Journal of Engineering Physics and Thermophysics, Vol. 80, No. 6, 2007

APPLICATION OF DENSITY-FUNCTIONAL THEORY TO CALCULATION OF FLOWS OF THREE-PHASE MIXTURES WITH PHASE TRANSITIONS

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The problem of mathematical modeling of flows of three-phase three-component mixtures with phase transitions has been investigated using density-functional theory. The analytical and numerical results demonstrating the efficient application of this approach to description of two-phase flows were obtained earlier. In the present work, methods extending the density-functional technique to the case of three-phase mixtures have been proposed. Numerical solutions for flows of three-phase mixtures, including those with phase transitions, have been given.

Density-functional theory enables one to describe a multicomponent multiphase mixture in a continuous manner without introducing density jumps and phase boundaries. This is achieved by inclusion of the density gradients squared of the components into the expression for the free energy of the mixture [1] (or into the expression for entropy [2]). As a result the dynamics of the multiphase mixture is described in a unified manner, i.e., the system of equations used has the same form at all points of the flow region. This removes a number of difficulties arising in the case where one uses a classical approach based on the use of Navier–Stokes equations with different viscosity values in different spatial domains (corresponding to different phases). The formulation of conditions at phase boundaries is the most substantial of such difficulties: indeed, the Laplace formula for a pressure jump ceases to hold at points with an infinite curvature of the phase boundary, and such points necessarily appear in coalescence or fragmentation of liquid droplets and gas cavities (bubbles). This problem does not exist in density-functional theory, since the distribution of all parameters in the flow region always remains continuous. Interphase regions are separated as regions of large density gradients of the components of the mixture, and the Laplace formula describes a change in the density in traversal of the interphase region [1].

Density-functional theory was applied earlier to analytical and numerical modeling of two-phase flows [3–7]. In the present work, we consider the application of the method of density functional to mathematical modeling of three-phase isothermal flows, including those with phase transitions.

We recall the basic propositions of the theory for an isothermal case [1]. The theory for nonisothermal flows has been set forth in [2, 5]. The dependence of all quantities on temperature will be omitted for simplicity.

Let a M-component mixture (gas or a liquid) fill the domain D with a piecewise smooth boundary ∂D corresponding to the contact with a stationary solid phase. We will use the notation n_i for the molar density of the component numbered i. It is assumed that the subscripts i, j, and k run through values of 1, ..., and M, which corresponds to the numbers of the components of the mixture, and the subscripts a, b, and c take values of 1, 2, and 3, corresponding to the Cartesian coordinates x^a. Summation is carried out over double subscripts, unless additionally specified. Also, we use a contracted notation for derivatives: $g_{,i} = \partial g/\partial n_i$ and $\partial_a g = \partial g/\partial x^a$.

The free-energy functional of the mixture is prescribed by the expression

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

where

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1062-0125/07/8006-1247

$$\omega = f + \frac{1}{2}\nu_{ij}\partial_a n_i \partial_a n_j + \rho\varphi \; ; \;\; f = f(n_i) \; ; \;\; f_* = f_*(n_i) \; ;$$

$$\nu_{ij} = \nu_{ij}(n_k) \; ; \quad \varphi = \varphi(x^a) \; ; \quad \rho = m_i n_i \; .$$

As the governing hydrodynamic equations for isothermal flows, we take ordinary density and momentum equations [8]:

$$\partial_t n_i + \partial_a (n_i v_a + Q_{ia}) = 0 \; , \tag{2}$$

$$\rho (\partial_t v_a + v_b \partial_b v_a) = \partial_b p_{ab} - \rho \partial_a \varphi \; . \tag{3}$$

