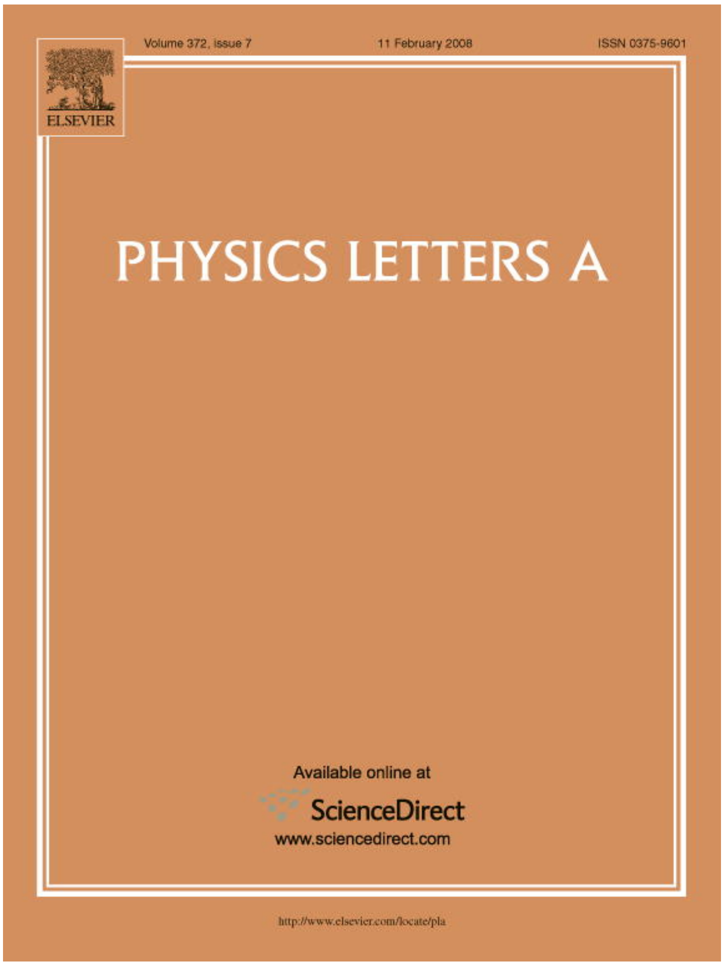

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Non-equilibrium effects in spinodal decomposition of a binary system

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Abstract

A model for diffusion and phase separation which takes into account relaxation of the solute diffusion flux is developed. It is shown that the model predicts non-linearity in the amplification rate of decomposition, which is governed by the ratio between diffusion and correlation lengths. The predicted amplification rate is tested against experimental data on a binary phase-separated glass.

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1. Introduction

A phase transformation in which both phases have equivalent symmetry but differ only in composition is well known as spinodal decomposition. This transformation has been theoretically described by Cahn and Hilliard [1,2].

In parallel with detailed analysis and tests against experimental data [3,4] the theory of Cahn and Hilliard has been further explored and developed. In particular, the theory has problems with the description of the early stages of decomposition. It has been demonstrated that experimental data extracted from light and X-ray scattering by phase-separated glasses [5,6] exhibit non-linear behavior in dispersion relation in contradiction with predictions of the Cahn–Hilliard theory. The theory predicts linear dispersion relation *versus* square of wave number that is only true for the long-range interaction [4]. Such linear dependence might be observed during intermediate or even latest stages of phase separation. However, due to high instability at earlier stages of decomposition (or for deeply supercooled systems below spinodal line), short-range interaction plays important role [7,8]. This leads to the pronounced influence of non-equilibrium effects and to possible non-linearity in characteristic functions of spinodal decomposition such as dispersion relation.

Few advancements were made for strongly non-equilibrium phase separation. Binder et al. [9] generalized the linearized Cahn–Hilliard theory to the case of the existence of a slowly relaxing variable. Their calculations show that the instability of the system is not of the standard diffusive type, but rather it is controlled by the relaxation of the slow structural variable. Recently, Cahn–Hillard theory has been modified by taking into account the relaxation of diffusion flux to its local steady state [10,11]. The flux is considered as an independent thermodynamic variable in consistency with the extended irreversible thermodynamics [12]. As a result, a partial differential equation of a hyperbolic type for phase separation with diffusion has been derived that can be called “a hyperbolic model for spinodal decomposition”. Theoretically, this model can predict spinodal decomposition for short periods of time, large characteristic velocities of the process, large concentration gradients, or deep supercoolings at the earliest stages of decomposition. Therefore, the present Letter gives a comparative analysis for both Cahn–Hilliard’s parabolic model and the hyperbolic model

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(modified Cahn–Hilliard) of spinodal decomposition. As a test for the hyperbolic model we compare its predictions with experimental data.

