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DESCRIPTION OF THE FLOWS OF TWO-PHASE MIXTURES WITH PHASE TRANSITIONS IN CAPILLARIES BY THE DENSITY-FUNCTIONAL METHOD

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The problem of mathematical modeling of flows of multicomponent mixtures with phase transitions has been considered. The free energy of a mixture is given as a functional containing squared density gradients of the components. This permits continuous description of multiphase mixtures without discontinuities at the interfaces. Numerical solutions for the flows of two-phase mixtures in capillaries with different wall wettability conditions have been obtained.

To solve many problems in chemical technology, one has to carry out mathematical modeling of the flows of multicomponent multiphase mixtures with phase transitions and chemical reactions. In so doing, the spatial arrangement of the phases and their characteristics are usually not known in advance; relevant information should be obtained as a component of the complete solution of the problem. Such a formulation makes it difficult to use the classical hydrodynamics based on the Navier–Stokes equations. Indeed, if the interface geometry is not known in advance, then it is also not known what viscosity values should be substituted into the Navier–Stokes equations in a given spatial domain. Moreover, a complication in the formulation of the interface conditions exists: the Laplace formula for pressure discontinuity assumes interface smoothness, which a fortiori excludes the observed phenomena of coalescence or splitting of liquid drops or gas bubbles.

The above problems disappear if one uses the density-functional method, which allows one to describe a multicomponent multiphase mixture continuously without introducing density discontinuities and interfaces. This is achieved by introducing into the expression for the free energy of the mixture [1] (or into the entropy expression [2]) squared density gradients of the components. As a result, the multiphase mixture dynamics is described in a unique manner, i.e., the system of equations used has one and the same form at all points of the flow region. One specific feature of the density-functional method is its account for the structure of the interphase region. The proposed method was used earlier to describe the liquid flow in a capillary with surface-active walls [3], the capillary-gravity waves [4], and the gas-condensate mixture flow in a capillary [5].

The present paper considers the employment of the density-functional method for mathematical modeling of two-phase isothermal flows with phase transitions. For simplicity, the temperature dependence will be omitted. Recall the salient points of the theory for the isothermal case [1]. The theory for nonisothermal flows is described in [2].

Let an M-component mixture (gas or liquid) fill the domain D with a sectionally smooth boundary ∂D corresponding to the contact with a stationary phase. It is assumed that indices i, j, and k take on values 1, ..., M, corresponding to the numbers of the mixture components; indices a, b, and c take on values 1, 2, and 3, denoting the Cartesian coordinates x^a. Summation is made over recurring indices. Abbreviated notations for derivatives will be used: $g_{,i} = \partial g/\partial n_i$, $\partial_a g = \partial g/\partial x^a$.

The functional of the mixture free energy is given by the expression

$$F = \int_D \omega dV + \int_{\partial D} f_* dA , \tag{1}$$

where

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$$\omega = f + \frac{1}{2}\nu_{ij}\partial_a n_i \partial_a n_j + \rho\varphi\ ; \quad f = f\,(n_i)\ ; \quad f_* = f_*\,(n_i)\ ; \quad \nu_{ij} = \nu_{ij}\,(n_k)\ ; \quad \varphi = \varphi\,(x^a)\ ; \quad \rho = m_i n_i\ .$$

The equilibrium states of the mixture are the critical points of functional (1) at a fixed number of particles of the mixture components:

$$N_i = \int_D n_i dV\ . \tag{2}$$

Calculating the variation of functional (1), we obtain the expression

$$\delta F = \int_D \Phi_i \delta n_i dV + \int_{\partial D} \Phi_{i*} \delta n_i dA\ , \tag{3}$$

$$\Phi_i = f_{,i} + m_i\varphi + \frac{1}{2}\nu_{jk,i}\partial_a n_j \partial_a n_k - \nu_{ij,k}\partial_a n_j \partial_a n_k - \nu_{ij}\Delta n_j\ ,$$

$$\Phi_{i*} = f_{*,i} - \nu_{ij} l_a \partial_a n_j\ , \quad \Delta = \partial_a \partial_a\ .$$

