Late stage of the decomposition of anisotropic solid solutions

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The theory of diffusion-controlled phase transitions in an anisotropic medium is discussed and applied to the decomposition of solid solutions. A gradient correction to the free-energy functional in tensor form is employed to take into account the anisotropy of the crystal structure. A generalization of the Cahn–Hillard equation is used to model the decomposition process. The most favorable directions of decomposition, determined by the properties of the gradient energy tensor, are described. The asymptotic growth of decomposition structures as a function of time at the stage of coalescence is determined. The exponent in the asymptotic law is expressed in terms of the dimensionality of the space and the degeneracy of the minimum eigenvalue of the gradient energy matrix. The results are statistically averaged over the equilibrium initial conditions.

1. INTRODUCTION

The most widely used description of spinodal decomposition of systems with one order parameter (binary mixtures, melts, and solid solutions) is the description given by Cahn and Hillard.[1] Their description is based on the system of equations[1,2]

$$\frac{\partial\varphi}{\partial t}=\nabla\Lambda\nabla\mu, \qquad (1)$$

$$F=\int\rho[F_0(\varphi)+\varkappa(\nabla\varphi)^2]d\mathbf{r}, \qquad (2)$$

$$\mu=\frac{1}{\rho}\frac{\delta F}{\delta\varphi}=\mu_0(\varphi)-2\varkappa(\varphi)\nabla^2\varphi-\varkappa_\varphi(\nabla\varphi)^2, \qquad (3)$$

where

$$\mu_0=\partial F_0/\partial\varphi,\quad \varkappa_\varphi=\partial\varkappa/\partial\varphi,$$

φ is the relative fraction of one component of the binary mixture, F is the free-energy functional in units of $k_B T$, μ is the reduced chemical potential, defined as a variational derivative of F, ρ is the number density, Λ is Onsager's coefficient, and $\varkappa$ is the gradient energy coefficient. According to Ref. 1, a functional of the form (2) describes the properties of isotropic systems and cubic crystals.

Solid solutions are anisotropic systems, to describe which it is necessary to generalize the expression (2). The gradient part of the free energy in this case must have the form[1,3]

$$\sum_{i,j=1}^{d}K_{ij}\frac{\partial\varphi}{\partial r_i}\frac{\partial\varphi}{\partial r_j}=(K\nabla\varphi,\nabla\varphi). \qquad (4)$$

Here d is the dimension of the space and the parentheses denote a scalar product. Based on its physical significance the quadratic form $(K\mathbf{x},\mathbf{x})$ is positive-definite, and the spectrum of the symmetric matrix K consists of positive real eigenvalues. A general theory of spinodal decomposition with a correction of the form (4) in the energy functional has not been previously constructed, probably because such a correction makes it much more difficult to study the process analytically, even at its initial stage. As will be shown below, if the decomposition process is described by an isotropic functional of the form (2), then one obtains results for anisotropic systems that are wrong.

The necessity of an anisotropic correction in order to describe the decomposition of solid solutions stems primarily from the fact that the most general functional of one variable φ is expressed in the long-wavelength approximation in terms of the quantity $F_0(\varphi)$ with the correction (4) (it is assumed that F is an analytic function of φ, $\Delta\varphi$,...).[3] The possibility of describing the process with the help of only one variable φ (the order parameter) in turn indicates that the other parameters of the system (strains in the crystal, the components of the stress tensor, etc.), vary over much shorter spatial scales and with much shorter relaxation times. For this reason they can be expressed in terms of the leading mode (the concentration mode). This principle for excluding fast modes is widely employed in the theory of self-organization of dynamic systems[4] and Cahn essentially used it implicitly to construct a theory with one order parameter.[5,6]

In Ref. 7 it was proposed that both the initial stage (separation of the mode of maximum growth) and the later stage of decomposition of anisotropic systems be studied by using the description (1)–(4). Nonlinear effects then become important. In this paper the description of the later stage of decomposition implemented in Ref. 7 for isotropic systems is extended to the anisotropic case. Thus spinodal decomposition in an anisotropic system can be described completely based on the nonlinear equation (1).[8]

2. LINEAR ANALYSIS: STATIONARY POINTS OF THE AMPLIFICATION FACTOR

We study the initial stage of decomposition with the help of the linearized equation (1). Transforming in Eq. (1), after linearization, to the Fourier components of the fluctuations about the average value φ_0, we obtain

$$\delta\varphi(\mathbf{q})'=R(\mathbf{q})\delta\varphi(\mathbf{q}),\quad R(\mathbf{q})=-\Lambda q^2[h+2(K\mathbf{q},\mathbf{q})]. \qquad (5)$$

Here $\delta\varphi(\mathbf{q})$ is the Fourier component of the fluctuation, $\mathbf{q}$ is the wave vector, and $h=\partial^2F_0/\partial\varphi^2$. For $h>0$ the Fourier components $\delta\varphi(\mathbf{q})$ decay for all q. For $h<0$ the Fourier components corresponding to the condition

$$2(K\mathbf{q},\mathbf{q})<-h, \qquad (6)$$

grow; modes for which $\mathbf{q}$ lies outside the ellipsoid (6) decay. The mode of maximum growth is determined by the condition

$$\partial R/\partial q_k=0, \quad k=1,\ldots,d. \tag{7}$$

The symmetry of K makes it possible to write the condition (7) in the form

$$2q^2K\mathbf{q}=-[h+2(K\mathbf{q},\mathbf{q})]\mathbf{q}. \tag{8}$$

From here we obtain the solution $\mathbf{q}=0$. If $\mathbf{q}\neq 0$, then, multiplying Eq. (8) by $\mathbf{b}_k$—the eigenvector of the matrix K corresponding to the eigenvalue λ_k—we obtain

$$[2q^2\lambda_k+h+2(K\mathbf{q},\mathbf{q})](\mathbf{q},\mathbf{b}_k)=0, \quad k=1,\ldots,d. \tag{9}$$

