



Solute dynamics in the liquid solution with stoichiometric compounds formation



V.G. Lebedev^{a,b}, A.A. Obukhov^a, M.G. Vasin^{c,*}

^a Department of Mathematics, Informatics and Physics, Udmurt State University, 426034 Izhevsk, Russia

^b Research center of metallurgical physics and materials science of UdmFRC UrB RAS, 426067 Izhevsk, Russia

^c Institute for High Pressure Physics of Russian Academy of Sciences, 142190 Moscow, Russia

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ABSTRACT

We show that in a binary solution in the presence of liquid phase of non-permanent composition, and a stoichiometric phase, for solute concentration exceeding some critical value, the instability mathematically described by the Cahn–Hilliard type equation can develop. Within the framework of the model system a dispersion relation is constructed. This relation allows to determine the concentration fluctuations dependence on time, and to investigate dynamics of structural factor and of amplification rate. The observed instability can explain the processes of slow non-monotonic relaxation in the glass-forming metal melts upon melting.

1. Introduction

Despite the significant progress achieved in the metallurgy, some processes of formation and dynamics of the internal microstructure in metal alloys have not been fully understood to this day. The main reason of this is that the scales of mesoscopic phenomena playing basic role in these processes, are too large to use such microscopic approaches as molecular dynamics, and at the same time are too small to study the phenomenon with the help of measurement technics.

One of these phenomena is the slow nonmonotonic relaxation of viscosity in the glass-forming metallic melts after melting [1,2]. For example, after melting of aluminum with small additions of yttrium or nickel, the relaxation time can reach several hours. In metallurgy, this relaxation is due to the processes of melting, caused by the slow dissolution of refractory materials in training. However, the kinetics of these relaxation processes can not be explained in the framework of linear diffusion model, the characteristic relaxation time in which should be in the order of few seconds.

The corresponding estimation of characteristic dissolution time of the initial inhomogeneity Al_3Y with the characteristic size 10^{-5} m was done in the paper [3] and is 10^{-2} s, which is much shorter than the relaxation time, observed on the experiment: $\tau \approx 10^4$ s. In addition, in some cases the relaxation is accompanied by an unusual nonmonotonic dependence of the melt viscosity [2,4–6] on time (see Fig. 1 and in Fig. 2). Firstly, for a certain period of time after melting, the melt viscosity decreases exponentially, but at the some point viscosity

suddenly begins to grow, reaching local maximum, and then returns to the normal exponentially decreasing mode. It was experimentally established that in the melts of Al–Y alloys the nonmonotonic viscosity behavior is observed both in the presence of other solutes and without them. One can assume that the nature of this unusual phenomenon is mainly related to the peculiarities of Al–Y melt relaxation. Therefore, initially for its description, we can limit ourselves to the consideration of the binary melt.

As the possible explanation of the phenomena under consideration (an abnormally slow relaxation and nonmonotonic dependence of viscosity on time) in [3] it was assumed that they are related to non-linear concentration dependence of the system chemical potential near the liquids line, leading to the phenomenon similar to the spinodal decomposition [7]. The appearance of spinodal decomposition by nature is related to the characteristic dependence of free energy (or Gibbs potential) on the solute concentration x .

2. The Cahn–Hilliard equation of spinodal decomposition

First of all, let us recall the main data about of the synodal decomposition, and start from the Cahn–Hilliard equation for isothermal phase separation [7], which has the following form:

$$\frac{\partial x}{\partial t} = M_D \nabla^2 \left(\frac{\delta \mathcal{F}}{\delta x} \right), \quad (1)$$

where $x(\mathbf{r}, t)$ is the order parameter (local deviation from the average

* Corresponding author.

E-mail address: dr_vasin@mail.ru (M.G. Vasin).

