Growth kinetics of structures in a nonlinear theory of spinodal precipitation

V. S. Mitlin

O. Yu. Shmidt Institute of Terrestrial Physics, Academy of Sciences of the USSR, Moscow
(Submitted 25 October 1988; resubmitted 3 January 1989)
Zh. Eksp. Teor. Fiz. **95**, 1826–1838 (May 1989)

Spinodal precipitation of a binary system during the coalescence stage is considered in the specific case of solid solutions. It is shown that a spatial structure formed during the exponential stage of growth of fluctuations may not satisfy immediately the condition of a weak interaction between neighboring nuclei. It is proposed to describe coalescence in such a structure on the basis of the nonlinear Cahn equation. Asymptotic methods are employed to derive an equation describing the change in the square of the wave number corresponding to the maximum of the structure factor. An analysis of this factor leads to scaling time dependences of the characteristic size of a structure. In the case of layer structures (when the problem is one-dimensional) the theory predicts a power exponent of 1/2, whereas in the case of two- and three- dimensional precipitation structures the exponent is 1/4. A description is given of the long-term evolution of the structure factor of a solid solution system.

INTRODUCTION

The coalescence occurring in solid solutions is often described using the classical theory of Lifshitz and Slezov[1] dealing with the time evolution of the size of a spherical nucleus and predicting a dependence $\lambda \propto t^{1/3}$ after a long time. The Lifshitz–Slezov theory[1] is based on the assumption that the interaction between nuclei is weak and that the ratio of their size to the average distance between them is small. The asymptotic behavior of $\lambda(t)$ predicted in Ref. 1 applies to a wide range of physical systems, as confirmed by numerous experiments.

The initial distribution of the nuclei, when they are far from one another, is typical of formation of a new phase by the mechanism of nucleation and growth when the parameters of the system in question lie in the range of stable states and the frequency of spontaneous nucleation is not too high at the stage of formation of a nucleus of critical size.[2] If a system can evolve rapidly beyond the spinodal without phase separation in accordance with the nucleation and growth mechanism in the range of metastable states, the next stage is spinodal precipitation of a solid solution. In this process there is no need for overcoming any energy barrier, and nuclei of the new phase may appear in the immediate vicinity of one another. In other words, during spinodal growth we can have situations when the interaction between nuclei cannot initially be regarded as weak.

Figure 1 shows the profile of the distribution of the fraction of one of the components of a binary mixture obtained by solving a one-dimensional equation describing spinodal precipitation and corresponding to the moment of termination of the stage of exponential growth of fluctuations; the initial calculation data were taken from Ref. 3. We can see that large-amplitude fluctuations, which form a modulated structure and can be regarded as nuclei of a new phase, are separated by distances equal to their spatial size. The continuum theory of spinodal precipitation, used in these calculations, was proposed in Ref. 4 and has been used widely since in describing the initial stage of precipitation of an unstable spatially homogeneous state and separation of a mode with a specific spatial scale.[5] Although the initial equation[4] is nonlinear, it is usual to employ only its linearized form and to ignore the stage of advanced instability. Recent results[3] suggest that a nonlinear Cahn equation can provide a unified description of the process of spinodal precipitation at the initial and later stages. The nonlinear terms make it possible to allow effectively for the interaction of nuclei, they limit the exponential growth of fluctuations in a thermodynamically stable region, and give rise to "coalescence" of a modulated structure, i.e., can result in modifications accompanied by an increase in the spatial scale. It would therefore be of interest to consider how the average size in a structure varies in accordance with a nonlinear theory of spinodal precipitation.

We shall try to provide such a description on the basis of the spinodal precipitation equation "truncated" in a certain manner and we shall estimate the validity of such truncation. We shall employ asymptotic methods to derive an equation describing the change in the wave number corresponding to the maximum of the structure factor. An analysis considered in the limit of long times yields simple dependences $\lambda(t)$, which are affected by the dimensionality of the precipitation region, and the power exponents are found to differ from 1/3.

1. DERIVATION OF THE TRUNCATED EQUATION

The spinodal precipitation equation can be written generally in the form[4–6]

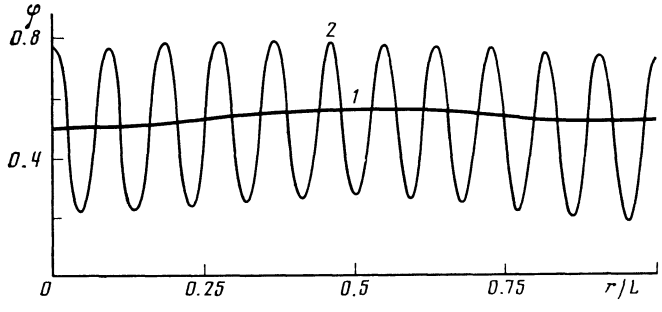

FIG. 1. Typical distribution of the concentrations (curve 2) at the end of the linear stage of the spinodal precipitation process. The amplitude modulation is governed by the initial condition (curve 1).

 0038-5646/89/051056-07$04.00

$$\dot{\varphi}=\nabla(\Lambda(\varphi)\nabla\mu), \tag{1}$$

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

$$\mu=\frac{1}{\rho}\frac{\delta F}{\delta\varphi}=\mu_0(\varphi)-2K(\varphi)\nabla^2\varphi-K_\varphi(\nabla\varphi)^2, \quad \mu_0=\frac{\partial F_0}{\partial\varphi} \tag{3}$$

The following notation is used in Eqs. (1)–(3): φ is the fraction of one of the components of a binary mixture; Λ is the Onsager coefficient; ρ is the number of molecules of the mixture per unit volume; F is the functional of the free energy of the system in units of $k_B T$; μ is the reduced chemical potential expressed in terms of the variational variable F. We shall consider the problem with impermeable boundaries in a rectangular parallelepiped of linear dimensions $L_1,\ldots,L_d$.

