EQUATIONS OF THERMOHYDROMECHANICS FOR DESCRIBING THE PROCESSES OF MASS CRYSTALLIZATION OUT OF SOLUTIONS AND THE GAS PHASE

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The equations of thermohydromechanics of a two-phase polydisperse medium, taking into account growth of crystals only, were obtained in [1]. In this paper, the process of mass crystallization is described taking into account the phenomena of homogeneous, heterogeneous, and secondary nucleation. Relations are obtained for the motive forces for nucleation and mass transfer accompanying the growth of crystals.

1. We shall examine a heterogeneous mixture of two phases, of which the first phase is the carrying phase (solution of gas), while the second phase is present in the form of separate particles of various diameters, under the assumptions used in [1, 2]. The nuclei can form by homogeneous as well as heterogeneous and secondary paths. The secondary nucleation arises due to abrasion of crystals by the carrying phase.

Let us introduce at each point of the volume, occupied by the mixture, the volume content of the phases α_i, α_3 ($i = 1, 2$). We assume that the nuclei are an independent phase:

$$1 = \alpha_1 + \int\limits_{r_3^+}^{R} frdr + n_3 r_3, \quad \rho = \rho_1 + \int\limits_{r_3^+}^{R} \rho_2^0 frdr + \rho_3,$$

where the dispersion is characterized by the function $f(r)dr$, which is the number of particles per unit volume whose size (volumes) falls in the range $r - dr$, $r + dr$; the indices are as follows: 1 indicates the carrying phase; 2 indicates the dispersed phase; 3 indicates the nuclei; r is the volume of a particle; ρ, ρ_1, and ρ_2^0 are the density of the entire mixture, the carrying phase, and of the crystal, respectively, n_3 is the number of nuclei per unit volume ($n_3 = f_3 r_3$, $\alpha_3 = r_3 n_3$, $\rho_3 = \rho_2^0 r_3 n_3$). Following [1], we introduce the concept of the r phase: a collection of particles whose sizes (volume) fall in the interval $(r - dr, r + dr)$. Let us denote by $\psi(r)dr$ the number of nuclei formed per unit time and unit volume from particles belonging to the r-th phase; let $I_3 = I_{31} + I_{3u}$ denote the number of nuclei arising per unit time and unit volume; I_{31} is the rate of homogeneous, heterogeneous nucleation; I_{3u} is the rate of secondary nucleation $\left(I_{3u} = \int\limits_{r_3^+}^{R} \psi(r)\,dr\right)$. Then, the equations for conservation of mass of the carrying (r-th) phase of nuclei and the masses of the component in volume τ will assume the form

$$\int\limits_{\tau} \frac{\partial}{\partial t} \rho_1 d\tau = -\int\limits_{S} \rho_1 v_1^n dS - \int\limits_{\tau} \sum_r \rho_2^0 f \eta \Delta r d\tau - \int\limits_{\tau} \rho_2^0 r_3 I_{31} d\tau,$$

$$\int\limits_{\tau} \frac{\partial}{\partial t} [\rho_2^0 fr\Delta r]\, d\tau = -\int\limits_{S} (\rho_2^0 fr\Delta r)\, v_2^n(r)\, dS + \int\limits_{\tau} \rho_2^0 r\, [f(r)\eta(r) - f(r+dr)\eta(r+\Delta r)]\, d\tau - \int\limits_{\tau} \rho_2^0 r_3 \psi(r)\, \Delta r d\tau,$$

$$\int\limits_{\tau} \frac{\partial}{\partial t} \rho_2^0 r_3 n_3 d\tau = -\int\limits_{S} \rho_2^0 r_3 n_3 v_3^n dS + \int\limits_{\tau} [\rho_2^0 r_3 I_3 - \rho_2^0 f_3 \eta_3 r_3]\, d\tau, \quad \int\limits_{\tau} \frac{\partial}{\partial t} \rho_1 c d\tau = -\int\limits_{S} \rho_1 c v_1^n dS - \int\limits_{\tau} \left[\sum_r \rho_2^0 f \eta \Delta r - \rho_2^0 r_3 I_{31}\right] d\tau,$$

where S is the surface of volume τ; η is the rate of change of the volume of a particle; c is the mass concentration of matter in the solution; v_i is the velocity of the i-th phase.

