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Mathematical Modeling of Nucleation and Growth Processes of Ellipsoidal Crystals in Binary Melts

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Abstract: The transient behavior of an ensemble of ellipsoidal particles in a supercooled binary melt is considered. The model laws, based on the Fokker-Planck type kinetic equation for the particle-volume distribution function, the thermal and mass integral balances for the binary melt temperature and solute concentration, as well as the corresponding boundary and initial conditions, are formulated and solved analytically. We show that the temperature and concentration increase with time due to the effects of impurity displacement and latent heat emission by the growing ellipsoidal particles. These effects are also responsible for metastability reduction. As this takes place, increasing the initial solute concentration in a metastable binary melt increases the intensity of its desupercooling. The theory is developed for arbitrary nucleation frequency with special consideration of two important nucleation kinetics according to the Meirs and Weber-Volmer-Frenkel Zel'dovich mechanisms. An analytical solution to the integrodifferential model equations is found in a parametric form. The theory contains all limiting transitions to previously developed analytical approaches. Namely, it contains the growth of spherical crystals in binary melts and ellipsoidal crystals in single-component melts.

Keywords: crystal growth; nucleation; ellipsoidal particles; particulate assemblages; binary melts

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Citation: Nikishina, M.A.; Alexandrov, D.V. Mathematical Modeling of Nucleation and Growth Processes of Ellipsoidal Crystals in Binary Melts. *Crystals* **2022**, *12*, 1495. https://doi.org/10.3390/cryst12101495

Academic Editor: Borislav Angelov

Received: 7 October 2022
Accepted: 19 October 2022
Published: 21 October 2022

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1. Introduction

It is well-known that a bulk crystallization process occurring from a metastable liquid state takes place in various natural phenomena (e.g., freezing of supercooled water, magma chambers, and lava lakes [1–6]). In addition, such a process is used in the chemical and pharmacological industries as well as materials science and metallurgy to obtain various substances (e.g., food additives and pharmaceuticals) with given properties [7–12]. The volumetric crystallization process is based on nucleation and crystal growth of a new phase in a metastable medium. At present, the theory of such a phase transformation is well developed for spherical crystals (see, among others, [13–20]). However, often the anisotropy of crystals transforms their shape by stretching the particles along one direction [21–28]. In this case, it is convenient to use the ellipsoidal approximation of growing particles to develop the theory. Previously, such an approach was developed for volumetric crystallization of pure (one-component) melts [29,30].

In this paper, the theory of ellipsoidal crystal growth in binary melts is constructed. The present study is based on two previously known methods for analyzing the evolution of a polydisperse crystal ensemble in a metastable binary melt: (i) the theory of spherical crystal ensemble growth in binary systems [31,32], and (ii) the theory of ellipsoidal crystal ensemble evolution in single-component systems [29,30]. The analytical approach under consideration has limiting transitions to these early known cases. Let us especially highlight that the theory under consideration taking a non-spherical shape of growing crystals into account can be used for the description of particle evolution in a metastable magnetic fluid [33], in the presence of buoyancy forces [34], polymerization [14] and removal mechanisms of product crystals from a crystallizer [35–37].

The main novelty of this paper is the theoretical consideration of the non-spherical (ellipsoidal) shape of crystals growing in binary supercooled melts. It should be noted that this theory generalizes previously known theories for ellipsoidal crystals evolving in one-component supercooled melts [29,30] and spherical crystals evolving in binary systems [31,32]. The paper is organized as follows. The growth rate of individual crystals in binary melts is considered in Section 2. An integrodifferential model of governing equations describing the evolution of a polydisperse ensemble of ellipsoidal particles is formulated and solved in Section 3 using this growth rate. Our conclusions and possible ways of developing the theory are formulated in Section 4.

2. Growth Rates of Individual Ellipsoidal Crystals in a Binary Melt

For the convenience of mathematical description of the growth of an ellipsoidal crystal, we use the coordinate system of a prolate ellipsoid.

