Theory for the nucleation of a crystalline droplet from the melt

Martin Grant and J. D. Gunton

Physics Department, Temple University, Philadelphia, Pennsylvania 19122

An expression is derived for the nucleation rate of a crystalline solid from its melt. In particular, the dynamical prefactor for the nucleation rate is obtained, using Langer's field theory of nucleation. The analysis makes use of the formalism of Ramakrishnan and Yussouff, as extended to solid-melt interfaces by Oxtoby, Haymet, and Harrowell. The theoretical result can be tested experimentally.

I. INTRODUCTION

In this paper we shall derive an expression for the rate at which crystalline droplets nucleate from a supercooled liquid matrix. Nucleation, the most commonplace of first-order phase transitions, has been the subject of considerable interest recently.[1] Homogeneous nucleation involves the decay of a metastable state, e.g., a supersaturated solution, by the spontaneous occurrence of large thermal fluctuations, that is, through the formation of droplets of the stable phase. Droplets which are larger than a critical size grow, and thus the stable phase results.

A description of this process requires a dynamical theory. The classical theory of Becker and Döring[2] has two main features: a phenomenological description of the critical droplet, and a Smoluchowski equation for the kinetics of a cluster of a given size. These ideas have been generalized and extended in statistical physics. Cahn and Hilliard[3] have obtained a description of the critical droplet through an examination of the saddle point of the coarse-grained free-energy functional. A first-principles theory of the kinetics of nucleation, which generalized earlier work by Landauer and Swanson,[4] has been provided by Langer.[5-7] We should also note that many experimental[8-10] and numerical studies[11] of metastable states have been undertaken.

These theories, either explicitly or implicitly, apply to systems where crystal structure is unimportant, for example, liquid-vapor systems. An early theory for nucleation in solid-melt and solid-solid systems, which is based on the Becker-Döring theory, is due to Turnbull and Fisher.[12] Our purpose here is to extend Langer's theory of nucleation to solid-melt systems, and so to generalize the earlier work of Turnbull and Fisher. It is worth noting that a fundamental question, which we shall not address, concerns the origin of the crystal structure from the interatomic potential. Instead, that crystal structure is simply assumed from the beginning, following work which we discuss below.

An equilibrium statistical-mechanical approach to freezing, that is, the solid-melt transition, was first given by Kirkwood and Munroe.[13] This involved an approximate solution to the equation for the density in the integral-equation hierarchy. A self-consistent solution was found for the first-order phase transition from melt to solid. Since the analysis involved uncontrolled approxi-

mations (e.g., replacing the pair-correlation function by its liquid-state form), however, the implication of their results was not clear. Recently, Ramakrishnan and Yussouff[14-16] have been able to reformulate the freezing problem in a manner somewhat analogous to the early work. They introduce order parameters corresponding to the crystalline structure of the solid phase.[17] Then, by treating the solid as an inhomogeneous fluid, they obtain a form for the free energy by standard liquid-state methods. Although they assume the crystal structure, a partial explanation of the origin of that structure is provided by an examination of three-body correlation functions. Their results, for body-centered-cubic lattices like sodium and face-centered-cubic lattices like argon, are in reasonable agreement with experimental work.

This theory has been extended in a series of papers by Oxtoby, Haymet, and Harrowell[18-20] to describe the solid-melt interface. They obtain an expression for the surface tension, and, in particular, an expression for the free energy of a critical droplet, in the manner of Cahn and Hilliard. The work of Oxtoby *et al.* appears to have certain limitations, however, which affect the present work. Basically those limitations are as follows. Because the crystal structure is assumed in the theory, some of the behavior intrinsic to a crystal is poorly represented. Hence, for example, surface reconstruction cannot presently be handled. Such effects are thought to be unimportant for solid-melt systems, but this means that the theory cannot be extended to, e.g., the study of solid-solid nucleation. To handle these effects would require a rather substantial generalization of the equilibrium theories of Refs. 14—20.

Herein, we concentrate our efforts on the kinetics of nucleation in the solid-melt system. Thus, our treatment is complementary to the work of Harrowell and Oxtoby on the free energy of a droplet. We obtain the rate at which crystalline droplets nucleate from the melt. That expression can be tested experimentally. The theory is probably best applicable to the study of the alkali metals such as sodium, potassium, and rubidium, to which the Ramakrishnan-Yusouff theory has already been successfully applied. The results are presented in a quite general form, however, and should be relevant to a wide class of solid-melt systems. The outline of the remainder of this paper is as follows.

In Sec. II we briefly review some of the results of

Langer's field theory of nucleation, and the formalism of Ramakrishnan and Yussouff, of which we shall make use. The dynamical prefactor for the nucleation rate is calculated in Sec. III. Following the program of Ramakrishnan and Yussouff, we continue to treat the solid as an inhomogeneous fluid. The circumstances under which this is justifiable, and the limitations of such a treatment, are discussed in the text. In Sec. IV the result for the statistical prefactor is presented, following which we present the expression for the nucleation rate. The predictions of this result are qualitatively sensible. The feasibility of an experimental, or computer-simulation, test is discussed. Finally, we examine the limitations of our approach and discuss directions for future research.