We shall transform Eq. (1) as follows. We shall consider fluctuations $\delta\varphi$ relative to the average value φ over the whole region, when the functions in Eq. (1) nonlinear in φ can be expanded as Taylor series. We shall then introduce Fourier components $\delta\varphi_{\mathbf{q}}$; it follows from the condition of impermeability that $\delta\varphi_{\mathbf{q}}=\delta\varphi_{-\mathbf{q}}$. We shall multiply the resultant equation by $\exp(-i\mathbf{qr})$, so that Eq. (1) reduces to a system of equations for $\delta\varphi_{\mathbf{q}}$. On the right-hand side of this system there are sums of the type

$$\sum_{\mathbf{q}_1,\ldots,\mathbf{q}_n}\delta\varphi_{\mathbf{q}_1}\ldots\delta\varphi_{\mathbf{q}_n}, \quad \mathbf{q}_1+\ldots+\mathbf{q}_n=\mathbf{q},$$

which are transformed into convolution-type integrals in accordance with the rule

$$\sum_{\mathbf{q}_1,\ldots,\mathbf{q}_n}\delta\varphi_{\mathbf{q}_1}\ldots\delta\varphi_{\mathbf{q}_n}$$

$$=u^{n-1}\int\delta\varphi(\mathbf{q}-\mathbf{q}_2-\ldots-\mathbf{q}_n)\delta\varphi(\mathbf{q}_2)\ldots\delta\varphi(\mathbf{q}_n)d\mathbf{q}_2\ldots d\mathbf{q}_n,$$

$$u=(2\pi)^{-d}\prod_{j=1}^{d}L_j. \tag{4}$$

The spatial derivatives in Eq. (1) transform in the usual way on adoption of the Fourier components. Expanding now the integrand $\delta\varphi(\mathbf{q}-\mathbf{q}_2-\ldots-\mathbf{q}_n)$ near $\mathbf{q}$, we obtain a system of partial differential equations with respect to $\mathbf{q}$ ($\mathbf{q}$ is a continuous quantity). Our truncation of this system results in retention of only the "bulk" terms and dropping all the terms with the derivatives with respect to $\mathbf{q}$. The use of such a system is permissible if the processes resulting in the smearing out of the spectrum by nonlocal interaction between modes are weak compared with the separation mechanism. Essentially this is equivalent to neglect of the diffusion terms in the diffusion + reaction equation. The problem of validity of this approximation will be considered separately in the last section of this paper.

We thus find that

$$\delta\dot{\varphi}_{\mathbf{q}}=-q^2\Lambda(\varphi_0+z)\left[\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}+2q^2K(\varphi_0+z)\right]\delta\varphi_{\mathbf{q}}, \tag{5}$$

which corresponds to the equation

$$\dot{\varphi}=\Lambda(\varphi_0+z)\nabla^2\left[\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}\varphi-2K(\varphi_0+z)\nabla^2\varphi\right]. \tag{6}$$

In Eqs. (5) and (6) we have $z=u\int\delta\varphi(\mathbf{q})d\mathbf{q}=\delta\varphi(\mathbf{r})|_{\mathbf{r}=0}$. It should be noted that Eqs. (5) and (6) do not include terms of Eq. (1) proportional to $K_\varphi(\nabla\varphi)^2$ and $\nabla\Lambda\nabla\mu$. This is due to the fact that in the adopted approximation they are expressed in terms of integrals $\int q_j\delta\varphi(\mathbf{q})d\mathbf{q}$, where $j=1,\ldots,d$, which vanish because $\delta\varphi(\mathbf{q})$ is even.

The structure of the truncated equation (5) obtained above represents generalization, to the case when Λ and K depend on φ, of the expression derived by Langer[7] starting from the functional equation of continuity of the density of the statistical distribution of configurations. Langer predicted the correct tendency of behavior of the solutions after a long time, namely that the maximum of the structure factor should shift toward longer wavelengths. It is shown above that the equations obtained in Ref. 7 can be derived directly from Eq. (1).

Having solved Eq. (5), we obtain

$$\delta\varphi(\mathbf{q})=C(\mathbf{q})\exp\left\{-q^2\int_0^t\Lambda(\varphi_0+z)\left[\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}+2K(\varphi_0+z)q^2\right]dt\right\}, \tag{7}$$

whereas integration of Eq. (7) with respect to $\mathbf{q}$ gives

$$z=u\int\delta\varphi(\mathbf{q})d\mathbf{q}, \quad C(\mathbf{q})=\delta\varphi(\mathbf{q})|_{t=0}. \tag{8}$$

2. EQUATION (5) IN THE LIMIT OF LONG TIMES

We shall be interested in the solutions of Eq. (5) after a long time, i.e., after the linear stage of the process shall rewrite Eq. (8) in the form

$$z=u\int C(\mathbf{q})\exp[-(Aq^2+Bq^4)t]d\mathbf{q}, \tag{9}$$

where

$$A=\frac{1}{t}\int_0^t\Lambda(\varphi_0+z)\frac{\mu_0(\varphi_0+z)-\mu_0(\varphi_0)}{z}dt,$$
$$B=\frac{2}{t}\int_0^t\Lambda(\varphi_0+z)K(\varphi_0+z)dt. \tag{10}$$

Since all the integrands in Eq. (10) are bounded, it follows that A and B are bounded functions of time. We shall introduce polar coordinates $q,\chi_1,\ldots,\chi_{d-1}$, in Eq. (9); here, χ_j are the angular variables. Then, Eq. (9) becomes

$$z=u\int C_*(q)S(q)\exp[-(Aq^2+Bq^4)t]dq, \tag{11}$$

where $C_*(q)$ is the average (over a sphere of radius q) initial distribution; $S(q)$ is the surface area of this sphere. In the one-dimensional case we have $S(q)=2$, since we are going over from an integral over the whole space to an integral in the region $q>0$, whereas for $d=2$ we find that $S=2\pi q$ and $S=4\pi q^2$ if $d=3$.

