

Variational Theory of Crystal Growth in Multicomponent Alloys

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Abstract: The provisions for a new variational theory of crystal growth in multicomponent metal melts were formulated. The developed theory is the generalization of the previously conducted studies of crystal growth under conditions of deviation from local equilibrium at the phase boundary. The description of the methods of non-equilibrium thermodynamics of interrelated physico-chemical processes occurring in the initial phase, on the interface of phases and inside the growing crystal, was compared with the variational description of the crystal growth as a macrobody. The developed approach made it possible to find the general expression for the crystal growth rate, considering the influence of thermal and diffusion processes, as well as taking into account the influence of nonstationary effects associated with deviation from the local equilibrium on the surface of the growing nucleus. The justification of the new method showed that when the condition of the local equilibrium on the surface of the growing crystal is satisfied, the resulting equations take the form of expressions that can be obtained by constructing the equation of a mass and internal energy balance for the system under consideration. As an example, the problem of crystal growth from a melt of eutectic composition was considered. The equation of the growth rate of the two-component nucleus of the stoichiometric composition was obtained, taking into account the influence of the local non-equilibrium effects on growth. The expressions obtained were compared with the known equations of the solute trapping theory.

Keywords: non-equilibrium thermodynamics; variational principles; diffusionless crystal growth; solute trapping



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1. Introduction

Recently, there has been an active development of theoretical methods for investigating crystal growth [1]. The task of the many studies has been to build universal models describing the patterns of crystal growth from multicomponent melt under various physico-chemical conditions. The classical approach [1–3] of this description assumes that crystal growth is limited by the diffusion of components from the melt and the local equilibrium is established on the crystal surface. Therefore, the equilibrium lines on the state diagram can be used to determine the concentration values of the components on the surface of the nucleus.

Meanwhile, this approach becomes inapplicable for a number of tasks related to the description of diffusionless growth [1,4,5]. For example, in supercooled metal melts, the effect of rapid crystal growth was observed. The crystallization front captures impurity atoms that do not have enough time to diffuse from the surface of the nucleus. Modeling of these effects has become the starting stage for constructing the solute trapping theory, which allows us to take into account the influence of deviation from the local equilibrium on the growth equations [4–11]. One of the directions of the theory development is the local non-equilibrium model, which allows describing the influence of solute trapping effects on the crystal growth rate [7–11].

A new method for taking these effects into account is the phase field theory [12–14]. The research with this approach has made it possible to conduct studies of crystals in

the nucleus, at the interface of phases and in the initial phase near the growing nucleus, have a key influence on the crystal growth. At the same time, for a short time interval, the system can be considered as isolated. With this definition, the entropy production of the system can be written as [3,19]

$$P = \int_{V^\Phi} \sigma^\Phi dV + \int_{V^\Psi} \sigma^\Psi dV + \int_{F^\Phi} \sigma^F dF, \quad (2)$$

where σ^Φ , σ^Ψ and σ^F are the rates of the entropy production in the corresponding phases and the volumes of the corresponding phases are at the interface, V^Φ and V^Ψ . Subsequently, we will use a well-known expression for the rate of entropy production [19] in the nucleus and melt phases

$$\sigma^\Phi = \mathbf{J}_q^\Phi \cdot \mathbf{X}_q^\Phi + \sum_{i=1}^n \mathbf{J}_i^\Phi \cdot \mathbf{X}_i^\Phi, \mathbf{X}_q^\Phi = \mathbf{grad} \left(\frac{1}{T} \right), \mathbf{X}_i^\Phi = -\frac{1}{T} [\mathbf{grad} \mu_i^\Phi]_T \quad (3)$$

$$\sigma^\Psi = \mathbf{J}_q^\Psi \cdot \mathbf{X}_q^\Psi + \sum_{j=1}^m \mathbf{J}_j^\Psi \cdot \mathbf{X}_j^\Psi, \mathbf{X}_q^\Psi = \mathbf{grad} \left(\frac{1}{T} \right), \mathbf{X}_j^\Psi = -\frac{1}{T} [\mathbf{grad} \mu_j^\Psi]_T \quad (4)$$

where μ_i^Φ and μ_j^Ψ are chemical potentials of the components in the corresponding phases. The quantities \mathbf{X}_q^Φ , \mathbf{X}_i^Φ , \mathbf{X}_q^Ψ , \mathbf{X}_j^Ψ represent thermodynamic forces, and \mathbf{J}_q^Φ , \mathbf{J}_i^Φ , \mathbf{J}_q^Ψ , \mathbf{J}_j^Ψ ($i = 1, \dots, n, j = 1, \dots, m$) are the corresponding thermodynamic fluxes. $[\mathbf{grad} \mu_i^\Phi]_T$ and $[\mathbf{grad} \mu_j^\Psi]_T$ are gradients of the chemical potentials, calculated under the condition of temperature constancy.

