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Two-Velocity Flow Containing Surfactant

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Abstract—A hydrodynamic theory of two-velocity fluid with surfactant is constructed in the present paper. The model takes into account both surface effects and impact of the concentration gradient on relative velocity of the components. The dependence of the nonstationary two-phase flow regimes on the surface tension gradient and the dependence of the relative drop velocity on the gradient of the surfactant concentration are investigated numerically on the base of volume control method.

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INTRODUCTION

A hydrodynamic system is considered, where two nonmiscible fluids are represented locally (e.g., oil drops and water containing them), with surfactant dissolved in them. In such systems, an additional local thermodynamic degree of freedom is the total surface area of the interface between the components. In the process of hydrodynamic evolution, the system performs work when the surface area of the interface changes.

In natural flows of water—oil mixtures, surfactants are always present. The fraction of alphaltenes, naphthenic acids, resins, etc. in flows of water—oil mixtures is negligible. However, in technological processes, interaction between alkalis and oil acids yields surfactants easily dissolvable in water, and they cause surface tension at the interface between oil droplets and the surrounding water to drop. These surfactants are adsorbed on the surface of oil droplets and affect the motion of nonmiscible fluids. As shown below, it is essential to analyze the impact surfactants have on dynamics of the mixture when computing phase fluxes. This analysis is described in the present article.

In [1], we can find the analysis of a select particle surrounded by a surfactant. It is shown that the gradient of surface tension creates additional drag for the moving particle, far exceeding viscous friction and Stokes friction. The present article demonstrates that, in the two-velocity medium, with the continual approach, there is always an additional characteristic reactive force in the presence of surfactants in the reversible hydrodynamic approximation. This force is proportional to the gradient of the concentration of surfactant dissolved in water. The hydrodynamic velocity determines the concentration of the surfactant distributed in space. In turn, the gradient of the surfactant generates the reaction forces in moving subsystems, which affect velocity of hydrodynamic transfer. As a result, hydrodynamic interaction appears, which results in a self-regulated velocity profile of subsystem motion. As shown below, the surfactant's influence at fairly low fluid flow rates is significant and affects phase velocities, which is key for analyzing mass phase fluxes through the cross section of the pipe.

The hydrodynamic theory of solutions in two-phase media differs from hydrodynamic theories reported in the literature [2—14]. The two-velocity equations are obtained based exclusively on fundamental physical principles (the first and second principles of thermodynamics, conservation laws). Specific particularities of the system under study are not taken into account. For example, the motion

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equations obtained hold true for an arbitrary class of equations of state of a two-velocity system. The equations of state have no influence on the form of the hydrodynamic motion equations. This situation is the same as when the classical Euler set of equations was obtained, where the equation of state was an external condition with respect to hydrodynamic equations and does not affect the character of motion equations. It is shown that the equations of hydrodynamic evolution of the two-velocity system depend only on the structure of the first principle of thermodynamics. The latter result is found in accordance with the logic of development of the one-velocity Euler set of hydrodynamic equations.

THERMODYNAMICS OF TWO-PHASE MEDIUM WITH SURFACTANT

Let us consider a two-phase medium with thermodynamic equilibrium in volume V, which is a fluid with droplets in it, and these droplets may be, for example, oil. Let us denote the water mass within the indicated volume as M_1, oil mass as M_2, and surfactant mass as M_c. The first principle of thermodynamics shown below introduces a version of the hydrodynamic system analyzed here:

$$d\tilde{E}_0 = Td\tilde{S} - pdV + \mu_1 dM_1 + \mu_2 dM_2 + \mu_c\, dM_c + \sigma d\Sigma. \tag{1}$$

Here $\tilde{E}_0$, $\tilde{S}$ are internal energy and entropy of the system within volume V; T is temperature; p is pressure; σ is surface tension at the interface between water and oil; $\Sigma = \varsigma J$ is total surface area of the interface between water and oil droplets; J is the number of droplets in the volume; μ_1, μ_2, μ_c are chemical potentials of components 1, 2 and surfactant. The pressure drop in “fluidic subsystems” may be neglected in further considerations. Equation (1) introduces chemical potentials [15].

For hydrodynamic description, we need to introduce physical densities:

$$\left(\tilde{E}_0, \tilde{S}, M_1, M_2, M_c, \Sigma\right) = \left(E_0, S, \rho_1, \rho_2, \rho_c, \varsigma J\right) V, \tag{2}$$

Substituting relationships from (2) into (1), we arrive at the first principle of thermodynamics for a unit volume of the medium:

$$dE_0 = TdS + \mu_1 d\rho_1 + \mu_2 d\rho_2 + \mu_c d\rho_c + \varsigma\sigma dJ. \tag{3}$$

Pressure can be found via the thermodynamic formula [16]

$$p = -E_0 + TS + \mu_1\rho_1 + \mu_2\rho_2 + \mu_c\rho_c + \varsigma\sigma J. \tag{4}$$

Let us introduce density of the medium containing water, oil, and surfactant:

$$\rho = \rho_1 + \rho_2 + \rho_c. \tag{5}$$

In terms of new variables, formula (3) takes the following form:

$$dE_0 = TdS + \mu_1 d\rho + \left(\mu_2 - \mu_1\right) d\rho_2 + \left(\mu_c - \mu_1\right) d\rho_c + \varsigma\sigma dJ. \tag{6}$$

Because the relationship $\rho_2 = M_2/V = m\,N/V = m\,J$ holds true, we arrive at the local form of the first principle of thermodynamics of a four-parameter thermodynamic system [17]

$$dE_0 = TdS + \mu_1 d\rho + \varsigma\bar{\sigma} dJ + \left(\mu_c - \mu_1\right) d\rho_c = TdS + \mu_1 d\rho + \frac{\varsigma\bar{\sigma}}{m} d\rho_2 + \left(\mu_c - \mu_1\right) d\rho_c, \tag{7}$$

$$\bar{\sigma} = \sigma + \frac{m}{\varsigma}\left(\mu_2 - \mu_1\right), \tag{8}$$

$$p = -E_0 + TS + \mu_1\rho + \left(\mu_c - \mu_1\right)\rho_c + \varsigma\bar{\sigma} J, \tag{9}$$

$$dp = SdT + \rho d\mu_1 + \rho_c d\left(\mu_c - \mu_1\right) + \varsigma J d\bar{\sigma}. \tag{10}$$

Here, m is mass of a droplet, $\mu_2 \neq \mu_1$.

Formula (7) describes a local thermodynamic equilibrium. For relative mutual motion of two components, we need to generalize the theory [18] for the case with no local equilibrium. The velocity difference $\mathbf{w} = \mathbf{u} - \mathbf{v}$ of the water–oil continuum may be considered a relaxing degree of freedom [19]:

$$\begin{aligned} dE_0 &= TdS + \mu_1 d\rho + \varsigma\bar{\sigma} dJ + \left(\mu_c - \mu_1\right) d\rho_c + \left(\mathbf{u} - \mathbf{v}\right) d\mathbf{j}_0 \\ &= TdS + \mu_1 d\rho + \frac{\varsigma\bar{\sigma}}{m} d\rho_2 + \left(\mu_c - \mu_1\right) d\rho_c + \left(\mathbf{u} - \mathbf{v}\right) d\mathbf{j}_0, \end{aligned} \tag{11}$$

$$p = -E_0 + TS + \mu_1 \rho + \left(\mu_c - \mu_1\right)\rho_c + \varsigma\bar{\sigma} J + \left(\mathbf{u} - \mathbf{v}\right)\mathbf{j}_0, \tag{12}$$

$$dp = SdT + \rho d\mu_1 + \rho_c d\left(\mu_c - \mu_1\right) + \varsigma J d\bar{\sigma} + \mathbf{j}_0 d\left(\mathbf{u} - \mathbf{v}\right). \tag{13}$$

Here, $\mathbf{j_0}$ is density of the relative momentum of two components; $\mathbf{u}$ is the velocity of the droplet continuum; $\mathbf{v}$ is the velocity of the water continuum. The kinetic term for the two-velocity medium was introduced as recommended by Landau [16].

If the system is in the constant gravity field with potential φ, it is necessary to adjust the chemical potentials in formula (3) for all components [19]:

$$dE_0 = TdS + \left(\mu_1 + \varphi\right) d\rho_1 + \left(\mu_2 + \varphi + \frac{\varsigma}{m}\sigma\right) d\rho_2 + \left(\mu_c + \varphi\right) d\rho_c. \tag{14}$$

The latter statement is due to additional energy of the system in the gravity field $\rho\varphi = \left(\rho_1 + \rho_2 + \rho_c\right)\varphi$. Analyzing the state of thermodynamic equilibrium as per [18], we arrive at the following conditions:

$$\begin{gathered} \nabla T = 0, \quad \mathbf{u} = \mathbf{v} = 0, \quad \nabla\left(\mu_1 + \varphi\right) = 0, \\ \nabla\left(\mu_2 + \frac{\varsigma}{m}\sigma + \varphi\right) \equiv \nabla\left(\varsigma\bar{\sigma}\right) = 0, \quad \nabla\left(\mu_c + \varphi\right) = 0. \end{gathered} \tag{15}$$

REVERSIBLE HYDRODYNAMIC EQUATIONS OF TWO-PHASE FLOW WITH SURFACTANT

Before developing a hydrodynamic model of the two-velocity medium, one need to develop reversible approximation [20], based on conservation laws of: mass, surfactant mass, number of droplets, entropy, momentum, energy

$$\frac{\partial\rho}{\partial t} + \operatorname{div}\left(\rho\mathbf{v} + \mathbf{j}_0\right) = 0, \tag{16}$$

$$\frac{\partial\rho_c}{\partial t} + \operatorname{div}\left(\rho_c\mathbf{v} + \mathbf{D}_0\right) = 0, \tag{17}$$

$$\frac{\partial J}{\partial t} + \operatorname{div}\left(J\mathbf{v} + \mathbf{G}_0\right) = 0, \tag{18}$$

$$\frac{\partial S}{\partial t} + \operatorname{div}\left(S\mathbf{v} + \mathbf{F}_0\right) = 0, \tag{19}$$

$$\frac{\partial j_i}{\partial t} + \partial_k\left(\rho v_i v_k + v_i j_{0,k} + v_k j_{0,i} + \Pi_{0,ik}\right) = \rho\mathbf{g}, \tag{20}$$

$$\frac{\partial E}{\partial t} + \partial_i \left(Q_{0,i} + \left(E_0 + (\mathbf{v}, \mathbf{j}_0) + \rho \mathbf{v}^2/2 + \rho\varphi \right) v_i + \mathbf{v}^2 j_{0,i}/2 + \Pi_{0,ki} v_k \right) = 0. \tag{21}$$

Here, $J = \rho_2/m$; $\mathbf{g} = -\nabla\varphi$ is free-fall acceleration. The flows denoted with the divergence sign are presented with accuracy of up to $\mathbf{j}_0$, $\mathbf{F}_0$, $\mathbf{D}_0$, $\mathbf{G}_0$, $\mathbf{Q}_0$, E_0 invariant parts of the Galileo transform [16]; $\mathbf{j} = \mathbf{j}_0 + \rho\mathbf{v}$ is momentum density of the system; $E = E_0 + (\mathbf{v}, \mathbf{j}_0) + \rho\mathbf{v}^2/2 + \rho\varphi$ is energy density [16]. These equations lack physical meaning because the flows are not defined.