We consider the evolution of an ellipsoidal particle in a supercooled binary melt. To find the temperature and solute concentration distributions as well as the particle growth rate we introduce a special curvilinear coordinate system illustrated in Figure 1 [38]. These new ellipsoidal coordinates (σ, τ, and φ) can be expressed in terms of the Cartesian coordinates x, y, and z as follows

$$\begin{aligned} x^2 &= a^2\left(\sigma^2-1\right)\left(1-\tau^2\right)\cos^2\varphi, \\ y^2 &= a^2\left(\sigma^2-1\right)\left(1-\tau^2\right)\sin^2\varphi, \\ z &= a\sigma\tau, \end{aligned} \tag{1}$$

where, the constant a describes a characteristic dimension of growing crystal, and $\sigma \geq 1$, $-1 \leq \tau \leq 1,\ 0 \leq \varphi \leq 2\pi$.

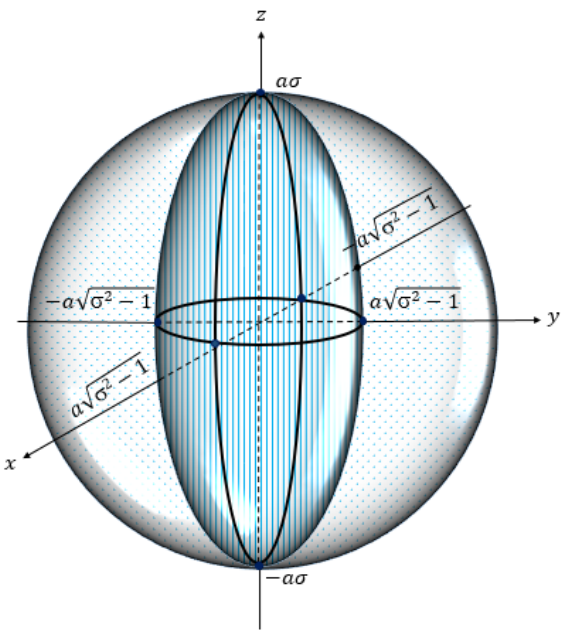

Figure 1. Special curvilinear coordinates σ, τ, and φ of the prolate ellipsoid.

The Lamé parameters defining differential operators in curvilinear coordinates can be written as follows

$$H_\sigma = a\sqrt{\frac{\sigma^2-\tau^2}{\sigma^2-1}},\ H_\tau = a\sqrt{\frac{\sigma^2-\tau^2}{1-\tau^2}},\ H_\varphi = a\sqrt{(\sigma^2-1)(1-\tau^2)}. \tag{2}$$

The reasonability of using an ellipsoidal coordinate system (1) is justified by the fact that (i) ellipsoidal coordinates of a prolate ellipsoid are a better approximation (as compared to spherical particles) of the evolution of crystals in supercooled and supersaturated liquids (see, for example, experimental data numerical simulations [21–28]), (ii) ellipsoidal coordinates of a prolate ellipsoid allow one to obtain much simpler laws of evolution of individual particles and ensembles of such particles (see, among others, Refs. [39,40]).

We will seek for a quasi-steady-state solution to the problem where the particle surface $\sigma = \sigma_0$ as well as the surfaces $\sigma > \sigma_0$ surrounding σ_0 represent the isothermal (isoconcentration) surfaces. In this case, the temperature T and solute concentration C satisfy the stationary equations $\nabla^2 T = 0$ and $\nabla^2 C = 0$ around the evolving crystal. Assuming the steady-state conditions, these functions only depend on the distance σ from the particle surface σ_0, i.e., $T = T(\sigma)$, and $C = C(\sigma)$. For the sake of simplicity, we consider the crystal temperature to be constant and neglect the diffusion mechanism in a crystal. Taking this into account, the heat and mass transfer problem becomes

$$\frac{d}{d\sigma}\left[\left(\sigma^2 - 1\right)\frac{dT}{d\sigma}\right] = 0,\ \frac{d}{d\sigma}\left[\left(\sigma^2 - 1\right)\frac{dC}{d\sigma}\right] = 0,\ \sigma \geq \sigma_0, \tag{3}$$

$$\dot{\sigma} = \frac{-\lambda_l}{a^2 \rho_s L}\frac{dT}{d\sigma} = \frac{\beta_*}{a}\left(T_p - mC - T\right),\ (1 - k_0)C\dot{\sigma} = -\frac{D}{a^2}\frac{dC}{d\sigma},\ \sigma = \sigma_0, \tag{4}$$

$$T \to T_l,\ C \to C_l,\ \sigma \gg 1, \tag{5}$$

where λ_l is the thermal conductivity parameter, $L_V = \rho_s L$ is the latent heat of solidification, β_* is the kinetic parameter, T_p is the phase transition temperature of pure melt, k_0 and m stand for the equilibrium segregation coefficient and liquidus slope, D is the solute diffusion coefficient, and T_l and C_l are the temperature and solute concentration far from the crystal surface.