Assuming the assumption of a linear relationship between thermodynamic fluxes and thermodynamic forces and using the well-known Onsager method, it is possible to transform the expressions (3) and (4) into the usual diffusion and thermal conductivity equations [3,19].

The situation is much more complicated with the description of the processes at the interface of phases. As mentioned earlier, the processes on the surface can be represented as chemical reactions (1) reflecting the transition of components through the phase interface. The rate of the entropy production for this process can be written as [3,19,20]

$$\sigma^F = \sum_{i=1}^n I_i A_i^*, A_i^* = A_i/T \quad (5)$$

where I_i is the molar rate of the product \aleph_i^Φ generation per unit area of the phase interface, and A_i is the affinity of the i th chemical reaction (1) at the boundary of the crystal-melt. The quantity I_i is the scalar flux of the i th component through the interface, and the quantity A_i^* is the corresponding thermodynamic force. In the case of a linear dependence of the quantities I_i and A_i^* , the application of the Onsager principle allows us to universally transform the Equation (5) [19]. Meanwhile, for several systems, when deviating from the local equilibrium, the linear dependence is not always preserved. Therefore, the methods of linear non-equilibrium thermodynamics are inapplicable for conditions of diffusionless growth, and the problem (1)–(5) has no direct solution within the framework of the described approach.

3. Variational Theory of Nucleus Growth in Multicomponent Melt

One of the well-known variational principles of non-equilibrium thermodynamics is the principle of minimum entropy production [19,24]. This principle assumes the condition of minimum entropy production at a given time. Within the framework of the classical approach for continuous systems, it is necessary to consider entropy production as a function of forces and fluxes at each point of the system. Therefore, finding the minimum of such a function leads to a complex integral expression that requires finding deriva-

tives of forces and fluxes in time at each point of the system. Such an equation has no simple solution.

We proposed a different approach [20]. For a wide class of problems related to primary crystallization, we can consider our system as isolated for a short time interval. It can then be argued that the minimum should not only be the production of entropy at a given time, but also the total production of entropy for the fixed period of time. The total entropy production can be defined by the function of the form $\Pi_{[t_1, t_2]} = \int_{t_1}^{t_2} P(t) dt$, where $P(t)$ is the entropy production at the time t , and $[t_1, t_2]$ is the time period under consideration. Subsequently, by analogy with the problems of mechanics [25,26], it can be argued that our system, being isolated from the external influences, would take the path of minimal length from the t_1 moment to the t_2 moment.

The function $P(t)$ depends on many quantities, including the function $R(t)$ (the radius of the growing nucleus), of interest to us. Let us consider the functional $\Pi_{[t_1, t_2]}(R) = \int_{t_1}^{t_2} P(t, R, \dot{R}) dt$. The minimum of entropy production at each time t will correspond to a set of functions satisfying this minimum. The deviation of any function would lead to a deviation of the integral from the minimum value. Therefore, if there is the function $R(t)$ for which the minimum condition for $\Pi_{[t_1, t_2]}$ is fulfilled, then replacing $R(t)$ with any $R(t) + \delta R(t)$ will increase the value of the functional $\Pi_{[t_1, t_2]}$. Applying to $\Pi_{[t_1, t_2]}$ the Euler–Lagrange equation [26], we obtain

$$\frac{d}{dt} \frac{\partial P}{\partial \dot{R}} - \frac{\partial P}{\partial R} = 0 \quad (6)$$

Thus, to solve the problem (1–5) in general, we can use expression (6). First, we need to find the value of the first term of Equation (6). The first two integrals (2) characterize the state of the phases Φ and Ψ ; they do not depend on the rate of change of the radius. Therefore, we can write

$$\frac{d}{dt} \frac{\partial P}{\partial \dot{R}} = \frac{d}{dt} \int_{F^\Phi} \frac{\partial}{\partial \dot{R}} \sum_{i=1}^n \frac{I_i A_i}{T} dF \quad (7)$$