The flow of the two-phase medium is characterized by two velocities, for this reason, to define these velocities, one needs two equations. The momentum conservation law (20) can be one of them. As the second equation, which would describe the motion of the carrier fluid, we selected the semi-linear motion equation whose right-hand side contains motion forces determined by gradients of thermodynamic variables from the first principle of thermodynamics (11) and becoming constants if there is thermodynamic equilibrium [21, 17, 18]:

$$\nabla T = 0, \quad \mathbf{u} = \mathbf{v} = 0, \quad \nabla(\mu_1 + \varphi) = 0, \quad \nabla(\mu_c - \mu_1) = 0, \quad \nabla(\varsigma\bar{\sigma}) = 0. \tag{22}$$

It should be noted that this is how the Euler equation is structured:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v},\, \nabla)\,\mathbf{v} = -\frac{\nabla p}{\rho} = -\nabla\mu - \frac{S}{\rho}\nabla T, \quad p = -E_0 + TS + \mu\rho. \tag{23}$$

It is a motion equation of ideal fluid. The conditions of thermodynamic equilibrium for the Euler set of equations can be reduced to absence of chemical potential gradient, temperature, and velocity: $\nabla\mu = 0$, $\nabla T = 0$, $\mathbf{v} = 0$. Here, p is pressure; μ is chemical potential from the first principle of thermodynamics $dE_0 = TdS + \mu d\rho$ for fluid. When there is thermodynamic equilibrium, it becomes a constant, just as temperature T.

The Euler equation may be obtained from the consistency conditions for conservation laws for mass, momentum, energy, entropy, and the first principle of thermodynamics. Such an approach leads to generalization of the motion equations for a wider class of hydrodynamic systems. Thus, according to the alternative idea of developing the Euler equation, the motion equation of the carrier fluid in the two-velocity continuum may be presented as [16, 17, 21]:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v},\, \nabla)\,\mathbf{v} = \xi_\mu \nabla(\mu_1 + \varphi) + \xi_T \nabla T + \xi_c \nabla(\mu_c - \mu_1) + \xi_\sigma \nabla(\varsigma\bar{\sigma}). \tag{24}$$

Equations (16)–(21), (24) should be consistent with each other and the first principle of thermodynamics (11), i.e., conservation laws should guarantee satisfaction of the first principle of thermodynamics. To this end, we differentiate the energy equation with respect to time. Taking into account (11), we have:

$$\frac{\partial E}{\partial t} = T\frac{\partial S}{\partial t} + \left(\mu_1 + \varphi + \frac{\mathbf{v}^2}{2} - (\mathbf{u}, \mathbf{v}) \right) \frac{\partial \rho}{\partial t} + (\mu_c - \mu_1)\frac{\partial \rho_c}{\partial t}$$
$$+ \left(\mathbf{j} - \rho\mathbf{u}, \frac{\partial \mathbf{v}}{\partial t} \right) + \left(\mathbf{u}, \frac{\partial \mathbf{j}}{\partial t} \right) + \varsigma\bar{\sigma}\frac{\partial J}{\partial t}. \tag{25}$$

When conservation laws (16)–(21) are satisfied identically, the motion equation (24) and formula (25) become identities. Substituting time derivatives from (16)–(21), (24) into (25), we arrive at the following equation:

$$\partial_i \left(Q_{0,i} - TF_{0,i} - (\mu_1 + \varphi)\, j_{0,i} - \varsigma\bar{\sigma} G_{0,i} - (\mu_c - \mu_1)\, D_{0,i} - (\Pi_{0,ki} - p\delta_{ki} - j_{0,k} w_i)\, w_k - (\mathbf{j}_0, \mathbf{w})\, w_i \right)$$
$$= -\left(\mathbf{F}_0 + \xi_T (\mathbf{j} - \rho\mathbf{u}) - S\mathbf{w} \right) \nabla T - (1 + \xi_\mu)(\mathbf{j} - \rho\mathbf{u})\nabla(\mu_1 + \varphi) - (\Pi_{0,ik} - p\delta_{ik} - j_{0,i} w_k)\, \partial_k u_i$$
$$- \left(\mathbf{J}_0 + \xi_\sigma(\mathbf{j} - \rho\mathbf{u}) - J\,\mathbf{w} \right) \nabla(\varsigma\bar{\sigma}) - \left(\mathbf{D}_0 + \xi_c(\mathbf{j} - \rho\mathbf{u}) - \rho_1\mathbf{w} \right) \nabla(\mu_c - \mu_1). \tag{26}$$

Relationship (27) ties together the Galileo invariants and should be satisfied identically. Therefore, summand $(\Pi_{0,ik} - p\delta_{ik} - j_{0,i}w_k)\,\partial_k u_i$ should disappear as it breaks the Galileo invariance. The latter condition determines the invariant part of the tensor of momentum flow density $\Pi_{0,ik} = p\delta_{ik} + j_{0,i}w_k$. As a result, Eq. (26) takes the following form:

$$\partial_i \left(Q_{0,i} - TF_{0,i} - (\mu_1 + \varphi)\, j_{0,i} - \varsigma\bar{\sigma}G_{0,i} - (\mu_c - \mu_1)\, D_{0,i} - (\mathbf{j}_0, \mathbf{w})\, w_i\right)$$

$$= - \left[\mathbf{F}_0 + \xi_T\,(\mathbf{j} - \rho\mathbf{u}) - S\mathbf{w}\right] \nabla T - (1 + \xi_\mu)\,(\mathbf{j} - \rho\mathbf{u})\, \nabla\,(\mu_1 + \varphi)$$

$$- \left(\mathbf{G}_0 + \xi_\sigma(\mathbf{j} - \rho\mathbf{u}) - J\mathbf{w}\right) \nabla\,(\varsigma\bar{\sigma}) - \left(\mathbf{D}_0 + \xi_c\,(\mathbf{j} - \rho\mathbf{u}) - \rho_c\mathbf{w}\right) \nabla\,(\mu_c - \mu_1)\,. \qquad (27)$$

Further extraction of total derivatives in the right-hand side of (27) yields spatial derivatives of velocities, which should not be present in reversible flows. Therefore,

$$\mathbf{Q}_0 = T\,\mathbf{F}_0 + (\mu_1 + \varphi)\,\mathbf{j}_0 + \varsigma\bar{\sigma}\,\mathbf{G}_0 + (\mu_c - \mu_1)\,\mathbf{D}_0 + (\mathbf{j}_0, \mathbf{w})\,\mathbf{w}. \qquad (28)$$

The sum of four differentials of independent thermodynamic variables identically equals zero only if the following coefficients identically equal zero:

$$\mathbf{F}_0 + \xi_T\,(\mathbf{j} - \rho\mathbf{u}) - S\mathbf{w} = 0, \quad \mathbf{G}_0 + \xi_\sigma\,(\mathbf{j} - \rho\mathbf{u}) - J\mathbf{w} = 0, \qquad (29)$$

$$\mathbf{D}_0 + \xi_c\,(\mathbf{j} - \rho\mathbf{u}) - \rho_c\mathbf{w} = 0, \quad 1 + \xi_\mu = 0. \qquad (30)$$

To find the flux $\mathbf{G}_0$, it is necessary to make assumptions regarding oil droplets transport with velocity $\mathbf{u}\,(\xi_\sigma = 0, \mathbf{G}_0 = J\,\mathbf{w})$:

$$\frac{\partial J}{\partial t} + \operatorname{div}\,(J\,\mathbf{u}) = 0. \qquad (31)$$

The parameter ξ_T defines the flow in the entropy conservation law, (19), and $\mathbf{F}_0 + \xi_T\,(\mathbf{j} - \rho\mathbf{u}) - S\mathbf{w} = 0$ must be an identity. If entropy transport is performed by both subsystems, then there is the only possibility to satisfy the identity by selecting $\xi_T = -S/\rho$. Repeating the same steps for the flux $\mathbf{D}_0$ in the mass conservation law for surfactant, (17), we arrive at this condition: $\xi_c = -\rho_c/\rho$.

Using (13), we can rewrite Eq. (24) as follows:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v},\, \nabla)\,\mathbf{v} = -\frac{\nabla p}{\rho} + \left(\xi_T + \frac{S}{\rho}\right) \nabla T + \left(\xi_c + \frac{\rho_c}{\rho}\right) \nabla\,(\mu_c - \mu_1)$$

$$+\varsigma \left(\xi_\sigma + \frac{J}{\rho}\right) \nabla\bar{\sigma} + \frac{1}{\rho}\,(\mathbf{j}_0, \nabla\mathbf{w}) - \nabla\varphi. \qquad (32)$$

Knowing ξ_μ, ξ_T, ξ_c, ξ_σ, we arrive at the equation for the carrier component motion:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v},\, \nabla)\,\mathbf{v} = -\frac{\nabla p}{\rho} + \varsigma\frac{J}{\rho}\nabla\bar{\sigma} + \frac{1}{\rho}\,(\mathbf{j}_0, \nabla\mathbf{w}) + \mathbf{g}. \qquad (33)$$

With reversible flows determined, the conservation laws in the continual theory of the two-velocity medium's hydrodynamics in reversible approximation acquire physical meaning:

$$\frac{\partial J}{\partial t} + \operatorname{div}\,(J\mathbf{u}) = 0 \quad (J = \rho_2/m)\,, \qquad (34)$$

$$\frac{\partial \rho}{\partial t} + \operatorname{div}\mathbf{j} = 0, \qquad (35)$$

$$\frac{\partial \rho_c}{\partial t} + \operatorname{div}\left(\frac{\rho_c}{\rho}\mathbf{j}\right) = 0, \tag{36}$$

$$\frac{\partial S}{\partial t} + \operatorname{div}\left(\frac{S}{\rho}\mathbf{j}\right) = 0, \tag{37}$$

$$\frac{\partial j_i}{\partial t} + \partial_k\left(\rho v_i v_k + v_i j_{0,k} + u_k j_{0,i} + p\delta_{ik}\right) = \rho g_i, \tag{38}$$

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v},\, \nabla)\,\mathbf{v} = -\frac{\nabla p}{\rho} + \varsigma\frac{J}{\rho}\nabla\bar{\sigma} + \frac{1}{\rho}\left(\mathbf{j}_0, \nabla\mathbf{w}\right) + \mathbf{g}, \tag{39}$$

$$\frac{\partial E}{\partial t} + \operatorname{div}\left((E+p)\frac{\mathbf{j}}{\rho} - \left(\varsigma\bar{\sigma}J + (\mathbf{j} - \rho\mathbf{v},\, \mathbf{u})\right)\left(\frac{\mathbf{j}}{\rho} - \mathbf{u}\right)\right) = 0, \tag{40}$$

$$\frac{\partial\left(\rho\varphi\right)}{\partial t} + \operatorname{div}\left(\mathbf{j}\varphi\right) = -\left(\mathbf{j}, \mathbf{g}\right). \tag{41}$$

The latter equality holds true when gravity is constant in time. To close the set of equations, one needs to present the equation of state and find the relationship between the relative velocity $\mathbf{u} - \mathbf{v}$ and relative momentum $\mathbf{j}_0$. The relative momentum is invariant, and at the same time, the only invariant present in the system is $\mathbf{u} - \mathbf{v}$, related to velocities of the medium. When the relative momentum is expanded into a series in terms of the relative velocity, just the first expansion term $\mathbf{j}_0 = \rho_s\left(\mathbf{u} - \mathbf{v}\right)$ would suffice. The proportionality coefficient ρ_s is partial density of the suspended (carried) phase: $\mathbf{j} = \mathbf{j}_0 + \rho\mathbf{v} = \rho_s\mathbf{u} + \rho_l\mathbf{v}$. Partial densities ρ_s, ρ_l are not affected by the velocity difference. In this case, the equations of the system may take the following form:

$$\frac{\partial J}{\partial t} + \operatorname{div}\left(J\,\mathbf{u}\right) = 0 \quad \left(J = \rho_2/m\right), \tag{42}$$

$$\frac{\partial \rho}{\partial t} + \operatorname{div}\mathbf{j} = 0, \quad \mathbf{j} = \rho_s\mathbf{u} + \rho_l\mathbf{v}, \quad \rho = \rho_s + \rho_l, \tag{43}$$

$$\frac{\partial \rho_c}{\partial t} + \operatorname{div}\left(\frac{\rho_c}{\rho}\mathbf{j}\right) = 0, \tag{44}$$

$$\frac{\partial S}{\partial t} + \operatorname{div}\left(\frac{S}{\rho}\mathbf{j}\right) = 0, \tag{45}$$

$$\frac{\partial j_i}{\partial t} + \partial_k\left(\rho_l v_i v_k + \rho_s u_i u_k + p\delta_{ik}\right) = \rho g_i, \tag{46}$$