Integrating Equation (3) with allowance for the boundary conditions (5), we come to the temperature and solute concentration distributions in liquid

$$T(\sigma) = T_l + C_1 \ln\left(\frac{\sigma - 1}{\sigma + 1}\right),\ C(\sigma) = C_l + C_2 \ln\left(\frac{\sigma - 1}{\sigma + 1}\right), \tag{6}$$

where C_1 and C_2 are constants.

Substituting Equation (6) into the first boundary condition (4), we arrive at

$$\dot{\sigma}_0 = \frac{-2\varepsilon_1 C_1}{\sigma_0^2 - 1},\ C_1 = \frac{\frac{\beta_*}{a}\left[T_p - T_l - mC_l - mC_2 \ln\left(\frac{\sigma_0 - 1}{\sigma_0 + 1}\right)\right]}{\frac{\beta_*}{a}\ln\left(\frac{\sigma_0 - 1}{\sigma_0 + 1}\right) - \frac{2\varepsilon_1}{\sigma_0^2 - 1}},$$

where $\varepsilon_1 = \lambda_l/(a^2 L_V)$. The second boundary condition (4) leads to another expression for C_1 in the form of

$$C_1 = \frac{DC_2}{a^2 \varepsilon_1 (1 - k_0)\left[C_l + C_2 \ln\left(\frac{\sigma_0 - 1}{\sigma_0 + 1}\right)\right]}.$$

Equating C_1 from these expressions, we obtain a quadratic equation for C_2

$$\alpha C_2^2 + \beta C_2 + \gamma = 0, \tag{7}$$

$$\alpha = \beta_* m a \varepsilon_1 (1 - k_0) \ln^2\left(\frac{\sigma_0 - 1}{\sigma_0 + 1}\right),$$

$$\gamma = -\beta_*(T_p - T_l - mC_l)a\varepsilon_1(1-k_0)C_l,\ \beta = -\frac{2\varepsilon_1 D}{\sigma_0^2 - 1} + \beta_* \ln\left(\frac{\sigma_0 - 1}{\sigma_0 + 1}\right)$$
$$\times\left[mC_l a\varepsilon_1(1-k_0) + \frac{D}{a} - (T_p - T_l - mC_l)a\varepsilon_1(1-k_0)\right].$$

The analytical solutions (6) and (7) show that the surface growth rate $\dot{\sigma}_0$ depends only on σ_0 and the binary melt temperature T_l and concentration C_l: $\dot{\sigma}_0 = \dot{\sigma}_0(\sigma_0, T_l, C_l)$. It means that the particle volume growth rate dV/dt also depends on three variables V, T_l and C_l and has the form

$$\frac{dV}{dt} = \frac{4}{3}\pi a^3\left[3\sigma_0^2(V) - 1\right]\dot{\sigma}_0(\sigma_0(V), T_l, C_l), \tag{8}$$

where $\sigma_0(V)$ is a real positive root of equation $\sigma_0^3 - \sigma_0 - V_1 = 0$ and $\dot{\sigma}_0 = \dot{\sigma}_0(\sigma_0(V), T_l, C_l)$ is determined by the analytical solution (6) and (7). Here $V_1 = 3V/(4\pi a^3)$. Note that the greater the parameter σ_0, the closer the shape of the crystal to spherical (Figure 2). To demonstrate the solution obtained let us introduce the dimensionless parameters as follows $\Delta_1 = \Delta T/T_l$, $t_1 = \beta_* T_l t/a$, and $\alpha_1 = \beta_*/(2a\varepsilon_1)$. Using these variables, we rewrite expression (8) as

$$G_R = \frac{dV_1}{dt_1} = \frac{(3\sigma_0^2 - 1)\left(\Delta_1 - (mC_2/T_l)\ln\frac{\sigma_0 - 1}{\sigma_0 + 1}\right)}{1 - \alpha_1(\sigma_0^2 - 1)\ln\frac{\sigma_0 - 1}{\sigma_0 + 1}}. \tag{9}$$