II. BACKGROUND

The order parameters in the Ramakrishnan-Yussouff[14-16] formalism for the solid-melt transition are introduced in the following way. The density ρ of the solid is written as

$$\rho(\mathbf{r}) = \rho_l \left[(1+\eta) + \sum_{\mathbf{G}} \mu_G e^{i\mathbf{G}\cdot\mathbf{r}} \right] , \qquad (2.1)$$

where ρ_l is the density of the liquid, η is the fractional density change upon melting, $\{\mu_G\}$ are the Fourier coefficients of the solid, and $\{\mathbf{G}\}$ are the reciprocal-lattice vectors of the crystalline solid. Since η and μ_G vanish in the liquid phase and are nonzero in the solid, they are identified as the order parameters. A free energy is then constructed by expanding in the quantity $[\rho(\mathbf{r}) - \rho_l]$ in a density-functional theory. The input to the theory is provided by the known liquid-state properties (that is, the structure factor) and the crystallographic basis for the solid.

Oxtoby, Haymet, and Harrowell[18-20] have generalized this approach to allow for inhomogeneities. In their treatment,

$$\eta \rightarrow \eta(\mathbf{r})$$

and

$$\mu_G \rightarrow \mu_G(\mathbf{r}) .$$

The free energy which is obtained can be written in the following way:

$$F(\eta, \mu, T) = \int d\mathbf{r} \left[f(\eta, \mu, T) + \tfrac{1}{2} K_0 (\nabla\eta)^2 \right. $$
$$\left. + \sum_{\mathbf{G}} \tfrac{3}{2} K_G \, | \widehat{\mathbf{G}} \cdot \nabla\mu_G |^2 \right] . \qquad (2.2)$$

In Eq. (2.2), f is the (gradient-free) bulk free energy calculated by Ramakrishnan and Yussouff, K_0 and $\{K_G\}$ are temperature-dependent constants, and $\widehat{\mathbf{G}}$ is the unit vector in the $\mathbf{G}$ direction. From this, Oxtoby, Haymet, and Harrowell have obtained the surface tension[18-20] and, in particular, the free energy of the critical droplet for nucleation.[20]

A shortcoming of this approach is evident immediately. Because the crystal structure of the solid is built into the theory, there is no mechanism for any reconstruction of the crystal. We will return to this point later in this paper, since it is the major limitation of our results. For the remainder of this section, we discuss some formal results of the theory of metastable states of which we shall make use.

We briefly review some of the results of classical theory[2,12] before discussing Langer's field theory of nucleation. In the droplet model the free energy of a spherical droplet of radius R is written

$$\Delta F = 4\pi R^2 \sigma - \frac{4\pi}{3} R^3 \Delta\Gamma , \qquad (2.3)$$

where σ is the solid-melt surface tension and $\Delta\Gamma$ is the free-energy difference, per unit volume, between the crystalline solid and the melt. From Eq. (2.3), small droplets will minimize the free energy by getting smaller, while large droplets will get larger. The critical droplet size R^* at which a crossover occurs is given by

$$\frac{\partial \Delta F}{\partial R} \bigg|_{R=R^*} = 0 , \qquad (2.4)$$

from which one obtains

$$R^* = \frac{2\sigma}{\Delta\Gamma} , \qquad (2.5)$$

and

$$\Delta F(R^*) = \frac{16}{3} \pi \frac{\sigma^3}{(\Delta\Gamma)^2} . \qquad (2.6)$$

Roughly speaking, then, the probability that a fluctuation corresponding to a critical droplet (which will grow and form the stable phase) will occur is $\exp[-\Delta F(R^*)/k_B T]$ where k_B is Boltzmann's constant and T is temperature. The rate at which droplets nucleate is proportional to this factor.

A more rigorous approach has been given by Cahn and Hilliard,[3] where the free energy at the saddle point, corresponding to the critical droplet, was calculated. Their treatment avoids the local equilibrium assumptions implicit in Eq. (2.3) above (i.e., the assumptions that the free energy can be decomposed into two additive parts and that the interface has no significant thickness). Harrowell and Oxtoby[20] have extended the approach of Cahn and Hilliard to the free energy given by Eq. (2.2) above.

A first-principles field-theoretic approach to nucleation has been given by Langer,[5-7] who generalized the earlier work of Landauer and Swanson.[4] In his theory, the nucleation rate I involves the analytic continuation of the free energy into the metastable state.[21-23] One way to express the formal result is that

$$I = \kappa \Omega_0 e^{-\Delta F(R^*)/k_B T} . \qquad (2.7)$$

In Eq. (2.7), ΔF is the free energy at the saddle point which was discussed above. The quantity Ω_0 is called the statistical prefactor. A formal expression for it is given in Refs. 5—7. Essentially, Ω_0 gives the amount of phase space accessible for a critical droplet fluctuation. Thus, it is proportional to the volume of the system. It will be discussed further in Sec. IV.

The quantity in Eq. (2.7) most interesting for our present purposes is κ. This is called the dynamical prefactor, since it gives the initial growth rate for a critical

droplet. In the following section we derive an expression for κ.

III. THE DYNAMICAL PREFACTOR

To calculate κ for the crystalline droplet nucleating from the supercooled melt, we will follow the related work by Langer and Turski[24,25] and Kawasaki[26] concerning liquid-vapor systems. Our analysis, as noted earlier, makes use of the dynamical formalism appropriate for an inhomogeneous fluid.[27-29] Before beginning our derivation, it is useful to discuss the physical rationale for this.