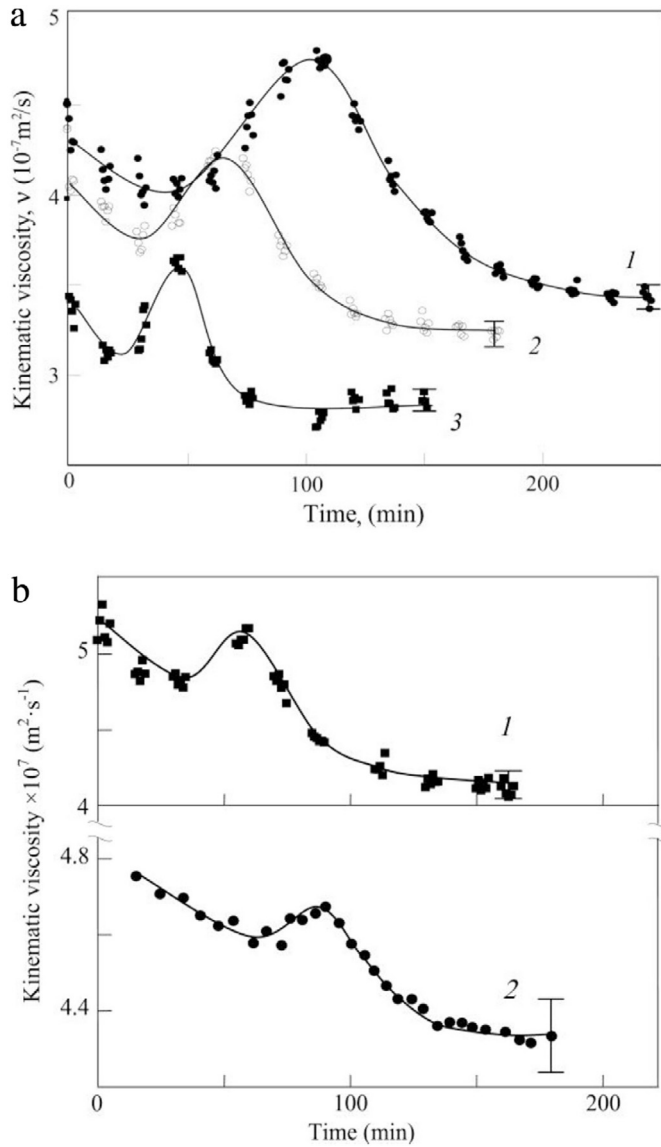


Fig. 1. The time dependencies of the liquid melt viscosity, $\text{Al}_{87}\text{Ni}_8\text{Y}_5$, at 900 °C (1), 1050 °C (2) and 1200 °C (3), obtained after heating from room temperature. b The time dependencies of the liquid melt viscosity, $\text{Al}_{86}\text{Ni}_8\text{La}_6$ (1) and $\text{Al}_{86}\text{Ni}_8\text{Ce}_6$ (2), at 1100 °C [5].

concentration of solute), M_D is transport coefficient (mobility) associated with diffusion coefficient, and

$$\mathcal{F} = \int \left(f(x) + \frac{1}{2} \varepsilon^2 (\nabla x)^2 \right) dV. \quad (2)$$

The Cahn–Hilliard equation plays a fundamental role in materials science, in description of the process of separation of the continuous medium into the regions with different concentrations. As a result of the stratification, a “worm-like” structure is formed. The coefficient ε^2 and the free energy density $f(x)$ are determined by the equilibrium properties of the system. If $f(x)$ has a single minimum, then the eq. (1) describes the usual diffusion with the characteristic dispersion relation [8] $\omega = -k^2(D + M_D \varepsilon^2 k^2)$ between the frequency ω and the wave number k , where the contribution of the gradient term $(\nabla x)^2$ is assumed to be small compared to the contribution of the free energy density. The value $D = M_D \partial^2 f(x) / \partial x^2$ is the diffusion coefficient, where M_D is a some positive kinetic factor (mobility). Spinodal decomposition occurs when $f(x)$ has two minima. Then, in the region between the minima, the diffusion coefficient $D < 0$ and the dispersion relation

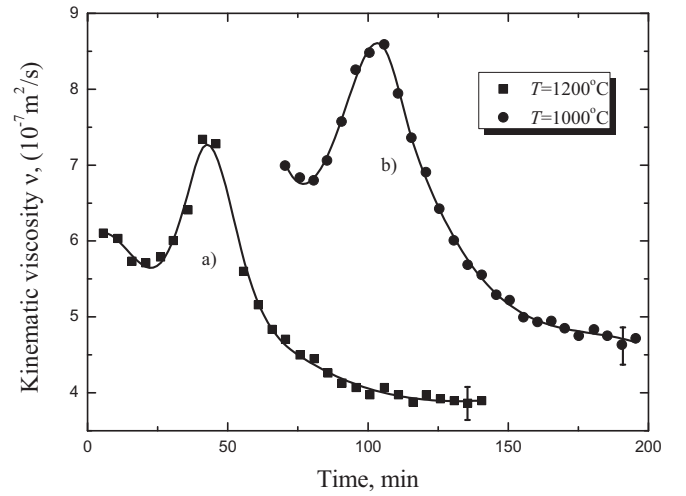


Fig. 2. The temporal dependencies of the viscosity of Al_{95}Y_5 (a) and $\text{Al}_{90}\text{Y}_{10}$ (b) melts at the various temperatures [5,6].

$\omega = k^2(|D| - M_D \varepsilon^2 k^2)$ indicate an important stabilizing role of the gradient term in the expression (2). The negative diffusion coefficient leads to instability, which results in a characteristic “worm-like” structure of the solute distribution over space.

Since visually it is very difficult to distinguish spinodal decomposition (homogeneous nucleation) from metastable state (heterogeneous nucleation), the concept of structural factor $S(k, t)$ is used [8]. The structural factor $S(k, t)$ is proportional to square of the Fourier component of the order parameter and usually increases as $S(k, t) \propto \exp(2A(k, t))$. The value $A(k, t)$ is called “the amplification rate”. Usually from experiments one finds dependence $A(k, t) \propto k^{-2}$ [8]. From the dispersion relation for the Cahn–Hilliard equation we can easily find that $A(k, t) k^{-2} = (|D| - M_D \varepsilon^2 k^2)$ gives a linear dependence by k^2 . One can note that the experimental data on the the amplification rate are characterized by significant nonlinearity [8]. Nevertheless, it is believed that the Cahn–Hilliard equation correctly reflects the essence of what is happening in the spinodal decay: the convexity of the potential leads to the instability, which is extinguished by the fourth derivative.

