Homogeneous Nucleation

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Significant progress has been made in recent years in measuring homogeneous nucleation rates in a variety of liquid–vapor and liquid–solid transitions. These studies have revealed serious shortcomings of classical nucleation theory. New theoretical work and simulation studies of simplified model systems have provided a better understanding of homogeneous nucleation, but many challenges remain. This article summarizes some recent developments, with an emphasis on the field-theoretic approach pioneered by Cahn and Hilliard in their study of nucleation in a two-component incompressible fluid in 1959.

1. INTRODUCTION

The kinetic transformation of supercooled matter via homogeneous nucleation is a topic of fundamental importance in science and technology which has a long and illustrious history. Gases can be compressed much beyond their equilibrium pressures without forming liquids. Liquids can be supercooled several decades below their freezing temperatures without crystallizing. The reason for such long lived metastable states is that their decay involves an activated process, which requires the surmounting of a free energy barrier between the metastable and more stable phase via a nucleating fluctuation in the form of a critical droplet. Since the free energy barrier is usually the dominant factor in determining the nucleation rate, most theoretical work has focused on calculating the critical droplet profile and its free energy. Because the nucleation rate depends exponentially on this free energy barrier, theoretical predictions for the barrier height which differ by small amounts can lead to predictions for nucleation rates which differ by orders of magnitude. Similarly, measurements of nucleation rates

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are extremely sensitive to experimental conditions such as temperature and impurities. Although the droplet free energy plays a dominant role in nucleation, the nucleation rate also includes an important kinetic contribution.

Historically, most studies of the gas to liquid transition measured the critical supersaturation, the pressure at which the nucleation rate changes from very small to very large. In recent years, however, experimentalists have provided a major breakthrough by making direct measurements of nucleation rates, which have revealed significant inadequacies of classical nucleation theory. Classical theory typically predicts rates that are too low at low temperatures and too high at high temperatures.[1] It also predicts crystal nucleation rates that are too low for liquids and glasses.[2] These discrepancies have led to a resurgence of theoretical activity and significant progress in calculating the critical droplet profile and the free energy barrier to nucleation. In particular, Reiss and colleagues have developed a more precise characterization of a cluster and its free energy of formation,[3] while Oxtoby and collaborators have focused on a density functional (field theoretic) approach,[1] using ideas and techniques developed in the theory of liquids. An important result of this work, as well as that of Klein and collaborators,[70] is that the properties of the critical nucleating droplet can be significantly different from those of the bulk stable phase that eventually develops. This is the case, for example, in crystal nucleation and in binary vapor–liquid transitions, in which one needs two order parameters to describe the droplet. In such cases one of these order parameters can dominate in the formation of the critical droplet, while the other evolves later on in the phase separation process.

This article summarizes recent developments in homogeneous nucleation, with the emphasis on the field theoretic approach to nucleation, which was pioneered by Cahn and Hilliard.[4, 5] It is not meant to be a comprehensive review of the field, as several excellent articles have recently appeared.[1, 2, 6–10] Many interesting areas for theoretical, simulation and experimental study exist, including homogeneous nucleation in systems more complex than simple fluids, such as polar fluids, colloids and proteins and the rapid solidification of metallic alloy systems. In addition, more attention needs to be given to the kinetic prefactor which appears in the expression for the nucleation rate, as is perhaps necessary, for example, to understand crystal nucleation at relatively deep undercoatings.[6, 7]

2. CLASSICAL NUCLEATION THEORY

2.1. Capillarity Approximation

Our theoretical understanding of the stability of phases has its origins in the classic work of Gibbs[11] on metastable and unstable states. Consider

for simplicity a mean field system with a critical point, such as a liquid–vapor transition. Imagine cooling the system from the vapor phase below the critical point into a region of the phase diagram in which thermodynamic equilibrium consists of a coexistence of the liquid and vapor phases. The vapor phase has to evolve dynamically into the equilibrium two phase state by fluctuations in the local order parameter (local density). Gibbs considered the effects of infinitesimal fluctuations on this state, separating into two categories fluctuations that are infinitesimal in degree but large in spatial extent (a small fluctuation of the order parameter extending over a large volume) and those that are large in degree but small in spatial extent (such as an infinitesimal droplet with the order parameter having a value close to the more stable phase). If a phase is unstable with respect to the former fluctuation, there is no barrier to a continuous transformation to the more stable phase; the system undergoes spinodal decomposition (or spontaneous ordering, depending on the dynamics of the system). Gibbs showed that this will occur if the initial cooling is to a region of phase space for which the isothermal compressibility is negative (the region of mechanical instability in this mean-field picture). The boundary of this unstable region is defined by the locus of points for which the inverse compressibility is zero—the meanfield spinodal. On the other hand, the metastable phase is always stable with respect to the formation of infinitesimal droplets, as long as there is a positive surface tension. Between this extreme and the other of the bulk stable phase, there is a critical size droplet, which is in unstable equilibrium. Gibbs calculated the work of formation of this critical droplet by using thermodynamics arguments developed for homogeneous systems. Thus, although he recognized that droplets would in general be spatially inhomogeneous, he treated the critical droplet as if it were spatially homogeneous up to the boundary separating it from the metastable background. To do this required a suitably defined surface energy. In this picture, the work of formation of a droplet of arbitrary radius R is given as the sum of the gain in the free energy of the new (stable phase) droplet and the cost in free energy due to the introduction of the interface:

$$\Delta\Omega = 4\pi R^2 \sigma - 4/3\pi R^3 \, \Delta F \tag{1}$$

where σ is the surface tension and ΔF is the (positive) bulk free energy difference per unit volume between the stable and metastable phases. The above is the capillarity approximation. One obtains the barrier height to nucleation $\Delta\Omega^*$ and the critical droplet size R_c by maximizing $\Delta\Omega(R)$ with respect to R. This yields the well known results

$$\Delta\Omega^* = (16\pi/3) \, \sigma^3/(\Delta F)^2 \tag{2}$$

and

$$R_c = 2\sigma/\Delta F \tag{3}$$

The surface tension σ is taken to be that of a planar interface between the two coexisting sizable phases. In the case of nucleation of a liquid from a supercooled vapor, the droplet free energy is usually written as

$$\Delta \Omega^* = (16\pi/3)\,\sigma^3/kT\rho_l \ln S)^2 \tag{4}$$

where $S = P/P_e$ is the supersaturation (the ratio of the actual pressure P to the equilibrium vapor pressure of the liquid at the same temperature) and ρ_l is the bulk liquid density. In the case of nucleation of a crystal from a supercooled liquid, the free energy barrier is usually expressed as

$$\Delta \Omega^* = (16\pi/3)\,\sigma^3 v^2/(\Delta\mu)^2 \tag{5}$$

where $\Delta\mu$ is the difference in chemical potential between the bulk solid and bulk liquid and v is the volume per particle in the solid.

The assumptions of the capillarity approximation, namely that the properties of the new phase at the center of the homogeneous droplet are the same as the new phase in bulk and that the surface tension of the curved droplet is the same as that of a planar interface, are in general incorrect for small critical droplets, such as occur at even moderate under-coolings. Thus one must go beyond classical theory. (It is also worth noting that in a strict mean field picture, such as describes certain long range force models, the lifetime of decay of a metastable state is infinite.)

2.2. Nucleation Rates

As is well known, the classical theory for the nucleation rate J is given by

$$J = J_0 \exp^{-\Delta\Omega^*/kT} \tag{6}$$

where the preexponential factor J_0 depends upon the kinetics of the system and $\Delta\Omega^*$ is given by Eq. (2). Classical nucleation theory is based on a microscopic description of cluster dynamics, as formulated by Becker and Daring, Volmer and Weber, Frenkel and others.[12–15] The starting point is a kinetic equation for the number density of droplets $n_i(t)$ of a given size i at time t. Assuming that such clusters grow or decay by gaining or losing single molecules, the net rate at which clusters of size i grow is

$$dn_i(t)/dt = J_{i-1} - J_i, \qquad i \geqslant 2 \tag{7}$$

where J_i is the rate per unit volume at which droplets of size i grow to droplets of size $i+1$, given by

$$J_i = R_i n_i(t) - R'_{i+1} n_{i+1}(t) \tag{8}$$

The coefficients R_i and R'_i are the forward and backward rates at which a cluster gains or loses particles and must be determined before the model is fully specified.[10] The nucleation rate is obtained from the steady state solution, $J_i = J$, of this equation, which involves a break-up of large droplets.[80] The classical nucleation theory for the gas–liquid transition is given by

$$J_0 = (2\sigma/\pi m)^{1/2} \, \rho_v^2/\rho_l \tag{9}$$

where ρ_v is the density of the supersaturated vapor and m is the mass of monomer molecules.

The classical theory of crystal nucleation from a supercooled liquid is due to Turnbull and Fisher.[16–18] Their kinetic model assumes that the molecules have to overcome an activation barrier Δ in jumping from the liquid to the solid phase, with the jump rate described by a self-diffusion model, satisfying an Arrhenius rate law. If one includes a Zeldovich correction[88] omitted in the original work, one can express J_0 as

$$J_0 = 2kT(\sigma/kT)^{1/2} \, v^{-2/3} \exp{-\Delta/kT} \tag{10}$$

where v is the molecular volume.[16, 2] One can also express this prefactor in terms of the liquid viscosity[6] or the coefficient of diffusion (using the Stokes–Einstein relation, modeling the jump rate via as a viscous flow). A thorough discussion of classical theory is given in a recent review by Wu.[10]

Actual nucleation rates for nonpolar fluids are in general larger than predicted by classical theory at low temperatures and smaller than predicted at high temperatures. Classical theory is qualitatively correct, however, for nonpolar fluids, in that it predicts nucleation rates that are accurate to within several orders of magnitude. (In homogeneous nucleation theory this is not too bad!) However, for strongly polar fluids classical theory is off by a much larger factor. A review of liquid–vapor nucleation, including a list of experimental references is given in ref. 8. Classical theory predicts crystal nucleation rates that are too low for liquids and glasses.[2] A recent comparison of theory (classical theory, several density functional theories and a diffuse interace model) and experiments for crystal nucleation is given in ref. 53. A summary of experimental, theoretical and simulation

studies of nucleation in liquid–solid and solid–solid transitions for molecular clusters is given in refs. 6 and 7.