The quantity B is always positive, since $\Lambda>0$ and $K>0$. The quantity A can generally be of any sign. We can easily

see that as long as φ_0 and $\varphi_0 + z$ correspond to the region below the spinodal, the integrand in the expression for A is negative. It follows from formal considerations that there are two types of asymptotic behavior of Eq. (11).

We shall now consider the case when $A<0$, which at any rate will be first to appear. Then, the function $I = -(Aq^2 + Bq^4)$ has a maximum at

$$q_*^2 = -A/2B. \tag{12}$$

Applying the steepest-descent method to Eq. (11), we obtain

$$z = uC_*(q_*)S(q_*)\exp\left(\frac{A^2t}{4B}\right)\left(-\frac{\pi}{2At}\right)^{1/2}. \tag{13}$$

If $A>0$, a maximum of I is located at the boundary of the integration domain and, moreover, we have $S(0)=0$ when $d>1$. We then find that $I'(0)=0$ and $I''(0)<0$. Let us assume that $d=1$ (one-dimensional case) and that $C_*(q)$ is a smooth function of q^2. We then obtain (p. 75 in Ref. 8)

$$z = uC_*(0)(\pi/At)^{1/2}. \tag{14}$$

If $d=2$, we can rewrite the integral in Eq. (11) in the form

$$\int C_*(q^2)\pi e^{tI}d(q^2) = \frac{\pi C_*(0)}{At}, \qquad z = \frac{u\pi C_*(0)}{At}. \tag{15}$$

If $d=3$, we can transform the integral in Eq. (11) as follows (p. 75 in Ref. 8):

$$\int C_*(q)4\pi q^2 e^{tI}dq = \int \frac{4\pi q^2 C_*(q)}{I't}d(e^{tI})$$

$$= -\int \frac{\partial}{\partial q}\left[\frac{4\pi q^2 C_*(q)}{I't}\right]e^{tI}dq = \left(\frac{\pi}{At}\right)^{1/2}\frac{2\pi C_*(q)}{t(2A+4Bq^2)}\Bigg|_{q=0},$$

$$z = uC_*(0)(\pi/At)^{3/2}. \tag{16}$$

Equations (14)–(16) can now be combined:

$$z = uC_*(0)(\pi/At)^{d/2}. \tag{17}$$

However, in the case of a formal change in A it is found that the type of a saddle point is modified (a singularity merges with a boundary). Therefore, in going over from $A>0$ to $A<0$ the asymptotes of Eqs. (13) and (17) should be refined in accordance with Ref. 8 (p. 499).

Equations (13) and (17) include integrals of type (10). The next transformation of Eq. (13) give rise to a pair of ordinary differential equations for A and B. We introduce

$$\begin{aligned} A_*(z) &= \Lambda(\varphi_0+z)[\mu_0(\varphi_0+z)-\mu_0(\varphi_0)]/z, \\ B_*(z) &= 2\Lambda(\varphi_0+z)K(\varphi_0+z), \\ G_-(A,B,t) &= uC_*(q_*)S(q_*)\exp(A^2t/4B)(-\pi/2At)^{1/2}, \end{aligned} \tag{18}$$

We apply to (13) the operators A_* and B_*:

$$A_*(z) = A_*(G_-), \qquad B_*(z) = B_*(G_-).$$

Equations (10) and (18) yield the required pair of equations:

$$\dot{A} = [A_*(G_-(A,B,t))-A]/t, \qquad \dot{B} = [B_*(G_-(A,B,t))-B]/t. \tag{19}$$

Similarly, introducing

$$G_+(A,t) = uC_*(0)(\pi/At)^{d/2},$$

we find from Eq. (10) one equation

$$\dot{A} = [A_*(G_+(A,t))-A]/t. \tag{20}$$

We shall be interested in future in the solutions of Eqs. (13) and (19), because these equations correspond to the motion of a maximum of the spectrum of fluctuations toward longer wavelengths.

The system can be closed by defining the function $C_*(q)$. It is known[4] that in the initial stage of spinodal precipitation the short-wavelength part of the spectrum, corresponding to the condition $q>q_c$, where $q_c^2 = -(\partial^2 F_0/\partial\varphi^2)/2K$, is suppressed. The process is concentrated at long wavelengths, which is simplest to allow for with the aid of C_*, which is constant in the range $q<q_c$ and is equal to zero for $q>q_c$. A characteristic value of C_* can be found from the normalization condition

$$z|_{t=0} = z_0 = u\int C\,d\mathbf{q},$$

which yields

$$C_* = z_0/uq_c^d R. \tag{21}$$

Here $R = 2, \pi, 4\pi/3$ applies when $d = 1, 2$, and 3, respectively.

