $X = (T_m/\Delta T)^2$ (Φ_{crystal} is the solid volume fraction). The dotted line gives the slope from which the surface tension should be extracted.

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Supplementary Material

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I. LANDAU THEORY OF NUCLEATION

In the following, we shall refer to the main text of the manuscript as MT.

A Landau theory of nucleation based on a Cahn-Hilliard-like functional [1] describing the free-energy cost of a diffuse interface between two phases — "solid" and "liquid", neglecting anisotropies — can be formulated as follows. Assume for simplicity a scalar order-parameter (OP) field $\phi(\mathbf{x})$. The Landau free energy is (Eq. (3) of MT):

$$\mathcal{G}[\phi]=\int \mathrm{d}^3x\,\left\{\frac{c}{2}(\nabla\phi)^2+\frac{\kappa}{2}(\nabla^2\phi)^2+g(\phi(\mathbf{x}))\right\}\,, \tag{1}$$

where $c,\kappa>0$ are "stiffness" parameters and $g(\phi)$ is the specific free energy (i.e., Gibbs free energy per unit volume) of the homogeneous system, the bulk liquid being the reference state where $\phi=0$. Exactly at coexistence, the OP values are $\phi_-=\phi_{s0}$ in the bulk solid and $\phi_+=0$ in the bulk liquid (i.e., $g(\phi_{s0})=g(0)=0$ and $g(\phi)>0$ otherwise). When boundary conditions are applied such that $\phi\to\phi_\pm$ for $z\to\pm\infty$, a planar interface orthogonal to z is forced to appear in the system. The corresponding z-dependent OP profile is the extremal point $\phi_0(z)$ of (1) that satisfies the boundary conditions:

$$c\phi_0''-\kappa\phi_0''''=\frac{\mathrm{d}g}{\mathrm{d}\phi}(\phi_0;T=T_m)\,,\quad \text{with }\ \phi_0(-\infty)=\phi_{s0}\ \text{ and }\ \phi_0(+\infty)=0\,. \tag{2}$$

Evidently, $\mathcal{G}[\phi_0]$ represents the free-energy cost of the solid-liquid interface.

Away from coexistence, the absolute minimum of $g(\phi)$ falls at $\phi=\phi_s>0$ for $\Delta T\equiv T-T_m<0$. This can be described by

$$g(\phi)=c_2\phi^2+c_3\phi^3+c_4\phi^4+\ldots \tag{3}$$

if we take $c_2=c_{20}+c_{20}'\Delta T$ ($c_{20},c_{20}'>0$), all other c_n coefficients being constant. Not far from T_m, the OP profile of a spherical solid cluster of radius $R\gg\sqrt{2c/c_{20}}$ is well described by $\phi_0(r-R)$, provided that the center of $\phi_0(z)$ is chosen at $z=0$. Based on these assumptions, the free energy of cluster formation becomes [2]:

$$\Delta G(R)=4\pi\int_0^{+\infty}\mathrm{d}r\,r^2\left[c\phi_0'^2(r-R)+2\kappa\phi_0''^2(r-R)\right]-4\pi c_{20}'|\Delta T|\int_0^{+\infty}\mathrm{d}r\,r^2\phi_0^2(r-R)\,. \tag{4}$$

A straightforward calculation then shows that:

$$\begin{aligned}
&\int_0^{+\infty} \mathrm{d}r\, r^2\phi_0^2(r-R) = \frac{1}{3}\phi_{s0}^2 R^3 + (I_2'-I_2) + 2(I_1'+I_1)R + (I_0'-I_0)R^2\,;\\
&\int_0^{+\infty} \mathrm{d}r\, r^2\phi_0'^2(r-R) = J_2 + 2J_1R + J_0R^2\,;\\
&\int_0^{+\infty} \mathrm{d}r\, r^2\phi_0''^2(r-R) = K_2 + 2K_1R + K_0R^2\,,
\end{aligned} \tag{5}$$

where, for $n=0,1,2$:

$$\begin{aligned}
I_n &= \int_0^{+\infty} \mathrm{d}z\, z^n\left(\phi_{s0}^2 - \phi_0^2(-z)\right) \quad \text{and} \quad I_n' = \int_0^{+\infty} \mathrm{d}z\, z^n\phi_0^2(z)\,;\\
J_n &= \int_{-\infty}^{+\infty} \mathrm{d}z\, z^n\phi_0'^2(z)\,;\\
K_n &= \int_{-\infty}^{+\infty} \mathrm{d}z\, z^n\phi_0''^2(z)\,.
\end{aligned} \tag{6}$$

