# Local Nonequilibrium Effect on Spinodal Decomposition in a Binary System

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# Abstract

A model for diffusion and phase separation which takes into account relaxation of the atomic diffusion flux to its local equilibrium state is explored. This model is described by a partial differential equation of a hyperbolic type that can be called "a hyperbolic model for spinodal decomposition". Analysis of the hyperbolic model is given to predict critical parameters of decomposition (such as amplification rate of decomposition, speeds for atomic diffusion, and critical time for instability) in comparison with the outcomes of the Cahn-Hilliard theory. From the analytical treatments it is shown that the hyperbolic model predicts non-linearity in the amplification rate of decomposition, which is governed by the ratio between diffusion length and correlation length.

Keywords:Spinodal, diffusion, relaxation, model, local nonequilibrium

# 1. Introduction

Phase transformation in which both phases have equivalent symmetry but differ only in composition is well-known as spinodal decomposition. This transformation was described by Cahn and Hilliard (1958) and Cahn (1961). It was widely investigated by using theoretical and experimental methods [see overviews of Skripov (1979); Beysens (1986); Binder and Fratzl (2001); Ustinovshchikov Pushkarev and (2006)]. Particularly, it has been shown that 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 exhibit non-linear behavior in dispersion relation in contradiction with predictions of the Cahn-Hillard theory [see Andreev et al. (1970)]. According to the theory, only systems with long-range interaction may behave linearly during the early stage of spinodal decomposition [see Binder (1984); Binder and Fratzl (2001)]. This theoretical result has not been observed experimentally in systems with shortrange interaction because non-linear or nonequilibrium effects become important for systems rapidly quenched or deeply supercooled into the spinodal region of a phase diagram.

Recently, the Cahn-Hillard theory has been modified by taking into account the relaxation of the atomic diffusion flux to its local steady state [Galenko (2001); Galenko and Jou (2005)]. The flux has been chosen as an additional independent thermodynamic variable in consistency with the extended irreversible thermodynamics of Jou, Casas-Vazquez and Lebon (2001). Using such a model, one can predict the very first stages of decomposition when the flux rapidly changes and relaxes to its local equilibrium steady state. Such description allows for prediction of the earliest stages of decomposition, intermediate regimes, and the latest stages of decomposition.

Recently, the hyperbolic model has been analyzed mathematically [see Gatti et al., 2005a] and, especially, tested against experimental data [see Galenko and Lebedev (2008)]. It has been demonstrated that the model has good agreement between theoretical prediction for amplification rate and experimental data extracted from light scattering on spinodally decomposed glass.

In the present article, the hyperbolic model of spinodal decomposition is further explored. We analyze the effect of local nonequilibrium on the amplification rate of decomposition, characteristic diffusion speeds and critical time for instability against perturbation of concentration.

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#### 2. Hyperbolic Spinodal Decomposition

Consider an isothermal binary system as an isotropic solid solution free from imperfections and with the molar volume independent of both atomic concentrations. Then, to describe rapid spinodal decomposition for such a system, the following entropy functional is used:

$$S = \int_{\Omega} \left[ s(c, \vec{J}) - \frac{1}{2} \varepsilon_c^2 \left| \nabla c \right|^2 \right] d\Omega \,. \tag{1}$$

where s is the entropy density based on the extended set  $\{c, \vec{J}\}$  of independent thermodynamic variables in which c is the concentration and  $\vec{J}$  is the atomic diffusion flux,  $\varepsilon_c^2$  the factor proportional to correlation length (i.e., so-called "gradient energy coefficient"), and a is the volume of the considered system.

In the functional (1) the gradient term is used to describe a spatial inhomogeneity within the diffusion field according to previously formulated models for phase transitions [see Ginzburg and Landau (1950); Cahn and Hilliard (1958); Allen and Cahn (1979)]. It is logical to include gradient terms in Equation (1) because the interest in description of the complete scenario from earliest to latest stages of decomposition is focused on interfaces between phases with both steep concentration gradients and small gradients. In addition to the classic approach of Ginzburg and Landau (1950), the entropy density *s* is based on the flux  $\vec{J}$  as the independent variable from the set  $\{c, \vec{J}\}$  of the thermodynamic variables.