Now we should ask ourselves the following question: can the spinodal decay, which is highly desirable [3] to explain the phenomena under consideration of abnormally slow relaxation and nonmonotonic dependence of viscosity on time, be observed in the Al–Y system because of its Gibbs potential? Obviously, the answer is no. The Gibbs potential of the Al–Y system, shown in Fig. 3 has a single minimum. Also, one can note the other feature of the solute presented in Fig. 3, this is the closely spaced vertical lines of stoichiometric compounds Al_2Y and Al_3Y attending in the initial samples. Therefore, one can assume that the presence of these compounds in initial solid can lead to presence of the local areas with a solute concentration exceeding the sample-average, in the melt. Moreover, it is well known that the physical processes taking place near peritectic, are quite complex and interesting, and continue to be researched until the present time [10,11].

The aim of this work is to study the solute redistribution processes between the liquid phase and stoichiometric compounds, which can result to the instability characteristic of the process of spinodal decomposition. For simplicity, we will limit ourselves to the convex potential model, for which it is possible to carry out up to the end analytical calculations and to analyze the dynamics of the system with liquid and stoichiometric phases. Since usually at the spinodal decomposition the separation of the region with a different solute concentration is discussed, but with one aggregate nature, below we will be talk not about the spinodal decay, but about the upward diffusion in the processes of melting.

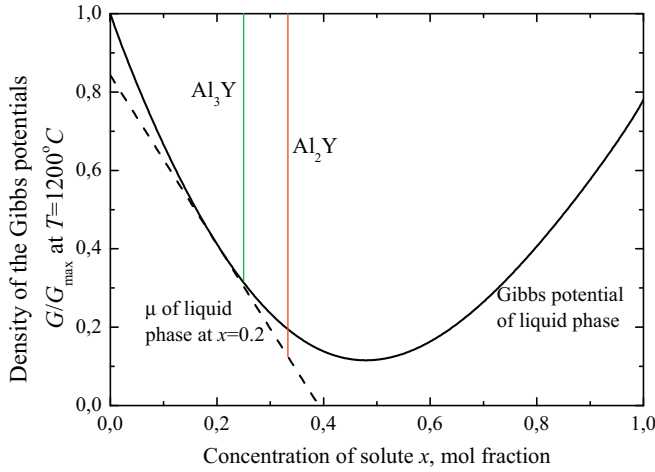


Fig. 3. Real Gibbs potentials of the liquid phase and two stoichiometric phases, Al_3Y and Al_2Y , in $Al–Y$ alloy at the temperature $T = 1200^\circ C$ [9].

3. Model of phase transformations in the presence of stoichiometric phase

Let us consider the model isothermal problem of phase transformations in a binary melt with a molar solute concentration x in the liquid (phase S). We suppose that the melt at the given concentration corresponds to the volume density of the Gibbs potential $G_S(x)$. For alloys in which there is a nonmonotonic relaxation of viscosity, the density of Gibbs potential is a convex downward function of the concentration, so to simplify the calculations, we restrict ourselves to the quadratic approximation

$$G_S = \frac{1}{2}g_0(x - x^*)^2,$$

where x^* is the $G_S(x)$ minimum position (Fig. 4).

Further we assume that this binary compound, in addition to the liquid, has another stoichiometric phase (phase F) of the fixed composition x_0 . For the stoichiometric phase the Gibbs potential also has the fixed value of G_F at the given temperature.

To describe the phase state of solution we restrict ourselves to the scalar field φ , such that for each unit of volume some share of the stoichiometric phase φ corresponds, and $(1 - \varphi)$ is the share of the liquid. In the solid (stoichiometric) phase F we assume that $\varphi = 1$, and in the liquid s the phase field is zero. Unlike the well-known ideology of

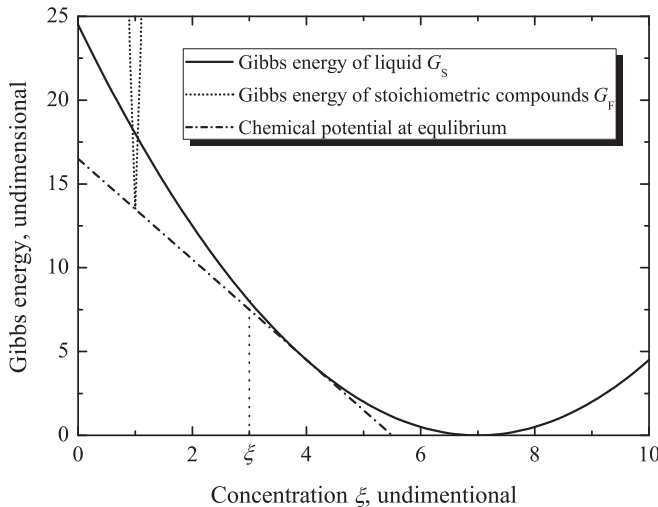


Fig. 4. The equilibrium conditions between phases at the given temperature.

