

## Analysis of the dispersion relation in spinodal decomposition of a binary system

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A model for diffusion and phase separation which takes into account hyperbolic relaxation of the solute diffusion flux is developed. Such a ‘hyperbolic model’ provides analysis of ‘hyperbolic evolution’ of patterns in spinodal decomposition of binary systems. Analytical results for the dispersion relation and critical parameters (such as wavelength and amplification rate of decomposition) are analyzed in comparison with outcomes of classic Cahn–Hilliard theory. It is shown that the hyperbolic model predicts the amplification rate behaviour that is typically observed in experiments on spinodal decomposition.

### 1. Introduction

The 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 a detailed analysis and tests against experimental data [3, 4] the theory of Cahn and Hilliard has been further explored and developed. In particular, it has been demonstrated that there is a boundary for the critical quenching above which the classic Cahn–Hilliard approach has to be extended to the case of strongly non-equilibrium decomposition provided by deep supercooling into the spinodal region of a phase diagram [5, 6].

Few advancements were made for strongly non-equilibrium phase separation. Binder *et al.* [7] 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, a classic model for spinodal decomposition has been modified by taking the relaxation of diffusion flux as an independent thermodynamic variable into consideration [8, 9]. This modification has been made consistent with extended irreversible thermodynamics [10]. As a result,

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a partial differential equation of hyperbolic type for phase separation with diffusion has been derived. It can be called ‘a hyperbolic model for spinodal decomposition’. Therefore, the present article gives a comparative analysis of both the Cahn–Hilliard parabolic model and the hyperbolic model (modified Cahn–Hilliard) of spinodal decomposition. As a first test we focus on a comparison of the dispersion relation in the parabolic and hyperbolic models of decomposition.

## 2. Hyperbolic spinodal decomposition

Consider an isothermal and isobaric binary system represented as an isotropic solid solution free from imperfections and with the 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, the free energy  $f$  is based on the selected set of independent thermodynamic variables  $\{c, \nabla c, \vec{J}\}$ , consisting of the 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  $\vec{J}$ . An analogous set of variables is generally analyzed within the context of extended thermodynamics [10, 11] and it is used for models of fast phase transformations [9]. In such a case, the free energy density can be written in the following form

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

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 [10],  $D$  the diffusion constant,  $\Delta\mu = \mu_A - \mu_B$  the difference of chemical potentials for components  $A$  and  $B$ , respectively, and  $\tau_D$  is the relaxation time of the diffusion flux to its steady state. Within the limits of instant relaxation, i.e.  $\tau_D \rightarrow 0$ , the term with fluxes vanishes and equation (1) gives the free energy density  $f(c, \nabla c)$  of Cahn–Hilliard form applicable for local equilibrium system.

Going beyond local equilibrium requires in-depth reexamination of such basic concepts as entropy, temperature, pressure or chemical potential under more general circumstances [10]. The free energy density (1) defines the thermodynamic potential with both the local equilibrium contribution  $f_h(c)$  and the purely local non-equilibrium contribution  $(\alpha_J/2)\vec{J}^2$  (under spatial inhomogeneity specified by the gradient term). For the local equilibrium part  $f_h(c)$  a local ergodicity (that is, the system needs to sample the phase space) is true. However, as soon as we postulate diffusion flux with a finite relaxation time, this means that the local non-equilibrium contribution  $(\alpha_J/2)\vec{J}^2$  assumes the existence of a slow physical process, which is the jump of solute atoms [13]. Considering ergodicity of a phase space for non-equilibrium situation, one may well refer to statistical effects in fast spinodal decomposition due to the existence of many particles (atoms and molecules) within local volumes. Since the phase demixing proceeds very fast, the particles do not have enough time to sample all the phase space. Thus, the number of microstates

accessible to each of them will be lower than in equilibrium. This will imply an increase in the free energy with respect to the local equilibrium contribution  $f_h(c)$ . This is one of the ways to interpret the non-equilibrium contribution  $(\alpha_J/2)J^2$  to the free energy (1).

