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ANALYTIC DESCRIPTION OF BINARY MELT CRYSTALLIZATION

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In [1, 2] an approach was developed for the analytic description of the crystallization of binary systems. Diffusion processes at the interphase boundary were assumed to occur so intensely that the concentration in the melt was independent of the local phase-boundary configuration. Such an approximation is physically justifiable if the crystallization process is limited to its kinetic stage. In the case where the characteristic rate of diffusion mass transfer in the concentration boundary layer is less than the maximum possible growth rate at specified temperature values and specified component concentrations in the melt core, we must consider the crystallization process in a diffusion regime. The growth rate and structural characteristics of the interphase zone are then determined by diffusion mass transfer to the phase boundary and the value of the concentration gradient which develops near the boundary.

The purpose of the present study is an analytic description of the crystallization of binary melts with consideration of diffusion in the melt. With a microscopic examination of the kinetics of elementary process we will obtain a system of finite-difference equations for the diffusion boundary layer near the surface of the growing crystal faces.

We will consider a lattice model of the binary crystal-melt system. We assume that atoms of the α and β components are located at lattice points and belong to either the liquid or solid phase. At each lattice point there is located only one such particle, the total number of which is equal to N . Interaction within the system will be described by the values of the effective binding energies of the most closely neighboring solid particles $\varphi_{11}^{\alpha\alpha}$, $\varphi_{11}^{\alpha\beta}$, $\varphi_{11}^{\beta\beta}$; of solid particles with liquid particles $\varphi_{10}^{\alpha\alpha}$, $\varphi_{10}^{\beta\beta}$, $\varphi_{10}^{\alpha\beta}$, $\varphi_{01}^{\alpha\beta}$; and of liquid particles $\varphi_{00}^{\alpha\alpha}$, $\varphi_{00}^{\alpha\beta}$, $\varphi_{00}^{\beta\beta}$ (the subscript 0 denotes the liquid phase, while the subscript 1 denotes the solid phase). As in [1, 2], the configuration of the distribution of atoms over the system is

specified by a set of parameters $g = \left\{ \begin{matrix} \xi_j \\ \eta_j \end{matrix} \right\}$, where $\eta_j = 1$ if at the j -th lattice point a solid particle exists and $\eta_j = 0$ if a liquid particle is present; ξ_j defines the type of particle at this point ($\xi_j = \alpha, \beta$). We denote by $\rho(g, t)$ the probability of finding the system at time t in a state with configuration g . The time evolution of the distribution function $\rho(g, t)$ in our model is the result of completion of elementary events of transition of liquid

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particles into the solid state, of solid particles into the liquid state, and of diffusion exchanges of place between pairs of adjacent particles. The characteristic time of the process τ is chosen sufficiently small so that over its course no more than one elementary act can occur.

We write the kinetic equation for $\rho(\mathbf{g}, t)$ in the form

$$\begin{aligned} & \frac{\partial \rho(\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N; t)}{\partial t} = \\ & = \sum_{i, \eta_i} W_{\eta_i \eta_i}^{\xi_i} \rho(\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N; t) + \\ & + \sum_{i, j \neq i} W_{\xi_i \eta_i}^{\xi_j \eta_j} \rho(\xi_1, \eta_1; \dots \xi_j, \eta_j; \xi_i, \eta_i; \dots \xi_N, \eta_N; t) - \\ & - \left[\sum_{i, \eta_i} W_{\eta_i \eta_i}^{\xi_i} + \sum_{i, j \neq i} W_{\xi_j \eta_j}^{\xi_i \eta_i} \right] \rho(\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N; t), \end{aligned} \quad (1)$$

where $W_{\eta_i \eta_i}^{\xi_i}$ is the frequency of transition of a ξ_i particle at the i -th lattice point from a phase state η_i to η_i ; $W_{\xi_j \eta_j}^{\xi_i \eta_i}$ is the frequency of diffusion exchange of place of a ξ_j particle located at the i -th point in a phase state η_i with a particle of the type ξ_j located at the j -th point in a phase state η_j . Summation in Eq. (1) is performed over all neighbors, adjacent to the point i , $j (j \in i)$, over all lattice points i , and over the phase states η_i . The first two terms in Eq. (1) describe the probability of transitions of some configuration of particle distribution in the system by the performance of a single elementary act into a configuration $\mathbf{g} = (\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N)$, while the last two terms are the probability of reverse transitions over a characteristic time τ .

