РОССИЙСКАЯ АКАДЕМИЯ НАУК

# ПИСЬМА В ЖУРНАЛ ЭКСПЕРИМЕНТАЛЬНОЙ И ТЕОРЕТИЧЕСКОЙ ФИЗИКИ

(ОТДЕЛЬНЫЙ ОТТИСК)

МОСКВА

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# Experimental Test for the Hyperbolic Model of Spinodal Decomposition in the Binary System

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A model has been presented for the physical decay with the relaxation of the diffusion flux described by the hyperbolic diffusion equation. The analysis of such a hyperbolic model provides the predictions for the critical parameters of the decay, which are compared with the conclusions of the Cahn–Hilliard theory. It has been shown that the hyperbolic model predicts the nonlinearity of the dispersion curve for the spinodal decay, which is controlled by the ratio of the diffusion and correlation lengths. The predicted behavior of the dispersion curve is compared with the experimental data on phase separation in binary glasses.

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A phase transition in which both phases have an equivalent symmetry and differ only in composition is known as spinodal decomposition. It was observed in many experiments with polymer mixtures [1], liquid solutions [2, 3], and metal systems [4]. Spinodal decomposition was described by Cahn and Hilliard [5, 6] and was theoretically examined and experimentally tested in [7, 8]. In particular, Andreev et al. [9, 10] showed that the experimental data obtained from the data on the scattering of light and x rays on layered glasses indicate a nonlinear dispersion relation in contradiction with the prediction of the Cahn–Hilliard theory [5, 6]. According to this theory, the linear change in the dispersion relation at early stages of the spinodal decomposition is characteristic of only the systems with long-range interaction [8]. This is not the case for the systems with short-range interaction, because nonlinear or nonequilibrium effects are important at rapid hardening or deep supercooling [11, 12].

In order to describe the strongly nonequilibrium phase separation, Binder et al. [13] generalized the Cahn–Hilliard theory by introducing a slowly relaxing variable. Their calculations show that the instability of the system is determined by the relaxation of the slowly relaxing structural variable rather than by the standard diffusion mechanism. The Cahn–Hilliard theory was recently modified with the inclusion of the relaxation of the diffusion flux to its steady state [14, 15]. The flux is considered as an independent thermodynamic variable in agreement with the formalism of extended irreversible thermodynamics [16]. As a result, a hyperbolic partial differential equation, which is called the hyperbolic model for spinodal decomposition, was obtained for phase separation with diffusion. This model can describe spinodal decomposition in short time intervals, at high characteristic rates of the process, for large density gradients, or for deep supercooling at early decomposition stages. For this reason, we present a comparative analysis of the Cahn–Hilliard parabolic model and hyperbolic model (modified Cahn–Hilliard model) of spinodal decomposition. In order to test the hyperbolic model, its predictions are compared with the experimental data.

Let us consider an isothermal and isobaric binary system which is an isotropic solid solution of atoms of the kinds A and B. Let the solution be free of imperfections and its molar volume be independent of the density of atoms. The spinodal region is determined by the negative curvature of the free energy, $\partial^2 f/\partial c^2 < 0$, and the spinodal is specified by the relation $\partial^2 f/\partial c^2 = 0$, where $f$ is the Helmholtz free energy per unit volume and $c$ is the density of atoms B.

The free energy at a given temperature $T$ depends on the behavior of the slow persistent variable, such as the density $c$, and fast nonpersistent variable, such as the diffusion flux $\mathbf{J}$, according to the model of rapid phase transitions [15]. In this case, the free energy density $f$ can be written as

$$f(c, \nabla c, \mathbf{J}) = f_h(c) + \frac{\varepsilon_c^2}{2}(\nabla c)^2 + \frac{\alpha_J}{2}J^2. \qquad (1)$$

Here, $\varepsilon_c^2 = (\partial^2 f/\partial(\nabla c)^2)_{\nabla c = 0}$ is proportional to the correlation length squared; the coefficient $\alpha_J = [\tau_D/D][\partial(\Delta\mu)/\partial c]_{T = \text{const}}$ determines non-Fick diffusion; $\Delta\mu = \mu_A - \mu_B$ is the difference between the chemical potentials of A and B atoms, respectively; and $\tau_D$ is the time of the relaxation of the diffusion flux to its steady state.