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

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

where  $v$  is 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 [8, 9] and applied to equation (2) one can obtain

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

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

where  $\omega$  is the outer surface of sub-volume  $v$ ,  $J_n$  is the diffusion flux pointed by the normal vector  $\vec{n}$ , and  $f'_c = \partial f_h / \partial c$ . As it follows from equation (4), the dissipative function includes the term  $\alpha_J \partial \vec{J} / \partial t$  which has a clear physical meaning: far from equilibrium, the diffusion flux provides additional ordering that is leading to increase of dissipation.

Around a steady state, the dissipative function (4) must decrease in time, so that the free energy of the entire system decreases. This condition implies a relation between fluxes and forces which, in the simplest case, is assumed to be linear [10]. For equation (4), it gives the following evolution equation for the diffusion flux

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

where  $M$  is the atomic mobility, so that  $\tau_D = M \alpha_J$ . Together with the atomic mass balance

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}, \quad (6)$$

equation (5) leads to the following governing equation

$$\tau_D \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = \nabla \cdot \left[ M \nabla (f'_c - \varepsilon_c^2 \nabla^2 c) \right], \quad (7)$$

which is the same as previously derived from the entropy functional [8, 9]. Equation (7) is a partial differential equation of hyperbolic type with the decomposition delay described by the term  $\tau_D \partial^2 c / \partial t^2$ .

As 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 equation (7) all terms not linear in  $c$ . This yields

$$\tau_D \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = M f''_{cc} \nabla^2 c - M \varepsilon_c^2 \nabla^4 c, \quad (8)$$

where  $f''_{cc} = \partial^2 f_h / \partial c^2$ . As  $\tau_D \rightarrow 0$ , equation (8) transforms into the classic Cahn–Hilliard equation [1, 2]. In the present form, equation (8) can be considered as a modified Cahn–Hilliard equation which is a linearized partial differential equation of hyperbolic type. This equation is true for spinodal decomposition with local non-equilibrium diffusion (diffusion with relaxation of the solute flux). This type of decomposition is expected for short periods of time, large characteristic velocities of the process, large concentration gradients, or for deep supercoolings.

### 3. Dispersion relation

Consider the elementary exponential solution of equation (8) in the following form

$$c(z, t) - c_0 = a_k \exp[i(kz - \omega(k)t)], \quad (9)$$

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

$$\omega(k) = -\frac{i}{2\tau_D} \pm \left( \frac{Mk^2(f''_{cc} + \varepsilon_c^2 k^2)}{\tau_D} - \frac{1}{4\tau_D^2} \right)^{1/2}. \quad (10)$$

The upper and lower signs for  $\omega(k)$  in equation (10) correspond to the branches which are responsible for the wave propagation in the positive and negative  $z$ -directions, respectively.

In the local equilibrium limit  $\tau_D \rightarrow 0$ , equation (10) gives the following approximation

$$\omega(k) \approx -\frac{i}{2\tau_D} [1 \pm (1 - 2\tau_D Mk^2(f''_{cc} + \varepsilon_c^2 k^2))]. \quad (11)$$

Equation (11) shows that one of the roots is going towards  $-\infty$  along the imaginary axis following the law  $\omega(k) \sim i/\tau_D$ . This leads to exponential decay of the solution (9). The second root of equation (11) is finite and it is equivalent to the well-known Cahn–Hilliard relation

$$\omega(k) \approx -iMk^2(f''_{cc} + \varepsilon_c^2 k^2). \quad (12)$$

Thus, the local equilibrium limit for the dispersion relation (10) gives two different roots: the first root is diverging and the second root is approaching to the dispersion relation (12) of Cahn and Hilliard.

## 4. Critical parameters for hyperbolic decomposition

### 4.1. Critical wavelength for decomposition

Cahn [2] has found a critical wavelength  $\lambda_c$  above which the infinitesimal sinusoidal fluctuations of the concentration are irreversibly growing. Particularly, he confirmed the concept of Hillert [12] that  $\lambda_c \rightarrow \infty$  with approaching the spinodal at which one has  $\partial^2 f / \partial c^2 = 0$ .

