Theory of Spinodal Decomposition

S. B. Goryachev

Laboratoire des Solides Irradiés, Ecole Polytechnique, 91128 Palaiseau Cedex, France

The general evolution equation describing spinodal decomposition in systems with conserved or non-conserved order parameter is developed. It is shown that if in the system thermodynamic potential expression the coefficients at order parameter square and at order parameter gradient square can change sign near the spinodal point, some different decomposition scenarios are possible, which result in system transformation from disordered to ordered, modulated, patterned, or ordered-patterned states.

When a system described by a scalar order parameter $\psi(\mathbf{x},t)$, depending on space and time, is rapidly quenched from the homogeneous high-temperature phase to the two-phase coexistence region, a dynamical phase separation process develops, which is called "spinodal decomposition" [1]. Usually, for theoretical analysis of spinodal decomposition dynamics two physically important models are considered [2]: a system with nonconserved order parameter (NCOP) and a system in which the order parameter is conserved (COP); i.e., ψ satisfies the condition

$$\int \psi\, d\mathbf{x} = N, \qquad (1)$$

where $N = L^d \bar{\psi}$, L is the system size, d is the system dimensionality, and $\bar{\psi}$ is the volume mean value of $\psi(\mathbf{x},t)$, which is constant in time. In both cases the system free energy expression in the Landau-Ginzburg [3] form is used,

$$F(\psi) = \tfrac{1}{2}\int d\mathbf{x}\{A\psi^2 + \tfrac{1}{2}B\psi^4 + C(\nabla\psi)^2\}, \qquad (2)$$

where B,C are positive constants, $A = A(T)$, T is temperature, and T_A is its phase transition value, defined by the condition $A(T_A) = 0$. The homogeneous order parameter distribution $\psi_0(\mathbf{x}) = 0$ is the extremal ·of (2) above ($T > T_A$, $A > 0$) and below ($T < T_A$, $A < 0$) the spinodal point. The NCOP dynamics near this extremal is defined by the Landau-Khalatnikov [4,5] evolution equation, which supposes the order parameter evolution rate to be proportional to the thermodynamic force,

$$\partial\psi/\partial t = -\Gamma\, \delta F/\delta\psi, \qquad (3)$$

where Γ is a constant and $\delta F/\delta\psi$ is a functional derivative. The COP dynamics near $\psi_0(\mathbf{x}) = 0$ is defined by Cahn's evolution equation [6]

$$\partial\psi/\partial t = M\nabla^2 \delta F/\delta\psi, \qquad (4)$$

where M is a constant. The latter is derived from Fick's law [7]

$$\mathbf{j} = -M\nabla\mu, \qquad (5)$$

which assumes the proportionality of COP current density $\mathbf{j}$ to the gradient of "local chemical potential" $\mu(\mathbf{x},t) = \delta F/\delta\psi$, and from the continuity equation

$$\partial\psi/\partial t + \nabla\mathbf{j} = 0, \qquad (6)$$

which is the differential form of (1). Introducing a Fourier transformation representation the free energy (2) and the evolution equations (3) and (4) can be written in linear approximation for ψ as

$$F = \tfrac{1}{2}\sum_{\mathbf{k}}\{[A + Ck^2]\psi(\mathbf{k},t)\psi(-\mathbf{k},t)\}, \qquad (7)$$

$$d\psi(\mathbf{k},t)/dt = -\gamma(\mathbf{k})\psi(\mathbf{k},t), \qquad (8)$$

where, for the NCOP,

$$\gamma(\mathbf{k}) = \Gamma(A + Ck^2), \qquad (9)$$

and, for the COP,

$$\gamma(\mathbf{k}) = Mk^2(A + Ck^2). \qquad (10)$$

In this form of representation the conservation condition (1) is simply the boundary condition in $\mathbf{k}$ space

$$\psi(\mathbf{k},t)|_{\mathbf{k}=0} = 0. \qquad (11)$$

From (8)–(10) it follows [1,4–6] that both systems are stable above the spinodal point against infinitesimal changes of the order parameter for all k. Below the spinodal point they are unstable, and the order parameter space inhomogeneities with $k < k_A$, where $k_A = \sqrt{-A/C}$, will grow exponentially. The maximum growth rate has inhomogeneities with $k_m = 0$ for the NCOP system and $k_m = \sqrt{-A/(2C)}$ for the COP system.