3. ASYMPTOTICS OF THE GROWTH OF PRECIPITATION STRUCTURES

We shall consider the model of spinodal precipitation in the case when $K = \text{const}$ and $\Lambda = \text{const}$ and use the Ginsburg–Landau potential

$$F = \int \rho[a\varphi^2 + b\varphi^4 + K(\nabla\varphi)^2]d\mathbf{r}. \tag{22}$$

The form (22) is obtained by expanding Eq. (2) as a Taylor series in $(\delta\varphi)^4$ and by a shift by a suitable constant; the remaining term of the $\text{const}_1\,\varphi + \text{const}_2$ type does not affect the growth kinetics. Since a fourth-degree polynomial is usually sufficient to approximate satisfactorily the concentration dependence of the free energy when, at a given temperature, there is only one interval of compositions corresponding to thermodynamically unstable states, and usually only the order of magnitude of K and Λ, are known, it follows that an analysis of such a model is a very important task.

We shall investigate the asymptotic change in the wave number corresponding to a maximum of the fluctuation spectrum. It follows from Eqs. (10), (12), and (22) that

$$q_*^2 = q_M^2 - \frac{3b\varphi_0}{Kt}\int_0^t z\,dt - \frac{b}{Kt}\int_0^t z^2\,dt, \qquad q_M^2 = \frac{q_c^2}{2}.$$

Using Eq. (13), we obtain

$$\frac{d(q_*^2 t)}{dt} = q_M^2 - \frac{3b\varphi_0}{K}uC_*(q_*)S(q_*)\exp(Bq_*^4 t)\left(-\frac{\pi}{2At}\right)^{1/2} - \frac{b}{K}\left[uC_*(q_*)S(q_*)\exp(Bq_*^4 t)\left(-\frac{\pi}{2At}\right)^{1/2}\right]^2. \tag{23}$$

We shall now adopt dimensionless variables $v = q_*^2/q_M^2$, and $\tau = tq_M^4 B$ (in other words, we shall use the dimensionless form of t during the initial stage of the process). It then follows from Eq. (21) that

$$dv/d\tau=[G(v,\tau)-v]/\tau,$$

where

$$G(v,\tau)=1-A_1\exp(v^2\tau)v^{(d-2)/2}/\tau^{1/2}-A_2\exp(2v^2\tau)v^{d-2}/\tau, \quad (24)$$

$$A_1=\frac{3b\varphi_0}{Kq_M^2}\gamma, \quad A_2=\frac{b}{Kq_M^2}\gamma^2, \quad \gamma=\frac{\pi^{1/2}dz_0}{2^{(d+2)/2}}. \quad (25)$$

Equation (23) plays the same role in the present analysis as the main equation in the Lifshitz–Slezov theory relating the supersaturation of the system to the radius of a nucleus.

Solving Eq. (23), we find that the expression in square brackets becomes

$$uC_*(q_*)S(q_*)\exp(Bq_*^4t)\left(-\frac{\pi}{2At}\right)^{1/2}$$
$$=\left\{\left[\left(\frac{3b\varphi_0}{K}\right)^2+\frac{4b}{K}\left(q_M^2-\frac{d(q_*^2t)}{dt}\right)\right]^{1/2}-\frac{3b\varphi_0}{K}\right\}\Big/\frac{2b}{K}. \quad (26)$$

If in Eq. (26) $d(q_*^2)t/dt$ the quantity is a rising function of time, then there is no solution for long times. If this quantity tends to a constant nonzero value, then $q_*^2t\propto t$, and $q_*^2\to$const in the limit $t\to\infty$, which again is physically meaningless. The solution (26) exists only if $d(q_*^2t)/dt$ decreases after a long time, which isequivalent to an asymptotic fall of q_*^2. But then the asymptotic behavior of the solution is governed by an equation which does not contain time derivatives:

$$uC_*(q_*)S(q_*)\exp(Bq_*^4t)\left(-\frac{\pi}{2At}\right)^{1/2}$$
$$=\left\{\left[\left(\frac{3b\varphi_0}{K}\right)^2+\frac{4bq_M^2}{K}\right]^{1/2}-\frac{3b\varphi_0}{K}\right\}\Big/\frac{2b}{K}. \quad (27)$$

In the case of the adopted initial condition (21), Eq. (27) is equivalent to

$$G(v,\tau)=0,$$

which yields the equation

$$\exp(v^2\tau)v^{(d-2)/2}/\tau^{1/2}=[(A_1^2+4A_2)^{1/2}-A_1]/2A_2=y. \quad (28)$$

The form of Eq. (28) depends on the dimensionality d of the problem.

If $d=1$, we can represent Eq. (28) in the form

$$4/y^4\tau=g/e^g, \quad g=4v^2\tau. \quad (29)$$

Then, for a sufficiently large value of τ the solution of Eq. (29) is a Bürmann–Lagrange series (p. 47 in Ref. 8):

$$g=\sum_{n=1}^{\infty}\left(\frac{4}{y^4\tau}\right)^n\frac{n^{n-1}}{n!}. \quad (30)$$

Using the Stirling formula, we can transform the n-term of the series (30) into

$$(4/y^4\tau)^ne^n/(2\pi n^3)^{1/2},$$

which shows that Eq. (30) converges when

$$\tau>4e/y^4. \quad (31)$$

For these values of τ, we find that

$$g=4/y^4\tau+O(\tau^{-2}). \quad (32)$$

It follows from Eq. (32) that at high values of d the spatial size λ of a structure increases in accordance with the law

$$\lambda=\lambda_M y\tau^{1/2}+O(\tau^{-1/2}), \quad \lambda_M=2\pi/q_M. \quad (33)$$