3. CAHN–HILLIARD THEORY

In two classic papers in 1958 and 1959 Cahn and Hilliard[4, 5] developed a theory for the description of a spatially inhomogeneous system, via a free energy functional given by

$$\Omega = \int \mathbf{dr}[K(\nabla \rho(\mathbf{r}))^2 + f(\rho(\mathbf{r})) - \mu \rho(\mathbf{r})] \qquad (11)$$

where f is the local Helmholtz free energy per unit volume of a homogeneous system of density ρ and the square gradient term represents the first approximation to a treatment of spatial inhomogeneities. The free energy f has a double well potential with a relative minimum at the metastable state and an absolute minimum at the stable phase. An assumption of this square gradient approximation is that the average density varies slowly on the coarse graining length scale implicit in the model, which is of the order of atomic distances or larger. A subsequent renormalization group theory by Kaski, Binder and Gunton makes this assumption explicit.[78, 79] (For example, the shape of the double well potential and the location of the spinodal depend on the coarse graining size.) In the second paper Cahn and Hilliard determined the saddle point of this free energy functional and analyzed the properties of the critical nucleus for a two component metastable fluid, which is a central component of nucleation theory. They found that in the limit of low supersaturation the properties of this droplet approach those predicted by classical theory, in which the nucleus is assumed to be homogeneous with an interfacial free energy that is independent of curvature. More importantly, they found that for increasing supersaturation, the properties of this critical droplet changed. In particular,[5] "(a) The work required for its formation becomes progressively less than that given by the classical theory, and approaches continuously to zero at the spinodal. (b) The interface with the exterior phase becomes more diffuse until eventually no part of the nucleus is even approximately homogeneous. (c) The concentration at the center of the nucleus approaches that of the exterior phase. (d) The radius and excess concentration in the nucleus at first decrease, then pass through a minimum and become infinite again at the spinodal." This work has been of seminal importance in the development of nucleation theory, in that it provides a description of the spatially inhomogeneous critical droplet, is not limited to planar interfaces and yields a work of formation which

vanishes at the mean field spinodal. It is the first of a series of density functional theories of nucleation which were refined and generalized much later. In what follows, we summarize some of these more recent developments.

4. FIELD THEORETIC NUCLEATION THEORY

The Cahn–Hilliard theory provides a useful starting point for a description of the critical droplet and nucleation barrier. However, a full nucleation theory requires a dynamical description, which Langer subsequently formulated in a continuum generalization of classical nucleation theory.[46] In this approach one starts with an appropriate Fokker–Planck (or corresponding Langevin) equation for the probability distribution functional $P([\psi_i], t)$ for the set of semi-macroscopic variables $[\psi_i]$ which are the relevant "slow" variables of the system:

$$\partial P/\partial t = -\sum_i \delta J_i/\delta \psi_i \tag{12}$$

where the probability current J_i is given by

$$J_i = \sum_j M_{ij}(\delta\Omega/\delta\psi_j + kT\,\delta P/\delta\psi_j) \tag{13}$$

The summation above stands for an integration over the spatial variable **r** and a sum over the semi-macroscopic variables. For a pure fluid, these variables are the hydrodynamic modes, which include viscous, thermal diffusion and sound wave modes. The matrix M_{ij} consists of a symmetric and an antisymmetric piece. The symmetric part corresponds to a set of generalized Onsager coefficients and the antisymmetric part corresponds to any nondissipative terms.

The decay of a metastable state corresponds to passing from a local minimum of Ω to another minimum of lower free energy, which involves improbable free energy fluctuations. The most likely path for this transition to occur when the nucleation barrier is high is via the saddle point, which corresponds to a critical droplet of the stable phase in a metastable background. The nucleation rate is given by a steady state solution of the Fokker–Planck equation which describes a finite probability current across the saddle point. The formal solution of this steady state current can be expressed as

$$J = \kappa\Omega_0 \exp -\Delta\Omega*/kT \tag{14}$$

where κ is a dynamical prefactor and Ω_0 is a statistical prefactor. The dynamical prefactor is the initial growth rate of a critical droplet, while the statistical prefactor essentially is the amount of phase space available for a fluctuation corresponding to a critical droplet.