Substituting Eqs. (5) into (4), we obtain the final expression for $\Delta G(R)$ (Eq. (2) of MT, with $C=0$):

$$\Delta G(R) = 4\pi R^2\widetilde{\sigma}\left(1 - \frac{2\widetilde{\delta}}{R} + \frac{\widetilde{\epsilon}}{R^2}\right) - \frac{4}{3}\pi R^3\rho_s|\Delta\mu|\,, \tag{7}$$

where

$$\begin{aligned}
&\widetilde{\sigma} = cJ_0 + 2\kappa K_0 - c_{20}'(I_0'-I_0)|\Delta T|\,;\\
&\widetilde{\sigma}\widetilde{\delta} = -cJ_1 - 2\kappa K_1 + c_{20}'(I_1'+I_1)|\Delta T|\,;\\
&\widetilde{\sigma}\widetilde{\epsilon} = cJ_2 + 2\kappa K_2 - c_{20}'(I_2'-I_2)|\Delta T|\,;\\
&\rho_s\Delta\mu = c_{20}'\phi_{s0}^2\Delta T\,.
\end{aligned} \tag{8}$$

In particular, the solid-liquid interface tension σ and the "Tolman length" δ are given by:

$$\begin{aligned}
\sigma &\equiv cJ_0 + 2\kappa K_0 = \int_{-\infty}^{+\infty} \mathrm{d}z\left[c\phi_0'^2(z) + 2\kappa\phi_0''^2(z)\right]\,;\\
\delta &\equiv -\frac{1}{\sigma}\left(cJ_1 + 2\kappa K_1\right) = -\frac{\int_{-\infty}^{+\infty}\mathrm{d}z\, z\left[c\phi_0'^2(z) + 2\kappa\phi_0''^2(z)\right]}{\int_{-\infty}^{+\infty}\mathrm{d}z\left[c\phi_0'^2(z) + 2\kappa\phi_0''^2(z)\right]}\,.
\end{aligned} \tag{9}$$

Note that, for $\kappa = 0$, the formula for δ reduces to that reported in [3]. A nonzero δ corresponds to a $\phi_0(z)$ that is not symmetric around 0, namely to an interface between phases of a different nature. Summing up, Eq. (7) describes the corrections to the classical nucleation theory (CNT) which arise by replacing the assumption of a sharp solid-liquid interface with a more realistic finite width.

II. CALCULATION OF THE SURFACE TENSION AND THE TOLMAN LENGTH

Given the form of g, one can compute the explicit values of σ and δ in Eqs. (9), and of $\epsilon = (cJ_2 + 2\kappa K_2)/\sigma$ (i.e., the value of $\widetilde{\epsilon}$ at T_m, see Eq. (8)), once the exact $\phi_0(z)$ is known. In turn, $\phi_0(z)$ follows from solving the boundary value problem (2), which can be simplified, after an integration by parts, to

$$\kappa\phi_0'\phi_0''' = \frac{c}{2}\phi_0'^2 + \frac{\kappa}{2}\phi_0''^2 - g(\phi_0)\,, \quad \text{with } \phi_0(-\infty) = \phi_{s0} \text{ and } \phi_0(+\infty) = 0\,. \tag{10}$$

A special case of g function is used in the MT, where at T_m we take

$$g(\phi) = c_{20}\phi^2\left(1 - \frac{\phi}{\phi_{s0}}\right)^2\left(1 + \tau\frac{\phi}{\phi_{s0}}\right) \equiv g_0(\phi)\left(1 + \tau\frac{\phi}{\phi_{s0}}\right)\,. \tag{11}$$

For this g, the differential equation (10) is still too difficult to solve in closed form for generic κ, even for $\tau = 0$. Hence, we decide to work perturbatively in κ and τ.