As the critical nucleus grows, its kinetics principally involves thermal diffusion from the surface of the solid droplet into the liquid. Since it is this diffusion into the melt which we want to describe, rather than diffusion into the solid, it is reasonable to treat the problem by considering the dynamics of a nonuniform fluid. Another way to put this is as follows. By simplifying the dynamics of the solid droplet in this manner, we will, of course, obtain a poor description of intrinsically crystalline dynamical properties, such as transverse sound waves and Rayleigh surface waves. These are, however, of negligible importance compared to the modes in the liquid matrix; excitations of the solid are unlikely because they involve wave numbers of order $1/R$, as compared to excitations in the liquid, which involve wave numbers of order $1/L$ (where L^3 is the volume of the system). This is in agreement with the intuitive picture that the droplets grow by diffusing latent heat into the supercooled melt rather than back into the droplet. An explicit demonstration of this for a liquid-vapor system is given in Ref. 24. This is not to say that our treatment gives a complete description of the solid-melt surface properties during nucleation. In fact, our analysis has some important limitations which we shall discuss later.

To derive an equation of motion for the time-dependent radius of a droplet (following Turski and Langer[25]) we must first obtain a set of "boundary conditions" for the long-lifetime thermodynamic variables near the solid-melt interface. These conditions implicitly contain the equation of motion for the nucleated droplet, as we shall see. Firstly, from the Navier-Stokes equation, the solid-melt surface tension is introduced. Next, by integrating the continuity equation, the velocity of the crystalline droplet's interface is obtained. Thirdly, from consideration of the equation of thermal conduction, the latent heat at the nonequilibrium interface is introduced. Finally, the nonequilibrium Gibbs-Thomson condition for the temperature field is obtained from the behavior of the chemical potential at the interface. We begin by considering the Navier-Stokes equation.

Conservation of momentum implies that the velocity field $u(\mathbf{r},t)$ satisfies

$$\frac{\partial}{\partial t}m\rho(\mathbf{r})u(\mathbf{r},t) = -\nabla\cdot\overset{\leftrightarrow}{\mathbf{P}} ,\tag{3.1}$$

where m is the mass, and $\overset{\leftrightarrow}{\mathbf{P}}$ is the pressure tensor, where we are neglecting viscosity. The derivation proceeds by considering the quasistationary limit, where $\partial m\rho u/\partial t \simeq 0$, and separating $\overset{\leftrightarrow}{\mathbf{P}}$ into two parts: a bulk piece, which is well behaved at the interface, and a surface piece, which is sharply peaked at the solid-melt interface, but vanishes in either of the two bulk phases. This will lead us to the analogue of the Laplace-Young condition[29] in the solid-melt system for the pressure differential over an interface. Our derivation will be somewhat schematic, since these manipulations are already well known from the study of liquid-vapor interfaces.

We will simplify our analysis by considering a small region of the droplet's surface. Then we can introduce Cartesian coordinates, $\mathbf{r}\equiv(x,y,z)$, of which we will choose the z axis to be orthogonal to the interface. The z component of Eq. (3.1) then gives

$$\frac{\partial}{\partial z}P^{\text{bulk}} = -\frac{\partial}{\partial z}P^{\text{surface}} ,\tag{3.2}$$

where P is the zz component of $\overset{\leftrightarrow}{\mathbf{P}}$. We have ignored off-diagonal parts of the pressure tensor since the liquid state cannot support a shear, and shear waves in the solid are irrelevant, by virtue of the argument given at the beginning of this section. It can be shown that the surface part of the pressure can be written as

$$\frac{\partial P^{\text{surface}}}{\partial z} = \rho(\mathbf{r})\frac{\partial}{\partial z}\frac{\delta}{\delta\rho(\mathbf{r})}F(\eta,\mu,T) ,\tag{3.3}$$

where $\delta/\delta\rho$ denotes a functional derivative, and F is the surface part of the free energy (to simplify notation, we will now drop the "surface" superscript). Thus, integrating Eq. (3.2), using Eq. (3.3), over the interface (which we will assume to be a small region located about $z=0$) we have

$$P_s - P_l = \int_{z\simeq 0}dz\rho(\mathbf{r})\frac{\partial}{\partial z}\frac{\delta F}{\delta\rho}$$

$$\simeq \int_{z\simeq 0}dz\frac{\rho(\mathbf{r})}{\rho_l}\frac{\partial}{\partial z}\left[\frac{\delta F}{\delta\eta} + \sum_{\mathbf{G}}\frac{\delta F}{\delta\mu_G}e^{-i\mathbf{G}\cdot\mathbf{r}}\right] ,\tag{3.4}$$

where the second approximate equality follows from Eq. (2.1). (The effects of temperature are not present in the integrand, because they are not surface effects, and so they appear implicitly on the left-hand side of the equation.) Linearizing Eq. (3.4), we have

$$P_s - P_l = \int dz \int d\mathbf{r}'\frac{\rho(\mathbf{r})}{\rho_l}\frac{\partial}{\partial z}\left[\frac{\delta^2 F}{\delta\eta\,\delta\eta}\delta\eta(\mathbf{r}') + \sum_{\mathbf{G}}\frac{\delta^2 F}{\delta\mu_{-G}\delta\mu_G}\delta\mu_G(\mathbf{r}')e^{-i\mathbf{G}\cdot\mathbf{r}}\right] ,\tag{3.5}$$