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Applying the Gauss—Ostrogradskii equation and passing to the limit $\Delta r \to 0$, we obtain the differential equations for balance of the number of particles, nuclei, conservation of mass of the carrying phase and the component

$$\frac{\partial}{\partial t} f + \operatorname{div}(f\mathbf{v}_2) + \frac{\partial}{\partial r} f\eta = -\psi \frac{r_3}{r}, \tag{1.1}$$

$$\frac{\partial}{\partial t} n_3 + \operatorname{div}(n_3\mathbf{v}_3) = I_3 - f_3\eta_3,$$

$$\frac{\partial}{\partial t} \rho_1 + \operatorname{div} \rho_1\mathbf{v}_1 = -\int\limits_{r_3^+}^{R} \rho_2^0 f\eta\, dr - \rho_2^0 r_3 I_{31},$$

$$\rho_1 \frac{d_1 c}{dt} = (c-1)\left[\int\limits_{r_3^+}^{R} \rho_2^0 f\eta\, dr + \rho_2^0 r_3 I_{31}\right], \quad \frac{d_1}{dt} = \frac{\partial}{\partial t} + v_1^k \nabla^k.$$

As in [1], we obtain an equation for conservation of the momenta of the phases, written in differential form:

$$\rho_1 \frac{d_1\mathbf{v}_1}{dt} = -\alpha_1 \nabla P + \nabla^k \boldsymbol{\tau}_1^k - \int\limits_{r_3^+}^{R} \rho_2^0 fr\mathbf{f}_{12}\, dr - \rho_3\mathbf{f}_{12}(r_3) + \rho_1\mathbf{F}_1 - \int\limits_{r_3^-}^{R} \rho_2^0 f\eta\,(\mathbf{v}_{12} - \mathbf{v}_1)\, dr - \rho_2^0 r_3 I_{31}(\mathbf{v}_{12}(r_3) - \mathbf{v}_1); \tag{1.2}$$

$$\rho_2^0 fr \frac{D_2\mathbf{v}_2}{Dt} = -fr\nabla P + \rho_2^0 fr\mathbf{f}_{12} + \rho_2^0 fr\mathbf{F}_2 + \rho_2^0 f\eta\,(\mathbf{v}_{12}(r) - \mathbf{v}_2); \tag{1.3}$$

$$\rho_3 \frac{d_3\mathbf{v}_3}{dt} = -\alpha_3 \nabla P + \rho_3\mathbf{f}_{12}(r_3) + \rho_3\mathbf{F}_3 + \rho_2^0 r_3 \int\limits_{r_3^-}^{R} \psi(r)\,[\mathbf{v}_2(r) - \mathbf{v}_3]\, dr \tag{1.4}$$

$$+ \rho_2^0 r_3 I_{31}(\mathbf{v}_{12}(r_3) - \mathbf{v}_3) - \rho_2^0 r_3 f_3 \eta_3 (\mathbf{v}_{12}(r_3) - \mathbf{v}_3),$$

$$\frac{D_2}{Dt} = \frac{\partial}{\partial t} + v_2^k \nabla^k + \eta \frac{\partial}{\partial r}, \quad \frac{d_3}{dt} = \frac{\partial}{\partial t} + v_3^k \nabla^k$$

(it was assumed that with the abrasion of particles with volume $\in (r - dr, r + dr)$, the momentum of the r-th phase did not change, while the nuclear phase acquired the momentum $\rho_2^0 r_3 \mathbf{v}_2(r)\,\psi(r)dr$). Here, $\mathbf{f}_{12}(r)$ is the force of interaction between the carrying phase and an inclusion of size r (volume); $\mathbf{F}_i$ is the external mass force, acting on the i-th phase (i = 1, 2, 3); and $\mathbf{v}_{12}(r)$ is the velocity of the carrying phase on the surface of contact between the phases.