If $d=2$, the solution of Eq. (28) is exact:

$$v^2=\ln(\tau y^2)/2\tau, \quad (34)$$

which exists for $\tau>y^{-2}$. If $\tau\gg y^{-2}$, the characteristic size of the structure is

$$\lambda=\lambda_M\left[\frac{2\tau}{\ln(\tau y^2)}\right]^{1/2}\left[1+O\left(\frac{1}{\ln\tau}\right)\right]. \quad (35)$$

In logarithmic coordinates we have, instead of Eq. (35),

$$\ln\frac{\lambda}{\lambda_M}=\frac{1}{4}\ln(2\tau)\left[1+O\left(\frac{\ln\ln\tau}{\ln\tau}\right)\right].$$

If $d=3$, we can represent Eq. (28) in the form

$$ge^g=4y^4\tau^3, \quad (36)$$

where g is defined by Eq. (29). At high values of τ the solution (36) is (p. 51 in Ref. 8)

$$g=\ln(4y^4\tau^3)-\ln\ln(4y^4\tau^3)+O\left(\frac{\ln\ln(4y^4\tau^3)}{\ln(4y^4\tau^3)}\right). \quad (37)$$

The solution (37) is defined if $\tau(4y^4)^{1/3}>1$. However, if $\tau\gg(4y^4)^{-1/3}$, we have

$$\lambda=\lambda_M\left[\frac{4\tau}{\ln(4y^4\tau^3)}\right]^{1/2}\left[1+O\left(\frac{1}{\ln\tau}\right)\right]. \quad (38)$$

Using logarithmic coordinates, we find that Eq. (38) becomes

$$\ln\frac{\lambda}{\lambda_M}=\frac{1}{4}\ln(4\tau)\left[1+O\left(\frac{\ln\ln\tau}{\ln\tau}\right)\right].$$

Therefore, when an analysis is made using logarithmic coordinates, after a long time the dependence of $\ln\lambda$ on $\ln\tau$ approaches a straight line with a slope 1/2 if $d=1$ and 1/4 if $d=2$ or $d=3$, and this slope is independent of the initial distribution of φ. The difference between the power exponents in the case of different dimensionalities d apparently reflects the fact that the boundaries of growing precipitation structures are planar if $d=1$, but are curved if $d>1$. If $d=1$, we obtain a larger power exponent than that in Ref. 1, whereas for $d>1$ we obtain a smaller exponent.

It is clear from Eq. (33) that the rate of growth of spinodal structures is different for $\varphi=\varphi_0$ and $\varphi=-\varphi_0$. This asymmetry of the solution is related to the fact that in both cases we use in Eq. (25) the same quantity z_0 from Eq. (21), so that the corresponding initial distributions $\varphi(\mathbf{r})$ are asymmetric relative to $\varphi=0$. The asymmetry disappears if opposite signs are attributed to z_0 in Eq. (25) for $\varphi=\varphi_0$ and $\varphi=-\varphi_0$.

These expressions can now be used to consider the problem of the influence of the rate of cooling of a solid-solution system on the kinetics of growth of precipitation structures. We must bear in mind that A_1 and A_2 are known functions of temperature and that the temperature depends on time.[9]

Allowance for the asymmetry of $F_0(\varphi)$ leads us to the problem of finding the roots of a polynomial of form (23)

and of degree higher than second. This simply alters the constant y in the resultant expressions. In general (if $\Lambda \neq \text{const}$, and $K \neq \text{const}$) we obtain equations of the (19)–(20) type.

4. EXAMPLE: PRECIPITATION IN FELDSPAR

We shall now use the expressions obtained above to estimate the parameters of the kinetics of spinodal precipitation of alkali feldspars belonging to a high albite–sanidine series ($NaAlSi_3O_8$–$KAlSi_3O_8$ solid solutions). The dependence of the free energy on the fraction of sanidine at $T = 500$ °C at a pressure 1 kbar was given in Ref. 10 where it was reduced to the symmetric Ginzburg–Landau form, as shown in Fig. 2. The energy converted to a value per one cell and normalized to $k_B T$ is characterized by $a = -0.58$ and $b = 3.68$. The scale L, representing the size of a monomineral grain, is $\sim 10^4$–10^7 Å. The volume of a unit cell in feldspars is of the order of 700 Å^3 at 500 °C (Ref. 10) and the distance between the neighboring lattice sites is 7–12 Å. The size λ_M of the spinodal structures at the end of the linear stage of the process was determined experimentally earlier[10] for the high albite–sanidine series and amounted to 75 ± 10 Å in a wide range of temperatures. The value of K, which in our derivation is independent of φ, can be estimated from

$$4\pi^2/\lambda_M^2 = -a/2K,$$

which gives 40 Å^2. If we consider the case when $\varphi_0 = 0$ (transition to an unstable region via a critical point) we find that $y = A_2^{1/2}$. The value of z_0 (representing the maximum deviation from the average composition at $\tau = 0$) is assumed to be 0.1; we also have $q_M = 2\pi/\lambda_M$. We shall define the times at which the expressions in the preceding section are valid:

$$v_*(1) = \frac{4e}{y^4}, \quad v_*(2) = \frac{e}{y^2}, \quad v_*(3) = \frac{e}{(4y^4)^{1/3}}. \tag{39}$$

We shall consider precipitation in a d-dimensional region with linear dimensions L, along each direction. The case $d = 1$ corresponds to coherent precipitation structures (cryptoperthites in the case of feldspars) in the form of platelets; $d = 2$ corresponds to cylindrical structures and

