$See \ discussions, stats, and author \ profiles \ for \ this \ publication \ at: \ https://www.researchgate.net/publication/274897845$ 

# On the mesoscopic description of locally nonequilibrium solidification of pure sustances

### Article in JETP Letters · January 2015

DOI: 10.1134/S0021364015020101

CITATIONS 3	5	reads 89	
3 authors, including:			
0	Vladimir Lebedev Udmurt State University 44 PUBLICATIONS 490 CITATIONS SEE PROFILE	8	Peter Galenko Friedrich Schiller University Jena 356 PUBLICATIONS 4,791 CITATIONS SEE PROFILE
Some of the authors of this publication are also working on these related projects:			

Project Microstructure formation in sintering of gradient materials by additive manufacturing, 2014-2016 View project

uK-China Royal Society Exchange View project

## On the Mesoscopic Description of Locally Nonequilibrium Solidification of Pure Substances

V. G. Lebedev<sup>a</sup>, \*, A. A. Lebedeva<sup>a</sup>, and P. K. Galenko<sup>b, c</sup>

<sup>a</sup> Udmurt State University, ul. Universitetskaya 1, Izhevsk, 426034 Russia

\* e-mail: lvg@udsu.ru

<sup>b</sup> Physikalisch–Astronomische Fakultät, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany <sup>c</sup> Ural Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia

Received December 1, 2014

A phase field model of locally nonequilibrium solidification of a supercooled melt of a pure substance has been proposed. To derive thermodynamically consistent equations of the model, the method of extended irreversible thermodynamics has been used. It has been assumed that Gibbs potentials describing thermodynamically equilibrium states in terms of experimental data are known. The limit of a sharp interface of the model has been considered and an analytical dependence of the velocity of a flat solidification front on the temperature has been obtained.

DOI: 10.1134/S0021364015020101

The idea of the use of a diffuse interface for the description of interphase phenomena goes back to van der Waals [1], Landau [2, 3], and Cahn, Hilliard, and Allen [4-6]. The first models with a diffuse interface for solidification processes were formulated and analyzed by Collins and Levine [7], Langer [8], and Caginalp [9]. The phase field method [10], which is an efficient method for the description of the evolution of microstructures in phase transitions, is a modern development of these models. However, nonisothermal phase-field models used at present have model phenomenological origin [11], which can be analyzed at thermodynamically consistent derivation of equations. The aim of this work is to derive a thermodynamically consistent model of solidification of pure substances based on locally nonequilibrium thermodynamics [12] and equilibrium Gibbs potentials [13]. The resulting equations of the phase field model are hyperbolic. For this reason, for their comparison with the equations of the Stefan hyperbolic problem [14], we used the sharp-interface limit [9, 15].

In order to describe states of a continuum medium of a solidifying system, we introduce the parameter  $\varphi$ (phase field), which is  $\varphi = 1$  in a solid phase (*S*) and  $\varphi = 0$  in a liquid phase (*L*). The definiteness of a local phase state is violated near the interface between phases, which has a small but finite thickness. The bulk properties of phases inside the diffuse interface are interpolated by the functions

$$p(\phi) = \phi^2(3 - 2\phi), \quad g(\phi) = \phi^2(1 - \phi)^2,$$
 (1)

which were chosen owing to the requirement of the stability of phases [16].

The potential determining the relaxation of the nonequilibrium nonisothermal system is the entropy thermodynamically conjugate with the temperature:

$$S = -\int \left(\frac{\partial G}{\partial T} + \frac{1}{T_{\rm m}}\varepsilon\right) dV, \qquad (2)$$

where G = G(T, P) is the Gibbs potential density and  $T_{\rm m}$  is the phase equilibrium temperature. The energy density

$$\varepsilon = \frac{1}{2} [\beta \mathbf{J}^2 + \gamma \dot{\phi}^2 + \sigma (\nabla \phi)^2]$$
(3)

includes the contribution from nonequilibrium effects [12]. In Eq. (3), **J** is the heat flux and  $\beta$ ,  $\gamma$ , and  $\sigma$  are the kinetic coefficients defined below. The dot over a symbol means the time derivative.

