GROWTH AND DISSOLUTION OF NUCLEI OF A NEW PHASE

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The kinetics of formation of nuclei of a new phase was investigated using the Ginzburg–Landau type equation for the order parameter. A distribution of the order parameter for the nuclei of different sizes was obtained for arbitrary values of the degree of metastability.

1. Formation of nuclei of a new phase is usually described by a phenomenological theory [1, 2] in which the conditions of a phase transition are assumed to be satisfied, and the properties of nuclei of a new phase are postulated. Within this framework, the concentration of the solution necessary for the phase transition, as well as the surface tension, cannot be calculated.

On the other hand, phase transformations are often described using the field of the order parameter [3, 4]. This theory is based on the Landau expansion of the free energy F in the order parameter $\xi(\mathbf{r}, t)$ near the critical point of the phase transition [3, 5], i.e.,

$$F = F_0 - \int (\lambda\xi^2 + B\xi^3 - \Gamma\xi^4 + \Omega(\nabla\xi)^2)\, d\mathbf{r}. \tag{1}$$

The relaxation of the field of the order parameter $\xi(\mathbf{r}, t)$ is given by the following equation [3, 4]:

$$\dot{\xi}(\mathbf{r}, t) = -\gamma \frac{\delta F[\xi]}{\delta\xi}, \tag{2}$$

where $\delta F[\xi]/\delta\xi$ is the variational derivative. The advantage of this approach is that the kinetics of formation of nuclei of a new phase can be described without introducing additional parameters (except the coefficients in Eqs. (1) and (2).) It should be noted that the nuclei, and their shape, appear in the inhomogeneous solutions of Eqs. (1) and (2), without any additional assumptions.

Recently, phase transitions have often been considered as a development of instability in a system of interacting particles in solution [6]. In such a description, the order parameter $\xi(\mathbf{r}, t)$ is the amplitude of the unstable mode, which corresponds to the particle concentration in the new phase. Separation of the amplitude of the unstable mode leads to an equation for the order parameter of the Ginzburg-Landau type:

$$\dot{\xi}(\mathbf{r}, t) = \tilde{\lambda}\xi + \tilde{B}\xi^2 - \tilde{\Gamma}\xi^3 + \tilde{\Omega}\Delta\xi, \tag{3}$$

which is formally equivalent to the equation for the order parameter obtained from Eqs. (1) and (2). Coefficients $\tilde{\lambda}$, $\tilde{B}$, $\tilde{\Gamma}$, $\tilde{\Omega}$ in Eq. (3) can be related to the parameters of kinetic equations which describe the behavior of the particles in solution [6].

This approach has been applied in [7, 8] to the system of point defects in irradiated metals. Long range attraction between the defects leads to instability of the uniform distribution of defects, and to formation of defect clusters.

It should be noted that the description of the phase transformations using the field of the order parameter agrees well with general energy considerations. Analysis of Eq. (1) for $F[\xi]$ shows that a new energy minimum appears in the system (Fig. 1) as it approaches the critical point. Therefore, the phase transformation is a transition into a state with the energetically more advantageous, finite order parameter:

$$\xi = 2\tilde{B}/9\tilde{\Gamma}.$$

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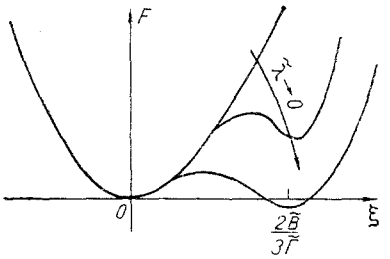

Fig. 1. Free energy F as a function of the homogeneous order parameter for different values of $\lambda < 0$.

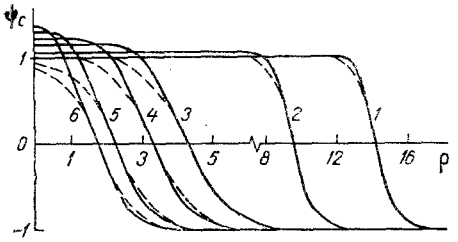

Fig. 2

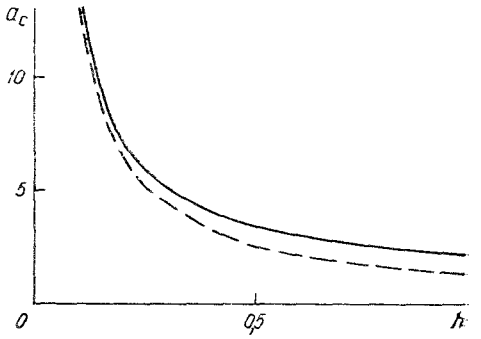

Fig. 3

Fig. 2. The field of the order parameter $\psi_c(\rho)$ for the critical size nuclei for different values of the degree of metastability: 1) h = 0.1; 2) 0.15; 3) 0.35; 4) 0.5; 5) 0.75; 6) 1.0.