The condition of detailed equilibrium allows us to express the ratio of the transition frequencies in terms of equilibrium distribution functions. We denote by $f(\xi_i, \eta_i; \xi_j, \eta_j)$ the probability of observation in the equilibrium state of a system with configuration \mathbf{g} , the i -th point of which corresponds to the parameter $\begin{pmatrix} \xi_i \\ \eta_i \end{pmatrix}$, and the j -th point ($j \in i$) of which corresponds to the parameter $\begin{pmatrix} \xi_j \\ \eta_j \end{pmatrix}$. From Eq. (1) we have

$$\frac{W_{\eta_i \eta_i}^{\xi_i}}{W_{\xi_j \eta_j}^{\xi_i \eta_i}} = \frac{f(\xi_i, \eta_i; \xi_j, \eta_j)}{f(\xi_i, \eta_i; \xi_j, \eta_j)}, \quad \frac{W_{\xi_j \eta_j}^{\xi_i \eta_i}}{W_{\xi_j \eta_j}^{\xi_i \eta_i}} = \frac{f(\xi_i, \eta_i; \xi_j, \eta_j)}{f(\xi_j, \eta_j; \xi_i, \eta_i)}. \quad (2)$$

To determine the explicit form of the functions $W_{\eta_i \eta_i}^{\xi_i}$, $W_{\xi_j \eta_j}^{\xi_i \eta_i}$ from the local configuration of particle distribution, we consider that at equilibrium

$$\begin{aligned} \frac{f(\xi_i, \eta_i; \xi_j, \eta_j)}{f(\xi_i, \eta_i; \xi_j, \eta_j)} &= \frac{\exp[-H(\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N)/kT]}{\exp[-H(\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N)/kT]}, \\ \frac{f(\xi_i, \eta_i; \xi_j, \eta_j)}{f(\xi_j, \eta_j; \xi_i, \eta_i)} &= \frac{\exp[-H(\xi_1, \eta_1; \dots \xi_i, \eta_i; \xi_j, \eta_j; \dots \xi_N, \eta_N)/kT]}{\exp[-H(\xi_1, \eta_1; \dots \xi_j, \eta_j; \xi_i, \eta_i; \dots \xi_N, \eta_N)/kT]}. \end{aligned} \quad (3)$$

The thermodynamic potential of the system $\Phi(\mathbf{g})$ plays the role of the Hamiltonian $H(\mathbf{g})$ for the order field \mathbf{g} , and $H(\mathbf{g})$ may be represented in the form

$$H(\mathbf{g}) = \sum_{\nu, \eta} N_{\eta}^{\nu} \tilde{\mu}_{\eta}^{\nu} + \sum_{\nu} N_{10}^{\nu \nu} \omega_{10}^{\nu \nu} + \sum_{\eta, \eta'} \bar{N}_{\eta \eta'}^{\alpha \beta} \omega_{\eta \eta'}^{\alpha \beta} + TS, \quad (4)$$

where $\tilde{\mu}_{\eta}^{\nu}$ is the chemical potential of the pure ν component located in the phase state η ; N_{η}^{ν} is the total number of $\nu - \eta$ particles; $N_{\eta \eta}^{\nu \xi}$ is the number of bonds between closest neighbors of types ν and ξ belonging to phase states η and η' , respectively; and $\omega_{\eta \eta}^{\nu \xi}$ is the heat of mixing of the components $\omega_{\eta \eta}^{\nu \xi} = \varphi_{\eta \eta}^{\nu \xi} - 1/2(\varphi_{\eta \eta}^{\nu \nu} + \varphi_{\eta' \eta'}^{\xi \xi})$. The last term in Eq. (4) describes the configuration component of the system entropy. If we do not consider diffusion processes in the solid phase, assuming that their characteristic times are much greater than those connected with growth rate and diffusion in the liquid phase, the configuration component of the

entropy will be equal to the entropy of mixing of the melt. In the single-particle approximation (condition of complete miscibility)

$$S = N_0^\alpha \ln c_0^\alpha + N_0^\beta \ln c_0^\beta, \quad (5)$$

where $c_0^\alpha = N_0^\alpha/N$ is the concentration of α particles in the melt and N is the total number of particles in the system. We define the chemical potentials of the solid and liquid phase components as the mean change over the ensemble of the Hamiltonian in the phase-transition process,

$$\begin{aligned} \mu_1^\nu &= \left\langle \left(\frac{\partial H}{\partial N_1^\nu} \right)_{N_0^\xi, N_1^\xi, N_0^\nu} \right\rangle, \\ \mu_0^\nu &= \left\langle \left(\frac{\partial H}{\partial N_0^\nu} \right)_{N_0^\xi, N_1^\xi, N_1^\nu} \right\rangle \quad (\xi \neq \nu). \end{aligned} \quad (6)$$

With consideration of Eq. (6),

$$\Delta\mu^\nu = \mu_0^\nu - \mu_1^\nu = \langle H(N_0^\xi, N_1^\xi, N_0^\nu + 1, N_1^\nu - 1) - H(N_0^\xi, N_1^\xi, N_0^\nu, N_1^\nu) \rangle \quad (\xi \neq \nu).$$

In the case of growth of stable crystalline faces in a stationary regime, $\Delta\mu^\nu$ has the sense of the difference between the chemical potentials of the volume phases, since the mean change in surface energy

$$\langle \Delta H \text{ surf} \rangle = \left\langle \Delta \left(\sum_{\nu, \xi} N_{10}^{\nu\xi} \omega_{10}^{\nu\xi} \right) \right\rangle = 0. \quad (7)$$