Just a cursory comparison of the foundations (1) and (2) and the resulting evolution equations (3) and (4), (8)–(10) shows some contradictions. For the NCOP model all above mentioned conclusions about its behavior can be seen already from the free energy expression (7) and it does not raise any doubts. For the COP model the same free energy expression (2) is used. It differs from the NCOP model only through condition (1), the influence of which must be displayed for the inhomogeneities with wave number near $k_L = 2\pi/L$. Therefore, the existence of the selected mode with wave number $k_m = \sqrt{-A/(2C)}$ depending on the constants A and C of the free energy (2) is very unnatural. For $k \gg k_L$ the COP evolution equation should turn continuously into the NCOP one, but this does not follow from (9) and (10) [8]. In my opinion all these contradictions are concerned with Cahn's equation (4) not having a sufficiently physical foundation and being incorrect. The main error in the

development of (4) is to use at the same time Fick's law (5), being a law of *linear thermodynamics*, and the free energy expression (2), which is outside of this thermodynamics. By writing (2) we violate the main linear thermodynamics supposition about *local system equilibrium* [3,7], since the local free energy in (2) is dependent not only on the order parameter ψ, but also on its space derivatives. Therefore the usual definition of a chemical potential conjugated to ψ loses sense and Fick's law cannot be utilized [7,9]. From my point of view, experimentally observed formation of spatial modulated structures during spinodal decomposition [1] is related, not with the conservation of the order parameter, as follows from Cahn's theory, but with the form of potentials (2) and must have the same nature in both the NCOP and COP systems.

This work contains three important results. First, a general evolution equation is developed, which describes the spinodal decomposition in both COP and NCOP systems. Second, it is shown that for a full description of the decomposition we must take into account the fifth-order spatial derivative of the order parameter in the free energy expression (2), and assume that not only A but also C can change the sign near the spinodal point. Third, it is demonstrated that there are some different decomposition scenarios connected with the order of sign changes of these coefficients during quenching, which result in system transitions from disordered to ordered, modulated, patterned, or ordered-patterned states.

To base these affirmations let us develop in detail the evolution equations for both NCOP and COP systems in the same way. Consider a system of constant volume L^d at constant temperature T, which is in a state of local equilibrium with respect to all parameters, except some order parameter $\psi(x,t)$. If the gradients of ψ are small, the system free energy may be written in the form

$$F(\psi) = \int dx\, f[\psi(x,t), \nabla\psi(x,t), \nabla^2\psi(x,t),\ldots] \quad (12)$$

by introducing a local free energy density $f(\psi, \nabla\psi, \nabla^2\psi, \ldots)$ which depends on the values of ψ and its space derivatives only at the point x. For the NCOP system, an extremum of free energy (12) defines the system extreme state [3,10]. The necessary extremum condition is

$$\delta F = \delta F/\delta\psi|_{\psi=\psi_0(x)}\delta\psi = 0, \quad (13)$$

and Eq. (3) describes the order parameter evolution near the extremal $\psi_0(x)$. When ψ is conserved the system extreme state is defined by the thermodynamic potential $\Omega = F - \mu N$ extremum. The constant μ, being conjugated to the variable N chemical potential [3,10], and the extremal $\psi_0(x)$ are found from the variation equation

$$\delta\Omega = (\delta F/\delta\psi|_{\psi=\psi_0(x)} - \mu)\delta\psi = 0 \quad (14)$$

and condition (1). For the weakly nonequilibrium state i.e., for small values of $\delta\Omega/\delta\psi$, we can suppose the evolution rate of $\delta\psi(x,t) = \psi(x,t) - \psi_0(x)$ to be proportional

to $\delta\Omega/\delta\psi$ by analogy with (3),

$$\partial\psi/\partial t = -\Gamma(\delta F/\delta\psi - \mu). \quad (15)$$

Here it should be remembered that from all the possible solutions of (15) only the ones which satisfy (1) are valid.