We neglect change in the volume at solidification, assuming that the phase transition occurs at a constant pressure and is completely controlled by the temperature. We determine the total Gibbs energy density as the interpolation in the Gibbs potential densities of each of the phases  $G^{(\alpha)}(T)$ :

$$G(T,\phi) = G^{(S)}(T)p(\phi) + G^{(L)}(T)[1-p(\phi)] + W_g(\phi),(4)$$

where W is the height of the potential barrier between the states S and L.

The dynamic equations follow from the condition of increasing entropy (2) during relaxation to equilibrium [17] and have the form

$$\begin{cases} \tau_{\varphi}\ddot{\varphi} + \dot{\varphi} = M_{\varphi} \bigg[ \sigma \nabla^{2} \varphi - \frac{T_{m}}{T} \frac{\partial G}{\partial \varphi} \bigg] \\ C_{p}\dot{T} + \nabla \cdot \mathbf{J} = - \bigg( \frac{\partial G}{\partial \varphi} - T \frac{\partial^{2} G}{\partial T \partial \varphi} \bigg) \dot{\varphi} \\ \tau_{T} \frac{\partial}{\partial t} \mathbf{J} + \mathbf{J} = -\kappa \nabla T. \end{cases}$$
(5)

The specific heat at constant pressure is defined as  $C_p = -T\partial^2 G(T, \varphi)/\partial T^2$ ;  $\tau_{\varphi} = M_{\varphi}\gamma$  and  $\tau_T = M_T(T)\beta/T_m$  are the characteristic relaxation times of the phase field and thermal flux, respectively;  $\kappa = M_T(T)/T^2$  is the thermal conductivity; and  $M_T(T) > 0$  and  $M_{\varphi}(T) > 0$  are the mobilities of the temperature and phase fields, respectively. In the locally equilibrium limit (i.e., at  $\tau_T = 0$  and  $\tau_{\varphi} = 0$ ), Eqs. (5) are reduced to the parabolic model of the phase field and the heat conduction equation with a source inside the diffuse interface (see [9, 16]).

Denoting differentiation with respect to the argument of a function by a prime,

$$p'(\phi) \equiv \frac{d}{d\phi} p(\phi), \quad \Delta G'(T) \equiv \frac{d}{dT} \Delta G(T),$$

and denoting the differences of the Gibbs potentials and internal energies (U = G - TG'(T)) as

$$\Delta G(T) = G^{(S)}(T) - G^{(L)}(T),$$
  
$$\Delta U(T) = U^{(S)}(T) - U^{(L)}(T),$$

we represent the right-hand sides of Eqs. (5) in the explicit form

$$\begin{cases} \tau_{\varphi}\ddot{\varphi} + \dot{\varphi} = M_{\varphi} \bigg\{ \sigma \nabla^{2} \varphi - \frac{T_{m}}{T} [Wg'(\varphi) + \Delta Gp'(\varphi)] \bigg\} \\ C_{p}\dot{T} + \nabla \cdot \mathbf{J} = -[Wg'(\varphi) + \Delta Up'(\varphi)]\dot{\varphi} \\ \tau_{T} \frac{\partial}{\partial t} \mathbf{J} + \mathbf{J} = -\kappa \nabla T. \end{cases}$$
(6)

In the case of equilibrium between the phases (i.e., at  $\dot{\phi} = 0$ ,  $\dot{T} = 0$ ,  $\mathbf{J} = 0$ ), from Eqs. (6) for the temperature, we obtain

$$c\nabla T = 0 \implies T = T_{\rm m} \equiv \text{const} \tag{7}$$

throughout the entire space. Equation (6) for the phase field is reduced to the expression

$$\sigma \nabla^2 \varphi - [Wg'(\varphi) + \Delta G(T_m)p'(\varphi)] = 0.$$
 (8)

Taking into account that the difference between Gibbs potentials at  $T = T_m$  is  $\Delta G(T_m) = \text{const}$ , we consider Eq. (8) in the one-dimensional case, denoting

JETP LETTERS Vol. 101 No. 2 2015

the coordinate along the solidification direction as *z*. Multiplying Eq. (8) by  $\varphi'(z)$  and integrating over an infinite interval taking into account the equality  $\varphi'(\pm \infty) = 0$ , we obtain the thermodynamic equilibrium condition in the form

$$\Delta G(T_{\rm m}) = 0 \Longrightarrow G^{(S)}(T_{\rm m}) = G^{(L)}(T_{\rm m}), \tag{9}$$

which determines the temperature  $T_{\rm m}$ .