At zeroth order, i.e., $\kappa = \tau = 0$, corresponding to ϕ^4 theory, the solution to (10) is

$$\bar{\phi}_0(z) = \frac{\phi_{s0}}{2}\left\{1 - \tanh\left(\frac{z - C}{\ell}\right)\right\} \tag{12}$$

with $\ell = \sqrt{2c/c_{20}}$ and arbitrary C. We fix C by requiring that the interface is centered at $z = 0$, i.e., by imposing

$$\int_{-\infty}^{+\infty} \mathrm{d}z\, z\bar{\phi}_0'(z) = 0 \tag{13}$$

(hence $C = 0$). Next, we take non-zero κ and τ, assumed to be of the same order of magnitude, and search for a first-order solution to (10) in the form

$$\phi_0(z) = \bar{\phi}_0(z) + \tau\psi_1(z) + \frac{\kappa}{c\ell^2}\chi_1(z)\,. \tag{14}$$

Upon inserting this function into Eq. (10), we obtain two independent equations for $\psi_1(z)$ and $\chi_1(z)$, namely

$$c\bar{\phi}_0'\psi_1' - g_0'(\bar{\phi}_0)\psi_1 = \frac{\bar{\phi}_0 g_0(\bar{\phi}_0)}{\phi_{s0}} \tag{15}$$

and

$$c\bar{\phi}_0'\chi_1' - g_0'(\bar{\phi}_0)\chi_1 = c\ell^2\left(\bar{\phi}_0'\bar{\phi}_0''' - \frac{1}{2}\bar{\phi}_0''^2\right)\,. \tag{16}$$

The solutions to Eqs. (15) and (16) such that each term in Eq. (14) separately meets a requirement analog to (13) are:

$$\psi_1(z) = -\frac{\phi_{s0}}{8\cosh^2(z/\ell)}\left(1 - \ln 2 + \frac{z}{\ell} - \ln\cosh\frac{z}{\ell}\right) \tag{17}$$

and

$$\chi_1(z) = \frac{\phi_{s0}}{\cosh^2(z/\ell)} \left(2 \tanh \frac{z}{\ell} - \frac{z}{\ell}\right) . \tag{18}$$

Upon plugging the by now specified $\phi_0(z)$ in the integrals defining σ, δ, and ϵ, we eventually obtain the final expressions quoted in Eq. (4) of MT.

III. DERIVATION OF THE INTERFACE HAMILTONIAN

We synthetically show how the interface Hamiltonian, Eq. (5) of MT, can be obtained from the Landau free energy (1). For this derivation, we build on Refs. [4, 5]. More details will be given in [2].

In the same spirit of a statistical field theory for vesicles, we wish to assign a free energy cost to each particular realization of the cluster interface, here assumed to be sharp and akin to a mathematical surface Σ. The goal here is to describe the effect of shape fluctuations — though, in practice, in order to make analytical progress, we shall be forced in the next paragraph to describe just small deviations around the spherical shape.

Let $\mathbf{R}(u, v)$ be the parametrization ("coordinate patch") of a tiny piece of Σ. For points $\mathbf{r}$ close to this small portion of Σ, we switch from 3D cartesian coordinates, $\mathbf{r} = (x, y, z)$, to new coordinates $q_\alpha = (u, v, \zeta)$ (tangential and normal to Σ):

$$\mathbf{r} = \mathbf{R}(u, v) + \zeta \widehat{\mathbf{n}}(u, v) , \tag{19}$$

where

$$\widehat{\mathbf{n}}(u, v) = \frac{\mathbf{R}_u \wedge \mathbf{R}_v}{|\mathbf{R}_u \wedge \mathbf{R}_v|} \tag{20}$$