Comparing (3) and (15) we see that both NCOP and COP systems may be described by a single evolution equation (15), and the NCOP system is a special case of the COP system, with $\mu = 0$, and condition (1) need not be used for the solution selection of Eq. (15) [11].

If $F(\psi)$ has the form (2), $\psi_0(x) = 0$ is the solution of Eqs. (13) above and below the spinodal point. We have for the COP system $N = 0$ in (1) and $\mu = 0$ in (14) and (15), so that $\Omega = F$ and both systems have the same evolution equations (3) or (8) and (9). They differ from each other only by conditions (1) or (11). From (8) and (9) we see that the maximum growth rate has the inhomogeneities with the minimum possible wave number, namely, $k = 0$ for the NCOP system and $k \to 0$ for the COP system. In other words, there are no order parameter spatial modulations with $k \gg k_L$ in both systems, as we have already discussed. One can see from (2) and (7) that for the appearance of this type of system instability it is necessary to assume that the C coefficient is negative, but then we should consider the next members of the series on the space derivatives to ensure the global system stability. In the most general form the local free energy density may be written as [12,13]

$$f = \tfrac{1}{2}A\psi^2 + \tfrac{1}{4}B\psi^4 + \tfrac{1}{2}C(\nabla\psi)^2 + \tfrac{1}{2}D(\Delta\psi)^2 + E\psi^2(\nabla\psi)^2. \quad (16)$$

The A and C coefficients may change signs independently of each other, so that the different system states arise. Their number and stability depend on proportions of A, B, C, D, and E coefficients and form a complex picture in general. We will restrict ourselves to consideration of the evolution of the system states near the state with homogeneous order parameter distribution. In this situation, as was shown above, $\Omega = F$ and both systems' evolution is defined by the same equation [14]:

$$\partial\psi/\partial t = -\Gamma(A\psi + B\psi^3 - C\Delta\psi + D\Delta^2\psi - E\psi^2\Delta\psi). \quad (17)$$

For the COP system, condition (1) with $\bar\psi = 0$ should be taken into account. In the linear approximation for $\delta\psi = \psi - \psi_0$, the order parameter evolution is described by Eq. (8) with

$$\gamma(k) = \Gamma(A + Ck^2 + Dk^4). \quad (18)$$

Introducing the structure function $S(k,t)$ as a Fourier transformation of correlation function $\langle\delta\psi(0,t)\delta\psi(x,t)\rangle$ [1], we have from (8)

$$dS(k,t)/dt = -2\gamma(k)S(k,t), \quad (19)$$

with $\gamma(k)$ defined by formula (18). The boundary condi-

tion for the COP system (11) has the form

$$S(\mathbf{k},t)|_{\mathbf{k}=0}=0. \tag{20}$$

On writing (3), (15), (17), and (19) we have neglected order parameter thermal fluctuations. If $\gamma(\mathbf{k}) > 0$, according to (19) any initial distribution $S(\mathbf{k},0)$ should fall to zero with time. On the other hand, it is well known that $S(\mathbf{k},\infty)$ is not zero [3,16]. For the NCOP system $S(\mathbf{k},\infty)$ is defined by the Ornstein-Zernike formula [3], which can be generalized for (16) as

$$S(\mathbf{k},\infty)=T/(A+Ck^2+Dk^4). \tag{21}$$

In the COP system thermal fluctuations are limited by the condition (20), so that the equilibrium correlation function $S(\mathbf{k},\infty)\to 0$ for $k\to 0$ ($k\ll k_L$) and $S(\mathbf{k},\infty)$ is given by (21) for $k\gg k_L$; therefore we have [17]

$$S(\mathbf{k},\infty)=[k^2/(k^2+k_L^2)]T/(A+Ck^2+Dk^4). \tag{22}$$

Equation (19), with thermal fluctuations, becomes

$$dS(\mathbf{k},t)/dt=-2\gamma(\mathbf{k})S(\mathbf{k},t)+2\Gamma Tk^2/(k^2+k_L^2). \tag{23}$$