One way to calculate κ is to linearize the Langevin equations corresponding to the Fokker–Planck equation around the (unstable) saddle point. There are a few cases in which this has been done.[80] One of the simpler cases corresponds to diffusion in a binary system, such as a binary alloy or binary fluid. In this case the formal analysis has been given in refs. 47 and 49. An equivalent, heuristic formulation has been given in ref. 48, based on a solution of the quasistationary diffusion equation, $\nabla^2 c = 0$, for the concentration field c in the neighborhood of a spherical droplet of radius R. This leads to an equation for the growth rate of the droplet:

$$dR/dt = (D \, \delta c/R \, \Delta c)(1 - R_c/R) \tag{15}$$

where δc is the supersaturation, D is the diffusion constant and Δc is the binary fluid miscibility gap.[80] If one linearizes this equation around the critical droplet size R_c, one obtains for the growth rate

$$|\kappa| = D \, \delta c/R_c^2 \, \Delta c \tag{16}$$

A similar derivation can be made to obtain κ for the case of a droplet of liquid in a supercooled vapor,[47, 49, 80] based on the assumption that the growth rate is determined by the rate at which the latent heat produced in the formation of the droplet of the nucleating phase can be dissipated. The result is

$$\kappa = 2\lambda\sigma T/l^2\rho_l R_c^3 \tag{17}$$

Grant and Gunton[83] have used the Langer formalism to calculate the nucleation rate for crystal nucleation. Their theory is probably most applicable to alkali metals, but it has been applied to a variety of other systems.[6, 7] The basic assumption of their calculation is that the critical droplet grows via the thermal conduction of latent heat. (A similar mechanism is involved in the theory of dendritic growth from supercooled liquids.) The equation of motion for a crystalline droplet of radius R is found to be

$$dR/dt = (2\lambda\sigma T/l^2\rho_l^2(1+\eta)^2 \, R)(1/R - 1/R_c) \tag{18}$$

where λ is the thermal conductivity, l is the latent heat of fusion, η is the fractional density change upon heating and R_c is the classical critical droplet size. Linearizing this equation about R_c yields for the growth rate

$$\kappa = 2\lambda\sigma T/l^2\rho_l^2(1+\eta)^2\,R_c^3 \tag{19}$$

This is to be contrasted with the classical Turnbull–Fisher expression in Eq. (10), in which the diffusion is expressed in terms of an activation energy. The underlying assumption of the classical theory seems to be that the latent heat is transported away before the critical droplet is formed, in contrast to the assumption above. Bartell has compared his experimental and simulation results for several molecular systems at deep undercoolings with both the classical theory and with the Grant–Gunton theory. It would appear that neither can explain the observed nucleation rates; for example, the Grant–Gunton theory apparently differs by several orders of magnitude from the experimental results (see refs. 6, 7, and 19 for a discussion of this). However, in addition to the complexity of the systems studied, at such deep undercoolings the critical droplet is quite small, so that it might be beyond the range of validity of these theories. In addition, the lack of knowledge of the surface tension makes comparison of experiment and theory difficult, as noted earlier. Skripov has also measured the nucleation rate for several metals and nonmetals and found that each seems to exhibit a maximum as a function of temperature, in at least qualitative agreement with the classical theory of nucleation.[21, 22] It would clearly be useful to have a more complete theory of crystal nucleation from the melt, particularly at deep undercoolings, including the dynamical prefactor.

Langer's original theory was developed for quenches near the coexistence curve, in which the nucleation barrier is large (strong first order transition). However, as Cahn and Hilliard had shown, this barrier vanishes at the mean field spinodal. Klein and collaborators subsequently extended Langer's theory to the case of nucleation near this spinodal, in the limit of a long range force model, for both gas–liquid[68, 69] and liquid–solid[70] nucleation. A summary of their results for crystal nucleation is given below.

5. DENSITY FUNCTIONAL APPROACH

The density functional theory of nucleation by Oxtoby and collaborators is a systematic theory of nucleation which has been applied to several different models for liquid–vapor and liquid–solid nucleation. The nucleation barrier is calculated by finding a saddle point and corresponding critical droplet profile for a given system. Nucleation rates are

typically calculated by combining the critical droplet free energy with the preexponential factor from classical nucleation theory, rather than by carrying out a full dynamical calculation ala Langer. (See, however, refs. 83 and 40.) The main difference with the Langer approach lies in the use of liquid–state perturbation theory to calculate the free energy functional. The interactions between the molecules are typically taken to be Lennard–Jones forces, which are then approximated as hard sphere interactions plus attractive tails. The free energy of the hard sphere system, f_{hs}, is treated in local density approximation, while the spherically symmetric attractive interaction, V, is treated by perturbation theory. The free energy functional for such a system is

$$\Omega[\rho(\mathbf{r})] = \int \mathbf{dr}\, f_{hs}(\rho(\mathbf{r})) + \iint \mathbf{dr}\, \mathbf{dr'}\, V(|\mathbf{r} - \mathbf{r'}|)\, \rho(\mathbf{r})\, \rho(\mathbf{r'})) \qquad (20)$$

As before, the saddle point is obtained by setting $\delta\Omega/\delta\rho(\mathbf{r})$ equal to zero, which yields a nonlinear integral equation for $\rho(\mathbf{r})$. This equation is solved by iteration, yielding the profile of the critical droplet and the corresponding work of formation, $\Delta\Omega^*$. The steady state nucleation rate is then given by Eq. (6), with the appropriate classical preexponential factor.