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v},\, \nabla)\,\mathbf{v} = -\frac{\nabla p}{\rho} + \varsigma\frac{J}{\rho}\nabla\bar{\sigma} + \frac{\rho_s}{2\rho}\nabla\mathbf{w}^2 + \mathbf{g}, \tag{47}$$

$$\frac{\partial E}{\partial t} + \operatorname{div}\left((E+p)\frac{\mathbf{j}}{\rho} + \frac{\rho_l}{\rho}(\mathbf{u}-\mathbf{v})(\varsigma\bar{\sigma}J + \rho_s(\mathbf{u}-\mathbf{v},\, \mathbf{u}))\right) = 0. \tag{48}$$

Equations (46), (47) yield the motion equation for droplets:

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u},\, \nabla)\,\mathbf{u} = -\frac{\nabla p}{\rho} - \frac{\rho_l}{\rho_s}\varsigma\frac{J}{\rho}\nabla\bar{\sigma} - \frac{\rho_l}{2\rho}\nabla\mathbf{w}^2 + \mathbf{g}, \tag{49}$$

and this equation for the velocity difference:

$$\frac{\partial \mathbf{w}}{\partial t}+(\mathbf{w},\,\nabla)\mathbf{w}+\frac{1}{2}\nabla \mathbf{w}^2+(\mathbf{w},\,\nabla)\,\mathbf{v}+(\mathbf{v},\,\nabla)\,\mathbf{w}=-\varsigma\frac{J}{\rho_s}\nabla\sigma. \tag{50}$$

Reversible motion Eq. (50) demonstrates that the gradient of surface tension ensures the relative phase velocity. It should be noted that this statement follows from the general procedure of hydrodynamic modeling based in the thermodynamic consistency condition. It may be beneficial to compare the latter equation with the way the corresponding formula is obtained in [1]. When obtaining (49), (50), the conservation law was taken into account:

$$\frac{\partial \rho_s}{\partial t}+\operatorname{div}\,(\rho_s\mathbf{u})=0. \tag{51}$$

Equations (42)–(48) represent ideal hydrodynamics of the two-velocity medium and are a consistent basis for real dissipative motion equations for the two-phase medium with surfactant. Equations (42)–(48) follow from the first principle of thermodynamics and from consistency conditions: these equations agree with the first principle of thermodynamics, (11), and identically satisfy the energy conservation law, (48). When obtaining these equations, assumptions regarding interactions within the system were not made. The most general thermodynamically consistent equations were obtained. Adding surfactant to the first principle of thermodynamics, which affected surface tension at the interface between water and oil, yields reversible hydrodynamic approximation of the force $\rho_l\,(\varsigma J\nabla\bar{\sigma}/\rho)$ acting on the unit volume of water in a certain medium. The force acting on the unit volume of oil in a certain element of the medium is $\rho_l\,(\varsigma J\nabla\sigma/\rho)$. This force is proportional to the gradient of surface tension due to oil droplets transport with the velocity $\mathbf{u}$. In a particular case, on the microscopic scales, this force was first calculated in [1]. The present paper showed that the nature of this force is more general. In [1], it is noted that extremely low concentrations of surfactant in the system may radically change the drag forces in the hydrodynamic flow, when flow rates are moderate. An important feature of these equations is the presence of reactive forces in the right-hand sides of equations:$\rho_l\nabla\mathbf{w}^2/2\rho$ and $-\rho_s\nabla\mathbf{w}^2/2\rho$. It is due to these forces we can ensure stability of reversible hydrodynamic approximation [18].

IRREVERSIBLE EQUATIONS OF TWO-VELOCITY FLOW WITH SURFACTANT

The complete set of equations taking into account dissipative effects can be obtained from set (42)–(48) by adding irreversible flows to corresponding reversible parts [20]:

$$\frac{\partial J}{\partial t}+\operatorname{div}\,(J\,\mathbf{u})=0\quad (J=\rho_2/m)\,, \tag{52}$$

$$\frac{\partial \rho}{\partial t}+\operatorname{div}\mathbf{j}=0,\quad \mathbf{j}=\rho_s\mathbf{u}+\rho_l\mathbf{v},\quad \rho=\rho_s+\rho_l, \tag{53}$$

$$\frac{\partial\,(c\rho)}{\partial t}+\operatorname{div}\left(c\mathbf{j}-\frac{\lambda_1}{T}\,(\mathbf{j}-\rho\mathbf{u})+\mathbf{L}\right)=0,\quad \rho_c=c\rho, \tag{54}$$

$$\frac{\partial S}{\partial t}+\operatorname{div}\left(\frac{S}{\rho}\mathbf{j}-\frac{\lambda}{T}\,(\mathbf{j}-\rho\mathbf{u})+\frac{\lambda_1\,(\mu_c-\mu_1)}{T^2}\,(\mathbf{j}-\rho\mathbf{u})+\frac{\mathbf{q}}{T}-\frac{(\mu_c-\mu_1)\,\mathbf{L}}{T}\right)=\frac{R}{T}, \tag{55}$$

$$\frac{\partial j_i}{\partial t}+\partial_k\left(\rho_s u_i u_k+\rho_l v_i v_k+p\,\delta_{ik}+\pi^s_{ik}+\pi^l_{ik}\right)=\rho g_i, \tag{56}$$

$$\frac{\partial \mathbf{v}}{\partial t}+(\mathbf{v},\nabla)\,\mathbf{v}=-\frac{\nabla p}{\rho}+\varsigma\frac{J}{\rho}\nabla\bar{\sigma}+\frac{\rho_s}{2\rho}\nabla\mathbf{w}^2+\lambda_1\nabla\left(\frac{(\mu_c-\mu_1)}{T}\right)+\lambda\frac{\nabla T}{T}+\mathbf{g}+\mathbf{f}, \tag{57}$$

$$\frac{\partial E}{\partial t} + \operatorname{div}(\mathbf{Q} + \mathbf{W}) = 0. \tag{58}$$

In Eqs. (52)–(58): R is a dissipative function; heat flow $\mathbf{q}$, surfactant mass flow $\mathbf{L}_1$, energy flow $\mathbf{W}$; irreversible densities of momentum flows are π^l_{ik}, π^s_{ik}; friction is $\mathbf{f}$. The equations should satisfy differential form (11) identically. The latter requirement enables us to find irreversible flows. To satisfy differential form (11), let us substitute time derivatives with respect to time from (52)–(58) into (25). After some minor simplifications, we obtain an equation whose right-hand side contains coupled products of unknown flows and thermodynamic forces that generate them:

$$\partial_i\left(W_i - q_i + \lambda\,(j_i - \rho u_i) - \pi^l_{ik}v_i - \pi^s_{ik}u_i\right) = -R - \frac{\mathbf{q}}{T}\nabla T - T\,\mathbf{L}\nabla\left(\frac{\mu_c - \mu_1}{T}\right)$$
$$-\frac{\pi^l_{ik}}{2}\,(\partial_k v_i + \partial_i v_k) - \frac{\pi^s_{ik}}{2}\,(\partial_k u_i + \partial_i u_k) - (j_i - \rho u_i)\left(f_i + \frac{\partial_k \pi^l_{ik}}{\rho_l}\right). \tag{59}$$

The left-hand side of the equation determines the irreversible flow of energy:

$$W_i = q_i - \lambda\,(j_i - \rho u_i) + \pi^l_{ik}v_i + \pi^s_{ik}u_i, \tag{60}$$

and the right-hand side, the dissipative function:

$$R = -\,(j_i - \rho u_i)\left(f_i + \frac{\partial_k \pi^l_{ik}}{\rho_l}\right) - \frac{\mathbf{q}}{T}\nabla T - T\,\mathbf{L}\nabla\left(\frac{\mu_c - \mu_1}{T}\right)$$
$$-\frac{\pi^l_{ik}}{2}\,(\partial_k v_i + \partial_i v_k) - \frac{\pi^s_{ik}}{2}\,(\partial_k u_i + \partial_i u_k). \tag{61}$$

The latter equation can be brought to the standard form: it is necessary to identify the diagonal in the flows of tensor dimension [22]:

$$R = -\left(f_i + \frac{\partial_k \pi^l_{ik}}{\rho_l}\right)(j_i - \rho u_i) - \mathbf{q}\,\frac{\nabla T}{T} - \mathbf{L}\,T\nabla\left(\frac{\mu_c - \mu_1}{T}\right)$$
$$-a^l \operatorname{div}\mathbf{v} - a^s \operatorname{div}\mathbf{u} - \frac{1}{2}A^l_{ik}v_{ik} - \frac{1}{2}A^s_{ik}u_{ik}. \tag{62}$$

Here, $\pi^{l,s}_{ik} = A^{l,s}_{ik} + a^{l,s}\delta_{ik}$, $\left(A^{l,s}_{ii} = 0\right)$, $v_{ik} = \partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\operatorname{div}\mathbf{v}$, $u_{ik} = \partial_k u_i + \partial_i u_k - \frac{2}{3}\delta_{ik}\operatorname{div}\mathbf{u}$.

The kinetic coefficients introduce the relationship between thermodynamic forces and thermodynamic flows of the same tensor nature:

$$f_i + \frac{\partial_k \pi^l_{ik}}{\rho_l} = -B_{11}(j_i - \rho u_i) - \lambda\frac{\partial_i T}{T} - \lambda_1\partial_i\left(\frac{\mu_c - \mu_1}{T}\right), \tag{63}$$

$$\mathbf{q} = -\lambda\,(\mathbf{j} - \rho\mathbf{u}) - B_{22}\frac{\nabla T}{T} - B_{23}\partial_i\left(\frac{\mu_c - \mu_1}{T}\right), \tag{64}$$

$$T\,\mathbf{L} = -\lambda_1\,(\mathbf{j} - \rho\mathbf{u}) - B_{32}\frac{\nabla T}{T} - B_{33}\partial_i\left(\frac{\mu_c - \mu_1}{T}\right), \tag{65}$$

$$A^l_{ik} = -\eta_l v_{ik} - \eta_{12}u_{ik}, \tag{66}$$

$$A^s_{ik} = -\eta_{12} v_{ik} - \eta_s u_{ik}, \tag{67}$$

$$a^l = -\zeta_l \operatorname{div} \mathbf{v} - \zeta_{12} \operatorname{div} \mathbf{u}, \tag{68}$$

$$a^s = -\zeta_{21} \operatorname{div} \mathbf{v} - \zeta_s \operatorname{div} \mathbf{u}, \tag{69}$$

where ζ_l, ζ_s, ζ_{12} are scalar kinetic coefficients; λ, λ_1, B_{11}, B_{22}, B_{33}, B_{23} are vector kinetic coefficients, and η_l, η_s, η_{12} are tensor kinetic coefficients.