2. The model

Consider an isothermal and isobaric binary system represented as an isotropic solid solution free from imperfections and with molar volume independent of concentration of A- and B-atoms. One assumes that a spinodal region is defined by the negative curvature for the free energy, $\partial^2 f/\partial c^2 < 0$, and the spinodal itself is defined as $\partial^2 f/\partial c^2 = 0$, where f is the Helmholtz free energy per unit volume and c is the concentration of B-atoms.

For a given temperature T, the free energy f is based on the selected set of independent thermodynamic variables $\{c, \nabla c, \vec{J}\}$, consisting of concentration, its gradient, and solute diffusion flux, respectively. This set represents a union of the slow conserved variable c and the fast non-conserved variable $\vec{J}$, much as for models of fast phase transformations [11]. In such a case, the free energy density can be written in the following form

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

where $\varepsilon_c = [(\partial^2 f/\partial(\nabla c)^2)_{\nabla c=0}]^{1/2}$ is the coefficient proportional to correlation length, $\alpha_J = [\tau_D/D][\partial(\Delta\mu)/\partial c]_{T=\text{const}}$ the coefficient specifying non-Fickian diffusion, D is the diffusion constant, $\Delta\mu = \mu_A - \mu_B$ the difference of chemical potentials for components A and B, respectively, and τ_D is the relaxation time of the diffusion flux to its steady state.

The free energy density (1) is defined for local non-equilibrium state. Microscopically, this state is characterized by impossibility for a system to cover all points of its phase space. This leads to necessity of introduction of relaxation for the flux $\vec{J}$ to its steady state in phenomenological description. In the limit of instantaneous relaxation, i.e., $\tau_D \to 0$, the term with fluxes vanishes and Eq. (1) gives the free energy density $f(c, \nabla c)$ of Cahn–Hilliard's form [1,2] applicable for local equilibrium system.

Taking Eq. (1), the total Helmholtz free energy as a free energy functional is given by

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

where v is a sub-volume of the system. Evolution of $F(c, \nabla c, \vec{J})$ with time t is described by $dF/dt = (dF/dt)_{\text{ex}} + (dF/dt)_{\text{in}}$, where $(dF/dt)_{\text{ex}}$ is the external exchange of the free energy and $(dF/dt)_{\text{in}}$ is the internal change of the free energy inside of the system. The latter is defined as a dissipative function. Using the procedure described in Refs. [10,11] and applied to Eq. (2) one can obtain $(dF/dt)_{\text{ex}} = \int d\omega [\varepsilon_c^2 (\nabla_n c)\partial c/\partial t + (-f_c' + \varepsilon_c^2 \nabla^2 c) J_n]$ and $(dF/dt)_{\text{in}} = \int dv\, \vec{J} \cdot [\nabla(f_c' - \varepsilon_c^2 \nabla_n^2 c) + \alpha_J \partial \vec{J}/\partial t]$, where ω is the outer surface of sub-volume v, J_n is the diffusion flux pointed by the normal vector $\vec{n}$, and $f_c' = \partial f_h/\partial c$. Around a steady state, the dissipative function $(dF/dt)_{\text{in}}$ must decrease in time, so that the free energy of the entire system is decreasing. It gives the following evolution equation for the diffusion flux

$$\vec{J} = -M\nabla\left(f_c' - \varepsilon_c^2 \nabla^2 c\right) - M\alpha_J \frac{\partial \vec{J}}{\partial t}, \tag{3}$$

where M is the atomic mobility which has a positive value, so that $\tau_D = M\alpha_J$. As we show below, the relaxation term $M\alpha_J \partial \vec{J}/\partial t$ in RHS of this equation has an important role in description of spinodal decomposition, especially at the very first stages of its evolution.

Together with the atomic mass balance $\partial c/\partial t = -\nabla \cdot \vec{J}$, Eq. (3) leads to the following governing equation [10,11]:

$$\tau_D \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = \nabla \cdot \left[M\nabla\left(f_c' - \varepsilon_c^2 \nabla^2 c\right)\right]. \tag{4}$$

Eq. (4) is a general partial differential equation of hyperbolic type with the decomposition delay described by the term $\tau_D \partial^2 c/\partial t^2$.