By definition it is taken that the diffusion flow does not transfer mass:

$$m_i Q_{ia} = 0 \; .$$

We impose the following boundary conditions on the dynamic variables under study: the sticking condition for the mass-mean velocity

$$v_a \,|_{\partial D} = 0 \; , \tag{4}$$

the nonflow condition for diffusion fluxes (where l_a is the internal normal to the surface ∂D)

$$l_a Q_{ia} \,|_{\partial D} = 0 \tag{5}$$

and the condition

$$\nu_{ij} l_a \partial_a n_j = f_{*,i} \; . \tag{6}$$

To close the hydrodynamic model with the dynamic equations (2) and (3) and boundary conditions (4)–(6) we must formulate the governing relations, i.e., the explicit expressions for the stress tensor p_{ab} and the diffusion fluxes Q_{ia}. These relations should be selected in accordance with the condition of decrease in the total energy including the free energy (1) and the kinetic energy of the mixture

$$E = F + \frac{1}{2}\int_D \rho v_a v_a dV \; . \tag{7}$$

Computation of the time derivative of the functional (7) with account for relations (2)–(6) yields

$$\frac{dE}{dt} = \int_D \Sigma dV \; , \tag{8}$$

$$\Sigma = -\,\tau_{ab}\partial_a v_b + Q_{ia}\partial_a \Phi_i \; , \tag{9}$$

$$\tau_{ab} = p_{ab} - \sigma_{ab} \; , \tag{10}$$

$$\sigma_{ab} = (\omega - \Phi_i n_i)\,\delta_{ab} - \nu_{ij}\partial_a n_i \partial_b n_j \; , \tag{11}$$

$$\Phi_i = f_{,i} + m_i\varphi + \frac{1}{2}\nu_{jk,i}\partial_a n_j \partial_a n_k - \nu_{ji,k}\partial_a n_j \partial_a n_k - \nu_{ij}\partial_a\partial_a n_j \, . \tag{12}$$

Here (10) should be interpreted as the viscous-stress tensor. Expression (11) is the tensor of static stresses in the mixture, since it is velocity-independent and makes no contribution to energy dissipation. In the case of a homogeneous mixture the tensor σ_{ab} is reduced to the ordinary stress tensor in an ideal liquid $\sigma_{ab} = -p\delta_{ab}$, where $p = n_i f_{,i} - f$ is the hydrostatic pressure.

For the integral of (8) to be of a nonnegative character, it is sufficient that the integrand (9) be nonnegative. For this purpose it is sufficient in turn to use the Navier–Stokes linear viscous model for the viscous-stress tensor

$$\tau_{ab} = \left(\mu_v - \frac{2}{3}\mu_s\right)\partial_c v_c \delta_{ab} + \mu_s\left(\partial_a v_b + \partial_b v_a\right) \tag{13}$$

and the generalized Fick law for diffusion fluxes

$$Q_{ia} = -D_{ij}\partial_a \Phi_j \, . \tag{14}$$

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

$$D_{ij} m_j = 0 \, . \tag{15}$$

In the absence of gravitation, the equilibrium states $n_i = n_i(x^1)$ and $v_a = 0$ with the dependence just on the coordinate x^1 satisfy the system of equations of second order

$$\Phi_i = \lambda_i \, , \tag{16}$$

where λ_i are certain constants. In explicit form, the system of equations (16) appears as

$$f_{,i} + \frac{1}{2}\nu_{jk,i}\partial_1 n_j \partial_1 n_k - \nu_{ij,k}\partial_1 n_j \partial_1 n_k - \nu_{ij}\partial_1\partial_1 n_j = \lambda_i \, . \tag{17}$$

System (17) can have solutions converging to different constant values for $x^1 \to \pm\infty$:

$$x^1 \to -\infty \, , \quad n_i \to n_{iA} \, , \tag{18}$$

$$x^1 \to +\infty \, , \quad n_i \to n_{iB} \, . \tag{19}$$

The existence of such solutions requires that the equalities $f_{,i}(n_{jA}) = f_{,i}(n_{jB})$ hold, which means the equality of the chemical potentials in phases A and B. Furthermore, as is easily checked directly, the quantity $\sigma_{11} = \omega - \lambda_i n_i - v_{ij}\partial_1 n_i \partial_1 n_j$ is the first integral of system (17). Therefore, the values of pressure in phases A and B are also coincident: $p(n_{iA}) = p(n_{iB})$. Thus, the solutions of problem (17)–(19) describe equilibrium two-phase states with a certain transition zone. Knowing the behavior of the solution in the interphase region, we can compute the coefficient of interphase surface tension [1]:

$$\gamma_{AB} = \int_{-\infty}^{+\infty} \nu_{ij}\partial_1 n_i \partial_1 n_j dx^1 \, . \tag{20}$$

Next, we carry out numerical modeling of three-phase three-component mixtures ($M = 3$) within the framework of density-functional theory. Gas and two immiscible liquids, e.g., can act as the phases. We prescribe a specific form of the free-energy function, the values of the coefficients of viscosity, diffusion, and surface tension on the contact of the mixture with the solid phase (vessel walls), and the coefficients ν_{ij}.

