On the possibility of forming periodic structures at the surface of stratifying solid solutions

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The subject of this paper is the stratification dynamics of solid-solution films in contact with their own vapor. It is shown that the spectrum of concentration waves for such films differs significantly from that of unbounded or isolated thin-film systems, being distinguished by stability of long-wavelength perturbations and an overall reduction of the size of the instability region. This has certain implications for the possibility of periodic structures forming in the early stages of stratification: specifically, that such structures must involve both concentration distributions and a modulation of the surface profile of the film.

The theory of spinodal decomposition in solid solutions has been the subject of a large number of papers, a bibliography of which can be found in the review Refs. 1 and 2. One of the most interesting implications of the theory of spinodal decomposition is the possibility that macroperiodic concentration distributions could form during the intermediate stages of the decomposition. The authors of Ref. 3 claimed that when the wave-number dependence of the attenuation rate of a periodic concentration perturbation is nonmonotonic, periodic structures can form even in the early stages of the stratification. However, in Ref. 4, this conclusion was shown to be erroneous. The objection raised there was essentially based on the fact that the ratio of the width of the instability region to the value of the wave number at which the maximum growth rate is achieved is of order unity, so that it is not possible to identify a single scale in the linear stages of the instability. In Ref. 5 it was shown that in the one-dimensional case macro-periodic concentration distributions correspond to metastable states, which may be encountered when a solid solution with appreciable anisotropy in its elastic constants undergoes decomposition.[6]

In the past, mechanisms for the formation of modulated structures have always applied to bulk samples. The study of spinodal decomposition in bounded samples raises additional questions related to surface segregation[7,8] and interaction of the solution that is undergoing stratification with the surrounding medium.[9,10] Crystallization of stratified alloys was investigated in Refs. 9 and 10; however, solid-state diffusion was not taken into account in these papers. The subject of this paper is the kinetics of spinodal decomposition of a thin film in contact with its own saturated vapor.

1. DESCRIPTION OF THE MODEL AND FORMULATION OF THE BASIC EQUATIONS

Let us consider a substitutional solid solution consisting of two types of atoms A and B and having an original concentration c_0 (where c_0 is the fraction of type-A atoms). We will further assume that for this composition the solution is unstable at some temperature, i.e.,

$$\left.\frac{\partial^2 f}{\partial c^2}\right|_{c=c_0}<0$$

(where f is the free-energy density of the solution). It is well-known that small perturbations will grow in this case, resulting in a local concentration c of the solution that differs from the average concentration c_0. If the solution is placed in contact with saturated vapor whose concentration corresponds to the average concentration of the solution c_0, then under stratification conditions the vapor is no longer in equilibrium and the shape of the surface of the solid solution will change. On the other hand, the appearance of uncompensated fluxes at the surface will change the form of the boundary conditions for the diffusion equation and, as we show below, can have a considerable effect on the spectrum of unstable concentration waves.

The free energy of the solid solution has the form

$$F=\int\left\{{}^1/_2\sigma(\nabla_\perp\xi)^2+\int_0^\xi[f(c)+{}^1/_2\gamma(\nabla c)^2]dz\right\}d\rho. \tag{1}$$

where ρ is the radius vector in the plane of the film and $\nabla_\perp=\partial/\partial\rho$; $z=0$ and $z=\xi(\rho)$ are the equations for the film-substrate boundary and the film-vapor boundary respectively. The first term in (1) is the contribution from the surface energy of the film-vapor boundary. We ignore surface segregation and assume that σ is independent of the solution concentration. Then Eq. (1) implies the following relations for the chemical potentials of atoms of type A and B:

$$\frac{\delta F}{\delta c}=\mu_A-\mu_B=\frac{df}{dc}-\gamma\Delta c,\qquad z\leqslant\xi, \tag{2}$$

$$\frac{\delta F}{\delta\xi}=c\mu_A+(1-c)\mu_B|_{z=\xi}=-\sigma\Delta_\perp\xi+[f(c)+{}^1/_2\gamma(\nabla c)^2]|_{z=\xi}. \tag{3}$$

In deriving Eq. (2) we have taken into account the fact that the difference in chemical potentials must be continuous. A consequence of the condition of continuity is the vanishing of the derivatives of the concentrations at the film boundary:

$$\left.\frac{dc}{dz}\right|_{z=0}=0,\qquad(\mathbf{n}\nabla c)|_{z=\xi}=0, \tag{4}$$

where $\mathbf{n}$ is a unit vector for the outward normal to the surface $z=\xi$. Relations (2) and (3) determine the chemical potential of the atoms located at the surface of the solid solution:

$$\mu_A|_{z=\xi}=f(c)+(1-c)\frac{df}{dc}+{}^1/_2\gamma(\nabla c)^2-\gamma(1-c)\Delta c-\sigma\Delta_\perp\xi, \tag{5}$$

$$\mu_B|_{z=\xi}=f(c)-c\frac{df}{dc}+{}^1/{}_2\gamma(\nabla c)^2+\gamma c\Delta c-\sigma\Delta_\perp\xi. \tag{6}$$