the phase field [12], we assume that the intermediate value of the field $0 \leq \varphi \leq 1$ does not describe the interface between the phases, but rather corresponds to the volume mixture of phases in the spirit of the quasi-equilibrium theory of crystallization [13]. Neglecting the change in volume during phase transformations of the solidifying liquid, we write down the Gibbs potential in the form of phase interpolation. Since we are not interested in the interface, we omit the gradient contribution of the field $(\nabla\varphi)^2$, in contrast to the approach of the phase field, but consider the similar contribution to the liquid concentration of x , assuming the existence of correlations of the solute concentration only in the liquid:

$$G = \int \left(\varphi G_F + (1 - \varphi)G_S(x) + \frac{1}{2}\varepsilon^2(\nabla x(1 - \varphi))^2 \right) dV, \quad (3)$$

that formally exactly coincides with the Cahn–Hilliard energy [7] at $\varphi = 0$, but in this case, unlike [7], the Gibbs potential of the liquid phase is always convex down $\partial^2 G_S / \partial x^2 \gg 0$. The coefficient ε^2 in (3) corresponds to the coefficient in the Cahn–Hilliard equation and is proportional to the square of the correlation length.

Note that the molar concentration of solute in the liquid x is not a constant value and can vary both due to changes in the phase fraction and due to diffusion. The average concentration of $\langle x \rangle$ per unit volume can be changed only by diffusion fluxes J_D in the liquid with a fraction $(1 - \varphi)$:

$$\frac{\partial}{\partial t} \langle x \rangle = -(1 - \varphi) \nabla \cdot J_D,$$

the choice of which is due to the requirement to reduce the total Gibbs energy of the system in the relaxation processes. The concentration average in phases can be written as

$$\langle x \rangle = \varphi x_0 + (1 - \varphi)x,$$

differentiation of which gives

$$\frac{\partial}{\partial t} \langle x \rangle = (1 - \varphi)\dot{x} + \dot{\varphi}(x_0 - x) = -(1 - \varphi) \nabla \cdot J_D, \quad (4)$$

where

$$\dot{x} \equiv \frac{\partial x}{\partial t}, \quad \dot{\varphi} \equiv \frac{\partial \varphi}{\partial t}.$$

From the expression (4) one can find the equation for solute in the liquid:

$$(1 - \varphi)\dot{x} = -\dot{\varphi}(x_0 - x) - (1 - \varphi) \nabla \cdot J_D. \quad (5)$$

Taking into account the eq. (5) we get the dynamic system of two independent variables $x(r, t)$, $\varphi(r, t)$, whose Lyapunov functional is the total Gibbs energy of the system (3).

4. Relaxation equations

In order to obtain the relaxation equations of the dynamical system (3) let us analyze the rate of change of the control potential by requiring the constant decrease of its value:

$$\frac{dG}{dt} = \int \left(\dot{\varphi} [G_F - G_S(x) + x\varepsilon^2 \nabla^2(x(1 - \varphi))] + \dot{x}(1 - \varphi) [\mu_S - \varepsilon^2 \nabla^2(x(1 - \varphi))] \right) dV \leq 0,$$

where

$$\mu_S \equiv \frac{\partial G_S}{\partial x}$$

is the chemical potential. Taking into account the conservation law (5), after integration in parts the rate of change of the Lyapunov functional is rewritten as

$$\frac{dG}{dt} = \int (\dot{\phi} [G_F - G_S(x) - (x_0 - x)\tilde{\mu}_S + x\varepsilon^2\nabla^2(x(1 - \phi))] + \mathbf{J}_D \nabla [(1 - \phi)\tilde{\mu}_S]) dV \leq 0,$$

where

$$\tilde{\mu}_S = \mu_S - \varepsilon^2\nabla^2(x(1 - \phi)). \tag{6}$$

According to the nonequilibrium thermodynamics [14] the simplest choice guaranteeing the decreasing of the Lyapunov functional, is

$$\begin{aligned} \dot{\phi} &= -M_\phi [G_F - G_S(x) - (x_0 - x)\tilde{\mu}_S + x\varepsilon^2\nabla^2(x(1 - \phi))], \\ \mathbf{J}_D &= -M_D \nabla [(1 - \phi)\tilde{\mu}_S], \end{aligned}$$

where $M_D > 0$, $M_\phi > 0$ are the kinetic coefficients of mobility. For diffusion processes in the liquid with Gibbs potential $G_S(x)$ the mobility is defined as $M_D = D/(\partial^2 G_S(x)/\partial x^2)$, where D is the diffusion coefficient. The kinetic coefficient M_ϕ determines the rate of phase growth and is usually empirical. Thus, taking into account the definition (6) and the conservation law (5), the dynamics of the system with the control functional (3) is determined by the equations

$$\begin{aligned} \dot{\phi} &= M_\phi [G_S(x) - G_F + (x_0 - x)\mu_S - x_0\varepsilon^2\nabla^2(x(1 - \phi))], \\ (1 - \phi)\dot{x} &= -(x_0 - x)\dot{\phi} + (1 - \phi)\nabla(M_D \nabla [(1 - \phi)\tilde{\mu}_S]). \end{aligned} \tag{7}$$

The obtained Eqs. (7) show that the phase transition velocity $\dot{\phi}$ is determined by the difference between the grand potentials of the phases ($\Omega_S = G_S(x) - x\mu_S$, and $\Omega_F = G_F - x_0\mu_S$), that coincides with the accepted point of view on the driving forces of phase transformations ([15,16]) in thermodynamic. The additional driving force of the phase transition is associated with concentration correlations defined by $\nabla^2(x(1 - \phi))$. In areas where function of the liquid concentration $x(1 - \phi)$ is convex upwards, the growth of the stoichiometric phase is accelerated, and where liquid concentration is convex downward its growth is slows.