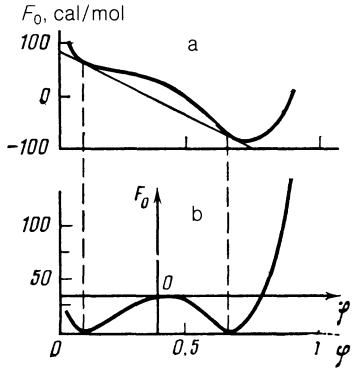

FIG. 2. a) Initial dependence $F_0(\varphi)$; b) replotted dependence $F_0(\varphi)$ representing—along the ordinate—the discrepancy between $F_0(\varphi)$ and the general tangent to the curve in Fig. 1a. The transition to this symmetric form occurs as a result of shift of the axes in Fig. 2b. This gives a function $a\varphi^2 + b\varphi^4$ which has minima at the points of minima of F_0 and passes through the origin of the coordinates.

$d = 3$ represents three-dimensional nearly spherical structures. These types of structure are encountered in crystalline solid solutions during precipitation at the postcrystallization stage. Precipitation of platelet, cylindrical, or spherical structures is due to the presence of certain specific most favorable crystallographic directions in the host lattice and it is along these directions that the process of perturbation is developing.[5] Substitution of the data for feldspars gives the following values of y: 4.44 for $d = 1$; 3.15 for $d = 2$; 2.97 for $d = 3$.

The expressions in the preceding section can be rewritten subject to Eq. (39):

$$\lambda = \lambda_M \tau^{1/2} \left(\frac{4e}{v_*}\right)^{1/4}, \quad d=1; \quad \lambda = \lambda_M \left(\frac{2\tau}{\ln(e\tau/v_*)}\right)^{1/4}, \quad d=2;$$
$$\lambda = \lambda_M \left(\frac{4\tau}{3\ln(e\tau/v_*)}\right)^{1/4}, \quad d=3. \tag{40}$$

Substituting the values of y, we find from Eq. (40) that

$$\lambda = \lambda_M \cdot 4{,}44\tau^{1/2}, \quad d=1; \quad \lambda = \lambda_M \left(\frac{2\tau}{2{,}3 + \ln\tau}\right)^{1/4}, \quad d=2;$$
$$\lambda = \lambda_M \left(\frac{4\tau}{3\ln\tau + 5{,}74}\right)^{1/4} \quad d=3. \tag{41}$$

We must bear in mind that if $\tau \sim 1$, the integrand in Eq. (11) does not yet have a sufficiently sharp maximum, so that expressions of the type given by Eq. (41) can be employed only for values of τ substantially larger than 1.

5. EVOLUTION OF THE STRUCTURE FACTOR OF THE SYSTEM

Using the results of Sec. 3, we shall obtain the asymptote of the change in the square of the Fourier component $\delta\varphi$. Using Eq. (7), we find that

$$\Gamma(\tilde{q}^2, \tau) = (\delta\varphi_q)^2/C^2 = \exp[2\tau\tilde{q}^2(2v - \tilde{q}^2)], \quad \tilde{q}^2 = q^2/q_M^2. \tag{42}$$

Substituting the expressions (33), (35), (38), and (39) in Eq. (42), we obtain

$$\ln\Gamma = 2\tilde{q}^2[(v_*/e)^{1/2} - \tilde{q}^2\tau], \quad d=1,$$
$$\ln\Gamma = 2\tilde{q}^2\{[2\tau\ln(\tau e/v_*)]^{1/2} - \tau\tilde{q}^2\}, \quad d=2, \tag{43}$$
$$\ln\Gamma = 2\tilde{q}^2\left\{\left[\tau\ln\left(\frac{\tau^3 e^3/v_*^3}{\ln(\tau^3 e^3/v_*^3)}\right)\right]^{1/3} - \tau\tilde{q}^2\right\}, \quad d=3.$$

The maximum value of $\ln\Gamma$ is equal to $2v^2\tau$ and it is attained at $\tilde{q}^2 = v$. We can see that it shifts with time toward longer wavelengths. It also follows from Eq. (43) that if $d = 1$, the value of $\ln\Gamma$ at the maximum decreases as τ^{-1}, whereas for $d = 2$ and $d = 3$ it rises as $\ln\tau$. If $\tilde{q}^2 = 2v$, the value of Γ falls from its maximum to 1. The effective width of the spectrum is thus $(2v)^{1/2}$. If $d = 1$, it decreases as $\tau^{-1/2}$ whereas for $d = 2$ it decreases as $(\tau^{-1}\ln\tau)^{1/4}$, whereas for $d = 3$ it decreases as $[\tau^{-1}\ln(\tau/\ln\tau)]^{1/4}$. The qualitative behavior of $\Gamma(\tilde{q}^2)$ is shown in Fig. 3.