where $\delta\eta$ and $\delta\mu_G$ are the small variations about which η and μ are linearized in the interfacial region. They will be discussed below. Cross terms involving $\partial^2 f/\partial\eta\,\partial\mu_G$ have been ignored to simplify notation; they do not affect the derivation. There are no $\delta^2 F/\delta\mu_{-G}\delta\mu_{G'}$ terms in the free energy.[14-20] Integrating this equation by parts, and making use of the form of $\rho(\mathbf{r})$ from Eq. (2.1), we have

$$P_s - P_l \simeq - \int dz \int d\mathbf{r}' \left[\frac{d\eta}{dz} + \sum_G \frac{d\mu_G}{dz} e^{i\mathbf{G}\cdot\mathbf{r}} \right] \left[\frac{\delta^2 F}{\delta\eta\,\delta\eta} \delta\eta(\mathbf{r}') + \sum_G \frac{\delta^2 F}{\delta\mu_{-G}\delta\mu_G} \delta\mu_G(\mathbf{r}') e^{-i\mathbf{G}\cdot\mathbf{r}} \right] , \tag{3.6}$$

The contribution from the gradient of $\exp(i\mathbf{G}\cdot\mathbf{r})$ has been neglected in comparison to the gradient of μ_G, which should be large in the surface region. Also, that term clearly does not involve a variation at the interface.

We now identify the variations of η and μ_G with the excitations corresponding to a uniform translation of the interface. Such a translation will leave a flat interface invariant, while it will correspond to the most simple growth mode of a spherical droplet. For example, we write the fluctuation in η as

$$\delta\eta = \eta(z + \zeta) - \eta(z) \simeq \zeta\, d\eta/dz , \tag{3.7}$$

where $\zeta(x,y,t)$ is the displacement of the interface. Similarly,

$$\delta\mu_G \simeq \zeta\, d\mu_G/dz . \tag{3.8}$$

In principle, the two ζ's in Eqs. (3.7) and (3.8) will be different. Nevertheless, since the interfacial region has been assumed to be of small extent, this difference is negligible. Using these expressions in Eq. (3.6) above, we obtain

$$P_s - P_l \simeq -\zeta \int dz \int d\mathbf{r}' \left[\frac{\delta^2 F}{\delta\eta\,\delta\eta} \frac{d\eta}{dz} \frac{d\eta}{dz'} \right.$$
$$\left. + \sum_G \frac{\delta^2 F}{\delta\mu_{-G}\delta\mu_G} \frac{d\mu_G}{dz} \frac{d\mu_G}{dz'} \right] . \tag{3.9}$$

The terms of order $\exp(i\mathbf{G}\cdot\mathbf{r})$, with nonzero $\mathbf{G}$, are negligible because they are rapidly varying in comparison to the other contributions. A specific approximation, which we shall use subsequently, clarifies this. We will assume that the reciprocal-lattice vectors at the surface of a growing droplet are, on average, randomly oriented[30] (or, to be more precise, this applies to the vectors on the surfaces of an ensemble of growing droplets). Thus,

$$\hat{\mathbf{G}}\hat{\mathbf{G}} \simeq \langle \hat{\mathbf{G}}\hat{\mathbf{G}} \rangle \simeq \tfrac{1}{3}\overleftrightarrow{\mathbf{I}} \tag{3.10}$$

at the surface of the droplet, where $\overleftrightarrow{\mathbf{I}}$ is the unit tensor and the angular brackets denote an ensemble average. This assumption limits us to systems where there is a negligible anisotropic contribution to the surface tension (this is the case in, for example, sodium[20]). It will give an inadequate description of a crystalline solid where faceting, or strong anisotropy, plays an important role in the phase transition, as is the case in solid-solid nucleation. However, it should be a reasonable approximation in the solid-melt system, except possibly at very large undercoolings. In any case, from Eq. (3.10) and a cumulant expansion, we obtain

$$e^{i\mathbf{G}\cdot\mathbf{R}} \simeq \langle e^{i\mathbf{G}\cdot\mathbf{R}} \rangle \simeq e^{-G^2 R^2/2} \ll 1 , \tag{3.11}$$

at the droplet's surface, where $\mathbf{R} \equiv R\hat{\mathbf{r}}$, and $G \equiv |\mathbf{G}|$. The last inequality follows because G is of the order of a lattice constant, and R is large.

Finally, we Fourier-transform the x-y plane with the kernel $\exp(iq_x x + iq_y y)$ and obtain from Eq. (3.9), using Eq. (3.10) and the form of F given in Eq. (2.2),

$$P_s - P_l \simeq \zeta q^2 \int dz \int dz' \left[K_0 \frac{d\eta}{dz} \frac{d\eta}{dz'} \right.$$
$$\left. + \sum_G K_G \frac{d\mu_G}{dz} \frac{d\mu_G}{dz'} \right] . \tag{3.12}$$

The terms involving f and gradients with respect to z vanish for the following reason. The solution for two coexisting phases separated by a flat interface is implicitly given by

$$\frac{\delta F}{\delta\eta(z)} = 0 \quad \text{and} \quad \frac{\delta F}{\delta\mu_G(z)} = 0 ,$$

or   (3.13)

$$\frac{d}{dz} \frac{\delta F}{\delta\eta(z)} = 0 \quad \text{and} \quad \frac{d}{dz} \frac{\delta F}{\delta\mu_G(z)} = 0 .$$