All kinetic coefficients are, generally, functions of S, ρ, c, J, $\mathbf{u} - \mathbf{v}$, that is, of the thermodynamic nonequilibrium state. The dissipative function is a quadratic form defined positively:

$$\begin{gathered}
R = B_{11} \left(\mathbf{j} - \rho \mathbf{u}\right)^2 + 2\lambda \frac{\nabla T}{T} \left(\mathbf{j} - \rho \mathbf{u}\right) + 2\lambda_1 \nabla \left(\frac{\mu_c - \mu_1}{T}\right) \left(\mathbf{j} - \rho \mathbf{u}\right) + B_{22} \left(\frac{\nabla T}{T}\right)^2 \\
+ B_{23} \nabla \left(\frac{\mu_c - \mu_1}{T}\right) \frac{\nabla T}{T} + B_{33} \left(\nabla \frac{(\mu_c - \mu_1)}{T}\right)^2 + \zeta_l \left(\operatorname{div} \mathbf{v}\right)^2 + \zeta_s \left(\operatorname{div} \mathbf{u}\right)^2 \\
+ 2\zeta_{12} \left(\operatorname{div} \mathbf{v}\right) \left(\operatorname{div} \mathbf{u}\right) + \frac{1}{2} \eta_l v_{ik}^2 + \frac{1}{2} \eta_s u_{ik}^2 + \eta_{12} u_{ik} v_{ik},
\end{gathered} \tag{70}$$

which is guaranteed by the following conditions:

$$\zeta_l \geq 0, \quad \zeta_l \zeta_s \geq \zeta_{12}^2, \tag{71}$$

$$B_{11} \geq 0, \quad B_{11} B_{22} \geq \lambda^2, \quad (B_{11} B_{33} - \lambda_1^2)(B_{11} B_{22} - \lambda^2) \geq (B_{11} B_{23} - \lambda \lambda_1)^2, \tag{72}$$

$$\eta_l \geq 0, \quad \eta_l \eta_s \geq \eta_{12}^2. \tag{73}$$

Irreversible flows (63)–(69) in (52)–(58) enable us to close the initial set of equations:

$$\frac{\partial J}{\partial t} + \operatorname{div} \left(J\, \mathbf{u}\right) = 0 \quad \left(J = \rho_2 / m\right), \tag{74}$$

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \mathbf{j} = 0, \quad \mathbf{j} = \rho_s \mathbf{u} + \rho_l \mathbf{v}, \quad \rho = \rho_s + \rho_l, \tag{75}$$

$$\frac{\partial \left(c\rho\right)}{\partial t} + \operatorname{div} \left(c_s \rho_s \mathbf{u} + c_l \rho_l \mathbf{v} + \tilde{\mathbf{L}}\right) = 0, \tag{76}$$

$$\frac{\partial S}{\partial t} + \operatorname{div} \left(S_s \mathbf{u} + S_l \mathbf{v} + \frac{\tilde{\mathbf{q}}}{T} - \frac{\left(\mu_c - \mu_1\right) \tilde{\mathbf{L}}}{T}\right) = \frac{R}{T}, \tag{77}$$

$$\begin{gathered}
\frac{\partial j_i}{\partial t} + \partial_k \left(\rho_s u_i u_k + \rho_l v_i v_k + p \delta_{ik} - \left(\zeta_s + \zeta_{12}\right) \delta_{ik} \operatorname{div} \mathbf{u} - \left(\zeta_l + \zeta_{12}\right) \delta_{ik} \operatorname{div} \mathbf{v} \right. \\
\left. - \left(\eta_s + \eta_{12}\right) u_{ik} - \left(\eta_l + \eta_{12}\right) v_{ik}\right) = \rho \mathbf{g},
\end{gathered} \tag{78}$$

$$\begin{gathered}
\frac{\partial v_i}{\partial t} + \left(\mathbf{v}, \nabla\right) v_i = -\frac{1}{\rho} \partial_i p + \varsigma \frac{J}{\rho} \partial_i \sigma + \frac{\rho_s}{2\rho} \partial_i \mathbf{w}^2 - B_{11} \left(j_i - \rho u_i\right) \\
+ \frac{1}{\rho_l} \partial_k \left(\eta_l v_{ik} + \eta_{12} u_{ik}\right) + \frac{1}{\rho_l} \partial_i \left(\zeta_l \operatorname{div} \mathbf{v} + \zeta_{12} \operatorname{div} \mathbf{u}\right) + g_i,
\end{gathered} \tag{79}$$

$$\frac{\partial E}{\partial t} + \partial_i \left((E+p)\frac{j_i}{\rho} + \frac{\rho_l}{\rho_s}(\varsigma\bar{\sigma} J + (\mathbf{j}_0,\, \mathbf{u}))\frac{j_{0,i}}{\rho} - 2\lambda(j_i - \rho u_i) + \pi^l_{ik} v_k + \pi^s_{ik} u_k + \tilde{q}_i \right) = 0. \tag{80}$$

As indicated above,

$$c_s\rho_s = c\rho_s + 2\frac{\lambda_1}{T}\rho_l, \quad S_s = \frac{\rho_s}{\rho}S + 2\left(\lambda - \lambda_1 \frac{\rho\,(\mu_c - \mu_1)}{T^2}\right)\frac{\rho_l}{\rho}, \tag{81}$$

$$c_l\rho_l = c\rho_l - 2\frac{\lambda_1}{T}\rho_l, \quad S_l = \frac{\rho_l}{\rho}S - 2\left(\lambda - \lambda_1 \frac{\rho\,(\mu_c - \mu_1)}{T^2}\right)\frac{\rho_l}{\rho}, \tag{82}$$

$$\tilde{\mathbf{L}} = -B_{32}\frac{\nabla T}{T^2} - \frac{B_{33}}{T}\nabla\left(\frac{\mu_c - \mu_1}{T}\right), \tag{83}$$

$$\tilde{\mathbf{q}} = -B_{22}\frac{\nabla T}{T} - B_{23}\nabla\left(\frac{\mu_c - \mu_1}{T}\right). \tag{84}$$

As a result, Eqs. (81), (82) yield a relationship between surfactant concentrations for each phase and surfactant concentration in the local element of the two-velocity medium $c_s\rho_s + c_l\rho_l = c\rho$, and dynamic equations as well:

$$\frac{\partial u_i}{\partial t} + (\mathbf{u}, \nabla)\, u_i = -\frac{\partial_i p}{\rho} - \frac{\rho_l}{\rho_s}\varsigma\frac{J}{\rho}\partial_i\bar{\sigma} - \frac{\rho_l}{2\rho}\partial_i \mathbf{w}^2 + \frac{\rho_l}{\rho_s}B_{11}\,(j_i - \rho u_i)$$

$$+\frac{1}{\rho_s}\partial_k\,(\eta_{12}v_{ik} + \eta_s u_{ik}) + \frac{1}{\rho_s}\partial_i\,(\zeta_{12}\operatorname{div}\mathbf{v} + \zeta_s\operatorname{div}\mathbf{u}) + g_i, \tag{85}$$

$$\frac{\partial v_i}{\partial t} + (\mathbf{v}, \nabla)\, v_i = -\frac{\partial_i p}{\rho} + \varsigma\frac{J}{\rho}\partial_i\bar{\sigma} + \frac{\rho_s}{2\rho}\partial_i \mathbf{w}^2 - B_{11}\,(j_i - \rho u_i)$$

$$+\frac{1}{\rho_l}\partial_i\,(\zeta_l\operatorname{div}\mathbf{v} + \zeta_{12}\operatorname{div}\mathbf{u}) + \frac{1}{\rho_l}\partial_k\,(\eta_l v_{ik} + \eta_{12}u_{ik}) + g_i \tag{86}$$

and the equation for velocity $\mathbf{w}$ of relative motion:

$$\frac{\partial w_i}{\partial t} + (\mathbf{w},\, \nabla)\, w_i + (\mathbf{w},\, \nabla)\, v_i + (\mathbf{v},\, \nabla)\, w_i + \frac{1}{2}\partial_i\mathbf{w}^2 = -\varsigma\frac{J}{\rho_s}\partial_i\bar{\sigma} - \frac{\rho_l}{\rho_s}\rho B_{11} w_i$$

$$+\frac{1}{\rho_s}\partial_i\,(\zeta_{12}\operatorname{div}\mathbf{v} + \zeta_s\operatorname{div}\mathbf{u}) - \frac{1}{\rho_l}\partial_i\,(\zeta_l\operatorname{div}\mathbf{v} + \zeta_{12}\operatorname{div}\mathbf{u})$$

$$+\frac{1}{\rho_s}\partial_k\,(\eta_{12}v_{ik} + \eta_s u_{ik}) - \frac{1}{\rho_l}\partial_k\,(\eta_l v_{ik} + \eta_{12}u_{ik})\,. \tag{87}$$

Let us omit viscous and nonlinear effects from consideration. Equation (87) is now simplified:

$$\frac{\partial \mathbf{w}}{\partial t} + \frac{\rho_l}{\rho_s}\rho B_{11}\mathbf{w} = -\varsigma\frac{J}{\rho_s}\nabla\bar{\sigma} \tag{88}$$

and it shows that it is the gradient of surface tension and interphase friction (and viscous friction, in the general case) determine the relative velocity of phases in the two-velocity system, under stationary conditions.

In the absence of hydrodynamic velocities and time derivatives, the set of Eqs. (74)–(80) can be reduced to:

$$\nabla \bar{\sigma} = 0, \quad \nabla p = \rho\, \mathbf{g}, \quad \operatorname{div} \tilde{\mathbf{q}} = 0, \quad \operatorname{div} \tilde{\mathbf{L}} = 0. \tag{89}$$

Taking into account the Gibbs–Duhem relationship, (13), as well as (83), (84), we can transform the set (88), (89) as follows:

$$S\nabla T + \rho\nabla\left(\mu_1 + \varphi\right) + \rho_c \nabla\left(\mu_c - \mu_1\right) = 0, \quad \nabla\bar{\sigma} = 0, \tag{90}$$

$$\operatorname{div}\left(B_{22}\frac{\nabla T}{T} + B_{23}\nabla\left(\frac{\mu_c - \mu_1}{T}\right)\right) = 0, \quad \operatorname{div}\left(B_{32}\frac{\nabla T}{T^2} + B_{33}\frac{1}{T}\nabla\left(\frac{\mu_c - \mu_1}{T}\right)\right) = 0. \tag{91}$$

The set of four equations for the four thermodynamic variables has the following solution:

$$\nabla T = 0, \quad \nabla\left(\mu_1 + \varphi\right) = 0, \quad \nabla\left(\mu_c - \mu_1\right) = 0, \quad \nabla\bar{\sigma} = 0 \tag{92}$$

with no entropy production:

$$R = B_{22}\left(\frac{\nabla T}{T}\right)^2 + B_{23}\nabla\left(\frac{\mu_c - \mu_1}{T}\right)\frac{\nabla T}{T} + B_{33}\left(\nabla\frac{\left(\mu_c - \mu_1\right)}{T}\right)^2. \tag{93}$$

Conditions (92) coincide with conditions of thermodynamic equilibrium (15).

Thus, Eqs. (74)–(80) follow from the first principle of thermodynamics, consistency conditions, and second principle of thermodynamics for irreversible flows. When obtaining these equations, no assumptions are made regarding interaction within the system. The motion equations obtained are consistent with thermodynamics and as general as possible for the continual approximation. The maximal value of kinetic coefficients and their functional dependence are shown.

EQUATION OF STATE FOR SOLUTION IN TWO-COMPONENT MEDIUM

Motion Eqs. (74)–(80) obtained above are determined by the first principle of thermodynamics, unambiguously:

$$dE_0 = TdS + \mu_1 d\rho + \left(\mu_c - \mu_1\right) d\rho_c + \left(\mu_2 - \mu_1 + \frac{\varsigma\sigma}{m}\right) d\rho_2 \tag{94}$$

and do not depend on the form of the equation of state $E_0 = E_0\left(S,\, \rho,\, \rho_c,\, \rho_2\right)$. Here, equations for the two-velocity medium are obtained in a way similar to that of obtaining the set of Euler equations [17, 18, 23].

With introduction of mass concentration $c = \rho_c/\rho$, the first principle of thermodynamics takes this form:

$$dE_0 = TdS + \mu d\rho + \left(\mu_2 - \mu_1 + \frac{\varsigma\sigma}{m}\right) d\rho_2 + Z\, dc, \tag{95}$$

$$Z = \left(\mu_c - \mu_1\right)\rho, \quad \mu = \mu_1 + c\left(\mu_c - \mu_1\right). \tag{96}$$

Our next goal is to express the chemical potentials (95) of the two-component system via the chemical potentials of its homogeneous thermodynamic subsystems.