According to the liquid concentration eq. (4) there are three different mechanisms of its redistribution, which are determined by the term $(x_0 - x)\dot{\phi}$: the solute diffuses either from the solid into liquid, when it is in excess supply, or from the liquid to the solid, if the solute concentration is not enough for the stoichiometry compound formation. The third way is the concentration redistribution influenced by the chemical potential (see (6) and (7)), which is specified by the expression

$$\begin{aligned} (1 - \phi)\nabla(M_D \nabla [(1 - \phi)\mu_S]) &= (1 - \phi)\nabla((1 - \phi)M_D (\partial\mu_S/\partial x) \nabla x) + \dots = \\ &= (1 - \phi)\nabla((1 - \phi)D \nabla x) + \dots, \end{aligned}$$

which describes usual diffusion in liquid. The last term, arising from substitution eq. (6) into (7), and defined by the summand with ε^2 , is analogous to the summand with fourth derivative in the Cahn–Hilliard equation, and serves to smooth short-wave perturbations.

The result is the system of coupled nonlinear equations that can be fully investigated only numerically. However, interested in the initial stages of the relaxation process close to equilibrium, we can get a qualitative idea of what is happening, using the Fourier analysis of small deviations from equilibrium.

5. The linearized equation

To simplify further analysis of the dynamics we proceed in the eqs. (7) to dimensionless variables. Considering the mobilities as constants, and marking out the characteristic scales in space and time as

$$L = \frac{\varepsilon}{\sqrt{g}}, \quad t_0 = \frac{1}{gM_\phi x_0^2},$$

after replacing

$$x = x_0\xi, \quad x^* = x_0\xi^*, \quad \tilde{G}_F = \frac{G_F}{gx_0^2},$$

where ξ is the dimensionless concentration variable, we come to the equations of the form

$$\begin{aligned} \dot{\phi} &= \frac{1}{2}(\xi - \xi^*)(2 - \xi - \xi^*) - \tilde{G}_F - \nabla^2(\xi(1 - \phi)), \\ (1 - \phi)\dot{\xi} &= -(1 - \xi)\dot{\phi} + D_0 \nabla^2((1 - \phi)(\xi - \xi^* - \nabla^2(\xi(1 - \phi)))), \end{aligned}$$

where $D_0 = gM_D/\varepsilon^2 x_0^2 M_\phi$. Note also that the region of change of dimensionless concentration in the new variables is $\xi \in [0, 1/x_0]$.

The graphs of stoichiometry and liquid phase potential in dimensionless variables are shown in Fig. 4. Stoichiometry is represented conditionally in the form of a narrow potential bounded from below by the G_F value. In our model the temperature formally is absent. However, the implicitly set temperature determines the relative position of the phase potentials, as well as the equilibrium concentration value, which also depends on temperature. Therefore, Fig. 4 corresponds to the certain temperature at which the stoichiometry and the liquid melt are in equilibrium.

Substituting the equation for $\dot{\phi}$ into the equation for ξ , we obtain

$$\begin{aligned} \dot{\phi} &= \frac{1}{2}(\xi - \xi^*)(2 - \xi - \xi^*) - \tilde{G}_F - \nabla^2(\xi(1 - \phi)), \\ (1 - \phi)\dot{\xi} &= (1 - \xi + D_0)\nabla^2(\xi(1 - \phi)) + D_0\xi^*\nabla^2\phi - \\ &- D_0\nabla^2[(1 - \phi)\nabla^2(\xi(1 - \phi))] + (\xi - 1)\left[\frac{1}{2}(\xi - \xi^*)(2 - \xi - \xi^*) - \tilde{G}_F\right]. \end{aligned}$$

As initial state we choose the equilibrium state, for which $\phi_0 = const$ and $\xi_0 = const$ satisfy the following condition:

$$\frac{1}{2}(\xi_0 - \xi^*)(2 - \xi_0 - \xi^*) = \tilde{G}_F.$$

For small deviations from the initial state $\phi(\mathbf{r}, t) = \phi_0 + \delta\phi(\mathbf{r}, t)$ and $\xi(\mathbf{r}, t) = \xi_0 + \delta\xi(\mathbf{r}, t)$, taking into account that

$$(1 - \phi)\xi \approx (1 - \phi_0)\delta\xi - \xi_0\delta\phi,$$

one get the linearization in the form of

$$\begin{aligned} \dot{\delta\phi} &= \xi_0 \nabla^2(\delta\phi) - (1 - \phi_0)\nabla^2(\delta\xi) + \alpha\delta\xi, \\ \delta\xi &= (1 + D_0 - \xi_0)\nabla^2(\delta\xi) - (1 - \phi_0)D_0\nabla^4(\delta\xi) + \\ &+ D_p \nabla^2(\delta\phi) + \beta\delta\xi, \end{aligned} \tag{8}$$