Under the equilibrium conditions, Eq. (8) becomes

$$\sigma \varphi'' = Wg'(\varphi), \tag{10}$$

which has a "kink" solution:

$$\varphi(x) = \frac{1}{2} [1 - \tanh(z/\delta)],$$
 (11)

where the parameter

$$\delta = \sqrt{\frac{2\sigma}{W}} \tag{12}$$

specifies the characteristic width of the diffuse interface.

The integration of the gradient contribution to potential (2) for equilibrium solution (11) gives the surface energy

$$\frac{1}{2}\sigma\int_{-\infty}^{\infty} \left[\varphi'(z)\right]^2 dz = \frac{\sigma}{6\delta} = \chi, \qquad (13)$$

where  $\chi$  is the surface tension coefficient of the interface. The coefficients  $\sigma$  and W are defined in terms of  $\delta$  and  $\chi$  as

$$\sigma = 6\chi\delta, \quad W = \frac{12\chi}{\delta}.$$
 (14)

In the absence of equilibrium between the phases,  $G^{(S)}(T) \neq G^{(L)}(T)$ , for the dynamics of the phase field in Eqs. (6), a driving force of a phase transition  $p'(\varphi)\Delta G(T)T_m/T$  appears, which is nonzero only inside the diffuse interface and determines the velocity of the solidification front.

We show that the Stefan hyperbolic problem [14] follows from the system of Eqs. (6) in the sharp-interface limit [9, 15]. For simplicity, we consider the onedimensional problem of directional crystallization in order to avoid the effect of the curvature of the interface.

The sharp-interface limit is based on the assumption of the existence of the small parameter  $\overline{\delta} = \delta/L$ , where *L* is the characteristic size of the region where the phase transition occurs. We use the dimensionless coordinate  $\overline{z} = z/L$  and time divided by the characteristic time of the thermal process,  $\overline{t} = t\lambda_i/L^2$ , where  $\lambda_i = \kappa_i/C_i$ ,  $\kappa_i = \kappa(T_i)$ ,  $C_i = C_p(T_i)$ , and  $T_i$  is the initial

temperature of the melt. Then, the equations of model (6) can be represented in the form

$$\begin{cases} \bar{\tau}_{\varphi}\ddot{\varphi} + \dot{\varphi} = \alpha \left\{ \nabla^{2}\varphi - \frac{T_{m}}{T} [2g'(\varphi)\bar{\delta}^{-2} + \overline{\Delta G}p'(\varphi)\bar{\delta}^{-1}] \right\} \\ \bar{C}_{p}\dot{T} + \nabla \cdot \mathbf{j} = -F(\varphi, T)\dot{\varphi} \\ \bar{\tau}_{T}\frac{\partial}{\partial f}\mathbf{j} + \mathbf{j} = -\bar{\kappa}\nabla T. \end{cases}$$
(15)

The function  $F(\varphi, T)$  is defined as

$$F(\varphi, T) = \theta g'(\varphi) + \Delta U p'(\varphi).$$
 (16)

Dimensionless quantities in Eqs. (15) and (16) are given by the expressions

$$\bar{\tau}_{\varphi} = \frac{\tau_{\varphi}\lambda_i}{L^2}, \quad \alpha = \frac{M_{\varphi}(T)\sigma}{\lambda_i}, \quad \theta = \frac{12\chi}{C_i\delta}, \quad \bar{\tau}_T = \frac{\tau_T\lambda_i}{L^2},$$
$$\overline{\Delta U} = \frac{\Delta U(T)}{C_i}, \quad \overline{\Delta G} = \frac{L\Delta G(T)}{6\chi},$$
$$\bar{\kappa} = \frac{\kappa(\varphi, T)}{\kappa_i}, \quad \bar{C}_p = \frac{C_p(\varphi, T)}{C_i}, \quad \mathbf{j} = \frac{\mathbf{J}L^2}{\kappa_i}.$$

Since the dimensionless coefficients do not change under a change in the scale, we consider the limiting transition  $\overline{\delta} \rightarrow 0$  in solutions of Eqs. (15).