Let us consider the first principle of thermodynamics for each of the three-parameter thermodynamic subsystem, introducing physical densities ρ_1^f, ρ_2^f. For the carrier water component with surfactant (mass concentration of surfactant being c_1) we have:

$$dE_1^f = TdS_1^f + \mu_1^f d\rho_1^p + \mu_{1c}^f d\rho_{1c}^p = dS_1^f + \mu_1^f d\left(\rho_1^f - \rho_{1c}^p\right) + \mu_{1c}^f d\rho_{1c}^p$$

$$= TdS_1^f + \mu_1^f d\rho_1^f + \left(\mu_{1c}^f - \mu_1^f\right) d\rho_{1c}^p = TdS_1^f + \bar{\mu}_1 d\rho_1^f + Z_1 dc_1, \tag{97}$$

$$\bar{\mu}_1 = \mu_1^f + \left(\mu_{1c}^f - \mu_1^f\right) c_1, \quad Z_1 = \left(\mu_{1c}^f - \mu_1^f\right) \rho_1^f, \quad \rho_1^f = \rho_1^p + \rho_{1c}^p. \tag{98}$$

For the fragmented oil component with surfactant (concentration being c_2), we have:

$$dE_2^f = TdS_2^f + \bar{\mu}_2 d\rho_2^f + Z_2 dc_2,$$

$$\bar{\mu}_2 = \mu_2^f + \left(\mu_{2c}^f - \mu_2^f\right) c_2, \quad Z_2 = \left(\mu_{2c}^f - \mu_2^f\right) \rho_2^f, \quad \rho_2^f = \rho_2^p + \rho_{2c}^p. \tag{99}$$

Here, index f denotes physical components of infinite homogeneous media with surfactant of which the hydrodynamic composite system is comprised; index p denotes partial density of the homogeneous phase. Physical chemical potentials μ_1^f, μ_2^f in thermodynamics are found via the first principle of thermodynamics with partial densities and are used in the so-called Gibbs phase rule.

Let us find the parameters representing the total of partial densities for homogeneous components: internal energy, entropy, and mass:

$$E_0 = E_1^f (1-\phi) + E_2^f \phi, \quad S = S_1^f (1-\phi) + S_2^f \phi, \quad \rho = \rho_1^f (1-\phi) + \rho_2^f \phi. \tag{100}$$

Here, ϕ is bulk fraction of oil droplets.

Let us calculate the differential for energy (100), using differentials of total entropy and density of the composite system. The result may be presented in the following form:

$$dE_0 = (1-\phi)\left(TdS_1^f + \bar{\mu}_1 d\rho_1^f + Z_1 dc_1\right) + \phi\left(TdS_2^f + \bar{\mu}_2 d\rho_2^f + Z_2 dc_2\right) + \left(E_2^f - E_1^f\right) d\phi$$

$$= TdS + \bar{\mu}_1 d\rho + \left(\bar{\mu}_2 - \bar{\mu}_1 + \frac{\varsigma\sigma}{m}\right)(1+c_2)\, d\rho_2 + (p_1 - p_2)\, d\phi$$

$$+ \left(\mu_{1c}^f - \mu_1^f\right) \rho_1 (1+c_1)\, dc_1 + \left[\bar{\mu}_2 - \bar{\mu}_1 + \left(\mu_{2c}^f - \mu_2^f\right)(1+c_2)\right] \rho_2 dc_2, \tag{101}$$

$$\rho_2 (1+c_2) = \phi\, \rho_2^f, \quad \rho_1 (1+c_1) = (1-\phi)\, \rho_1^f, \quad \rho = \rho_1 + \rho_2 + \rho_c, \tag{102}$$

$$p_1 = -E_1^f + TS_1^f + \bar{\mu}_1 d\rho_1^f, \quad p_2 = -E_2^f + TS_2^f + \bar{\mu}_2 d\rho_2^f. \tag{103}$$

Combining the two subsystems together, we find concentration no longer arbitrary but part of the combined system at certain proportions determined either by the Gibbs rule or by Langmuir condition (if the surfactant is concentrated on the surface of the oil droplets). However, pressure in (40) is determined for arbitrary concentrations for each identified subsystem. In the composite system, components' pressure will be $p_1 = p_2$, but neither will coincide with pressure p of the composite system. For low concentrations, Eq. (101) may be rewritten as follows:

$$dE_0 = TdS + \bar{\mu}_1 d\rho + \left(\bar{\mu}_2 - \bar{\mu}_1 + \frac{\varsigma\sigma}{m}\right) d\rho_2 + \lambda \rho_1 dc_1 + \nu \rho_2 dc_2, \tag{104}$$

$$\rho_2 = \rho_s = \phi\, \rho_2^f, \quad \rho_1 = \rho_l = (1-\phi)\, \rho_1^f, \quad \rho = \rho_1 + \rho_2 + \rho_c, \tag{105}$$

$$\lambda = \mu_{1c}^f - \mu_1^f, \quad \nu = \mu_{2c}^f - \mu_2^f. \tag{106}$$

To connect composite variables with those of the thermodynamic system under study, let us use the following relationship:

$$\rho c = c_1 \rho_1 + c_2 \rho_2, \tag{107}$$

$$\frac{c_1}{c_2} = \frac{c_{01}}{c_{02}} + \theta\left(T\right), \quad \theta\left(T\right) = \Phi_c \left(T - T_0\right), \quad \Phi_c = const, \quad \mu^f_{1c} \neq \mu^f_{2c}. \tag{108}$$

The second formula from (108) represents the Langmuir isotherm, that is, the curve of equilibrium adsorption, which holds true in the low concentration domain. Concentrations c_{10}, c_{20} characterize the initial distribution of concentrations at temperature T_0. It is assumed that the time needed for local equilibrium adsorption to establish is small. The term linear with respect to temperature describes the temperature shift for the equilibrium curve. The pressure shift for the equilibrium adsorption curve is not taken into account. Generally, one needs to consider kinetics of local adsorption.

Formula (104) must be identical to (11):

$$dE_0 = TdS + \mu d\rho + \left(\mu_2 - \mu_1 + \frac{\varsigma\sigma}{m}\right) d\rho_2 + Zdc, \tag{109}$$

$$\mu = \mu_1 + \left(\mu_c - \mu_1\right) c, \quad Z = \left(\mu_c - \mu_1\right) \rho, \tag{110}$$

$$p = -E_0 + TdS + \mu\rho + \left(\mu_2 - \mu_1 + \frac{\varsigma\sigma}{m}\right) d\rho_2. \tag{111}$$

Bringing (104) to the same form as (109), we arrive at the relationship between parameters μ, μ_1, μ_2, Z and the corresponding thermodynamic variables related to the subsystem. To this end, it is necessary to transform expression $\lambda\rho_1 dc_1 + \nu\rho_2 dc_2$ from (104) in terms of variables used in the first principle of thermodynamics (109). Taking into account (107), (108), we have two equations for finding differentials of concentrations in components:

$$\rho_1 dc_1 + \rho_2 dc_2 = \rho dc + \left(c - c_1\right) d\rho + \left(c_1 - c_2\right) d\rho_2, \tag{112}$$

$$c_2 dc_1 - c_1 dc_2 = \Phi_c\, c_2^2 dT. \tag{113}$$

The essence of the procedure performed is identifying the dependence of concentration differentials on differentials of thermodynamic variables in (109). Let us introduce this parameter:

$$\mu_r = \mu^f_{1c} - \left(\mu^f_1 \frac{\rho_1 c_1}{\rho c} + \mu^f_2 \frac{\rho_2 c_2}{\rho c}\right). \tag{114}$$

As a result, the solution to the set of Eqs. (112), (113) determines this sum:

$$\lambda\rho_1 dc_1 + \nu\rho_2 dc_2 = \mu_r \rho dc + \mu_r \left(c - c_1\right) d\rho + \mu_r \left(c_1 - c_2\right) d\rho_2 + \left(\lambda - \nu\right) \frac{\rho_1\rho_2}{\rho} \frac{c_2^2}{c} \Phi_c dT. \tag{115}$$

Using (108), we can bring (101) to the following form:

$$d\bar{E}_0 = Td\bar{S} + \left(\bar{\mu}_1 + \mu_r \left(c - c_1\right)\right) d\rho + \left(\bar{\mu}_2 - \bar{\mu}_1 + \mu_r \left(c_1 - c_2\right) + \frac{\varsigma\sigma}{m}\right) d\rho_2 + \mu_r \rho dc. \tag{116}$$

This equation corresponds to pressure as per its thermodynamic definition:

$$p = -\bar{E}_0 + T\bar{S} + \left(\bar{\mu}_1 + \mu_r \left(c - c_1\right)\right) \rho + \left(\bar{\mu}_2 - \bar{\mu}_1 + \mu_r \left(c_1 - c_2\right) + \frac{\varsigma\sigma}{m}\right) \rho_2. \tag{117}$$

On the other hand, we have a combined definition of pressure based on the relationship below:

$$E_0 = (1-\phi)\,E_1 + \phi E_2 = (1-\phi)\left(-p_1 + TS_1 + \bar{\mu}_1\rho_1^f\right) + \phi\left(-p_2 + TS_2 + \bar{\mu}_2\rho_2^f\right)$$

$$= -\left((1-\phi)\,p_1 + \phi p_2\right) + TS + \bar{\mu}_1\rho + (\bar{\mu}_2 - \bar{\mu}_1)\,\rho_2\,(1+c_2)\,, \qquad (118)$$

which is definitely true. We find pressure form the latter equation ($p_1 = p_2$):

$$p_1 = p_2 = \left((1-\phi)\,p_1 + \phi p_2\right) = -E_0 + TS + \bar{\mu}_1\rho + (\bar{\mu}_2 - \bar{\mu}_1)\,\rho_2 + (\bar{\mu}_2 - \bar{\mu}_1)\,\rho_2 c_2. \qquad (119)$$

This expression is invariant with respect to this transform:

$$\bar{E}_0 = E_0 + (\nu - \lambda)\,\frac{\rho_1\rho_2 c_2^2}{\rho c}\Phi_c T, \quad \bar{S} = S + (\nu - \lambda)\,\frac{\rho_1\rho_2 c_2^2}{\rho c}\Phi_c. \qquad (120)$$

Let us demonstrate that pressure p_1 and pressure p_2 differ from pressure p by the same value. Indeed,

$$p_1 = p - (\bar{\mu}_2 - \bar{\mu}_1)\,\rho_2 c_2 + \mu_r c_1 \rho_c, \quad p_2 = p - (\bar{\mu}_2 - \bar{\mu}_1)\,\rho_2 c_2 + \mu_r c_1 \rho_c. \qquad (121)$$

The difference between p_1 or p_2 and p of the composite system is based on dependence of concentrations c_1, c_2 on phase equilibrium condition or Langmuir equilibrium adsorption curve, while p_1 and p_2 characterize the homogeneous system with arbitrary concentrations of surfactants in it.

Equation (116) represents the first principle of thermodynamics for the composite system. We assume that internal energy and entropy are determined by (120). Only in this case will the first principle of thermodynamics (116) hold true.

