

Nucleation and the Solid–Liquid Interfacial Free Energy

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Abstract

This article reviews the current understanding of the fundamentals of nucleation theory and its use to extract values for the solid–liquid interfacial free energy from experimental and simulation data.

Keywords: clusters, density functional theory, field theoretic models, interfaces, interfacial free energy, molecular dynamics, nucleation kinetics.

Introduction

Ever since Gibbs¹ formulated the work necessary to form a heterophase fluctuation, or cluster, as the sum of a bulk and an interfacial term, nucleation experiments have been central to the study of solid–liquid interfaces and measurements of the interfacial free energy. This picture has since become considerably more complicated: several structures may compete, even in simple liquids (fcc, bcc, icosahedral, etc.); the size of the critical cluster is similar to the thickness of the molecularly diffuse interface; the interior of the critical cluster may not have macroscopic bulk properties; the shape of the cluster may be nonspherical or even highly irregular (see Figure 1); and the interfacial free energy may depend on curvature and temperature. Furthermore, the formulation of the kinetic model that translates these energetics into a nucleation rate requires considerable care. This article takes a brief, critical look at our current understanding.

Reversible Work to Form a Cluster Thermodynamics

Gibbs¹ made the connection between interfacial free energy and the reversible work W to form a cluster of a new phase in (unstable) equilibrium with a parent phase:

$$W = -(p - p_0)V + A\gamma, \quad (1)$$

where p , V , and A are, respectively, the pressure, volume, and area of the cluster; p_0 is the pressure of the parent phase; and γ is the interfacial free energy. For all but the earliest theory of nucleation rate,² the extension of the reversible work to noncritical sizes is required, yet there is no universal agreement on the nature of the size-dependent reversible work. While Gibbs did not identify W with a specific free energy, later workers have variously equated W for arbitrary size to the change in Gibbs free energy,³ Helmholtz free energy,⁴ or grand potential⁵ when the system is held, respectively, at constant (NTp) , (NTV) , or (μTV) conditions. Here N is the total number of molecules, assuming a pure system; T is the temperature; and μ is the chemical potential.

For nucleation from a condensed phase, the dominant viewpoint is that W is the change in Gibbs free energy, which for a single-component system is

$$W_n = -\Delta\mu_\infty n + A\gamma, \quad (2)$$

where n is the number of molecules in the cluster and $\Delta\mu_\infty$ is the difference in the bulk chemical potentials of the two phases. Actually, this expression cannot be the true Gibbs free energy change, for because of the Laplace pressure and the Gibbs–Duhem relation, the chemical poten-

tial of a small cluster ought to differ from the bulk value. Abraham has noted this discrepancy and attributed it to the assumption that the new phase is incompressible,⁴ that is, W looks like an apparent Gibbs free energy only because of incompressibility. On the other hand, Abraham's view that W is the change in the Helmholtz free energy at constant (NTV) may be at odds with a steady-state theory for the nucleation rate, because a density difference between the two phases implies a change in driving force as the transformation proceeds.

Recent analysis⁶ shows that the correct reversible work for forming a cluster of arbitrary size is the change in the availability of energy, or exergy,

$$W = \Delta U - T_0\Delta S + p_0\Delta V - \mu_0\Delta N, \quad (3)$$

where U and S are, respectively, the internal energy and the entropy; the subscripted intensive variables, T_0 , p_0 , and μ_0 , are properties of the reservoir in contact with the parent phase; and the differences of extensive variables are calculated for the system in contact with the reservoir. This result is correct regardless of the type of constraint imposed by the reservoir. In particular, for (NTp) , W is not the change in Gibbs free energy because p is not homogeneous in the system when a cluster is formed; for (μTV) , W is not the change in the grand potential because μ is not homogeneous when a (noncritical) cluster is formed; and for (NTV) , W is not the change in Helmholtz free energy unless the effect of latent heat can be ignored and the temperature of a cluster is the same as that of the parent phase. These observations have important implications for the interpretation of computer simulations or theoretical calculations aimed at obtaining the form of the nucleation barrier.

As for the appropriate constraint for a steady-state nucleation theory, (μTV) keeps the driving force constant and is thus most natural. Under this constraint, W for cluster formation takes the explicit form

$$W_n = -(p - p_0)V - \Delta\mu n + A\gamma, \quad (4)$$

where $\Delta\mu$ is the actual difference in chemical potential between the parent phase and the small cluster. Generalization to multi-component systems is straightforward. If the stable phase is incompressible, this expression reduces to the conventional expression (Equation 2), in agreement with Abraham's observation,⁴ but for cavitation, in which the internal phase is a compressible gas, the general expression must be used. We note that in the thermodynamic limit where the total number of particles N be-