The free energy density given by Eq. (1) is defined for the locally nonequilibrium state. This state is microscopically characterized by the impossibility of the system to pass through all the points of the phase space in a short time interval in a local volume. This situation leads to the necessity of the inclusion of the relaxation of the flux **J** in the steady value at the phenomenological description level [17]. In the instantaneous relaxation limit, $\tau_D \longrightarrow 0$, the contribution from the flux **J** disappears and Eq. (1) determines the free energy density $f(c, \nabla c)$ for the locally equilibrium system [5, 6].

In view of Eq. (1), the total free energy can be written in the functional form

$$F(c, \nabla c, \mathbf{J}) = \int\limits_v \left[f_h(c) + \frac{\varepsilon_c^2}{2}(\nabla c)^2 + \frac{\alpha_J}{2}J^2\right]dv, \quad (2)$$

where $v$ is the volume of the system. The evolution of $F(c, \nabla c, \mathbf{J})$ in time $t$ is described as $dF/dt = (dF/dt)_{\text{ex}} + (dF/dt)_{\text{in}}$, where $(dF/dt)_{\text{ex}} + (dF/dt)_{\text{in}}$ are the changes in the free energy due to the exchange with the external medium and inside the system defined as the dissipative function. The application of the standard procedure described in [14, 15] to Eq. (2) yields

$$\left(\frac{dF}{dt}\right)_{\text{ex}} = \int\limits_\Omega \left[\varepsilon_c^2(\nabla_n c)\frac{\partial c}{\partial t} + (-f'_c + \varepsilon_c^2\nabla^2 c)J_n\right]d\Omega, \quad (3)$$

$$\left(\frac{dF}{dt}\right)_{\text{in}} = \int\limits_v \mathbf{J}\cdot\left[\nabla(f'_c - \varepsilon_c^2\nabla_n^2 c) + \alpha_J\frac{\partial \mathbf{J}}{\partial t}\right]dv, \quad (4)$$

where $\Omega$ is the outer surface of the volume $v$, $J_n$ is the diffusion flux directed along the normal vector **n**, and $f'_c = \partial f_h/\partial c$. According to Eq. (4), the diffusion flux includes the term $\alpha_J \partial \mathbf{J}/\partial t$ whose physical meaning is as follows: the diffusion flux far from equilibrium ensures additional ordering that leads to an increase in dissipation.

Near the stable state, diffusion flux (4) must decrease in time so that the free energy of the entire system decreases. This condition in the simplest case implies a linear relation between the thermodynamic flux and conjugate force [16]. Then, the flux appearing in Eq. (4) satisfies the evolution equation

$$\mathbf{J} = -M\nabla(f'_c - \varepsilon_c^2\nabla^2 c) - M\alpha_J\frac{\partial \mathbf{J}}{\partial t}, \quad (5)$$

where $M$ is the mobility of atoms, so that $\tau_D = M\alpha_J$. Equation (5), together with the mass balance equation $\partial c/\partial t = -\nabla\cdot\mathbf{J}$, provides the transport equation

$$\tau_D\frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = \nabla[M\nabla(f'_c - \varepsilon_c^2\nabla^2 c)], \quad (6)$$

which coincides with the equation previously derived from the entropy functional [14, 15]. Equation (6) is a general hyperbolic partial differential equation involving the delay of the decay described by the term $\tau_D\partial^2 c/\partial t^2$.

At the initial decay stages, i.e., when large density gradients exist and short time intervals are important, we disregard the terms nonlinear in $c$ in Eq. (6). In this case,

$$\tau_D\frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = Mf''_{cc}\nabla^2 c - M\varepsilon_c^2\nabla^4 c, \quad (7)$$

where $f''_{cc} = \partial^2 f_h/\partial c^2$. In the limit $\tau_D \longrightarrow 0$, Eq. (7) is modified to the Cahn–Hilliard equation [5, 6]. Equation (7) can be treated as a modified Cahn–Hillard equation, which is a linearized hyperbolic equation. It is valid for spinodal decomposition with locally nonequilibrium diffusion [diffusion with the relaxation of diffusion flux (5)].