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

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

where $n_{i\mathrm{A}}$ is the unperturbed value of the mole density for phase A. Analogous expressions can be written for phases B and C:

$$f_{\mathrm{B}}(n_i) = f_{0\mathrm{B}} + f_{i\mathrm{B}}(n_i - n_{i\mathrm{B}}) + \phi_{\mathrm{B}}\,, \quad \phi_{\mathrm{B}} = 2^{-1} f_{ij\mathrm{B}}(n_i - n_{i\mathrm{B}})(n_j - n_{j\mathrm{B}})\,,$$

$$f_{\mathrm{C}}(n_i) = f_{0\mathrm{C}} + f_{i\mathrm{C}}(n_i - n_{i\mathrm{C}}) + \phi_{\mathrm{C}}\,, \quad \phi_{\mathrm{C}} = 2^{-1} f_{ij\mathrm{C}}(n_i - n_{i\mathrm{C}})(n_j - n_{j\mathrm{C}})\,.$$

Let us assume that phases A, B, and C can coexist in equilibrium. This means the equality of the corresponding chemical potentials and pressures:

$$f_{i\mathrm{A}} = f_{i\mathrm{B}} = f_{i\mathrm{C}}\,, \tag{21}$$

$$f_{i\mathrm{A}} n_{i\mathrm{A}} - f_{0\mathrm{A}} = f_{i\mathrm{B}} n_{i\mathrm{B}} = f_{0\mathrm{B}} = f_{i\mathrm{C}} n_{i\mathrm{C}} - f_{0\mathrm{C}}\,. \tag{22}$$

For states of the mixture not necessarily close to the A, B, and C states, the free energy f is determined as follows:

$$f = f_{0\mathrm{A}} + f_{i\mathrm{A}}(n_i - n_{i\mathrm{A}}) + \frac{\phi_{\mathrm{A}}\phi_{\mathrm{B}}\phi_{\mathrm{C}}}{\phi_{\mathrm{A}}\phi_{\mathrm{B}} + \phi_{\mathrm{B}}\phi_{\mathrm{C}} + \phi_{\mathrm{A}}\phi_{\mathrm{C}}}\,. \tag{23}$$

By virtue of relations (21) and (22) we reduce expression (23) near phases A, B, and C respectively to f_{A}, f_{B}, and f_{C} accurate to the increments in density of fourth order. The coefficients $f_{0\mathrm{A}}$ and $f_{i\mathrm{A}}$ are not involved in the hydrodynamic equations and are used just for computation of the initial unperturbed pressures and chemical potentials. It is only the coefficients $f_{ij\mathrm{A}}$, $f_{ij\mathrm{B}}$, and $f_{ij\mathrm{C}}$ that are important for hydrodynamic modeling; they are selected in accordance with the data on the modulus of dilatation for phases A, B, and C:

$$E_{\mathrm{A}} = f_{ij\mathrm{A}} n_{i\mathrm{A}} n_{j\mathrm{A}}\,, \quad E_{\mathrm{B}} = f_{ij\mathrm{B}} n_{i\mathrm{B}} n_{j\mathrm{B}}\,, \quad E_{\mathrm{C}} = f_{ij\mathrm{C}} n_{i\mathrm{C}} n_{j\mathrm{C}}\,.$$

Viscosity. The values of the shear and volume viscosity for unperturbed phases A, B, and C are assumed to be known. Furthermore, the vectors $n_{i\mathrm{A}}$, $n_{i\mathrm{B}}$, and $n_{i\mathrm{C}}$ are taken to be linearly independent. The viscosity values for arbitrary values of the density of the components are computed from the empirical interpolation formulas

$$\mu_{\mathrm{s}} = \left(y_{\mathrm{A}} \mu_{\mathrm{sA}}^{1/3} + y_{\mathrm{B}} \mu_{\mathrm{sB}}^{1/3} + y_{\mathrm{C}} \mu_{\mathrm{sC}}^{1/3} \right)^3, \tag{24}$$