As a result, using Eqs. (4), (6), and (7), we have

$$\Delta\mu^\nu = \tilde{\Delta}\mu^\nu + \gamma_0^\nu \omega_{00}^{\alpha\beta} - \gamma_1^\nu \omega_{11}^{\alpha\beta} + T \langle (\partial S / \partial N_0^\nu) - (\partial S / \partial N_1^\nu) \rangle.$$

Here γ_η^ν is the η -phase structural factor, describing the degree of its close order:

$$\gamma_\eta^\nu = \left\langle \left(\frac{\partial N_{\eta\eta}^{\alpha\beta}}{\partial N_\eta^\nu} \right) \right\rangle.$$

In the approximation (5), we obtain the usual expression for the difference between the chemical potentials:

$$\begin{aligned} \Delta\mu^\nu &= \tilde{\Delta}\mu^\nu + l c_0^\nu \omega_{00}^{\alpha\beta} - \gamma_1^\nu \omega_{11}^{\alpha\beta} + T \ln c_0^\nu, \\ \tilde{\Delta}\mu^\nu &= \frac{\tilde{L}^\nu}{k \tilde{T}_{eq}^\nu} \frac{\tilde{T}_{eq}^\nu - T}{T}, \end{aligned} \quad (8)$$

where \tilde{T}_{eq}^ν is the fusion temperature; $\tilde{L}^\nu = (Z/2)(\varphi_{00}^{\nu\nu} - \varphi_{11}^{\nu\nu})$ is the heat of transition of the pure ν component; and Z is the coordination number. In the case of crystallization from solutions, a different form of Eq. (8) will be more convenient:

$$\Delta\mu^\nu = \Delta\mu_0^\nu + \Delta\mu_1^\nu, \quad \Delta\mu_1^\nu = \omega_{11}^{\alpha\beta} [(\gamma_1^\nu)_{eq} - \gamma_1^\nu],$$

according to which supersaturation of the system (the moving force of the crystallization process $\Delta\mu^\nu$) is equal to the sum of the supersaturation of the liquid $\Delta\mu_0^\nu$ and solid $\Delta\mu_1^\nu$ phases. The parameter γ_1^ν then characterizes the degree of supersaturation of the crystal related to disordering of its structure in the growth process.

Considering Eqs. (3) and (4), instead of Eq. (2) we obtain

$$\frac{W_{01}^{\xi i}}{W_{10}^{\xi i}} = \exp \left[- \frac{1}{kT} \sum_{\nu, \eta} l_{\eta}^{\xi i \nu} (\varphi_{0\eta}^{\xi i \nu} - \varphi_{1\eta}^{\xi i \nu}) + \theta_{\xi i} \right], \quad \sum_{\nu, \eta} l_{\eta}^{\xi i \nu} = l; \quad (9)$$

$$\begin{aligned} \frac{W_{\alpha_i 0}^{\beta_j 0}}{W_{\beta_j 0}^{\alpha_i 0}} &= \frac{f(\alpha_i, 0; \beta_j, 0)}{f(\beta_j, 0; \alpha_i, 0)} = \exp \left[\frac{(l-1 - l_0^{\alpha_i \alpha} - l_0^{\beta_j \beta}) (\varphi_{00}^{\alpha\alpha} + \varphi_{00}^{\beta\beta} - 2\varphi_{00}^{\alpha\beta})}{kT} - \right. \\ &\quad - \frac{l_1^{\alpha_i \alpha} (\varphi_{01}^{\alpha\alpha} + \varphi_{00}^{\beta\beta} - \varphi_{01}^{\beta\alpha} - \varphi_{00}^{\alpha\beta})}{kT} - \frac{l_1^{\alpha_i \beta} (\varphi_{01}^{\alpha\beta} + \varphi_{00}^{\beta\beta} - \varphi_{01}^{\beta\beta} - \varphi_{00}^{\alpha\beta})}{kT} \\ &\quad \left. - \frac{l_1^{\beta_j \beta} (\varphi_{01}^{\beta\beta} + \varphi_{00}^{\alpha\alpha} - \varphi_{01}^{\alpha\beta} - \varphi_{00}^{\alpha\beta})}{kT} - \frac{l_1^{\beta_j \alpha} (\varphi_{01}^{\beta\alpha} + \varphi_{00}^{\alpha\alpha} - \varphi_{01}^{\alpha\alpha} - \varphi_{00}^{\alpha\beta})}{kT} \right], \end{aligned} \quad (10)$$

where $\theta_{\xi_i} = \theta_i^{\xi_i} - \theta_{o_i}^{\xi_i}$, and $z_{\eta'}^{\xi_i \nu}$ is the number of neighbors adjacent to the particle ξ_i located at node i of type ν in phase state η' . We now take $\varphi_{o_i}^{\xi_i \nu} = \varphi_{o_o}^{\xi_i \nu}$. Then