Entropy density *s* is an additive function of its local equilibrium contribution  $s_{eq}(c)$  and its pure non-equilibrium contribution  $s_{nea}(J)$ , i.e.

$$s(c, \vec{J}) = s_{eq}(c) + s_{neq}(\vec{J})$$
. (2)

Non-equilibrium contribution in Equation (2) can be expanded in series as follows

$$s_{neq}(\vec{J}) = \frac{\partial s}{\partial \vec{J}} \vec{J} + \frac{1}{2} \frac{\partial^2 s}{\partial J^2} J^2 + \frac{1}{6} \frac{\partial^3 s}{\partial \vec{J}^3} \vec{J}^3 + \dots$$
(3)

Taking linear proportionality for the derivative [Jou et al., 2001],  $\partial s / \partial \vec{J} = \alpha_J \vec{J}$ , one can omit terms with the power of quadratic and higher order in the expansion (3) for the first order of approximation. Then, Equation (2) holds

$$s(c, \vec{J}) = s_{eq}(c) + \frac{\alpha_J}{2} J^2,$$
 (4)

where  $\alpha_J$  is the coefficient independent on the fast variable  $\vec{J}$ .

Equation (4) shows that the entropy s has a standard local equilibrium contribution  $s_{eq}$  and contribution  $s_{neq}$  explicitly dependent on fast variables. As it is well established in classic **22** Int. J. of Thermodynamics, Vol. 11 (No. 1)

irreversible thermodynamics [see Prigogine (1967); Glansdorff and Prigogine (1971)], thermodynamic functions (entropy, free energy, chemical potential) are strictly defined only for locally equilibrium states. Therefore, Equation (4) can be specially explained in the following way. For the local equilibrium part  $s_{eq}$  a local ergodicity (that is, the system needs to sample the phase space) is true. However, as soon as we postulate diffusion flux with its own finite relaxation times, this means that the local nonequilibrium contribution  $\alpha_J J^2/2$  assumes the existence of slow physical processes, which are the thermal conduction and/or jump of solute atoms [Jou and Galenko (2006)]. Considering ergodicity of a phase space for non-equilibrium situation, one may well refer to statistical effects in fast phase transition due to the existence of many particles (atoms and molecules) within local volumes. Since we consider the phase transition in high frequency approximation, the particles have not 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 a decrease in the entropy with respect to the local equilibrium contribution  $s_{eq}$ . This is one of the ways to interpret the non-equilibrium contribution  $s_{nea}$  to the entropy (4).

Using Equation (4), the nonlinear equation for spinodal decomposition derived from the entropy functional (1) [see Galenko (2001); Galenko and Jou (2005)] is described by

$$\tau_{D} \frac{\partial^{2} c}{\partial t^{2}} + \frac{\partial c}{\partial t} = \nabla \cdot \left[ M \nabla \left( f_{c}^{'} - \varepsilon_{c}^{2} \nabla^{2} c \right) \right], \quad (5)$$

Here: t the time,  $\tau_D$  the time for relaxation of the diffusion flux to its steady state, M the atomic mobility, and  $f'_c = df/dc$  the derivative from free energy density f with respect to concentration. For the initial stages of decomposition one can neglect all terms nonlinear in concentration. Then Equation (5) yields

$$\tau_D \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = M f_{cc}^{"} \nabla^2 c - M \varepsilon_c^2 \nabla^4 c, \qquad (6)$$

where  $f_{cc}^{"} = d^2 f / dc^2$ .

Equation. (6) has been characterized by Gatti et al. (2005b) as a singularly perturbed Cahn-Hilliard type equation. Indeed, this equation is interpreted in consistency with classification of linear equations of the second order, then it might be treated as the singularly perturbed equation (due to assumption of a small coefficient  $\tau_D$  at the second derivative with respect to time). However, one may also consider

Eq. (6) as a limiting equation from the hyperbolic side which is characterized by a large value for the coefficient  $1/\tau_D$  at the first derivative with respect to time. In this limiting case, there are not singularities and Equation (6) might be considered as hyperbolic.

#### 3. Dispersion Relation

Considering the elementary exponential solution of Equation (6) of the form

$$c(z,t) - c_0 = a_k \exp[i(kz - \omega(k)t)], \qquad (7)$$

one can write the dispersion relation  $\omega(k)$  as

$$\omega(k) = -\frac{i}{2\tau_D} \pm \left(\frac{Mk^2 \left(f_{cc}^* + \varepsilon_c^2 k^2\right)}{\tau_D} - \frac{1}{4\tau_D^2}\right)^{1/2}, \quad (8)$$

The upper and lower signs for  $\omega(k)$  in Equation (8) correspond to the branches which are responsible for the wave propagation in the positive and negative *z*-directions, respectively.