The case of the general position corresponds to the case in which all eigenvalues of the matrix K nondegenerate. In this case there are several possibilities of solving Eq. (9) for $\mathbf{q}$. The relation

$$(\mathbf{q},\mathbf{b}_k)=0 \tag{10}$$

cannot hold for all k if $\mathbf{q}\neq 0$, since the vectors $\mathbf{b}_k$ form an orthogonal basis.[9] If the condition (10) is violated for only one value of k, then because $\mathbf{b}_k$ and $\mathbf{b}_l$ are orthogonal for $k\neq l$ the eigenvector $\mathbf{b}_l$, determined to within a constant factor, will be a solution of the system (9). The length of $\mathbf{b}_l$ is given by the relation

$$2q^2\lambda_l+h+2(K\mathbf{q},\mathbf{q})=0. \tag{11}$$

Since $(K\mathbf{q},\mathbf{q})=\lambda_l q^2$ Eq. (11) can be rewritten in the form

$$q^2=-h/4\lambda_l. \tag{12}$$

Finally, if the vector $\mathbf{q}$ is orthogonal to less than $d-1$ eigenvectors $\mathbf{b}_k$, then at least two of the d relations (9) can be written in the form (12). By assumption, all λ_k are nondegenerate, so that the last possibility cannot be realized.

Thus, except at $\mathbf{q}=0$, the function $R(\mathbf{q})$ has another d stationary points corresponding to the eigenvectors of the matrix K with the normalization (12). The value of the amplification factor at these points is

$$R(\mathbf{q})=2\Lambda\lambda_l q^4=\Lambda h^2/8\lambda_l, \quad \lambda_1<\lambda_2<\ldots, \tag{13}$$

i.e., smaller values of $R(\mathbf{q})$ correspond to larger values of λ. Comparing Eqs. (6) and (13) one can see that all stationary points lie inside the region $\{\mathbf{q}:R(\mathbf{q})\geqslant 0\}$.

If the eigenvalues of the matrix K are degenerate, the wave vector space must be represented as a direct sum of the invariant subspaces Q_l of the eigenvectors of the matrix K corresponding to different values of λ_l. As is well known, vectors from the different subspaces Q_l are orthogonal.[9] It can be shown that the stationary points of the function $R(\mathbf{q})$, except $\mathbf{q}=0$, lie in the intersection of Q_l and the sphere Z_l determined by the relation (12). For stationary points $\mathbf{q}\in Q_l\cap Z_l$, $R(\mathbf{q})$ is constant and equal to (13).

In the case of one eigenvalue with degeneracy d any vector is an eigenvector of K and the appropriate vectors lie on the sphere (12). This is not the general case, where $R(\mathbf{q})$ has only d stationary points.

3. KINETICALLY FAVORED DIRECTIONS OF DECOMPOSITION

To determine which solutions of Eq. (7) give the function $R(\mathbf{q})$ an extremum we shall study the definiteness of the quadratic form

$$(B(\mathbf{q})\mathbf{x},\mathbf{x})=\sum_{k,l=1}^{d}B_{kl}(\mathbf{q})x_kx_l, \quad B_{kl}=\frac{1}{\Lambda}\frac{\partial^2R}{\partial q_k\partial q_l}. \tag{14}$$

Differentiating $R(\mathbf{q})$ we obtain from Eq. (14)

$$B_{kl}=-2h\delta_{kl}-4K_{kl}q^2-4\delta_{kl}(K\mathbf{q},\mathbf{q})-8q_k\sum_{j=1}^{d}K_{lj}q_j-8q_l\sum_{j=1}^{d}K_{kj}q_j, \tag{15}$$

where δ_{kl} is the Kronecker δ function. One can see from Eq. (15) that the amplification factor $R(\mathbf{q})$ is minimum when $\mathbf{q}=0$, since $(B(0)\mathbf{x},\mathbf{x})=-2hx^2>0$, if $\mathbf{x}\neq 0$.

Let the stationary point being considered as an extremum lie in the intersection $Q_l\cap Z_l$. Substituting into Eq. (15) the expression (11) for h we obtain, using the properties of an eigenvector

$$\sum_{i=1}^{d}K_{ji}q_i=\lambda_l q_j, \quad (K\mathbf{q},\mathbf{q})=\lambda_l q^2 \tag{16}$$

the following expression for $(B(\mathbf{q})\mathbf{x},\mathbf{x})$:

$$(B(\mathbf{q})\mathbf{x},\mathbf{x})=4\lambda_l q^2x^2-4q^2(K\mathbf{x},\mathbf{x})-16\lambda_l(\mathbf{q},\mathbf{x})^2. \tag{17}$$