Note that expression (9) transforms to its analog for one-component melts at $C_2 = C_l = 0$ [30,41]. On the other hand, if crystals are almost spherical ($\sigma_0 \gg 1$), the growth rate tends to the corresponding law for spherical particles [42]. Figure 3 shows that the volume growth rate G_R increases with increasing the crystal volume V_1 and binary melt supercooling Δ_1. In addition, the presence of dissolved impurities in the supercooled melt reduces the growth rate of individual crystals. An important point is that this rate enters the Fokker-Planck equation for the particle-volume distribution function and defines the evolution of a polydisperse ensemble of ellipsoidal crystals in a supercooled binary melt. This question is studied in the next section in more detail.

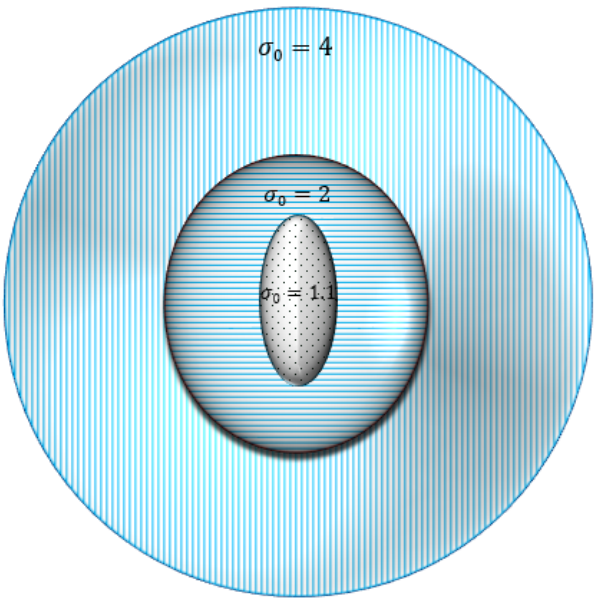

Figure 2. Ellipsoidal particles with different σ_0.

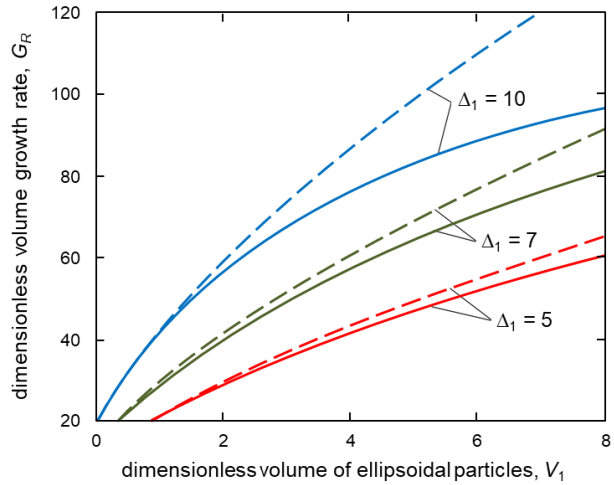

Figure 3. The growth rate G_R of ellipsoidal crystals as a function of their volume V_1 at a different melt supercooling Δ_1. The solid and dashed curves are plotted for binary ($C_l = 55$ at%) and one-component ($C_l = 0$) melts, respectively. The model parameters are [43]: $\lambda_l/(\rho_s L) = 2.75 \cdot 10^{-8}$ m^2 K^{-1} s^{-1}, $a = 1.26 \cdot 10^{-8}$ m, $\beta_* = 10^{-4}$ m K^{-1} s^{-1}, $m = 8.78$ K at%$^{-1}$, $k_0 = 0.86$, $D = 5.27 \cdot 10^{-9}$ m^2 s^{-1}, $T_l = 2 \cdot 10^3$ K.