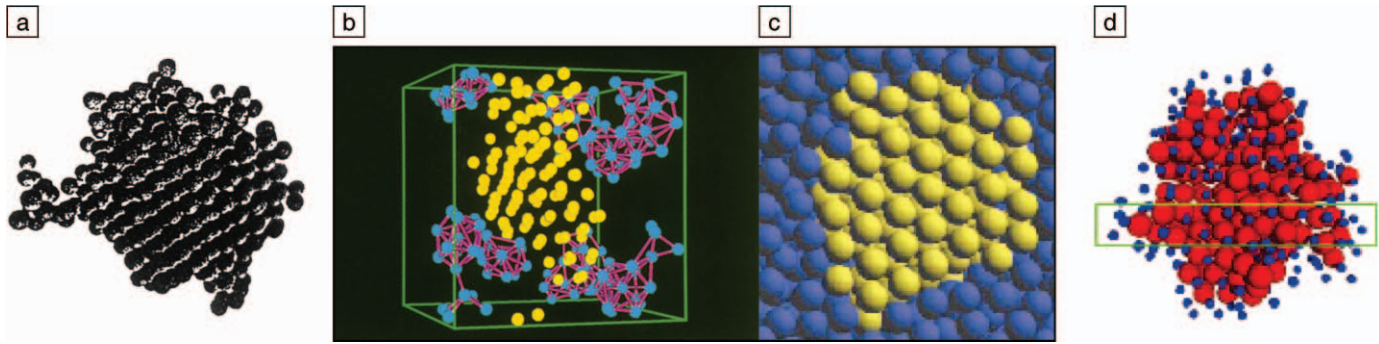


Figure 1. Four examples of crystal nuclei in atomistic simulations and experiment: (a) in a Lennard–Jones liquid,⁷⁹ (b) in a Lennard–Jones glass,⁸⁰ (c) in a hard-sphere fluid,⁸¹ and (d) in a colloidal suspension recorded by scanning laser confocal microscopy.⁸² Note the crystal-like atomic order at the central part of the fluctuations and the irregular shape of the surface.

comes very large, W is invariant to the constraint because the change in the driving force with the formation of a single cluster becomes negligible; however, in computer simulations where N is small, the various constraints differ to leading order by terms proportional to $(n/N)^2$.⁶

Connection between Thermodynamics and Kinetics

Nucleation is inherently a kinetic process and can be modeled as a series of bimolecular reactions involving clusters of the new phase. If these clusters are assumed to grow only by the addition and subtraction of monomers (one-step approximation), the net flux in size space between sizes n and $(n + 1)$ is

$$J_{n \rightarrow n+1} = \beta_n f_n - \alpha_{n+1} f_{n+1}, \quad (5)$$

where β_n and α_n are, respectively, the forward and backward rate constants for the n cluster and f_n is the number density of clusters of the new phase. In most cases, a model for β exists (e.g., kinetic theory for condensation and transition state theory for crystallization), but one for α is lacking. Nevertheless, a formal solution for the steady-state nucleation rate is facilitated by the introduction of a zero-flux distribution, z_n , that satisfies $0 = \beta_n z_n - \alpha_{n+1} z_{n+1}$. Given the boundary condition $z_1 = f_1$, this distribution can be found recursively and written in the form $z_n = f_1 \exp(-\Phi_n/k_B T)$, where the kinetic potential Φ is defined as

$$\Phi_n = k_B T \sum_{i=2}^n \ln(\alpha_i/\beta_{i-1}), \quad (6)$$

with k_B being the Boltzmann constant. Solved under the no-depletion condition for the monomers, the steady-state nucleation rate is

$$J = \left(\sum_{n=1}^{\infty} 1/[\beta_n z_n] \right)^{-1}. \quad (7)$$

Since we expect Φ to reach a maximum at a critical size n^* (kinetic bottleneck), $1/[\beta_n z_n]$ should peak around n^* , which means that this sum is dominated by terms in the vicinity of n^* . In the manner of Frenkel and Zeldovich,^{3,8} this sum can be replaced by an integral and evaluated using the Laplace method⁹ (asymptotic analysis):

$$J = \frac{f_1 \beta_{n^*}}{\sqrt{2\pi} w} \exp\left\{-\frac{\Phi_{n^*}}{k_B T}\right\}, \quad (8a)$$

where

$$w = \sqrt{-k_B T/\Phi_{n^*}''} \quad (8b)$$

is the approximate width or standard deviation of the kinetic bottleneck, and all quantities with a subscripted $*$ are evaluated at the critical size. Thus far, no specific assumptions about the kinetic potential have been made besides the existence of a bottleneck, so this result is subject only to the accuracy of the one-step approximation and the asymptotic analysis. For the latter, the estimate is expected to be accurate if n^* and $\Phi_{n^*}/k_B T$ are large and n^*/w is moderately large, compared to 1. On the other hand, because the general multistep process is nonlinear, the accuracy of linear analysis¹⁰ is hard to assess; therefore, the importance of multistep reactions remains an open problem, although it might be argued that because the mobility of crystalline clusters in a liquid is low, higher-order reactions, which do not involve monomers, should not contribute significantly to the nucleation rate. Interpreted through the general expression in Equation 8a, nucleation rate measurements allow estimates of the height and width of the kinetic bottleneck as well as the forward rate constant at the bottleneck, although not independently.

In order to derive the rate ascribed to the classical nucleation theory (CNT), additional

assumptions and approximations are required. The first is the so-called constrained equilibrium hypothesis (CEH): $\Phi = W$. Since z_n is now proportional to $\exp(-W_n/k_B T)$, a probability for fluctuations about equilibrium derived from statistical mechanics,¹¹ it is an equilibrium distribution. This distribution is only hypothetical and hence unmeasurable, because it cannot persist without constraints in the presence of a driving force for phase change.¹² CEH shifts a kinetic problem, that of determining the set of α_n , to a thermodynamic one, that of determining $\Delta\mu_{\infty}$ and γ in Equation 2 for an incompressible new phase. Another simplification is the capillarity approximation, whereby γ is assumed to be size-independent and is equal to the interfacial free energy for coexistence equilibrium at the temperature of interest: $\gamma = \gamma_{\text{eq}}$. Next, for solidification from the melt, because $\Delta\mu_{\infty}$ is difficult to measure for large undercooling, it is often taken to be $\Delta H_f \Delta T/T_m$ (equal specific heats),¹³ where ΔH_f is the heat of fusion per unit volume, T_m is the melting temperature, and ΔT is the undercooling $T_m - T$. Finally, the Turnbull–Fisher form for β ¹⁴ is used (transition-state theory), supplemented by an estimate for the number of accommodation sites on the surface of a sphere.¹⁵ Altogether, these lead to the CNT form for the steady-state nucleation rate:⁷