$$\frac{W_{\alpha_i 0}^{\beta_j 0}}{W_{\beta_j 0}^{\alpha_i 0}} = \exp[(l-1 - l_0^{\alpha_i \alpha} - l_1^{\alpha_i \alpha} - l_0^{\beta_j \beta} - l_1^{\beta_j \beta} (\varphi_{00}^{\alpha \alpha} + \varphi_{00}^{\beta \beta} - 2\varphi_{00}^{\alpha \beta})/kT]$$

is determined by only one energy parameter — the heat of mixing of the liquid phase. If the close order of the component distribution in the melt is insignificant, the frequency of diffusion transitions can be considered independent of the number of adjacent neighbors and

$$W_{\alpha_i 0}^{\beta_j 0} = W_{\beta_j 0}^{\alpha_i 0} = W_{\beta}^{\alpha} \quad (11)$$

for any pair i, j of liquid nodes. We will also assume Eq. (11) to be valid in the general case, relying on experimental data, according to which the diffusion coefficient is independent in order of magnitude of the type of system, comprising $\sim 10^{-5}$ cm²/sec. It can be hoped that the approximation (11) will have no significant effect on the quantitative results of the calculations. The ratio of the transition frequencies (9) from one phase to the other with consideration of $\varphi_{o_i}^{\xi_i \nu} = \varphi_{o_o}^{\xi_i \nu}$ has the form

$$\frac{W_{01}^{\xi_i}}{W_{10}^{\xi_i}} = \exp\left[-\frac{l_1^{\xi_i \alpha} \Phi_{\xi_i \alpha} + l_1^{\xi_i \beta} \Phi_{\xi_i \beta}}{kT} + \theta_{\xi_i}\right], \quad (12)$$

$$\Phi_{\xi_i \nu} = \varphi_{00}^{\xi_i \nu} - \varphi_{11}^{\xi_i \nu}.$$

As in [1, 2], to find the explicit form of $W_{o_1}^{\xi_i}$, $W_{10}^{\xi_i}$ we assume that the activation energy for uniting a liquid particle to the crystal is independent of the local configuration of component distribution. Then, if the type of particle being joined is known,

$$W_{10}^{\alpha} = W_{10}^{\beta} = \omega \exp\left(-\frac{u}{kT}\right) = W_{10} \quad (13)$$

(where ω is the frequency factor). Thus, Eqs. (11)-(13) specify all the frequency characteristics of elementary processes in the system in thermodynamic equilibrium. For the future we will assume that these relationships maintain their form for nonequilibrium systems.

We will solve Eq. (1) in the two-particle approximation of the distribution function, which can be related to the close-order parameters. To do this, we consider the concentration of solid-solid $c_{11}^{\nu\gamma}(i, k)$, solid-liquid $c_{o_1}^{\nu\gamma}(i, k)$, and liquid-liquid $c_{o_0}^{\nu\gamma}(i, k)$ closest-neighbor bonds in the lattice ($\nu, \gamma = \alpha, \beta$),

$$c_{11}^{\nu\gamma}(i, k) = \sum_{\mathbf{g}} \eta_i \eta_k \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \rho(\mathbf{g}, t) = \sum_{\eta_i, \xi_i, \eta_k, \xi_k} \eta_i \eta_k \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t),$$

$$c_{o_1}^{\nu\gamma}(i, k) = \sum_{\eta_i, \xi_i, \eta_k, \xi_k} (1 - \eta_i) \eta_k \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t),$$

$$c_{o_0}^{\nu\gamma}(i, k) = \sum_{\eta_i, \xi_i, \eta_k, \xi_k} (1 - \eta_i) (1 - \eta_k) \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t).$$

Here $\rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t)$ is the two-particle distribution function,

$$\sum_{\nu, \gamma, \eta, \eta'} c_{\eta\eta'}^{\nu\gamma}(i, k) = 1.$$

Multiplying the left and right sides of Eq. (1) by $\eta_i \eta_k \delta_{\xi_i \nu} \delta_{\xi_k \gamma}$ and summing over all configurations, we obtain

$$\frac{dc_{11}^{\nu\gamma}(i, k)}{dt} = \sum_{\xi_i, \eta_i, \xi_k, \eta_k} \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \left\{ \sum_{j \in i} (1 - 2\eta_i) \eta_k W_{1-\eta_i, \eta_i}^{\xi_i} \rho^{(7)}(\xi_i, \eta_i; t) + \sum_{j \in k} (1 - 2\eta_k) \eta_i W_{1-\eta_k, \eta_k}^{\xi_k} \rho^{(7)}(\xi_k, \eta_k; t) \right\}. \quad (14)$$