## Region external with respect to the diffuse interface.

We multiply the phase field equation in Eqs. (15) by  $\overline{\delta}^2$ and pass to the limit  $\overline{\delta} \rightarrow 0$ . Then, the phase field equation is reduced to the form

$$g'(\phi)=0.$$

This relation is automatically satisfied beyond the diffuse interface because  $\varphi = 0$  and  $\varphi = 1$  in the volume of a phase. Since  $\varphi$  is constant in the volumes of the phases,  $\dot{\varphi} = 0$ . As a result, the remaining equations in Eqs. (15) are written in the form

$$\begin{cases} \overline{C}_{p}\dot{T} + \nabla \cdot \mathbf{j} = 0\\ \overline{\tau}_{T}\frac{\partial}{\partial t}\mathbf{j} + \mathbf{j} = -\overline{\kappa}\nabla T. \end{cases}$$
(17)

Equations (17) are equivalent to the nonstationary heat conduction equation at  $\bar{\tau}_T = 0$  or to its singular expansion at  $\bar{\tau}_T \neq 0$  [12].

**Region inside the diffuse interface.** In the reference frame of the interface  $\bar{x} = \bar{z} - y(\bar{t})$ , moving with nondimensionality velocity  $v = \dot{y}$  and acceleration  $a = \ddot{y}$ , we take the coordinate origin corresponding to  $\varphi =$  1/2. In this case, the system of equations (15) has the form

$$\begin{cases} \alpha_{e} \varphi''(\xi) + (v + \bar{\tau}_{\varphi} a) \varphi'(\xi) \bar{\delta} \\ = \alpha \frac{T_{m}}{T} [2g'(\varphi) + \overline{\Delta G} p'(\varphi) \bar{\delta}] \\ \kappa_{e} T'(\xi) + j(\xi) \bar{\delta} = \bar{\tau}_{T} v^{2} F(\varphi, T) \varphi'(\xi) \\ v \bar{\tau}_{T} j'(\xi) - j(\xi) \bar{\delta} = \bar{\kappa} T'(\xi), \end{cases}$$
(18)

where  $\alpha_e = \alpha - \bar{\tau}_{\phi} v^2$ ,  $\kappa_e = \bar{\kappa} - \bar{\tau}_T v^2 \bar{C}_p$ , and the coordinate  $\bar{x} = \xi \bar{\delta}$  is introduced for convenient asymptotic analysis. Indeed, the width of the diffuse interface in the limit  $\bar{\delta} \rightarrow 0$  becomes infinite  $(-\infty < \xi < \infty)$  and independent of  $\bar{\delta}$ . Furthermore, it is taken into account in Eqs. (18) that the factor  $\bar{\delta}^{-1}$  appears in the derivatives with respect to the spatial coordinates under such a change. After a change of coordinates and scaling of variables, the factor  $\bar{\delta}^2$  appears in Eqs. (18). Here and below, it is assumed that the coefficients are positive, i.e.,  $\kappa_e > 0$  and  $\alpha_e > 0$ .

We seek the solution of system (18) for the functions  $\varphi(\xi)$ ,  $T(\xi)$ , and  $\mathbf{j}(\xi)$  in the form of asymptotic series,

$$f(\xi) = f_0(\xi) + f_1(\xi)\bar{\delta} + \dots,$$
(19)

in the powers of the small dimensionless parameter  $\overline{\delta}$ .