We can see from (16)–(23) that there are some important system states defined by the signs of the A and C coefficients. It is useful to represent these states on the coordinate plane (A,C). For simplicity, let us begin with the NCOP system. If $A > 0$, $C > 0$ (region I), $\psi_0(\mathbf{x})=0$ is the single stable stationary solution of (17), or in other words the system is in the one-phase homogeneous state (disordered state) [3]. If $A < 0$, $C > 0$ (region II), Eq. (17) has two stable stationary solutions $\psi_0(\mathbf{x})=\pm\sqrt{-A/(2B)}$; i.e., the system is in the two-phase homogeneous state (ordered state) [3]. If $A > 0$, $C < 0$ (region IV), Eq. (17) has a stationary homogeneous solution $\psi_0(\mathbf{x})=0$ and some stationary space-periodical ones [19], the common property of which is $\bar\psi_0=0$. Therefore, we can say that the system is in the one-phase inhomogeneous state. In region IV', where $C > -2\sqrt{AD}$, $\psi_0(\mathbf{x})=0$ is the single stable solution, as in region I. However, the equilibrium correlation function (21) has a maximum not at $|\mathbf{k}|=0$, but at $|\mathbf{k}|=k_C$, where $k_C=\sqrt{-C/(2D)}$. This signifies that a thermal fluctuation induced transition to the modulated state takes place. In the region IV'', where $C < -2\sqrt{AD}$, the solution $\psi_0(\mathbf{x})=0$ is unstable and Eq. (17) admits stationary one-, two-, and three-dimensional space-periodical solutions [15,19]; i.e., the system is in the one-phase patterned state (or, more simply, patterned state). It can be shown [12] that in region III ($A < 0$, $C < 0$), Eq. (17) has unstable stationary homogeneous solutions $\psi_0(\mathbf{x})=0$, $\pm\sqrt{-A/(2B)}$ and stable stationary space-periodical solutions with $\bar\psi_0=\pm\sqrt{-A/(2B)}$ and k near k_C. This means that in region III the system is in the two-phase patterned state (ordered-patterned state).

There are some different system transformations connected with the sign change of the A and C coefficients. The transformation I$\to$II is the well-known disorder-

order phase transition [5]. Any order parameter inhomogeneity with $k < k_A$ grows during decomposition until the moment when equilibrium values are achieved, and then the coalescence process begins. The maximum growth rate has inhomogeneities with the wave number $k_m=0$. The transformation I$\to$IV is the transition to the inhomogeneous state. The transition I$\to$IV' is the one from the disordered state to the modulated state and results in the appearance of a new maximum of the equilibrium correlation function $S(\mathbf{k},\infty)$ at $k=k_C$. The transition I$\to$IV'' is the one from the disordered state to the patterned state [15]. Any order parameter inhomogeneity with $k_{C1} < k < k_{C2}$, where $k_{C1,C2}=(k_C^2\pm\sqrt{k_C^4-A})^{1/2}$, grows exponentially and inhomogeneities with wave number $k_m=k_C$ have a maximum growth rate. It can be shown [12] that after the II$\to$III and IV$\to$III transitions the system symmetry changes take place with splitting of the ordered state and the patterned state on the ordered-patterned states. The A and C coefficients depend on T, so that the critical values T_A and T_C [the latter defined from condition $C(T_C)=0$] are in general not coincident. Thus, the system transition I$\to$III from the disordered ($T > T_A$, $T > T_C$) to the ordered-patterned state ($T < T_A$, $T < T_C$) may be realized in three different ways: I$\to$II$\to$III ($T_A > T_C$); I$\to$IV$\to$III ($T_A < T_C$); I$\to$0$\to$III ($T_A=T_C$). So, three transitions I$\to$II, I$\to$III, and I$\to$IV result in the decomposition of the disordered state. Two of these, I$\to$II and I$\to$III, are related to spinodal decomposition, although the first does not result in spatial modulated structure ($k_m=0$). On the contrary, during the I$\to$IV transition these structures are formed ($k_m=k_C$), but it is not really spinodal decomposition, since the system does not come below the spinodal temperature T_A.