We shall end this section by comparing the results obtained with one of the best known nonlinear theories of spinodal precipitation, proposed by Langer,[7] as well as with the results of mathematical modeling of spinodal precipitation in three-dimensional space by the methods of molecular dynamics. As pointed out in Sec. 1, Langer generalized Cahn's

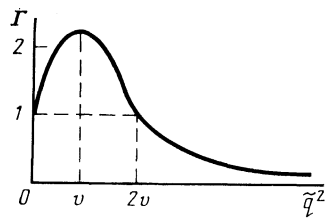

FIG. 3. Dependence of the structure factor on the square of the dimensionless wave number.

theory and obtained an equation for the density of the statistical distribution over all possible configurations.[11] Certain consequences follow from this equation for various moments of the distribution function. In particular the "mean-field approximation"[11] is obtained for the structure factor of the system $G_2(\mathbf{q},t)$ on the assumption that the density of the distribution is of Gaussian form with zero average. In this approximation the relevant equations are as follows:

$$\partial G_2(\mathbf{q},t)/\partial t = 2R(\mathbf{q},t)G_2(\mathbf{q},t), \tag{44}$$

$$R(\mathbf{q},t) = -\Lambda q^2\left(\frac{\partial \mu_0}{\partial \varphi}\bigg|_{\varphi=\varphi_0} + \frac{1}{2}\frac{\partial^3 \mu_0}{\partial \varphi^3}\bigg|_{\varphi=\varphi_0}\langle u^2\rangle + 2Kq^2\right), \tag{45}$$

$$\langle u^2\rangle = \frac{1}{(2\pi)^3}\int G_2(\mathbf{q},t)\,d\mathbf{q}. \tag{46}$$

We can easily see that Eqs. (44)–(46) for G_2 represent a particular case of Eq. (5) for $\delta\varphi(\mathbf{q},t)$. The whole asymptotic analysis of this investigation can be repeated verbatim for Eqs. (44)–(46): the same results are obtained, apart from the constant y.

Allowance for the asymmetry of the fluctuations and for the influence of the thermal noise results in generalization of Eqs. (44)–(46) (Ref. 7). However, the asymptotics of the growth of structures is once again governed by an exponent close to 1/4. Figure 4a shows variation of the spatial size $\lambda = q^{-1}$ corresponding to a maximum of $G_2(\mathbf{q})$ calculated in Ref. 7 (see also review in Ref. 12). An analysis of the results in Ref. 7 can be carried out using the coordinates $\ln\lambda$ and $(1/4)\ln t$. We can see that the slope of the line governing the change in the size of the structures is close to a straight line with a slope of 45°. This means that according to the Langer theory the structures grow with an exponent close to 1/4. Some deviation from the exact 1/4 law may occur because of a logarithmic correction in Eq. (38).

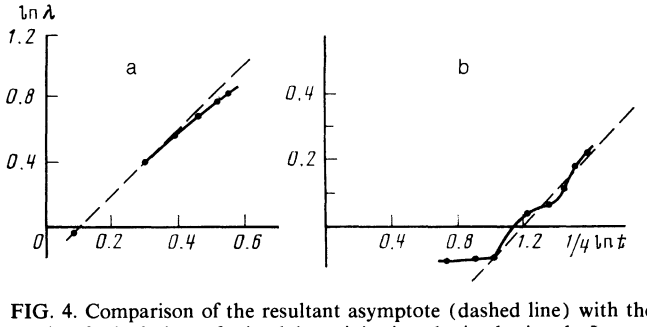

FIG. 4. Comparison of the resultant asymptote (dashed line) with the results of calculations of spinodal precipitation obtained using the Langer theory (a) and with the results of modeling of the process by the methods of molecular dynamics (b).

Allowance for the thermal fluctuations in the Langer theory gives rise on the right-hand side of Eq. (44) to the term

$$2\Lambda k_B T q^2. \tag{47}$$

A comparison of our results with a numerical analysis of the gain factor in Ref. 7 shows that deviation of $(q^2G_2)^{-1}\partial G_2/\partial t$ from a linear dependence occurs mainly in the range of large values for $\mathbf{q}$ where the main contribution comes from the thermal fluctuations and the gain factor $(q^2G_2)^{-1}\partial G_2/\partial t$ reaches a horizontal asymptote. In the long-wavelength range the dominant term is $2RG_2$ of Eq. (44), describing the intrinsic nonlinear kinetics of the process. In the absence of the term (47) in the theory, the dependence of the gain factor on q^2 is linear, as expected on the basis of the above analysis. The logarithm of the maximum of the structure factor in the Langer theory increases as $\ln t$, which is in agreement with our analysis of the $d = 3$ case.

The Monte Carlo method was used in Ref. 13 to model spinodal precipitation in a binary alloy and to study the behavior of the structure factor. Figure 4b shows, using the coordinates $\ln\lambda$ and $(1/4)\ln t$, the evolution of the spatial size corresponding to the maximum of the structure factor. The first three points represent the linear stage of the process when the characteristic spatial size remains constant. This size then increases: it is clear from Fig. 4b that the points representing calculations of Ref. 13 are grouped near a straight line with a slope of 45°. This implies growth of structures with an exponent close to 1/4.

A comparison with the Langer theory and with the results of mathematical modeling of the process demonstrates a good agreement between the calculated asymptotes and the numerical results published earlier. Calculations made using another familiar theory of spinodal precipitation, proposed by Binder,[14] also predict growth of structures characterized by an exponent smaller than 1/3. It is important to note that in this case the situation can be treated analytically, whereas in Refs. 7, 13, and 14 it was ultimately necessary to carry out more or less cumbersome numerical calculations.