Using expression (3), we can write out the equation for the nonequilibrium states with the Lagrange factors Λ_i:

$$\delta F - \Lambda_i \delta N_i = 0\ ,$$

leading to the system of elliptic equations

$$\Phi_i - \Lambda_i = 0 \tag{4}$$

and boundary conditions

$$\Phi_{i*} = 0\ . \tag{5}$$

The Lagrange factor Λ_i should be determined by solving problem (4), (5) for the unknown fields of component densities n_i from the additional integral conditions (2). As constitutive hydrodynamic equations for isothermal flows, the ordinary density and pulse equations

$$\partial_t n_i + \partial_a I_{ia} = 0\ , \tag{6}$$

$$\rho\,(\partial_t v_a + v_b \partial_b v_a) = \partial_b p_{ab} - \rho\partial_a \varphi\ , \tag{7}$$

where $v_a = \rho^{-1} m_i I_{ia}$ are taken [6]. Let us introduce the following auxiliary quantities:

$$Q_{ia} = I_{ia} - n_i v_a\ , \quad \tau_{ab} = p_{ab} - \sigma_{ab}\ , \quad \sigma_{ab} = (\omega - \Phi_i n_i)\,\delta_{ab} - \nu_{ij}\partial_a n_i \partial_b n_j\ . \tag{8}$$

In the hydrodynamic description, the following boundary conditions that are usual for dynamic variables are used:

the adhesion boundary condition

$$v_a \big|_{\partial D} = 0\ , \tag{9}$$

and the nonrunning boundary condition for diffusion flows

$$l_a Q_{ia} \big|_{\partial D} = 0\ . \tag{10}$$

It is also assumed that in dynamics, as in statics, the boundary conditions (5) are fulfilled.

Determine the total energy functional of the system, including the free energy (1) and the kinetic energy of the mixture:

$$E = F + \frac{1}{2}\int_D \rho v_a v_a dV . \tag{11}$$

Direct calculation of the time derivative of functional (11) in view of expression (3) and Eqs. (5)–(10) leads to the relation

$$\frac{dE}{dt} = \int_D \Sigma dV , \tag{12}$$

where

$$\Sigma = -\tau_{ab}\partial_a v_b + Q_{ia}\partial_a \Phi_i . \tag{13}$$

The hydrodynamic model should be dissipative, i.e., it is essential that the following inequality, which is an analog of the nonnegativity condition of energy production, hold:

$$\frac{dE}{dt} \le 0 . \tag{14}$$

In view of relations (12) and (13), for inequality (14) to hold, the condition

$$\Sigma \le 0 \tag{15}$$

should be fulfilled.

Note that relations (12) and (13) allow one to interpret τ_{ab} as a viscous stress tensor, since precisely this component of the complete stress tensor p_{ab} makes a contribution to the dissipation. Accordingly, σ_{ab} should be interpreted as a tensor of static stresses in the mixture, since it is rate-independent and is only determined by the density distribution of the mixture components.

For the hydrodynamic problem (6)–(10), (5) to be closed, constituent relations, i.e., expressions for the quantities τ_{ab} and Q_{ia} are needed. These expressions should be consistent with inequality (15). Of greatest interest is the model that is a minimum generalization of the model of a multicomponent mixture [6, 7]. For instance, for the viscous stress tensor the linearly viscous Navier–Stokes model

$$\tau_{ab} = \left(\mu_v - \frac{2}{3}\mu_s\right)\partial_c v_c \delta_{ab} + \mu_s\left(\partial_a v_b + \partial_b v_a\right), \tag{16}$$

is taken. Here μ_v and μ_s are positive coefficients of the volume and shear viscosities.

For diffusion flows, relations generalizing the Fick law are taken:

$$Q_{ia} = -D_{ij}\partial_a \Phi_j . \tag{17}$$

Here D_{ij} is a symmetric nonnegative matrix satisfying the additional condition

$$D_{ij} m_j = 0 . \tag{18}$$

It is reasonable to discuss the physical meaning of the static stress tensor σ_{ab}. In the case of a homogeneous mixture, it is reduced to the ordinary stress tensor in an ideal liquid

$$\sigma_{ab} = -p\delta_{ab} ,$$

where $p = n_i f_{,i} - f$.