By means of linear nonequilibrium thermodynamics we find for the diffusion current of atoms of type A:

$$\mathbf{j}_{AD}=-D\nabla(\mu_A-\mu_B). \tag{7}$$

where D is the kinetic diffusion coefficient. The partial currents from the vapor equal

$$j_A=\omega_A[\mu_A(c_0)-\mu_A(c)]|_{z=\xi}, \tag{8}$$

$$j_B=\omega_B[\mu_B(c_0)-\mu_B(c)]|_{z=\xi}. \tag{9}$$

Here $\omega_{A,B}$ are the kinetic coefficients, which will be set equal, i.e., $\omega_A=\omega_B=\omega$. In writing down (8) and (9) we have built in the fact that the vapor is saturated for a solution with concentrations c_0.

Condition (4) constitutes the first pair of boundary conditions for the diffusion equation

$$\frac{\partial c}{\partial t}=\Omega D\Delta\left(\frac{\partial f}{\partial c}-\gamma\Delta c\right), \tag{10}$$

where Ω is the specific volume of the solid solution. Here and in what follows we will assume the specific volumes of the components are equal, $\Omega_A=\Omega_B=\Omega$. We obtain the equations for the surface profile ξ and the second pair of boundary conditions for Eq. (10) from the condition for conservation of the number of particles of types A and B at the boundaries of the film. At the boundary with the vapor these conditions have the form[11]

$$Vc=\Omega(j_A-j_{AD}^{(z)})|_{z=\xi}, \tag{11}$$

$$V(1-c)=\Omega(j_B-j_{BD}^{(z)})|_{z=\xi}. \tag{12}$$

Here $j^{(z)}_{AD,BD}$ are the z components of the diffusion currents of A and B atoms, respectively, and V is the translation velocity of the boundary along the z-axis. Conditions (11) and (12) express the law of conservation of the number of particles A and B, taking into account diffusion and exchange of particles between the vapor and the solution. Combining Eqs. (11) and (12), we obtain the following equation for the surface profile:

$$\frac{\partial\xi}{\partial t}=\Omega(j_A+j_B). \tag{13}$$

Assuming the absence of diffusion at the boundary with the substrate, we have

$$j_{AD}^{(z)}|_{z=0}=0. \tag{14}$$

In order to determine the explicit dependence of the particle currents on the concentration of the solution we will assume that the concentration dependence of the free energy density for temperatures below the critical stratification temperature has the form

$$f(c)=f(c_0)-{}^1/{}_2\alpha(c-c_0)^2+{}^1/{}_4\beta(c-c_0)^4, \tag{15}$$

where α and β are positive coefficients.

2. DYNAMICS OF SMALL PERTURBATIONS

Let us investigate small departures of the concentration from its average. Introducing the Fourier transform of the surface profile and the concentration

$$\xi_\mathbf{p}=\int\xi(\boldsymbol{\rho})e^{-i\mathbf{p}\boldsymbol{\rho}}\,d\boldsymbol{\rho},\qquad \eta_\mathbf{p}=\int(c-c_0)e^{-i\mathbf{p}\boldsymbol{\rho}}\,d\boldsymbol{\rho}$$

we find after linearizing (in what follows the label **p** will be omitted) that

$$\frac{\partial\xi}{\partial t}=\gamma\Omega\omega(1-2c_0)\left[(k_c^2-p^2)\eta+\frac{\partial^2\eta}{\partial z^2}\right]\Bigg|_{z=h}-2\Omega\omega\sigma p^2\xi, \tag{16}$$

$$\frac{\partial\eta}{\partial t}=-\gamma\Omega D\left[p^2(p^2-k_c^2)\eta+(k_c^2-2p^2)\frac{\partial^2\eta}{\partial z^2}+\frac{\partial^4\eta}{\partial z^4}\right], \tag{17}$$

where $k_c^2=\alpha/\gamma$. The boundary conditions in this approximation acquire the form

$$\frac{\partial\eta}{\partial z}\bigg|_{z=0}=\frac{\partial\eta}{\partial z}\bigg|_{z=h}=\frac{\partial^3\eta}{\partial z^3}\bigg|_{z=0}=0,$$
$$\frac{\partial^3\eta}{\partial z^3}=\varkappa\left[(k_c^2-p^2)\eta+\frac{\partial^2\eta}{\partial z^2}\right]\Bigg|_{z=h},\qquad \varkappa=\frac{\omega}{D}(1-2c_0+2c_0^2). \tag{18}$$