Since the vanishing contributions in Eq. (3.13) are proportional to the $q=0$ limit of the integrand of Eq. (3.9), we obtain the result given by Eq. (3.12). The term in the large parentheses of (3.12) is, however, the Oxtoby-Haymet-Harrowell surface tension σ,[18-20] which we have simplified somewhat.[29] Thus, we have

$$P_s - P_l \simeq \zeta q^2 \sigma , \tag{3.14a}$$

or, since ζq^2 is the curvature of the interface,[27]

$$P_s - P_l \simeq 2\sigma/R \tag{3.14b}$$

for a large spherical droplet of radius R. This provides the equation of state for the interface, which is usually called the Laplace-Young equation. It should be noted that Eq. (3.14) is the analogue of the solution of the eigenvalue problem at the droplet interface, given by Langer and Turski for the liquid-vapor system. Furthermore, it is now implicit that we are considering an isotropic surface tension, since the droplet is spherical, so we have made the approximation noted in Eq. (3.10) above. An anisotropic surface tension will lead to a nonspherical droplet, as determined by, for example, the Wulff construction.[31] Of course, averaging over an ensemble of critical droplets, which would be randomly oriented in the melt, will lead to some averaged value of that surface tension. Zia and Wallace[23] have discussed some of the ways in which this can affect a first-order phase transition.

Equation (3.14) is not an unexpected result from this formalism. It does show, however, some of the limitations of our results. In principle, the Laplace-Young equation for a solid-liquid interface should involve the surface stress σ'.[32-34] This is identical to the surface tension σ in a liquid-vapor, or binary fluid system, but there can be differences at a solid interface. One reason for this is that the surface can cause a "reconstruction" of the

bulk, so that the pressure deep within the crystal is not the equilibrium pressure. This effect is not naturally present in this formalism, since we assume a crystal structure. The surface is modeled only by decreasing the intensity of the Bragg peaks due to the **G**'s near the interface. Thus, strictly speaking, the result given above is only true in the limit

$$\left| \frac{\sigma - \sigma'}{\sigma} \right| \ll 1 \; . \tag{3.15}$$

Gibbs[33] has suggested that this may be a reasonable approximation in the limit where the solid can be considered incompressible, which is indeed the limit we are considering. In any case, the effect of a non-negligible $[1 - (\sigma'/\sigma)]$ on nucleation would be of interest, particularly in solid-solid systems where elastic effects play an important role. Note, for example, that σ' can be negative, unlike the positive-definite surface tension. Surface stress is briefly discussed again below, in the text following Eq. (3.29).

The velocity of the interface of the growing droplet can be obtained from the continuity equation

$$\frac{\partial}{\partial t} \delta\rho(\mathbf{r},t) = -\nabla \cdot \rho(\mathbf{r})\mathbf{u}(\mathbf{r},t) \simeq -\frac{d}{dz}\rho(\mathbf{r})u(\mathbf{r},t) \; , \tag{3.16}$$

where the second approximate equality uses the fact that gradients along the surface are of order $1/R$, and so are negligible, u is the z component of $\mathbf{u}$, and $\delta\rho$ is the fluctuation in ρ. Close to the interface, we make use of Eqs. (3.7) and (3.8) to express the right-hand side of this equation as

$$\rho_l \frac{\partial \zeta}{\partial t} \left[\frac{d\eta}{dz} + \sum_{\mathbf{G}} \frac{d\mu_{\mathbf{G}}}{dz} e^{i\mathbf{G}\cdot\mathbf{r}} \right] \simeq -\frac{d}{dz}\rho(\mathbf{r})u(\mathbf{r},t) \; . \tag{3.17}$$

Integrating this over the interfacial region $z \simeq 0$ gives

$$\frac{\partial \zeta}{\partial t} \simeq \frac{\rho_l}{\rho_s(\mathbf{R}) - \rho_l}(u_l - u_s) - u_s \; ,$$

or

$$\frac{\partial R}{\partial t} + u_s \simeq \frac{\rho_l}{\rho_s(\mathbf{R}) - \rho_l}(u_l - u_s) \; , \tag{3.18}$$

where u_l and u_s denote the velocities in the two bulk phases, liquid and solid, respectively,

$$\rho_s(\mathbf{R}) \equiv \rho_l \left[1 + \eta + \sum_{\mathbf{G}} \mu_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{R}} \right] \; , \tag{3.19}$$

and η and $\mu_{\mathbf{G}}$ are the bulk solid values of the order parameters. We shall set u_s to zero, which corresponds to a choice of an inertial frame. We have not set $\rho_s(\mathbf{R}) \simeq \langle \rho_s \rangle$, as in Eq. (3.10) above, because this is not a good approximation to make in $\rho_s - \rho_l$, when η is small.