For definiteness we shall assume that the magnitude of the vector $\mathbf{x}$ is equal to 1. This is not important for the subsequent check, since the function (17) is a homogeneous function of $\mathbf{q}$ and $\mathbf{x}$. We shall study first the case $\lambda_l=\lambda_1$, where λ_1 is the smallest eigenvalue in the spectrum. The fact that λ_1 is the minimum eigenvalue implies $(K\mathbf{x},\mathbf{x})\geqslant\lambda_1$, (see, e.g., Gel'fand[9]), whence we have $(B(\mathbf{q})\mathbf{x},\mathbf{x})\leqslant -16\lambda_1(\mathbf{q},\mathbf{x})^2$. The quadratic form $(K\mathbf{x},\mathbf{x})$ is minimum if and only if $\mathbf{x}$ is the eigenvector corresponding to the eigenvalue λ_1. Hence if λ_1 is not degenerate, the form (17) takes on only negative values. Indeed, if $\mathbf{x}$ is not an eigenvector corresponding to λ_1, then the sum of the first two terms on the right side of Eq. (17) is strictly less than zero. If $\mathbf{x}$ is such an eigenvector, then the sum of these terms is equal to zero, but because $\mathbf{q}$ and $\mathbf{x}$ are collinear the third term is less than zero. Hence if λ_1 is not degenerate, the function $R(\mathbf{q})$ has an unconditional maximum at the corresponding stationary point, it is evident from Eq. (13) that this maximum will be a global maximum. If λ_1 is degenerate, then a global maximum is reached at all points in $Q_1\cap Z_1$ and it will be a conditional maximum.

The stationary points corresponding to λ_l with $l>1$ can be studied in an analogous manner. Analyzing Eq. (17) it can be shown that at these points $R(\mathbf{q})$ does not have a local maximum. The directions of $\mathbf{x}$ in which the form (17) is positive are determined by the eigenvectors from Q_i with $i<l$; the directions in which the form (17) is negative are determined by the vectors from Q_i with $i>l$ and from the set $\mathbf{x}\in Q_l$, $(\mathbf{q},\mathbf{x})\neq 0$.

Thus the amplification factor $R(\mathbf{q})$ has one local minimum at $\mathbf{q}=0$ and one global maximum in the set $Q_l\cap Z_l$; all remaining stationary points will be saddle points. This shows that in the anisotropic case of the general position both the kinetically favored spatial size of the structures and the direction of decomposition are determined at the initial stage (in contrast to the isotropic case, when all modes whose wave vectors lie on the sphere (12) grow with the same amplification factor).

4. NONLINEAR STAGE OF DECOMPOSITION

Following Ref. 7, we shall use a reduced form of Eq. (1) to study the later stage of decomposition (the coalescence stage, at which the structures grow). This equation is constructed by rewriting Eq. (1) in terms of the Fourier coefficients of the fluctuations φ, expanding in a Taylor series integrals of the type

$$\int \delta\varphi(\mathbf{q}-\mathbf{q}_2-\ldots-\mathbf{q}_n)\,\delta\varphi(\mathbf{q}_2)\ldots\delta\varphi(q_n)\,d\mathbf{q}_2\ldots d\mathbf{q}_n$$

which arise in the nonlinear terms, and dropping all terms containing derivatives with respect to **q**. This approximation corresponds to the point-equation approximation in the theory of autowave processes.[10] In Ref. 7 it is shown that going from Cahn's equation to the reduced equation is equivalent to the "mean-field approximation" in the well-known nonlinear theory of spinodal decomposition.[11] The analytical dependences given in Ref. 7 were compared with the results obtained by modeling the decomposition process by the methods of molecular dynamics and with calculations based on the theory of Ref. 11. The result showed that the asymptotic expressions given in Ref. 7 agree well with earlier numerical results.

We study the decomposition process in a region in the shape of a rectangular parellelipiped of volume V with impermeable boundaries. The reduced equation has the form

$$\delta\varphi(\mathbf{q})'=-q^2\Lambda(\varphi_0+z)\left[\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}+2(K(\varphi_0+z)\mathbf{q},\mathbf{q})\right]\delta\varphi(\mathbf{q}),\quad (18)$$

$$z=u\int\delta\varphi(\mathbf{q})\,d\mathbf{q}=\delta\varphi(\mathbf{r})\,|_{\mathbf{r}=0},\quad u=V/(2\pi)^d\quad (19)$$

We represent Eq. (18) in the form

$$\delta\varphi(\mathbf{q})=C(\mathbf{q})\exp\left\{-q^2\int_0^t\Lambda(\varphi_0+z)\times\left[\frac{\mu_0(\rho_0+z)-\mu_0(\varphi_0)}{z}+2(K(\varphi_0+z)\mathbf{q},\mathbf{q})\right]dt\right\},$$

where $C(\mathbf{q})=\delta\varphi(\mathbf{q})|_{t=0}$. Integrating over **q** we obtain, using Eq. (19),

$$z=u\int C(\mathbf{q})\exp\left\{-q^2\int_0^t\Lambda(\varphi_0+z)\times\left[\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}+2(K(\varphi_0+z)\mathbf{q},\mathbf{q})\right]dt\right\}d\mathbf{q}.\quad (20)$$

Let us study Eq. (20) at times much longer than the duration of the linear stage of the process. We write Eq. (20) in the form

$$z=u\int C(\mathbf{q})\exp\{-[Aq^2+q^2(D\mathbf{q},\mathbf{q})]t\}d\mathbf{q},\quad (21)$$

$$A=\frac{1}{t}\int_0^t\Lambda(\varphi_0+z)\,\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}\,dt,$$

$$D=\frac{2}{t}\int_0^t\Lambda(\varphi_0+z)K(\varphi_0+z)\,dt.\quad (22)$$

The form $(D\mathbf{q},\mathbf{q})$ is positive definite since $(K\mathbf{q},\mathbf{q})$ is positive definite and Λ is positive; generally speaking, A can be positive or negative. Below, as in Ref. 7, we shall be interested in the solution of Eq. (21) for $A<0$, since this case is always realized first and corresponds to the motion of the maximum of the structure factor in the region of small **q**.