Order  $\overline{\delta}_0$ . We have the system of equations

$$\begin{cases} \alpha_{0e} \varphi_{0}^{"}(\xi) = 2 \frac{\alpha_{0} T_{m}}{T_{0}(\xi)} g^{'}(\varphi_{0}) \\ \kappa_{0e} T_{0}^{'}(\xi) = \bar{\tau}_{T} v^{2} F_{0} \varphi_{0}^{'}(\xi) \\ \kappa_{0e} j_{0}^{'}(\xi) = v \bar{\kappa}_{0} F_{0} \varphi_{0}^{'}(\xi), \end{cases}$$
(20)

where the coefficients are calculated on the solutions  $\varphi_0$  and  $T_0$ , in particular,  $\alpha_{0e} = \alpha_0 - \bar{\tau}_{\varphi}v^2$ ,  $\kappa_{0e} = \bar{\kappa}_0 - \bar{\tau}_T v^2 \bar{C}_p^0$ ,  $\alpha_0 = \alpha(T_0)$ ,  $\bar{\kappa}_0 = \bar{\kappa}(\varphi_0, T_0)$ ,  $\bar{C}_p^0 = \bar{C}_p(\varphi_0, T_0)$ , and  $F_0 = F(\varphi_0, T_0)$ .

At  $\xi \to \pm \infty$ , the limiting conditions for the phase field and temperature in the zeroth order should be consistent with the external functions:

$$\lim_{\xi \to -\infty} \varphi_0(\xi, t) = 1, \qquad (21)$$

$$\lim_{\xi \to \infty} \phi_0(\xi) = \lim_{\xi \to \pm \infty} \phi'_0(\xi) = 0, \qquad (22)$$

$$\lim_{\xi \to \pm \infty} T_0(\xi) = 0, \qquad (23)$$

$$\lim_{\xi \to \pm \infty} T_0(\xi) = T(\bar{x})|_{0 \pm 0}, \qquad (24)$$

JETP LETTERS Vol. 101 No. 2 2015

where  $T(\bar{x})|_{0\pm 0}$  are the temperatures in the external regions to the right (+0) and left (-0) of the diffuse interface (at  $\bar{x} = 0$ ).

In the case of locally nonequilibrium relaxation  $(\bar{\tau}_T > 0)$ , the temperature has a jump at the interface. The difference between the temperature on the right and left sides of the diffuse interface is

$$T|_{+0} - T|_{-0} = \tau_T v^2 \int_{-\infty}^{\infty} \frac{1}{\kappa_{0e}} F_0 \varphi'_0(\xi) d\xi.$$

Under the assumption of smallness  $\bar{\tau}_T v^2 \ll 1$  and weakly varying thermophysical properties, this temperature jump can be estimated as

$$T|_{+0} - T|_{-0} \approx -\tau_T v^2 \kappa_{*e}^{-1} \overline{\Delta U}^*,$$

where the coefficients were calculated at the temperature  $T^*$  at a certain internal point of the diffuse interface. The flux jump is given by a similar expression

$$|j|_{+0} - j|_{-0} = v \int_{-\infty}^{\infty} \frac{\overline{\kappa}_0}{\kappa_{0e}} F_0 \varphi'_0(\xi) d\xi \approx -v \overline{\kappa}_* \kappa_{*e}^{-1} \overline{\Delta U}^*$$

The phase field and temperature profiles inside the diffuse interface in the locally nonequilibrium case at a given velocity of the front v can be determined only numerically.

In the limit  $\bar{\tau}_T \rightarrow 0$ , the continuity of the temperature  $(T_0(\xi) \equiv \text{const})$  at the interface follows from Eqs. (20) and the expression for the flux jump becomes

$$|j|_{+0} - j|_{-0} = -v\overline{\Delta U}(T_0)$$

Under asymptotic conditions (21) and (22), the phase field profile is again given by Eq. (11) with the width of the diffuse interface smaller by a factor of  $\sqrt{\alpha_{0e}T_0/\alpha_0T_m}$ .