Because we focus on the analysis of the initial stages of decomposition (i.e., when large concentration gradients exist and short periods of time are important) one may neglect in Eq. (4) all terms not linear in c. This yields

$$\tau_D \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = M f_{cc}'' \nabla^2 c - M\varepsilon_c^2 \nabla^4 c, \tag{5}$$

where $f_{cc}'' = \partial^2 f_h/\partial c^2$. As $\tau_D \to 0$, Eq. (5) transforms into the Cahn–Hilliard equation [1,2]. In the present form, Eq. (5) can be considered as a modified Cahn–Hilliard equation which is a linearized partial differential equation of a hyperbolic type. This equation is true for spinodal decomposition with local nonequilibrium diffusion (diffusion with relaxation of the solute flux).

3. Analysis of the dispersion relation

Consider the elementary exponential solution of Eq. (5) in the following form

$$c(z, t) - c_0 = a_k \exp\left[i\left(kz - \omega(k)t\right)\right], \tag{6}$$

where k is the wave-vector and the dispersion relation $\omega(k)$ is given by

$$\omega(k) = -\frac{i}{2\tau_D} \pm \left(\frac{Mk^2(f_{cc}'' + \varepsilon_c^2 k^2)}{\tau_D} - \frac{1}{4\tau_D^2}\right)^{1/2}. \tag{7}$$

The upper and lower signs for $\omega(k)$ in Eq. (7) correspond to the branches which are responsible for the wave propagation in the positive and negative z-directions, respectively.

Within local equilibrium limit $\tau_D \to 0$, Eq. (7) gives the following approximation

$$\omega(k) \approx -\frac{i}{2\tau_D}\left[1 \pm \left(1 - 2\tau_D M k^2\left(f_{cc}'' + \varepsilon_c^2 k^2\right)\right)\right]. \tag{8}$$

Eq. (8) shows that one of the roots is going to $-\infty$ along the imaginary axis by the law $\omega(k) \sim i/\tau_D$. This leads to an exponential decay of the solution (6). The second root of Eq. (8) is finite and it is equivalent to the well-known Cahn–Hilliard relation

$$\omega(k) \approx -iMk^2\big(f''_{cc} + \varepsilon_c^2 k^2\big). \tag{9}$$

Local equilibrium limit for the dispersion relation (7) gives two different roots: the first root is divergent and the second root approaches to the relation (9).

From Eqs. (7) and (9) one can obtain a critical wavelength λ_c above which infinitesimal sinusoidal fluctuations of concentration irreversibly grow. This yields

$$k_c = 2\pi/\lambda_c = \big(-f''_{cc}/\varepsilon_c^2\big)^{1/2}, \quad f''_{cc} < 0. \tag{10}$$

Therefore, with $f''_{cc} < 0$ and for $\lambda > \lambda_c$, the free energy decreases, and decomposition starts to proceed. Eq. (10) clearly shows that as the composition tends to the values lying in the spinodal, $f''_{cc} = 0$, the critical wavelength approaches to infinity, $\lambda_c \to \infty$ [2].

Using Eq. (7), the imaginary part of the frequency at $k < k_c$ is given by

$$\omega_\pm = (2\tau_D)^{-1}\Big[-1 \pm \big(1 - 4k^2\tau_D M\big(f''_{cc} + \varepsilon_c^2 k^2\big)\big)^{1/2}\Big]. \tag{11}$$

In this expression, the "plus" and "minus" signs correspond to the growth or decay of solution (6), respectively. After expanding the square root in Eq. (11) for $4k^2\tau_D M[f''_{cc} + \varepsilon_c^2 k^2] \ll 1$ one gets in the local equilibrium limit the imaginary part of Eq. (9). This expression is the kinetic amplification rate obtained by Cahn [2] for a pure diffusion regime. Eq. (11) can be interpreted as the kinetic amplification rate for both dissipative and propagative regimes of atomic transport described by Eq. (5). The extremum of Eq. (11) gives the maximum frequency of the form

$$\omega_m(k_m) = i(2\tau_D)^{-1}\Big[-1 + \big(1 + \tau_D M\big(f''_{cc}/\varepsilon_c\big)^2\big)^{1/2}\Big] \tag{12}$$

at

$$k_m = 2\pi/\lambda_m = \big(-f''_{cc}/\big(2\varepsilon_c^2\big)\big)^{1/2}, \quad f''_{cc} < 0. \tag{13}$$

Consequently, the maximum wavelength (13) is exactly $\sqrt{2}$ times larger than the critical wavelength (10) of instability against fluctuations of concentration.