We note that a procedure analogous to the one presented above for the complete equation (1) leads to an expression of the form (21), and A is determined in terms of an expression of the form

$$\left[\int\delta\varphi(\mathbf{q}-\mathbf{q}_2-\ldots-\mathbf{q}_n)\,\delta\varphi(\mathbf{q}_2)\ldots\delta\varphi\times(\mathbf{q}_n)\,d\mathbf{q}_2\ldots d\mathbf{q}_n\right]\Big/\ \delta\varphi(\mathbf{q}).$$

Our approximation (18) means that these **q**- and t-dependent expressions are replaced by a function of t only.

We shall now apply to the integral on the right side of Eq. (21) the multidimensional Laplace method.[12] In so doing we shall employ the results of Sec. 3, since the form of the function $R(\mathbf{q})$ is similar to that of the argument of the exponential function in Eq. (21) and in Eq. (21) time is a parameter. In the case of the general position the spectrum of the matrix D consists of nondegenerate eigenvalues. The argument of the exponential in Eq. (21) assumes a maximum value for the eigenvector $\mathbf{q}_*$ corresponding to the minimum eigenvalue λ_D in the spectrum of the matrix D and having the length $q_*^2=-A/2\lambda_D$. The asymptotic value of the integral in Eq. (21) is given by the expression

$$z=2\frac{uC(\mathbf{q}_*)\exp(A^2t/4\lambda_D)\,(2\pi/t)^{d/2}}{|\det I_{\mathbf{qq}}(\mathbf{q}_*)|^{1/2}},\quad (23)$$

where $I(\mathbf{q})=-q^2[A+(D\mathbf{q},\mathbf{q})]$ and $I_{\mathbf{qq}}$ is the matrix of the second derivatives of the function I with respect to the components of the wave vector (the 2 appears in Eq. (23) because there are two symmetric maxima, one at $\mathbf{q}_*$ and another at $-\mathbf{q}_*$). Substituting Eqs. (15) and (16) we obtain

$$I_{\mathbf{qq}}(\mathbf{q}_*)=2q_*^2(-D+\lambda_DE-4\lambda_DP),\quad P_{kl}=\frac{q_{*,k}}{q_*}\frac{q_{*,l}}{q_*},$$
$$\det I_{\mathbf{qq}}(\mathbf{q}_*)=2^dq_*^{2d}\det(\lambda_DE-D-4\lambda_DP).\quad (24)$$

The remaining analysis is simplest for the case of φ-independent Λ and K. In this case the elements of the matrix P, expressed in terms of the direction cosines of the vector $\mathbf{q}_*$, are constant, just like the elements of the matrix D and the quantity Λ. Introducing the notation

$$\sigma=|\det(D-\lambda_DE-4\lambda_DP)|,$$

we obtain instead of Eq. (23), using Eq. (24),

$$z=u_1C(\mathbf{q}_*)\exp(A^2t/4\lambda_D)(-\pi/At)^{d/2},\quad (25)$$

where $u_1=2u(2\lambda_D)^{d/2}/\sigma^{1/2}$. For $d=1$ we have $\det P=1$, $\sigma=4\lambda_D$, $\lambda_D=2\Lambda\varkappa$, $u_1=u/2^{1/2}$ and Eq. (25) goes over to

Eq. (13) of Ref. 7.

An equation for the squared wave vector $\mathbf{q}_*$, corresponding to the maximum of the structure factor of the anisotropic system, can be derived from Eq. (25).

5. ASYMPTOTIC GROWTH OF STRUCTURES

We study the case $F_0 = a\varphi^2 + b\varphi^4$, which corresponds to the Ginzburg–Landau form of the free-energy functional extended to the anisotropic case:

$$F=\int \rho[a\varphi^2+b\varphi^4+(K\nabla\varphi, \nabla\varphi)]d\mathbf{r}. \tag{26}$$

The expression (26) is obtained by approximating F_0 by a quartic polynomial and shifting by a corresponding constant; the term of the form $\text{const}_1\varphi + \text{const}_2$ remaining after we do this does not affect the kinetics. From Eqs. (26) and (22) and the definition of q_*^2 we obtain

$$q_*^2=q_M^2-\frac{3b\varphi_0}{\lambda_1 t}\int_0^t z\,dt-\frac{b}{\lambda_1 t}\int_0^t z^2\,dt. \tag{27}$$

Here λ_1, as above, is the minimum eigenvalue in the spectrum of the matrix K, $\lambda_D = 2\Lambda\lambda_1$, and $q_M^2 = -h/4\lambda_1$. We rewrite Eq. (27) in the form

$$(tq_*^2)'=q_M^2-\frac{3b\varphi_0}{\lambda_1}z-\frac{b}{\lambda_1}z^2. \tag{28}$$