Similarly

$$\begin{aligned}
\frac{dc_{01}^{v\gamma}(i, k)}{dt} &= \sum_{\xi_i, \eta_i; \xi_k, \eta_k} \delta_{\xi_i v} \left\{ \sum_{j \in i} [\delta_{\xi_i v} (2\eta_i - 1) \eta_k W_{1-\eta_i, \eta_i}^{\xi_i} \rho^{(7)}(\xi_i, \eta_i; t) + \right. \\
&+ \delta_{\xi_i v} (1 - \eta_j) - \delta_{\xi_i v} (1 - \eta_i) \eta_k W_{\xi_j \eta_j}^{\xi_i \eta_i} \rho^{(3)}(\xi_i, \eta_i; \xi_k, \eta_k; \xi_j, \eta_j; t)] + \\
&+ \sum_{j \in k} \delta_{\xi_i v} (1 - \eta_i) (1 - 2\eta_k) W_{1-\eta_k, \eta_k}^{\xi_k} \rho^{(7)}(\xi_k, \eta_k; t) \Big\}; \\
\frac{dc_{00}^{v\gamma}(i, k)}{dt} &= \sum_{\xi_i, \eta_i; \xi_k, \eta_k} \left\{ \sum_{j \in i} \delta_{\xi_i v} \delta_{\xi_k v} (2\eta_i - 1) (1 - \eta_k) W_{1-\eta_i, \eta_i}^{\xi_i} \rho^{(7)}(\xi_i, \eta_i; t) + \right. \\
&+ \sum_{j \in k} \delta_{\xi_i v} \delta_{\xi_k v} (1 - \eta_i) (2\eta_k - 1) W_{1-\eta_k, \eta_k}^{\xi_k} \rho^{(7)}(\xi_k, \eta_k; t) + \\
&+ \sum_{j \in i, j \neq k} [\delta_{\xi_i v} (1 - \eta_j) - \delta_{\xi_i v} (1 - \eta_i)] \delta_{\xi_k v} (1 - \eta_k) W_{\xi_j \eta_j}^{\xi_i \eta_i} \rho^{(3)} \times \\
&\times (\xi_i, \eta_i; \xi_k, \eta_k; \xi_j, \eta_j; t) + \sum_{j \in k, j \neq i} [\delta_{\xi_j v} (1 - \eta_j) - \delta_{\xi_k v} (1 - \eta_k)] \delta_{\xi_i v} (1 - \\
&- \eta_i) W_{\xi_j \eta_j}^{\xi_k \eta_k} \rho^{(3)}(\xi_i, \eta_i; \xi_k, \eta_k; \xi_j, \eta_j; t) + (\delta_{\xi_k v} \delta_{\xi_i v} - \delta_{\xi_i v} \delta_{\xi_k v}) (1 - \eta_i) (1 - \eta_k) W_{\xi_k \eta_k}^{\xi_i \eta_i} \rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t) \Big\}, \quad (15)
\end{aligned}$$

where $\rho^{(7)}(\xi_i, \eta_i; t)$ is the seven-particle distribution function with central point i and z adjacent neighbors $j \in i$; $\rho^{(3)}(\xi_i, \eta_i; \xi_k, \eta_k; \xi_j, \eta_j; t)$ is the three-particle distribution function, while the point j here is a closest neighbor to the point i if $j \neq k$ and to the point k if $j \neq i$. We introduce the two-particle distribution function approximation in the superposition approximation:

$$\begin{aligned}
\rho^{(7)}(\xi_i, \eta_i; t) &= \rho^{(1)}(\xi_i, \eta_i; t) \prod_{j=1}^z \frac{\rho^{(2)}(\xi_i, \eta_i; \xi_j, \eta_j; t)}{\rho^{(1)}(\xi_i, \eta_i; t)}, \quad j \in i, \\
\rho^{(3)}(\xi_i, \eta_i; \xi_k, \eta_k; \xi_j, \eta_j; t) &= \rho^{(2)}(\xi_i, \eta_i; \xi_j, \eta_j; t) \frac{\rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t)}{\rho^{(1)}(\xi_i, \eta_i; t)}, \quad j \in i, \\
\rho^{(3)}(\xi_i, \eta_i; \xi_k, \eta_k; \xi_j, \eta_j; t) &= \rho^{(2)}(\xi_k, \eta_k; \xi_j, \eta_j; t) \frac{\rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t)}{\rho^{(1)}(\xi_k, \eta_k; t)}, \quad j \in k.
\end{aligned} \quad (17)$$

Substituting Eqs. (14)-(16) into Eq. (17) and summing over all configurations, we obtain a system of equations describing the evolution of the close-order, and thus the distant-order, parameters $c_{\eta}^v = \sum_{\eta} c_{\eta}^{v\gamma}$ with time.