To find the critical wavelength for decomposition under local non-equilibrium diffusion, we expand  $f_h(c)$  in equation (2) about some concentration  $c_0$  that is  $f_h(c) = f(c_0) + (c - c_0)(f'_c)_{c=c_0} + 0.5(c - c_0)^2(f''_{cc})_{c=c_0} + \dots$  Along the  $z$ -axis,

composition is represented by a series of sinusoidal waves with components of the following form:  $c - c_0 = a_c \cos(kz)$ , where  $a_c$  is the amplitude. Substituting  $c - c_0$  into the expression for  $f_h(c)$  we perform integration of the functional (2) over the volume  $v_c$ . Then, for the difference of the Helmholtz free energy,  $\Delta F = F(c, J) - \int_v f_h(c_0) dv$ , between a system with sinusoidal concentration and a homogeneous system, respectively, one gets:

$$\frac{\Delta F}{v} = \frac{a_c^2}{4} [f''_{cc} + \varepsilon_c^2 k_z^2]. \quad (13)$$

For the reasonable cases of the positive surface tension,  $\varepsilon_c^2 > 0$ , one can consider two important points. First, with  $f''_{cc} > 0$  the solution is stable against fluctuation of concentration of any wavelength: the free energy only increases in this case,  $\Delta F > 0$ . Second, with  $f''_{cc} < 0$  the solution is unstable with respect to the critical wavelength for decomposition which can merely be found by taking the zero value for the square bracket in equation (13):

$$k_c = 2\pi/\lambda_c = (-f''_{cc}/\varepsilon_c^2)^{1/2}, \quad f''_{cc} < 0. \quad (14)$$

Therefore, with  $f''_{cc} < 0$  and for  $\lambda > \lambda_c$ , the free energy decreases,  $\Delta F < 0$ , and decomposition starts to proceed. Equation (14) clearly shows that as the composition tends to the values lying in the spinodal,  $f''_{cc} = 0$ , the critical wavelength approaches infinity,  $\lambda_c \rightarrow \infty$  [2, 12].

#### 4.2. Amplification rate of decomposition

Using equation (10), the imaginary part of the frequency at  $k < k_c$  is defined by

$$\omega_{\pm} = (2\tau_D)^{-1} \left[ -1 \pm (1 - 4k^2\tau_D M(f''_{cc} + \varepsilon_c^2 k^2))^{1/2} \right]. \quad (15)$$

In this expression, the 'plus' and 'minus' signs correspond to the growth or to the decay of solution (9), respectively. After expanding the square root in equation (15) for  $4k^2\tau_D M[f''_{cc} + \varepsilon_c^2 k^2] \ll 1$  one gets in the local equilibrium limit the expression:

$$\lim_{\tau_D \rightarrow 0} \omega_+ = -k^2 M(f''_{cc} + \varepsilon_c^2 k^2), \quad (16)$$

which is the kinetic amplification rate obtained by Cahn [2] for a purely diffusion regime. Therefore, equation (15) can be interpreted as the kinetic amplification rate for both dissipative and propagative regimes of atomic transport described by equation (8).

From the amplification rate  $\omega_+$  the maximum can be obtained by differentiation of equation (15) with respect to  $k$ . The extremum condition,  $\partial\omega_+/\partial k = 0$ , gives maximum frequency

$$\omega_m(k_m) = i(2\tau_D)^{-1} \left[ -1 + (1 + \tau_D M(f''_{cc}/\varepsilon_c^2))^2 \right]^{1/2} \quad (17)$$

at

$$k_m = 2\pi/\lambda_m = (-f''_{cc}/(2\varepsilon_c^2))^{1/2}, \quad f''_{cc} < 0. \quad (18)$$