3. Evolution of a Particulate Ensemble of Ellipsoidal Crystals

Let us consider a binary melt which is initially supercooled by the value $\Delta T_0 = T_p - T_0 - mC_0$ (T_0 and C_0 represent the initial temperature and solute concentration). We assume that the melt is homogeneous and that, initially, it did not contain any particles. The initial supercooling ΔT_0 generates crystal nucleation and growth and partial supercooling reduction due to the release of latent heat. Here we assume that each crystal evolves changing its volume V and surface σ_0 according to the theory developed in the previous section (see also Figure 3). Taking possible fluctuations in particle growth rates into account [44–47], we have the following kinetic equation for the particle-volume distribution function $f(V,t)$, which reads as

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial V}\left(\frac{dV}{dt} f\right) = \frac{\partial}{\partial V}\left(D_V \frac{\partial f}{\partial V}\right), \; t > 0, \; V > V_*. \tag{10}$$

This equation should be supplemented by the initial and boundary conditions

$$f = 0, \; t = 0; \; \frac{dV}{dt} f - D_V \frac{\partial f}{\partial V} = I(\Delta T), \; V = V_*; \; f \to 0, \; V \to \infty, \tag{11}$$

where V_* is the critical volume of nucleating particles. Here, the "diffusion" coefficient D_V of crystals in the space of their volumes includes the rate of particle fluctuations. For the sake of simplicity, we consider the case when D_V is proportional to the rate of particle growth $g = dV/dt$ [31,44] and has the form

$$D_V = d_0 \frac{g(t)}{R(V)}, \tag{12}$$

where d_0 is a constant parameter, and $R(V)$ is defined by the minimal work needed to produce a crystal with volume V [44].

The frequency of nucleation I can be considered changing with the melt supercooling ΔT according to the Weber-Volmer-Frenkel Zel'dovich (WVFZ) or Meirs nucleation kinetics, i.e., (see, among others, [31,48,49])

$$I(\Delta T) = \begin{cases} I_* \exp\left[-p(1 - mC_l/T_p)\dfrac{\Delta T_0^2}{\Delta T^2}\right], \text{ WVFZ} \\ I_*(\Delta T)^p, \text{ Meirs} \end{cases},$$

where the parameters p and I_* are different for WVFZ and Meirs kinetics are assumed to be constant.

The heat and mass balance laws taking such fluctuations into account read as [31]

$$\frac{dT_l}{dt} = K \int_{V_*}^{\infty} \left(\frac{dV}{dt} f - D_V \frac{\partial f}{\partial V} \right) dV, \ t > 0, \ K = \frac{L_V}{\rho_m C_m}, \tag{13}$$

$$\frac{dC_l}{dt} = C_l(1 - k_0) \int_{V_*}^{\infty} \left(\frac{dV}{dt} f - D_V \frac{\partial f}{\partial V} \right) dV, \ t > 0. \tag{14}$$

Note that we have formulated the thermal and mass balances (13) and (14) through the particle volume and not through the radius, as was done for spherical crystals [31].

It is significant that the balance laws (13) and (14) can be integrated using the kinetic Equation (10) in the form of

$$T_l(t) = T_0 + K \int_{V_*}^{\infty} V f dV, \ t > 0, \tag{15}$$

$$C_l(t) = C_0 \exp\left[(1 - k_0) \int_{V_*}^{\infty} V f dV \right], \ t > 0. \tag{16}$$

As this takes place, the binary melt supercooling is given by [50]

$$\Delta T = T_p - mC_l - T_l, \ t > 0. \tag{17}$$

Let us especially underline that this model was previously used to study the evolution of particulate assemblages of spherical crystals in Refs. [19,31,51] for pure and binary supercooled liquids. Here we extend this analysis to the case of ellipsoidal crystals.

For the sake of convenience, we introduce dimensionless variables and parameters as follows

$$\begin{gathered} \tau = \frac{t}{t_0}, \ s = \frac{V}{V_0}, \ F = V_0^2 f, \ s_* = \frac{V_*}{V_0}, \ z = s - s_*, \ u_0 = \frac{d_0}{V_0}, \ w = \frac{\Delta T}{\Delta T_0}, \\ T_{dl} = \frac{T_l}{\Delta T_0}, \ C_{dl} = \frac{C_l}{C_0}, \ T_{d0} = \frac{T_0}{\Delta T_0}, \ T_{dp} = \frac{T_p}{\Delta T_0}, \ \xi_1 = \frac{K}{\Delta T_0}, \\ V_0 = \left(\frac{\beta_* \Delta T_0}{I_0} \right)^{3/4}, \ t_0 = (\beta_*^3 \Delta T_0^3 I_0)^{-1/4}, \ I_0 = I(\Delta T_0), \text{ and} \\ g_0(t) = \frac{ds}{dt} = \frac{t_0}{V_0} g \end{gathered} \tag{18}$$

at $\tau \geq \tau_*$ and $g_0(t) = 0$ at $\tau < \tau_*$, where τ_* is the initiation time of a critical crystallite.