Let us consider the elementary solution of Eq. (7) in the form of the plane wave

$$c(z, t) - c_0 = a_k\exp[i(kz - \omega(k)t)], \quad (8)$$

where $k$ is the wave vector and the dispersion relation has the form

$$\omega(k) = -\frac{i}{2\tau_D} \pm \left(\frac{Mk^2(f''_{cc} + \varepsilon_c^2 k^2)}{\tau_D} - \frac{1}{4\tau_D^2}\right)^{1/2}. \quad (9)$$

The upper and lower signs for $\omega(k)$ in Eq. (9) correspond to the propagation of waves in the positive and negative directions of the $z$ axis.

In the locally equilibrium limit, $\tau_D \longrightarrow 0$, Eq. (9) takes the form

$$\omega(k) \approx -\frac{i}{2\tau_D}[1 \pm (1 - 2\tau_D Mk^2(f''_{cc} + \varepsilon_c^2 k^2))]. \quad (10)$$

One of the roots given by Eq. (10) tends to $-\infty$ along the imaginary axis as $\omega(k) \sim i/\tau_D$. This gives rise to the exponential damping of solution (8). The second of the roots given by Eq. (10) is finite and coincides with the known solution [5, 6]

$$\omega(k) \approx -iMk^2(f''_{cc} + \varepsilon_c^2 k^2). \quad (11)$$

The critical WL $\lambda_c$ above which the irreversible increase in small density perturbations occurs can be obtained from Eqs. (9) and (11) in the form

$$k_c = 2\pi/\lambda_c = (-f''_{cc}/\varepsilon_c^2)^{1/2}, \quad f''_{cc} < 0. \quad (12)$$

For $f''_{cc} < 0$ and $\lambda > \lambda_c$, the free energy decreases and spinodal decomposition occurs. Relation (12) shows that, if the composition is close to the spinodal one, $f''_{cc} = 0$, the critical WL increases infinitely, $\lambda_c \longrightarrow \infty$ [6].

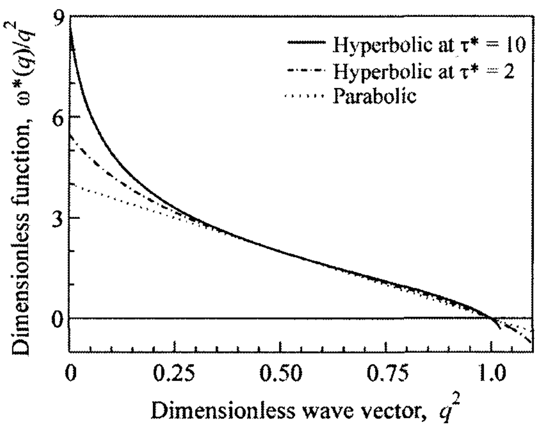

**Fig. 1.** Dimensionless function $\omega^*(q^2)/q^2$ for (dotted line) the parabolic diffusion equation (Cahn–Hilliard equation) and hyperbolic equation of spinodal decomposition for the parameter $\tau^* = \tau_D M(-f''_{cc})/[\varepsilon_c^2/(-f''_{cc})] = l_D^2/l_C^2 =$ (solid line) 10 and (dash-dotted line) 2, which determines the ratio of the diffusion length $l_D$ and correlation length $l_C$.

