

Formation of nucleation centers in a crystal

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A theory is derived for the critical nucleation center in the course of a first-order phase transition in a solid. The critical nucleation center turns out to be very oblate, because this shape lowers the elastic energy of the deformations which arise because of the difference between the densities of the two phases. The energy of formation of such this nucleation center is derived on the basis of an analogy with the crack problem. The possibility of a transition from nonspherical to spherical nucleation centers as the supersaturation increases is discussed.

The rate at which the new phase is nucleated in the course of a first-order phase transition is determined by the equilibrium distribution function of the nucleation centers and by their growth kinetics (Ref. 1, for example). Putting aside anisotropy effects, we conclude that since there are equilibrium vacancies and interstitial atoms in the interior of a crystal, the stage of nucleation in the immediate vicinity of the transition should not differ in any way from (for example) the process by which liquid droplets are nucleated in supersaturated vapor. Kinetic reasons, however, may make a different nucleation path more effective as we get away from the transition point.

We ignore the equilibrium defects in the crystal. A deformation must then arise around the nucleation center of the new phase, because of the difference between the densities of the two phases. As Lifshits and Guild² have pointed out, this deformation changes the picture of the nucleation process substantially. Motorin³ has shown, however, that the assertion in Ref. 2 that there is an equilibrium striction-related hysteresis is incorrect. The nucleation center discussed in Ref. 2 was spherical, while an oblate shape is more favorable.

In this letter we offer a solution to the problem of the critical nucleation center in an isotropic crystal. This solution can be found thanks to the use of the exact results found by Griffith⁴ and Sneddon⁵ in the theory of cracks.

The change in free energy upon the formation of a nucleation center of the new phase is

$$\Delta F = \int f_s dV_{s0} + F_L + \int \alpha dS - f_{s0} dV_0. \quad (1)$$

Here f_s and f_{s0} are the free energy densities of the deformed and undeformed (initial) crystal, respectively. They satisfy

$$f_s - f_{s0} = \frac{1}{2} \sigma_{ik} u_{ik}, \quad (2)$$

where σ_{ik} and u_{ik} are the stress and strain tensors (for simplicity we are assuming that the phase transition occurs at a zero external pressure), and dV_{s0} is the volume element in the integration over the volume of the undeformed state of the crystal (not including the volume of the nucleation center). In this integral, the integration runs over the entire volume of the initial state. The quantity α is the surface energy of the interface, and F_L is the bulk free energy of the nucleation center of the new phase, given by

$$F_L = \mu N - PV. \quad (3)$$

For definiteness, we will speak in terms of a melting for the time being; i.e., the new phase, which contains N particles and occupies a volume V , is a homogeneous melt with a chemical potential μ and a pressure P .

We write the energy in (1) in the form

$$\Delta F = \int (f_s - f_{s0}) dV_{s0} + (\mu - Pv_s - f_{s0}v_s)N - P(V - v_s N) + \int \alpha dS, \quad (4)$$

where v_s is the atomic volume of the crystal at zero pressure. Substituting (2) in here, and integrating by parts (for the equilibrium strain field), we reduce the first term in (4) to the following integral over the boundary of the nucleation center:

$$\int (f_s - f_{s0}) dW_{s0} = -\frac{1}{2} \int \sigma_{in} u_n dS = \frac{1}{2} P \int u_n dS. \quad (5)$$

The latter inequality is correct if we ignore surface-tension effects⁶ in the mechanical-equilibrium boundary conditions. Since the medium is continuous, we have the following expression for the volume of the melt:

$$V = Nv_L(P) = Nv_s + \int u_n dS, \quad (6)$$

where $v_L(P)$ is the atomic volume of the liquid at pressure P , and the last term describes the change in the volume of the crystal upon deformation. Finally, using (5) and (6), we put expression (4) in the form

$$\Delta F = (\mu - Pv_s - f_{s0}v_s)N - \frac{1}{2} P \int u_n dS + \int \alpha dS. \quad (7)$$

We consider a nucleation center which is a very oblate circular lune of radius R and height $h \ll R$. In a first approximation, we will then ignore the height of the lune in solving the elastic-theory problem. In this case the pressure P exerted on the crystal by the liquid is given on a plane circular cut within the radius R . This problem is completely equivalent to the crack problem.^{4,5} We need only the normal component of the displacement vector, $u_n = u_z$, at the interface [see (7)]:

$$u_z = 4P(1 - \sigma^2)(R^2 - r^2)^{1/2} / \pi E \quad (8)$$

(Ref. 5). Here σ is the Poisson ratio, and E the Young's modulus.

The divergence of the stress near the edge of a crack has been discussed at length in the literature. However, the stress becomes significant only at atomic distances, as in the case of dislocations and point defects.

To calculate the pressure P we use the Gibbs–Thomson phase-equilibrium condition. In this condition, in the leading approximation in the small deviation from the phase-transition point, we can ignore capillary and striction-related corrections:

$$\mu(P) = (P + f_{s0})v_s \quad (9)$$

Expanding the chemical potential μ in P , we find

$$P = \Delta\mu / (v_L - v_s), \quad (10)$$

where v_L is the atomic volume of the liquid at zero pressure, and the quantity

$$\Delta\mu = v_s f_{s0} - \mu(0) \quad (11)$$

specifies the deviation from the phase-transition point.