is the unit normal to Σ. For a patch that deviates only slightly from planarity, we may adopt a free energy of $\mathcal{G}[\phi_0(\zeta(x, y, z))]$, thus arriving, by Eq.(1), to the surface Hamiltonian

$$\mathcal{H}_s = \int \mathrm{d}u \, \mathrm{d}v \, \mathrm{d}\zeta \, |J| \left\{ \frac{c}{2} \left(\nabla \phi_0(\zeta)\right)^2 + \frac{\kappa}{2} \left(\nabla^2 \phi_0(\zeta)\right)^2 + g(\phi_0(\zeta)) \right\} \tag{21}$$

with $J = |\mathbf{r}_u \cdot (\mathbf{r}_v \wedge \mathbf{r}_\zeta)| = \widehat{\mathbf{n}} \cdot (\mathbf{r}_u \wedge \mathbf{r}_v)$. In order to compute the explicit form of J as well as those of the gradient and Laplacian of a function of ζ only, it is convenient to take a patch parametrization in terms of orthonormal, arc-length coordinates, i.e., one such that $\mathbf{R}_u \cdot \mathbf{R}_v = 0$ all over the patch and $|\mathbf{R}_u| = |\mathbf{R}_v| = 1$. Although this can rigorously be done only for surfaces with zero Gaussian curvature ($K = 0$) [6], we can reasonably expect to make small errors of order K for quasi-planar interfaces. It then follows that

$$\begin{aligned}
\frac{\partial \mathbf{r}}{\partial \zeta} &= \widehat{\mathbf{n}}\,; \\
\frac{\partial \mathbf{r}}{\partial u} &= (1-\zeta\kappa_n^{(1)})\mathbf{R}_u - \zeta\tau_g\mathbf{R}_v\,; \\
\frac{\partial \mathbf{r}}{\partial v} &= -\zeta\tau_g\mathbf{R}_u + (1-\zeta\kappa_n^{(2)})\mathbf{R}_v\,,
\end{aligned} \tag{22}$$

where $\kappa_n^{(1)}$ and $\kappa_n^{(2)}$ are the normal curvatures of the u- and v-lines respectively, and $\tau_g \equiv \tau_g^{(1)} = -\tau_g^{(2)}$ is the geodetic torsion. From Eqs. (22), one can derive the metric tensor $g_{\alpha\beta}$ of the transformation (19) and the Jacobian:

$$g_{\alpha\beta} \equiv \frac{\partial \mathbf{r}}{\partial q_\alpha}\cdot\frac{\partial \mathbf{r}}{\partial q_\beta} = \begin{pmatrix} \left(1-\zeta\kappa_n^{(1)}\right)^2+\zeta^2\tau_g^2 & -2\zeta\tau_g+\zeta^2\tau_g\left(\kappa_n^{(1)}+\kappa_n^{(2)}\right) & 0 \\ -2\zeta\tau_g+\zeta^2\tau_g\left(\kappa_n^{(1)}+\kappa_n^{(2)}\right) & \left(1-\zeta\kappa_n^{(2)}\right)^2+\zeta^2\tau_g^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{23}$$

and

$$J = \left(1-\zeta\kappa_n^{(1)}\right)\left(1-\zeta\kappa_n^{(2)}\right) - \zeta^2\tau_g^2 \equiv \sqrt{g}\,, \tag{24}$$

g being the determinant of (23). Considering that covariant and contravariant components of a vector $\mathbf{v} = \sum_{i=1}^{3}(\mathbf{v}\cdot\widehat{\mathbf{x}}_i)\,\widehat{\mathbf{x}}_i$ are built by projecting $\mathbf{v}$ on the bases ∇q_α and $\partial\mathbf{r}/\partial q_\alpha$, respectively, we can calculate the gradient of a scalar field ϕ and the divergence of a vector field $\mathbf{A}$ in local coordinates as follows:

$$\nabla\phi = \frac{\partial\phi}{\partial q_\alpha}g^{\alpha\beta}\frac{\partial\mathbf{r}}{\partial q_\beta} \quad \text{and} \quad \nabla\cdot\mathbf{A} = \frac{1}{\sqrt{g}}\frac{\partial}{\partial q_\alpha}\left(\sqrt{g}A^\alpha\right)\,, \tag{25}$$