where

$$\begin{aligned} D_p &= \frac{D_0\xi^* - (D_0 + 1 - \xi_0)\xi_0}{1 - \phi_0}, \\ \alpha &= \frac{1}{2} \frac{\partial}{\partial \xi} [(\xi - \xi^*)(2 - \xi - \xi^*)]_{\xi=\xi_0} = 1 - \xi_0, \\ \beta &= \frac{1}{1 - \phi_0} \left(\frac{1}{2} \frac{\partial}{\partial \xi} [(\xi - 1)(\xi - \xi^*)(2 - \xi - \xi^*)]_{\xi=\xi_0} - \tilde{G}_F \right) = \\ &= \frac{1}{1 - \phi_0} \left(3\xi_0 \left(1 - \frac{1}{2}\xi_0 \right) - \xi^* \left(1 - \frac{1}{2}\xi^* \right) - 1 - \tilde{G}_F \right). \end{aligned}$$

The eqs. (8) show that the coefficient at the second derivative of the concentration becomes negative, if the initial concentration ξ_0 at the given temperature exceeds some value $\xi_0 > 1 + D_0$.

6. Fourier analysis of deviation from the equilibrium

Let us consider the dynamics of small deviations from the equilibrium position over time t assuming the presence of small phase fluctuations $\delta\phi_0$ and the composition $\delta\xi_0$ inside the melt at the initial time. For simplicity, we restrict ourselves to a one-dimensional infinite region, the points of which are numbered by the coordinate z , assuming that

$$\begin{cases} \delta\phi = C_1 e^{\Omega t + i q z}, \\ \delta\xi = C_2 e^{\Omega t + i q z}, \end{cases} \tag{9}$$

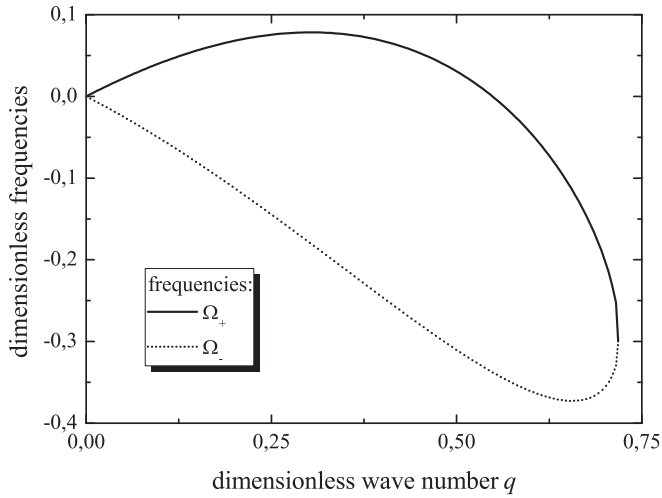


Fig. 5. Dispersion dependence at small wave numbers.

where Ω is the frequency, q is the wave number.

Substituting (9) into the eqs. (8), one can find the dispersion relation

$$(\beta - \Omega - (1 + D_0 - \xi_0)q^2 - D_0(1 - \varphi_0)q^4)(\Omega + \xi_0 q^2) - D_p q^2 (\alpha + (1 - \varphi_0)q^2) = 0,$$

which is reduced to the quadratic equation for Ω ,

$$\Omega^2 + B\Omega + C = 0$$

with the following coefficients:

$$B = (1 + D_0)k^2 + (1 - \varphi_0)D_0 k^4 - \beta,$$

$$C = (1 - \varphi_0)\xi_0 q^6 + (1 + D_0 - \xi_0)\xi_0 q^4 + (1 - \varphi_0)D_p q^4 + D_p \alpha q^2 - \beta \xi_0 q^2.$$

For model calculations the following parameters were adopted: $D_0 = 0.1$, $\xi^* = 7$, $\varphi_0 = 0.25$, $\xi_0 = 1.2$, $\tilde{C}_F = 17.98$. The dependence of roots of the dispersion equation

$$\Omega_{\pm} = \frac{1}{2}(-B \pm \sqrt{B^2 - 4C})$$

for the selected parameter values is shown in Fig. 5–6. In Fig. 5 one can see for small wave numbers there is a region of positive real values Ω_+ , which corresponds to the upward diffusion. The second root Ω_- is negative and corresponds to the solutions that fade monotonically over time. When the wave number increases the real roots disappear, and appear complex-conjugate ones. This is the area of periodic damped solutions. With further increase in Fig. 6, the roots again become real,

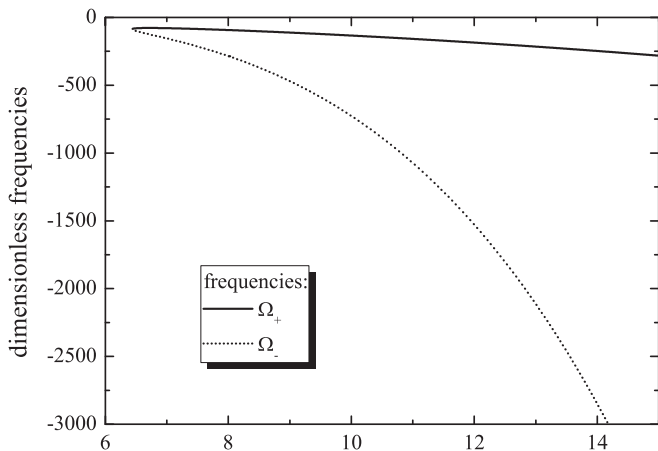


Fig. 6. Dispersion dependence at high wave numbers.

and the corresponding solutions are monotonically damped. Therefore, we limit ourselves further to the area with small wave numbers.