Qualitative behavior for  $\omega(k)$  is shown in Fig. 1. The real part of  $\omega(k)$  begins to exist only from some critical value  $k = k_0$ , Figure 1(a). This value defines the confluence of two branches for the imaginary part of  $\omega(k)$ , Figure 1(b). Also, one can define two other critical values for the wavevector k. The critical value  $k = k_c$  defines a point from which  $\omega$ takes positive values of its imaginary part, Fiure. 1(b). For  $k < k_c$  solution (7) exponentially grows in time and decomposition begins to irreversibly proceed. The critical value  $k = k_m$  gives a maximal positive value for  $\omega$ , Figure 1(b). Frequency  $\omega(k_m)$  defines the mostly unstable mode with which a pattern evolves during phase decomposition.

Note that Equations. (7)-(8) describe the evolution of patterns in spinodal decomposition under local nonequilibrium conditions. It can be seen by taking the real part of solution (7) in the following form:

$$c(z,t) - c_0 = a_k(k,0) \exp[\omega(k)t] \exp(kz) .$$
(9)

Then the solution of Equation (6) is described by:

$$\omega(k)\left[1+\omega(k)\tau_D\right] = -Mk^2 \left[f_{cc}^{"}+\varepsilon_c^2 k^2\right]. \quad (10)$$

From this it follows that with low frequency for concentration propagation, i.e. for  $\omega \tau_D \ll 1$ , the usually applied "hydrodynamic approximation" is true. In this case, one can neglect the term with relaxation time in Euation. (6). However, at a high frequency of concentration propagation, i.e. for  $\omega \tau_D \gg 1$ , violation of "hydrodynamic approximation" occurs for the system. In such a case, approximation of local equilibrium relaxes within the system which has to be described by Equation (6).

# 4. Characteristics of Spinodal Decomposition

In the present section we summarize results on the main features of hyperbolic spinodal decomposition described by Equation (6). These are the amplification rate of decomposition, speeds for atomic diffusion (namely, phase speed and group speed), and critical time for instability.



Figure 1. Dispersion relations for hyperbolic (the presently modified Cahn-Hilliard) equation, Eq. (8). (a) Real part of frequency,  $\operatorname{Re}(\omega(k))$ . (b) Imaginary part of frequency,  $\operatorname{Im}(\omega(k))$ .

#### 4.1. Amplification rate of decomposition

Using a dispersion relation (8) one can find the rate of decomposition which is characterized by the irreversibly growing wavelength of decomposition. For the region of phase diagram, in which spinodal decomposition proceeds,  $f_{cc}^{"} < 0$ , this yields [see Galenko and Lebedev (2008)]:

$$\frac{\omega^*}{q^2} = \frac{1}{q^2} \cdot \frac{\omega(k)}{\omega(k_m)}$$

or

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$$\frac{\omega^*}{q^2} = \frac{1}{q^2} \cdot \frac{1 - \sqrt{1 + q^2 (1 - q^2) (l_D / l_C)^2}}{1 - \sqrt{1 + (l_D / l_C)^2}}.$$
 (11)

Equation (11) can be interpreted as the kinetic amplification rate for both dissipative and propagative regimes of atomic transport as described by Equation (6).

The following notations are used in Equation (11):

$$l_D = (D\tau_D)^{1/2}$$
 and  $l_C = \varepsilon_C / (-f_{cc})^{1/2}$  (12)

are the diffusion length and correlation length, respectively;  $D = -Mf_{cc}^*$  is the diffusion constant;  $\omega^* = \omega(k) / \omega(k_m)$  is the dimensionless amplification rate in which

$$\omega(k) = \frac{-1 + \sqrt{1 + 4l_D^2 k^2 (1 - l_C^2 k^2)}}{2\tau_D}$$
(13)

is the dimensional amplification rate,

$$\omega(k_m) = M \left[ f_{cc}'' / (2\varepsilon_c) \right]^2 = \frac{(l_D / l_C)^2}{4\tau_D}$$
(14)

is the dimensional amplification rate at the wave number  $k_m$  and wavelength  $\lambda_m$ 

$$k_m = 2\pi / \lambda_m = 1/(\sqrt{2}l_C),$$
 (15)

giving a maximum amplification rate (see *Figure 1*);

$$k_c = 2\pi / \lambda_c = 1/l_C \tag{16}$$

is the critical wave number  $k_c$  and wavelength  $\lambda_c$ (see *Figure 1*); and  $q = k/k_c$  is the dimensionless wave number with respect to its critical value  $k_c$ . As it follows from Equations. (15) and (16), the maximum amplification rate allows for the wavelength  $\lambda_m$  greater in exactly  $\sqrt{2}$  times the critical wavelength  $\lambda_c$  of instability against fluctuations of concentration.