$$J = 24 \left(\frac{2\Omega}{9\pi} \right)^{1/3} \frac{Df_1}{\lambda^2} \sqrt{\frac{\gamma_{\text{eq}}}{k_B T}} \times \exp\left\{-\frac{16\pi T_m^2}{3k_B(\Delta H_f)^2} \frac{\gamma_{\text{eq}}^3}{T(\Delta T)^2}\right\}, \quad (9)$$

where Ω is the atomic volume in the crystal, D is the diffusion coefficient in the liquid, and λ is a jump distance.

A comparison of CNT to measurements of J shows a mixed picture.¹⁶ While the tem-

perature variation of the argument of the exponential is approximately correct in most cases, the predicted prefactor is several orders of magnitude too low for metals (10^{-7} in Hg) and typically 20–25 orders of magnitude too low for glasses. It should be pointed out, however, that independent determination of γ_{eq} for condensed systems is difficult; in most cases, it is treated as a fit constant, and when it is allowed to depend on T linearly, the disparity between the predicted and fitted prefactors is greatly reduced. As for glasses, D is obtained from the viscosity η via the Stokes–Einstein relation, and changing assumptions about the T -dependence of η or $\Delta\mu_{\infty}$ can greatly affect the value of the fitted prefactor.

An additional source for the uncertainty in γ arises from the morphology of a cluster in the vicinity of the critical size. As shown in Figure 1, crystalline clusters observed in both experiments and computer simulations have a rough morphology, contrary to the CNT assumption of spherical clusters. This result can be understood qualitatively by comparing the relaxation time for surface diffusion, τ_{rel} , to the mean lifetime of a critical cluster, τ_{life} . Since $\tau_{\text{rel}} = \lambda^2/2D$, and

$$\tau_{\text{life}} = (\alpha_* + \beta_*)^{-1} \leq \beta_*^{-1} = \lambda^2/(6mD), \quad (10)$$

where m is the number of accommodation sites on the surface of the cluster,¹⁴ the ratio $\tau_{\text{rel}}/\tau_{\text{life}} \geq 3m$. Even if the cluster were spherical, this ratio would exceed 100 for n^* as small as 25.¹⁵ Thus, a critical cluster is expected to be rough because it changes size many times before surface diffusion can smooth out the irregularities caused by repeated attachment and detachment of molecules at its surface. This has implications for interpretation of measurements using Equation 9: (1) the estimate of γ_{eq} may only be an upper bound because the actual surface area of the critical cluster is larger than that for a sphere; (2) the prefactor ought to be larger because β_* is proportional to surface area (although this cannot explain the orders-of-magnitude discrepancy between the CNT prefactor and the fitted value when γ_{eq} is assumed to be constant). More generally, one could question whether γ_{eq} , a quantity defined at equilibrium for a planar interface, has relevance for a rough cluster that fluctuates in size and morphology faster than the process for structural relaxation. It may be that γ inferred from nucleation rate measurements in solidification is a dynamic, rather than a static, property. This underscores the importance of ultimately developing a molecular theory of nucleation.

Interfacial Free Energy Dependence of Interfacial Free Energy on Temperature and Size

There are good reasons, related to the entropy loss due to ordering of the liquid near the interface, why γ could increase with T . In the CNT analysis of his nucleation data in Hg, Turnbull¹³ pointed out that a normal prefactor implied a linearly increasing $\gamma(T)$. Gránásy^{17,18} and Spaepen^{19,20} reached a similar conclusion with phenomenological theories of the diffuse interface. The parameters in Spaepen's analysis are consistent with the interface width and entropy loss in a static hard-sphere model of the interface.^{21,22} An analysis by Gránásy,^{23,24} using various nonclassical cluster models, of the temperature-dependence of γ for

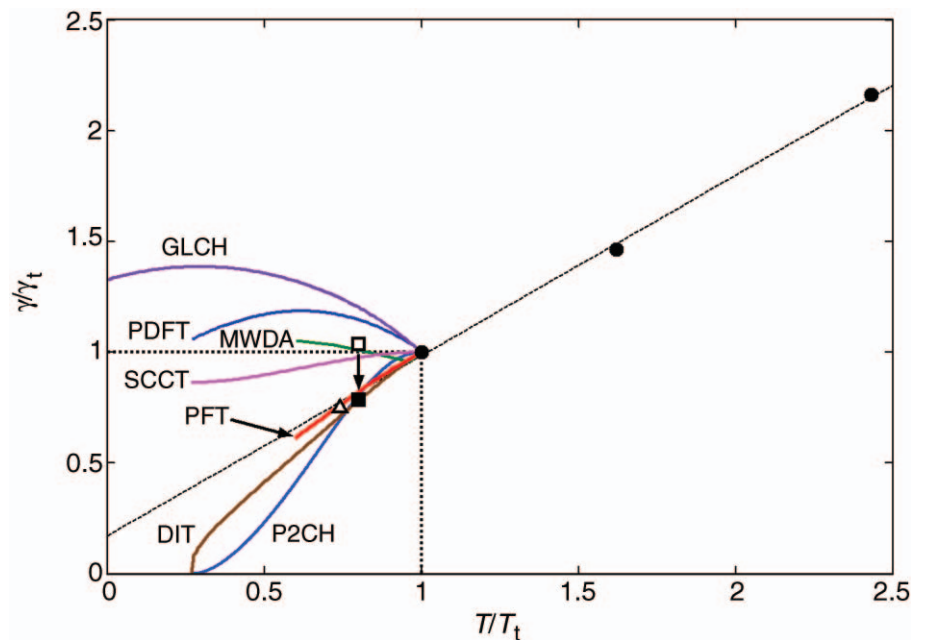
critical clusters in the Lennard–Jones (LJ) system is shown in Figure 2.