For a heterogeneous mixture, the tensor σ_{ab} can differ from the stress tensor of an ideal liquid in the region where the density gradients of the components reach an appreciable value. To elucidate the role of these gradients in the stress tensor, it is convenient to consider the equilibrium two-phase state with the dependence on only one coordinate x^1. In this case, $n_i = n_i(x^1)$ and $v_a = 0$. As $x^1 \to \pm\infty$ the densities of the components and the stresses converge to the densities and stresses in the phases A and B:

$$x^1 \to -\infty\,,\quad n_i \to n_{i\mathrm{A}}\,,\quad \sigma_{ab} \to -p_{\mathrm{A}}\delta_{ab}\,;\quad x^1 \to +\infty\,,\quad n_i \to n_{i\mathrm{B}}\,,\quad \sigma_{ab} \to -p_{\mathrm{B}}\delta_{ab}\,.$$

As is known [1], from the thermodynamic equilibrium conditions of the state under consideration, the mechanical equilibrium condition $\partial_1\sigma_{11} = 0$ follows. From this and from the foregoing, the relations

$$\sigma_{11} = -p_{\mathrm{A}} = -p_{\mathrm{B}}\,,$$

$$\sigma_{22} = \sigma_{33} = \sigma_{11} + \nu_{ij}\partial_1 n_i \partial_1 n_j = -p_{\mathrm{A}} + \nu_{ij}\partial_1 n_i \partial_1 n_j$$

follow.

Thus, the density gradients make a contribution to the transverse components of the stress tensor. In so doing, they are responsible for the appearance of tension in the interphase area. The integral over the longitudinal coordinate of this distributed tension should be identified with the interphase surface tension coefficient [1]

$$\gamma = \int_{-\infty}^{+\infty} \nu_{ij}\partial_1 n_i \partial_1 n_j dx^1\,. \tag{19}$$

In the present paper, in terms of the density-functional theory, numerical simulation of two-phase, two-component mixtures was performed. In so doing, for numerical calculations of two-phase media of the type "liquid–liquid" or "gas–liquid" it is necessary to specify a concrete form of the free energy function, the values of the coefficients of viscosity, diffusion, and surface tension at the mixture–solid phase contact, as well as the coefficients ν_{ij}.

Free energy. If the deviations of the densities from certain fixed equilibrium values are small, then the free energy of one phase (phase A) can be represented by the quadratic polynomial

$$f_{\mathrm{A}}(n_i) = f_{\mathrm{A}0} + f_{\mathrm{A}i}(n_i - n_{i\mathrm{A}}) + 2^{-1} f_{\mathrm{A}ij}(n_i - n_{i\mathrm{A}})(n_j - n_{j\mathrm{A}})\,. \tag{20}$$

The coefficients $f_{\mathrm{A}0}$ and $f_{\mathrm{A}i}$ do not enter into the hydrodynamics equations; they are only used to calculate the initial undisturbed pressure and chemical potentials. These coefficients can be assumed to be equal to zero. For hydrodynamic modeling, only the coefficients $f_{\mathrm{A}ij}$ are important; they are selected in accordance with the data on the bulk modulus for the phase A:

$$E_{\mathrm{A}} = f_{\mathrm{A}ij} n_{i\mathrm{A}} n_{j\mathrm{A}}\,. \tag{21}$$

In the case of a two-phase flow (phases A and B), the free energy f is determined by the expressions for $f_{\mathrm{A}}(n_i)$, $f_B(n_i)$ as follows:

$$f = f_{\mathrm{A}} f_{\mathrm{B}} / (f_{\mathrm{A}} + f_{\mathrm{B}})\,. \tag{22}$$

Viscosity. The values of the shear and volume viscosities for each phase are assumed to be known. The viscosity values for arbitrary values of component densities are calculated by the empirical formulas that permit determining the mixture viscosity by its known values for the components (see formula (VIII-54) in [8]):

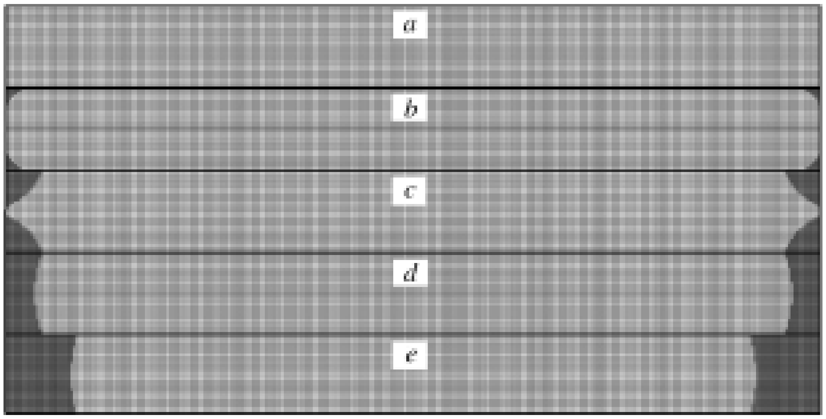

Fig. 1. Binodal decomposition of the mixture with homogeneous wettability conditions on the capillary walls.