Equation (11) is true for both regimes: (i) regime with finite  $\tau_D$  (local nonequilibrium situation with violation of the standard "hydrodynamic approximation"); and (ii) regime with vanishing relaxation time (local equilibrium situation described by the standard "hydrodynamic approximation"). The first regime (i) occurs for significant deviations from local equilibrium in the diffusion field. It exists at the initial stages of decomposition in which the short range interaction between atoms (particles) becomes significant. Therefore Equation (11) predicts the behavior, when the length of local nonequilibrium is larger or comparable with the correlation length,  $l_D \ge l_C$ . The second regime (ii) occurs when the correlation prevails in the system,  $l_C >> l_D$ . It is described by the Cahn-Hilliard scenario, which 24 Int. J. of Thermodynamics, Vol. 11 (No. 1)

can be obtained from Equation (11) for the small ratio  $l_D / l_C$  as

$$\frac{\omega^{*}}{q^{2}} = \frac{1}{q^{2}} \cdot \frac{\omega(k)}{\omega(k_{m})} = 4(1 - q^{2}).$$
(17)

This equation exhibits linear dependence of  $\omega^*/q^2$  from  $q^2$  which occurs only in systems with long range interaction [Binder (1984)] and practically is not observable [Binder and Frantzl (2001)].

From Equations. (11)-(17) it follows that the ratio  $l_D/l_C$  between diffusion and correlation lengths governs the mechanism of transition from a homogeneous unstable state to heterogeneous metastable and stable states. This fact is clearly shown in Figure 2. At the early stage of decomposition, when the effects of local nonequilibrium plays a crucial role, the length of nonequilibrium  $l_D$  is essentially larger than the length of correlation  $l_C$ . In this case, one gets  $l_D >> l_C$  and non-linearity is clearly seen in the amplification rate (see the solid line in *Figure 2*). With the formation of developed patterns, the correlation length  $l_C$  increases in comparison with the diffusion length  $l_D$ . With  $l_D \ll l_C$ , amplification rate tends to linear law predicted by Cahn and Hilliard (see dashed-dotted and dotted lines in Figure 2).



Figure 2. Comparison of the function  $\omega^* / q^2$ predicted by the parabolic diffusion equation (Cahn-Hilliard model) and the hyperbolic diffusion equation (presently the modified Cahn-Hilliard model). Curves are given for various values of the ratio  $l_D / l_C$  between diffusion length and correlation length, respectively.

# 4.2. Phase speed

If the expression under square root of Equation (8) is positive, then the speed of propagation has the real finite value. Values of the wave vector  $k_0$  above which relation (8) has the real part, *Figure 1(a)*, is found from condition

$$k_0^2 = \frac{1}{2\varepsilon_c^2} \left( \sqrt{\left( -f_{cc}^{"} \right)^2 + \frac{\varepsilon_c^2}{\tau_D M}} - f_{cc}^{"} \right).$$
(18)

For  $k^2 > k_0^2$ , one can obtain from Equation (8) the real part of the phase speed:

$$v_p = \operatorname{Re}(\omega) / \operatorname{Re}(k) \tag{19}$$

$$=\tau_D^{-1} \left( \tau_D M(f_{cc}^* + \varepsilon_c^2 k^2) - (2k)^{-2} \right)^{1/2}.$$

This expression describes propagation in both positive and negative spatial directions.

The speed  $v_p$  incorporates a motion for one of the separated single harmonics. It can be compared with the predictions of the partial differential equation of a hyperbolic type for solute diffusion without phase separation. Indeed, analysis of dispersion relation for mass transport Equation (6) at  $\varepsilon_c = 0$  leads to the following expression [see, e.g., Galenko (2002)]:

$$v_p = \left(\frac{2D}{\tau_D + (\tau_D^2 + \omega^{-2})^{1/2}}\right)^{1/2}.$$
 (20)

Equation (19) arrives at Equation (20) with  $\varepsilon_c = 0$ and  $-Mf_{cc}^{"} = D$ . Using the proportionality  $k \propto \omega$ for the high frequency of disturbance's propagation, one can see that both expressions (19) and (20) lead to the same result:

$$v_p = (D / \tau_D)^{1/2} = V_D$$
 with  $\omega \to \infty$ . (21)

Therefore, phase speed  $v_p$  is equal to solute diffusion speed  $V_D$  which is a maximal speed for propagation of the solute diffusion disturbance (profile).