From the heat equation, for the time dependence of the temperature field in the quasistationary limit, we obtain[25,27,28]

$$T \int d\mathbf{r} \frac{\delta P(\mathbf{r}')}{\delta T(\mathbf{r})} \frac{du}{dz'} \simeq -\lambda \frac{d^2 T}{dz^2} \; . \tag{3.20}$$

This equation asserts that the temperature generated at the interface is thermally conducted away, which gives the minus sign, where λ is the thermal conductivity, and we

again neglect gradients along the interface. Integrating this over the interface gives

$$(u_l - u_s)\left[T\frac{\partial P}{\partial T} \right]_0 \simeq -\lambda \left[\left[\frac{dT}{dz} \right]_{0+} - \left[\frac{dT}{dz} \right]_{0-} \right] \; , \tag{3.21}$$

where 0^+ and 0^- denote, respectively, a position slightly above the interface in the melt and a position in the solid below the interface, and we are assuming that

$$T\frac{\delta P(\mathbf{r}')}{\delta T(\mathbf{r})} \simeq \delta(\mathbf{r} - \mathbf{r}')\left[T\frac{\partial P}{\partial T} \right]_0 \tag{3.22}$$

in the interfacial region. The quantity in large parentheses will be obtained below.

To evaluate the right-hand side of Eq. (3.21), we require the form of the temperature field in the two phases. In the simplest case,[25] $T(\mathbf{r})$ must satisfy Laplace's equation in the two phases. Physically, we must have the following. Far from the droplet, in the melt, the system must be at the temperature T, to which it had been supercooled. The crystalline droplet, however, will be in local equilibrium at a higher temperature T_s, because of the latent heat which has been released. Note, in particular, that T, the supercooled temperature of the melt, is the nonequilibrium quantity which will equilibrate to T_s, through the thermal diffusion of latent heat. The solution of Laplace's equation which is consistent with these boundary conditions is[25]

$$T(\mathbf{r}) = T_s, \quad r < R^- \tag{3.23}$$

and

$$T(\mathbf{r}) = T + (T_s - T)\frac{R}{r}, \quad r > R^+ \tag{3.24}$$

where we have changed notation slightly. To be consistent, $\partial/\partial z$ and $z = 0^+$ in Eq. (3.21) should be replaced by $\partial/\partial r$ and $r = R^{\pm}$. Thus, using the result above to eliminate $u_l - u_s$ in Eq. (3.18), we have

$$\frac{\partial R}{\partial t} \simeq \frac{\rho_l}{\rho_s(\mathbf{R}) - \rho_l} \frac{\lambda}{R(T\partial P/\partial T)_0}(T_s - T) \; . \tag{3.24}$$

It remains to relate $(T\partial P/\partial T)_0$ to the latent heat, and $T_s - T$ to the pressure difference over the interface, and so to the surface tension.

To evaluate $(T\partial P/\partial T)_0$, we introduce a surface projection operator S. The appropriate choice is[35]

$$S\{A\} \equiv -\frac{\rho_l}{\rho_s(\mathbf{R}) - \rho_l} \int dz\, A\left[\frac{d\eta}{dz} + \sum_{\mathbf{G}} \frac{d\mu_{\mathbf{G}}}{dz} e^{i\mathbf{G}\cdot\mathbf{r}} \right] \; , \tag{3.25}$$

which projects a quantity A onto uniform displacements of the interface. Thus, we have

$$\left[T\frac{\partial P}{\partial T} \right]_0 = -\frac{\rho_l}{\rho_s(\mathbf{R}) - \rho_l} \left[\int dz \frac{d\eta}{dz} T\frac{\partial P}{\partial T} \right. $$
$$\left. + \int dz \sum_{\mathbf{G}} \frac{d\mu_{\mathbf{G}}}{dz} e^{i\mathbf{G}\cdot\mathbf{r}} T\frac{\partial P}{\partial T} \right] \; .$$

Furthermore, we write $\partial P/\partial T$ in terms of volume and structural dependences as[14]

$$T\frac{\partial P}{\partial T} \equiv T\left[\frac{\partial P}{\partial T}\right]_{G=0} + \sum_{\mathbf{G}} T\left[\frac{\partial P}{\partial T}\right]_G e^{-i\mathbf{G}\cdot\mathbf{r}} , \quad (3.26)$$

so that, after doing the integral, we obtain

$$\left[T\frac{\partial P}{\partial T}\right]_0 \simeq \frac{\rho_l}{\rho_s(\mathbf{R})-\rho_l}\left[\eta T\left[\frac{\partial P}{\partial T}\right]_{G=0} \right.$$
$$\left. + \sum_{\mathbf{G}}\mu_G T\left[\frac{\partial P}{\partial T}\right]_G \right] , \quad (3.27a)$$

where we again have no "unmatched" favors of $\exp i(\mathbf{G}\cdot\mathbf{R})$, by virtue of the arguments presented earlier. From Refs. 14, 18, and 19, the quantity in the large square brackets is proportional to the latent heat, i.e.,

$$\left[T\frac{\partial P}{\partial T}\right]_0 \simeq \frac{\rho_l}{\rho_s(\mathbf{R})-\rho_l}[\rho_l(1+\eta)l] , \quad (3.27b)$$

where l is the latent heat of fusion, which can now be used in Eq. (3.24) for $\partial R/\partial t$.