The imaginary part of frequency (9) for $k < k_c$ is given by the expression

$$\omega_\pm = (2\tau_D)^{-1}[-1 \pm (1 - 4k^2\tau_D(f''_{cc} + \varepsilon_c^2 k^2))^{1/2}], \quad (13)$$

where the plus and minus signs correspond to the increase and decrease of solution (8). The expansion of the square root in Eq. (13) in the small parameter $4k^2\tau_D[f''_{cc} + \varepsilon_c^2 k^2] \ll 1$ provides $\omega_+ = -k^2 M(f''_{cc} + \varepsilon_c^2 k^2)$ in the local equilibrium limit $r_D \longrightarrow 0$. This expression coincides with the kinetic rate of increasing instability that was obtained by Cahn [6] for the purely diffusion regime. For this reason, expression (13) can be treated as the kinetic instability index for both the dissipative and ballistic regimes of the atomic transport described by Eq. (7). The extremum (maximum frequency)

$$\omega_m(k_m) = i(2\tau_D)^{-1}[-1 + (1 + \tau_D(f''_{cc}\varepsilon_c)^2)^{1/2}] \quad (14)$$

of expression (13) occurs at

$$k_m = 2\pi/\lambda_m = (-f''_{cc}/(2\varepsilon_c^2))^{1/2}, \quad f''_{cc} < 0. \quad (15)$$

According to Eq. (15), the WL $\lambda_m$ for the maximum instability index is $\sqrt{2}$ times larger than the critical wavelength $\lambda_c$ determined by Eq. (12) for density perturbation increase.

In the Cahn–Hilliard theory, the instability index in spinodal decomposition is determined by Eq. (11). The normalization of this expression to the imaginary part $\omega_m(k_m) = iM(f''_{cc}/2\varepsilon_c)^2$, which is obtained from Eq. (14) in the limit $\tau_D \longrightarrow 0$, provides the relations

$$\omega^*(q)/q^2 = [\omega(k)/\omega(k_m)]/q^2 = 4(1 - q^2), \quad (16)$$

where $q = k/k_c$ and $k_c$ is given by Eq. (12).

The instability index in the hyperbolic model, $\omega_+$, is given by Eq. (13). Therefore, in view of Eqs. (12) and (14),

$$\omega^*(q)/q^2 = [\omega_+(k)/\omega(k_m)]/q^2$$
$$= \frac{1}{q^2}\frac{[1 + q^2(1 - q^2)\tau_D M(-f''_{cc}/\varepsilon_c)^2]^{1/2} - 1}{[1 + \tau_D M(-f''_{cc}/\varepsilon_c)]^{1/2} - 1}. \quad (17)$$

This expression is transformed to Eq. (16) in the limit $\tau_D \longrightarrow 0$.

Figure 1 shows the quantity $\omega^*(q)/q^2$ as a function of $q^2$ given by Eqs. (16) and (17). It is seen that the Cahn–Hilliard theory predicts a linear dependence (the dotted line in Fig. 1), which is not observed experimentally [8]. However, the hyperbolic model is sufficiently flexible for describing the nonlinear behavior (dash-dotted and solid lines in Fig. 1). Such a nonlinear behavior is usually observed in the experiments [7–9]. Let us show that this nonlinearity is controlled by the parameter $\tau^* = \tau_D M(-f''_{cc})^2/\varepsilon_c^2$ in Eq. (17).

Assuming that the diffusion coefficient is defined as $D = -Mf''_{cc}$, we introduce the diffusion length $l_D = (D\tau_D)^{1/2}$ and the equilibrium part of the free energy density $f_h = f_0 c^2(1 - c^2)$. Therefore, $f''_{cc} = 2f_0(1 - 4c)|_{c=0.5} = -2f_0$, where $f_0$ is the barrier height. In this case, the parameter $\tau^*$ in Eq. (17) determines the square of the ratio between the diffusion length $l_D$ and correlation length $l_C = \varepsilon_c/\sqrt{2f_0}$, so that $\tau^* = l_D^2/[\varepsilon_c^2/(2f_0)]$. Thus, an increase in the correlation length with respect to the diffusion length reduces the parameter $\tau^*$ and the nonlinear behavior of the function $q^{-2}\omega^*(q)$ is modified to the Cahn–Hilliard linear regime (see Fig. 1).