Fig. 3. Dependence of the size of the critical nucleus a_c ($\psi(\rho = a_c) = 0$) on the degree of metastability h.

The purpose of this study is to investigate the kinetics of growth and dissolution of nuclei during phase transitions of the first order by directly solving the Ginzburg-Landau equation (3) for the order parameter.

2. It is convenient to introduce a new dimensionless function ψ and new variables ρ, τ so that Eq. (3) becomes

$$\dot{\psi}(\rho, \tau) = \Delta\psi + 2\psi(1 - \psi^2) + h(\psi + 1), \qquad (4)$$

where $h = 4(1 - \lambda/\lambda_c)$; $\lambda_c = -2\tilde{B}^2/9\tilde{\gamma}$; $\rho = r/\chi$; $\chi = \sqrt{8\Omega/\Gamma\xi_0^2}$; $\tau = 8t/\tilde{\Gamma}\xi_0^2$; $\xi_0 = 2\tilde{B}/3\tilde{\Gamma}$; $\psi = 2\xi/\xi_0 - 1$.

It should be stressed that the resulting equation (4) for the order parameter is universal in the sense that a variety of conditions of phase transitions in different materials is described by a single parameter h which is the degree of metastability of the system. Equation (4) differs from the equation for the order parameter investigated earlier for $h \ll 1$ [4]. The latter equation was derived for a model system in external field and undergoing a second-order phase transition. Formally, this difference leads to an additional term $h\psi$ in Eq. (4).

It has been shown earlier that, for $h > 0$, nuclei of arbitrary shape quickly attain a spherical shape [4, 9]. Therefore, in the following we consider only that part of the space of initial parameters which lead to the values of the degree of metastability $h > 0$. We first seek the solution of Eq. (4) which corresponds to the nuclei of critical size. By definition, the critical nucleus does not grow or dissolve and corresponds, therefore, to the stationary inhomogeneous solution of the equation for the order parameter. The problem is thus reduced to the solution of the stationary equation for the order parameter (4), i.e., the ordinary differential equation of the second order. We must also specify the boundary conditions. At large distances from the nucleus, the order parameter corresponds to the old phase $\xi(r \to \infty) = 0$, $\psi(\rho \to \infty) = -1$ and inside the nucleus to the new phase $\xi(r = 0) = 2\tilde{B}/3\tilde{\Gamma}$, $\psi(\rho = 0) = \psi_H \equiv (1 + \sqrt{1 + 2h})/2$. Due to nonlinearity of Eq. (4), for arbitrary values of h the solutions have only been found numerically. The results of

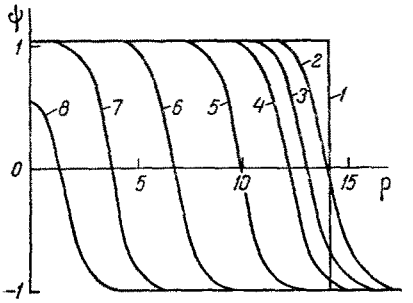

Fig. 4. Relaxation of the field of the order parameter for h = 0.1 and a_0 = $0.99a_c$: 1) τ = 0; 2) 2; 3) 260; 4) 330; 5) 410; 6) 440; 7) 456; 8) 460.