Within the hyperbolic model, the amplification rate for decomposition ω_+ is given by Eq. (11). Therefore, using Eqs. (10) and (12), one can get the following relation

$$\begin{aligned}\omega^*(q)/q^2 &= \big[\omega_+(k)/\omega(k_m)\big]/q^2 \\ &= \frac{1}{q^2}\,\frac{[1 + q^2(1-q^2)\tau_D M(-f''_{cc}/\varepsilon_c)^2]^{1/2} - 1}{[1 + \tau_D M(-f''_{cc}/\varepsilon_c)^2]^{1/2} - 1}.\end{aligned} \tag{14}$$

With $\tau_D \to 0$, it transforms into the prediction of Cahn–Hilliard theory:

$$\omega^*(q)/q^2 = \big[\omega_+(k)/\omega(k_m)\big]/q^2 = 4\big(1 - q^2\big). \tag{15}$$

Eqs. (14) and (15) give expression for $\omega^* = \omega_+/\omega_m$, i.e., they are normalized on the imaginary part of expression $\omega_m(k_m) = iM[f''_{cc}/(2\varepsilon_c)]^2$ (that is found from Eq. (12) in the limit $\tau_D \to 0$). Also, it is assumed that $q = k/k_c$, where k_c is given by Eq. (10).

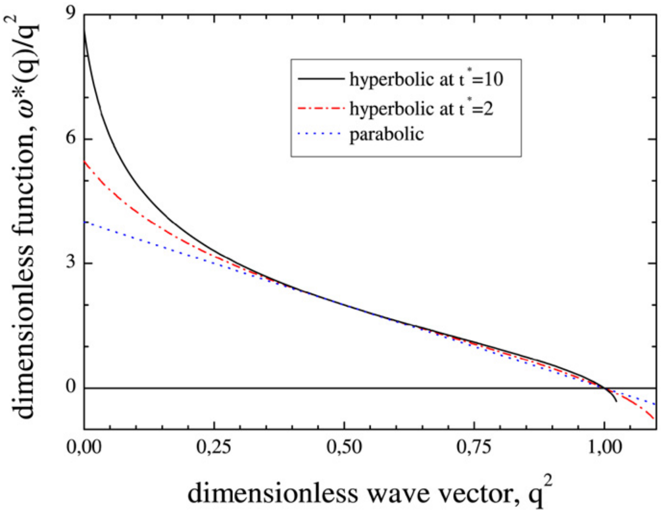

Fig. 1. Comparison of the function ω^*/q^2 for the parabolic diffusion equation (Cahn–Hilliard equation) and the hyperbolic equation (modified Cahn–Hilliard equation). Curves for the hyperbolic equation are given for various values of the parameter $\tau^* = \tau_D M(-f''_{cc})/[\varepsilon_c^2/(-f''_{cc})]$.

4. Discussion

Fig. 1 shows the relationship "$\omega^*(q)/q^2$ *versus* q^2" given by Eqs. (14) and (15). As it can be seen, Cahn–Hilliard's theory predicts the linear law (dotted line in Fig. 1) that is practically not observable [4]. The present model is flexible enough to describe non-linear behavior (dashed-dotted and solid lines in Fig. 1). Such non-linear behavior is typically observed in experiments [3,5]. In what follows, we show that this non-linearity can be controlled by the parameter $\tau^* = \tau_D M(-f''_{cc})^2/\varepsilon_c^2$ in Eq. (14).

Now, assume that the diffusion constant is given by $D = -Mf''_{cc}$, the diffusion length is defined by $l_D = (D\tau_D)^{1/2}$, and the equilibrium part of the free energy density is described by the double-well $f_h = f_0 c^2(1 - c^2)$. From this it follows $f''_{cc} = 2f_0(1 - 4c)|_{c=0.5} = -2f_0$, where f_0 is the characteristic height of the free energy. Then, the parameter τ^* in Eq. (14) specifies the ratio between diffusion length l_D and correlation length $l_c = \varepsilon_c/\sqrt{2f_0}$, i.e., $\tau^* = (l_D/l_c)^2$. Thus, with the increasing of the correlation length (relatively to the length of diffusion), parameter τ^* decreases and the non-linear behavior of the function $q^{-2}\omega^*(q)$ tends to the linear law predicted by Cahn and Hilliard, Fig. 1.