2. We shall use the hypothesis that the fundamental thermodynamic characteristics are additive with respect to the masses of the phases. As in [1, 2], we shall introduce the surface component of the internal energy of the mixture, taking into account the surface effect:

$$\rho u = \rho_1 u_1 + \int\limits_{r_3^+}^{R} (\rho_2^0 fru_2 + fu_\sigma^1)\, dr + \rho_3 u_3,$$

$$\rho K = \frac{1}{2}\rho_1 v_1^2 + \int\limits_{r_3^+}^{R} \rho_2^0 fr \frac{v_2^2}{2}\, dr + \rho_3 \frac{v_3^2}{2},$$

where u, u_1, and $u_2(r)$ are the specific internal energy of the entire mixture and that of the carrying and r-th phases, respectively; $u_\sigma^1 = 4\pi a^2 u_\sigma$; u_σ^1 and u_σ are the surface energies, for a single inclusion and per unit surface, respectively; a is the radius of a particle; u_3 is the internal energy of a nucleus; K is the kinetic energy of the mixture. Reasoning as in [1, 2], we obtain the differential equations for the internal energies of the phases and the separation surface of the phases:

$$\rho_1 \frac{d_1 u_1}{dt} = \frac{\alpha_1 P}{\rho_1^0} \frac{d\rho_1^0}{dt} + \tau_1^{kl} e_1^{kl} + \int\limits_{r_3^+}^{R} \varkappa_1 \rho_2^0 f r \mathbf{f}_{12}(r)(\mathbf{v}_1 - \mathbf{v}_2)\, dr \tag{2.1}$$

$$+ \varkappa_1(r_3)\rho_3 \mathbf{f}_{12}(r_3)(\mathbf{v}_1 - \mathbf{v}_3) - \int\limits_{r_3^+}^{R} \rho_2^0 f \eta \frac{(\mathbf{v}_{12} - \mathbf{v}_1)^2}{2}\, dr - \rho_2^0 I_{31} r_3 \frac{(\mathbf{v}_{13} - \mathbf{v}_1)^2}{2}$$

$$- \nabla \mathbf{q}_1 + \int\limits_{r_3^+}^{R} \left[- \rho_2^0 f \eta x_{1(12)}(r) - q_{1\sigma}(r) \right] dr - \rho_2^0 r_3 I_{31} x_{1(12)}(r_3) - q_{1\sigma}(r_3) + \rho_1 Q_1;$$

$$\rho_2^0 f r \frac{D_2 u_2}{Dt} = f \frac{r}{\rho_2^0} P \frac{d}{dt} \rho_2^0 + \varkappa_2 \rho_2^0 f r \mathbf{f}_{12}(r)(\mathbf{v}_1 - \mathbf{v}_2) \tag{2.2}$$

$$+ \rho_2^0 f \eta \frac{(\mathbf{v}_{12} - \mathbf{v}_2)^2}{2} - \rho_2^0 f \eta x_{2(12)}(r) - q_{2\sigma} + \rho_2^0 f r Q_2;$$

$$f \frac{D_2 u_\sigma^1}{Dt} = f \eta \frac{2\sigma}{a} - \rho_2^0 f \eta x_{\sigma(12)}(r) + q_{1\sigma}(r) + q_{2\sigma}(r); \tag{2.3}$$

$$\rho_3 \frac{d_3}{dt} u_3 = \frac{P}{\rho_2^0} \alpha_3 \frac{d}{dt} \rho_2^0 + I_{31} A_{31} + \int\limits_{r_3^+}^{R} \psi(r) A_{3u}(r)\, dr \tag{2.4}$$

$$- \varkappa_2(r_3)\rho_3 \mathbf{f}_{12}(r_3)(\mathbf{v}_1 - \mathbf{v}_3) + \rho_2^0 r_3 I_{31} \frac{(\mathbf{v}_{12}(r_3) - \mathbf{v}_3)^2}{2}$$

$$- \rho_2^0 r_3 f_3 \eta_3 \frac{(\mathbf{v}_{12}(r_3) - \mathbf{v}_3)^2}{2} + \rho_2^0 r_3 \int\limits_{r_3^+}^{R} \psi(r) \frac{(\mathbf{v}_2(r) - \mathbf{v}_3)^2}{2}\, dr + q_{1\sigma}(r_3) - \rho_2^0 r_3 I_{31} x_3 - \rho_2^0 r_3 \int\limits_{r_3^+}^{R} \psi(r) x_{3u}\, dr,$$

where $x_{i(12)}(r)$ are the fluxes of heat from the i-th phase to the matter undergoing the transformation 1→2; $q_{i\sigma}(r)$ are the heat fluxes from the i-th phase to the surface separating the phases; σ is the surface tension of the interphase boundary; x_3 and x_{3u} are the heat fluxes related to the formation of nuclei by different methods (homogeneous, heterogeneous, and secondary paths); A_{31} and A_{3u} are the work of formation of a nucleus, per single inclusion from the carrying phase and due to abrasion, respectively; the coefficient $\varkappa_i(r)$ shows the fraction of the kinetic energy of the mixture transforming into the internal energy of the i-th phase, due to the force interaction between the carrying phase and particles of size r:

$$\left(\int\limits_{r_3^+}^{R} [\varkappa_1(r) + \varkappa_2(r)]\, dr + \varkappa_1(r_3) + \varkappa_2(r_3) \right) = 1;$$

$\rho_1 Q_1$ and $\rho_2^0 f r Q_2$ are the intensities of the volume sources of heat; a is the radius of a particle.

