Figure 1 shows the function $\varphi(Fo)$ obtained by numerical solution of the heat conduction equation (2) with the boundary and initial conditions (3). The numerical solution was obtained on a uniform grid with step $\Delta x = 0.01$ by means of an implicit difference scheme. The integral in Eq. (10) was calculated by the trapezium method.

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HYDRODYNAMICS OF FILMS OF SURFACE-ACTIVE SUBSTANCES

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UDC 532.5

Investigation of the motion of films of surface-active substances, which change the surface tension at an interface of two liquids or a liquid and a gas, is of great interest for chemical technology [1], and also in many biological processes [2]. These substances affect the motion of liquids by changing the boundary conditions on the interfaces, the moving film of surface-active substance setting in motion the adjoining layer of liquid [1-3].

The experiments of [1] show that sufficiently concentrated films of surface-active substances do not have a homogeneous structure but consist of aggregates of condensed molecules. The regions of two-dimensional condensation are analogous to ordinary three-dimensional drops in multiphase mixture, i.e., they are two-dimensional drops. These two-dimensional drops exchange molecules with both the ambient film of the surface-active substance as well as with the adjoining liquid. Thus, films of surface-active substances should be regarded as multiphase films.

Single-component and multicomponent single-phase films of surface-active substances were investigated in [4-12]. Various models of multicomponent single-phase films were considered by Gogosov and Chyong Za Bin.* The hydrodynamics of three-dimensional multiphase mixtures was considered in [13-15].

In the present paper, we derive equations describing the motion of a film of surfaceactive substance at the interface of two three-dimensional phases. The film is assumed to consist of m two-dimensional phases and n components that react chemically with one another. The three-dimensional phases are assumed to be single phases and consist of n components, which can be adsorbed and desorbed at the interface. The interface exchanges matter, momentum, and energy with the three-dimensional phases and is thus an open system. Using the methods of the thermodynamics of nonequilibrium processes, we obtain expressions for the two-dimensional stress tensors of all phases the diffusion fluxes of the surface-active substance in the two-dimensional phases, the heat fluxes within the phases and the heat transfer between the phases, the rates of the surface chemical reactions and the two-dimensional phase on the interface, the rates of adsorption and desorption of molecules from the three-dimensional solutions on the surface, the heat fluxes from the volume to the surface, the frictional forces of the two-dimensional

 * V. V. Gogosov and Chyong Za Bin, Paper Presented at L. I. Sedov's Seminar.

Saransk. Translated from Izvestiya Akademii Nauk SSSR, Mekhanika Zhidkosti i Gaza, No. 4, pp. 150-157, July-August, 1982. Original article submitted November 24, 1980. phases with the adjoining liquids, and also the frictional forces between the two-dimensional phases. The surface variables are defined as in [9], and not as excess variables in Gibbs's method [1].

We write the equation of the interface in the form

$$x^r = x^r (u^{\alpha}, t); r = 1, 2, 3; \alpha = 1, 2$$

where x^r are curvilinear coordinates used to consider the motion of the three-dimensional phases and the interface, and u^{α} are two-dimensional coordinates on the interface. We choose the coordinates u^{α} in such a way as to satisfy the equation [9]

 $\partial x^r / \partial t = u_n n^r$

Here, u_n is the velocity of the surface in the normal direction, and n^r is the unit normal to the surface oriented in such a way that the vectors $e_1 = \partial r / \partial u^i$, $e_2 = \partial r / \partial u^2$, n form a right-handed triplet, r being the radius vector. In Eq. (1) and what follows, all the partial derivatives with respect to the time of the surface variables are taken for fixed coordinates u^{α} .