Thus, for the medium representing the two-component system with surfactant, densities of internal energy and entropy are not additive functions as per (116). Evidently, when these equations hold true:

$$\mu_1 = \bar{\mu}_1 - \mu_r c_1, \quad \mu_2 = \bar{\mu}_2 - \mu_r c_2, \quad \mu_c = \bar{\mu}_1 + \mu_r\,(1 - c_1) \qquad (122)$$

Eq. (116) becomes (109). Therefore, the first principle of thermodynamics of the two-component system has this form:

$$dE_0 = TdS + \mu d\rho + \left(\mu_2 - \mu_1 + \frac{\varsigma\sigma}{m}\right) d\rho_2 + Zdc, \qquad (123)$$

where chemical potentials are related with chemical potentials of homogenous subsystems as per (122). To identify the link between concentrations c_1, c_2, concentration c, and densities ρ, ρ_2, one should use the following formulas:

$$c_2 = \frac{\rho c}{\rho\theta + \rho_2\,(1-\theta)}, \quad c_1 = \frac{\rho c\,\theta}{\rho\theta + \rho_2\,(1-\theta)}, \qquad (124)$$

$$\mu_1^f = \mu_1^f\,(p, T, c_1)\,, \quad \mu_{1c}^f = \mu_{1c}^f\,(p, T, c_1)\,, \quad \mu_{2c}^f = \mu_{2c}^f\,(p, T, c_2)\,. \qquad (125)$$

The kinetic correction (quadratic with respect to velocities) to the equation of state (123) is calculated based on (11) [18]:

$$E_0 = \left.E_0\right|_{\mathbf{u}-\mathbf{v}=0} + \frac{\rho_s}{2}\,(\mathbf{u} - \mathbf{v})^2\,. \qquad (126)$$

DIFFERENTIAL SCHEME FOR TWO-VELOCITY EQUATIONS

The computational algorithm for numerical analysis of the two-velocity continual hydrodynamic system is based on the method of controlled volume [24, 25]. Discretization of the key equations for this model is performed using a uniform rectangular grid (Fig. 1), where the computational nodes for the vector components of velocities (grids s^1, s^2) are shifted with respect to the computational nodes for other variables of the model (grid s^0).

The scheme used is entirely implicit with respect to time. When approximating convective summands to compute the flows via the faces of control volumes, the HLPA (Hybrid Linear/Parabolic Approximation) scheme of the second order [26] is realized, which satisfied the quantitative accuracy requirement and the convection boundedness criterion (CBC). When approximating diffusive summands, the central difference scheme is used. To compute the pressure field coordinated with the flow field, a scheme similar to the IPSA (Inter-Phase Slip Algorithm) procedure [27] is realized. When approximating the summands determining the forces between interacting phases, an entirely implicit scheme is used. Within the framework of the computational algorithm developed, the continuity equation is not solved explicitly. Its discrete counterpart:

$$\left(\rho^{n+1}_{l,i,j} - \rho^{n}_{r,i,j}\right) \frac{\Delta x \Delta y}{\Delta t} + \left((\rho_l v_x)^{n+1}_{i+1/2,j} - (\rho_l v_x)^{n+1}_{i-1/2,j}\right) \Delta y$$

$$+ \left((\rho_l v_y)^{n+1}_{i,j+1/2} - (\rho_l v_y)^{n+1}_{i,j-1/2}\right) \Delta x = 0 \qquad (127)$$

is used when obtaining discrete counterparts for all other equations and when obtaining the correction equation for pressure.

As a result of this approach and using the selected approximation scheme, the discrete counterpart of the motion equation for the component v_x of the velocity vector of the carrier component takes this form:

$$a_{v,i+1/2,j} v^{n+1}_{x,i+1/2,j} = a_{v,i+3/2,j} v^{n+1}_{x,i+3/2,j} + a_{v,i-1/2,j} v^{n+1}_{x,i-1/2,j}$$

$$+ a_{v,i+1/2,j+1} v^{n+1}_{x,i+1/2,j+1} + a_{v,i+1/2,j-1} v^{n+1}_{x,i+1/2,j-1} + \frac{\rho^{n+1}_{l,i+1/2,j}}{\rho^{n+1}_{i+1/2,j}} \left(P^{n+1}_{i,j} - P^{n+1}_{i+1,j}\right) \Delta y$$

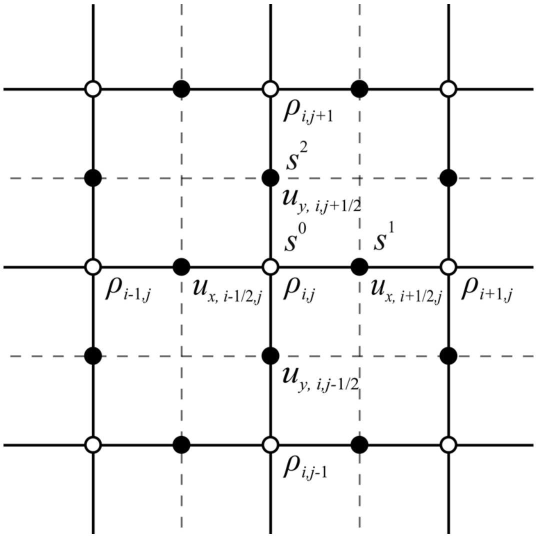

Fig. 1. The computational grid.

$$+\pi r_b^2 J^{n+1}_{i+1/2,j}\frac{\rho^{n+1}_{l,\,i+1/2,j}}{\rho^{n+1}_{i+1/2,j}}\left(\sigma^{n+1}_{i+1,j}-\sigma^{n+1}_{i,j}\right)\Delta y+b_{v,\,i+1/2,j}, \tag{128}$$

$$a_{l,\,i+1/2\pm 1,j}=\left(\rho_l v_x^{\mp}\right)^{n+1}_{i+1/2\pm 1/2,j}\Delta y+\frac{4}{3}\frac{1}{Re_l}\frac{\Delta y}{\Delta x}\eta^{n+1}_{l,\,i+1/2\pm 1/2,j},$$

$$a_{l,\,i+1/2,j\pm 1}=\left(\rho_l v_y^{\mp}\right)^{n+1}_{i+1/2,j\pm 1/2}\Delta x+\frac{1}{Re_l}\frac{\Delta x}{\Delta y}\eta^{n+1}_{l,\,i+1/2,j\pm 1/2},$$

$$a_{l\,,i+1/2,j}=a_l^n+a_{l,\,i+3/2,j}+a_{l,\,i-1/2,j}+a_{l,\,i+1/2,j+1}+a_{l,\,i+1/2,j-1}+b\rho^{n+1}_{l,\,i+1/2,j}\Delta x\Delta y,$$

$$a_l^n=\rho^n_{l,\,i+1/2,j}\frac{\Delta x\Delta y}{\Delta t},$$

$$b_{l,\,i+1/2,j}=a_l^n v^n_{x,\,i+1/2,j}+b\rho^{n+1}_{l,\,i+1/2,j}u^{n+1}_{x,\,i+1/2,j}\Delta x\Delta y+\omega^{n+1}_{l,\,i+1/2,j}+\tau^{n+1}_{l,\,i+1/2,j}.$$

In Eqs. (127), (128), the superscript index denotes the time step number,

$$v^{\mp}_{x,i+1/2\pm 1/2,j}=\max\left(\mp v_{x,\,i+1/2\pm 1/2,j},0\right),\quad v^{\mp}_{y,i+1/2,j\pm 1/2}=\max\left(\mp v_{y,i+1/2,j\pm 1/2},0\right),$$

$\omega^{n+1}_{l,\,i+1/2,j}$ includes nonlinear antidiffusion corrections in accordance with the HLPA scheme, while $\tau^{n+1}_{l,\,i+1/2,j}$ is a result of integrating diffusive summands. Discrete counterparts for all other equations in this model are found in a similar way. We have studied hydrodynamic problems involving different types of boundary condition. For example, for the motion equation at the boundary Γ, we either set pressure $p|_\Gamma = const$, or velocity vectors $\mathbf{u}|_\Gamma = const$, $\mathbf{v}|_\Gamma = const$, or we approximate the infinity $(\partial\mathbf{u}/\partial y)|_\Gamma = 0$, $(\partial\mathbf{v}/\partial y)|_\Gamma = 0$, $(\partial\mathbf{u}/\partial x)|_\Gamma = 0$, $(\partial\mathbf{v}/\partial x)|_\Gamma = 0$. Differential approximation of boundary conditions in both cases is done similarly and is based on the scheme of the second order [28].

To compute the velocity field, which would satisfy the continuity equation and the pressure field coordinated with it, a version of iterative procedure SIMPLE [24] was realized, which is similar to IPSA. When passing to the next time step, the initial assumption regarding an approximate value of the pressure field P^* is made, and the true value is found via correction P':

$$P=P^*+P'. \tag{129}$$

Similarly, corrections for velocity vector components are introduced:

$$v_x=v_x^*+v_x',\quad v_y=v_y^*+v_y',\quad u_x=u_x^*+u_x',\quad u_y=u_y^*+u_y'. \tag{130}$$

Further on, by subtracting the exact and the approximate discrete counterparts for motion equations and eliminating several summands as allowed by the basic version of the SIMPLE procedure, the following corrections are introduced:

$$v'_{x,\,i+1/2,j}=\frac{\Delta y}{a_{l,\,i+1/2,j}}\frac{\rho_{l,\,i+1/2,j}}{\rho_{i+1/2,j}}\left(P'_{i,j}-P'_{i+1,j}\right), \tag{131}$$

$$v'_{y,\,i,j+1/2}=\frac{\Delta x}{a_{l,\,i,j+1/2}}\frac{\rho_{l,\,i,j+1/2}}{\rho_{i,j+1/2}}\left(P'_{i,j}-P'_{i,j+1}\right), \tag{132}$$

$$u'_{x,\,i+1/2,j}=\frac{\Delta y}{a_{s,\,i+1/2,j}}\frac{\rho_{s,\,i+1/2,j}}{\rho_{i+1/2,j}}\left(P'_{i,j}-P'_{i+1,j}\right), \tag{133}$$

$$u'_{y,\,i,j+1/2} = \frac{\Delta x}{a_{s,\,i,j+1/2}} \frac{\rho_{s,\,i,j+1/2}}{\rho_{i,j+1/2}} \left(P'_{i,j} - P'_{i,j+1}\right). \tag{134}$$

A special feature of the IPSA is using a discrete counterpart for the continuity equation, which would be general with respect to the phases, to obtain the pressure correction equation:

$$\left(\rho_{i,j} - \rho^n_{i,j}\right) \frac{\Delta x \Delta y}{\Delta t} + \Big((\rho_s u_x)_{i+1/2,j} - (\rho_s u_x)_{i-1/2,j} \Big) \Delta y + \Big((\rho_l v_x)_{i+1/2,j} - (\rho_l v_x)_{i-1/2,j} \Big) \Delta y$$

$$+ \Big((\rho_s u_y)_{i,j+1/2} - (\rho_s u_y)_{i,j-1/2} \Big) \Delta x + \Big((\rho_l v_y)_{i,j+1/2} - (\rho_l v_y)_{i,j-1/2} \Big) \Delta x = 0. \tag{135}$$

Substituting (130)–(134) in (135), we arrive at the set of equations for computing the pressure field (linear coefficients are not listed here due to being cumbersome and also not informative):

$$A_{i,j} P'_{i,j} = A_{i+1,j} P'_{i+1,j} + A_{i-1,j} P'_{i-1,j} + A_{i,j+1} P'_{i,j+1} + A_{i,j-1} P'_{i,j-1} + B_{i,j}, \tag{136}$$

where $B_{i,j}$ contains residuals of the continuity equations and is a necessary indicator of convergence for the iterative process. The step-by-step application scheme for this procedure is as follows: 1) Initial assumption regarding the approximate pressure field P^*; 2) solving discrete counterparts (128) in order to find the velocity vector components for the approximate field $\left(u^*_x, u^*_y\right)$ and $\left(v^*_x, v^*_y\right)$; 3) finding pressure correction P' by solving correction Eq. (135); 4) computing the new pressure field P from (130); 5) computing the new fields for velocity vector components (u_x, u_y) and (v_x, v_y) via (131)–(134); 6) solving discrete counterparts for other equations of the model; recalculating the density and temperature fields using the equation of state, expressions for surface tension and chemical potential of surfactant; 7) presenting the corrected pressure field P as new P^*, returning to Step 2 and repeating the procedure until the iterative process converges.

To solve numerically the systems of linear algebraic equations for discrete counterparts of core equations and correction equation for pressure, the method of alternating direction and the PARDISO solver parallel to the line are used, the latter realized as part of the mathematical library Intel MKL [29].