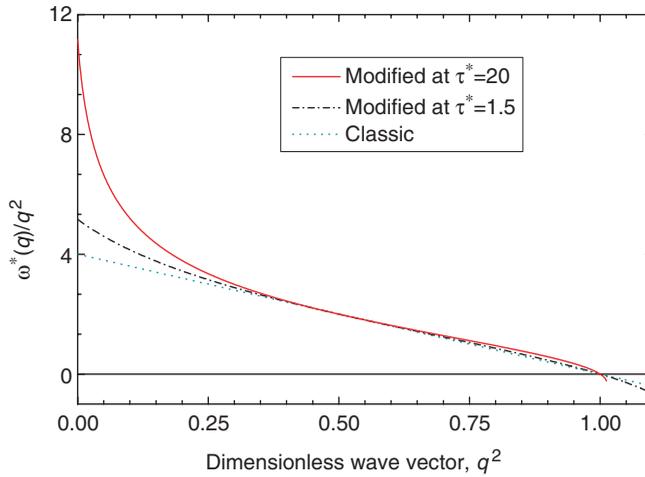


Figure 1. Comparison of the function  $\omega^*/q^2$  for the parabolic diffusion equation (classic Cahn–Hilliard equation for  $\tau_D \rightarrow 0$ ) and the hyperbolic equation (modified Cahn–Hilliard equation). Curves for the hyperbolic equation are given for various values of the parameter  $\tau^* = \tau_D M(-f''_{cc})^2/\varepsilon_c^2 = (l_D/l_c)^2$  that specifies the square of the ratio between diffusion length  $l_D = \sqrt{D\tau_D}$  and correlation length  $l_c = \varepsilon_c/\sqrt{2f_0}$ . Non-linear behaviour is predicted with  $l_D/l_c = 1.225$  (dashed-dotted) and  $l_D/l_c = 4.472$  (solid line).

Consequently, the maximum wavelength (18) is exactly  $\sqrt{2}$  times larger than the critical wavelength (14) of instability against fluctuations of concentration.

## 5. Discussion

For the Cahn–Hilliard theory, the amplification rate for decomposition is given by equation (12). Normalizing this expression on the imaginary part of the expression  $\omega_m(k_m) = iM[f''_{cc}/(2\varepsilon_c)]^2$  (that is found from equation (17) in the limit  $\tau_D \rightarrow 0$ ) one gets the following relation

$$\omega(q)^*/q^2 = [\omega(k)/\omega(k_m)]/q^2 = 4(1 - q^2), \quad q = k/k_c, \quad (19)$$

where  $k_c$  is given by equation (14).

Within the hyperbolic model, the amplification rate for decomposition  $\omega_+$  is given by equation (15). Therefore, using equations (14) and (17), one can get the following relation

$$\omega(q)^*/q^2 = [\omega_+(k)/\omega(k_m)]/q^2 = \frac{1}{q^2} \frac{[1 + q^2(1 - q^2)\tau_D M(-f''_{cc}/\varepsilon_c)^2]^{1/2} - 1}{[1 + \tau_D M(-f''_{cc}/\varepsilon_c)^2]^{1/2} - 1}, \quad (20)$$

which transforms into equation (19) in the local equilibrium limit  $\tau_D \rightarrow 0$ .

Figure 1 shows the relationship  $\omega^*(q)/q^2$  versus  $q^2$ , given by equations (19) and (20). As can be seen, Cahn–Hilliard theory predicts the linear law (dotted line in figure 1) which is practically not observable [4]. The present model

(modified Cahn–Hilliard model based on the hyperbolic equation) is flexible enough to describe non-linear behaviour (dashed-dotted and solid lines in figure 1). Such non-linear behaviour is typically observed in experiments (see, e.g., plots with experimental data for amplification rates of spinodally decomposing glasses [3]) and it directly depends on the parameter  $\tau^* = \tau_D M(-f''_{cc})^2 / \varepsilon_c^2$  in equation (20).

Now, we 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 that  $f''_{cc} = 2f_0(1 - 4c)|_{c=0.5} = -2f_0$ , where  $f_0$  is the characteristic height of the free energy. Then, the parameter  $\tau^*$  in equation (20) is defined by the square of the ratio between the 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 increase of the correlation length (in comparison with the length of diffusion), the parameter  $\tau^*$  decreases and the non-linear behaviour of the function  $q^{-2}\omega^*(q)$  tends to the linear law predicted by Cahn and Hilliard, figure 1.

## 6. Conclusion

The model of hyperbolic spinodal decomposition [8] which is a special case of the model of rapid phase transformations [9] has been further developed. Through the analysis of the dispersion relation, it has been shown that the hyperbolic model predicts the non-linear relationship ' $\omega^*(q)/q^2$  versus  $q^2$ '. This is typically observed in experiments on spinodal decomposition.

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