The imaginary part of the phase speed,  $Im(v_p) = i/(2\tau_D k)$ , specifies the amplification rate for a given harmonic. With  $k < k_0$ , harmonics do not move with possible changing of their own amplitudes. For both real and imaginary parts of  $v_p$ , i.e., with  $k > k_0$ , the harmonics move and change their own amplitudes. The behavior is shown in *Figure 3* for  $v_p$ .

#### 4.3. Group speed

Concentration disturbances propagating by diffusion can be considered as an undistorted wave packet moving with the group speed given by

$$\partial \omega(k) / \partial k = \pm W(k) \,. \tag{22}$$

Using Equation (8) calculation of the group speed W gives

$$W(k) = \frac{2kM(f_{cc}^{"} + 2\varepsilon_c^2 k^2)}{\left(4\tau_D^2 k^2 M(f_{cc}^{"} + \varepsilon_c^2 k^2) - 1\right)^{1/2}} \cdot (23)$$

Dependence W(k) is shown in *Figure 3* and it specifies a speed for a concentration profiles envelope. One may see that, as for the phase speed  $v_p$ , the real values for W given by Equation (23) exist only at  $k > k_0$ . In contrast with the behavior of  $v_p$ , the imaginary part of W(k) may exist only at  $k < k_0$ .



Figure 3. Phase and group speeds for hyperbolic Cahn-Hilliard equation. (a) Real part  $\operatorname{Re}(v_p)$  of phase speed (solid line) and real part  $\operatorname{Re}(W)$  of group speed (dashed-dotted line). (b) Imaginary part  $\operatorname{Im}(v_p)$  of phase speed (solid line), and imaginary part  $\operatorname{Im}(W)$  of group speed (dasheddotted line).

#### 4.4. Critical time for instability

Let us evaluate the time of the transitive period from the beginning of instability (with the beginning of growth of infinitesimal perturbation) up to arriving into the new metastable state. For the fastest growth of infinitesimal perturbation the maximal frequency  $\omega(k_m)$  is responsible. Therefore substitution of Equation (14) into dispersion relation (8) leads to

$$\omega_m(k_m) = -\frac{i}{2\tau_D} \left[ l \pm (1 + M\tau_D(f_{cc}^{"})^2 / \varepsilon_c^2)^{1/2} \right]$$

$$= -\frac{i}{2\tau_D} \left[ l \pm (1 + (l_D / l_C)^2)^{1/2} \right]$$
(24)

Equation (24) adopts both real and imaginary parts for  $\omega$  and, using the maximal frequency (24), solution (7) can be rewritten as

$$c(z,t) - c_0 = a_k \exp(ikz) \exp(t/t_c), \qquad (25)$$

where

$$t_{c} = \frac{2\tau_{D}}{\left[1 + M\tau_{D}(f_{cc}^{"})^{2} / \varepsilon_{c}^{2}\right]^{1/2} - 1}, \qquad (26)$$
$$= \frac{2\tau_{D}}{\left[1 + (l_{D} / l_{C})^{2}\right]^{1/2} - 1}$$

is the time for developing coherent structure due to instability in the system under spinodal decomposition. Equation (26) can be used to evaluate the transitive period from one metastable state to the other one.

If the time for decomposition is of the order of or smaller than the relaxation time,  $t_c \leq \tau_D$ , then the effects of local nonequilibrium in the diffusion field become pronounced. Therefore, using Equation (26), one can predict that the effect of local non-equilibrium on decomposition becomes very significant if one has the following inequality:  $l_D > 2\sqrt{2}l_C$ . In this case, the traditional "hydrodynamic approximation" (which is true for long wavelengths and low frequencies of disturbances propagation) breaks and the system needs to be described by the local nonequilibrium model. The simplest model with local nonequilibrium effect of atomic diffusion on spinodal decomposition is presented by the hyperbolic Equations. (5) and (6).

Within the local equilibrium limit,  $\tau_D \rightarrow 0$ , one can expand square root in Equation (26) for  $M\tau_D (f_{cc}^{"})^2 / \varepsilon_c^2 = (l_D / l_C)^2 \ll 1$ . In this case, we arrive at the following approximation

$$t_c = \frac{4\varepsilon_c^2}{M(f_{cc}^{"})^2}$$
 (27)

This expression for the time of instability is found from the predictions of the pure diffusion theory (parabolic transport equation) of Cahn and Hilliard.