Subsequently, we write down the expression for the affinity of the i th chemical reaction (2). To do this, we will use Prigogine’s expression for multiphase systems [27]

$$A_i = - \left(\sum_{j=1}^m v_{ij} \mu_j^\Psi + v_i \mu_i^\Phi \right) \quad (8)$$

where $v_{ij} = -M_{N_j^\Psi} n_{ij}$, $v_i = M_{N_i^\Phi}$, $M_{N_i^\Phi}$ is the molecular mass of the corresponding component. The quantity A_i does not depend on the rate of radius change, but it depends rather on the radius due to the influence of the surface tension. This effect can be neglected for not very small, supercritical particles. Therefore, considering the spherical symmetry of our system, we can rewrite (7) in the form

$$\frac{d}{dt} \frac{\partial P}{\partial \dot{R}} = 4\pi \frac{d}{dt} \left(R^2 \sum_{i=1}^n \frac{A_i}{T} \frac{\partial I_i}{\partial \dot{R}} \right) \quad (9)$$

We can now consider the second term of expression (6). Using the formula of the derivative of the integral with a variable upper limit and the spherical symmetry of the system, we can write for the first two terms (2)

$$\frac{\partial}{\partial R} \int_{V^\Phi} \sigma^\Phi dV + \frac{\partial}{\partial R} \int_{V^\Psi} \sigma^\Psi dV = 4\pi R^2 \left[\sigma^\Phi - \sigma^\Psi \right]_{r=R} \quad (10)$$

To find the derivative $\frac{\partial}{\partial R} \int_{F^\Phi} \sigma^F dF$, it is necessary to use (5) and (8) to separate the parameters related to the phases Φ and Ψ . Furthermore, with certain assumptions, applying the Gauss–Ostrogradsky equation to the inner and outer sides of the surface F , we can write [18]

$$\frac{\partial P}{\partial R} = 4\pi R^2 \left[\sigma^\Phi + \text{div}(\mathbf{n}_F \sigma^F) - \sigma^\Psi \right]_{r=R} \tag{11}$$

Below we will consider only the processes on the surface of the nucleus; therefore, for the simplicity of expression, we will not separately highlight the $r = R$ condition. Finally, combining (6), (9) and (11) and using (3)–(5) for more detailed conclusions, we write

$$R^2 \left[(\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi) \cdot \mathbf{grad} \left(\frac{1}{T} \right) - \frac{1}{T} \left(\sum_{i=1}^n \mathbf{J}_i^\Phi \cdot [\mathbf{grad} \mu_i^\Phi]_T - \sum_{j=1}^m \mathbf{J}_j^\Psi \cdot [\mathbf{grad} \mu_j^\Psi]_T \right) + \text{div} \left(\mathbf{n}_F \sum_{i=1}^n I_i \frac{A_i}{T} \right) \right] - \frac{d}{dt} \left(R^2 \sum_{i=1}^n \frac{A_i}{T} \frac{\partial I_i}{\partial R} \right) = 0 \tag{12}$$

The resulting equation is the general expression that allows calculating the growth rate of the nucleus together with the equations describing the processes in the volumes of the phases taking into account the interrelated thermal and diffusion processes at the boundary of the phases. At the same time, the expression does not use simplified linear non-equilibrium thermodynamics, which makes it possible to take into account the non-linear effects related to the deviation from equilibrium on the surface of the growing nucleus.

4. Incorporation of Existing Theories into the Developed Variational Technique

The resulting equation (12) is a convenient expression for practical calculations and it has been used to study the various systems [20–23]. In the present work, we additionally transform expression (12) for comparison with the results of other researchers. To do this, we use the expression $\mu_i = h_i - Ts_i$, which connects the chemical potential with the specific entropy s_i and enthalpy h_i .