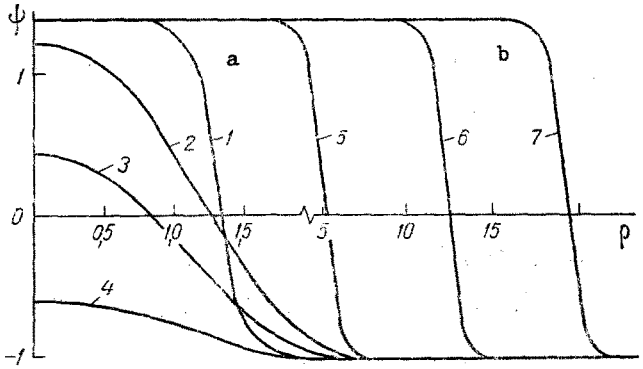

Fig. 5. Relaxation of the field of the order parameter for h = 1: a) a_0 = $0.66a_c$; 1) τ = 0.01; 2) 0.15; 3) 0.48; 4) 0.93; b) a_0 = $1.05a_c$; 5) τ = 10.3; 6) 19.1; 7) 26.7.

calculations are shown in Figs. 2 and 3. Up to the value h = 0.2, the critical nuclei are structures with a very thin transition layer (the layer width is much smaller than the nucleus size.) Distributions of the order parameter of this type will be called nucleus-like provided they differ from the critical nucleus only in the general displacement of the transition layer. In this region (h < 0.2), one can find an analytic function which describes well the field of the order parameter for the critical nucleus (dashed curves in Figs. 2 and 3), i.e.,

$$\psi_c(\rho) \simeq \mathrm{th}(a_c - \rho), \quad h \ll 1. \tag{5}$$

Expression (5) was obtained taking into account that ψ = ±thX is the exact solution of the homogeneous equation for the order parameter for h = 0.

For nucleus-like solutions (h < 0.2), for which the nucleus size can be determined uniquely from (ψ(ρ = a) = 0), the dependence of the critical size of nuclei on the degree of metastability (Fig. 3) can be approximated by a function $a_c = \alpha/h(\alpha = 1.3\text{-}1.4)$. It should be noted that an analogous functional dependence of the critical size on supersaturation (for Δ ≪ 1) can be obtained from the phenomenological theory. Indeed, assuming that the new phse corresponds to lower energy and that the formed nuclei have a boundary, it is easy to see [1] that only the nuclei with sizes greater than

$$a_c = 1/\ln(1+\Delta)\left(\Delta \equiv \frac{c-c_0}{c_0}\right), \tag{6}$$

where the dimensional parameter is 2σv'/T, will grow.

With increasing values of the degree of metastability, the transition layer (Fig. 2) becomes diffuse, and for values h > 0.5, the critical nucleus has no sharply defined boundary. For these values of h, the analytical approximation (5) still describes the behavior of solution correctly, but gives incorrect value for the order parameter inside the nucleus. For large values of h, the determination of the size of critical nuclei becomes difficult;

in this case the width of the transition layer is comparable to the nucleus size. If we continue to use as the critical size a_c the value defined for $h \ll 1$, i.e., a_c: $\psi(\rho = a_c) = 0$, we obtain the dependence of the critical size a_c on h, which, for all values of h, can be approximated by a function

$$a_c = \alpha/\ln(1+h). \tag{7}$$

Similarity between the dependence of the critical size on the supersaturation Δ and the degree of metastability h, obtained using different approaches, is apparently related to the identical role of these parameters. Both h and Δ determine the critical size of nuclei of the new phase, and the values $h = 0$ and $\Delta = 0$ correspond to the critical point. It also follows from Eqs. (6) and (7) that the characteristic length scale in the phenomenological theory can be expressed in terms of the corresponding microscopic parameters

$$2\sigma v'/T \simeq \alpha\chi. \tag{8}$$

3. Behavior of the different size nuclei of the new phase (see Figs. 4 and 5) was investigated by solving the spherically-symmetric equation for the order parameter (4) numerically. The initial distribution was taken to be a step function of size a_0 and the ampplitude of the new phase $\psi(\rho, \tau = 0) = (\psi_H + 1)\eta(a_0-\rho)-1$, where η is the step function. For small values of the degree of metastability ($h < 0.2$) and large initial sizes ($a_0 \gg 1$), the initial distribution becomes nucleus-like (see fig. 4) on a very short time scale (much shorter than the characteristic times of growth or dissolution.) Analysis of the numerical solution of dissolution of subcritical nuclei for small values of h has shown that the dissolution takes place in two stages. The displacement of the nucleus boundary up to the size of the order of the width of the transition layer ρ_0, with a constant value of the order parameter inside the nucleus, takes place in the first stage. After that, during the second stage, the characteristic size of the inhomogeneity is almost constant but the value of the order parameter inside the nucleus decreases.

Thus, during the first stage, dissolution of the new phase occurs only at the nucleus boundary, while during the second stage dissolution occurs in the whole nucleus, i.e., the concentration of the new phase inside the nucleus decreases.