Solving Eq. (28) for z, using Eq. (25), we obtain

$$z=u_1C(\mathbf{q}_*)\exp\left(\frac{A^2t}{8\lambda_1\Lambda}\right)\left(\frac{-\pi}{At}\right)^{d/2}=\left\{-\frac{3b\varphi_0}{\lambda_1}\right.$$
$$\left.\pm\left[\left(\frac{3b\varphi_0}{\lambda_1}\right)^2+\frac{4b}{\lambda_1}(q_M^2-(q_*^2t)')\right]^{1/2}\right\}\Big/\frac{2b}{\lambda_1}. \tag{29}$$

The "+" sign in front of the square root in Eq. (29) corresponds to $C>0$ and the "−" sign corresponds to $C<0$. If in Eq. (29) $(q_*^2t)'$ is an increasing function of time, then at long times a solution does not exist. If $(q_*^2t)'$ approaches a constant nonzero value, then $q_*^2 t\sim t$ and in the limit $t\to\infty\, q_*^2\to\text{const}\neq 0$, which is also physically meaningless. The solution (29) exists when at longtimes $(q_*^2t)'$ decreases to zero. This is equivalent to q_*^2 decreasing. But then the asymptotic behavior of the solution is determined by an equation with no derivatives (for definiteness we assume $C>0$):

$$u_1C(\mathbf{q}_*)\exp\left(\frac{A^2t}{8\lambda_1\Lambda}\right)\left(\frac{-\pi}{At}\right)^{d/2}$$
$$=\left\{-\frac{3b\varphi_0}{\lambda_1}\pm\left[\left(\frac{3b\varphi_0}{\lambda_1}\right)^2+\frac{4b}{\lambda_1}q_M^2\right]^{1/2}\right\}\Big/\frac{2b}{\lambda_1}=g_\pm. \tag{30}$$

As noted above, at the initial stage of decomposition the short-wavelength part of the spectrum of fluctuations is suppressed. The decomposition process is concentrated in the long-wavelength region; this can be taken into account with the leap of the initial condition, constant in the sphere $q^2<2q_M^2$ and equal to zero outside it. The quantity C is determined from the normalization condition $z|_{t=0}=z_0=u\int Cd\mathbf{q}$:

$$C=z_0/uq_M{}^d2^{d/2}\gamma_d, \tag{31}$$

where γ_d is equal to 2, π, and $4\pi/3$ and d = 1, 2, and 3.

Transferring to the dimensionless variables $v = q_*^2/q_M^2$ and $\tau = 2q_M^4\Lambda\lambda_1 t$ (putting t into a dimensionless form in which the duration of the initial stage of the process corresponds to unity), we obtain from Eq. (30)

$$\frac{dv}{d\tau}=\frac{G(v,\tau)-v}{\tau},\quad G=1-A_1\frac{\exp(v^2\tau)}{(v\tau)^{d/2}}-A_2\frac{\exp(2v^2\tau)}{(v\tau)^d},$$
$$A_1=\frac{3b\varphi_0}{\lambda_1q_M^2}\frac{z_0\pi^{d/2}\lambda_1^{d/2}}{\gamma_d\nu^{1/2}2^{(d-2)/2}},\qquad A_2=\frac{b}{\lambda_1q_M^2}\frac{z_0^2\lambda_1^d\pi^d}{\nu\gamma_d^22^{d-2}}.$$

here $\nu = |\det(K-\lambda_1E-4\lambda_1P)|$. The condition (30) is equivalent to the equation $G(v,\tau) = 0$, whence

$$\exp(v^2\tau)/(v\tau)^{d/2}=[(^1/_4A_1^2+A_2)^{1/2}-{}^1/_2A_1]/A_2=y. \tag{32}$$

Raising Eq. (32) to the power $4/d$, we write Eq. (32) in the form

$$p/e^p=4/dy^{4/d}\tau,\quad p=(4/d)v^2\tau. \tag{33}$$

For sufficiently large τ the solution of Eq. (33) is given by the Burman–Lagrange series[12]

$$p=\sum_{n=1}^{\infty}\left(\frac{4}{dy^{4/d}\tau}\right)^n\frac{n^{n-1}}{n!}. \tag{34}$$

The series (34) converges for $\tau>4e/dy^{4/d}$ and then $v^2=y^{-4/d}\tau^{-2}+O(\tau^{-3})$. The spatial size ξ of the decomposition structures grows as

$$\xi=\xi_M\tau^{1/2}y^{1/d}+O(\tau^{-1/2}),\quad \xi_M=2\pi/q_M. \tag{35}$$

Thus for any d the growth exponent of the structures in an anisotropic system is equal to 1/2. However as the degeneracy of λ_1 increases the asymptotic behavior changes. If the degeneracy is equal to m, then the general form of Eq. (32) will be

$$\frac{\exp(v^2\tau)v^{(m-1)/2}}{(v\tau)^{(d-m+1)/2}}=\frac{\exp(v^2\tau)}{v^{(d-2m+2)/2}\tau^{(d-m+1)/2}}=y. \tag{36}$$