The velocity of the particles of the surface-active substance on the interface relative to the system of coordinates x^r can be written in the form [9]

 $v_s^r = v_{ns}n^r + v_s^{\alpha}x_{\alpha}^r, \quad x_{\alpha}^r = \partial x^r / \partial u^{\alpha}, \quad v_{ns} = v_s^r n_r$

Here and in what follows, summation over repeated Greek and Latin indices is understood. We shall use the index s to distinguish the surface variables from the corresponding volume variables. The general balance equation for the two-dimensional density of some surface variable ψ_s has the form [9]

$$\frac{\partial \psi_s}{\partial t} = -\nabla_\alpha (\psi_s v_s^\alpha + Q_s^\alpha) + 2Ku_n \psi_s - \{\psi(v_n - u_n)\} - \{Q^r n_r\} + F_s + f_s \quad K = \frac{1}{2} a^{\alpha\beta} b_{\alpha\beta}$$
(3)

Here, ∇_{α} is the covariant derivative, K is the mean curvature of the surface, $a^{\alpha\beta}$ and $b_{\alpha\beta}$ are the first (fundamental) and second tensors of the surface, respectively, [16], Q_s^{α} is the surface flux density vector of ψ_s , Q^r is the three-dimensional flux density vector of ψ , \mathbf{F}_s is the source of ψ_s due to the external surface influences, \mathbf{f}_s is the production of ψ_s on the surface, \mathbf{v}_n is the normal component of the velocity of convective transport of ψ in the volume, $\{A\} = A_2 - A_1$ is the discontinuity of a three-dimensional variable at the interface (we denote the variables referring to the volume phase for which the normal n to the interface is exterior and interior by the indices 1 and 2, respectively), and, finally, the variables without index s represent the three-dimensional phases.

We write the continuity equation for component k in the i-th two-dimensional phase, the momentum equation for the i-th two-dimensional phase, and the equation representing the variation of the total energy of the i-th two-dimensional phase in the form

$$\frac{\partial \rho_{\epsilon i k}}{\partial t} = -\nabla_{\alpha} (\rho_{\epsilon i k} v_{\epsilon i k}) + 2K \rho_{\epsilon i k} v_{n \epsilon i} - \epsilon_{\epsilon i} \{\rho_{k} (v_{n} - v_{n \epsilon i})\} - \epsilon_{\epsilon i} \{\rho_{k} (v_{k n} - v_{n})\} + \varkappa_{\epsilon i k} + \sum_{j=1}^{m} (m_{\epsilon(j i)}^{k} - m_{\epsilon(i j)}^{k}))$$

$$\frac{\partial \rho_{\epsilon i} v_{\epsilon i}^{r}}{\partial t} = -\nabla_{\beta} (\rho_{\epsilon i} v_{\epsilon i}^{r} v_{\epsilon i}^{\beta} - \varkappa_{\alpha}^{r} \Pi_{i}^{\alpha \beta}) + 2K \rho_{\epsilon i} v_{\epsilon i}^{r} v_{n \epsilon i} + \epsilon_{\epsilon i} \{t_{n i}^{r}\} - \epsilon_{\epsilon i} \{\rho v^{r} (v_{n} - v_{n \epsilon i})\} + \sum_{j=1}^{m} R_{\epsilon(j i)}^{r} + \sum_{j=1}^{m} (m_{\epsilon(j i)} v_{\epsilon(j i)}^{r} - m_{\epsilon(i j)} v_{\epsilon(i j)}^{r}))$$

$$\frac{\partial}{\partial t} \rho_{\epsilon i} \left(U_{\epsilon i} + \frac{v_{\epsilon i}^{2}}{2} \right) = -\nabla_{\beta} \left[\rho_{\epsilon i} v_{\epsilon i}^{\beta} \left(U_{\epsilon i} + \frac{v_{\epsilon i}^{2}}{2} \right) - \Pi_{i}^{\alpha \beta} v_{\epsilon i \alpha} + q_{\epsilon i}^{\beta} \right] + 2K \rho_{\epsilon i} v_{n \epsilon i} \left(U_{\epsilon i} + \frac{v_{\epsilon i}^{2}}{2} \right) + \epsilon_{\epsilon i} \{t_{n i}^{r} v_{r}\} - \epsilon_{\epsilon i} \left\{ \rho (v_{n} - v_{n \epsilon i}) \left(U + \frac{v^{2}}{2} \right) \right\} - \epsilon_{\epsilon i} \{q_{n}\} + \sum_{j=1}^{m} w_{\epsilon(j i)} + \sum_{j=1}^{m} m_{\epsilon(j i)} \left(U_{\epsilon(j i)} + \frac{v_{\epsilon(j i)}^{2}}{2} \right) - \sum_{j=1}^{m} m_{\epsilon(i j)} \left(U_{\epsilon(i j)} + \frac{v_{\epsilon(i j)}^{2}}{2} \right)$$

$$(6)$$

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(1)

