Elastic Effects on the Kinetics of a Phase Transition

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The kinetics of the nucleation and growth of a new phase in the course of a first-order phase transition in a solid is described. The growing center of a new phase is very oblate, because this shape lowers the elastic energy of the deformations which arise due to the difference in the densities of the two phases. An analogy with the crack problem is emphasized. The growth of the nucleus is governed by the combination of the elastic effects and the diffusion of the latent heat. The elastic cracklike effects lead to the selection of the growth mode which is substantially different from the ordinary dendrite. [S0031-9007(99)08492-6]

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Nucleation and growth phenomena occur in conjunction with a first-order phase transition. There a critical nucleus is formed by thermodynamical fluctuations. This nucleus afterward grows in a deterministic way. The growth of a crystal from the melt or from a solution is a typical example of such a process. Due to the well-known Mullins-Sekerka instability [1] the dendritic patterns often form.

Novel aspects of the kinetics of phase transitions appear if the initial metastable phase is a crystal. Because of a difference in the densities of the two cooperating phases, a part of the crystal around a nucleation center of the new phase becomes deformed, which modifies the system's behavior, in comparison with an unstressed situation. The critical nucleus has an oblate shape, which is more favorable compared to a spherical shape because it lowers the elastic energy [2,3]. The energy of the formation of this nucleation center and some other thermodynamic properties have been derived in [3] on the basis of the analogy with the crack problem. The elastic deformation leads to a substantial increase in the energy of the formation of the nucleus in comparison with the unstressed situation. While in the usual growth phenomena the deviation from the spherical shape appears due to the Mullins-Sekerka instability; in our case the shape is very oblate even for the equilibrium critical nucleus.

The main purpose of this Letter is to describe the growth of a supercritical nucleus in the presence of the elastic effects. The motion of a growing interface is governed by the interplay between the irreversible diffusion of the latent heat (diffusional growth) and the reversible work done for elastic deformation and the formation of a new surface area. The kinetics of this process and pattern formation during this type of diffusional growth is substantially modified due to the elastic effect. We will find a new growth law for the evolution of the nucleus which is quite different from the customary dendritic growth law [4].

For definiteness, we will speak in terms of melting for the time being. The melting process of crystals is usually initiated at heterogeneous sites such as grain boundaries or free surfaces. [5]. However, providing the heterogeneous nucleation can be avoided by means of experimental techniques; crystals can be superheated above the equilibrium melting point [6,7]. Thus we assume that the new phase, which contains N particles and occupies a volume W, is a homogeneous melt with a chemical potential μ and a pressure P (we assume that the external pressure is zero). Because of the conservation of mass, we have the following expression for the volume of the melt:

$$W = N v_L = N v_s + \int u_n \, dS \,, \tag{1}$$

where v_L and v_s are the atomic volumes of the liquid and solid phases, and the last term describes the change in the volume of the crystal upon deformation (u_n is the normal component of the displacement vector at the interface).

The center is assumed to be a very oblate lentil of radius R and height $h \ll R$. In a first approximation, we can ignore the height of the lentil in solving the elastic 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 equivalent to the crack problem and its solution gives us the normal component of the displacement vector at the interface (see, for example, [8]).

The equilibrium Gibbs-Thomson condition at the interface is [9,10]

$$v_s \left[f_{s0} + P + \frac{\tilde{\sigma}_{rr}^2 + \tilde{\sigma}_{\phi\phi}^2 - 2\nu \tilde{\sigma}_{rr} \tilde{\sigma}_{\phi\phi}}{2E} + \alpha K \right] = \mu(P) \,. \tag{2}$$

Here f_{s0} is the free energy density of the undeformed (initial) crystal and we have introduced cylindrical coordinates (r, ϕ, z); $\tilde{\sigma}_{ik} = \sigma_{ik} - \sigma_{zz} = \sigma_{ik} + P$, σ_{ik} is the stress tensor, ν and E are the Poisson and Young coefficients, and K is the curvature of the interface (considered positive for a convex solid).