5.1. Liquid–Vapor Nucleation

A variety of density functional calculations have been carried out by Oxtoby and collaborators for nucleation of the supercooled vapor. Some of the important conclusions include the following:

• The breakdown of classical theory was studied within the context of a Yukawa potential by Oxtoby and Evans.[32] They found that as the range of this attractive tail was increased, the agreement between density functional and classical theory disappeared, with discrepancies of many orders of magnitude developing between the corresponding theoretically predicted nucleation rates. They concluded that the qualitative agreement between the classical nucleation theory and experimental results for the magnitude of the nucleation rate is somewhat fortuitous. Namely, if physical systems had somewhat longer attractive potentials, classical theory would be in gross error.

• Zeng and Oxtoby[34] analyzed a Lennard–Jones potential with a temperature dependent diameter for the hard sphere potential. This model presumably describes simple substances such as the noble gases. Unfortunately, accurate experimental data is not available for such systems. However, they found qualitative agreement with the temperature and

supersaturation dependence for the nucleation rate found in several experimental studies of alcohols, toluene and alkanes.[45, 43, 44] Although spherically symmetric potentials such as the Lennard–Jones type are not accurate descriptions of these systems, the qualitative agreement is nevertheless encouraging.

• Talanquer and Oxtoby[40] carried out a more complete density functional calculation, extending earlier work[34, 32] to include a calculation of the prefactor J_o that occurs in the expression for the nucleation rate. The earlier calculations had assumed that this prefactor was given by classical nucleation theory. By calculating the forward and backward rates that occur in the cluster dynamics model described in Section II, they found results that were not much different than those obtained in,[34, 32] but differed from classical nucleation theory. Classical nucleation theory overestimates the nucleation rate at small supersaturation by considering incompressible liquid droplets, whereas it underestimates the rate at large supersaturation via an overestimate of the surface tension of small droplets.

• As noted in the preceding section, Langer and Turski[47] carried out a calculation of the preexponential factor J_o near the critical point, using the full hydrodynamic equations appropriate to the fluid. In spite of being a more complete theory, their results did not differ significantly from the Becker–Döring theory, as modified to include modern scaling laws and critical exponents.

5.2. Crystal Nucleation

The nucleation of crystals from a supercooled liquid is much less well understood than the gas–liquid transition, due in large part to the broken symmetry of the liquid–solid transition. In addition, it is extremely difficult to measure the interfacial free energy that occurs in the expression for J. This interfacial free energy can only be measured at the melting temperature and even there it is only known within rather limited accuracy.[53] Since many of the nucleation experiments are at moderate to deep undercoolings, one can only estimate the interfacial free energies at such temperatures. Thus in contrast to the relatively straightforward measurements of σ for liquids, which allow one to make direct tests of classical nucleation theory, it is in general not possible to carry out such tests for crystal nucleation. However, various indirect tests have been carried out. A comparison of a variety of experimental results with several theories for crystal nucleation is given in ref. 53.

In the liquid–gas transition the critical droplet is described by a local density $\rho(\mathbf{r})$. However, in the liquid–solid transition the crystalline droplet

has both a local density and a local periodic structure. The spatial variation of these two variables need not be the same. For example, changes in density occur after the crystalline structure appears for liquids whose molecules are small, whereas in colloids and proteins one can have the density change occurring first, followed by the development of a periodic structure in the droplet.[36] Such effects can play a significant role in nucleation and in particular invalidate classical nucleation theory.

Density functional theory treats the solid as an inhomogeneous fluid. The starting point for a calculation of crystal nucleation rates is a Fourier expansion of $\rho(\mathbf{r})$ in terms of the reciprocal lattice vectors $\mathbf{k}_i$,

$$\rho(\mathbf{r}) = \rho_o + \rho_s \sum m_i \exp i\mathbf{k}_i \cdot \mathbf{r} \tag{21}$$

where ρ_o is the average density, ρ_s is the average density of the solid and the Fourier coefficients are structural order parameters that determine the crystal structure. Since the m_i would be zero in the liquid, one models the nucleation process by letting the m_i's be spatially dependent. The saddle point is found as usual by minimizing the grand canonical potential functional Ω with respect to $\rho(\mathbf{r})$. Different truncations of the above expansion have been made, in order to facilitate actual calculations, with the crystal symmetry usually assumed known. One approximation that has been made is to write the density as a sum of Gaussians, centered about the lattice sites of the crystal. All of the m_i's are then determined in terms of the first one, m_1. The Gaussian approximation then yields two ordinary differential equations for the average density $\rho_o(r)$ and the structural order parameter $m_1(r)$:

$$\delta\Omega/\delta\rho_o(r) = 0 \tag{22}$$

$$\delta\Omega/\delta m_1(r) = 0 \tag{23}$$

One then solves these equations for a system of Lennard–Jones atoms, for example, using a free energy functional of the type discussed above and assuming a fcc crystal symmetry. Some interesting results include the following:

• Shen and Oxtoby[38] found that the critical droplet is different at large undercoolings from that at large superheating due to the absence of a spinodal in their solid free energy functional. In addition, they found that the classical theory for the free energy of formation of the critical droplet is found to exceed that obtained in the density functional calculation.

• In an interesting extension of this work,[39] the same authors introduced an order parameter that continuously distorts a crystal with fcc

symmetry into one with bcc symmetry, to allow for the possibility that precritical bcc crystallites form which then transform to critical fcc droplets. The latter had been found in a earlier simulation of a Lennard–Jones system.[65] Their calculation of the free energy functional showed a metastable bcc state close to the stable fcc phase. This metastable bcc phase induces a saddle point which serves as the lowest free energy barrier between the liquid and crystal, with the minimum free energy interface passing close to this saddle point. This has significant consequences for nucleation, in that a small critical droplet is largely of bcc structure at the center and evolves into the stable fcc structure as it grows. It is interesting that this precursor bcc structure was also predicted earlier[70] in a theoretical study of spinodals in crystal nucleation, as discussed next.

• One issue that is still under discussion is whether there is a spinodal in crystal nucleation, which should manifest itself in a divergence in the structure factor at a nonzero wave vector. (The idea that there might be an instability in the freezing transition dates back to theoretical work by Kirkwood and Monroe.[58]) There is no experimental evidence for such a divergence, however. In addition, current density functional calculations of crystal nucleation[38] support these experimental observations. On the other hand, theoretical work by Klein and Levraz[70] suggests that one should expect to see effects of a spinodal in crystal nucleation, although these might be somewhat subtle. These authors base their arguments on an analysis of a system interacting with weak, long-range repulsive potentials. (In the limit of an infinitely weak, but infinitely long-ranged potential this model has a mean-field spinodal.) The authors calculate the critical droplet profile and show that near the spinodal it is a small amplitude fluctuation with a bcc symmetry (in three dimensions). The instability associated with the spinodal is characterized by a structure factor that diverges at a nonzero wave vector. In addition, the droplet with crystalline symmetry appears with no initial latent heat release. The nucleation barrier near the spinodal differs from what one would obtain in classical theory, which is based on the assumption of a finite surface tension. In contrast, the surface tension vanishes as one approaches the spinodal. Klein and Levraz suggest that crystalline nucleation in deeply quenched liquids with finite-range forces might be similar to that found for the weak, long-range force models, although they cannot explain the apparent lack of a divergence in the structure factor in experiments. Finally, as noted earlier, Klein and collaborators have discussed the nucleation mechanism to be found in deeply supercooled vapors and in Ising models, within the framework of a fractal or ramified droplet picture analogous to that summarized here for crystal nucleation.[68, 69, 71–73] An interesting discussion of how nucleation

clusters arise from the coalescence of critical phenomena fluctuations associated with a mean field spinodal is given in ref. 76.

6. DIFFUSE INTERFACE MODEL

Although the density functional approach provides, in principle, a systematic approach to the calculation of nucleation rates, it requires an accurate intermolecular potential to describe real materials. In addition the square gradient approximation which occurs in several applications of the density functional approach has been criticized as being an inaccurate description of the interface in certain instances. As a consequence other more phenomenological approaches have been developed which try to improve the capillarity approximation which is clearly incorrect for small droplets. For typical nuclei which contain a few tens to a few hundred molecules, the nuclei are dominated by their interfaces. This suggests a size-dependent surface tension, for which there are many theories (see, e.g., ref. 30). One particular approach to calculate the work of formation is the so-called diffuse interface model developed by Granasy and collaborators.[56, 54, 55, 52] (A similar theory has been proposed by Spaepen.[30, 31]) This model assumes that the center of the droplet can be characterized by the physical properties of the bulk and that a "diffuse interface" thickness is size independent. Specifically, the work of formation of the droplet is written formally as

$$\Delta\Omega = \int \mathbf{dr}[\,\Delta h(r) - T\,\Delta s(r)\,] \tag{24}$$

where Δh and Δs describe the local enthalpy and entropy densities of the droplet. One then writes this as