# 5. Conclusions

Following the thermodynamic approach to rapid phase transitions, a model for kinetics of fast

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spinodal decomposition has been further developed. The present model gives the modified Cahn-Hilliard equation, Equation (5), which describes the spinodal decomposition for both diffusion and wave propagation of atoms. In such a case, the equation predicts a rate for fast separation which is compatible with the atomic diffusion speed.

The analysis leads to the obtaining of the phase and group atomic speeds. The real values for the speeds define the finite propagation of a single harmonic (for the phase speed) and a packet of harmonics (for the group speed). The group speed always has a finite value. Thus, we consider the present equation for spinodal decomposition (6) as a limiting equation from the hyperbolic side but with a large coefficient at the first derivative with respect to time.

The model is able to give prediction for scenario from very earliest up to latest stages of decomposition. spinodal Particularly, for  $l_D >> l_C$  and  $t_c \leq \tau_D$ , the usual "hydrodynamic approximation" breaks and one has to describe the process by taking into account local nonequilibrium. In the present work we used a hyperbolic model adopting the final diffusion speed (so-called "modified model of Cahn and Hilliard"). Such a model works properly at the very first stages of decomposition under local nonequilibrium conditions. It predicts a gradual transformation from local nonequilibrium decomposition existing at the very first stages to the latest stages existing with  $l_D \ll l_C$  and  $t_c >> \tau_D$ . The latter inequalities characterize the "hydrodynamic standard approximation" describing parabolic type of equation for diffusion and phase separation during spinodal decomposition (classic Cahn-Hilliard model).

As a final note, several generalizations of the present model can be outlined. First, an introduction into the model fluctuations in a manner of Cahn-Hilliard-Cook model [see Cook (1970)] can be made. As an extension of the present linear Equation (6), fluctuations can be introduced using analysis of a generalized diffusion equation as described by Jou and Galenko (2006). 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 nonlinear equation (5) have 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. (1975) or using "power's expansion" suggested by Grant et al. (1985). Comparison of the outcomes from non-linear hyperbolic model

and from the well-known non-linear theories based on the parabolic diffusion equation [see Cook (1970); Langer et al. (1975); Grant et al. (1985)] can be seen as a very attractive point of investigation.

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#### Nomenclature

- $a_k$ amplitude for concentration (atomic fraction)
- concentration (atomic fraction) c
- D diffusion constant  $(m^2/s)$
- free energy density  $(J/m^3)$ f
- imaginary unit i
- Ĵ vector of atomic diffusion flux (atomic fraction m/s)
- k wave – vector  $(m^{-1})$
- $k_c$ critical wave-number for beginning of the irreversible growth of instability (m<sup>-1</sup>)
- $k_m$ wave-number for the selected maximum wavelength  $(m^{-1})$
- value for wave vector above which  $k_0$ dispersion relation has a real part  $(m^{-1})$
- correlation length (m)  $l_{C}$
- diffusion length (m)  $l_D$
- atomic mobility  $(m^{5}(atomic fraction)^{2}/s/J)$ M
- dimensionless wave number q
- S total entropy in a system (J/K)
- entropy density (J/K/m<sup>3</sup>) S
- equilibrium part of the entropy density  $S_{eq}$  $(J/K/m^3)$
- non-equilibrium part of entropy density  $S_{neq}$  $(J/K/m^3)$
- time (s) t
- time for instability (s)  $t_c$
- phase speed (m/s)
- $v_p V_D$ diffusion speed (m/s)
- W group speed (m/s)
- spatial coordinate (m)  $\overline{Z}$

### Greek

- thermodynamic coefficient  $\alpha_{J}$  $(Js^2/m^5/(atomic fraction)^2)$
- $\varepsilon_c^2$ factor proportional to correlation length ("gradient energy coefficient")  $(m/J^{1/2}m^{3/2})$
- critical wavelength of instability (m)  $\lambda_c$
- maximum wavelength of the irreversibly  $\lambda_m$ growth pattern (m)
- mathematical constant, 3.1415926...  $\pi$
- time for relaxation of the diffusion flux (s)  $\tau_D$

- Ω the volume of the considered system  $(m^3)$
- $\omega(k)$ dispersion relation (cyclic frequency of the planar wave,s<sup>-1</sup>)
- $\omega$ dimensionless amplification rate

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