The capillarity approximation may also break down at small size and require what is commonly called a curvature correction. We will first consider the vapor–liquid interface because it is simpler and has been studied more intensively.

The most famous theory for a curvature-dependent γ is by Tolman:²⁵

$$\gamma = \gamma_{\infty}/(1 + \delta_T/R), \quad (11)$$

where δ_T is the Tolman length, γ_{∞} is the planar limit, and R is the radius of the particle. However, in the size range of the critical nuclei, the Tolman length is a strong



GLCH	Cahn–Hilliard theory with Ginzburg–Landau free energy
PDFT	Perturbative density functional theory
MWDA	Modified weighted density approximation
SCCT	Self-consistent classical theory
PFT	Phase field theory
DIT	Diffuse interface theory
P2CH	Cahn–Hilliard theory with double parabolic free energy

Figure 2. The reduced interfacial free energy (γ/γ_t) of critical fluctuations for the Broughton–Gilmer-type modified Lennard–Jones system as a function of reduced temperature (T/T_t), as predicted by various nonclassical cluster models. Here, γ_t is the interface free energy for the equilibrium planar solid–liquid interface at the triple point (T_t). The reduced interfacial free energy has been defined as $\gamma/\gamma_t = (W_*/W_*^{\text{CNT}})^{1/3}$, where W_* is the work of forming a critical fluctuation in the nonclassical theory, and W_*^{CNT} is the classical work of formation calculated with γ_t and the bulk Gibbs free energy difference (for details of the calculations, see References 23 and 24). For the sake of comparison, molecular dynamics results for the equilibrium planar interface $\gamma_{\infty}(T)$ (solid circles), an interfacial free energy value deduced from the nucleation rate of Báez and Clancy⁸³ (open triangle), and the results from Monte Carlo simulations⁸⁴ (squares) are also shown; the open square has been calculated with inconsistent data, while the solid square was calculated with consistent data (see Reference 23).

function of R .^{26,27} The usefulness of Tolman's theory for nucleation is thus questionable.

An alternative theory by McGraw and Laaksonen specifically devised for vapor–liquid nucleation predicts that γ for the critical cluster has a correction inversely proportional to surface area, i.e., $\gamma = \gamma_\infty + C(T)/A_*$, where C is an arbitrary function.^{28,29} Their theory assumes that CNT correctly predicts the critical size; thus, the only correction to the CNT's reversible work is the "interfacial curvature free energy," $C(T)$. The most important consequences of their theory are thus: $n_* = n_*^{\text{CNT}}$ and $W_* = W_*^{\text{CNT}} + C(T)$. These relations compare favorably to density functional calculations^{28,29} and computer simulation using umbrella sampling,³⁰ both for a LJ fluid, and to empirical observations in H_2O , D_2O , alcohols, and n -nonane (see references in Reference 31). For H_2O , Wölk et al.³¹ showed that data compiled from different groups using diverse methods such as nucleation pulse chamber, expansion chamber, shock tube, and supersonic nozzle measured over an extended range of T and supersaturation ratio S compares favorably to the empirical correction factor³²

$$J/J^{\text{CNT}} = \exp(-27.56 + 6.5 \times 10^3 T^{-1}), \quad (12)$$

although there is some scatter due to a relatively weak S dependence. If the CNT prefactor for vapor–liquid nucleation is assumed to be correct (a view supported by molecular theory³³ and computer simulations of condensation),³⁴ the discrepancy between CNT and vapor–liquid nucleation measurements can be attributed essentially to $C(T)$. Interestingly, molecular dynamics studies of planar vapor–liquid interfaces using periodic boundary conditions report that, relative to the infinite size limit, γ also has a correction inversely proportional to the area of the interface for a LJ fluid³⁵ and a molten KI salt,³⁶ in agreement with the prediction of a Gaussian model of capillary waves.³⁷ This suggests that rather than depending on curvature per se, deviations of γ from constancy for the vapor–liquid interface are a finite size effect.

Hale et al.^{38–40} performed Monte Carlo simulations on the cluster energetics of water clusters, unary and binary LJ systems, and binary sulfuric acid–water. They found that when the differential Helmholtz energy, $F_n - F_{n-1}$, is plotted versus $n^{-1/3}$ [essentially $n^{2/3} - (n-1)^{2/3}$], the data points fit well to a straight line down to n as small as 5–10, which suggests that even very small clusters already exhibit bulklike behavior. However, this observation is diffi-

cult to reconcile with ten Wolde and Frenkel's LJ simulation,³⁰ which shows that small liquid clusters have very diffuse density profiles and that the density at the center of mass of a cluster does not even reach the bulk value until n is nearly 100; thus it would seem improbable that a much smaller cluster could already exhibit bulklike behavior, or, alternatively, that its interface is fully as wide as that of a large cluster. This paradox can be resolved using kinetic arguments, as we show in the next section.