We obtain a relation for the total derivative of the total energy of the mixture $\rho E = \rho u + \rho K$

$$\rho \frac{dE}{dt} = \rho_1 \frac{d_1 E_1}{dt} + \int\limits_{r_3^+}^{R} \rho_2^0 f r \frac{d_2 E_2}{dt}\, dr + \int\limits_{r_3^+}^{R} f \frac{d_2 E_\sigma^1}{dt}\, dr \tag{2.5}$$

$$+ \rho_3 \frac{d_3}{dt} E_3 + \int\limits_{r_3^+}^{R} \rho_2^0 f \eta (E_2 - E_1)\, dr + \rho_2^0 r_3 I_{31} [E_3 - E_1] + \int\limits_{r_3^+}^{R} \rho_2^0 r_3 \psi(r) \left[E_3 - \left(E_2 + \frac{E_\sigma^1}{\rho_2^0 r} \right) \right] dr.$$

Starting from the definition (2.5) and the equations for the components of the energy of the mixture (2.1)-(2.4) and momenta (1.2)-(1.4), we present an explicit expression for the total derivative of the total energy of the mixture in the form

$$\rho\frac{dE}{dt}=\int_{r_3^+}^{R}-\rho_2^0 f\eta\left[u_1+\frac{P}{\rho_1^0}-u_2-\frac{P}{\rho_2^0}-\frac{2\sigma}{\rho_2^0 a}+x_{1(12)}+x_{2(12)}+x_{\sigma(12)}\right]dr$$

$$-\rho_2^0 r_3 I_{31}\left[u_1+\frac{P}{\rho_1^0}-u_3-\frac{P}{\rho_2^0}-\frac{A_{31}}{\rho_2^0 r_3}+x_{1(12)}(r_3)+x_3\right]+\rho_2^0 r_3\int_{r_3^+}^{R}\psi\left[u_3-\left(u_2+\frac{u_\sigma^1}{\rho_2^0 r}\right)-\frac{A_{3u}}{\rho_2^0 r_3}-x_{3u}\right]dr-\nabla\alpha_1 P\mathbf{v}_1$$

$$-\int_{r_3^+}^{R}\nabla(frP\mathbf{v}_2)\,dr-\nabla(\alpha_3 P\mathbf{v}_3)+\nabla^k\tau_1^{kl}v_1^l-\nabla\mathbf{q}_1+\rho_1\mathbf{F}_1\mathbf{v}_1+\int_{r_3^+}^{R}\rho_2^0 rf\mathbf{F}_2\mathbf{v}_2dr+\rho_3\mathbf{F}_3\mathbf{v}_3+\rho_1Q_1+\int_{r_3^+}^{R}\rho_2^0 frQ_2dr.$$

From the definition of dE/dt, it follows that the change in the total energy of the mixture is determined only by the external action. Then, the expressions on the right side (energy source type) must equal zero:

$$x_{1(12)}+x_{2(12)}+x_{\sigma(12)}=i_2-i_1,\quad x_{1(12)}(r_3)+x_3=u_3+\frac{P}{\rho_2^0}+\frac{A_{31}}{\rho_2^0 r_3}-i_1,$$

$$x_{3u}=u_3-\left(u_2+\frac{u_\sigma^1}{\rho_2^0 r}\right)+\frac{A_{3u}}{\rho_2^0 r_3}.$$