(2)

$$\sum_{k=1}^{n} x_{sik} = 0, \qquad \sum_{i=1}^{m} \sum_{j=1}^{m} (m_{s(ji)}^{k} - m_{s(ij)}^{k}) = 0$$

$$\sum_{i=1}^{m} \sum_{j=1}^{m} (R_{s(ji)}^{r} + m_{s(ji)}v_{s(ji)}^{r} - m_{s(ij)}v_{s(ij)}^{r}) = 0$$

$$\sum_{i=1}^{m} \sum_{j=1}^{m} \left[q_{s(ji)} + w_{s(ji)} + m_{s(ji)} \left(U_{s(ji)} + \frac{v_{s(ji)}^{2}}{2} \right) - m_{s(ij)} \left(U_{s(ij)} + \frac{v_{s(ij)}^{2}}{2} \right) \right] = 0, \qquad \sum_{j=1}^{m} R_{s(ji)} = -\alpha_{i}\nabla_{s}\varepsilon_{si} + \sum_{j=1}^{m} F_{s(ji)}$$

$$m_{s(ji)} = \sum_{k=1}^{n} m_{s(ji)}^{k}, \qquad m_{s(ij)} = \sum_{k=1}^{n} m_{s(ij)}^{k}, \qquad \sum_{i=1}^{m} \varepsilon_{si} = 1, \qquad v_{si}r = \frac{1}{\rho_{si}}\sum_{k=1}^{n} \rho_{sik}v_{sik}^{r}$$

$$\rho_{sik} = \varepsilon_{si}\rho_{sik}, \qquad \rho_{si} = \varepsilon_{si}\rho_{si}^{\circ}, \qquad \rho_{si}^{\circ} = \sum_{k=1}^{n} \rho_{sik}^{\circ}, \qquad \rho_{s} = \sum_{i=1}^{m} \rho_{si}$$

Here, ρ_{sik}° is the true density of component k in phase i, ρ_{sik} is the mean density of component k in phase i, ρ_{si}° and ρ_{si} are, respectively, the true density and mean density of phase i, ρ_s is the density of the surface mixture (the surface density is defined as the mass of the substance per unit area), $\epsilon_{\rm Si}$ is the fraction of the surface occupied by phase i, v_{sik} is the velocity of component k in phase i, v_{si} is the mass-average velocity of the i-th two-dimensional phase, vkn is the normal component of the velocity of the k-th three-dimensional component, \varkappa_{sik} is the rate of production of component k in phase i per unit time on unit area due to the surface chemical reactions, $m_{s(ji)}^{k}$ is the rate of production of component k in phase i due to the phase transition $j \rightarrow i$, $m_{s(ij)}^{k}$ is the rate of transition of component k from the i-th to the j-th phase $(m_{s(ij)}^{k})$ and $m_{s(ji)}^{k}$ are introduced in the same way as the corresponding quantities in three-dimensional hydrodynamics [15], t_{ni} is the stress on the surface of the i-th two-dimensional phase exerted by the three-dimensional phase, $\Pi_i^{lphaeta} = \epsilon_{si}(\alpha_i a^{lphaeta} + \pi_i {}^{lphaeta})$ is the partial transfer of the internal stresses in phase i, α_i is the coefficient of surface tension of phase i, $\epsilon_{si}\pi_i^{\alpha\beta}$ is the nonequilibrium (viscous) part of the stress tensor of phase i, $R_{s(ii)}$ is the force with which phase j acts on phase i per unit area, $F_{s(ji)}$ is the nonequilibrium part of the force of interaction of the phases, $v_{s(ji)}$ is the velocity of the matter in the phase transition $j \rightarrow i$, U_{si} is the internal energy of unit mass of the i-th two-dimensional phase, $v_{si}^2/2$ is the kinetic energy of unit mass of phase i, q_n is the density of the heat flux from the volume to the surface, q_{si}^{α} is the vector of the heat flux density in phase i, $q_{s(ji)}$ is the heat transfer between phases j and i, $U_{s(ji)}$ is the internal energy of the substance making the phase transition $j \rightarrow i$, $w_{s(ji)}$ is the transition of energy from phase j to phase i due to the work of the interaction force $R_{s(ii)}$, and $\nabla_{\mathbf{s}} = \mathbf{e} \, \alpha \nabla_{\alpha}$.