$$\Delta\Omega = (4\pi/3)(R_H^3\,\Delta h_c - R_S^3\,\Delta s_c) \tag{25}$$

where R_H and R_S denote the positions of the "enthalpy" and "entropy" surfaces, respectively, and $\Delta h_c = \Delta h(0)$ and $\Delta s_c = \Delta s(0)$. One assumes that $R_S - R_H$ is independent of the droplet size and undercooling and is equal to its melting point value $\delta = -\sigma_f/\Delta h_f$. (The physical significance of this length seems unclear.) The free energy of the critical droplet can then be calculated and used together with the classical preexponential factor in Eq. (6) to obtain the nucleation rate. It has been shown that this model is consistent with the experimental data on crystal nucleation in molten metals, oxide glasses and hydrocarbons,[53, 50, 51] as is a semiempirical single order parameter Cahn–Hilliard model.[35, 53]

7. NUMERICAL SIMULATIONS

Numerical simulations of microscopic models of interacting molecules have become a powerful tool for the study of homogeneous nucleation. The two common methods are Monte Carlo and molecular dynamics (MD), with the latter being increasingly used to study the kinetics of first order phase transitions. Another fruitful approach has been the simulation of nonlinear Langevin equations, which appear in the field theoretic approach. We summarize a few highlights of such simulations, focusing primarily on MD studies.

• MD studies of crystal nucleation from the melt have been carried out using simple isotropic potentials such as Lennard–Jones.[64, 74, 75, 65] Earlier simulation studies were carried out by quickly cooling a liquid to temperatures much below its freezing temperature and then determining the time until the first signs of solidification appear.[57, 59–63] This is a straightforward method but has the disadvantage that it only works at deep undercoolings (in order to have observable nucleation events). More recent studies use biasing techniques, such as umbrella sampling, in order to sample frequently configurations with a large free energy (such as occur near the top of the nucleation barrier), to circumvent this difficulty. For example, ten Wolde *et al.*[65] used umbrella sampling to determine the nucleation barrier for a Lennard–Jones system at moderate undercooling and calculated the rate at which the barrier is crossed by MD. They found that although the Lennard–Jones system studied had a stable fee phase below the melting curve, the precritical nuclei were primarily a metastable bcc phase which transformed to fcc *before* the critical nucleus was reached. They also found that the density profile falls off more rapidly in the interface than that of the structural order parameter, as predicted by Harrowell and Oxtoby.[42] In addition, the kinetic prefactor was approximately two orders of magnitude larger than predicted by classical nucleation theory at the moderate undercoatings studied. The possibility of the formation of a phase from the melt that is not the most stable, but rather the phase closest in free energy to the liquid phase, is known as the Ostwald "step rule"[90] and has been the subject of considerable theoretical development.[77, 70] (Earlier, interesting simulations of crystal growth of a fcc crystal in contact with its melt were carried out for a Lennard–Jones system by Broughton *et al.*[85, 89])

• Bartell and collaborators have carried out experimental and MD studies on a variety of molecular clusters.[23–29, 6, 7] The MD studies were motivated by the observation of both freezing and certain solid–solid transitions in electron diffraction measurements of deeply undercooled, small

molecular clusters in a supersonic beam. Since the clusters were small, the simulations did not involve biasing but rather were straightforward studies of small clusters at deep undercooling. Experimental observations of freezing in liquid clusters have been made for carbon tetrachloride, cycloheptane, ammonia, water and a variety of other systems.[7] Typical simulations treated the molecules as rigid polyhedra (e.g., Se–F octahedra) with pairwise additive Lennard–Jones potential interactions and ranged in size from about 100 to 500 molecules. Simulations of freezing transitions have been carried out for several systems, including molten salt and chalcogen hexafluorides (SF_6, SeF_6 and TeF_6). clusters. In addition, studies of solid–solid transitions (from one structural phase to another) have been carried out for several systems, including t-butyl chloride and a series of hexafluorides. In spite of the relative simplicity of the Lennard–Jones potentials for the various molecules studied, relatively good results were obtained for the various phase transitions. Recent reviews of this work are contained in refs. 6 and 7.

• The nature of the critical droplet for strongly polar fluids such as acetonotrile has been a subject of some interest.[93–95] In order to clarify this, a recent simulation of the liquid–gas transition was carried out[67] for a Stockmayer model, for which the potential is a Lennard–Jones 6–12 interaction plus a dipole–dipole interaction. The simulation showed that homogeneous gas–liquid nucleation is initiated by chain-like clusters. Beyond a certain size, the clusters condense and form compact droplets. The interface of these droplets differs significantly from planar interfaces, however, due to the existence of chains. The existence of the chain-like precritical nuclei is significant, in that it affects the nucleation barrier. It was shown that classical nucleation theory underestimates the size of the critical droplet and the magnitude of the nucleation barrier.