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It was found [3] that the radius of the critical nucleus is related to the pressure P by the Griffith formula,

$$R_c = \frac{\pi E \alpha}{2(1 - \nu^2) P_c^2}. \quad (3)$$

and the mean lentil height is

$$h_c/R_c = 16(1 - \nu^2) v_s \delta\mu/[3\pi E (v_L - v_s)^2]. \quad (4)$$

Here the quantity $\delta\mu = v_s f_{s0} - \mu(0)$ gives the deviation from the phase-transition point and it is related to the pressure P_c,

$$\delta\mu = P_c(v_L - v_s). \quad (5)$$

Our basic assumption requires the ratio (4) to be small, as is the case for a small deviation from the phase-transition point and a not too small difference in the atomic volumes of the phases.

The critical nucleus is unstable and continues to grow if its radius R is larger than R_c. Latent heat is absorbed by the front and should be delivered to the front by thermodiffusion. The temperature field in the solid phase obeys the diffusion equation and the following boundary conditions:

$$D\nabla^2 u = \partial u/\partial t, \quad (6)$$

$$v_n = -D\vec{n} \cdot \nabla u|_{\text{int}}, \quad (7)$$

$$u|_{\text{int}} = \Delta(1 - P/P_c). \quad (8)$$

Here $u = (T_\infty - T)c_p/L_p$ is the rescaled temperature field, measured from the temperature at infinity T_∞, c_p is the specific heat, D the thermal diffusion constant, and L_p the latent heat. In terms of these parameters,

$$\Delta = (T_\infty - T_M)c_p/L_p = \delta\mu T_M c_p/(L_p^2 v_s)$$

is the dimensionless superheating (T_M is the melting temperature). The physics underlying Eqs. (6)–(8) is quite simple. A melting front absorbs latent heat that diffuses as expressed by (6); the requirement of heat conservation at the interface gives (7) ($\vec{n}$ is the normal to the interface and v_n is the normal velocity). Equation (8) is the local equilibrium condition (2) where we have neglected elastic and capillary corrections. Under this condition, the field u inside the melt is constant and equal to its interfacial value (8).

The local equilibrium also requires that the pressure P inside the nucleus is related to the radius R by the equilibrium Griffith formula (3) as it is for the critical nucleus,

$$P^2 = \frac{\pi E \alpha}{2(1 - \nu^2) R}. \quad (9)$$

This pressure decreases when R increases. Then the interface equilibrium condition, Eq. (8), can be rewritten as

$$u|_{\text{int}} = \Delta(R) = \Delta(1 - \sqrt{R_c/R}). \quad (10)$$

If the radius of the nucleus R is smaller than the diffusion length $(Dt)^{1/2}$, we can solve the Laplace equation instead of the diffusion equation, and, using the well-known analogy with the electrostatic problem [11], we can find the temperature field around the nucleus. The field far away from the growing nucleus, $\tilde{r} \gg R$, decays as

$$u(\tilde{r}, t) = \frac{2R\Delta(R)}{\pi\tilde{r}}, \quad (11)$$

where $\tilde{r} = \sqrt{r^2 + z^2}$. The global heat conservation law requires that

$$\frac{d}{dt}[\pi R^2(t) h(t)] = 8DR\Delta(R), \quad (12)$$

where h is the mean height of the nucleus.

The mass conservation law, Eq. (1), reads

$$(v_L - v_s)\pi R^2 h/v_s = \int u_n \, ds = \frac{16(1 - \nu^2)}{3E} P R^3. \quad (13)$$