Using (7)–(9), we find the energy of formation of the nucleation center to be

$$\Delta F = -\frac{1}{2}P \int u_n dS + \int \alpha dS = -8P^2(1 - \sigma^2)R^3/3E + 2\pi R^2\alpha. \quad (12)$$

This expression is precisely the same as the expression for the energy of a crack. The radius of the critical nucleation center, which corresponds to the extremum of energy (12), is

$$R_c = \pi E \alpha / 2(1 - \sigma^2)P^2, \quad (13)$$

and the energy of the nucleation center is [we are using (10)]

$$\Delta F_c = \pi^3 \alpha^3 E^2 (v_L - v_s)^4 / 6(1 - \sigma^2)^2 (\Delta\mu)^4. \quad (15)$$

From (6), (8), (10), and (13) we find the total number of particles in the critical nucleation center to be

$$N_c = 2\pi^3 \alpha^3 E^3 (v_L - v_s)^4 / 3(1 - \sigma^2)^2 (\Delta\mu)^5. \quad (15)$$

The lune height h can be found from

$$bhR^2 = v_s N, \quad (16)$$

where the numerical factor b depends on the shape of the nucleation center. From (11), (13), (15), and (16) we find the relation

$$h_c/R_c \sim (1 - \sigma^2)v_s \Delta\mu / E(v_L - v_s)^2. \quad (17)$$

In our approximation the energy of the nucleation center does not depend on the detailed shape. It is not difficult to verify that in the leading approximation the nucleation center is a figure bounded by two small spherical segments. The primary shape-dependent correction in Gibbs–Thomas condition (9) arises from a capillary effect ($\alpha K v_s$, where K is the curvature of the surface); the shape dependence of the deformation correction can be ignored. As a result, the curvature K turns out to be a constant.

A critical nucleation center thus exists for an arbitrarily small $\Delta\mu$, so there is no hysteresis. However, the striction effect, due to the difference between the atomic volumes of the phases, leads to a substantial increase in the energy of formation of the nucleus: $\Delta F_c \propto (\Delta\mu)^{-4}$ instead of the customary $\Delta F_c \propto (\Delta\mu)^{-2}$. It can be seen from (17) that at small angles of $\Delta\mu$ the height of the lune is much smaller than its radius and that the nucleation center becomes more rounded as $\Delta\mu$ increases. According to Ref. 2, for $\Delta\mu$ greater than a critical $\Delta\mu_c$ given by

$$\Delta\mu_c = (v_L - v_s)^2 E (1 + 2\beta) / 3v_s (1 + \sigma) (1 + \beta)^2,$$

$$\beta = 2E / 3(1 + \sigma)k, \quad (18)$$

where k is the bulk modulus of the liquid, a solution corresponding to a spherical nucleation center exists [with $\Delta\mu \sim \Delta\mu_c$, we find $h_c/R_c \sim 1$ from (17)]. In the region $\Delta\mu_c < \Delta\mu < \Delta\mu_s$, however, this solution is unstable with respect to a shape perturbation of the type

$$R = R_c + \delta Y_{20}(\theta), \quad (19)$$

where Y is the second spherical harmonic. A simple but lengthy calculation yields the following expression for $\Delta\mu_s$:

$$\Delta\mu_s = f(\sigma, \beta) \Delta\mu_c,$$

where the function $f \gg 1$ is extremely complicated. A transition from nonspherical to spherical critical nucleation center can thus occur at $\Delta\mu > \Delta\mu_s$. Since a term cubic in δ in the energy is not prohibited by symmetry for the case of perturbation (19), this transition is not continuous. At the point of the transition, the energies of the critical nucleation centers (spherical and nonspherical) are equal. However, even if the critical nucleation center is spherical, it loses its stability with respect to a perturbation of the type in (19) once it reaches a size R_s , i.e., the size of a spherical critical nucleation center under the condition $\Delta\mu = \Delta\mu_s$:

$$R_s = 2\alpha / (\Delta\mu_s - \Delta\mu_c). \quad (20)$$

The evolution of this instability and the shape of the growing nucleation center are problems which cannot be solved in a thermodynamic treatment; they require solution of the kinetic problem.

In the 2D case this transition from noncircular to circular critical nucleation centers may be continuous, since in the case of a perturbation of the radius at the harmonic $\delta \cos 2\theta$, which loses stability, the symmetry forbids a term in the energy cubic in δ (the states δ and $-\delta$ differ by a rotation through $\pi/2$). Otherwise, the results in the 2D case are analogous to the 3D results. In particular, here are the parameters of the critical nucleation center for small values of $\Delta\mu$ (cf. Ref. 4):

$$u_z = 2P(1 - \sigma^2)(R^2 - r^2)^{1/2}/E, \quad (8a)$$

$$R_c = 2E\alpha/\pi(1 - \sigma^2)P^2, \quad (13a)$$

$$\Delta F_c = 4\alpha^2 E (v_L - v_s)^2 / \pi(1 - \sigma^2) (\Delta\mu)^2. \quad (14a)$$

In the course of a solid-phase transition, in which the nucleation center of the new phase is also a crystal, the condition that the pressure be constant within the nucleation center is not mandatory. However, the solution found above is an extremum again in this case. We might add that for transitions involving a small volume defect (e.g., for magnetic transitions and for transitions which are approximately second-order transitions) a situation may arise in which it is difficult for crystal defects (vacancies, interstitial atoms, and dislocations) to form at the interface. Since the interface is coherent in this case, there is the additional condition that the displacement vector must be continuous at this interface [see condition (II,6) in Ref. 7]. Under this restriction, nucleation is possible only if a critical supersaturation $\Delta\mu_c$ is exceeded, and the nucleation center is spherical.⁷

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