$$\mu_{\mathrm{v}} = \left(y_{\mathrm{A}} \mu_{\mathrm{vA}}^{1/3} + y_{\mathrm{B}} \mu_{\mathrm{vB}}^{1/3} + y_{\mathrm{C}} \mu_{\mathrm{vC}}^{1/3} \right)^3, \tag{25}$$

$$y_{\mathrm{A}} = \left| \Delta_{\mathrm{A}}/\Delta \right|, \quad y_{\mathrm{B}} = \left| \Delta_{\mathrm{B}}/\Delta \right|, \quad y_{\mathrm{C}} = \left| \Delta_{\mathrm{C}}/\Delta \right|,$$

$$\Delta_{\mathrm{A}} = \begin{vmatrix} n_1 & n_2 & n_3 \\ n_{1\mathrm{B}} & n_{2\mathrm{B}} & n_{3\mathrm{B}} \\ n_{1\mathrm{C}} & n_{2\mathrm{C}} & n_{3\mathrm{C}} \end{vmatrix}, \quad \Delta_{\mathrm{B}} = \begin{vmatrix} n_1 & n_2 & n_3 \\ n_{1\mathrm{A}} & n_{2\mathrm{A}} & n_{3\mathrm{A}} \\ n_{1\mathrm{C}} & n_{2\mathrm{C}} & n_{3\mathrm{C}} \end{vmatrix},$$

$$\Delta_C = \begin{vmatrix} n_1 & n_2 & n_3 \\ n_{1A} & n_{2A} & n_{3A} \\ n_{1B} & n_{2B} & n_{3B} \end{vmatrix}, \quad \Delta = \begin{vmatrix} n_{1A} & n_{2A} & n_{3A} \\ n_{1B} & n_{2B} & n_{3B} \\ n_{1C} & n_{2C} & n_{3C} \end{vmatrix}.$$

Diffusion. To calculate the matrix D_{ij} we use the property that, on condition that $\nu_{ij} = 0$, formula (14) yields the following expression for the concentration flux of the components:

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

where $n = \sum_{i=1}^{3} n_i$ is the total density, $c_i = n_i/n$, and $\kappa_i = f_{,i}$. Thus, the matrix of diffusion coefficients d_{ij} which determines the diffusion flux in relation to the concentration gradients is related to the matrix D_{ij} by the equation

$$d_{ij} = n^{-1} D_{ik} \left(\frac{\partial \kappa_k}{\partial c_j}\right)_n . \tag{26}$$

The matrices of coefficients d_{ijA}, d_{ijB}, and d_{ijC} for many actual phases are usually the well-known tabulated data. The diffusion matrix d_{ij} is computed from the known values in phases using the interpolation formula

$$d_{ij} = y_A d_{ijA} + y_B d_{ijB} + y_C d_{ijC} . \tag{27}$$

If the free energy has been prescribed (see (23)), Eq. (26) enables us to uniquely determine the matrix D_{ij} from the matrix d_{ij}.

Surface Tension on the Mixture–Solid Body Contact is taken in the form of the linear function of the densities of the components

$$f_* = \xi_{1i} n_i + \xi_0 . \tag{28}$$

The parameters ξ_0 and ξ_{1j} are computed from the known values of the surface tension θ_A, θ_B, and θ_C on the contact with a solid body for phases A, B, and C based on the equation

$$\theta_A = \xi_{1i} n_{iA} + \xi_0 , \quad \theta_B = \xi_{1i} n_{iB} + \xi_0 , \quad \theta_C = \xi_{1i} n_{iC} + \xi_0 . \tag{29}$$

The system of linear equations (29) for ξ_0 and ξ_{1j} always has a solution (since the vectors n_{iA}, n_{iB}, and n_{iC} are assumed to be linearly independent) but it is not unique. The arbitrariness of selection of dependences (29) influences the distribution of the components near a solid wall but has no effect on the wetting angles. Furthermore, the parameter ξ_0 influences neither the dynamic equations nor the boundary conditions. Therefore, it is sufficient to assign an arbitrary value to the parameter ξ_0 and to compute the parameters ξ_{1j} from Eqs. (29).