This equation together with the Griffith formula (9) gives the relation between h and R,

$$h = \sqrt{\rho R}, \quad (14)$$

where the characteristic length scale

$$\rho = \frac{128\alpha(1 - \nu^2) v_s^2}{9\pi E (v_L - v_s)^2} \quad (15)$$

depends only on material parameters. Eliminating h from Eq. (12), we find a closed equation for the evolution of the nucleus radius $R(t)$,

$$\frac{d}{dt}[R^{3/2}] = \frac{24D\Delta(R)}{5\pi\sqrt{\rho}}. \quad (16)$$

In a close vicinity of R_c the radius R grows exponentially with time $(R - R_c) \sim \exp(\lambda t)$ with $\lambda = 8D\Delta/(5\pi R_c h_c) \sim \Delta^4$. This parameter λ is an important ingredient of the nucleation theory. For $R \gg R_c$, $\Delta(R) \approx \Delta$ and Eq. (16) gives the growth law,

$$R(t) = \left[\frac{24Dt}{5\pi\sqrt{\rho}}\Delta\right]^{2/3}. \quad (17)$$

We can also find the shape of the growing nucleus. The temperature field u in the vicinity of the nucleus, which obeys the Laplace equation, is given by the solution of the corresponding electrostatic problem [11]. The evolution equation (7) reads

$$\dot{z} = \frac{2D\Delta}{\pi\sqrt{R^2 - r^2}}. \quad (18)$$

This equation can be easily integrated to find a self-similar shape of the nucleus,

$$\frac{z(r,t)}{h(t)} = \frac{5}{8}\left(\frac{r}{R}\right)^{1/2} \int_{r/R}^{1} \frac{ds}{s^{3/2}\sqrt{1 - s^2}}, \quad (19)$$

where $R(t)$ and $h(t)$ are given by Eqs. (17) and (14), respectively. For $x = (R - r) \ll R$, the shape is parabolic, $z \sim \sqrt{\rho x}$, where ρ is given by Eq. (15). A closer inspection shows that, as for the static case [3], in the small vicinity of the edge, the elastic and capillary effects should be taken into account and the edge remains singular.

We have used the hydrostatic approximation and have neglected the viscous flow necessarily present inside the nucleus due to mass redistribution. The characteristic difference in pressure, arising from the viscous flow with the velocity of the order of $\dot{R}$, is $\delta P \sim \eta \dot{R} R/h^2$ where η is the viscosity. This pressure is small compared to the hydrostatic pressure P [Eq. (9)],

$$\frac{\delta P}{P} \sim \frac{\eta D E (v_L - v_s)^3}{\alpha^2 v_s^3} \Delta \ll 1, \qquad (20)$$

if the deviation from the equilibrium is small, $\Delta \ll 1$. Thus, the used hydrostatic approximation is legitimate.

The smooth shape of a growing nucleus should undergo a Mullins-Sekerka instability. In the usual case of the spherical nucleus this happens when the radius of the nucleus becomes a few times larger than the critical radius [1]. In our case, in which the nucleus has an oblate shape an instability occurs when the radius R is close to R_c. Indeed, the threshold of the instability can be roughly estimated from the condition $\lambda_{MS} \sim R$ where the Mullins-Sekerka length is $\lambda_{MS} \sim (d_0 D/\dot{h})^{1/2}$ and $d_0 = \alpha T_M c_p / L_p^2$ is the capillary length. Using Eqs. (14) and (16), we find for the threshold of the instability $(R - R_c) \sim h_c \ll R_c$. This instability should lead to the development of sidebranches behind the moving edge in the same way as it happens in the customary dendritic growth [4].

The growth law $R(t) \sim t^{2/3}$ crosses over to the constant velocity regime at time t_c, when the radius R becomes of the order of the diffusion length, $R(t_c) \sim (D t_c)^{1/2}$ and the diffusion equation should be used instead of the Laplace equation. Using the growth law, Eq. (17), we can estimate t_c and the velocity in the asymptotic regime,

$$v \sim \frac{D}{\rho} \Delta^2. \qquad (21)$$

This result corresponds to the stationary moving Ivantsov parabolic solution $z \sim \sqrt{\rho x}$ where the selection of the particular parabola is due to the elastic effects. In addition to the small scale ρ the developed "dendritic" structure has the macroscopic length scale (the distance between the independent branches) of the order of $R(t_c) \sim D/v \sim \rho/\Delta^2$. It is important that not only the selected radius ρ is very different from the ordinary dendritic radius, but also the whole shape which is oblate in our case differs from the rather needle shape of three-dimensional dendrites.