The terms in the curly brackets in Eqs. (4)-(6) characterize the exchange of matter, momentum, and energy between the interface and the three-dimensional phases; the terms containing the curvature of the surface are associated with the influence of its shape on the variation of the surface variables. The factors ε_{si} in front of the curly brackets indicate that the exchange of mass, momentum, and energy between the i-th surface phase and the volume does not take place on the entire interface but on the fraction ε_{si} of it occupied by phase i. Equations (7) are a consequence of the conservation laws for mass, momentum, and energy in the chemical reactions, the phase transition, and the energy transfer between the surface phases.

Introducing the vector $J_{sik}^{\alpha} = \rho_{sik} (v_{sik}^{\alpha} - v_{si}^{\alpha})$ of the diffusion flux density of component k relative to phase i, we can write the continuity equation (4) as

$$\frac{\partial \rho_{sik}}{\partial t} = -\nabla_{\alpha}(\rho_{sik}v_{si}^{\alpha}) - \nabla_{\alpha}I_{sik}^{\alpha} + 2K\rho_{sik}v_{nsi} - \varepsilon_{si}\{\rho_{k}(v_{n} - v_{nsi})\} - \varepsilon_{si}\{\rho_{k}(v_{kn} - v_{n})\} + \varkappa_{sik} + \sum_{i=1}^{m} (m_{s(ij)}^{k} - m_{s(ij)}^{k})$$
(8)

Summing Eqs. (8) over k, we obtain the continuity equation for phase i:

$$\frac{\partial \rho_{si}}{\partial t} = -\nabla_{\alpha} (\rho_{si} v_{si}^{\alpha}) + 2K \rho_{si} v_{nsi} - \varepsilon_{si} \{\rho (v_n - v_{nsi})\} + \sum_{j=1}^{m} (m_{s(ji)} - m_{s(ij)})$$
(9)

Comparing Eqs. (5), (6), and (8) with Eq. (3), we can establish the form of the

functions Q_s^{α} , F_s , and f_s .

The particularization of the form of the functions Q_S^{α} , F_s , and f_s is the assumption made when a model of the film of surface-active substance is constructed.

From Eqs. (5) and (9) we obtain an equation for the variation of the kinetic energy of phase i:

$$\frac{\partial}{\partial t} \frac{\rho_{si} v_{si}^{2}}{2} = -\nabla_{\alpha} \left(\frac{1}{2} \rho_{si} v_{si}^{\alpha} v_{si}^{2} \right) + K \rho_{si} v_{si}^{2} v_{nsi} + \frac{1}{2} \varepsilon_{si} v_{si}^{2} \{\rho (v_{n} - v_{nsi})\} - \frac{1}{2} v_{si}^{2} \sum_{j=1}^{m} (m_{s(ji)} - m_{s(ij)}) + \varepsilon_{si} v_{si}^{r} \{t_{rni}\} - \varepsilon_{si} v_{si}^{r} \{\rho v_{r} (v_{n} - v_{nsi})\} + v_{si\alpha} \nabla_{\beta} \prod_{i}^{\alpha\beta} + \prod_{i}^{\alpha\beta} b_{\alpha\beta} v_{nsi} + \sum_{j=1}^{m} v_{si}^{r} R_{rs(ji)} + v_{rsi} \left(\sum_{j=1}^{m} m_{s(ji)} v_{s(ji)}^{r} - \sum_{j=1}^{m} m_{s(ij)} v_{s(ij)}^{r} \right)$$