CONCLUSIONS

We shall now consider in greater detail the validity of our truncation of Eq. (1), corresponding to the approximation of point equations in the theory of spontaneous wave processes.[15] For simplicity, we shall consider the case when $\Lambda = \text{const}$, $K = \text{const}$. Then, in estimating the contribution of the diffusion of modes to the intermode interaction we have to compare quantities

$$\delta\varphi(q)\int\delta\varphi(q)S(q)\,dq, \quad \frac{\partial^2\delta\varphi(q)}{\partial a^2}\int q^2 S(q)\,\delta\varphi(q)\,dq. \tag{48}$$

Substituting Eq. (42) into Eq. (48) and differentiating, we can see that at high values of τ we obtain

$$\frac{\partial^2\delta\varphi(q)}{\partial a^2}\int q^2 S(q)\,\delta\varphi(q)\,dq/\delta\varphi(q)\int\delta\varphi(q)S(q)\,dq \propto v^2\tau \tag{49}$$

If $d = 1$ we have $v^2\tau \propto \tau^{-1}$. Thus, in the one-dimensional case we can say that the calculated asymptote describes accurately the process after a long time. If $d > 1$, we obtain $v^2\tau \propto \ln\tau$. This means that in the multidimensional case the correction terms are not generally small compared with

those already allowed for. It is quite clear that since the process in question is related to the collapse of the spectrum at long wavelengths, the diffusion of modes should be manifested most strongly in the multidimensional case. Inclusion of mode diffusion may limit the growth of the maximum of the structure factor after a long time. The study demonstrates a good agreement between the analytic results obtained here and those of numerical calculations carried out using the familiar theories of spinodal precipitation. This may mean that mutual compensation of the correction terms of higher orders is possible. In any case, we were able to carry out the first analytic calculations in the case of nonlinear kinetics of spinodal precipitation within the framework of the Cahn equation. The method developed here can be used to analyze nonlinear integrodifferential equations of the type encountered in the Langer theory.

The $d < 3$ cases discussed above describe extremely anisotropic states of a solid solution, because all the characteristics depend only on the modulus of the wave vector. If $d = 1$, this means that precipitation along a certain straight line is preferred from the point of view of minimization of the elastic energy rather than precipitation on a plane perpendicular to this straight line. If $d = 2$, then energy considerations make it likely that a solid solution becomes stratified along two spatial directions. In general, the anisotropy of precipitation should be manifested by an anisotropy of the scattering of particles passing through a solid solution. The corresponding generalization of the theory yields a free energy functional of the form

$$F = \int \rho \left[F_0(\varphi) + \sum_{j,l} K_{jl} \frac{\partial \varphi}{\partial r_j} \frac{\partial \varphi}{\partial r_l} \right] d\mathbf{r}, \tag{50}$$

where

$$K_{jl} = \frac{1}{4} \frac{\partial^2 (1/S_2)}{\partial q_j \partial q_l},$$

whereas the quantity

$$S_2(q) = \rho \int d\mathbf{r} \exp(-i\mathbf{q}\mathbf{r}) \langle \delta\varphi(\mathbf{r}) \delta\varphi(0) \rangle$$

is proportional to the scattering cross section of particles transferring a momentum $\mathbf{q}$ in a medium.[16] An asymptotic analysis of Eq. (1) with the potential (50), similar to that described above, can be carried out using a multidimensional version of the steepest-descent method.

The approach to the description of the late stages of precipitation in a one-dimensional system, other than that described above, is based on the observation that transition to a full thermodynamic equilibrium causes the system to become stabilized consecutively near unstable but long-lived stationary (steady-state) solutions of Eq. (1) (Ref. 3). Averaging of the law describing the fall of the energy (Eq. (44)] over such stationary states yields a second-order equation for slowly varying parameters of stationary solutions.[17] The need for such a procedure, apart from the importance of obtaining the asymptotes of the process, is related largely to the fact that the exact solutions of Eq. (1) describing precipitation are not known.

The author is grateful to I.Ya. Erukhimovich and L.I. Manevich for valuable discussions.

[1]I. M. Lifshitz and V. V. Slezov, Zh. Eksp. Teor. Fiz. **35**, 479 (1958) [Sov. Phys. JETP **8**, 331 (1959)].
[2]M. Volmer and A. Weber, Z. Phys. Chem. (Leipzig) **119**, 277 (1926).
[3]V. S. Mitlin and L. I. Manevich, Vysokomol. Soedin. A **30**, 9 (1988).
[4]J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).
[5]V. P. Skripov and A. V. Skripov, Usp. Fiz. Nauk **128**, 193 (1979) [Sov. Phys. Usp. **22**, 389 (1979)].
[6]V. S. Mitlin, L. I. Manevich, and I. Ya. Erukhimovich, Zh. Eksp. Teor. Fiz. **88**, 495 (1985) [Sov. Phys. JETP **61**, 290 (1985)].
[7]J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. A **11**, 1417 (1975).
[8]M. V. Fedoryuk, *Asymptotics: Integrals and Series* [in Russian], Nauka, Moscow (1987).
[9]E. L. Huston, J. W. Cahn, and J. E. Hilliard, Acta Metall. **14**, 1053 (1966).
[10]N. R. Khisina, *Subsolidus Transformations of Solid Solutions of Rock-Forming Minerals* [in Russian], Nauka, Moscow (1987), p. 118.
[11]J. S. Langer, Ann. Phys. (N.Y.) **65**, 53 (1971).
[12]Yu. I. Ustinovshchikov, *Precipitation of a Second Phase in Solid Solutions* [in Russian], Nauka, Moscow (1988), p. 39.
[13]J. Marro, A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, Phys. Rev. B **12**, 2000 (1975).
[14]K. Binder, Phys. Rev. B **15**, 4425 (1977).
[15]V. A. Vasil'ev, Yu. M. Romanovskiĭ, and V. G. Yakhno, *Spontaneous Wave Processes* [in Russian], Nauka, Moscow (1987), p. 12.
[16]Shang-Keng Ma, *Modern Theory of Critical Phenomena*, W. A. Benjamin, Reading, MA (1976).
[17]V. S. Mitlin and L. I. Manevich, Vysokomol. Soedin. B **30**, 597 (1988).

Translated by A. Tybulewicz