Thus the equations for η and ξ are decoupled. Solving Eq. (17) with the boundary conditions (18) and substituting the solution we find into (16) allows us to determine the law of variation of the surface profile ξ. The solution to Eq. (17) can be sought in the form

$$\eta=\sum_n e^{-\lambda_n t}R_n(z).$$

After standard procedures we obtain the dispersion relation

$$\nu\mu(\nu^2-\mu^2)[\nu\mu(\nu^2-\mu^2)\operatorname{sh}(\mu h)\operatorname{sh}(\nu h)$$
$$-(\mu\varphi_\nu\operatorname{sh}(\mu h)\operatorname{ch}(\nu h)-\nu\varphi_\mu\operatorname{sh}(\nu h)\operatorname{ch}(\mu h))]=0, \tag{19}$$

where

$$\mu^2=p^2-\frac{k_c^2}{2}+Q,\qquad \nu^2=p^2-\frac{k_c^2}{2}-Q,$$
$$\varphi_{\mu,\nu}=\varkappa\left(\frac{k_c^2}{2}\pm Q\right),\qquad Q=\left[\frac{k_c^4}{4}+\frac{\lambda_n}{\gamma\Omega D}\right]^{1/2}.$$

The solution of the dispersion relation we obtain is difficult to work with in its general form; therefore, we will analyze the dependence of the decay rate λ_n on the longitudinal wave number qualitatively. We can show that the roots of Eq. (19), which are determined by the relations $\nu=\mu=0$ and $\nu^2=\mu^2$, correspond to the trivial solution $\eta=0$. The equation for the roots that give the decay rate λ_n has the form

$$\operatorname{sh}(\nu h)[\mu\operatorname{sh}(\mu h)-\varkappa\operatorname{ch}(\mu h)]=0, \tag{20}$$
$$\nu^2=p^2-k_c^2,\qquad \mu=p.$$

From (20) it follows that there exist two series of roots. The roots of the first series satisfy the relation

$$p_{1,n}^2=k_c^2-q_n^2,\qquad q_n=\frac{\pi}{h}n,\qquad n=0,\pm1,\pm2\dots. \tag{21}$$

The roots of the second series are imaginary for $n\neq0$ and their absolute values satisfy the equation

$$p_{2,n}\operatorname{tg}(p_{2,n}h)=-\varkappa.$$

For the zero mode ($n=0$) there exists a real root

$$p_{2,0}\,\mathrm{th}(p_{2,0}h)=\varkappa, \tag{22}$$

such that

$$p_{2,0}\sim\begin{cases}(\varkappa/h)^{1/2}, & h\varkappa<1,\\ \varkappa, & h\varkappa>1.\end{cases}$$

Let us write the decay rate in the form

$$\lambda_n=\gamma\Omega D(p^2-p_{1,n}^2)(p^2-p_{2,n}^2). \tag{23}$$

If the solid-solution film is sufficiently thick ($hk_c>1$), there exists an unstable perturbation of arbitrarily long wavelength. For thin films ($hk_c<1$) the situation is qualitatively different: only the zero mode is unstable in the range of wavelengths $k_c<p<p_{2,0}$ or $p_{2,0}<p<k_c$ (see Fig. 1). We note that when the film is not in contact with its vapor ($\varkappa=0$), as $h\to\infty$ Eq. (23) reduces to the well-known expression for the decay rate in a bulk sample

$$\lambda=\gamma\Omega D(k^2-k_c^2)k^2,$$

where k is the three-dimensional wave number.

3. DISCUSSION OF RESULTS

From the analysis given here it follows that the spectrum of unstable concentration waves in a thin ($hk_c<1$) film in contact with its own vapor is quite different from spectra of unbounded samples or isolated thin films. The salient feature of this spectrum is the stability of long-wavelength perturbations. Consider the case where $k_c>p_{2,0}$ or $\varkappa<hk_c^2$. In this case for small values of the longitudinal wave number we can neglect the nonlocal terms in the expressions for the chemical potentials (2) and (3), and in particular for $p=0$ we obtain the following equations for the concentration

$$\frac{\partial\eta}{\partial t}=-\alpha D\frac{\partial^2\eta}{\partial z^2},\quad \left.\frac{\partial\eta}{\partial z}\right|_{z=0}=0,\quad \left.\frac{\partial\eta}{\partial z}\right|_{z=h}=\varkappa\eta.$$