The function of the amplification rate (11) predicted by the hyperbolic model can be compared with experimental data of Andreev et al. on phase-separated glasses [5]. With this aim, the amplification rate is taken in the following form

$$\omega_+ = \frac{[1 + 4D\tau_D k^2(1 - \varepsilon_c^2 k^2/f''_{cc})]^{1/2} - 1}{2\tau_D}. \tag{16}$$

Also, we assume that the free energy of a binary system can be replaced by

$$f_h(T, c) = f_0\big[(T/T_c - 1)(c - c_c)^2 + B_0(c - c_c)^4\big], \tag{17}$$

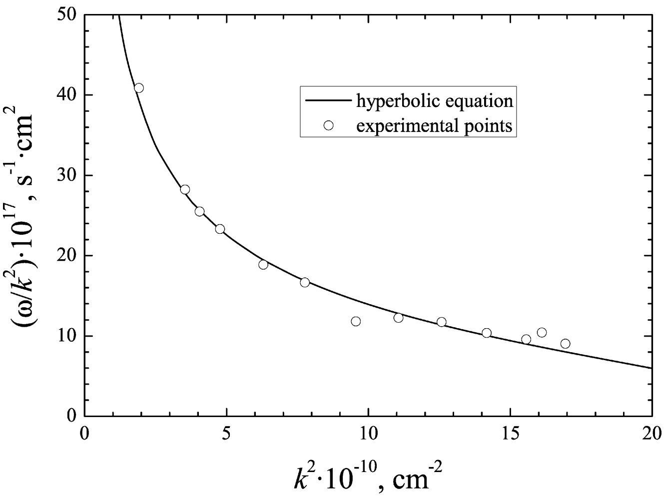

Fig. 2. Dependence ω_+/k^2 upon k^2 given by the hyperbolic model [solid line, Eqs. (16) and (17)] and scattering data of visible light [points, Refs. [5,6]]. Experimental points were obtained on phase-separated SiO_2–12 wt% Na_2O glass at $T = 803$ K.

where T_c and c_c are the critical temperature and concentration, respectively, $T < T_c$, and $B_0 > 0$. Eq. (17) is often used in analysis of kinetics of spinodal decomposition in glasses [14] and the parameters f_0 and B_0 are treated as phenomenological input parameters of the theory, which are fitted to experiment [4].

Fig. 2 shows data for the relationship "ω_+/k^2 *versus* k^2" extracted from experiments on a binary phase-separated glass [5,6]. They exhibit non-linear behavior as predicted by Eqs. (16) and (17) for the following material parameters: $D = 2.3 \times 10^{-14}$ cm²/s, $\tau_D = 7.2 \times 10^{-11}$ s, $\varepsilon_c = 6.2 \times 10^{-8}$ $\mathrm{cm}\sqrt{\mathrm{J}/(\mathrm{mole\,cm}^3)}$, $T/T_c = 0.85$, $B_0 = 0.15$, $f_0 = 1.88 \times 10^4$ $\mathrm{J}/(\mathrm{mole\,cm}^3)$, and $c - c_c = 0.8$ mole fraction.

In Fig. 2 it is shown that good agreement is achieved between theory and experiment. This result is due to the fact that both lengths: correlation length $l_c = \varepsilon_c/\sqrt{2f_0}$ and diffusion length $l_D = (D\tau_D)^{1/2}$ appear in the theory. It makes the theory flexible enough to predict non-linear behavior for amplification rate typically observed in experiments, Fig. 1, and to quantitatively describe experiments, Fig. 2.

The hyperbolic model predicts a transition from spinodal decomposition with the short-range interaction to decomposition with long-range interaction. The ratio l_D/l_c dictates the transition: spinodal decomposition tends to the Cahn–Hilliard's scenario with the increase of the correlation length in comparison with the diffusion length (see Fig. 1). With $l_c \approx l_D$, one can accept the long range interaction within the system and the Cahn–Hilliard scenario takes effect. This conclusion supports results developed theoretically [7] and numerically [8]. With short-range interaction, i.e., with $l_c < l_D$, the kinetics of spinodal decomposition deviates from the predictions of the Cahn–Hilliard theory. With $l_c \ll l_D$, effects of local non-equilibrium in the diffusion field becomes much more pronounced and a clear-cut non-linearity in amplification rate is fixed (see Fig. 2). Thus, the interplay between two lengths, i.e., the ratio l_D/l_c, governs the transition from short-range interaction to long-range interaction during phase decomposition.