For simplicity, we will consider the crystallization of a binary melt into a simple cubic lattice ($z = 6$). A cross section of the crystal-melt system is shown in Fig. 1 (R is the crystallization rate). We divide the interphase zone and adjacent volumes of solid and liquid phases into atomic layers parallel to the xy plane. The z axis corresponds to the growth direction of the face (001), and whole number coordinates along the z axis correspond to the atomic layers. Each layer will be characterized by a concentration of solid-solid $c_{11}^{v\gamma}(z)$, solid-liquid $c_{10}^{v\gamma}(z)$, and liquid-liquid $c_{00}^{v\gamma}(z)$ bonds of adjacent neighbors of all types in the xy plane and also by concentrations of solid-solid $c_{11}^{v\gamma}(z, z-1)$, solid-liquid $c_{01}^{v\gamma}(z, z-1)$, and liquid-liquid $c_{00}^{v\gamma}(z, z-1)$ bonds along the growth direction. Let xyz be integral coordinates defining the position of a lattice point in a layer; $\eta_{xyz} = 1$ if at the point with coordinates xy in layer z a solid atom exists, while $\eta_{xyz} = 0$ if a liquid particle is located there. We will limit our consideration to system states corresponding to interphase boundary configurations without impendency. This means that in the atomic column along the direction of the growth rate v only one solid atom has a neighbor in the liquid state beneath it. With consideration of this,

$$W_{10}^{\xi xyz} = W_{10} \eta_{xy, z-1} (1 - \eta_{xyz}). \quad (18)$$

Since diffusion is considered only in the melt,

$$W_{\xi k}^{\xi i} = (\delta_{\xi_i \alpha} \delta_{\xi_k \beta} + \delta_{\xi_i \beta} \delta_{\xi_k \alpha}) (1 - \eta_i) (1 - \eta_k) W_{\beta}^{\alpha}. \quad (19)$$

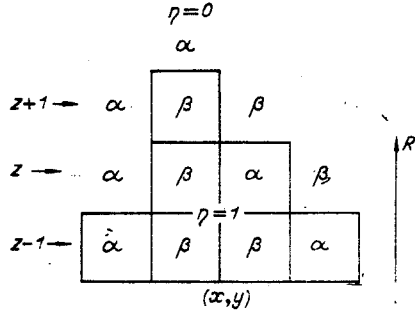


Fig. 1

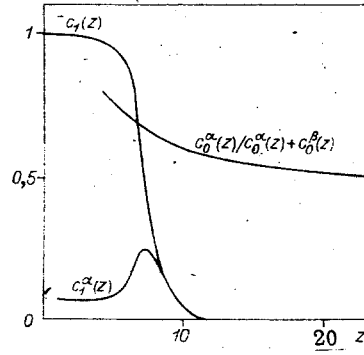


Fig. 2

Thus, the problem reduces to obtaining, with the consideration of Eqs. 14)-(19), a system of 28 finite-difference equations in the 24 adjacent neighbor bond concentrations $c_{\eta\eta}^{\nu\gamma}(z)$, $c_{\eta\eta}^{\nu\gamma}(z, z-1)$ and the four particle concentrations $c_{\eta}^{\nu}(z)$, of which only 14 of the variables are linearly independent. We chose as the independent variables $c_{11}^{\alpha\alpha}(z, z-1)$, $c_{11}^{\beta\beta}(z, z-1)$, $c_{01}^{\alpha\alpha}(z, z-1)$, $c_{01}^{\beta\beta}(z, z-1)$, $c_{00}^{\alpha\alpha}(z, z-1)$, $c_{11}^{\alpha\alpha}(z)$, $c_{11}^{\beta\beta}(z)$, $c_{11}^{\alpha\beta}(z)$, $c_{01}^{\alpha\alpha}(z)$, $c_{01}^{\beta\beta}(z)$, $c_{00}^{\alpha\alpha}(z)$, $c_{00}^{\beta\beta}(z)$, $c_1^{\alpha}(z)$, $c_1^{\beta}(z)$. Averaging in Eqs. (9)-(11) in the two-particle approximation of the distribution function, we have