$g^{\alpha\beta}$ being the inverse of (23). In particular,

$$\nabla\phi(\zeta) = \phi'(\zeta)\widehat{\mathbf{n}} \quad \text{and} \quad \nabla^2\phi(\zeta) = \phi''(\zeta) + \phi'(\zeta)\nabla\cdot\widehat{\mathbf{n}}\,, \tag{26}$$

where

$$\nabla\cdot\widehat{\mathbf{n}} = \frac{1}{\sqrt{g}}\left(-\kappa_n^{(1)} - \kappa_n^{(2)} - 2\zeta\tau_g^2\right)\,. \tag{27}$$

Finally, the mean and Gaussian curvatures of the patch are given by

$$H = \frac{1}{2}\nabla\cdot\widehat{\mathbf{n}}\bigg|_{\zeta=0} = -\frac{1}{2}\left(\kappa_n^{(1)}+\kappa_n^{(2)}\right) \tag{28}$$

and

$$K = \widehat{\mathbf{n}}\cdot\left(\frac{\partial\widehat{\mathbf{n}}}{\partial u}\wedge\frac{\partial\widehat{\mathbf{n}}}{\partial v}\right)\bigg|_{\zeta=0} = \kappa_n^{(1)}\kappa_n^{(2)} - \tau_g^2\,. \tag{29}$$

We are now in a position to simplify Eq. (21). Upon using Eq. (2) to eliminate $g(\phi_0)$ in favor of $(c/2)\phi_0'^2 - \kappa\left[(\phi_0'\phi_0'')' - (3/2)\phi_0''^2\right]$, and inserting Eqs. (24), (26), (28), and (29), we eventually get [2] the classic Canham-Helfrich Hamiltonian for fluid membranes,

$$\mathcal{H}_s[\Sigma] = \int_\Sigma \mathrm{d}S\,\left(\bar{a} + \bar{b}H + \bar{c}H^2 + \bar{d}K\right)\,, \tag{30}$$

with the following explicit expressions for the coefficients:

$$\begin{aligned}
\bar{a} &= \int_{-\infty}^{+\infty} \mathrm{d}\zeta\,\left[c\phi_0'^2(\zeta) + 2\kappa\phi_0''^2(\zeta)\right]\,;\\
\bar{b} &= 2\int_{-\infty}^{+\infty} \mathrm{d}\zeta\,\zeta\,\left[c\phi_0'^2(\zeta) + 2\kappa\phi_0''^2(\zeta)\right]\,;\\
\bar{c} &= 2\kappa\int_{-\infty}^{+\infty} \mathrm{d}\zeta\,\phi_0'^2(\zeta)\,;\\
\bar{d} &= \int_{-\infty}^{+\infty} \mathrm{d}\zeta\,\left\{\zeta^2\left[c\phi_0'^2(\zeta) + 2\kappa\phi_0''^2(\zeta)\right] - \kappa\phi_0'^2(\zeta)\right\}\,.
\end{aligned} \tag{31}$$

A few remarks are now in order: a) in deriving Eq. (30), all subleading corrections to the H^2 and K terms were ignored. b) H and K are reparametrization invariants, hence no ambiguity arises from the arbitrariness of the parametrization used. c) The above derivation actually applies for just one Σ patch. However, upon viewing Σ as the union of many disjoint patches, the Hamiltonian (30) holds for Σ as well. d) As anticipated, the coefficient $\bar{d}$ of the K term in (30) is possibly different from the quoted one since a parametrization in terms of orthonormal coordinates does not generally exist. However, as far as we only allow for clusters with the topology of a sphere, $\int_\Sigma \mathrm{d}S\,K$ takes the constant value of 4π by the Gauss-Bonnet theorem and the K term in $\mathcal{H}_s$ can be dropped. Comparing the definition of $\bar{a}$ and $\bar{b}$ in Eqs. (31) with Eq. (9), we can rewrite Eq. (30) in the form