Let us write down the expression $\mathbf{grad} \frac{\mu_i}{T} = \frac{1}{T} [\mathbf{grad} \mu_i]_T + h_i \mathbf{grad} \left(\frac{1}{T} \right)$ [17]. Thus, converting the second to the last term (12) and additionally using (8), we obtain

$$\text{div} \left(\mathbf{n}_F \sum_{i=1}^n I_i \frac{A_i}{T} \right) = \sum_{i=1}^n \frac{A_i}{T} \mathbf{div}(\mathbf{n}_F I_i) - \sum_{i=1}^n \frac{I_i \mathbf{n}_F}{T} \cdot \left(\sum_{j=1}^m v_{ij} [\mathbf{grad} \mu_j^\Psi]_T + v_i [\mathbf{grad} \mu_i^\Phi]_T \right) - \sum_{i=1}^n I_i \left(\sum_{j=1}^m v_{ij} h_i^\Psi + v_i h_i^\Phi \right) \mathbf{n}_F \cdot \mathbf{grad} \left(\frac{1}{T} \right) \tag{13}$$

We introduce an additional designation for the molar enthalpy of the product formation \aleph_i^Φ

$$\Delta H_i = \sum_{j=1}^m v_{ij} h_i^\Psi + v_i h_i^\Phi \tag{14}$$

Substituting (13) and (14) into (12), we obtain

$$R^2 \left[\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi - \sum_{i=1}^n I_i \Delta H_i \mathbf{n}_F \right] \cdot \mathbf{grad} \left(\frac{1}{T} \right) - \frac{R^2}{T} \left[\sum_{i=1}^n [\mathbf{grad} \mu_i^\Phi]_T \cdot (\mathbf{J}_i^\Phi + \mathbf{n}_F v_i I_i) + \sum_{j=1}^m [\mathbf{grad} \mu_j^\Psi]_T \cdot \left(\sum_{i=1}^n v_{ij} I_i \mathbf{n}_F - \mathbf{J}_j^\Psi \right) \right] + R^2 \sum_{i=1}^n \frac{A_i}{T} \mathbf{div}(\mathbf{n}_F I_i) - \frac{d}{dt} \left(R^2 \sum_{i=1}^n \frac{A_i}{T} \frac{\partial I_i}{\partial R} \right) = 0 \tag{15}$$

For further transformation of this equation, the expression for the growth rate of the nucleus is considered. The growth rate is determined by the sum of the molar rates of the product formation I_i for each of the components [20]

$$\rho^\Phi \dot{R} = \sum_{i=1}^n M_{N_i^\Phi} I_i^\Phi \tag{16}$$

Without taking into account the cross effects associated with the diffusion of various components and using (13), we can simply write an expression of the form [20]

$$I_i = \chi_i \frac{\rho^\Phi}{M_{N_i^\Phi}} \dot{R} \tag{17}$$

the quantities χ_i can be considered as the coefficients of the participation of the i th component in the formation of a new phase. In the first approximation, the coefficient χ_i can be assumed to be equal to the average concentration c_i^Φ of the i th component in the growing nucleus.

The molar rate of the product formation I_i is determined only at the interface of the phases and does not depend on r . Therefore, taking into account the spherical symmetry of the system and the expression (17), it is possible to simplify the expression for the second to last term (15)

$$R^2 \sum_{i=1}^n \frac{A_i}{T} \mathbf{div}(\mathbf{n}_F I_i) = 2R \sum_{i=1}^n \frac{A_i}{T} I_i \tag{18}$$

Subsequently, taking into account (17), we write

$$\frac{d}{dt} \left(R^2 \sum_{i=1}^n \frac{A_i}{T} \frac{\partial I_i}{\partial R} \right) = \frac{d}{dt} \left(R^2 \sum_{i=1}^n \frac{\rho_i^\Phi}{M_{N_i^\Phi}} \frac{A_i}{T} \right) = 2R \sum_{i=1}^n \frac{A_i}{T} I_i + R^2 \sum_{i=1}^n \frac{\rho_i^\Phi}{M_{N_i^\Phi}} \frac{d}{dt} \left(\frac{A_i}{T} \right) \tag{19}$$

and we will rewrite (15) in the form

$$\begin{aligned} & \left[\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi - \sum_{i=1}^n I_i \Delta H_i \mathbf{n}_F \right] \cdot \mathbf{grad} \left(\frac{1}{T} \right) - \\ & - \frac{1}{T} \left[\sum_{i=1}^n \left[\mathbf{grad} \mu_i^\Phi \right]_T \cdot \left(\mathbf{J}_i^\Phi + \mathbf{n}_F v_i I_i \right) + \sum_{j=1}^m \left[\mathbf{grad} \mu_j^\Psi \right]_T \cdot \left(\sum_{i=1}^n v_{ij} I_i \mathbf{n}_F - \mathbf{J}_j^\Psi \right) \right] \\ & - \sum_{i=1}^n \frac{\rho_i^\Phi}{M_{N_i^\Phi}} \frac{d}{dt} \left(\frac{A_i}{T} \right) = 0 \end{aligned} \tag{20}$$