Indeed, if we choose in the wave space a basis consisting of the eigenvectors of the matrix K, transform in the subspace Q_1 to the coordinates

$$q_\lambda=\left(\sum_{i=1}^m q_i^2\right)^{1/2},\ \beta_1,\dots,\beta_{m-1}$$

(β_j are angular variables), and integrate over β_j, then the integral in Eq. (21) is transformed into an integral over a space with dimension $d-m+1$. The minimum eigenvalue of the matrix K in the new space is nondegenerate. Using the scheme described in this section we obtain Eq. (36), and the factor $v^{(m-1)/2}$ appears in the numerator, because on transforming to a lower-dimensional space the surface area of an m-dimensional sphere with radius q_λ appears in the integrand. It can be shown that for $d-2m+2>0$ the quantity $\xi=2\pi/q_*$ grows with the exponent $(d-m+1)/(2d-4m+4)$. For $d-2m+2\leqslant 0$, the quantity ξ grows as $(\tau/\ln\tau)^{1/4}$;[12] this case is close to the isotropic case studied in Ref. 7. The following results were obtained for an isotropic solution with $d>1$ $(m=d)$:

$$\begin{aligned}\xi&=\xi_M[2\tau/\ln(\tau y^2)]^{1/4}[1+O(1/\ln\tau)],\quad d=2,\\ \xi&=\xi_M[4\tau/\ln(4y^4\tau^3)]^{1/4}[1+O(1/\ln\tau)],\quad d=3,\end{aligned} \tag{37}$$

i.e., the structures grow with an exponent of 1/4. It is well known that the Lifshitz–Slezov theory[13] gives an exponent of 1/3; at the same time some authors[14] obtained by one or another method exponents less than 1/3. It follows from the results obtained above the anisotropic decomposition in a multidimensional system proceeds as a quasi-dimensional process and predominantly in the direct $\mathbf{q}_*$. We also note that isotropic decomposition is slower than anisotropic decomposition. This is connected with the quasi-one-dimensionality of the anisotropic decomposition, in which there is virtually no competition between decomposition in the most favorable spatial direction and in other directions. This situation is different from the isotropic situation, in which modes with wave vectors of the same length are equally suitable irrespective of the direction of the vector.

6. AVERAGING OVER THE INITIAL CONDITIONS

Equations (35) and (37) contain the quantity z_0, which is the maximum deviation of the composition in the sample (monomineral grain) from the average value at $t = 0$. Estimates of z_0 may not be available or they may not be very accurate, so that it is more convenient to represent the asymptotic expressions as an average over an ensemble of equilibrium initial distributions of φ. Assume that initially the system has a temperature T_0 above the spinodal, and decomposition occurs by means of quite rapid cooling to the temperature T. We average over all possible distributions of the form (31). We rewrite Eq. (30) in the form

$$\frac{u_2^2}{g_\pm^2}C^2=\frac{(v\tau)^d}{\exp(2v^2\tau)},\qquad u_2=\frac{2\pi^{d/2}q_M{}^d\lambda_1{}^d u}{\nu^{1/2}}. \tag{38}$$

The Gibbs distribution has the form[3]

$$w\propto\exp\left\{-\int\rho[(a_0+6b_0\varphi_0^2)(\delta\varphi)^2+(K_0\nabla\delta\varphi,\nabla\delta\varphi)]d\mathbf{r}\right\},$$

where the zero index denotes the quantities a, b, and K at T_0. Substituting Eq. (31), we obtain

$$w\propto\exp(-\rho VuC^2\gamma_d 2^{d/2}q_M{}^d\alpha),$$

$$\alpha=\int[a_0+6b_0\varphi_0^2+(K_0\mathbf{q},\mathbf{q})]d\mathbf{q}\Big/$$

$$\times\int d\mathbf{q}=a_0+6b_0\varphi_0^2+\left(2q_M{}^2\sum_{i=1}^{d}\lambda_{i,0}\right)\Big/(d+2). \tag{39}$$

Averaging Eq. (38) over the distribution (39), allowing for the fact that $g_\pm=g_+$, if $C>0$ and $g_\pm=g_-$ if $C<0$ we obtain after transformations the equation

$$\exp(v_*^2\tau)/(v_*\tau)^{d/2}=y_*,$$

where v_* is the average of v obtained in the manner indicated,

$$y_*=\left(\frac{g_+^2g_-^2}{g_+^2+g_-^2}\,\frac{2^{(3d+2)/2}\rho\gamma_d\nu\alpha}{q_M{}^d\lambda_1{}^d}\right)^{1/2},$$

$$\frac{g_+^2g_-^2}{g_+^2+g_-^2}=\frac{2q_M{}^4}{(3b\varphi_0/\lambda_1)^2+2bq_M{}^2/\lambda_1} \tag{40}$$

Correspondingly, Eq. (35) assumes the form

$$\xi_*=\xi_M\tau^{1/2}y_*^{1/d}.$$

If the denominator is estimated to be of the order of λ_1^d in order of magnitude and the initial state is not too close to the spinodal, then Eq. (40) can be simplified as follows:

$$y_*=\left[\frac{g_+^2g_-^2}{g_+^2+g_-^2}\,\frac{2^{(3d+2)/2}(a_0+6b_0\varphi_0^2)\rho\gamma_d}{q_M{}^d}\right]^{1/2},$$

$$q_M{}^2=-\frac{a+6b\varphi_0^2}{2\lambda_1}. \tag{41}$$

In the isotropic case y in Eq. (37) must be replaced by

$$y_*=\left(\frac{g_+^2g_-^2}{g_+^2+g_-^2}\,\frac{2^{(3d+6)/2}\pi^{d-1}\rho\alpha}{\gamma_d d^2 q_M{}^d}\right)^{1/2}, \tag{42}$$

$$\alpha=a_0+6b_0\varphi_0^2+2d\varkappa_0 q_M{}^2/(d+2),$$

and in the definition of $g_\pm$ λ_1 must be everywhere replaced by $\varkappa$.