$$\mathcal{H}_s[\Sigma] = \int_\Sigma \mathrm{d}S\,\left(\sigma - 2\sigma\delta H + 2\lambda H^2\right)\,, \tag{32}$$

where $\lambda = \bar{c}/2$. e) The term linear in H is related to the *spontaneous curvature* of Σ, $H_0 = -\bar{b}/(2\bar{c})$, which is proportional to the Tolman length δ. A nonzero value of H_0 entails a difference in energy between inward and outward interface protrusions, with the effect of producing a nonzero Tolman length δ. The realization that in systems where, as in the Ising model, the symmetry is perfect between the two phases then $\delta = 0$, has long been known [3].

IV. FIELD THEORY FOR THE INTERFACE HAMILTONIAN

We consider a single solid cluster in a supercooled-liquid host. We model the cluster surface Σ as being subject to random fluctuations distributed according to $\exp\{-\beta\mathcal{H}_s[\Sigma]\}$ with $\beta = 1/(k_B T)$ and $\mathcal{H}_s[\Sigma]$ given as in Eq. (5) of MT. We stress that this form of interface Hamiltonian is only valid slightly below T_m, where the curvature of the cluster surface is small. The cost in free energy of a cluster of volume V is then taken to be

$$\Delta G(V) = -\rho_s|\Delta\mu|V + F_s(V)\,, \tag{33}$$

where the surface free energy $F_s = -(1/\beta)\ln Z_s$ with

$$Z_s(V) = a^3 \int \mathcal{D}\Sigma\, \delta(\mathcal{V}[\Sigma] - V)\exp\{-\beta\mathcal{H}_s[\Sigma]\}\,. \tag{34}$$

In the above equation, $a = \rho_s^{-1/3}$ is a characteristic system length, $\mathcal{V}[\Sigma]$ is the volume enclosed by Σ, and $\mathcal{D}\Sigma$ is a suitable integral measure (see below). Neglecting overhangs and liquid inclusions in the cluster, let $r = R(\theta,\phi)$ be the equation of Σ in spherical coordinates. To proceed further, we assume only small deviations from a sphere, i.e., $R(\theta,\phi) = R_0[1+\epsilon(\theta,\phi)]$, with $\epsilon(\theta,\phi) \ll 1$. Then, we expand $\epsilon(\theta,\phi)$ in real spherical harmonics,

$$\epsilon(\theta,\phi) = \sum_{l=1}^{\infty}\sum_{m=-l}^{l} x_{l,m}Y_{l,m}(\theta,\phi)\,, \tag{35}$$

and we agree to ignore, from now on, all terms beyond second-order in the coefficients $x_{l,m}$. With these specifications, the enclosed volume and area of Σ are approximated as

$$\mathcal{V}[\Sigma] = \frac{4}{3}\pi R_0^3 + R_0^3\sum_{l>0,m} x_{l,m}^2 \equiv \frac{4}{3}\pi R_0^3\, f(\{x\}) \tag{36}$$

and

$$\mathcal{A}[\Sigma] = 4\pi R_0^2 + \frac{R_0^2}{2}\sum_{l>0,m}\left(l^2+l+2\right)x_{l,m}^2 \equiv 4\pi R_0^2\, g(\{x\})\,, \tag{37}$$

respectively, $f(\{x\})$ and $g(\{x\})$ being close-to-1 factors. In order to evaluate the mean curvature H, we move from

$$\nabla\cdot\widehat{\mathbf{n}} = \frac{2}{R(\theta,\phi)}\left(1+\frac{1}{2}L^2\epsilon(\theta,\phi) - \frac{1}{2}\epsilon(\theta,\phi)L^2\epsilon(\theta,\phi)\right)\,, \tag{38}$$

where

$$L^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\,. \tag{39}$$

Eventually, we obtain [2]:

$$\begin{aligned}\int_\Sigma \mathrm{d}S\left(\sigma - 2\sigma\delta H + 2\lambda H^2\right) &= 4\pi\sigma R_0^2 + \frac{\sigma R_0^2}{2}\sum_{l>0,m}(l^2+l+2)x_{l,m}^2 \\ -8\pi\sigma\delta R_0 - \sigma\delta R_0\sum_{l>0,m} l(l+1)x_{l,m}^2 &+ 8\pi\lambda + \frac{\lambda}{2}\sum_{l>1,m} l(l+1)(l-1)(l+2)x_{l,m}^2 \,. \end{aligned} \tag{40}$$