Finally, to obtain $T_s - T$ we have followed the local equilibrium arguments of Turski and Langer. Since this involves only a transcription of that treatment, with similar generalizations to those given above, we will merely present the result, after a short discussion. The physics behind the algebra proceeds as follows. First note that the chemical potentials $\phi_s(R)$ and $\phi_l(R)$ in the crystalline nucleus and the liquid matrix are equal. [Note, however, our discussion following Eq. (3.29) below.] Furthermore, the chemical potentials are equal when the two phases coexist across a flat interface. Thus,[25,29] we may write

$$\int_{\phi_s(\infty)}^{\phi_s(R)} d\phi = \int_{\phi_l(\infty)}^{\phi_l(R)} d\phi . \quad (3.28)$$

By integrating the Gibbs-Duhem equation (or rather its appropriate generalization for a solid), one then obtains a relationship between P_s and P_l, and $T_s - T$. Eliminating P_l in terms of the critical droplet radius R^*, and P_s by use of the Laplace-Young equation, Eq. (3.14), gives

$$T_s - T \simeq \frac{2\sigma T}{l\rho_l(1+\eta)}\left[\frac{1}{R^*}-\frac{1}{R}\right] . \quad (3.29)$$

[Alternatively, one may proceed by again considering the Navier-Stokes equation (3.1) above, but for the time dependence of the velocity field, rather than the momentum density. This serves to eliminate the density piece which was studied above, and, from the remaining temperature piece, Eq. (3.29) can be obtained.]

For the same reason as we discussed following Eq. (3.14) above, this result is only correct to order $1-(\sigma'/\sigma)$. In fact, it should be noted that the chemical potential is difficult to define at a solid-liquid interface.[32-34] An additional factor of $2(\sigma'-\sigma)/R$ enters the equation for the equality of the chemical potentials across a spherical surface of radius R.[32] If we put the factors of σ' in "by hand," we find that they cancel in intermediate steps, the eventual result still being Eq. (3.29). This is, perhaps, not surprising. One would naturally expect the nucleation

rate, which we obtain below, to involve the positive-definite σ rather than the (possibly negative) σ'. Nonetheless, it is not obvious what effect a large negative surface stress would have on the nucleation rate, and as we have mentioned above, this question cannot be answered with the formalism which we are using here.

The equation of motion for a droplet of radius R can now be obtained from Eqs. (3.24), (3.27b), and (3.29):

$$\frac{\partial R}{\partial t} \simeq \frac{2\lambda\sigma T}{l^2\rho_l^2(1+\eta)^2}\frac{1}{R}\left[\frac{1}{R^*}-\frac{1}{R}\right] . \quad (3.30)$$

The physical picture implied by this equation is the following: large droplets grow, while small ones shrink. The rate-limiting process for the dynamics will involve droplets of radii slightly larger than the critical droplet. Linearizing around R^* gives $R - R^* \propto e^{\kappa t}$ for those droplets, where

$$\kappa \simeq \frac{2\lambda\sigma T}{l^2\rho_l^2(1+\eta)^2(R^*)^3} \quad (3.31)$$

is the dynamical prefactor for the nucleation rate. Further discussion of this result will be deferred to the following section.

For late times, after the birth of droplets no longer plays an important role, Eq. (3.31) is apparently consistent with $R \sim t^{1/3}$ Lifshitz-Slyozov[36] growth. In that case, the dynamics proceeds by large droplets growing at the expanse of small droplets, by condensation and evaporation from their respective surfaces. An important qualification of this is that anisotropies, defects, and lattice mismatches, which will certainly play important roles in the late-time dynamics, are absent from our treatment.

IV. STATISTICAL PREFACTOR AND DISCUSSION

We shall now present the result for the statistical prefactor Ω_0, without derivation. The treatment is the same as that given by Langer and Turski[24] for the liquid-vapor system. Basically Ω_0 has two parts: a piece proportional to the volume of the system (which is the most important contribution), arising from the Jacobian of the transformation from spatial coordinates to an order-parameter description, and the fluctuation corrections to the critical droplet's free energy $\Delta F(R^*)$ [Eq. (2.6)]. To simplify the analysis, we have followed Harrowell and Oxtoby[20] and considered a "one-order-parameter description." This is thought to be a reasonable approximation for body-centered-cubic solids, like sodium or one of the other alkali metals. The single order parameter μ_1 is chosen so that its corresponding reciprocal-lattice wave number $|\mathbf{G}|$ is in the position of the observed first peak of the structure factor for the supercooled melt. All other μ_G are set to zero. Furthermore, following Ref. 20, we assume that $K_0 \simeq 0$ in Eq. (2.2). It is then quite straightforward to obtain the statistical prefactor, which we find to be

$$\Omega_0 \simeq \left[\frac{L}{\xi}\right]^3\left[\frac{2}{3\sqrt{3}}\right]\left[\frac{\sigma\xi^2}{k_B T}\right]^{3/2}\left[\frac{R^*}{\xi}\right]^4 , \quad (4.1)$$

where L^3 is the volume of the system, and we have introduced

$$\xi \equiv \left[\frac{1}{K_1} \frac{\partial^2 f}{\partial \rho_l^2} \right]^{-2} , \qquad (4.2)$$

which is a small "correlation" length. This, then, completes our analysis. For the remainder of the paper, we shall discuss our results.

Using the results for $\Delta F(R^*)$, κ, and Ω_0 derived above [in Eqs. (2.6), (3.31), and (4.1), or with the more complete expression for ΔF given by Harrowell and Oxtoby[20]], we obtain the nucleation rate I from Eq. (2.7). Our main interest here concerns the dynamical prefactor κ. The result above is qualitatively sensible: The nucleation rate is faster for transitions which are almost second order (i.e., where l is small, as in the alkali metals), and is slower when the thermal diffusivity, which is proportional to the thermal conductivity λ, is small (as is the case for noble solids, compared to metals).