Kinetic Theory for Finite Size Correction

As pointed out earlier, the constrained equilibrium hypothesis (CEH) is a central assumption of classical nucleation theory (CNT). Katz et al. have developed kinetic theories of nucleation without appealing to CEH for condensation¹² and crystallization.⁴¹ Wu⁷ has shown that their theories are logically equivalent to the self-consistent classical theory (SCCT), for which the kinetic potential is defined as $\Phi_n = W_n^{\text{CNT}} - W_1^{\text{CNT}}$. SCCT was originally developed by Girshick and Chiu⁴² for condensation in order to remove the inconsistency $W_1^{\text{CNT}} \neq 0$. Wu⁷ has shown that SCCT can be derived by the kinetic assumption that for all $n > 1$,

$$\Phi_n - \Phi_{n-1} = W_n^{\text{CNT}} - W_1^{\text{CNT}}, \quad (13)$$

which is equivalent to

$$k_B T \ln(\alpha_n / \beta_{n-1}) = -\Delta\mu_\infty + (36\pi\Omega^2)^{1/3} \gamma_{\text{eq}} \{n^{2/3} - (n-1)^{2/3}\} \quad (14)$$

and asserts that the ratio of backward to forward rate constants takes on bulk behavior for all sizes, no matter how small. Supplemented by the self-consistent boundary condition $\Phi_1 = 0$, Φ_n is then uniquely determined by summing the differential relation. The finite size effect, as far as kinetic behavior is concerned, can be defined by violation of the differential relation for small size:⁴³ Given some criterion for kinetic convergence, i.e., a size n_0 such that Equation 14 is satisfied to within some tolerance for $n > n_0$, then $\Phi_n = W_n^{\text{CNT}} + C$ for $n > n_0$, where C , in this case, is the sum of the self-consistency correction and a "kinetic excess." For this model to accommodate the breakdown of the capillarity approximation, γ_{eq} in Equation 14 and in the definition of C ought to be replaced by γ_z , which can in principle depend on both T and p , although for crystallization this is a moot point if γ_{eq} is unknown. An analy-

sis⁴³ of McGraw and Laaksonen's results²⁸ shows that depending on the supersaturation, γ_{eq} exceeds the result from SCCT by 4–31%.

A number of connections can now be made with previous discussions on theory, simulation, and experiments on condensation:

1. The simulation results of Hale et al.^{38–40} can be interpreted within this kinetic model, as n_0 is the largest size at which the data points deviate from bulk, straight-line behavior, and the slope is $\gamma_\infty(36\pi\Omega^2)^{1/3}$.
2. For condensation from ideal gas, $\Delta\mu_\infty = k_B T \ln S$ (supersaturation), and the assumptions that β_n is proportional to S and α_n is independent of S are reasonable;¹² thus, the only pressure-dependence of C comes from the self-consistency correction

$$W_1^{\text{CNT}} = -k_B T \ln S + \gamma_{\text{eq}}(36\pi\Omega^2)^{1/3}, \quad (15)$$

which is a relatively weak dependence. Therefore, for $n_0 < n^*$, this theory reproduces McGraw and Laaksonen's interfacial curvature free energy $C(T)$ in the critical reversible work^{28,29} and ascribes its origin to finite size kinetic effects rather than curvature. That their theory describes measured rates in H_2O at conditions⁴⁴ where n^* is as small as 10 supports the value of n_0 deduced from Hale et al.'s calculations.^{38–40}

3. That ten Wolde and Frenkel's simulation³⁰ shows much slower convergence to bulk behavior for the density does not contradict the small experimental and simulational estimates for n_0 because thermodynamic convergence may be slower than kinetic convergence, for which the ratio α_n / β_{n-1} is of interest, rather than the individual rate constants. The usefulness of this kinetic theory for condensation suggests its extension to solid–liquid nucleation. The chief concern for its applicability has to do with n_0 . For condensation, it appears to be 10 or less, so that the use of the general Equation 8a to interpret J is fully justified except at extremely high S when asymptotic analysis for the evaluation of J breaks down. For crystallization, n_0 is unknown, although one might expect it to be larger because crystalline clusters are probably rougher and farther away from equilibrium than liquid clusters. However, even in the large size limit, a growing solid–liquid interface may be rough, so roughness may be an intrinsic property of the solid–liquid interface in some cases, which would remove its role in determining n_0 . Moreover, higher roughness is expected to increase both α_n and β_{n-1} , so their ratio may be largely independent of roughness. It is thus plausible that n_0 may

be only modestly large for crystallization from an undercooled melt. Because p is held constant, the kinetic potential should take the same form as McGraw and Laaksonen's theory,^{28,29} $\Phi_n = W_n^{\text{CNT}} + C(T)$. The sign of C can be either positive or negative, depending on whether $\ln(\alpha_n/\beta_{n-1})$ for the smallest clusters is predominantly greater than or less than that for bulk behavior; it may even change with T , as is the case for H₂O condensation.³¹

Field Theoretic Models

The small heterophase fluctuations can be naturally handled in the framework of *continuum* (field theoretic) models, which are able to address local physical states (e.g., interfacial states) that differ from the bulk crystal or liquid states. The starting point of the field theoretic approaches is a free energy functional that depends on coarse-grained order parameter(s) that characterize the local physical state. The critical fluctuation represents an extremum of the free energy functional (saddle point in the appropriate function space), which can be found by solving the respective Euler–Lagrange equation(s).