The COP system has the same evolution equations of disordered state decomposition (8) and (18) as the NCOP system, but the supplementary condition (11). For the practically important case $k\gg k_L$ any difference in their behavior must not be observed, because of the small influence of this condition. In the other cases the decomposition consideration demands more detailed analysis of system boundary conditions influence on the pattern selection process [12,15].

I note some circumstances in conclusion. First, I cannot make in this short communication the full comparison of our theoretical conclusions with numerous experimental data for the spinodal decomposition problem [1]. From more interesting results, I note that this approach removes one of the most important discrepancies between experiment and Cahn's theory, namely, the amplification factor $-\gamma(\mathbf{k})$ dependence of wave number k. According to Cahn's theory $-\gamma(\mathbf{k})/k^2$ should be a linear function of k^2, whereas all experimental evidence shows [1,20] that there are considerable deviations from the linear relation especially for small k. Second, the exponential growth of the structure function $S(\mathbf{k},t)$ in (19) and (23) is evidently related with the evolution equation (17)

linearization. Taking into account the nonlinear effects, for example by the LBM method [1], has no principal difficulties [12], although the evolution equation (17) is much more complicated than that of Cahn (2) and (4) [21]. Third, discussion about critical dynamics of systems with "global" and "local" order parameter conservation laws [22] is related, in my opinion, to the impossibility of formulation of the "local" conservation law without using Fick's law (i.e., without the supposition about the local system thermodynamic equilibrium) in the theory and to artificial methods of its realization in computer simulation models. Recent computer simulation results are consistent with those presented here and demonstrate that systems with global conservation laws and those with no conservation laws are in the same dynamical universality class [23]. Finally, the decomposition process depends on proportion of $A(T)$ and $C(T)$ coefficients, i.e., on the concurrence of short- and long-range attractive and repulsive interactions of the system elements. Therefore, the effects discussed in this article must be observed in systems where this concurrence is significant, for example, some binary alloys and liquids, oxide compounds, uniaxial ferromagnetic films, lipid monolayers, ferrofluid systems, etc. [20,24].

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[8] The k_L value is not present at all in (10), and the coefficient M has a different dimensionality than Γ

without any physical explanation.

[9] Utilization of Fick's law (5) in Cahn's theory to derive (4) is not correct already because (5) does not take into account the next member of space derivatives expansion being proportional to $\nabla^3\mu$, that gives the contribution of the same $\nabla^4\psi$ order, that has been held.

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[11] If to believe approximately that local free energy f in (12) does not depend on spatial derivatives of ψ, then $\mu(x,t)=\delta F/\delta\psi=\partial F/\partial\psi$ really is the local chemical potential and Fick's law is the approximate diffusion law of linear thermodynamics for $k \ll k_L$ [7]. If $f=f(\psi,\nabla\psi, \nabla^2\psi,...)$, then $\delta F/\delta\psi$ is not the chemical potential because f depends on some independent variables ψ, $\nabla\psi, \nabla^2\psi,...$, and formally giving this sense for $\delta F/\delta\psi$ does not signify the possibility to use it in (5).

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[13] Terms $\psi\Delta\psi$, $\psi\Delta^2\psi$, and $\psi^3\Delta\psi$ are reduced to the written ones and $(\nabla\psi)^2\psi\Delta\psi$, $\psi^3\Delta^2\psi$, and $\psi^2(\Delta\psi)^2$ to $(\nabla\psi)^4$ by means of system volume integration, if the system surface effects are being neglected. It is easy to show [12] that for general system stability the B, D, and E must be positive; therefore the member $(\nabla\psi)^4$ can be neglected.

[14] The particular cases of this equation are the Landau-Khalatnikov one ($B>0$, $C>0$, $D=0$, $E=0$) and Swift-Honenberg one ($A>0$, $B>0$, $C<-2\sqrt{AD}$, $D>0$, $E=0$). The latter and other similar equations appear as the model evolution equations describing Rayleigh-Bénard convection in nonequilibrium fluid systems [15].

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