The instability index can be compared to the experimental data on phase separation in glasses [9]. To this end, Eq. (13) is written in the form

$$\omega_+ = \frac{[1 + 4D\tau_D k^2(1 - \varepsilon_c^2 k^2/f''_{cc})]^{1/2} - 1}{2\tau_D}. \quad (18)$$

In addition, the free energy of the binary system can be written as [18]

$$f_h(T, c) = f_0[(T/T_c - 1)(c - c_c)^2 + B_0(c - c_c)^4], \quad (19)$$

where $T_c$ and $c_c$ are the critical temperature and density, respectively; $T < T_c$; $B_0 > 0$; and the phenomenological parameters $f_0$ and $B_0$ are determined from the experiment [8].

Figure 2 shows $\omega_+/k^2$ values measured for the binary glass with PS at various $k^2$ values [9, 10]. The experimental procedure and details of the measurements were described and discussed in [7, 9, 10]. These experimental data were comparatively analyzed in the Cahn–Hil-

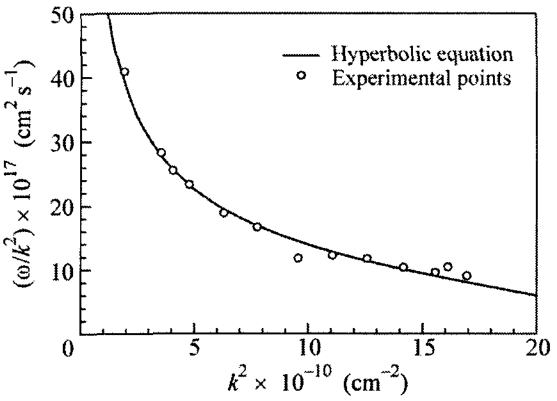

**Fig. 2.** Quantity $\omega_+/k^2$ vs. $k^2$ for (solid line) the hyperbolic model given by Eqs. (18) and (19) and (points) experimental data [9, 10] on the scattering of visible light obtained for the spinodal decomposition of BG $SiO_2$–12 wt % $Na_2O$ at $T = 803$ K.

liard theory [7] and Langer–Baron–Miller theory [19]. They exhibit the same nonlinear behavior for $\omega_+(k^2)/k^2$ as, e.g., in spinodal decomposition in crystalline binary systems [20]. Such a behavior is usually observed in systems with short-range interaction and at the initial stages of spinodal decomposition [8]. According to Fig. 2, the experimental data are well reproduced by Eqs. (18) and (19) of the hyperbolic model with the parameters $D = 2.3 \times 10^{-14}$ cm$^2$/s, $\tau_D = 7.2 \times 10^{-11}$ s, $\varepsilon_c = 6.2 \times 10^{-8}$ cm $\sqrt{\text{J/mol cm}^3}$, $T/T_c = 0.85$, $B_0 = 0.15$, $f_0 = 1.88 \times 10^4$ J/mol cm$^3$, and $c - c_c = 0.8$ at %.

Figure 2 shows good agreement between the theory and experiment. This result is due to the fact that a new length scale, diffusion length $l_D = (D\tau_D)^{1/2}$, appears in the theory in addition to the correlation length $l_C = \varepsilon_c/\sqrt{-f''_{cc}}$. Owing to this fact, the theory is sufficiently flexible to predict the nonlinear NE behavior in the experiments (Fig. 1) and to quantitatively describe the experimental data (see Fig. 2).

Note that the hyperbolic model predicts the features of spinodal decomposition in the systems with both the short- and long-range interactions. The ratio $l_D/l_C$ between the diffusion length $l_D$ and correlation length $l_C$ determines the transition between different regimes: spinodal decomposition becomes close to the Cahn–Hilliard scenario when this ratio decreases (see Fig. 1). At $l_C \approx l_D$, the system can be treated as long-range and the Cahn–Hilliard scenario occurs. This conclusion is in agreement with the theoretical [11] and numerical [12] results. For the short-range interaction, i.e., for $l_C < l_D$, the kinetic of spinodal decomposition differs from the prediction of the Cahn–Hilliard theory. For $l_C \ll l_D$, the local-nonequilibrium effects in the diffusion field are important, which is manifested in the pronounced nonlinearity in the instability index (see Fig. 2). Thus, the ratio of two scales, $l_D/l_C$, controls the mechanism of spinodal decomposition in the transition from the short-range interaction to the long-range interaction in the PD process.

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