COMPUTATION RESULTS: CHARACTERISTICS OF FORCED TWO-PHASE FLOW

Computational domain is set as a rectangular annulus of characteristic dimensions $L_x = 0.5$ m, $L_y = 0.2$ m, limited from above and below by nonmoving horizontal planes. Gravity has components $\mathbf{g} = (0,\, g)$ (see Fig. 2).

Formulation of the problem: On the top and bottom surfaces, there are no orthogonal or vertical velocity components. These planes serve as adiabatic insulation. Between the inlet and outlet boundaries, the pressure drop Δp is set. At the inlet boundary of the computational domain, the Dirichlet conditions for surfactant concentration and temperature of the medium are set. At the outlet boundary of the computational domain, the Neumann conditions for surfactant concentration and temperature of the medium are set. Computations are performed for a dispersed mix of viscous, barely compressible

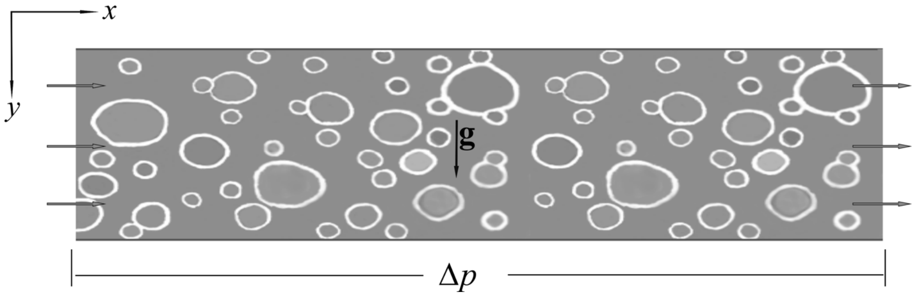

Fig. 2. Computational domain for a flat annulus. The water–oil mix with surfactant is flowing through its sides, left to right.

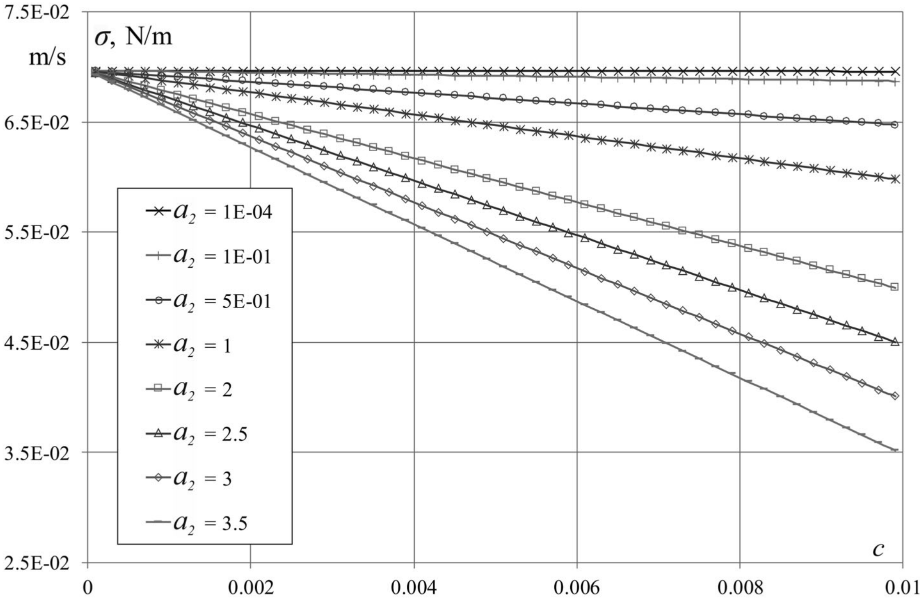

Fig. 3. The linear interval of the curve representing dependence of surface tension on surfactant concentration for different surface activity.

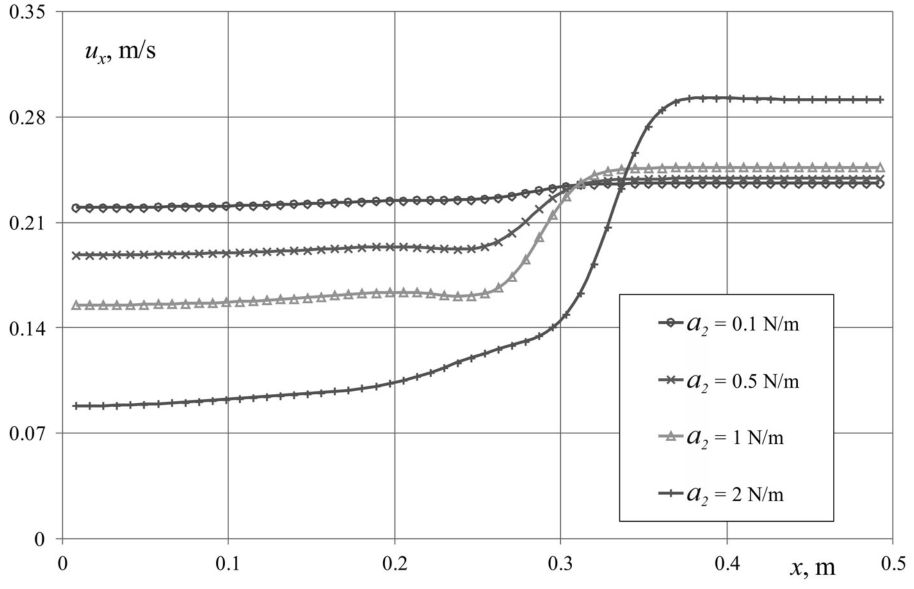

Fig. 4. The velocity profile for oil motion at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

fluids. Physical parameters of the dispersed phase (oil droplets, flow rate $\mathbf{u}$) correspond to the technical data for oils: $\rho_s^f = 880$ kg/m^3, $\alpha_s = 1.2 \cdot 10^{-10}$ Pa^{-1}, $\eta_s = 0.1$ kg/(m s). For the carrier phase (water, flow rate $\mathbf{v}$), physical parameters correspond to the technical data for water: $\rho_l^f = 998$ kg/m^3, $\alpha_l = 4.7 \cdot 10^{-9}$ Pa^{-1}, $\eta_l = 0.001$ kg/(m s). The bulk fraction of water at the initial moment of time is $\phi = 0.5$. Thermodynamic parameters are linked as follows:

$$\delta\rho = \rho\alpha\,\delta p - \rho\beta\,\delta T, \quad \delta s = c_p \delta T/T - \beta\delta p/\rho. \tag{137}$$

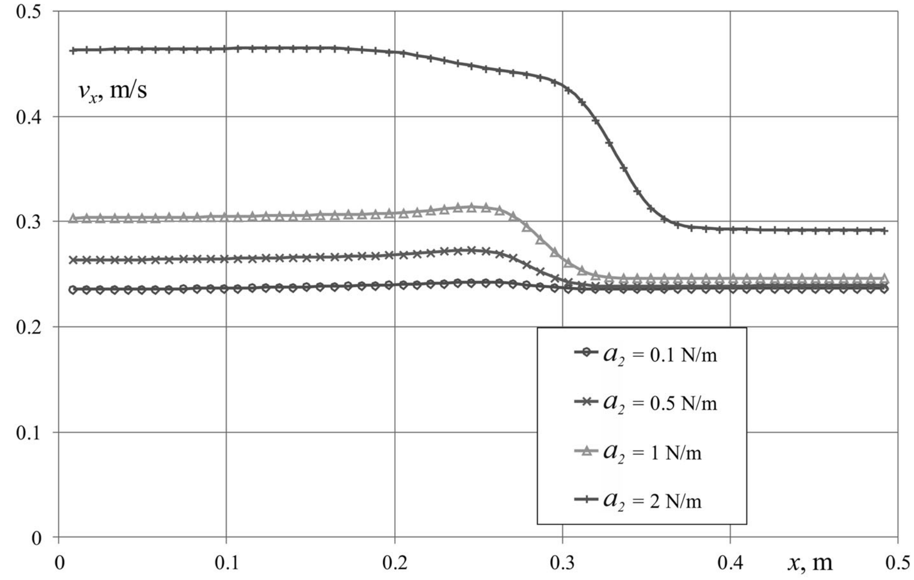

Fig. 5. The velocity profile for water motion at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

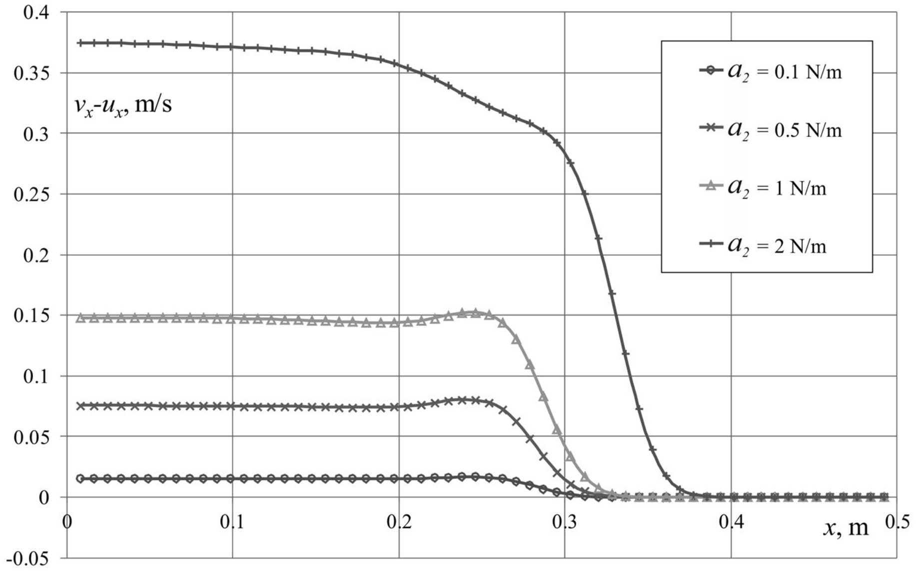

Fig. 6. The velocity profile for water–oil relative motion at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

The chemical potential of surfactant was described with this dependence:

$$\mu_1 = d_1\, P + d_2\, T + R^* T \ln\, c, \tag{138}$$

where $d_1 = 0.1$ m^3/kg, $d_2 = 0.001$ m^2/(K s^2), R^* is the gas constant. Surface tension was found via

$$\sigma = a_1(T_c - T)/(T_c - T_{ref}) - a_2 \ln(1 + a_3 c)\,, \tag{139}$$

where $T_c = 513$ K, $T_{ref} = 293$ K, $a_1 = 7 \cdot 10^{-2}$ N/m, $a_2 = 0.1, 0.5, 1, 2$ N/m, $a_3 = 1$.