The Matrix of Coefficients ν_{ij} is assumed to be constant and proportional to the diagonal matrix $\nu_{ij} = \zeta_i \delta_{ij}$ (here no summation over i is carried out). Unknown coefficients ζ_i are determined from expression (20) for the surface tension between phases A and B for the static solution and by analogous expressions for γ_{BC} and γ_{CA}. From the equations for γ_{AB}, γ_{BC}, and γ_{CA}, we can numerically determine three coefficients ζ_i. It is noteworthy that this problem is nonlinear, since the equilibrium distribution of the components is also dependent on ζ_i (see (17)).

The system of equations (2)–(6), (11), (13), (14), and (23)–(25) with the corresponding determinations of the diffusion, surface tension on the walls, and matrix ν_{ij} has been solved numerically using an explicit conservative difference scheme of 2nd order of accuracy with a staggered arrangement of the nodes [9].

We calculated, in a two-dimensional formulation, the following model problems for the three-component mixture:

(1) incidence of a droplet, under gravity, on the boundary of the other two phases;

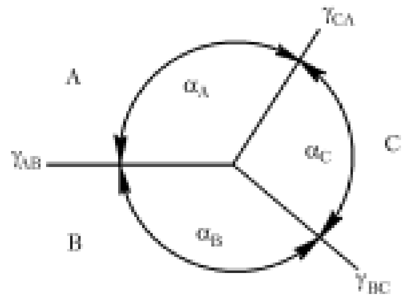

Fig. 1. Layout of the angles at the point of contact of phases A, B, and C.

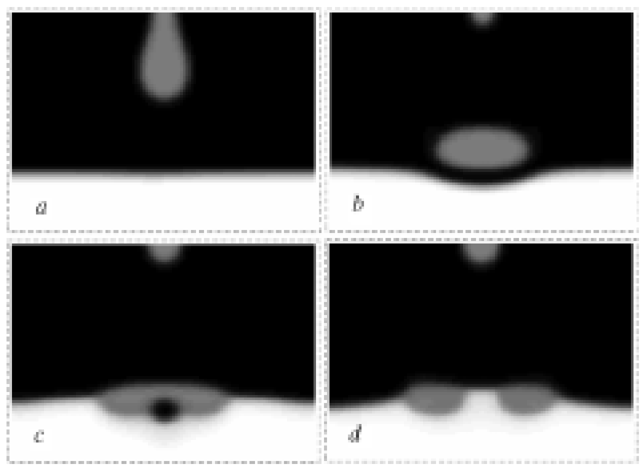

Fig. 2. Problem 1. Incidence of the first droplet: a) t = 0.465, b) 0.512, c) 0.542, and d) 0.561 sec.

(2) binodal disintegration of the mixture in the capillary into two phases in the presence of the third phase.

Modeling was carried out using the program developed by the authors of the paper; the time of calculation on a personal computer with an Athlon 4400+ x2 processor was ~30 min for the first problem and ~1 h for the second problem.

Visualization of the processes modeled was carried out from the calculation results. The regions of the mixture with the first component predominant are shown in white, those with the second component predominant are shown in black, and the regions with the third component predominant are shown in gray.

Problem 1. The model represents a square plane (2D) vessel installed in the gravity field so that the lines of force are directed along one dimension, from top to bottom. Initially, the vessel is filled with two equal volumes of different liquids (phases) in an equilibrium manner, i.e., a heavy liquid (phase B, white color) occupies the lower half of the vessel, whereas a gas (phase C, black color) occupies the upper half. The initial velocity fields are zero. We considered the motion of the droplets of the third phase (light liquid, phase A, gray color) in the gravity field with their subsequent incidence on the interface of phases B and C. Phase A in equilibrium was assumed to represent a virtually pure 1st component, phase B was assumed to represent the 2nd component, and phase C, the 3rd component. Thus, the mutual solubility of the components was low and occurred just as a result of the deviation from equilibrium in flow.

Phase A entered the vessel continuously with a constant flow rate of 0.35 cm^2/sec via two cells located at the center of the model's upper side. On the lower side, the mixture was extracted in an amount necessary for ensuring a constant average pressure throughout the vessel.