Rewriting the model (10)–(17) in dimensionless variables (19), one can get

$$\frac{\partial F}{\partial x_1} + \frac{\partial F}{\partial z_1} = u_0 \frac{\partial^2 F}{\partial z_1^2}, \ x_1 > 0, \ z_1 > 0, \tag{19}$$

$$F = 0,\ \tau = 0;\ F \to 0,\ z_1 \to \infty, \tag{20}$$

$$F - u_0 \frac{\partial F}{\partial z_1} = \frac{\exp(p\varphi(w(x_1))}{\mu(x_1)} \equiv J(x_1),\ z_1 = 0, \tag{21}$$

where $\mu = g_0$ at $s = s_*$ and the modified time (x_1) and space (z_1) variables are used by analogy with Refs. [19,31,51]

$$x_1 = \int_0^\tau g_0(\bar{\tau}) R(V_0 s(\bar{\tau})) d\bar{\tau},\ z_1 = \int_0^z R_1(\bar{z}) d\bar{z},\ R_1(z) = R(V_0(z + s_*)), \tag{22}$$

$$\varphi = \ln w \text{ (Meirs kinetics)},\ \varphi = 1 - \kappa C_{dl} - \frac{1 - \kappa C_{dl}}{w^2} \text{ (WVFZ kinetics)},$$

and $\kappa = mC_0/T_p$.

Equation (19) supplemented by the initial and boundary conditions (20) and (21) can be solved by means of the Laplace integral transform with respect to x_1 (note that $x_1 = 0$ corresponds to $\tau = 0$). So, omitting tedious mathematical manipulations, we arrive at [52]

$$F(x_1, z_1) = \int_0^{x_1} J(x_1 - y_1)\gamma(y_1, z_1) dy_1, \tag{23}$$

$$\gamma(y_1, z_1) = \frac{1}{2u_0} \exp\left(\frac{2z_1 - y_1}{4u_0}\right) \left[\frac{2\sqrt{u_0}}{\sqrt{\pi y_1}} \exp\left(\frac{-z_1^2}{4u_0 y_1}\right)\right.$$
$$\left. - \exp\left(\frac{z_1}{2u_0} + \frac{y_1}{4u_0}\right) \operatorname{erfc}\left(\frac{z_1}{2\sqrt{u_0 y_1}} + \frac{\sqrt{y_1}}{2\sqrt{u_0}}\right)\right].$$

Now, assuming that $R_1(\bar{z}) = \bar{z}$ [44] and substituting F from (23) into the heat and mass balances (15) and (16), we come to the temperature and concentration of impurity

$$T_{dl}(x_1) = T_{d0} + \xi_1 G_0(x_1),\ C_{dl}(x_1) = \exp[(1 - k_0)G_0(x_1)], \tag{24}$$

$$G_0(x_1) = \int_0^{x_1} J(x_1 - y_1) h(y_1) dy_1,\ h(y_1) = \int_0^\infty \frac{(\sqrt{2z_1} + s_*)\gamma(y_1, z_1)}{\sqrt{2z_1}} dz_1. \tag{25}$$

Now, combining expressions (17) and (24), one can obtain the supercooling w in the form

$$w(x_1) = T_{dp} - T_{d0} - \xi_1 G_0(x_1) - \frac{mC_0}{\Delta T_0} \exp[(1 - k_0)G_0(x_1)]. \tag{26}$$

Expressions (24)–(26) enable us to express w, C_{dl}, and G_0 as functions of T_{dl}:

$$w(T_{dl}) = T_{dp} - T_{dl} - \frac{mC_0}{\Delta T_0} \exp[(1 - k_0)(T_{dl} - T_{d0})/\xi_1], \tag{27}$$

$$C_{dl}(T_{dl}) = \exp[(1 - k_0)(T_{dl} - T_{d0})/\xi_1],\ G_0(T_{dl}) = \frac{T_{dl} - T_{d0}}{\xi_1}. \tag{28}$$