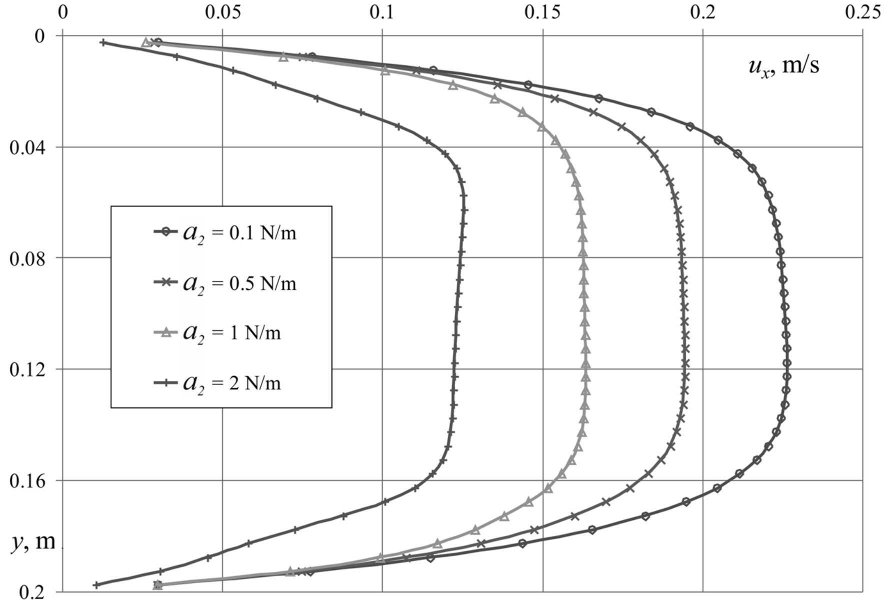

Fig. 7. The velocity profile for oil motion at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

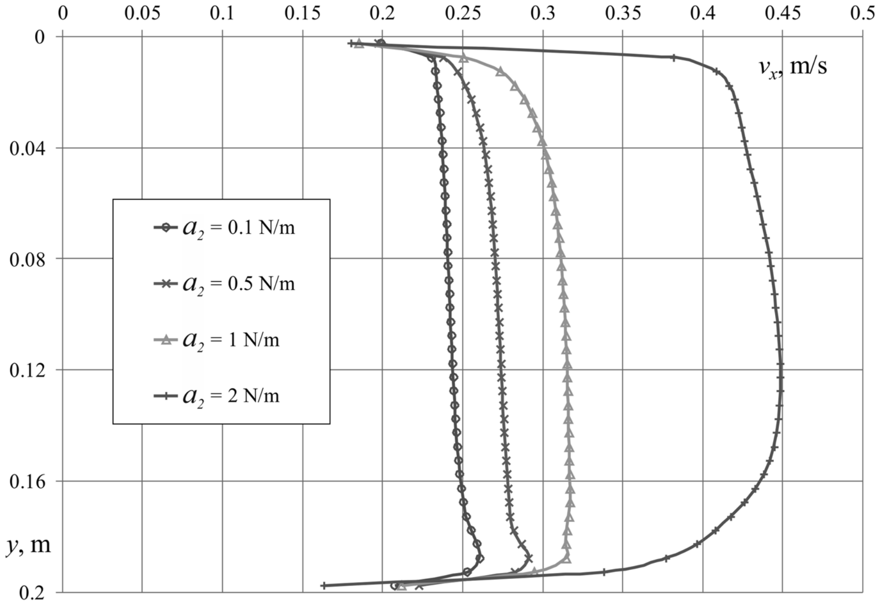

Fig. 8. The velocity profile for water motion at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

In the computations, dissipative parameters were used: $\lambda_1 = 10^{-6}$, $\lambda_2 = 10^{-2}$ kg/(m·s^2). The diffusion coefficient for surfactant in water is set at $D = 2 \cdot 10^{-9}$ m^2/s. Thermal conductivity is typically defined as $\kappa = B_{22}/T$. Because $\chi = \kappa/\rho c_p$, we have $\chi = B_{22}/\rho c_p T$: $\chi = 1.34 \cdot 10^{-7}$ m^2/s. Computations were performed using a 80 × 60 grid with the time step $\Delta t = 10^{-3}$ s. When performing numerical analysis in the full set of equations, we did not take into account: mutual ($\eta_{12} = 0$) and bulk ($\zeta_{12,s,l} = 0$) viscosities of the components, and thermodiffusion ($B_{23} = 0$).

Oil components, which include various compounds, affect physics and chemistry of oil. Of special interest are organic compounds whose presence can be assumed when oil contains oxygen, sulfur, and other elements. The amount of these compounds (naphthenic acids, asphaltenes, and resins) in natural oil is negligible. However, oxygen and sulfur-containing compounds have significant influence on properties of interfaces between layers within the formation, on distribution of fluids and gases in the

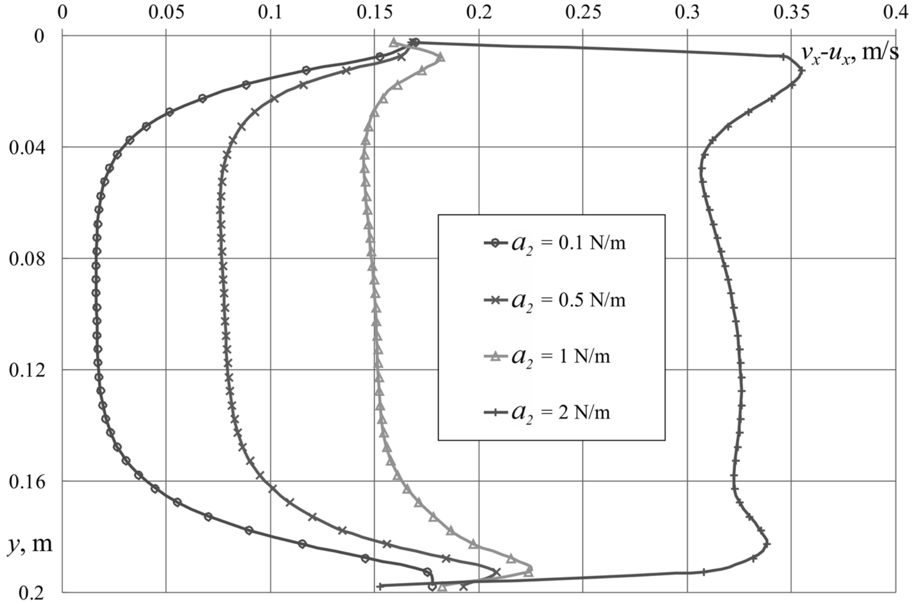

Fig. 9. The velocity profile for water–oil relative motion at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

borehole flow, and motion patterns of components. Sulfur content in oil may reach 6%. Sulfur is present in the free state or as hydrogen sulfide, but more often it may be part of the sulfur compounds or resins. Oxygenated oil components include naphthenic and fatty acids, phenols, ketones, and other compounds. The contents of naphthenic and fatty acids vary from hundredth fractions of percent to 2%. Because oil contains naphthenic and fatty acids, alkalis can be used to increase oil recovery. Later, these compounds enter the borehole shaft and affect subsequent dynamics of the multiphase mix. Interaction between alkalis and oil acid yields water-soluble surfactants, which decrease surface tension at the interface between oil and water. Macromolecular oil compounds containing nitrogen, sulfur, oxygen, and metals are resins and asphaltenes. Their special feature is the ability to adsorb on the phase surface and affect fluid and gas motion when the water–oil system travels along pipes. For this reason, it is essential to analyze the impact surfactants have on dynamics of the mixture.

Below, it is assumed that dependence of surface tension on surfactant concentration is (139). As we consider only the linear interval of the curve, we can set $a_1 = 1$ without violating the generality of discussion (Fig. 3).

The parameter a_2 characterizes the derivative of surface tension as a function of surfactant concentration and determines its surface activity. Surface tension at the interface between water and oil is between 50 mJ/m^2 and 10 mJ/m^2. These boundaries are, obviously, tentative because solvable surfactants are always present in natural oil at different concentrations. The parameter a_2 for specialized surfactants may be 100 mJ/m^2 and up, and can reach tens of thousands. As we had in mind natural surfactants, we intentionally set very low a_2 when studying surfactant's role in the two-phase flow. The results obtained are likely the estimates of the lower limit of this effect. There are no exact data reported for dependence $\sigma(c, T)$ for surfactants like resins and asphaltenes, which contain sulfur and oxygen. Also, there are no such data for soluble paraffins, silica gels, and other natural surfactants found in water–oil mixtures. Information of this kind is kept as a trade secret.

A strong impact of a_2 on the motion of water and oil motion is due to low flow rates. As one can see from dynamic equations (106), (107):

$$\rho_s \frac{\partial \mathbf{u}}{\partial t} + \rho_s (\mathbf{u}, \nabla)\, \mathbf{u} = -\frac{\rho_s}{\rho} \nabla p - \rho_l \varsigma \frac{J}{\rho} \nabla \sigma + \ldots, \tag{140}$$

$$\rho_l \frac{\partial \mathbf{v}}{\partial t} + \rho_l (\mathbf{v}, \nabla)\, \mathbf{v} = -\frac{\rho_l}{\rho} \nabla p + \rho_l \varsigma \frac{J}{\rho} \nabla \sigma + \ldots, \tag{141}$$

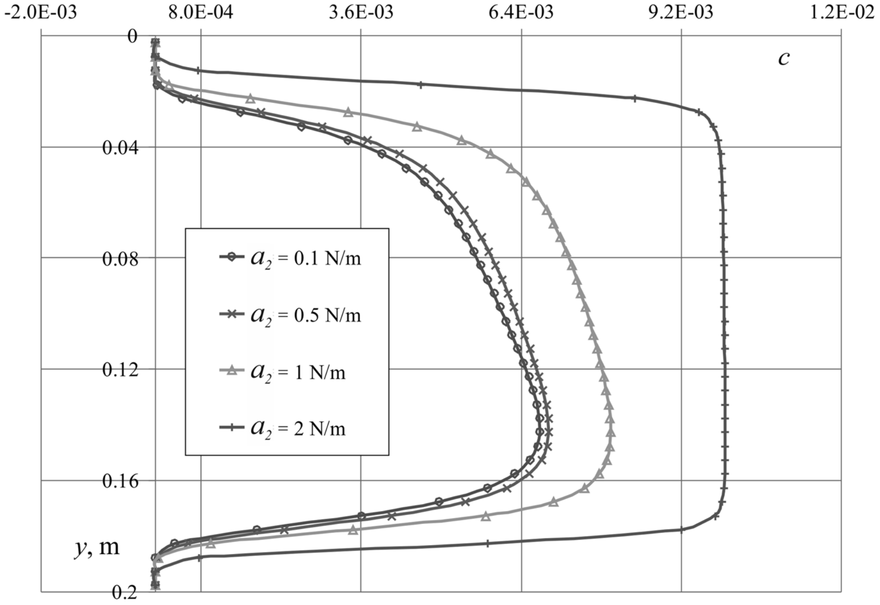

Fig. 10. The velocity profile for surfactant distribution at $\Delta p = 50$ Pa and different surface activity for the moment of time $t = 2.2$ s.

it is the pressure gradient $\nabla p \leq 0$ and surface tension gradient $\nabla \sigma \geq 0$ that act as the moving forces in the system. These two forces accelerate water and decelerate oil. Below, Figs. 4–6 demonstrate longitudinal profiles for corresponding velocities where the pressure drop $\Delta p = 50$ Pa is applied to the system. The profiles cross the center of the flat cannel. The bends on the curve are due to the bends on the spatial distribution curve for the surfactant concentration.

When surface activity is low and varies within the neighborhood of 0.1–2.0 H/m, one can observe a strong influence on velocities of components (oil and water) and on their difference; see the figure showing the changes in velocity to the left from the front. The greatest impact on the dynamic process is observed when surface activity reaches $a_2 = 2$.

Figures 7–9 show cross-section profiles for corresponding velocities at $\Delta p = 50$ Pa. The profiles cross the center of the computational domain.

The profiles are shown for the moment of time $t = 2.2$ s for the cross section going through the center of the computational domain. When surface activity changes from 0.1 N/m to 2.0 N/m, oil velocity drops by almost half while water velocity almost doubles. Of special interest are cross-section profiles of surfactant distribution shown in Fig. 10. The profile crosses the center of the computational domain.

CONCLUSIONS

Thus, with the two-component model whose carrier component contains dissolved surfactant, we were able to demonstrate the impact of surfactant on fluid dynamics. The surfactant accelerates the carrier component and considerably decelerates the motion of the oil droplets continuum in the nonstationary fluid flow. This fact requires considerable adjustments to phase flow rates computed taking into account hydrodynamics of multiphase flows. If we do not take into account the above, significant errors will be introduced to measurements of the mass phase ratios via the cross section of the pipe.

The hydrodynamic analysis of the system is based on the physical two-velocity model of the medium whose equations were obtained exclusively from the conditions of satisfying the conservation laws and the first principle of thermodynamics for the two-velocity system.

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