In the past decades, various field theoretic models have been worked out for crystal nucleation. Many of them are direct descendants of the single-order-parameter *gradient theories* by van der Waals⁴⁵ and Cahn and Hilliard (CH),⁴⁶ which approximate the free energy functional of the inhomogeneous system (liquid + critical fluctuation) by the form

$$W_{\text{CH}} = \int d^3r \{ \Delta\omega[m(\mathbf{r})] + c(\nabla m)^2 \}, \quad (16)$$

where m is, in this case, a structural order parameter (e.g., the amplitude of the dominant Fourier component of the crystal singlet density), c is a constant, the grand potential density $\Delta\omega$ measured relative to the mother phase has a double-well form, and the square-gradient term $(\nabla m)^2$ gives rise to the diffuse interface. The critical fluctuation (nucleus) represents a saddle point of the W_{CH} functional. The respective $m(\mathbf{r})$ emerges as a nontrivial solution of the Euler–Lagrange equation,

$$0 = \partial\Delta\omega/\partial m - 2c\nabla^2 m, \quad (17)$$

under boundary conditions $m \rightarrow m_0$ for $|\mathbf{r}| \rightarrow \infty$ and $\nabla m \rightarrow 0$ for $|\mathbf{r}| \rightarrow 0$, where $m_0 = 0$ is the order parameter of the supersaturated liquid. For spherical symmetry (the anisotropy of the interface free energy γ is weak), the Euler–Lagrange equation reduces to an ordinary differential equation. If the free energy density is of piecewise parabolic form, the Euler–Lagrange equation

becomes linearized, and the solution can be found analytically. This method has been used to study crystal nucleation and growth in one-component liquids,^{47,48} hard-sphere crystallization,⁴⁹ and crystallization in the presence of metastable phases.⁵⁰

The density functional technique (DFT) offers a microscopic (molecular), rather than phenomenological, route to crystallization, which considers either the crystalline structure and/or molecular interactions. Applications to crystal nucleation include the perturbative DFT by Harrowell and Oxtoby,⁵¹ the modified weighted density approximation by Shen and Oxtoby,⁵² and the Ginzburg–Landau method adopted by Iwamatsu and Horii⁵³ and by Gránásy and Pusztai.⁵⁴ Critical comparison with experiment has been presented by Gránásy and Iglói⁵⁵ and Gránásy and James.^{56,57} The DFT successfully addresses such long-standing problems as the role of metastable bcc structure during fcc solidification⁵⁸ and the effect of the metastable critical point on crystal nucleation,⁵⁹ essential for understanding protein crystallization.

Important generalizations of the Cahn–Hilliard theory are the Hohenberg–Halperin⁶⁰ C-type field theoretic models in which the time evolution of the nonconserved structural order parameter is coupled to other fields of conserved dynamics. In the *phase field theory*, the conserved fields are the heat or chemical composition or both.^{61–64} This approach emerges as the method of choice for modeling complex solidification morphologies.^{65,66} In the phase field simulations, the proper statistical mechanical treatment of the nucleation process requires the introduction of uncorrelated Langevin noise terms into the governing equations with amplitudes that are determined by the fluctuation-dissipation theorem.^{67–70} This approach has been used to treat the nucleation of primary dendritic and eutectic particles with different crystal orientations.²⁴ The differences in crystal orientation were described by a nonconserved orientational order parameter, which assumes fluctuating random values in the liquid to model short-range order.²⁴ Other polycrystalline solidification morphologies that can be modeled include the disordered dendritic morphologies observed in clay–polymer films, fractal-like crystalline aggregates, and spherulites.^{71,72} Nucleation of different crystallographic orientations at the growth front is also captured by this model.⁷³

The phase field theory can also be used to calculate the height of the nucleation barrier.^{24,74} When the model parameters are set so that the free energy and thickness of the equilibrium planar interface are recovered, good quantitative agreement has been

achieved, *without adjustable parameters*, with the results of LJ computer simulations and with experiments on ice nucleation in undercooled water.²⁴ For Ni–Cu alloys, reasonable values have been obtained for the temperature- and composition-dependence of the interfacial free energy, to match critical undercoolings measured in electromagnetically levitated droplets. Similar results have been obtained in a phase field theory that relies on two fields (structural order parameter and density) for crystal nucleation in the hard-sphere fluid.⁷⁵

The continuum models predict different temperature dependencies for the nuclei, as reviewed by Gránásy and Iglói⁵⁵ and Gránásy and James^{56,57} and summarized in Figure 2. Some of the density functional approaches predict a negative temperature coefficient for γ at small undercoolings for the LJ system. It seems to be in contradiction with a recent finding by molecular dynamics⁷⁶ that $\gamma_{\infty} \propto T$ for the equilibrium solid–liquid interface. In contrast, a realistic positive temperature coefficient is obtained from the Cahn–Hilliard theories based on piecewise parabolic free energies.^{55,48} A Cahn–Hilliard theory with triple-parabolic free energy⁴⁸ has been used to derive the Tolman length. In agreement with earlier results for liquid droplets, the Tolman length is strongly size-dependent.