7. The structure factor dynamics

In order to study the instability dynamics we consider the structural factor of the model as the value measured in the x-ray scattering experiments. By definition, the structural factor for the solute is $S(q, t) = N_q |\xi_q(t)|^2$. Choosing the eigenvectors corresponding to the frequencies Ω_{\pm} , in the form of

$$\mathbf{V}_{\pm} = \begin{pmatrix} \Omega_{\pm} + \xi_0 q^2 \\ -(\alpha + (1 - \varphi_0)q^2) \end{pmatrix}.$$

one can represent the solutions for Fourier components (9) of the equation system (8) in the following form:

$$\begin{pmatrix} \delta \xi \\ \delta \varphi \end{pmatrix} = (C_{1q} \mathbf{V}_+ e^{\Omega_+ t} + C_{2q} \mathbf{V}_- e^{\Omega_- t}) e^{iqz}.$$

Assuming for simplicity that fluctuations are present at all wave numbers with the same amplitude, which can be taken as one, from the initial conditions we find the values of the integration constants:

$$C_{1q} \mathbf{V}_+ + C_{2q} \mathbf{V}_- = \begin{pmatrix} 1 \\ 1 \end{pmatrix},$$

from which the expression for the structural factor is

$$S(q, t) = N_q [(\Omega_+ + \xi_0 q^2) C_{1q} e^{\Omega_+ t} + (\Omega_- + \xi_0 q^2) C_{2q} e^{\Omega_- t}]^2.$$

The normalization factor is chosen from the condition $S(q, 0) = 1$. The type of structural factor, given the choice of normalization, for different time moments is shown in Fig. 7–8. At the initial time moment the maximum of the structural factor is significantly shifted towards smaller wave numbers (large characteristic distances). In subsequent time moments the shift stops, and at some characteristic scales the concentration increases.

More detailed information about the structural factor behavior can be obtained from the dependence of the amplification rate on the wave number and time, $A(q, t) = S^{-1} dS/dq$, shown in Fig. 9. The figure shows that the positive part of the amplification rate, which provides instability of the process, with time tends to some limit distribution.

For comparison, we can give the normalized amplification rate, $A(q, t)q^{-2}$, in Fig. 10, which commonly used in the analysis of spinodal decomposition processes. Comparing with the available data of [17], it is possible to note their great similarity, although formally no spinodal decay occurs in this system.

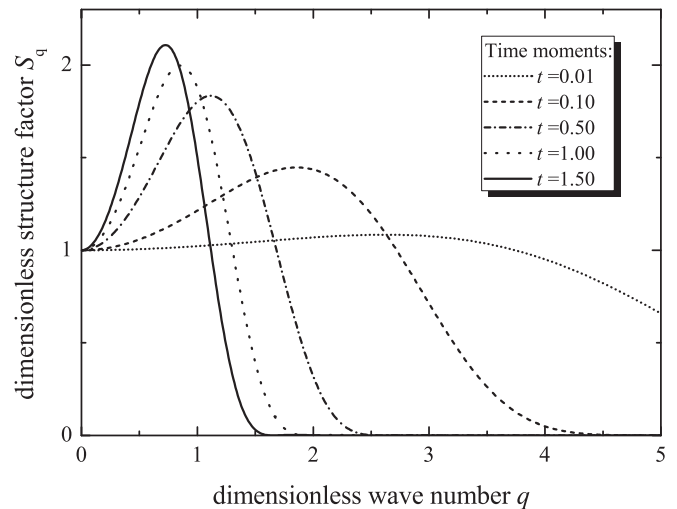


Fig. 7. The structure factor at the initial moments of time.

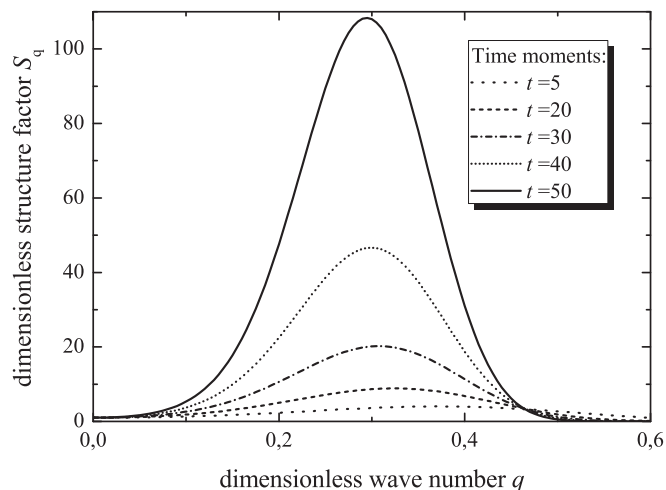


Fig. 8. The structural factor in later time points.