**Order**  $\bar{\delta}_1$ . The velocity of the front can be found from the conditions of solvability of the equations in the first order in  $\bar{\delta}$ :

$$\begin{cases} \hat{L}_{11}\phi_1(\xi) + \hat{L}_{12}T_1(\xi) = \Phi_{\phi}(\phi_0, T_0) \\ \hat{L}_{21}\phi_1(\xi) + \hat{L}_{22}T_1(\xi) = \Phi_T(\phi_0, T_0), \end{cases}$$
(25)

where

$$\Phi_{\varphi}(\varphi_0, T_0) = \frac{\alpha_0 T_m}{\alpha_{0e} T_0} \overline{\Delta G}_0 p'(\varphi_0) - \frac{v + \tilde{\tau}_{\varphi} a}{\alpha_{0e}} \varphi'_0(\xi), \quad (26)$$

$$\Phi_T(\varphi_0, T_0) = -\frac{j_0}{\overline{\kappa}_{0e}}, \qquad (27)$$

$$\hat{L}_{11}\phi_1(\xi) = \phi_1''(\xi) - \frac{2\alpha_0 T_m}{\alpha_{0e} T_0} g''(\phi_0) \phi_1(\xi), \quad (28)$$

JETP LETTERS Vol. 101 No. 2 2015

$$\hat{L}_{12}T_1(\xi) = -T_1(\xi)\frac{\partial}{\partial T_0} \left[\frac{2\alpha_0 T_m}{\alpha_{0e} T_0}g'(\varphi_0)\right], \qquad (29)$$

$$\hat{L}_{21}\phi_{1}(\xi) = -\tau_{T} v^{2} \left[ \frac{F_{0}}{\kappa_{0e}} \phi_{1}'(\xi) \right]$$
(30)

$$+ \varphi'_{0}(\xi) \frac{\partial}{\partial \varphi_{0}} \left( \frac{F_{0}}{\kappa_{0e}} \right) \varphi_{1}(\xi) ],$$
$$\hat{L}_{22} T_{1}(\xi) = T'_{1}(\xi)$$

$$-\tau_T v^2 \varphi'_0(\xi) \frac{\partial}{\partial T_0} \left( \frac{F_0}{\kappa_{0e}} \right) T_1(\xi), \qquad (31)$$

$$j_0(\xi) = \int_{-\infty}^{\infty} \frac{\overline{\kappa}_0}{\tau_T v} T_0'(y) dy.$$
(32)

The asymptotic limiting conditions at  $\xi \to \pm \infty$  for the phase field and temperature in the first order has the form

$$\lim_{\xi \to \pm \infty} \varphi_1(\xi) = \lim_{\xi \to \pm \infty} \varphi'_1(\xi) = 0, \qquad (33)$$

$$\lim_{\xi \to \pm \infty} T_1(\xi) = 0, \qquad (34)$$

$$\lim_{\xi \to \pm \infty} T'_1(\xi) = T'(\bar{x})|_{0 \pm 0}, \qquad (35)$$

where  $T'(\bar{x})|_{0\pm 0}$  are the temperature gradients taken from the external regions on the right (+0) and left (-0) of the diffuse interface (at  $\bar{x} = 0$ ).

The system of equations (25) is linear with respect to the variables  $\varphi_1$  and  $T_1$ . The general solution of this system is a sum of the general solution of the homogeneous system and a partial solution of the inhomogeneous system. The direct differentiation with respect to the coordinate  $\xi$  of the system

$$\begin{cases} \varphi_{0}^{"}(\xi) = 2 \frac{\alpha_{0} T_{m}}{\alpha_{0e} T_{0}(\xi)} g'(\varphi_{0}) \\ T_{0}'(\xi) = \frac{\bar{\tau}_{T} v^{2}}{\kappa_{0e}} F_{0} \varphi_{0}'(\xi), \end{cases}$$

which is equivalent to the system of equations (20), indicates that the functions  $\varphi'_0(\xi)$  and  $T'_0(\xi)$  are the solutions of homogeneous system (25). The presence of these functions on the right-hand side of Eqs. (25) means the existence of resonance solutions of the inhomogeneous system, which violates the monotonicity and smoothness of the expansion in  $\overline{\delta}$ . In order to eliminate resonances, we introduce the condition of the orthogonality of the vector ( $\varphi'_0(\xi)$ ),  $T'_0(\xi)$ ) to the vector  $(\Phi_{\varphi}, \Phi_T)$  on the right-hand side of system (25) with respect to the scalar product

$$\int_{-\infty}^{\infty} (\phi'_0 \Phi_{\phi} + T'_0 \Phi_T) d\xi = 0.$$
(36)