We took the following parameters of the mixture: m_1 = 250 kg/mole, m_2 = 18 kg/mole, and m_3 = 16 kg/mole; ρ_A = 800 kg/m^3, ρ_B = 1000 kg/m^3, and ρ_C = 1.5 kg/m^3; $E_A = 1.2 \cdot 10^9$ Pa, $E_B = 2.2 \cdot 10^9$ Pa, and $E_C = 1.1 \cdot 10^5$ Pa; $\mu_{sA} = 2 \cdot 10^{-3}$ Pa·sec, $\mu_{sB} = 1.5 \cdot 10^{-3}$ Pa·sec, and $\mu_{sC} = \cdot 10^{-4}$ Pa·sec; $\mu_{vA} = 2 \cdot 10^{-2}$ Pa·sec, $\mu_{vB} = 1.5 \cdot 10^{-2}$

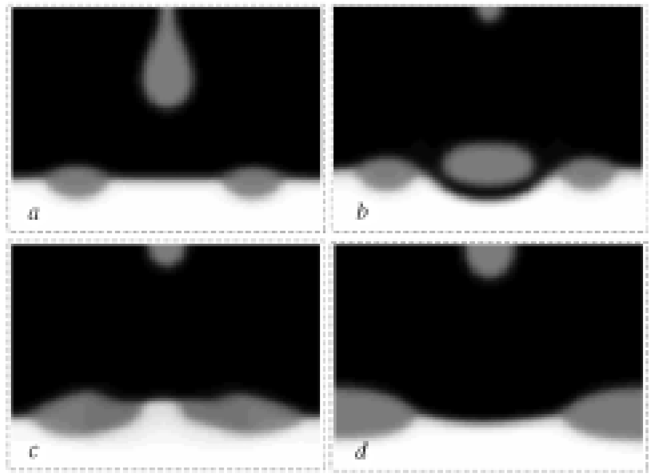

Fig. 3. Problem 1. Incidence of the second droplet: a) t = 0.924, b) 0.968, c) 1.012, and d) 1.1 sec.

Pa·sec, and $\mu_{vC} = \cdot 10^{-3}$ Pa·sec. The equilibrium angles at the point of contact of three phases (Fig. 1) were $\alpha_A = 75^o$, $\alpha_B = 121^o$, and $\alpha_C = 164^o$. The coefficients of interphase surface tension were γ_{AB} = 0.15 N/m, γ_{CA} = 0.47 N/m, and γ_{BC} = 0.53 N/m. We recall that the equilibrium angles at the point of contact of three phases are related to the surface-tension coefficients by the relation

$$\frac{\sin \alpha_A}{\gamma_{BC}} = \frac{\sin \alpha_B}{\gamma_{CA}} = \frac{\sin \alpha_C}{\gamma_{AB}},$$

whose fulfillment was checked using the results of the numerical modeling. The vessel walls had neutral wettability in relation to all the three phases: $\theta_A = \theta_B = \theta_C = 0$.

The matrices (26) for the three phases were restored from the values taken for the diffusion of components 2 and 3 in phase A, components 3 and 1 in phase B, and components 1 and 2 in phase C: $d_{22A} = 10^{-9}$ m^2/sec, $d_{33A} = 6.1 \cdot 10^{-9}$ m^2/sec, $d_{11B} = 1.5 \cdot 10^{-9}$ m^2/sec, $d_{33B} = 3.5 \cdot 10^{-9}$ m^2/sec, $d_{11C} = 2 \cdot 10^{-5}$ m^2/sec, and $d_{22C} = 10^{-5}$ m^2/sec.

The geometric dimensions of the model in question were 2 × 2 cm; the computational domain was approximated using 100 × 100 square cells.

The beginning of the process corresponded to the instant of time t = 0 sec. Figure 2 shows the development of the process to form the first droplet (Fig. 2a), its approach to the phase interface (Fig. 2b), the contact of the droplet with the surface of the heavy liquid to form a gas cavity (Fig. 2c), and the rupture of the droplet into halves (Fig. 2d). Figure 3 shows the continuation of the process to form the second droplet (Fig. 3a), its approach to the phase interface (Fig. 3b), the coalescence with the halves of the previous droplet (Fig. 3c), and the separation of the formed large fragments of phase A with their subsequent attachment to the vertical vessel walls (Fig. 3d).