• Solidification of supercooled eutectic liquids provides rich examples of nucleation and spinodal decomposition phenomena. These have been studied via simulations of nonlinear Langevin equations for isothermal solidification[81] and nonisothermal solidification.[82]

• ten Wolde and Frenkel[66] studied crystal nucleation in a model of a colloidal system which has a *metastable* vapor–liquid critical point. They found for supercoolings far from this metastable critical point, the critical droplet was classical, with its crystalline order comparable to the stable bulk crystal. However, for supercoolings close to the metastable critical point the critical droplet was disordered. They suggested that the minimum crystal nucleation barrier (and optimal crystal growth rate) corresponded to this nonclassical critical droplet. A density functional study of this phenomena has subsequently been carried out,[36] to further elucidate the

role of a metastable critical point in crystal nucleation. This showed significant increases in nucleation rates near this critical point, which would have major consequences for the nucleation of colloids and proteins from solution.

• In many systems long range interactions, such as elastic interactions in solids, play an important role in nucleation and growth. A preliminary step toward the study of such phenomena was taken through the simulation of nucleation in a Langevin model with non-local interactions.[84]

8. SUBCRITICAL BUBBLES AND THE ELECTROWEAK TRANSITION

The adiabatic expansion of the early universe and its concommitant cooling is thought to involve first order phase transitions, such as the electroweak transition. The kinetics of such transitions and in particular that of homogeneous nucleation has been a subject of considerable research. In particular, Gleiser and collaborators[92, 91] have investigated the effects of large amplitude fluctuations which play an important role in weak first order transitions. The standard field theoretic approach to homogeneous nucleation is strictly applicable to strong first order phase transitions, in which there is a large barrier between the metastable and stable phases. In this case, the large barrier suppresses large amplitude thermal fluctuations of the order parameter and one can regard the initial metastable state as homogeneous, in that only very small amplitude fluctuations occur. In weak first order phase transitions, on the other hand, such as the isotropic to nematic transition in certain liquid crystals, large amplitude fluctuations of the nematic phase can occur. Indeed, they have been observed *above* the phase transition temperature. As a consequence, it would seem natural that in order to develop a theory for weak first order transitions, one should expand around an *inhomogeneous* background which includes large amplitude fluctuations. Attempts to achieve this have been carried out in recent years both above and below the phase transition temperature T_c. Initial work treated the equilibrium distribution of so-called subcritical bubbles of the broken symmetric phase within the symmetric phase at temperatures above T_c. A kinetic equation for the number density of these sub-critical fluctuations was derived and solved analytically, using different mechanisms for the destruction of these bubbles.[92] A later work[91] argued that the subcritical fluctuations provide an additional free energy-density in the system and hence change the free energy barrier to nucleation below T_c. That is, these subcritical fluctuations renormalize the original Cahn–Hilliard free energy functional. This results in a renormalized free energy barrier for the formation of a critical size bubble

and hence a change in the nucleation rate as compared with one based on the original free energy functional. These ideas were implemented in a study of the model in two dimensions, in which a renormalized free energy functional was obtained, using an approximate form for the distribution function and free energy for these bubbles. The predicted nucleation rate was shown to be in reasonable agreement with numerical simulations of the model. Although this is interesting work, it is difficult to judge its validity.

9. MISCELLANEOUS

There are several important topics currently under investigation which have not been discussed here. Among these are the following:

• The classical cluster approach to nucleation in the gas–liquid transition has been a subject of considerable discussion in recent decades, dating back to work of Lothe and Pound[96, 97] who argued that classical theory neglected significant contributions from translational and rotational degrees of freedom of the critical droplet. An apparent resolution of such issues has been made recently by Reiss et al.[3]

• Nucleation and growth. Although homogeneous nucleation in itself is a subject of intrinsic importance, a full understanding of the dynamics of decay of a metastable state involves both nucleation and growth. Droplet growth depends on the particular dynamics which govern the system, such as whether the order parameter is conserved or nonconserved, whether hydrodynamic modes are important, etc. A recent theory of nucleation and growth for phase separating systems for which droplet growth proceeds by the Lifshitz–Slyzov diffusion mechanism is given in refs. 86 and 87, which also contains a summary of earlier work on this subject.

• Atmospheric nucleation. Important examples of homogeneous and heterogeneous nucleation occur in the earth's atmosphere. A summary of some recent advances in this field is given in ref. 8.

• Binary nucleation. Although classical nucleation theory gives a qualitatively correct description of condensation in simple fluids, it can give rise to the unphysical prediction of negative numbers of particles in the critical droplet in the case of binary fluids.[1] Density functional theory can avoid such difficulties and has provided useful information on the critical droplet profile.[8, 1]

• Amphiphilic molecules. A particularly interesting application of nucleation system is the case in which two incompatible systems are brought together by means of a third, amphiphilic component. One such system includes immiscible water and nonane, with butanol as the

amphiphilic molecule which acts as a surfactant. Density functional theory has been useful in clarifying the composition of the critical ternary droplet.[1, 37]

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