This condition can be rewritten in the form

$$\int_{-\infty}^{\infty} \frac{\alpha_0 T_{\rm m}}{\alpha_{0e} T_0} \overline{\Delta G}_0 p'(\varphi_0) \varphi'_0(\xi) d\xi$$
$$- (v + \tilde{\tau}_{\varphi} a) \int_{-\infty}^{\infty} \frac{{\varphi'_0}^2(\xi)}{\alpha_{0e}} d\xi \qquad (37)$$

$$-\tau_T v^3 \int_{-\infty}^{\infty} \frac{\overline{\kappa}_0}{\overline{\kappa}_{0e}^2} F_0 \phi'_0(\xi) \left[ \int_{-\infty}^{\xi} \frac{1}{\overline{\kappa}_{0e}} F_0 \phi'_0(y) dy \right] d\xi = 0.$$

Expression (37), together with the systems of equations (20) and (17), specifies the relation of the kinematics of motion (velocity v and acceleration a) of the flat solidification front of pure substances to the thermodynamic quantities of the Gibbs energies and internal energies of the phases. With the existing results of molecular dynamics simulation [18] (or natural experiments), Eq. (37) makes it possible to determine the temperature dependence of the mobility of the phase field of pure substances. In particular, at  $\tau_{\phi} = 0$  and  $\tau_T = 0$ , we find  $T_0 = \text{const}$  and

$$v = -6\alpha_0 \sqrt{\frac{T_{\rm m}}{T_0}} \overline{\Delta G_0} \,,$$

which directly expresses the dimensionless mobility  $\alpha_0$  in terms of the velocity of the front and the temperature on the flat solidification front.

To summarize, a thermodynamically consistent phase-field model of the solidification of pure substances in the absence of local equilibrium has been developed with the use of the Gibbs potentials of real substances. The relation between the velocity of the flat front and the temperature on the solidification front has been obtained in the sharp interface limit.

This work was supported by the Russian Foundation for Basic Research (project nos. 13-02-01149A and 14-29-10282ofi\_m).

#### REFERENCES

- 1. J. D. van der Waals, J. Stat. Phys. 20, 197 (1979).
- 2. L. D. Landau, Zh. Eksp. Teor. Fiz. 7, 19 (1937).
- V. I. Ginzburg and L. D. Landau, Zh. Eksp. Teor. Fiz. 20, 1064 (1950).
- 4. J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 28, 258 (1958).
- 5. J. W. Cahn, Acta Metall. 8, 554 (1960).
- S. M. Allen and J. W. Cahn, Acta Metall. 27, 1085 (1979).
- J. B. Collins and H. Levine, Phys. Rev. B 31, 6119 (1985).
- 8. J. S. Langer, in *Directions in Condensed Matter Physics* (World Scientific, Singapore, 1986), p. 166.
- 9. G. Caginalp, Arch. Rat. Mech. Anal. 92, 205 (1986).
- 10. N. Provatas and K. Elder, *Phase-Field Methods in Materials Science and Engineering* (Wiey-VCH, Weinheim, 2010).
- 11. J.-R. Li, D. Calhoun, and L. Brush, J. Comp. Phys. **228**, 8945 (2009).
- 12. P. Galenko and D. Jou, Phys. Rev. E 71, 046125 (2005).
- 13. A. T. Dinsdale, CALPHAD 15, 317 (1991).
- 14. P. K. Galenko and D. A. Danilov, Phys. Lett. A **278**, 129 (2000).
- 15. O. Penrose and P. C. Fife, Phys. D 43, 44 (1990).
- S. Wang, R. Sekerka, A. Wheeler, B. Murray, S. Coriell, R. Braun, and G. McFadden, Phys. D: Nonlin. Phenom. 69, 189 (1993).
- 17. D. A. Danilov, V. G. Lebedev, and P. K. Galenko, J. Non-Equilib. Thermodyn. **39**, 93 (2014),
- M. Berghoff, M. Selzer, and B. Nestler, Sci. World J. 2013, Article ID 564272 (2013).

Translated by R. Tyapaev