A Cahn–Hilliard theory of ice nuclei with quartic free energy function predicts a positive temperature coefficient for the interface free energy.⁷⁷ The latter model has been used to evaluate interfacial properties from nucleation experiments on oxide glasses.⁷⁸ The model parameters were fitted to the nucleation barrier heights deduced from experiments by CNT; using these parameters, values for the magnitude of the interfacial free energy and the interface thickness were found in agreement with atomistic simulations for simpler systems. Remarkably, often the centers of the nuclei did not have bulk crystal properties.

The success of the phase field theory in predicting the nucleation barrier is attributable to the assumption that the coefficient of the gradient term and the height of the free energy barrier between the solid and liquid minima is proportional to the temperature,²⁴ yielding $\gamma_{\infty} \propto T$ and a constant thickness for an equilibrium solid–liquid interface, in good agreement with recent atomistic LJ simulations.⁷⁶ The temperature plot for the curvature-corrected interfacial free energy, though slightly curved, has a positive temperature coefficient.²⁴ These calculations show that under typical conditions, the size of the critical fluctuations is similar to the interface thick-

ness, and usually the center of the fluctuations does not have bulk properties.

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References

- J.W. Gibbs, *The Scientific Papers of J.W. Gibbs*, Vol. 1 (Dover, New York, 1961).
- M. Volmer and A. Weber, *Z. Phys. Chem.* **119** (1925) p. 277.
- J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, Oxford, 1946).
- F.F. Abraham, *J. Atmospheric Sci.* **25** (1968) p. 47.
- D.W. Oxtoby and R. Evans, *J. Chem. Phys.* **89** (1988) p. 7521.
- L. Zhuo and D.T. Wu, to be published.
- D.T. Wu, in *Solid State Physics*, Vol. 50, edited by H. Ehrenreich and F. Spaepen (Academic Press, San Diego, 1997) p. 37.
- J.B. Zeldovich, *Acta Physicochim. U.R.S.S.* **18** (1943) p. 1.
- C.M. Bender and S.A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers I* (Springer, New York, 1999).
- J.L. Katz, H. Saltsburg, and H. Reiss, *J. Colloid Interface Sci.* **21** (1966) p. 560.
- A. Einstein, *Ann. Phys.* **33** (1910) p. 1275.
- J.L. Katz and H. Wiedersich, *J. Colloid Interface Sci.* **61** (1977) p. 351.
- D. Turnbull, *J. Chem. Phys.* **20** (1952) p. 411.
- D. Turnbull and J.C. Fisher, *J. Chem. Phys.* **17** (1949) p. 71.
- K.F. Kelton, A.L. Greer, and C.V. Thompson, *J. Chem. Phys.* **79** (1983) p. 6261.
- K.F. Kelton, in *Solid State Physics*, Vol. 45, edited by H. Ehrenreich and D. Turnbull (Academic Press, Boston, 1991) p. 75.
- L. Gránásy, *J. Non-Cryst. Solids* **162** (1993) p. 301.
- L. Gránásy, *Europhys. Lett.* **24** (1993) p. 121.
- F. Spaepen, *Mater. Sci. Eng. A* **178** (1994) p. 15.
- F. Spaepen, in *Solid State Physics*, Vol. 47, edited by H. Ehrenreich and D. Turnbull (Academic Press, Boston, 1994) p. 1.
- F. Spaepen, *Acta Metall.* **23** (1975) p. 729.
- F. Spaepen, *Scripta Metall.* **10** (1976) p. 257.
- L. Gránásy, *Int. J. Non-Equilib. Process.* **11** (1998) p. 113.
- L. Gránásy, T. Börzsönyi, and T. Pusztai, *Phys. Rev. Lett.* **88** (2002) p. 206105-1.
- R.C. Tolman, *J. Chem. Phys.* **17** (1949) p. 333.
- H. Tomino, I. Kusaka, K. Nishioka, and T. Takai, *J. Crystal Growth* **113** (1991) p. 633.
- V. Talanquer and D. Oxtoby, *J. Chem. Phys.* **99** (1995) p. 2865.
- R. McGraw and A. Laaksonen, *Phys. Rev. Lett.* **76** (1996) p. 2754.
- R. McGraw and A. Laaksonen, *J. Chem. Phys.* **106** (1997) p. 5284.
- P.R. ten Wolde and D. Frenkel, *J. Chem. Phys.* **109** (1998) p. 9901.
- J. Wölk, R. Strey, C.H. Heath, and B.E. Wyslouzil, *J. Chem. Phys.* **117** (2002) p. 4954.
- J. Wölk and R. Strey, *J. Phys. Chem.* **105** (2001) p. 11683.
- V. Talanquer and D.W. Oxtoby, *J. Chem. Phys.* **100** (1994) p. 5190.
- P.R. ten Wolde, M.J. Ruiz-Montero, and D. Frenkel, *J. Chem. Phys.* **110** (1999) p. 1591.
- L.-J. Chen, *J. Chem. Phys.* **103** (1995) p. 10214.