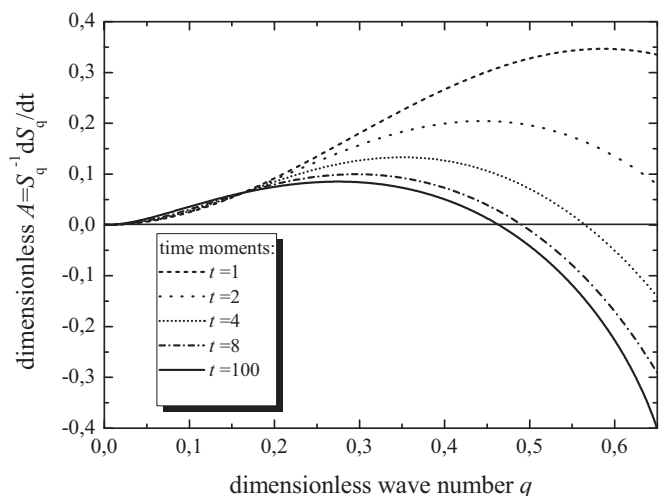


Fig. 9. Amplification rate at different times.

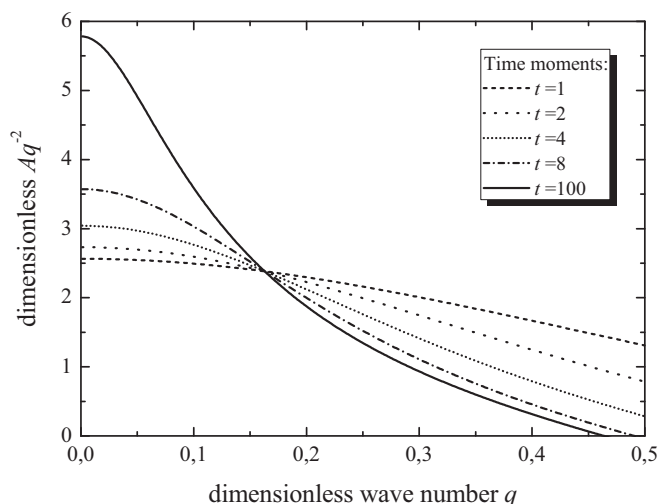


Fig. 10. The adjusted amplification rate at different times.

Thus, the obtained structure factor and the amplification rate for the redistribution of solute in melt in the presence of stoichiometrical phases are very close in appearance to corresponding values in the

spinodal decay. Moreover, the nonlinearity of the amplification rate in the considered model is closer to the observed dependence for spinodal decay [17].

One can conclude that although the real Gibbs potential of liquid is an unimodular function, the presence of phase transition processes leads to an effective Gibbs potential, the second derivative of which determines the negative diffusion coefficient. Thus, assuming that the initial alloy is heterogeneous over impurity concentration, after melting in the areas with high impurity content, the “effective upward diffusion” can arise.

This is equivalent to the local realization of the effective double-well Gibbs potential, that can lead to appearance of the dynamic properties characteristic for bistable systems. From the spinodal decomposition theory one well knows that this leads to very slow relaxation. Also, from the physics of non-linear systems one knows that in like these bistable systems the appearance of Kramers oscillations [18] is possible. The mechanism of the appearance of these oscillations in melts was described in [19,20], and in [3] one shown that the system with double-well model Gibbs potential could demonstrate the non-monotonic relaxation dynamics. Thus, the theory admits the possibility of local in space and time growth of inhomogeneity as a result of fluctuation processes in non-linear system, and the “effective upward diffusion” can explain the slowness and non-monotonicity of the relaxation processes observed in the experiment.

8. Conclusions

Thus, a model describing the processes of melting–solidification in a two–phase system consisting of a liquid and stoichiometric phase is proposed. The resulting equations, under certain conditions, have the diffusion instability and behave similarly to the Cahn–Hilliard equation. From the Fourier analysis of small deviations from the equilibrium position, expressions for the structural factor and the amplification rate are obtained, the study of which shows that in the presence of stoichiometric phase in solutions, upward diffusion processes similar to spinodal decomposition are possible.

Note that the mechanism of upward diffusion considered in this paper, is different from the spinodal Cahn–Hilliard decay [7]. If during the spinodal decomposition the instability is associated with the potential convexity upwards, then our instability is due to the redistribution of solute between the phases. If at some point of time in the solution locally there is a concentration of solute exceeding some critical value, the excess of this concentration leads to formation of the stoichiometric phase taking away quite a certain part of solute. The excess solute is displaced into the liquid phase, leading to an increase in instability. Formally, mathematically, the model of such process turns out to be quite equivalent to the Cahn–Hilliard model, although, as noted earlier, the potential of the liquid phase always remains a convex function.

Another consequence of this study is the qualitative confirmation of the possible origin of long-term relaxation and nonmonotonic behavior of viscosity in the melting processes based on the using of the Cahn–Hilliard eq. [3]. Of course, this work is based on the model system, so the resulting picture needs both additional theoretical study on real materials and additional experimental data, preferably obtained on matrix X–ray diffraction units. It is such equipment that can give data on the growth rate of the structural factor in the melting of solid solutions of Al–Y and Al–Ni.

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