5. Conclusions

A non-equilibrium binary system with diffusion and phase separation has been considered. Taking into account relaxation of the solute diffusion flux, a principal parameter, as the ratio l_D/l_c, is appeared in the theory of phase separation. As soon as the range of local non-equilibrium effects covers the characteristic spatial scale for correlation between particles, i.e., $l_D \gg l_c$, clear non-linearity appears in the dispersion relation in comparison with the prediction of the model of Cahn and Hilliard (see Fig. 1). Interplay between diffusion length l_D and correlation length l_c governs the transition from short-range interaction to long range interaction. It makes the model predictions flexible enough to describe experimental data (see Fig. 2).

The model is able to predict earliest stages of decomposition ($l_D \gg l_c$), intermediate regimes ($l_D \approx l_c$), and latest states of decomposition when the role of local non-equilibrium effects disappears ($l_D \ll l_c$). It is manifested through gradual degeneration of the second derivative from concentration with respect to time with the factor of short time τ_D in Eq. (5). On the large time scale this term is negligible, and the characteristic diffusion length vanishes, i.e., $l_D = (D\tau_D)^{1/2} \to 0$. In the latter case, the outcomes of hyperbolic model of decomposition transforms into the solutions of the Cahn–Hillard theory based on parabolic diffusion equation.

The present model tests effect of local non-equilibrium on amplification rate in spinodal decomposition. As a perspective, several generalizations of the present model can be outlined. First, introduction into the model fluctuations in a manner of Cahn–Hilliard–Cook model [15] can be made. As an extension of the present linearized equation (5), fluctuations can be introduced using analysis of generalized diffusion equation as described in Ref. [13]. It might give partial contribution from local non-equilibrium effects and partial contribution of fluctuations into non-linearity of the main characteristics (such as amplification rate, structural factor, etc.) of spinodal decomposition. Second, solutions of the non-linear equation (4) has to be tested with regard to the influence of non-linear effects during initial stages of decomposition. It might be treated, e.g., in a manner of the "decoupling approximation" of Langer et al. [16] or using "power's expansion" suggested by Grant et al. [17]. Comparison of the outcomes from non-linear hyperbolic model and from the well-known non-linear theories based on the parabolic diffusion equation [15–17] can be seen as a very attractive point of investigation.

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References

[1] J.W. Cahn, J.E. Hilliard, J. Chem. Phys. 28 (1958) 258.
[2] J.W. Cahn, Acta Metall. 9 (1961) 795.
[3] V.P. Skripov, A.V. Skripov, Usp. Fiz. Nauk 128 (1979) 193, Sov. Phys. Usp. 22 (1979) 389.
[4] K. Binder, P. Fratzl, in: G. Kostorz (Ed.), Phase Transformations in Materials, Wiley, Weinheim, 2001, p. 409.
[5] N.S. Andreev, G.G. Boiko, N.A. Bokov, J. Non-Cryst. Solids 5 (1970) 41.
[6] N.S. Andreev, E.A. Porai-Koshits, Discuss. Faraday Soc. 50 (1970) 135.
[7] K. Binder, Phys. Rev. A 29 (1984) 341.
[8] M. Laradji, M. Grant, M.J. Zuckermann, W. Klein, Phys. Rev. B 41 (1990) 4646.
[9] K. Binder, H.L. Frisch, J. Jäckle, J. Chem. Phys. 85 (1986) 1505.
[10] P. Galenko, Phys. Lett. A 287 (2001) 190.
[11] P. Galenko, D. Jou, Phys. Rev. E 71 (2005) 046125.
[12] D. Jou, J. Casas-Vazquez, G. Lebon, Extended Irreversible Thermodynamics, second ed., Springer, Berlin, 1996.
[13] D. Jou, P. Galenko, Physica A 399 (2006) 149.
[14] E.P. Feldman, L.I. Stefanovich, Zh. Eksp. Teor. Fiz. 98 (1990) 1695, Sov. Phys. JETP 71 (1990) 951.
[15] H.E. Cook, Acta Metall. 18 (1970) 297.
[16] J.S. Langer, M. Baron, H.D. Miller, Phys. Rev. A 11 (1975) 1417.
[17] M. Grant, M. San Miguel, J. Viñals, J.D. Gunton, Phys. Rev. B 31 (1985) 302.