It is easy to see that the zero mode is stable in this case. As the inhomogeneity appears along the film, a diffusive flux begins to flow, which increases the nonuniformity; the value of this current is proportional to the wave number p. As we pass through the value $p^2\approx\varkappa/h$, the concentration distribution loses its stability. For further increases in p we reach a value $p\approx k_c$ at which the perturbation under discussion once more becomes stable. This dependence of the decay rate on the longitudinal wave number coincides with the dependence determined by Eq. (23) for λ_0. It follows from Eq. (16) that the decay rates of harmonics of the surface profile coincide with the decay rate for concentration waves. Consequently, the shape of the surface is "tuned" as the concentration distribution is formed.

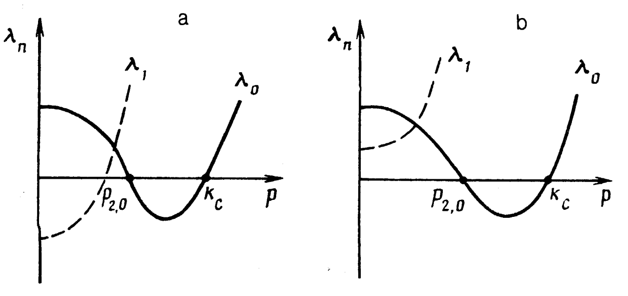

FIG. 1. Qualitative dependence on the longitudinal wave number of the decay rate for the zero-order (solid curves) and first-order (dashed curves) modes: a—$hk_c>1$, b—$hk_c<1$

An important feature of the spectrum under discussion here is the dependence of the decay-rate roots on the external parameters. In fact, the root $p_{2,0}$ depends on the thickness of the film and the temperature, while the root $p_{1,0}=k_c$ depends only on the ratio of the sample temperature to the critical stratification temperature. When the condition $|p_{1,0}-p_{2,0}|\ll p_{1,0}$ is satisfied, harmonics with longitudinal wave vector magnitudes of order k_c are unstable. This reduction in size of the region of instability leads to the possibility of macroperiodic structures forming at early stages of the stratification. Analysis of the system in linear approximation suggests that two-dimensional perturbations with certain wave vector magnitudes will be singled out. In order to determine the symmetry of the possible periodic structures we investigate the first nonlinear correction to the solutions we have obtained by perturbation theory. Analysis of the general system of equations shows that the nonlinear corrections are quadratic in η. Representing the solution in the form

$$\eta=\eta_0+\eta_1+\dots,$$

we obtain the following equation for η_1:

$$\frac{\partial\eta_1}{\partial t}=-\gamma\Omega D\Delta(k_c^2\eta_1+\Delta\eta_1),$$

$$\left.\frac{\partial\eta_1}{\partial z}\right|_{z=0}=\left.\frac{\partial\eta_1}{\partial z}\right|_{z=h}=\left.\frac{\partial^3\eta_1}{\partial z^3}\right|_{z=0}=\eta_1(z,\rho,t=0)=0,$$

$$\frac{\partial}{\partial z}\Delta\eta_1=\varkappa(k_c^2\eta_1+\Delta\eta_1)+\frac{\omega}{D}(c_0-1/2)$$

$$\times(3k_c^2\eta_0^2+4\eta_0\Delta\eta_0+(\nabla\eta_0)^2)|_{z=h}. \tag{24}$$

From Eq. (24) it follows that two concentration waves with wave vectors $\mathbf{p}'$ and $\mathbf{p}-\mathbf{p}'$ will excite a concentration wave with wave vector $\mathbf{p}$. For the case of a sufficiently narrow range of instabilities, waves with the same wave vector modulus $|\mathbf{p}|\approx|\mathbf{p}-\mathbf{p}'|\approx|\mathbf{p}'|\approx k_c$ will have the maximum rate of growth. This implies that the squared nonlinearity leads to the formation of a hexagonal lattice with dimensions of the unit cell $\approx 1/k_c$.

Thus, it is possible for macroperiodic structures to form at the surface of a stratifying solid-solution film in contact with its own vapor during the early stages of stratification. The structures are combined concentration distributions and modulations of the profile of the film surface; for the case of an isotropic solution they have hexagonal symmetry. In order for such periodic structures to arise it is necessary to fulfill at least two conditions. First of all the film must be sufficiently thin ($hk_c<1$), and secondly the region of instability for concentration waves must be small ($|k_c-p_{2,0}|\ll k_c$).

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