$$\begin{aligned}
 dc_{\eta\eta}^{\nu\gamma}(z, z-1)/dt = & [c_{01}^{\nu\gamma}(z+1, z) Q_{\nu\gamma}(z, z-1) Q_{\nu}^{\delta}(z) - \\
 & - c_{01}^{\nu\gamma}(z, z-1)] \delta_{\eta'1} (\delta_{\eta 0} - \delta_{\eta 1} \delta_{\nu\gamma}) W_{10}^{\gamma} - [c_{01}^{\nu\gamma}(z, z-1) Q_{\nu}(z-1, z-2) Q_{\nu}^{\delta} \times \\
 & \times (z-1) - c_{00}^{\nu\gamma}(z, z-1) c_{01}^{\nu\delta}(z-1, z-2) [c_0^{\nu}(z-1)]^{-1}] \times \\
 & \times \delta_{\eta 0} (\delta_{\eta'1} - \delta_{\eta'0} \delta_{\nu\gamma}) W_{10}^{\gamma} + [c_{\eta\eta'}^{\mu\nu}(z, z-1) [c_{\eta}^{\mu}(z)]^{-1} [c_{\eta\eta'}^{\mu\nu}(z+1, z) + \\
 & + 2c_{\eta\eta'}^{\mu\nu}(z)] - c_{\eta\eta'}^{\nu\gamma}(z, z-1) [c_{\eta}^{\nu}(z)]^{-1} [c_{\eta\eta'}^{\nu\gamma}(z+1, z) + 2c_{\eta\eta'}^{\nu\gamma}(z)]] \delta_{\eta 0} (\delta_{\eta'0} + \\
 & + \delta_{\eta'1}) (1 - \delta_{\mu\nu}) W_{\beta}^{\alpha} + [c_{\eta\eta'}^{\mu\nu}(z, z-1) [c_{\eta}^{\mu}(z-1)]^{-1} [c_{\eta\eta'}^{\mu\nu}(z-1, z-2) + \\
 & + 2c_{\eta\eta'}^{\mu\nu}(z-1)] - c_{\eta\eta'}^{\nu\gamma}(z, z-1) [c_{\eta}^{\nu}(z-1)]^{-1} [c_{\eta\eta'}^{\mu\nu}(z-1, z-2) + 2c_{\eta\eta'}^{\nu\gamma}(z-1)]] \delta_{\eta 0} \delta_{\eta'0} (1 - \delta_{\mu\nu}) W_{\beta}^{\alpha}; \quad (20)
 \end{aligned}$$

$$\begin{aligned}
 \frac{dc_{\eta\eta'}^{\nu\gamma}(z)}{dt} = & \psi \left[\begin{pmatrix} \nu \\ \eta \end{pmatrix}, \begin{pmatrix} \gamma \\ \eta' \end{pmatrix} \right] + \psi \left[\begin{pmatrix} \gamma \\ \eta' \end{pmatrix}, \begin{pmatrix} \nu \\ \eta \end{pmatrix} \right], \quad \psi \left[\begin{pmatrix} \nu \\ \eta \end{pmatrix}, \begin{pmatrix} \gamma \\ \eta' \end{pmatrix} \right] = \\
 = & c_{01}^{\nu\delta}(z, z-1) [c_0^{\nu}(z)]^{-1} [c_{01}^{\nu\gamma}(z) \delta_{\eta'1} f_1 + c_{00}^{\nu\gamma}(z) \delta_{\eta'0} f_2] W_{10}^{\gamma} + \\
 & + c_{01}^{\nu\delta}(z+1, z) [c_1^{\nu}(z)]^{-1} Q_{\nu}(z, z-1) Q_{\nu}^{\delta}(z) [c_{10}^{\nu\delta}(z) \delta_{\eta'0} f_3 + \\
 & + c_{11}^{\nu\delta}(z) \delta_{\eta'1} \exp(-\Phi_{\nu\gamma}/kT) f_4] W_{10}^{\gamma} + [c_{\eta\eta'}^{\mu\nu}(z) [4c_{\eta}^{\mu}(z)]^{-1} \times \\
 & \times [3c_{\eta\eta'}^{\mu\nu}(z) + 2c_{\eta\eta'}^{\mu\nu}(z, z-1) + 2c_{\eta\eta'}^{\mu\nu}(z+1, z)] [2\delta_{\eta'1} + (4-3\delta_{\nu\gamma}) \delta_{\eta'0}] - \\
 & - c_{\eta\eta'}^{\nu\gamma}(z) [2c_{\eta}^{\nu}(z)]^{-1} [3c_{\eta\eta'}^{\mu\nu}(z) + 2c_{\eta\eta'}^{\mu\nu}(z, z-1) + 2c_{\eta\eta'}^{\mu\nu}(z+1, z)] \delta_{\eta 0} (\delta_{\eta'0} + \delta_{\eta'1})] (1 - \delta_{\mu\nu}) W_{\beta}^{\alpha}, \quad (21)
 \end{aligned}$$

where

$$\begin{aligned}
 f_1 = & \delta_{\eta 1} (2 - \delta_{\nu\gamma}) 2^{-1} - \delta_{\eta 0}; \quad f_2 = \delta_{\eta 1} (1 + \delta_{\nu\gamma}) - \delta_{\eta 0}; \\
 f_3 = & \delta_{\eta 0} (2 - \delta_{\nu\gamma}) 2^{-1} - \delta_{\eta 1}; \quad f_4 = \delta_{\eta 0} (1 + \delta_{\nu\gamma}) - \delta_{\eta 1}; \\
 Q_{\nu\gamma}(z, z-1) = & c_{11}^{\nu\gamma}(z, z-1) [c_1^{\nu}(z)]^{-1} \exp(-\Phi_{\nu\gamma}/kT + \theta_{\nu}); \\
 Q_{\nu}(z, z-1) = & Q_{\nu\alpha}(z, z-1) + Q_{\nu\beta}(z, z-1); \\
 Q_{\nu}(z) = & c_{11}^{\nu\gamma}(z) [c_1^{\nu}(z)]^{-1} \exp(-\Phi_{\nu\gamma}/kT) + \\
 & + c_{11}^{\alpha\beta}(z) [2c_{11}^{\alpha\beta}(z)]^{-1} \exp(-\Phi_{\alpha\beta}/kT) + c_{10}^{\nu\delta}(z) [2c_1^{\nu}(z)]^{-1}; \\
 c_{0\eta}^{\nu} = & c_{0\eta}^{\alpha\nu} + c_{0\eta}^{\beta\nu}; \quad c_{1\eta}^{\nu} = c_{1\eta}^{\alpha\nu} + c_{1\eta}^{\beta\nu}.
 \end{aligned}$$