The work of formation of a nucleus out of the homogeneous phase on surfaces (dust particles, impurities) equals, respectively, [3]

$$A_{31}(\text{hom})=\frac{\sigma 4\pi a_3^2}{3},\quad A_{31}(\text{het})=\frac{\sigma 4\pi a_3^2}{3}[2(1-\cos\theta-\sin^2\theta\cos\theta],$$

where θ is the contact angle. In order to specify the model it is necessary to determine the energies $x_k(ij)$. We shall postulate these relations as follows:

$$x_{1(12)}(r)=x_{2(12)}(r)=0,\ r\in[r_3,\ R],\ x_{\sigma(12)}=i_2-i_1,\ r\neq r_3,$$

$$x_n=\begin{cases} i_3-i_1-\dfrac{\sigma}{\rho_2^0 a_3} & \text{for homogeneous,}\\ i_3-i_1+\dfrac{\sigma}{\rho_2^0 a_3}\dfrac{[2(1-\cos\theta)-\sin^2\theta\cos\theta-8]}{4} & \text{for heterogeneous nucleation.}\end{cases}$$

3. Let us assume that $\varkappa_1=1,\ \varkappa_2(r)=0,\ r\in[r_3,\ R],\ v_{12}(r)=v_2(r)$, and $q_{i\sigma}=4\pi a^2\beta_i(T_i-T_\sigma)$. Then, the system of equations describing the interpenetrating motion of the two-phase polydispersed mixture taking into account the growth and formation of nuclei has the form

$$\frac{\partial}{\partial t}\rho_1+\operatorname{div}\rho_1\mathbf{v}_1=-\int_{r_3^+}^{R}\rho_2^0 f\eta dr-\rho_2^0 I_{31}r_3,\tag{3.1}$$

$$\frac{\partial}{\partial t}f+\operatorname{div}f\mathbf{v}_2+\frac{\partial}{\partial r}f\eta=-\frac{\psi}{r}r_3,$$

$$\rho_1\frac{d_1c}{dt}=(c-1)\left[\int_{r_3^+}^{S}\rho_2^0 f\eta dr+\rho_2^0 r_3 I_{31}\right],$$

$$\rho_2^0 r_3^2\left[\frac{\partial}{\partial t}f_3+\operatorname{div}f_3\mathbf{v}_3\right]=\rho_2^0 r_3 I_3-\rho_2^0 f_3\eta_3 r_3,$$

$$\rho_1\frac{d_1\mathbf{v}_1}{dt}=-\alpha_1\nabla P+\nabla^k\tau_1^k-\int_{r_3^+}^{R}\rho_2^0 fr\mathbf{f}_{12}dr-\rho_3\mathbf{f}_{12}(r_3)+\rho_1\mathbf{F}_1-\int_{r_3^+}^{R}\rho_2^0 f\eta(\mathbf{v}_2-\mathbf{v}_1)\,dr-\rho_2^0 I_{31}r_3(\mathbf{v}_3-\mathbf{v}_1),$$

$$\rho_2^0 fr\frac{D_2\mathbf{v}_2}{Dt}=-fr\nabla P+\rho_2^0 fr\mathbf{f}_{12}+\rho_2^0 fr\mathbf{F}_2,$$

$$\rho_3 \frac{d_2}{dt}\mathbf{v}_3 = -\alpha_3 \underline{\nabla} P + \rho_3 \mathbf{f}_{12} + \rho_3 \mathbf{F}_2(r_3) + \rho_2^0 r_3 \int\limits_{r_3^+}^{R} \psi(r)\left[\mathbf{v}_2(r) - \mathbf{v}_3\right] dr,$$

$$\rho_1 \frac{d_1 u_1}{dt} = \frac{\alpha_1 P}{\rho_1^0}\frac{d}{dt}\rho_1^0 + \tau_1^{kl} e_1^{kl} + \int\limits_{r_3^+}^{R} \rho_2^0 f r \mathbf{f}_{12}(\mathbf{v}_1 - \mathbf{v}_2)\, dr$$

$$+ \rho_3 \mathbf{f}_{12}(r_3)(\mathbf{v}_1 - \mathbf{v}_3) - \int\limits_{r_3^+}^{R} \rho_2^0 f \eta \frac{(\mathbf{v}_2 - \mathbf{v}_1)^2}{2}\, dr - \rho_2^0 I_{31} r_3 \frac{(\mathbf{v}_3 - \mathbf{v}_1)^2}{2}$$

$$- \nabla \mathbf{q}_1 - \int\limits_{r_3^+}^{R} 4\pi a^2 f \beta_1 (T_1 - T_\sigma)\, dr - 4\pi a_3^2 n_3 \beta_1 (T_1 - T_3) + \rho_1 Q_1,$$