In concluding this section we shall explain more precisely what the case $d<3$ studied above means. For $d=1$, the initial conditions for Eq. (1) are such (in the three-dimensional space) that they do not depend on two spatial coordinates. For $d=2$, the initial conditions remain constant along one coordinate axis. Accordingly, for $d=1$ the quantity ρ in Eq. (2) is the linear density of lattice sites along the coordinate axis along which the initial condition varies and it has the dimension of inverse length. For $d=2$, ρ has the dimensions of inverse length squared. Such states are in principle possible for some specific character of the ordering of the solid solution at the temperature T_0, but it is clear that in themselves they are exceptional. The fundamental result of this work is the following property of anisotropic decomposition: asymptotically the process is organized as a one-dimensional process.

7. COMPUTATIONAL EXAMPLE; DISCUSSION

An example of calculations based on Eqs. (37) is given in Ref. 7, where decomposition in feldspars (the solid solution $NaAlSi_3O_4$–$KAlSi_3O_8$) was studied. According to Ref. 15, this is an isostructural solid solution. The theory here is especially suited precisely for such solutions, since the development of spinodal structures in them reduces to the motion of cations in a relatively inert framework, which remains continuous throughout the entire crystal. In Ref. 7 the quantity z_0 was set equal to 0.1. Averaging over the initial conditions changes the formulas. The starting data for feldspars were taken from Ref. 16. In Ref. 7 the reduction of the free energy of mixing to a symmetric form gave $b=3.68$ and $a=-0.58$. Decomposition at $T=773$ K was studied; at this temperature the unit cell is $\sim10^{-9}$ m in size, whence we get $\rho\approx10^{9d}$ m^{-d}. The size of the spinodal structures at the end of the linear stage of the process is $\xi_M=(75\pm10)\times10^{-10}$ m. The quantity λ_1 can be estimated using the formula

$$4\pi^2/\xi_M{}^2=-(a+6b\varphi_0^2)/2\lambda_1,$$

whence $\lambda_1\approx4\times10^{-19}$ m^2. If the solid solution is isotropic, then $\varkappa$ can be determined using a similar formula. Let the spinodal decomposition proceed by means of a transition through the critical temperature T_c, i.e., $\varphi_0=0$. For definiteness let $a_0=-a$, i.e., $T_c-T\approx T_0-T_c$. Performing the calculations using the relations (41) and (42) we find that in the anisotropic case with $d = 1$, 2, and 3 the quantity y_* is equal to 0.71, 1.6, and 3.1, respectively. The growth of the structures can be described in the form (35) with the coefficient $y_*^{1/d}$ equal to 0.71, 1.25, and 1.48 with $d = 1$, 2, and 3, respectively. In the isotropic case with $d = 2$ and 3 the quantity y_* is equal to 0.9 and 1.6, respectively. The product in the argument of the logarithm in Eq. (37) has the form 0.81τ for $d = 2$ and $25.2\tau^3$ for $d = 3$. the expressions obtained should be used for values of τ much greater than unity.

Equations (35), (37), and (40)–(42) can serve as a basis for the calculation of the kinetics of the growth of structures in the process of spinodal decomposition of anisotropic and isotropic systems. In addition, if we transform in Eqs. (35) and (37) to dimensional variables and assume that Onsager's coefficient and the parameters of the thermodynamic potential are functions of the time-dependent temperature, we can study the effect of the rate of cooling on the kinetics of decomposition. This question is important in application to problems in metal science and geochemistry.

The approximation of $F_0(\varphi)$ by a quartic polynomial is not a significant restriction. In the general case, one seeks the roots of a polynomial of the type (28) of degree higher than two; this merely changes the constant y in the formulas obtained.

We note that the correctness of using the reduced equation in the nonlinear analysis was studied in detail in Refs. 17 and 18, where the results of the numerical solution of Eqs. (1) and (2) in the two-dimensional case were compared with calculations based on simpler theories. The results of these works agree very well with the time dependences of the characteristic size of decomposition structures obtained in the Cahn–Hillard theory and in Langer's approximation. Moreover, calculations based on the more complicated theory of Langer, Bar-on, and Miller[19] not only give qualitatively the same time dependence for the sizes of the structures, but in addition yield a dependence which is quantitatively not very different.

8. CONCLUSIONS

In conclusion we shall discuss the generality of these results. Consider the most general form of the equation describing a diffusion-controlled phase transition in a system with one order parameter:

$$\frac{\partial\varphi}{\partial t}=\sum_{i,j=1}^{d}\frac{\partial}{\partial r_i}\left(\Lambda_{ij}\frac{\partial}{\partial r_j}\frac{\delta F}{\delta\varphi}\right). \tag{43}$$

Here Λ_{ij} is an element of the symmetric matrix of the kinetic coefficients (for simplicity we assume below that Λ_{ij} are constants). We multiply Eq. (43) by $\delta F/\delta\varphi$ and integrate over the space. Using the identity

$$\int\frac{\delta F}{\delta\varphi}\frac{\partial\varphi}{\partial t}\,d\mathbf{r}=\frac{dF}{dt},$$

we obtain

$$\frac{dF}{dt}=-\int\sum_{i,j=1}^{d}\Lambda_{ij}\frac{\partial}{\partial r_i}\frac{\delta F}{\delta\varphi}\frac{\partial}{\partial r_j}\frac{\delta F}{\delta\varphi}\,d\mathbf{r}.$$