In the case of one-component melts and Meirs kinetics, the melt supercooling can be written in the form [52] ($C_{dl} = 0$ and $w = T_{dp} - T_{dl}$)

$$w(x_1) = [(2-p)H(x_1) + 1]^{1/(2-p)},\ p \neq 2 \qquad w(x_1) = \exp[H(x_1)],\ p = 2 \tag{29}$$

It is significant that Equation (22) enables us to find the following dependence between the dimensionless (τ) and modified (x_1) times

$$\tau(x_1) = \int_0^{x_1} \frac{dx_2}{g_0(T_l(x_2))R_1(z(x_2))}. \tag{30}$$

Note that Equations (27) and (28) determine w and C_{dl} as functions of T_{dl} whereas $T_{dl}(x_1)$ and $\tau(x_1)$ are given by Equations (24) and (30). Expressions (23), (27), (28) and (30) represent a complete analytical solution obtained in a parametric form (with the decision variable x_1). The present solution contains limiting transitions to previously studied cases of a pure melt with ellipsoidal crystals [30] and a binary melt with spherical crystals [31].

Our analytical solution is shown in Figures 4 and 5, where the dynamics of the melt temperature, solute concentration, and supercooling are illustrated. As would be expected, the solute concentration increases due to the effect of impurity displacement by growing crystals. In addition, the latent heat of phase transformation released by them leads to an increase in temperature. Both of these evolutionary dependencies are demonstrated in Figure 4 (scales of values are marked on the left and right vertical axes). Desupercooling dynamics in a binary melt are illustrated in Figure 5. As is easily seen, the melt supercooling w decreases with time as a result of latent heat emission. Moreover, the higher the initial solute concentration (higher mC_0), the faster the supercooling decreases. This faster decay of supercooling corresponds to the previously constructed solution of the similar problem about the evolution of an ensemble of spherical crystals in a supercooled binary melt [31]. This is caused by the fact that increasing the solute concentration decreases the crystallization temperature of a binary system and, consequently, decreases its supercooling.

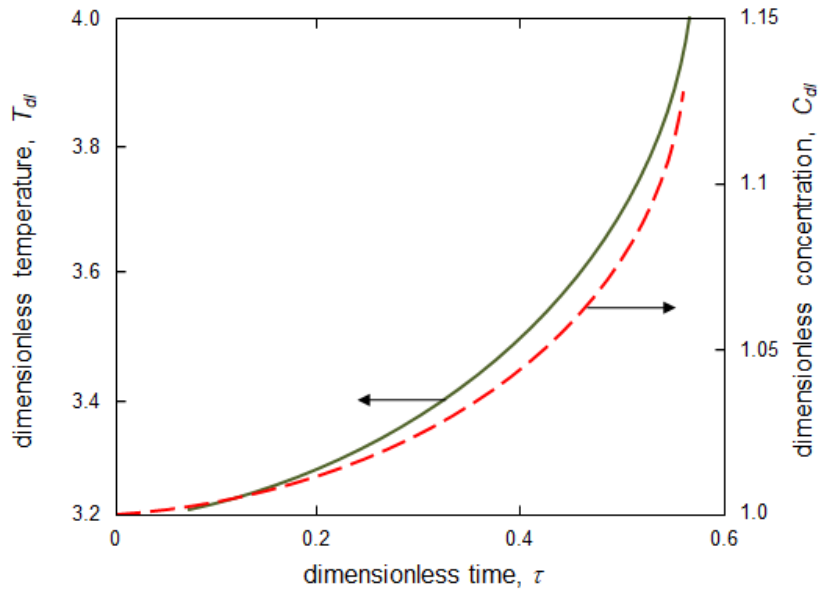

Figure 4. Dimensionless temperature T_{dl} and solute concentration C_{dl} in a binary supercooled melt as functions of dimensionless time τ.