- W.S. Aguado and P.A. Madden, *J. Chem. Phys.* **115** (2001) p. 8612.
- M.P. Gelfand and M.E. Fisher, *Physica A* **166** (1990) p. 1.
- B.N. Hale, *Aust. J. Phys.* **49** (1996) p. 425.
- J. Kiefer and B.N. Hale, in *Nucleation and Atmospheric Aerosols 2000*, edited by B.N. Hale and M. Kulmala (AIP Press, Melville, NY, 2000) p. 260.
- S.M. Kathmann and B.N. Hale, *J. Phys. Chem. B* **105** (2001) p. 11719.
- J.L. Katz and F. Spaepen, *Phil. Mag. B* **37** (1978) p. 137.
- S.L. Girshick and C.P. Chiu, *J. Chem. Phys.* **93** (1990) p. 1273.
- D.T. Wu, unpublished.
- Y.J. Kim, B.E. Wyslouzil, G. Wilemski, J. Wölk, and R. Strey, *J. Phys. Chem. A* **108** (2004) p. 4365.
- J.D. van der Waals, *Verhand. Koninkl. Akad. Wetensch. Amsterdam* **1** (1893) p. 1.
- J.W. Cahn and J.E. Hilliard, *J. Chem. Phys.* **31** (1959) p. 688.
- C.K. Bagdassarian and D.W. Oxtoby, *J. Chem. Phys.* **100** (1994) p. 2139.
- L. Gránásy and D.W. Oxtoby, *J. Chem. Phys.* **112** (2000) p. 2399.
- R. Wild and P. Harrowell, *Phys. Rev. E* **56** (1997) p. 3265.
- L. Gránásy and D.W. Oxtoby, *J. Chem. Phys.* **112** (2000) p. 2410.
- P. Harrowell and D.W. Oxtoby, *J. Chem. Phys.* **80** (1984) p. 1639.
- Y.C. Shen and D.W. Oxtoby, *J. Chem. Phys.* **105** (1996) p. 6517.
- M. Iwamatsu and K. Horii, *J. Phys. Soc. Jpn.* **65** (1996) p. 2311.
- L. Gránásy and T. Pusztai, *J. Chem. Phys.* **117** (2002) p. 10121.
- L. Gránásy and F. Iglói, *J. Chem. Phys.* **107** (1997) p. 3634.
- L. Gránásy and P.F. James, *Proc. R. Soc. London, Ser. A* **454** (1998) p. 1745.
- L. Gránásy and P.F. James, *J. Non-Cryst. Solids* **253** (1999) p. 210.
- Y.C. Shen and D.W. Oxtoby, *Phys. Rev. Lett.* **77** (1996) p. 3585.
- V. Talanquer and D.W. Oxtoby, *J. Chem. Phys.* **109** (1998) p. 223.
- P.C. Hohenberg and B.I. Halperin, *Rev. Mod. Phys.* **49** (1977) p. 435.
- R. Kobayashi, *Physica D* **63** (1993) p. 410.
- J.A. Warren and W.J. Boettinger, *Acta Metall. Mater.* **43** (1995) p. 689.
- A. Karma and W.-J. Rappel, *Phys. Rev. E* **57** (1998) p. 4323.
- M. Conti, *Phys. Rev. E* **61** (2000) p. 642.
- W.J. Boettinger, J.A. Warren, C. Beckermann, and A. Karma, *Annu. Rev. Mater. Res.* **32** (2002) p. 163.
- J.J. Hoyt, M. Asta, and A. Karma, *Mater. Sci. Eng., R* **41** (2003) p. 121.
- K.R. Elder, F. Drolet, J.M. Kosterlitz, and M. Grant, *Phys. Rev. Lett.* **72** (1994) p. 677.
- F. Drolet, K.R. Elder, M. Grant, and J.M. Kosterlitz, *Phys. Rev. E* **61** (2000) p. 6705.
- S.G. Pavlik and R.F. Sekerka, *Physica A* **268** (1999) p. 283.
- S.G. Pavlik and R.F. Sekerka, *Physica A* **277** (2000) p. 415.
- L. Gránásy, T. Pusztai, J.F. Douglas, J.A. Warren, T. Börzsönyi, and V. Ferreiro, *Nature Mater.* **2** (2003) p. 92.
- L. Gránásy, T. Börzsönyi, and T. Pusztai, in *Interface and Transport Dynamics, Computational Modelling*, Vol. 32, edited by H. Emmerich, B. Nestler, and M. Schreckenberg (Springer, Berlin, 2003) p. 190.
- L. Gránásy, T. Pusztai, T. Börzsönyi, J.A. Warren, and J.F. Douglas, *Nature Mater.* **2** (2004) p. 92.
- A. Roy, J.M. Rickman, J.D. Gunton, and K.R. Elder, *Phys. Rev.* **56** (1998) p. 2610.
- L. Gránásy, T. Pusztai, G. Tóth, Z. Jurek, M. Conti, and B. Kvamme, *J. Chem. Phys.* **119** (2003) p. 10376.
- R.L. Davidchack and B.B. Laird, *J. Chem. Phys.* **118** (2003) p. 7651.
- L. Gránásy, *J. Mol. Struct.* **485-486** (1999) p. 523.
- L. Gránásy, T. Pusztai, and P.F. James, *J. Chem. Phys.* **117** (2002) p. 6157.
- P.R. ten Wolde, M.J. Ruiz-Montero, and D. Frenkel, *J. Chem. Phys.* **104** (1996) p. 9932.
- F. Yonezawa, in *Solid State Physics*, Vol. 45, edited by H. Ehrenreich and D. Turnbull (Academic Press, Boston, 1991) p. 179.
- S. Auer and D. Frenkel, *Nature* **409** (2001) p. 1020.
- U. Gasser, E.R. Weeks, A. Schofield, P.N. Pusey, and D.A. Weitz, *Science* **292** (2001) p. 258.
- L.A. Báez and P. Clancy, *J. Chem. Phys.* **102** (1995) p. 8138.
- P.R. ten Wolde, M.J. Ruiz-Montero, and D. Frenkel, *Phys. Rev. Lett.* **75** (1995) p. 2714. □



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