We would expect these same tends to be seen experimentally, although it should be noted that nucleation experiments are notoriously difficult. This is because of the exponential factor in I, which tends to make the results of a detailed theory (in particular, the form of κ) difficult to observe. Nonetheless, a rigorous experimental or molecular-dynamics test[8-11] of theory could be performed on, for example, a system with an anomalously small, or strongly-temperature-dependent, thermal conductivity.[10(a)] In such a system, it is the dynamics which effectively limits the rate of nucleation of the solid droplets, rather than the volume factor from Ω_0. All the quantities necessary for a test of theory (particularly σ and l), with the exception of λ, can be calculated from this formalism.[14-20] This is important for σ, since the solid-melt surface tension is difficult to measure and, indeed, is often obtained experimentally from nucleation rates. (Also, since there is no critical point here, we cannot appeal to universal critical behavior to simplify the form of expressions like σ, as was done for liquid-vapor systems.[24-26]) Despite the possible difficulty of experiments, however, we stress they would be of great interest: At present, there is no experimental test which can distinguish the results of Langer's first-principles theory of nucleation from those of classical theory.

One difficulty which complicated interpretation of experimental data for fluids was as follows. There, experimentalists often measured a "completion time" rather than a nucleation rate, that being the time taken for droplets to grow to an experimentally detectable size.[8,9,21] That growth period was of importance because of critical slowing down in the fluids. A fundamental theory of the simultaneous birth and growth of droplets remains a difficult and unsolved problem, though some progress has been made.[37] Although the present theory only applies to the birth of droplets, it is important to note that this may be separable from the growth stage in some solid-melt system: According to numerical simulations,[11] the growth regime can be extremely rapid, and so the rate at which macroscopic droplets form may indeed be limited by the nucleation rate, thus rendering a test of theory somewhat more tractable.

The result we obtain generalizes the expression derived via classical arguments by Turnbull and Fisher:[12]

$$I \simeq \left[\frac{k_B T}{h} e^{-\Delta A / k_B T} \right] N e^{-\Delta F / k_B T} , \qquad (4.3)$$

where h is Planck's constant, ΔA is an activation energy for diffusion, and N is the number of particles. This may be compared to Eq. (2.7) and the subsequent results [Eqs. (2.6), (3.31), and (4.1)]: The term in the large parentheses is the dynamical prefactor, while N is the statistical prefactor. There is an important difference in the expressions for κ: Turnbull and Fisher express the diffusivity as an undetermined activation energy for diffusion, while in Eq. (3.31) we write it explicitly in terms of the conductivity, and the field-theoretic expressions for the surface tension and the latent heat. This statistical-mechanical form for κ is the main new result of our first-principles treatment and provides an important generalization of the result of classical theory. Our result for I is similar to that of Turski and Langer[25] for the liquid-vapor system. It should be noted, however, that implicit in the expressions for σ and l [Eqs. (3.12) and (3.14), and (3.27)] is the structural information about the crystalline nucleus. In fact, these quantities can be, and indeed have been,[14-20] calculated from this formalism, as we have mentioned above.

Let us now turn to some of the limitations of our treatment. The first qualification is standard.[24,25] It is not clear whether fluctuations have been correctly taken into account in the expression for the solid-melt surface tension. That is, should σ, in the expressions above, be interpreted as the bare or renormalized surface tension. The special difficulty here is that the ingredients of the theory include the experimental (and thus, of course, the "renormalized") structure factor of the melt. For the time being we will simply assume that the difference between the bare and renormalized σ's is negligible. Although this is an important conceptual problem, it probably is not of significant consequence compared to the related problem discussed below: the description of the crystal.

While our treatment should provide a reasonable description of a crystalline droplet nucleating from the melt, several aspects concerning the description of the crystal will handicap generalizations to other problems. For example, one cannot handle surface reconstruction with this formalism, or any of the physics involved with defects in the crystal structure. Thus, the above approximate description cannot be extended to a solid-vapor interface. Anisotropic stresses and modes in solids are not present in the dynamical formulation. Thus, nucleation of a liquid droplet in a superheated solid cannot be described, nor can solid-solid nucleation. Late-time dynamics, which must involve, for example, lattice-mismatch effects, cannot be correctly described. Higher-order effects, involving modes in the crystalline nucleus, cannot be adequately explained by this formalism. Also, as we have noted several times in the paper, a subtle point not present in the analysis is the possible difference between surface stress (the mechanical difference in pressures at an interface) and surface tension (the surface free energy per unit area).[32-34] All of these remarks have their source in the somewhat artificial treatment of the solid by liquid-state methods. Properties involving the

crystalline structure of the nucleated droplet, and, in particular, the origin of that crystal structure, thus require further theoretical analysis for a complete and satisfying description encompassing solid-solid and solid-vapor systems, as well as solid-melt nucleation.

Despite these qualifications, we believe that this work provides a useful first step towards such a complete theory. We have shown that Langer's field theory of nucleation can be applied to study the birth of a crystalline droplet from a supercooled melt. Our work extends the previous program of Ramakrishnan and Yussouff and of Oxtoby, Haymet, and Harrowell, for the freezing transition, and generalizes the classical theory of Turnbull and Fisher. An experimental test of the result would be of interest.

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