Dissolution and growth of large nuclei can be described by a simple relaxation equation which takes into account the nucleus-like nature of the solution up to the values $a \sim \rho_0$. Indeed, assuming that the nucleus relaxation is limited to the displacement of its boundary, we seek the solution of the nonstationary equation for the order parameter in the form

$$\psi(a(\tau),\ \rho) = \psi_c(a(\tau) - \rho). \tag{9}$$

Substitution of Eq. (9) into the equation for the order parameter (4) leads to a well known [4] equation for the nonconserved order parameter

$$\dot{a}(\tau) = \frac{2}{a_c} - \frac{2}{a}. \tag{10}$$

The values of the critical size a_c are shown in Fig. 3. It should be noted that the results for a_c differ from those obtained in [4] (shown by a dashed curve in Fig. 3). It follows from Eq. (10) that the subcritical size nuclei dissolve and supercritical size nuclei grow. The growth (or dissolution) of the new phase takes place in the transition layer of the nucleus.

The nuclei of size $a \lesssim a_c$ are the slowest to dissolve. At this stage of dissolution, the dependence of the nucleus size on time is accurately described by Eq. (10). For $h \ll 1$, the region of size $a \sim \rho_0$ makes only a small contribution to the lifetime of a large nucleus. Taking this into account, the lifetime of a nucleus ($a_c \gtrsim a \gg 1$) can be written explicitly

$$\tau_0 = \frac{a_c^2}{2} \ln \frac{a_c}{a_c - a_0}. \tag{11}$$

Expression (11) for the lifetime of a large nucleus was obtained by integrating Eq. (10).

An interesting case arises when the degree of metastability is large. In this case, for nuclei of size $a \sim a_c$ (as well as for small nuclei for $h \ll 1$), the width of the transition layer between the new and old phases is comparable to the nucleus size. It can be seen in Fig. 5 that only the second stage of dissolution of nuclei takes place, i.e., the

order parameter (or the concentration of the new phase) decreases simultaneously throughout the nucleus volume.

Just as for small values of h, the growth of nuclei for large values of h takes place by formation of the new phase in the transition layer of the nucleus (see Fig. 5). However, in the latter case, the nuclei have wider transition layers. For large values of h, it can be shown that the growth of nuclei with sizes $a \gg \rho_0$ is given by Eq. (10).

It should be stressed that with increasing degree of metastability h, the width of the transition layer between the old and new phases in the nucleus increases. As a result, for large values of the degree of metastability, there is no sharp separation between the volume and surface. This separation is used in the phenomenological theory to obtain the equation (6) for the critical size of the nucleus.

The advantage of the approach to describe the formation of the new phase which is used here is that all the characteristic quantities can be expressed in terms of the coefficients of the equation for the order parameter, which, in turn, can be expressed in terms of the microscopic parameters of solution [7, 8]. For example, the microscopic approach to phase transitions in molybdenum bombarded with helium ions He^+ gives $\chi \approx 10$ Å, in good agreement with an estimate of this quantity obtained using the phenomenological parameters (8). It should be noted that the nuclei of the new phase, and their shape, appear in the solution of the equation for the order parameter, and the growth and dissolution of the nuclei can be studied without assuming special conditions [1, 2] at the nucleus boundary.

NOTATION

$\xi(r, t)$, field of the order parameter; ($\psi(\rho, \tau)$, dimensionless field); r, position vector (ρ is the dimensionless position vector); χ, characteristic length for scaling r; t, time and τ is the dimensionless time; $F[\xi]$, free energy of the system undergoing a phase transition; F_0, free energy of the system far from the critical point; λ, B, Γ, Ω, coefficients in the Landau expansion [1]; γ, kinetic coefficient which is independent of ξ; $\tilde{\lambda}$, $\tilde{B}$, $\tilde{\Gamma}$, $\tilde{\Omega}$, coefficients in the equation for the order parameter, obtained from the kinetic equations using the approach developed in [6-9]; a_c, critical nucleus size; α, a numerical factor; σ, surface tension; v', molecular volume of the new phase; T, temperature of the medium; Δ, supersaturation; c, real concentration of solution; c_0, concentration at the critical point; $a(\tau)$, time-dependent nucleus size; and $\psi_c(a_c-\rho)$, solution of the stationary equation for the order parameter [4].

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