$$\rho_2^0 f r \frac{D_2 u_2}{Dt} = \frac{\alpha_2 P d}{\rho_2^0 dt}\rho_2^0 - 4\pi a^2 \beta_2 f (T_2 - T_\sigma) + \rho_2^0 f r Q_2,$$

$$f \frac{D_2 u_\sigma^1}{Dt} = f\eta \frac{2\sigma}{a} + 4\pi a^2 \beta_1 f (T_1 - T_\sigma) + 4\pi a^2 f \beta_2 (T_2 - T_\sigma) - \rho_2^0 f \eta (i_2 - i_1),$$

$$\rho_3 \frac{d_3}{dt} u_3 = \alpha_3 \frac{P}{\rho_2^0}\frac{d}{dt}\rho_2^0 + \rho_2^0 r_3 \int\limits_{r_3^+}^{R} \psi \frac{(\mathbf{v}_2 - \mathbf{v}_3)^2}{2}\, dr + 4\pi a_3^2 n_3 \beta_1 (T_1 - T_3)$$

$$+ \rho_2^0 r_3 I_{31} \frac{2\sigma}{\rho_2^0 a_3} - \rho_2^0 r_3 I_{31}[i_3 - i_1] - \rho_2^0 r_3 \int\limits_{r_3^+}^{R} \left[u_3 - \left(u_2 + \frac{u_\sigma^1}{\rho_2^0 r}\right)\right] \psi\, dr + \rho_3 Q_3.$$

4. The additivity of the entropy of the mixture follows from the additivity hypothesis:

$$\rho S = \rho_1 S_1 + \int\limits_{r_3^+}^{R} \left[\rho_2^0 f r S_2 + f S_\sigma^1\right] dr + n_3 S_3^1 \left(S_3^1 = \rho_2^0 r_3 S_3\right).$$

Using the Gibbs relations, having the form

$$\rho_1 \frac{d_1 S_1}{dt} = \frac{\rho_1}{T_1}\frac{d_1}{dt} u_1 + \rho_1 \frac{P}{T_1}\frac{d_1}{dt}\frac{1}{\rho_1^0} - \frac{\mu_{1c}}{T_1}\frac{dc_{1c}}{dt} - \frac{\mu_{1S}}{T_1}\frac{dc_{1S}}{dt},$$

$$\rho_2^0 f r \frac{d_2 S_2}{dt} = \rho_2^0 f \frac{r}{T_2}\frac{d_2 u_2}{dt} + \rho_2^0 f \frac{r}{T_2}\frac{d_2}{dt}\frac{1}{\rho_2^0},$$

$$f \frac{d_2 S_\sigma^1}{dt} = \frac{f}{T_\sigma}\frac{d_2 u_\sigma^1}{dt} - f \frac{\sigma}{T_\sigma} d 4\pi a^2, \quad n_3 \frac{d_2 S_3^1}{dt} = \frac{n_3}{T_3}\frac{d_2 u_3^1}{dt} - n_3 \frac{\sigma}{T_3} d 4\pi a_3^2$$

[where μ_{ik} is the chemical potential of the k-th component in the carrying phase; c_{1c} and c_{1S} are the mass concentrations of the component and solvent (for simplicity, we assumed that only a single component participates in the phase transition)], and the equations for the heat inflows and conservation of the components (2.1)-(2.4), (1.1), and (3.1), we write an explicit expression for the total derivative of the entropy of the mixture

$$\frac{DS}{Dt} = \left[-\frac{1}{T_1}\nabla \mathbf{q}_1 + \rho_1 \frac{Q_1}{T_1} + \int\limits_{r_3^+}^{R} \rho_2^0 f \frac{r Q_2}{T_2}\, dr + \rho_3 \frac{Q_3}{T_3}\right] \tag{4.1}$$

$$+ \frac{1}{T_1}\tau^{kl} e_1^{kl} + \frac{1}{T_1}\left[\int\limits_{r_3^+}^{R} \rho_2^0 f r \mathbf{f}_{12}(\mathbf{v}_1 - \mathbf{v}_2)\, dr + \rho_3 \mathbf{f}_{12}(r_3)(\mathbf{v}_1 - \mathbf{v}_3)\right]$$