To simplify the resulting expression, let us consider the second term separately. We transform the resulting equation to the balance equation of the known type. It follows from the Gibbs–Duhem equation [26] that at constant pressure $\sum_{i=1}^n c_i^\Phi \left[\mathbf{grad} \mu_i^\Phi \right]_T = 0$ and $\sum_{j=1}^m c_j^\Psi \left[\mathbf{grad} \mu_j^\Psi \right]_T = 0$. Therefore, the following condition is satisfied

$$- \frac{1}{T} \left[\sum_{i=1}^n c_i^\Phi \left[\mathbf{grad} \mu_i^\Phi \right]_T - \sum_{j=1}^m c_j^\Psi \left[\mathbf{grad} \mu_j^\Psi \right]_T \right] \mathbf{n}_F \sum_{k=1}^n v_k I_k = 0 \tag{21}$$

$$\begin{aligned} & \left[\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi - \sum_{i=1}^n I_i \Delta H_i \mathbf{n}_F \right] \cdot \mathbf{grad} \left(\frac{1}{T} \right) - \\ & - \frac{1}{T} \sum_{i=1}^n \left[\mathbf{grad} \mu_i^\Phi \right]_T \cdot \left(\mathbf{J}_i^\Phi + \mathbf{n}_F v_i I_i - c_i^\Phi \mathbf{n}_F \sum_{k=1}^n v_k I_k \right) - \\ & - \frac{1}{T} \sum_{j=1}^m \left[\mathbf{grad} \mu_j^\Psi \right]_T \cdot \left(\sum_{i=1}^n \left(v_{ij} + c_j^\Psi v_i \right) I_i \mathbf{n}_F - \mathbf{J}_j^\Psi \right) - \sum_{i=1}^n \frac{\rho_i^\Phi}{M_{N_i^\Phi}} \frac{d}{dt} \left(\frac{A_i}{T} \right) = 0 \end{aligned} \tag{22}$$

To compare the obtained expression with the existing models, we consider separately the case of the local equilibrium on the surface of the growing nucleus and the case when the condition of local equilibrium is not satisfied.

4.1. The Case of Local Equilibrium

The last term of expression (22) characterizes non-linear effects [18–21]. Indeed, under the condition of the local equilibrium, the equalities $A_i = 0$ and $dA_i/dt = 0$ are fulfilled, and the last term of the expression vanishes. Expression (22) takes the following form

$$\begin{aligned} & \left[\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi - \sum_{i=1}^n I_i \Delta H_i \mathbf{n}_F \right] \cdot \mathbf{grad} \left(\frac{1}{T} \right) - \\ & - \frac{1}{T} \sum_{i=1}^n \left[\mathbf{grad} \mu_i^\Phi \right]_T \cdot \left[\mathbf{J}_i^\Phi + \mathbf{n}_F v_i I_i - c_i^\Phi \mathbf{n}_F \sum_{k=1}^n v_k I_k \right] - \\ & - \frac{1}{T} \sum_{j=1}^m \left[\mathbf{grad} \mu_j^\Psi \right]_T \cdot \left[\sum_{i=1}^n \left(v_{ij} + c_j^\Psi v_i \right) I_i \mathbf{n}_F - \mathbf{J}_j^\Psi \right] \end{aligned} \quad (23)$$

Let us now consider the system under various particular conditions.