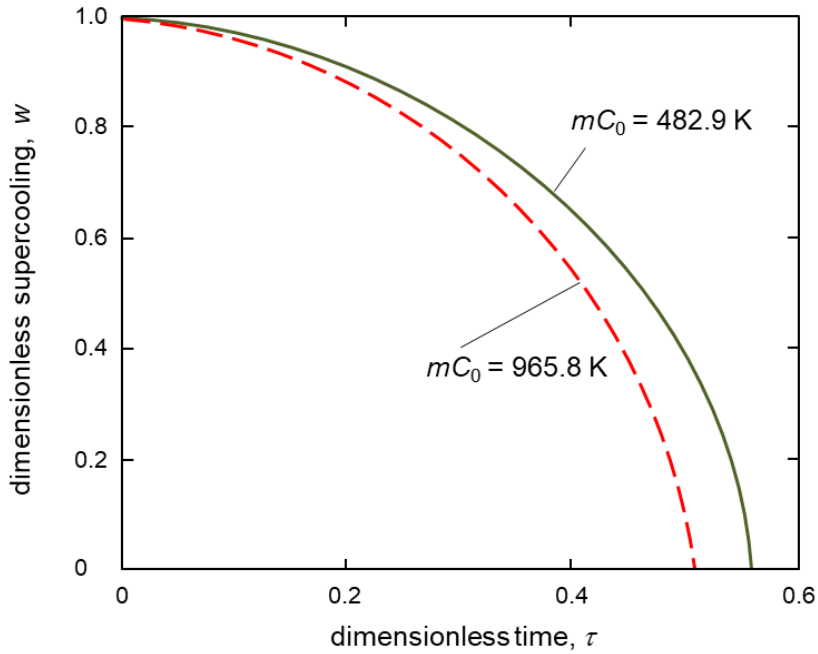

Figure 5. Dimensionless supercooling w in a binary melt as a function of dimensionless time τ at two initial concentrations C_0.

4. Conclusions

In summary, in this paper, we develop a theory of nucleation and evolution for a polydisperse ensemble of ellipsoidal particles in a supercooled binary alloy. This theory is developed with allowance for the "diffusion" mechanism of crystals in the space of their volumes. Physically it means taking into account possible fluctuations in the particle growth rates. The theory is developed for arbitrary nucleation frequency with special consideration of two popular nucleation kinetics according to the Meirs and WVFZ mechanisms. An analytical solution to the integrodifferential model equations is found in a parametric form. We show that the melt temperature and solute concentration increase with time. This is caused due to the effects of impurity displacement by the surfaces of growing crystals and latent heat release during the bulk phase transformation. What is more, we show that the melt supercooling decreases faster with increasing the initial solute concentration. The theory contains all limiting transitions to previously developed analytical approaches. Namely, it contains the growth of spherical crystals in binary melts [31,32] and ellipsoidal crystals in single-component melts [29,30].

The theory under consideration is developed for a pure bulk phase transition process when crystals appear and grow in the volume of an unbounded liquid. One of the most significant factors playing an important role is to consider the walls, as well as the cooling of the system through these walls. This can be done by analogy with the previously developed theory [53–55] for spherical particles. Another important effect that should be taken into account in future studies is the phase transition temperature shift due to the curvature of the crystal surface and the kinetics of atoms joining it. Such a theory for ellipsoidal particles can be developed by analogy with Ref. [56]. It also seems important to consider the possibility of joint implementation of bulk and directional crystallization. Directional phase transition (in addition to the bulk one) appears in the presence of a temperature gradient along with one of the spatial directions (for example, as a result of melt cooling). The development of the present theory to such a more general phase transformation process can be conducted in the spirit of Refs. [57–59]. The present analytical approach, taking a non-spherical shape of growing crystals into account, can be used when considering particle evolution in external fields (e.g., metastable magnetic fluids [33], buoyancy forces [34],

polymerization [14], external heat and mass exchange with the environment and removal mechanisms of product crystals from a crystallizer [35–37]).

Author Contributions: Conceptualization, D.V.A.; methodology, D.V.A.; software, M.A.N.; validation, M.A.N. and D.V.A.; formal analysis, M.A.N. and D.V.A.; investigation, M.A.N. and D.V.A.; writing—original draft preparation, M.A.N. and D.V.A.; writing—review and editing, M.A.N. and D.V.A.; visualization, M.A.N.; discussion, M.A.N. and D.V.A.; supervision, D.V.A.; project administration, D.V.A.; funding acquisition, D.V.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Russian Science Foundation (project no. 18-19-00008).

Data Availability Statement: All data generated or analyzed during this study are included in this published article.

Conflicts of Interest: The authors declare no conflict of interest.

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