The only constraint on the theory is that the free energy must not increase with time,

$$dF/dt\leqslant 0,$$

here the equality holds only on the stationary solutions $\mu = \text{const}$. For this reason the form $\Sigma\Lambda_{ij}q_iq_j$ should be positive-definite, which is equivalent to the possibility of rotating the coordinates so that Eq. (43) assumes the form

$$\frac{\partial\varphi}{\partial t}=\sum_{i=1}^{d}\Lambda_i\frac{\partial^2}{\partial r_i^2}\frac{\delta F}{\delta\varphi},\quad \Lambda_i>0.$$

Next, performing the transformation $r_i \to r_i(\Lambda/\Lambda_i)^{1/2}$, where Λ is the characteristic scale of the kinetic coefficient, we obtain Eq. (1). As noted above, in the long-wavelength approximation the free-energy functional has the general form

$$F=\int\rho[F_0(\varphi)+(K\nabla\varphi,\nabla\varphi)]\,d\mathbf{r}. \tag{44}$$

The coordinate transformations indicated above transform K once again into a symmetric matrix. Thus the description of a diffusion-controlled transition with one order parameter reduces to solving the problem (1) with the functional (44). Most importantly, in the dynamic description an anisotropic form cannot be reduced to an isotropic form, as can be done by rotating and then changing scales along the axes when analyzing the statics of critical phenomena based solely on the functional (44). This fact was apparently ignored in the theory of spinodal decomposition which was constructed initially precisely for applications to solid solutions. Attempts to take into account the differences between decomposition in an isotropic medium and decomposition superposed on a medium having higher symmetry were limited to the case of a cubic crystal.[6] A general analysis of decomposition in an anisotropic system was not performed. The constructive development of a general theory, performed above, was made possible by the use of two quite simple, but fundamental, assumptions. The first assumption consists of the introduction of an order parameter, which means that the relaxation times of all other parameters are much shorter. These parameters actually change with their own equilibrium values, which depend on the order parameter, and thereby they are eliminated from the analysis. The second assumption consists of using the energy functional in its general form and the diffusion equation for the anisotropic system in the long-wavelength approximation.

Thus it is possible to propose, starting from first principles, a quite general scenario of phase separation in diffusion-controlled systems with one order parameter. Whether the decomposition is isotropic or anisotropic depends on the properties of the gradient-energy tensor, whose components can be determined from small-angle scattering data. The exponent in the law of growth of the structures depends on the type of decomposition. The simplest form of the equation of decomposition in the anisotropic scenario is

$$\frac{\partial\varphi}{\partial t}=\nabla^2\left(-\varphi+\varphi^3-\sum_{i=1}^{d}\lambda_i\frac{\partial^2\varphi}{\partial r_i^2}\right),$$

which can be derived by transforming the dependent and independent variables after retaining in Eq. (1) nonlinearities up to and including the cubic terms.

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APPENDIX

We show here how to solve Eq. (36). We write Eq. (36) in the form

$$\frac{\exp(v^2\tau)}{(v^2\tau)^{(d-2m+2)/4}} = y\tau^{d/4}. \tag{A.1}$$

Next, three cases are distinguished. for $d - 2m + 2 = 0$ Eq. (A.1) can be solved exactly:

$$v^2=\tau^{-1} \ln (y\tau^{d/4}).$$

For $d - 2m + 2 > 0$, introducing $p = 4v^2\tau/(d - 2m + 2)$ we obtain instead of Eq. (A1)

$$\frac{p}{e^p} = \frac{4}{d-2m+2} y^{-4/(d-2m+2)}\tau^{-d/(d-2m+2)}. \tag{A2}$$

The leading term in the asymptotic expansion of the solution of Eq. (A.2) is

$$v^2=y^{-4/(d-2m+2)}\tau^{-(2d-2m+2)/(d-2m+2)}.$$

For $d - 2m + 2 < 0$, introducing $p = 4v^2\tau/(2m - d - 2)$, we obtain from Eq. (A1)

$$pe^p = \frac{4}{2m-d-2} y^{4/(2m-d-2)}\tau^{d/(2m-d-2)}=f. \tag{A3}$$

The leading term in the solution of Eq. (A3) is

$$v^2 = \frac{2m-d-2}{4\tau} (\ln f + \ln \ln f).$$

One can see from the solutions presented that for $d = 3$, the exponent in the growth law is equal to 1/2 for $m = 1$, 1 for $m = 2$, and 1/4 for $m = 3$. Thus as one goes from an anisotropic situation ($m = 1$) to an isotropic situation ($m = 2$) the exponent changes from 1/2 to 1/4 nonmonotonically. In other words, for every d there exists a critical dimension of the manifold of wave vectors that correspond to modes of maximum growth,

$$m_* = (d+2)/2,$$

which marks the boundary between decomposition with a "quasi-isotropic" asymptotic law ($m \geqslant m_*$, the exponent is equal to 1/4) and decomposition with an "anisotropic" asymptotic law ($m < m_*$, the exponent is greater than or equal to 1/2).

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