$$+ \left[\int\limits_{r_3^+}^{R} q_{1\sigma}\left(\frac{1}{T_\sigma} - \frac{1}{T_1}\right) dr + q_{1\sigma}(r_3)\left(\frac{1}{T_3} - \frac{1}{T_1}\right) + \int\limits_{r_3^+}^{R} q_{2\sigma}\left(\frac{1}{T_\sigma} - \frac{1}{T_2}\right) dr\right]$$

$$+\int_{r_3^+}^{R}\rho_2^0 f\eta\left[\frac{\mu_{1c}}{T_1}-\frac{\mu_{1c}c_{1c}}{T_1}-\frac{\mu_{1s}c_{1s}}{T_1}+\frac{i_1}{T_\sigma}-\frac{i_2}{T_\sigma}+S_2-S_1-\frac{(\mathrm{v}_2-\mathrm{v}_1)^2}{2T_1}\right]dr$$

$$+\rho_2^0 r_3 I_{31}\left[\frac{\mu_{1c}}{T_1}-\frac{\mu_{1c}c_{1c}}{T_1}-\frac{\mu_{1s}c_{1s}}{T_1}+\frac{i_1}{T_3}-\frac{i_3}{T_3}+S_3-S_1-\frac{(\mathrm{v}_3-\mathrm{v}_1)^2}{2T_1}\right]$$

$$+\rho_2^0 r_3\int_{r_3^+}^{R}\psi(r)\left\{\left[S_3-\left(S_2+\frac{S_\sigma^1}{\rho_2^0 r}\right)\right]-\left[\frac{u_3}{T_3}-\frac{\left(u_2+\frac{u_\sigma^1}{\rho_2^0 r}\right)}{T_3}\right]+\frac{1}{2T_3}(\mathrm{v}_2-\mathrm{v}_3)^2\right\}dr.$$

The first term in (4.1) (the expression in the first bracket) determines the increase in entropy of the mixture due to the inflow of entropy from outside due to exchange with the external medium, and the remaining terms determine the increase in entropy of the mixture due to internal irreversible processes within a phase or between phases (always nonnegative) and represent the sum of products of thermodynamic forces by thermodynamic fluxes. The fluxes are assumed to be as follows: $J^{kl} = \tau_1^{kl}$ is the flux of viscous stresses; $J^F = f_{12}$ is the flux of the mechanical interaction force between phases; $J^{i\sigma} = q_{i\sigma}$ is the heat flux from the i-th phase to the phase separation surface; $J_{12}(r) = \rho_2^0 f\eta dr$ is the flux of mass out of the carrying phase into the r-th phase; $J_{13} = \rho_2^0 r_3 I_{31}$ is the flux of mass out of the carrying phase into the nuclear phase; $J_{23} = \rho_2^0 r_3\psi dr$ is the flux of mass out of the r-th phase into the nuclear phase. Let us enumerate the motive forces: $X^{kl} = e^{kl}/T_1$ is the reduced tensor of the deformation velocities of the carrying phase; $X^F = [\mathrm{v}_2(r) - \mathrm{v}_1]$ is the motive force arising due to the fact that the phase velocities do not coincide; $X^{ij} = (1/T_j - 1/T_i)$ ($i = 1, 2$, $j = \sigma, 3$) is the motive force arising due to the temperature nonequilibrium between the j-th and i-th phase;

$$X_{12}=\frac{\mu_{1c}}{T_1}-\frac{\mu_{1c}c_{1c}}{T_1}-\frac{\mu_{1s}c_{1s}}{T_1}+\frac{i_1}{T_\sigma}-\frac{i_2}{T_\sigma}+S_2-S_1-\frac{(\mathrm{v}_2-\mathrm{v}_1)^2}{2T_1}\qquad(4.2)$$

is the moving force of mass transfer of matter from the carrying phase into the r-th phase;

$$X_{13}=\frac{\mu_{1c}}{T_1}-\frac{\mu_{1c}c_{1c}}{T_1}-\frac{\mu_{1s}c_{1s}}{T_1}+\frac{i_1}{T_3}-\frac{i_3}{T_3}+S_3-S_1-\frac{(\mathrm{v}_3-\mathrm{v}_1)^2}{2T_1}\qquad(4.3)$$

is the motive force for transition of matter out of the carrying phase into the nuclear phase;

$$X_{23}=[S_3-\overline{S}_2]-\frac{[u_3-\overline{u}_2]}{T_3}+\frac{1}{2T_3}(\mathrm{v}_2-\mathrm{v}_3)^2\qquad(4.4)$$

$$\left(\overline{S}_2=S_2\,\frac{\rho_2^0 r+S_\sigma^1}{\rho_2^0 r},\quad \overline{u}_2=u_2\,\frac{\rho_2^0 r+u_\sigma^1}{\rho_2^0 r}\right)$$

is the motive force for transition of matter out of the r-th phase into the nuclear phase (secondary nucleation).