Problem 2. Here the model represents a rectangular vessel filled with a mixture of three phases as follows. The lower part of the vessel is two-fifths full of phase B. The remaining volume is filled with a mixture of the 1st and 3rd components in 80%:20% ratio respectively. The mixture with such a composition is locally thermodynamically stable but unstable to finite perturbations. It is assumed that phases A and B do not wet capillary walls ($\theta_A = \theta_B$ = 0.05 N/m), whereas phase C wets them (θ_C = –0.1 N/m). It is expedient to note once again that, in the formulation in question, the solution is dependent on the differences $\theta_A - \theta_C$ and $\theta_B - \theta_C$ rather than on the absolute values of θ_A, θ_B, and θ_C. Gravitation is disregarded. The remaining parameters of the phases are taken such as those in problem 1. The geometric dimensions of the model are 3.2 × 1.6 cm; the computational domain is approximated by 64 × 32 square cells.

The initial state of the system corresponds to the instant of time t = 0 (Fig. 4a). The binodical disintegration of the mixture of components 1 and 3 begins in the two upper corners of the vessel and at the boundary of the mixture and phase B. Next, the released phase C, being wetting, displaces phase B and moves to the lower corners of the

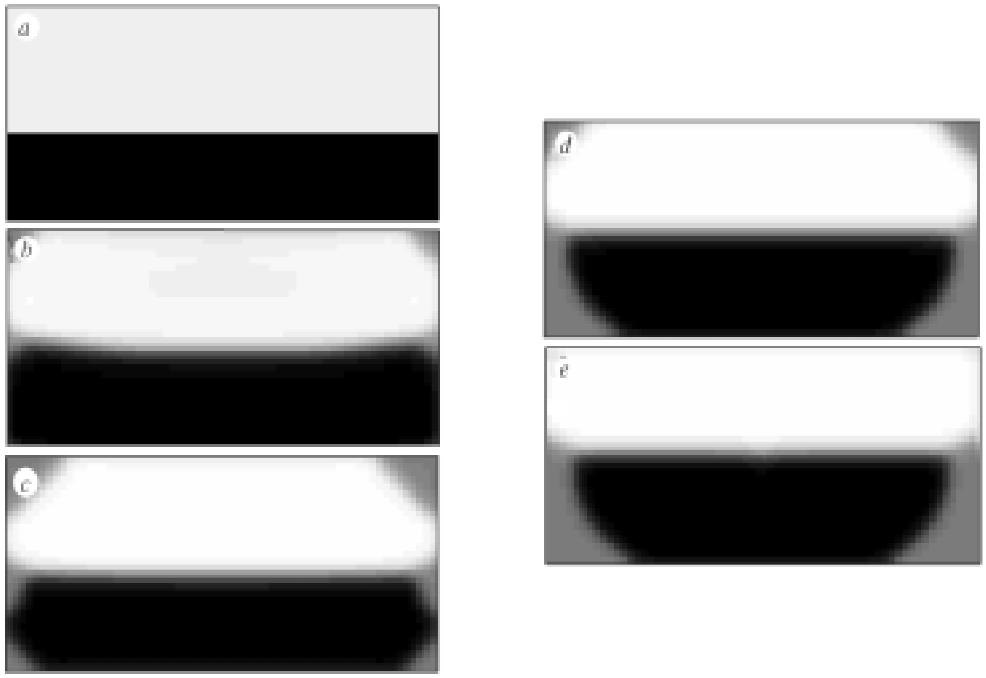

Fig. 4. Problem 2. Binodal disintegration of the mixture into two phases (A and C) in the presence of the third phase B (phase A, white color, B, black, and C, gray): a) $t = 0$, b) 7.2, c) 80.5, d) 706.9, and c) 2120.7 min.

vessel. Finally, equilibrium sets in when phase C is accumulated near the lower corners of the model and the boundary of phases A and B. A successive change of states is shown in Fig. 4b–e.

Thus, it has been demonstrated with specific examples that one can efficiently describe different hydrodynamic processes on three-phase mixtures, including those with phase transitions, using the method of density functional. The same computational program is used; only the boundary and initial conditions are changed. Noteworthy is the fact that a fairly good description of the rupture and coalescence of droplets and the occurrence and evolution of a new phase, i.e., phenomena that are difficult to model within the framework of other approaches, has been obtained on comparatively small grids.