$$(10)$$

Subtracting Eq. (10) from Eq. (6), we find the equation for the heat supply for phase i:

$$\frac{\partial}{\partial t} \rho_{si} U_{si} = -\nabla_{\beta} (\rho_{si} U_{si} v_{si}^{\alpha}) + 2K \rho_{si} U_{si} v_{nsi} + \varepsilon_{si} \{t_{rni} (v^{r} - v_{si}^{r})\} - \varepsilon_{si} \{\rho_{si} U_{si} v_{si}^{\alpha} + 2K \rho_{si} U_{si} v_{nsi} + \varepsilon_{si} \{t_{rni} (v^{r} - v_{si}^{r})\} - \varepsilon_{si} \{q_{n}\} + \Pi_{i}^{\alpha\beta} \nabla_{\alpha} v_{si\beta} - \nabla_{\alpha} q_{si}^{\alpha} + \sum_{j=1}^{m} q_{s(ji)} + \sum_{j=1}^{m} (w_{s(ji)} - v_{rsi} R_{s(ji)}^{r}) - \Pi_{i}^{\alpha\beta} b_{\alpha\beta} v_{nsi} + \sum_{j=1}^{m} m_{s(ji)} \left[\frac{(v_{s(ji)} - v_{si})^{2}}{2} + U_{s(ji)} \right] - \sum_{j=1}^{m} m_{s(ij)} \left[\frac{(v_{s(ij)} - v_{si})^{2}}{2} + U_{s(ij)} \right]$$

$$(11)$$

We now particularize the model of the film by making the assumption $w_{s(ji)} = R_{s(ji)}^{r} v_{rsi}$.

Assuming that each two-dimensional phase is locally in equilibrium, and that the internal energy U_{si} of phase i depends on the entropy S_{si} of unit mass of phase i, the surface mass concentration $c_{sik} = \rho_{sik}/\rho_{si}$, and the true density ρ_{si}° of phase i and does not depend explicitly on the shape of the surface, the two-dimensional deformations, etc., we postulate the Gibbs identity for phase i in the form

$$dU_{si} = T_{si} \, dS_{si} + \sum_{h=1}^{n} \xi_{sih} \, dc_{sih} + \alpha_i d \, \frac{1}{\rho_{si}^{\circ}} \tag{12}$$

Here, T_{si} is the temperature of phase i, and ξ_{sik} is the chemical potential of unit mass of component k in phase i. All the two-dimensional phases are assumed to be compressible.

The Gibbs identity (12) can also be written in the form

$$d\rho_{si} U_{si} = T_{si} d\rho_{si} S_{si} + \sum_{k=1}^{n} \xi_{sik} d\rho_{sik} + \alpha_i d\varepsilon_{si}$$
(13)

We define the entropy S_S of unit mass of the surface mixture as follows:

$$\rho_s S_s = \sum_{i=1}^m \rho_{si} S_{si} \tag{14}$$

Using the continuity and heat supply equations, we obtain from Eqs. (13) and (14)

$$\frac{\partial}{\partial t} \rho_{s} S_{s} = -\nabla_{\alpha} \left[\sum_{i=1}^{m} \left(\rho_{si} S_{si} v_{si}^{\alpha} + \frac{q_{i}^{\alpha}}{T_{si}} \right) - \sum_{i=1}^{m} \sum_{k=1}^{n} \frac{\xi_{sik} I_{sik}^{\alpha}}{T_{si}} \right] - \sum_{i=1}^{m} \left\{ \varepsilon_{si} J_{ni} S \right\} + 2K \sum_{i=1}^{m} v_{nsi} \rho_{si} S_{si} - \sum_{i=1}^{m} \frac{\alpha_{i}}{T_{si}} \frac{d_{i} \varepsilon_{si}}{dt} - \sum_{i=1}^{m} \left\{ \left(\frac{1}{T_{si}} - \frac{1}{T} \right) \left[\varepsilon_{si} \left(q_{n} + w J_{ni} \right) \right] \right\} + \sum_{i=1}^{m} \left\{ \varepsilon_{si} \tau_{ni} \frac{\mathbf{v} - \mathbf{v}_{si}}{T_{si}} \right\} - \left\{ \frac{1}{T} \left(q_{n} - \sum_{k=1}^{n} I_{kn} \xi_{k} \right) \right\} +$$