The remaining concentrations are found from the balance conditions

$$\begin{aligned}
 c_1^{\nu}(z) = & c_{01}^{\nu\delta}(z+1, z) + c_{11}^{\nu\gamma}(z+1, z) + c_{11}^{\nu\delta}(z+1, z) = \\
 = & c_{11}^{\nu\alpha}(z, z-1) + c_{11}^{\nu\beta}(z, z-1) = c_{11}^{\nu\gamma}(z) + [c_{11}^{\nu\gamma}(z) + c_{10}^{\nu\delta}(z)]/2 \quad (\gamma \neq \nu), \\
 c_0^{\nu}(z) = & c_{00}^{\nu\delta}(z+1, z) = c_{00}^{\nu\delta}(z, z-1) + c_{01}^{\nu\alpha}(z, z-1) + c_{01}^{\nu\beta}(z, z-1) = \\
 = & c_{00}^{\nu\gamma}(z) + [c_{00}^{\nu\gamma}(z) + c_{01}^{\nu\alpha}(z) + c_{01}^{\nu\beta}(z)]/2.
 \end{aligned}$$

The velocity of the interphase boundary motion is defined in the form

$$R = \sum_z \sum_v [dc_v^\alpha(z)/dt] W_{10}^{-1}.$$

Figure 2 shows a full section of the solid phase in the two-phase zone $c_1(z) = c_1^\alpha(z) + c_1^\beta(z)$, and distributions of the concentrations $c_1^\alpha(z)$ and $c_0^\alpha(z)/[c_0^\alpha(z) + c_0^\beta(z)]$ over atomic layers for an α component concentration in the core of the melt $c_0^\alpha(z)|_{z=\delta} = 0.25$. The thickness of the diffusion layer for the model example considered $\delta = 4$. This value was calculated from the atomic layer in which $c_1^\alpha(z) + c_1^\beta(z) = 0$. The results were obtained for a eutectic-type binary system [1, 2] with following parameter values: $\phi_{\alpha\alpha} = 300$ cal/mole; $\phi_{\alpha\beta} = 200$ cal/mole; $\phi_{\beta\beta} = 1500$ cal/mole; $\theta_\alpha = 1$; $\theta_\beta = 3$; and $W_\beta^\alpha = W_{10}$. The results indicate the strong dependence of interphase zone structure, concentration gradient in the melt, and crystallization rate on the value of the diffusion coefficient W_β^α .

An interesting peculiarity in the dynamics of solid-phase structure formation should be noted. In the curve $c_1^\alpha(z)$ (Fig. 2) there is a nonmonotonic dependence on z , corresponding to the fact that upon crystallization of some fixed atomic layer the rate of its filling by α particles is positive when $c_1^\alpha(z) + c_1^\beta(z) \leq 0.7$ and negative when the solid phase section exceeds the value 0.7. This nonmonotonic effect increases with increase in the component concentration discontinuity on the kinetic phase diagram.

In the one-particle approximation of the distribution function there remain as functions to be found only the component concentrations $c_n^v(z)$ for which $\sum_{v,\eta} c_n^v(z) = 1$. In [1, 2] it was shown that the single-particle approximation may be used for regular melts [3, 4], for which close order in the solid phases may be neglected.

Thus, the system of equations (20)-(22) offers a solution of the problem of a diffusion boundary layer without additional artificial assumptions as to the form of boundary conditions on the interphase boundary inherent to the Stefan problem. The approach proposed not only permits analysis of the dependence of concentration gradients in the melt on growth rate, but allows description in a self-consistent manner of the kinetics of crystalline-phase structure formation. Far from the interphase boundary, where $c_1^\alpha(z) + c_1^\beta(z) \equiv 0$, in the single-particle approximation of the distribution function, Eqs. (20)-(22) in the central difference approximate the conventional diffusion equation in the melt,

$$\frac{dc_0^\alpha(z)}{dt} = [c_0^\alpha(z+1) + c_0^\alpha(z-1) - 2c_0^\alpha(z)] W_\beta^\alpha.$$

The analytic description presented in the present study may also be used for the case of crystallization from solutions. Computer calculations were performed by G. T. Gidrikhson.

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