- (1) Let us have a one-component system. The concentrations of the components do not change in the system (the second and third terms are reset to zero). The expression (23) takes the form of a well-known expression for the heat release rate at the boundary [3]

$$\mathbf{J}_q^\Psi - \mathbf{J}_q^\Phi + \mathbf{n}_F \sum_{i=1}^n I_i \Delta H_i = 0 \quad (24)$$

- (2) The temperature of the system and the concentrations of the components in phase Ψ do not change (the first and third terms are reset to zero). Expression (23) in scalar form takes the form of the expression for the densities of diffusion fluxes in the phase Φ

$$J_i^\Phi = c_i^\Phi \sum_{k=1}^n v_k I_k - v_i I_i \quad (25)$$

- (3) The temperature of the system and the concentrations of components in the phase Φ do not change (the first and second terms are reset to zero). Expression (23) in scalar form takes the form of the expression of the densities of diffusion fluxes in the phase Ψ

$$J_j^\Psi = \sum_{i=1}^n \left(v_{ij} + c_j^\Psi v_i \right) I_i \quad (26)$$

Expressions (25) and (26) can be derived from the mass balance expressions for phase Φ and phase Ψ [3,19], respectively.

Meanwhile, it should be noted that expressions (24)–(26) do not take into account the effects associated with high-speed movement of the phase interface. Therefore, with a local deviation from the equilibrium, expressions (24)–(26) cannot be applied. The fluxes in these equations are “equilibrium” fluxes corresponding to the conditions of the local equilibrium.

4.2. The Locally Non-Equilibrium Case

Let us consider a more general case where the condition of the local equilibrium on the surface of the growing nucleus is not fulfilled. Considering the expression for affinity (8) and equality $v_i = M_{N_i^\Phi}$, we rewrite the last term of expression (22)

$$- \sum_{i=1}^n \frac{\rho_i^\Phi}{M_{N_i^\Phi}} \frac{d}{dt} \left(\frac{A_i}{T} \right) = \frac{1}{T^2} \sum_{i=1}^n \frac{\rho_i^\Phi A_i}{M_{N_i^\Phi}} \frac{dT}{dt} + \frac{1}{T} \sum_{j=1}^m \frac{d\mu_j^\Psi}{dt} \sum_{i=1}^n \frac{\rho_i^\Phi v_{ij}}{M_{N_i^\Phi}} + \frac{1}{T} \sum_{i=1}^n \rho_i^\Phi \frac{d\mu_i^\Phi}{dt} \quad (27)$$

Substituting (27) into (22), we obtain

$$\begin{aligned}
 & -\frac{1}{T^2} \left[\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi - \sum_{i=1}^n (I_i \Delta H_i \mathbf{n}_F) \right] \cdot \mathbf{grad} T + \frac{1}{T^2} \sum_{i=1}^n \frac{\rho_i^\Phi A_i}{M_{N_i}^\Phi} \frac{dT}{dt} - \\
 & -\frac{1}{T} \sum_{i=1}^n [\mathbf{grad} \mu_i^\Phi]_T \cdot \left(\mathbf{J}_i^\Phi + \mathbf{n}_F v_i I_i - c_i^\Phi \mathbf{n}_F \sum_{k=1}^n v_k I_k \right) + \frac{1}{T} \sum_{i=1}^n \rho_i^\Phi \frac{d\mu_i^\Phi}{dt} - \\
 & -\frac{1}{T} \sum_{j=1}^m [\mathbf{grad} \mu_j^\Psi]_T \cdot \left(\sum_{i=1}^n (v_{ij} + c_j^\Psi v_i) I_i \mathbf{n}_F - \mathbf{J}_j^\Psi \right) + \frac{1}{T} \sum_{j=1}^m \frac{d\mu_j^\Psi}{dt} \sum_{i=1}^n \frac{\rho_i^\Phi v_{ij}}{M_{N_i}^\Phi}
 \end{aligned} \quad (28)$$

The resulting expression differs from (23) by nonstationary terms that reflect non-linear thermal and diffusion effects on the surface of the growing nucleus. When we approach the local equilibrium at the phase interface, these terms vanish. We obtain the known linear equations of non-equilibrium thermodynamics (23)–(26).

Considering the obtained nonstationary terms, we can draw an analogy with the well-known local non-equilibrium model [7–11]. The presence of the nonstationary terms [16] determines the change in the growth rate of the nucleus due to deviation from the local equilibrium. In the next section, it will be shown that in the practical description of the simplified two-component system, the resulting equations have obvious similarities.

Thus, we have obtained a general solution to the system of equations of nucleus growth in multicomponent metal melt both for the case of the local equilibrium at the interface of phases and for the local non-equilibrium case.