$$\mu_s = (c_A \mu_{sA}^{1/3} + c_B \mu_{sB}^{1/3})^3\,, \quad \mu_v = (c_A \mu_{vA}^{1/3} + c_B \mu_{vB}^{1/3})^3\,; \quad c_A = z_B/(z_A + z_B)\,, \quad c_B = z_A/(z_A + z_B)\,;$$

$$z_A = \left(\sum_{i=1}^{2} (n_i - n_{iA})^2 \right)^{1/2}, \quad z_B = \left(\sum_{i=1}^{2} (n_i - n_{iB})^2 \right)^{1/2} . \tag{23}$$

Diffusion. To calculate the matrix D_{ij}, we use the condition according to which at $\nu_{ij} = 0$ from (17) the expression for the ith component flow

$$q_{ia} = n^{-1} Q_{ia} = - n^{-1} D_{ij} \left(\frac{\partial \kappa_j}{\partial c} \right)_n \partial_a c - n^{-1} D_{ij} \left(\frac{\partial \kappa_j}{\partial n} \right)_c \partial_a n$$

follows. Here $n = \sum_{i=1}^{2} n_i$; $c = n_1/n$; $\kappa_i = f_{,i}$.

Thus, the tabulated diffusion coefficient d for component 1 in the mixture is related to the matrix D_{ij} by the relation

$$d = n^{-1} D_{1j} \left(\frac{\partial \kappa_j}{\partial c} \right)_n . \tag{24}$$

The diffusion coefficient d is calculated by the known values in the phases d_A and d_B: $d = c_A d_A + c_B d_B$. If the free energy is given (see (20)–(22)), then in the case of a two-component mixture, by the coefficient d from Eq. (24) in view of (18) the matrix D_{ij} is calculated uniquely.

The surface tension at the mixture–solid contact is assumed to be a linear function of the component densities:

$$f_* = \xi_{1i} n_i + \xi_0 . \tag{25}$$

The parameters ξ_0 and ξ_{1i} are calculated by the known values of the surface tension at the contact with a solid for the phases A and B:

$$\theta_A = \xi_{1i} n_{iA} + \xi_0\,, \quad \theta_B = \xi_{1i} n_{iB} + \xi_0 . \tag{26}$$

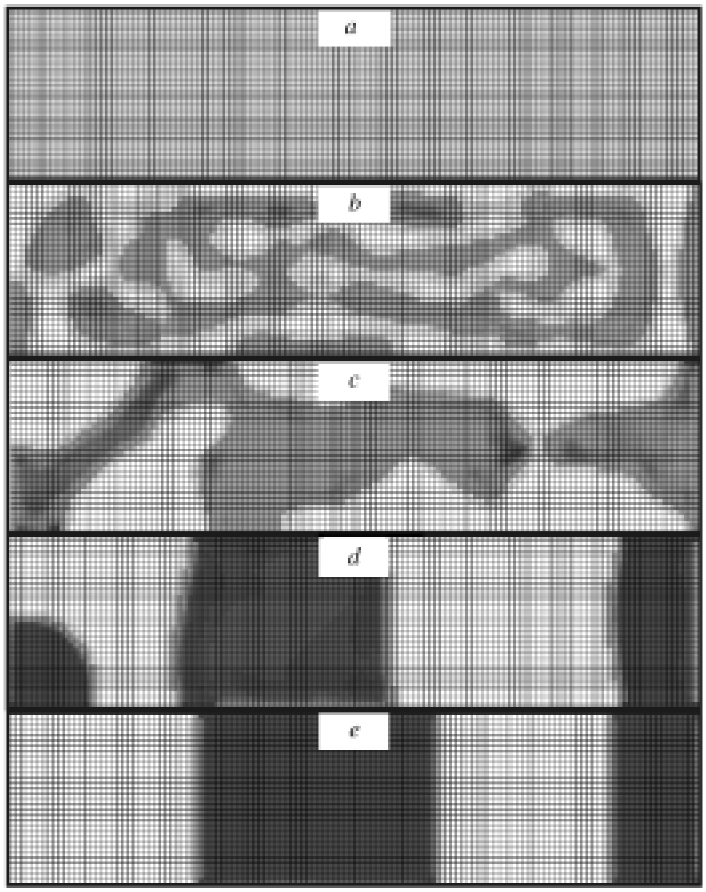

Fig. 2. Spinodal decomposition of the mixture with inhomogeneous wettability conditions on the capillary walls.