NOTATION

c_i, mole concentration of the component i; D, spatial domain; dA, surface element, m^2; ∂D, boundary of the spatial domain; dV, volume element, m^3; D_{ij}, symmetric nonnegative matrix, sec·mole^2/(m^3·kg); d_{ij}, matrix of diffusion coefficients in the mixture, m^2/sec; $d_{ij\mathrm{A}}$, $d_{ij\mathrm{B}}$, and $d_{ij\mathrm{C}}$, matrix of diffusion coefficients in phases A, B, and C, m^2/sec; E, total energy of the mixture, J; E_A, E_B, and E_C, dilatation modulus of phases A, B, and C, Pa; F, total free energy of the mixture, J; f, free energy of a homogeneous mixture per unit volume, Pa; f_*, free energy of a homogeneous mixture per unit surface, Pa·m; f_A, f_B, and f_C, free energy of phases A, B, and C, Pa; $f_{0\mathrm{A}}$, $f_{0\mathrm{B}}$, and $f_{0\mathrm{C}}$, coefficients of the zero degree of the quadratic polynomial of free energy of phases A, B, and C, Pa; $f_{i\mathrm{A}}$, $f_{i\mathrm{B}}$, and $f_{i\mathrm{C}}$, coefficients of the first of the first degree of the quadratic polynomial of free energy of phases A, B, and C, kg·m^2/(sec·mole); $f_{ij\mathrm{A}}$, $f_{ij\mathrm{B}}$, and $f_{ij\mathrm{C}}$, coefficients of the second degree of the quadratic polynomial of free energy of phases A, B, and C, kg·m^5/(sec·mole); g, arbitrary auxiliary function; l_a, internal normal to the surface; M, number of components in the mixture; m_i, mole weight of the ith component, kg/mole; n, total mole density of the mixture, mole/m^3; n_i, mole density of the ith component, mole/m^3; $n_{i\mathrm{A}}$, $b_{i\mathrm{B}}$, and $n_{i\mathrm{C}}$, unperturbed value of the mole density of the ith component in phases A, B, and C, mole/m^3; p, pressure, Pa; p_{ab}, stress tensor in the mixture, Pa; Q_{ia}, vector of the diffusion flux of the ith component, mole/(sec·m^2); q_{ia}, concentration flux of the ith component, m/sec; v_a, mass-mean velocity, m/sec; t, time, sec; x^a, Cartesian coordinate, m; y_A, y_B, and y_C, auxiliary dimensionless quantities; α_A, α_B, and α_C, angles at the point of contact of three phases; γ_{AB}, γ_{BC}, and γ_{CA}, coefficients of interphase surface tension between phases A and B, B and C, and C and A, kg·m^2/sec; δ_{ab}, unit matrix; Δ, Δ_A, Δ_B, and Δ_C, auxiliary functions, mole^3/m^9; ζ_i, auxiliary quantities, kg·m^7/(sec·mole^2); θ_A, θ_B, and θ_C, surface tension for phases A, B, and C on the contact with a solid body, N/m; κ_i, chemical potential of the ith component, kg·m^2/(sec·mole); μ_s, shear-viscosity coefficient, Pa·sec; μ_{sA}, μ_{sB}, and μ_{sC}, shear-viscosity coefficient of phases A, B, and C, Pa·sec; μ_v, volume-viscosity coefficient, Pa·sec; μ_{vA}, μ_{vB}, and μ_{vC}, volume-viscosity coefficients of phases A, B, and C, Pa·sec; ν_{ij}, coefficients of a symmetric positive-definite matrix, kg·m^7/(sec·mole^2); ξ_0, auxiliary quantity, Pa·m; ξ_{1i}, auxiliary quantity, Pa·m^4/mole; ρ, mass density of the mixture, kg/m^3; Σ, auxiliary function, Pa/sec; σ_{ab}, tensor of static stresses in the mixture, Pa; τ_{ab}, tensor of viscous stresses in the mixture, Pa; φ, gravitational potential, m^2/sec^2; Φ_i, generalized chemical potential of the ith component in the volume, kg·m^2/(sec·mole); φ_A, φ_B, and φ_C, quadratic part of free energy for phases A. B, and C, Pa; ω, energy of a homogeneous mixture per unit volume, Pa. Subscripts and superscripts: a, b, and c, to the Cartesian coordinates; i, j, and k, to the components of the mixture; s, shear; v, volume.

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