5. Crystal Growth in Two-Component Melt of an Eutectic Composition

The obtained expressions can be used to build general models of crystal growth taking into account the influence of thermal and diffusion processes in the nucleus and melt phase. This approach assumes a description of processes in the nucleus and melt phase using the diffusion and thermal conductivity equations, as well as use of the obtained equations to describe processes at the interface of phases. The resulting description represents the Stefan problem, which can be solved numerically.

Meanwhile, for a number of tasks, a simplified approach to estimating the growth rate of the nucleus can be applied directly on the basis of the obtained equations for the phase interface. Based on this method, we carried out practical calculations for various systems [20–23]. This paper presents a general theoretical derivation of the expression for the rate of crystal growth from eutectic melt.

Crystals of various phases can form in the melt of a eutectic composition. Continuing the reasoning of the previous section, let us consider the growth of a nucleus of one of the phases of stoichiometric composition N^Φ from a multicomponent eutectic melt. With this definition, since $n = 1$, equations (1) are reduced to one equation

$$n_1 \mathfrak{R}_1^\Psi + n_2 \mathfrak{R}_2^\Psi + \dots + n_m \mathfrak{R}_m^\Psi \rightarrow N^\Phi \quad (29)$$

Because our nucleus has an invariable stoichiometric composition, the diffusion fluxes in the nucleus are zero. Accordingly, expression (12) can be rewritten as

$$R^2 \left[(\mathbf{J}_q^\Phi - \mathbf{J}_q^\Psi) \cdot \mathbf{grad} \left(\frac{1}{T} \right) + \frac{1}{T} \sum_{j=1}^m \mathbf{J}_j^\Psi \cdot [\mathbf{grad} \mu_j^\Psi]_T + \text{div} \left(\mathbf{n}_F I \frac{A}{T} \right) \right] - \frac{d}{dt} \left(R^2 \frac{A}{T} \frac{\partial I}{\partial R} \right) = 0 \quad (30)$$

We subsequently consider the case when the local non-equilibrium conditions can be determined only by diffusion processes. Equation (24) can then be applied to our expression. Transforming (30) and taking into account the spherical symmetry of the system, we write in scalar form

$$\frac{R^2}{T^2} I \Delta H \frac{\partial T}{\partial r} + \frac{R^2}{T} \sum_{i=1}^m J_i^\Psi \left[\frac{\partial \mu_i^\Psi}{\partial r} \right]_T + I \frac{\partial}{\partial r} \left(r^2 \frac{A}{T} \right) - \frac{d}{dt} \left(R^2 \frac{A}{T} \frac{\partial I}{\partial R} \right) = 0 \quad (31)$$

Given (17) for $n = 1$, it is possible to rewrite the last term of the expression

$$\frac{d}{dt} \left(R^2 \frac{A}{T} \frac{I}{R} \right) = 2R \frac{A}{T} I + R^2 \frac{\rho^\Phi}{M_{N\Phi}} \frac{d}{dt} \left(\frac{A}{T} \right) \quad (32)$$

Finally, taking into account (32), we will rewrite (31) in the form

$$I = \frac{\sum_{i=1}^m J_i^\Psi \left[\frac{\partial \mu_i^\Psi}{\partial r} \right]_T - T \frac{\rho^\Phi}{M_{N\Phi}} \frac{d}{dt} \left(\frac{A}{T} \right)}{\frac{\Delta H}{T} \frac{\partial T}{\partial r} + T \frac{\partial}{\partial r} \left(\frac{A}{T} \right)} \quad (33)$$

The resulting expression allows us to calculate the growth rate of the nucleus. At the same time, the second term $-T \frac{\rho^\Phi}{M_{N\Phi}} \frac{d}{dt} \left(\frac{A}{T} \right)$ in the numerator reflects the influence of the non-linear effects associated with deviation from the local equilibrium. Under the conditions of the local equilibrium this term vanishes, and expression (33) takes on the simplified form

$$I = \frac{\sum_{i=1}^m J_i^\Psi \left[\frac{\partial \mu_i^\Psi}{\partial r} \right]_T}{\frac{\Delta H}{T} \frac{\partial T}{\partial r} + T \frac{\partial}{\partial r} \left(\frac{A}{T} \right)} \quad (34)$$