The system of linear equations (26) always has a solution, but it is not unique. The arbitrariness in the choice of dependence (25) influences the component distribution near the solid wall but does not influence the wetting angle. Moreover, the parameter ξ_0 influences neither the dynamic equations nor the boundary conditions. Therefore, it suffices to make the parameters ξ_{1i} consistent with the given difference

$$\Delta\theta = \theta_B - \theta_A = \xi_{1i}\,(n_{iB} - n_{iA})\,,$$

and assign an arbitrary value to the parameter ξ_0.

The matrix of coefficient ν_{ij} is assumed to be constant and proportional to the unit matrix: $\nu_{ij} = \nu\delta_{ij}$. The unknown coefficient ν is determined from the expression for the surface tension (19) between the phases A and B for the static solution. It should be noted that at a known coefficient γ Eq. (19) is nonlinear with respect to ν, since the equilibrium distribution of components also depends on ν_{ij} (see [4]).

The system of equations (6)–(10), (16), (17) was solved numerically by means of an explicit conservative difference scheme. In the two-dimensional formulation, the following model problems were calculated:

1) binodal decomposition of a two-component mixture in a capillary with wetted walls;

2) spinodal decomposition of a two-component mixture in a capillary whose walls contain alternating wetted and nonwetted areas.

In both cases, for phases A and B a core with mole concentrations of the first and second components that are close, respectively, to unity was taken. The other parameters of the phases and components were: $\mu_{sA} = \mu_{sB} = 10^{-3}$ Pa·sec, $\mu_v = 10\mu_s$ for the phases A and B, $\rho_A = 1000$ kg/m^3, $\rho_B = 800$ kg/m^3, $m_1 = 18$ kg/kmole, and $m_2 = 200$ kg/kmole.

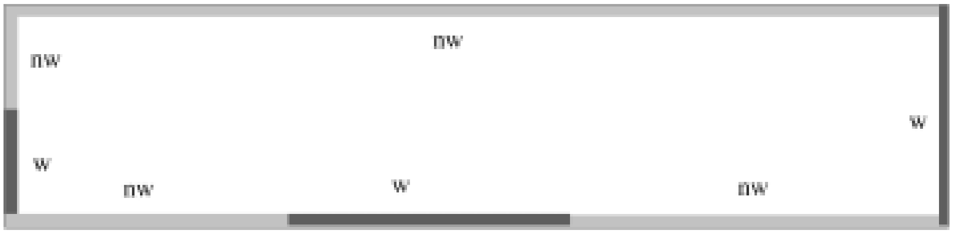

Fig. 3. Scheme of the distribution of wettable and nonwettable areas at the capillary boundaries.

The gray color gradations in the calculated cells presented in Figs. 1 and 2 show the concentration distribution of one of the components present, which practically corresponds to the spatial distribution of the corresponding phase.

Problem 1. As initial conditions, a homogeneous state of a mixture (Fig. 1a) with a zero flow field is given. The initial molar composition of the mixture is 0.7 of the first component and 0.3 of the second one. This composition corresponds to the local thermodynamic stability of the mixture (the matrix $f_{,ij}$ is positive definite). At the same time, the mixture is thermodynamically unstable in the sense of finite disturbances. The mixture is in a capillary with walls wetted by the phase B at $\Delta\theta = -0.04$ N/m, $\gamma = 0.24$ N/m. The calculated field consists of 320 × 32 square cells with dimensions of $5\cdot10^{-4}$ m. Figure 1b–e shows the process of the appearance and growth of the wetting phase as a result of the interaction between the mixture and the capillary walls.

Problem 2. The mixture is in a capillary with a variable surface tension on the walls (the scheme of the distribution of wettable (w) and nonwettable (nw) areas of the boundary is given in Fig. 3). In this case, $\Delta\theta = -0.01$ N/m for wettable and $\Delta\theta = 0.01$ N/m for nonwettable areas, $\gamma = 0.24$ N/m. As initial conditions, a homogeneous state of a mixture (Fig. 2a) with a zero flow field is given. The initial molar composition of the mixture is 0.5 of the first component and 0.5 of the second one. This composition corresponds to the locally thermodynamically unstable mixture (the matrix $f_{,ij}$ has a negative eigenvalue). The calculated field consists of 128 × 32 square cells with dimensions of $5\cdot10^{-4}$ m. Figure 2b–e shows the process of mixture decomposition into phases (spinodal decomposition), which, as a result of the local instability, involves the entire volume (see Fig. 2b) as opposed to the case of binodal decomposition, where the growth of a new phase started at the corner points (see Fig. 1b). At later stages of spinodal decomposition the interrelated hydrodynamic and diffusion processes lead to a spatial separation (see Fig. 2c–e).