Finally, we specify the integral measure in (34):

$$\int \mathcal{D}\Sigma = \int_{-\infty}^{+\infty}\prod_{l>0,m}\left(\frac{S}{s}\,\mathrm{d}x_{l,m}\right)\int_0^{+\infty}\frac{\mathrm{d}R_0}{a}\,, \tag{41}$$

where $S = (36\pi)^{1/3}V^{2/3}$ is the area of the spherical surface of volume V and $s = 4\pi a^2$. Equation (41) follows from requiring that the present theory be the continuum limit of the field theory for a solid-on-solid (SOS) model whose heights are defined on nodes uniformly placed over a sphere of radius $\sqrt{S/(4\pi)}$ [2].

We can now compute the partition function (34). We calculate first the integral on R_0 by rearranging the delta function in Z_s as

$$\delta\left(\frac{4}{3}\pi R_0^3 f(\{x\}) - V\right) = \frac{\delta\left(R_0 - [4\pi f(\{x\})/(3V)]^{-1/3}\right)}{(36\pi)^{1/3}V^{2/3}f(\{x\})^{1/3}}\,. \tag{42}$$

After doing the trivial integral over R_0, we remain with a factor $f(\{x\})^{-1/3}$ which, within a quadratic theory, can be treated as follows:

$$f(\{x\})^{-1/3} = \left(1 + \frac{3}{4\pi}\sum_{l>0,m}x_{l,m}^2\right)^{-1/3} \simeq 1 - \frac{1}{4\pi}\sum_{l>0,m}x_{l,m}^2 \simeq \exp\left\{-\frac{1}{4\pi}\sum_{l>0,m}x_{l,m}^2\right\}\,. \tag{43}$$

In the end, we arrive at a Gaussian integral which is readily computed:

$$\begin{aligned} Z_s &= (36\pi)^{-1/3}\left(\frac{V}{a^3}\right)^{-2/3}\exp\left\{\beta\rho_s|\Delta\mu|V - \beta\sigma S - 8\pi\beta\lambda + 8\pi\beta\sigma\delta\left(\frac{3V}{4\pi}\right)^{1/3}\right\} \\ &\times \left(\frac{2\pi S}{s}\right)^3\prod_{l>1}\left\{\left(\frac{s}{2\pi S}\right)^2\left[1 + \frac{\beta\sigma S}{2}(l^2+l-2) + 2\pi\beta\lambda\, l(l+1)(l-1)(l+2)\right.\right. \\ &- \left.\left. 4\pi\beta\sigma\delta\sqrt{\frac{S}{4\pi}}(l^2+l-2)\right]\right\}^{-(l+1/2)}\,. \end{aligned} \tag{44}$$

Without a proper ultraviolet cutoff $l_{\max}$, the l sum in $F_s = -k_BT\ln Z_s$ does not converge. This is a typical occurrence for field theories on the continuum, which do not take into account the granularity of matter at the most fundamental level. We fix $l_{\max}$ by requiring that the total number of (l, m) modes be equal to the average number of SOS heights/atoms on the cluster surface. It thus follows:

$$l_{\max} = \frac{\sqrt{S}}{a} - 1\,. \tag{45}$$

With this cutoff, the surface free energy becomes $F_s = \gamma(S)S$, with a surface tension $\gamma(S)$ dressed by thermal fluctuations:

$$\begin{aligned} \gamma(S) \;&=\; \sigma + \frac{k_BT}{2S} \sum_{l=2}^{\sqrt{S}/a-1} (2l+1) \ln\left[A + B(l^2+l-2) + C(l^2+l-2)^2\right] \\ &-\; 2\sigma\delta\left(\frac{4\pi}{S}\right)^{1/2} - 2\frac{k_BT}{S}\ln\left(\frac{S}{a^2}\right) - 3\frac{k_BT}{S}\ln\left(\frac{2\pi a^2}{s}\right) + \frac{8\pi\lambda}{S}\,. \end{aligned} \tag{46}$$