We should note that the quasistatic (Laplace) approximation, which has been used for the description of the initial and intermediate stages of the evolution of the nucleus, is legitimate if $d_0/\rho \ll 1$. This is possible if the difference in the densities is small enough. Otherwise, even the initial stage of the evolution should be described in the framework of the full diffusion equation. In this case, after the initial transient we go directly to the final asymptotics (21) without an intermediate asymptotics (17).

The discussed growth problem is closely related to other diffusional growth problems. Equation (18) corresponds to a free-boundary problem, where the temperature at the interface is assumed to be constant along the interface and equal to the equilibrium melting temperature. Equation (18) has a family of solutions where $R \sim t^{\beta}$ and $h \sim t^{(1-\beta)}$. The value of $\beta = 1/2$ corresponds to the spherical shape (or a circular shape for the two-dimensional problem), while $1 > \beta > 1/2$ corresponds to the oblate shape. A particular selection of β depends on the physics involved in the problem under consideration.

In the customary dendritic growth, capillarity plays the role of a singular perturbation and the anisotropy of the surface energy is a prerequisite for the existence of the dendritic solution [4]. The basic result is that the so-called stability parameter $\sigma = 2 D d_0/(\rho_t^2 v)$ is supposed to be equal to $\sigma^*(\epsilon)$ and depends only on the anisotropy of the surface tension. Here ρ_t is the radius of the curvature of the dendritic tip, v is the tip velocity, and ϵ is the strength of the anisotropy. Together with the heat conservation, it leads to the selection of the velocity and length scale of the dendritic structure [4,12]. In particular, for the intermediate Laplace asymptotics of the two-dimensional growth it gives a growth law with $\beta = 3/5$ [13,14].

Another example of the related diffusional growth problem is the so-called noise-reduced diffusion limited aggregation on two-dimensional lattices described analytically in [15]. In addition to the conservation law, the fact was used that the length scale of the growing tip ρ is restricted only by the lattice distance. This leads to the growth law with $\beta = 2/3$ as in our case. However, the physics leading to the selection of ρ in the form of (15) in our case is quite different in that this selection is due to the elastic effects.

The dendriticlike structures during melting have been observed experimentally (see, for example, [16], and references therein). However, the used materials are very plastic and it is unclear whether the elastic effects have been very pronounced in these experiments.

In a recent paper [17] the problem of the nucleation in a superheated crystal has been discussed in the context of a homogeneous nucleation catastrophe for melting. The authors also took into account elastic effects due to the difference of densities but they traditionally used only the spherical shape. The oblate shape of the nucleus, which lowers the elastic energy, would change their results.

The presented theory should be applicable not only to the melting process but also to the other types of first-order phase transitions inside a solid phase. The growth of gaseous cracklike pores from supersaturated solid solutions (see, for example, [18], and references therein) requires

diffusion of the impurities towards the crack, while elastic deformations arise in order to compensate the volume difference. Another example is a transition of a metastable metallic crystal phase into an insulating amorphous state which is accompanied by an increase of specific volume. A stepwise annealing was used in [19] to investigate the temperature dependence of the conductivity of a two-phase material. On the basis of the obtained results the authors came to the conclusion that the growing amorphous phase has very oblate shape producing two-dimensional insulating surfaces inside of the parent metallic phase.

In summary, the combination of the surface tension effects with the elastic effects near the singular edge (Griffith formula) leads to the selection condition in the form of (14) and, eventually, to the new growth laws, Eqs. (17) and (21). This elastic dendrite is different from the customary dendrite. In the latter case, selection is mostly governed by the anisotropic surface tension and the singularities of the interface equation of motion are located in the complex plane [4]. It is quite remarkable that the physical mechanism which controls the development of the diffusional instability can be so different for solidification and melting. We note that the described elastic effects should be very pronounced also at the latest coarsening stage of the phase separation leading, in mean field approximation, to the coarsening law $R \sim t^{1/2}$ [20] instead of the customary law $R \sim t^{1/3}$. We believe that those findings will stimulate new experiments in the broad field of the kinetics of phase transitions in solid.

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