Thus, it has been shown that for thermodynamically unstable mixtures the density-functional method permits effective description of the interrelated processes of viscous flow, diffusion, phase transitions, and surface tension. This makes it possible to use this method in modeling a wide class of processes of chemical technology.

Visualization of the results of the calculations (Figs. 1 and 2) was carried out by means of the VR-Geo program (limited company "Service-Nafta").

NOTATION

c, concentration of component 1; c_A, c_B, auxiliary variables; D, spatial domain; d, diffusion coefficient, m^2/sec; ∂D, spatial domain boundary; D_{ij}, matrix of diffusion coefficients, sec·mole^2/(m^3·kg); d_A, diffusion coefficient in phase A, m^2/sec; d_B, diffusion coefficient in phase B, m^2/sec; dA, surface element, m^2; dV, volume element, m^3; E, total energy functional, J; E_A, modulus of dilatation of phase A, Pa; F, free energy functional, J; f, free energy of a homogeneous mixture per unit volume, Pa; f_*, free energy of the mixture per unit surface, Pa·m; f_A, free energy of phase A, Pa; f_B, free energy of phase B, Pa; f_{A0}, coefficient at the zero degree of the free energy quadratic polynomial of phase A, Pa; f_{Ai}, coefficient at the first degree of the free energy quadratic polynomial of phase A, kg·m^2/(sec·mole); f_{Aij}, coefficient at the second degree of the free energy quadratic polynomial of phase A, kg·m^2/(sec·mole); g, arbitrary auxiliary function; I_{ia}, flow vector of the ith component, mole/(sec·m^2); l_a, internal normal to the surface; M, number of mixture components; m_i, molar mass of the ith component, kg/mole; N_i, number of particles of the ith component of the mixture; n, total molar density of the mixture, mole/m^3; n_i, molar density of the ith component, mole/m^3; p_A, phase A pressure, Pa; p_B, phase B pressure, Pa; p_{ab}, stress tensor in the mixture, Pa; Q_{ia}, diffusion flow of the ith component, mole/(sec·m^2); q_{ia}, flow of the ith component, m/sec; v_a, mass-mean flow rate, m/sec; t, time, sec; x^a, Cartesian coordinate, m; z_A, z_B, auxiliary variables, mole, m^3; γ, interphase surface tension coefficient, N/m; δ_{ab}, unit matrix; $\Delta\theta$, surface tension difference between phases A and B, Pa·m; θ_A, surface tension at the phase-A–solid contact, Pa·m; θ_B, surface tension at the phase-B–solid contact, Pa·m; κ_i, chemical potential of the ith component, kg·m^2/(sec·mole); Λ_i, Lagrange factors, kg·m^2/(sec·mole); μ_v, volume coefficient of viscosity, Pa·sec; μ_{vA}, volume coefficient of viscosity of phase A, Pa·sec; μ_{vB}, volume coefficient of viscosity of phase B, Pa·sec; μ_s, shear-viscosity coefficient, Pa·sec; μ_{sA}, shear-viscosity coefficient of phase A, Pa·sec; μ_{sB}, shear-viscosity coefficient of phase B, Pa·sec; ν_{ij}, coefficients of the positive symmetric matrix, kg·m^7/(sec^2·mole^2); ξ_0, auxiliary parameter, Pa·m; ξ_{1i}, auxiliary parameters, kg·m^3/(sec·mole); p, mass density of the mixture, kg/m^3; ρ_A, mass density of phase A, kg/m^3; ρ_B, mass density of phase B, kg/m^3; Σ, auxiliary function, kg/(sec^2·m); σ_{ab}, tensor of static stresses in the mixture, Pa; τ_{ab}, tensor of viscous stresses in the mixture, Pa; Φ_i, generalized chemical potential of the ith component of the mixture in the bulk, kg·m^2/(sec·mole); Φ_i^*, generalized chemical potential of the ith component of the mixture on the surface; kg·m^3/(sec·mole); φ, gravitational potential, m^2/sec^2; ω, auxiliary function, Pa; a, b, c, indices of Cartesian coordinates; i, j, k, indices of mixture components.

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