Let us compare the obtained expression with the known equations of the solute trapping theory [4–11]. To do this, we consider a particular case of the nucleus growth in the system consisting of two components A and B . In addition, we will assume that thermal processes on the surface of the growing nucleus do not significantly affect its growth. Thus, the expression (33), taking into account the relationship of diffusion fluxes, will take the form

$$I = \frac{J_A^\Psi \left(\left[\frac{\partial \mu_A^\Psi}{\partial r} \right]_T - \left[\frac{\partial \mu_B^\Psi}{\partial r} \right]_T \right) - \frac{\rho^\Phi}{M_{N\Phi}} \frac{dA}{dt}}{\frac{\partial A}{\partial r}} \quad (35)$$

Furthermore, taking into account the expression for the affinity of the chemical reaction (8), using the ideal solutions theory $\mu_i^\Psi = \mu_i^{\Psi 0} + R_\Gamma T \ln c_i^\Psi$, as well as taking into account the constancy of the concentration of the product inside the nucleus and equality $c_A^\Psi + c_B^\Psi = 1$, we write down the expression (35) in the new form

$$I = \frac{M_A c_B^\Psi + M_B c_A^\Psi}{M_A c_B^\Psi - M_B c_A^\Psi} J_A^\Psi - \frac{\rho^\Phi}{M_{N\Phi}} \frac{dc_A^\Psi/dt}{\partial c_A^\Psi/\partial r} \quad (36)$$

In addition, taking into account (16), it is finally possible to write down the expression for the growth rate of the nucleus

$$\dot{R} = \frac{M_{N\Phi}}{\rho^\Phi} \frac{M_A c_B^\Psi + M_B c_A^\Psi}{M_A c_B^\Psi - M_B c_A^\Psi} J_A^\Psi - \frac{dc_A^\Psi/dt}{\partial c_A^\Psi/\partial r} \quad (37)$$

The first term of this expression determines the contribution of the diffusion of components in the process of nucleus growth. The second term defines non-linear effects. Under the condition of the local equilibrium, this term vanishes.

When we analyze the resulting expression, an analogy can be drawn with the well-known expression of the local non-equilibrium model [7–11]

$$J(r, t) = -D \nabla c - \tau_D \frac{\partial J(r, t)}{\partial t} \quad (38)$$

where c is concentration of the impurity component, $J(r, t)$ is the impurity flux to the surface of the growing nucleus, and D is the diffusion coefficient. The relaxation time τ_D

is zero when the local equilibrium condition is satisfied. In this case, the term $\tau_D \frac{\partial J(r,t)}{\partial t}$ characterizes the influence of the solute trapping effects.

The resulting expression (36) differs from expression (37), since our expression reflects the growth rate of the crystal, and expression (38) is the expression of the impurity flux to the surface of the crystal. Meanwhile, it is possible to compare the second terms reflecting the influence of the nonstationary effects on the growth of the nucleus. As can be seen, both equations reflect nonstationary concentration effects on the interface of the phases. Comparative calculations based on both methods may become a further direction for research.

6. Conclusions

In this paper, for the first time it has been possible to obtain detailed theoretical justification for the new theoretical approach to the description of crystal growth in multicomponent metal melts by methods of non-equilibrium thermodynamics. The use of the new variational method made it possible to find a solution to the obtained equations under conditions of deviation from the local equilibrium. The substantiation of the new method showed that if the condition of the local equilibrium at the surface of the growing crystal is satisfied, the resulting equations take the form of expressions that can be obtained by constructing the equation of mass balance and internal energy balance for the system under consideration. Such a generalized description of the nucleus–melt system makes it possible to apply the methods of non-equilibrium thermodynamics to nonlinear growth problems when the condition of the local equilibrium is not met. In the case of deviation from the local equilibrium, the growth equations of the nucleus are obtained, including the additional nonstationary terms. At the same time, the separately considered particular case of crystal growth from the two-component eutectic melt showed the correspondence of the obtained expressions to the equations of the solute trapping theory.

Based on the general description of the nucleus–melt system by non-equilibrium thermodynamic methods, an important feature of our approach is the possibility of its expansion to take into account the influence of additional factors affecting the crystal growth. As an example, we can consider the effect of changes in the average concentration of components in the system. Such a special case of the application of growth equations in the description of macro-crystallization processes is considered in one of our research papers [21]. This feature of the method can be used for joint studies of crystal growth using the various methods.

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