The quantities A, B, and C in Eq. (46) are given by

$$A = \frac{A_0}{S^2}\,,\quad B = \frac{2C_0}{S^2} + \frac{D_0}{S\sqrt{S}} + \frac{B_0}{S}\,,\quad C = \frac{C_0}{S^2}\,, \tag{47}$$

where

$$A_0 = \frac{s^2}{4\pi^2}\,,\quad B_0 = \frac{\beta\sigma s^2}{8\pi^2}\,,\quad C_0 = \frac{\beta\lambda s^2}{2\pi}\,,\quad D_0 = -\frac{\beta\sigma\delta s^2}{2\pi\sqrt{\pi}}\,. \tag{48}$$

By the Euler-Mac Laurin formula, the residual sum in Eq. (46) can be evaluated explicitly. After a tedious and rather lengthy derivation, we obtain (for $\lambda \neq 0$):

$$\begin{aligned} &\gamma(S) = \sigma + \frac{k_BT}{2a^2}\left[\ln\frac{B_0}{a^2e^2} + \left(1 + \frac{B_0a^2}{C_0}\right)\ln\left(1 + \frac{C_0}{B_0a^2}\right)\right] \\ &+ \left[-2\sigma\delta + \frac{k_BTD_0}{4C_0\sqrt{\pi}}\ln\left(1 + \frac{C_0}{B_0a^2}\right)\right]\left(\frac{4\pi}{S}\right)^{1/2} - \frac{7}{6}k_BT\frac{\ln(S/a^2)}{S} \\ &+ \Bigg[8\pi\beta\lambda - 3\ln\frac{2\pi a^2}{s} - \frac{11}{6}\ln\frac{B_0}{a^2} + 3 - \frac{5}{3}\ln 2 - \frac{25}{96} + \frac{121}{46080} \\ &+ \frac{D_0a}{4C_0} - \frac{D_0^2}{4B_0C_0} - \frac{1}{6}\ln\left(\frac{B_0}{a^2} + \frac{C_0}{a^4}\right) + \frac{1}{8C_0(B_0a^2+C_0)^2} \\ &\times \Bigg(-4B_0C_0D_0a^3 - 18B_0C_0^2a^2 - 2C_0^2D_0a - \frac{28}{3}C_0^3 - \frac{26}{3}B_0^2C_0a^4 \\ &-2B_0^2D_0a^5 + 2B_0D_0^2a^4 + 2C_0D_0^2a^2\Big)\Big]\,\frac{k_BT}{S}\,, \end{aligned} \tag{49}$$

up to terms $o(S^{-1})$. We wrote a computer code to evaluate the sum in (46) numerically, and so checked that every single term in Eq. (49) is correct. In the notation of MT, the interface free energy $\gamma(S)$ has the form:

$$\gamma = \widetilde{\sigma}\left(1 - \frac{2\widetilde{\delta}}{R} + \frac{\widetilde{\epsilon}}{R^2}\right) - \frac{7}{3}k_BT\frac{\ln(R/a)}{4\pi R^2}\,, \tag{50}$$

with $R = [3V/(4\pi)]^{1/3}$ and T-dependent expressions for $\widetilde{\sigma}, \widetilde{\delta}$, and $\widetilde{\epsilon}$ that can be read in Eq. (49). At coexistence, the values of $\widetilde{\sigma}$ and $\widetilde{\delta}$ for a quasi-spherical cluster differ from those in Landau theory (i.e., σ and δ) for fluctuation corrections which are the effect of thermally excited capillary waves on the cluster surface.

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