We introduce the notation: $\Theta_{is} = |(T_i - T_s)/T_s|$, $\Theta_{i\sigma} = |(T_i - T_\sigma)/T_\sigma|$, where T_s is the saturation temperature. For sufficiently small deviations of the phase temperatures T_i ($i = 1, 2$) from the saturation temperature T_s ($\Theta_{is} \ll 1$, $\Theta_{i\sigma} \ll 1$), the linearized (relative to deviations from the equilibrium state) equations of state of the phases have the form

$$i_1=i_{2s}+\Delta h+C_1(T_1-T_s),\ i_2=i_{2s}+C_2(T_2-T_s).\qquad(4.5)$$

Substituting (4.5) into the expressions for the motive forces (4.2) and (4.3), neglecting terms higher than first order infinitesimals relative to Θ_{ij} and taking into account also the relations [4]

$$i_1-T_1S_1=c_{1c}\mu_{1c}+c_{1s}\mu_{1s},\ i_2-T_2S_2=\mu_2,$$

$$i_3-T_3S_3=\frac{\sigma 4\pi a_3^2}{\rho_2^0 r_3}+\mu_3,\quad \overline{i}_2-T_2\overline{S}_2=\frac{\sigma 4\pi a^2}{\rho_2^0 r}+\overline{\mu}_2,$$

we represent the motive forces for growth and formation of crystals in the form

$$X_{12}=\left[\frac{\mu_{1c}}{T_1}-\frac{\mu_{2c}}{T_2}\right]+\left[\Delta h\left(\frac{1}{T_\sigma}-\frac{1}{T_1}\right)+i_{2s}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]-\left[\frac{1}{2}\frac{(\mathbf{v}_2-\mathbf{v}_1)^2}{T_1}\right]; \tag{4.6}$$

$$X_{13}=\left[\frac{\mu_{1c}}{T_1}-\frac{\mu_3}{T_3}-\frac{\sigma 4\pi a_3^2}{T_3\rho_2^0 r_3}\right]+i_1\left[\frac{1}{T_3}-\frac{1}{T_1}\right]-\left[\frac{(\mathbf{v}_3-\mathbf{v}_1)^2}{2T_1}\right]; \tag{4.7}$$

$$X_{23}=\left[\frac{\overline{\Phi}_2}{T_2}-\frac{\overline{\Phi}_3}{T_3}\right]+i_2\left[\frac{1}{T_3}-\frac{1}{T_2}\right]+\left[\frac{1}{2T_3}(\mathbf{v}_2-\mathbf{v}_3)^2\right]+\left[\frac{1}{\rho_2^0 r_3}\,\frac{2}{3}\,\frac{(a-a_3)}{aT_3}\,\sigma 4\pi a_3^2\right], \tag{4.8}$$

where

$$\overline{\Phi}_2=\overline{\mu}_2+\frac{\sigma 4\pi a^2}{\rho_2^0 r};\quad \Phi_3=\mu_3+\frac{\sigma 4\pi a_3^2}{\rho_2^0 r_3}.$$

The difference between (4.6) and the generally accepted expression for the motive force of mass transfer stems from the presence of the two last terms, owing to the temperature and velocity nonequilibrium of the phases. Due to the smallness of the mass of the nuclei, the difference in the temperatures T_3 and T_1, the velocities $\mathbf{v}_3$ and $\mathbf{v}_1$ can be neglected; then, the relation X_{13} coincides with the expression for the motive force of nucleation (homogeneous, heterogeneous), obtained in [5], and is written in the form

$$X_{13}=\mu_{1c}-\mu_3-\frac{\sigma 4\pi a_3^2}{\rho_2^0 r_3}.$$

It has been determined empirically that secondary nucleation depends on the velocities of the flow around a crystal, the surface tension force, and the temperature of the solution, which agrees with relation (4.8).

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