$$\sum_{i=1}^{m} \sum_{k=1}^{n} \left\{ \varepsilon_{\epsilon i} J_{ikn} \left[\frac{\xi_{\epsilon ik}}{T_{\epsilon i}} - \frac{\xi_{k}}{T} - \frac{(\mathbf{v} - \mathbf{v}_{\epsilon i})^{2}}{2T_{\epsilon i}} \right] \right\} + \sum_{i=1}^{m} \varepsilon_{\epsilon i} \pi_{i}^{*\alpha\beta} \frac{E_{i\alpha\beta}^{*}}{T_{\epsilon i}} + \sum_{i=1}^{m} \varepsilon_{\epsilon i} \pi_{i}^{\alpha} \nabla_{\alpha} \frac{1}{T_{\epsilon i}} - \sum_{i=1}^{m} \sum_{k=1}^{n-1} J_{\epsilon ik}^{\alpha} \nabla_{\alpha} \frac{\xi_{\epsilon ik} - \xi_{\epsilon mn}}{T_{\epsilon i}} + \sum_{i=1}^{m-1} \sum_{j=1}^{m} q_{\epsilon(ji)} \left(\frac{1}{T_{\epsilon i}} - \frac{1}{T_{\epsilon m}} \right) - \sum_{i=1}^{m-1} \sum_{j=1}^{m} R_{s(ji)} \frac{\mathbf{v}_{\epsilon i} - \mathbf{v}_{\epsilon m}}{T_{\epsilon m}} - \sum_{i=1}^{m} \sum_{k=1}^{n-1} J_{\epsilon ik}^{\alpha} \nabla_{\alpha} \frac{\xi_{\epsilon ik} - \xi_{\epsilon mn}}{T_{\epsilon i}} + \sum_{i=1}^{m} \sum_{j=1}^{m} m q_{\epsilon(ji)} \left(\frac{1}{T_{\epsilon i}} - \frac{1}{T_{\epsilon m}} \right) - \sum_{i=1}^{m-1} \sum_{j=1}^{m} R_{s(ji)} \frac{\mathbf{v}_{\epsilon i} - \mathbf{v}_{\epsilon m}}{T_{\epsilon m}} - \sum_{i=1}^{m} \sum_{k=1}^{n-1} \frac{\xi_{\epsilon ik} - \xi_{\epsilon in}}{T_{\epsilon i}} \chi_{aik} + \sum_{i=1}^{m-1} \sum_{j=1}^{m} \sum_{k=1}^{n} (m_{s(ji)}^{k} \chi_{\epsilon(ji)}^{k} - m_{\epsilon(ij)}^{k} \chi_{\epsilon(ij)}^{k}) - \sum_{i=1}^{k} R_{s(ji)} \frac{\mathbf{v}_{\epsilon i} - \mathbf{v}_{\epsilon m}}{T_{\epsilon m}} - \sum_{i=1}^{m} \sum_{k=1}^{n-1} \frac{\xi_{\epsilon(ik} - \xi_{\epsilon in}}{T_{\epsilon i}} \chi_{aik} + \sum_{i=1}^{m-1} \sum_{j=1}^{m} \sum_{k=1}^{n} (m_{s(ji)}^{k} \chi_{\epsilon(ji)}^{k} - m_{\epsilon(ij)}^{k} \chi_{\epsilon(ij)}^{k}) - \sum_{i=1}^{n} \xi_{\epsilon(ik} - \xi_{\epsilon mk}} \chi_{\epsilon(ij)} - \frac{(\mathbf{v}_{\epsilon(ji)} - \mathbf{v}_{\epsilon i})^{2}}{2T_{\epsilon i}} - \frac{(\mathbf{v}_{\epsilon(ji)} - \mathbf{v}_{\epsilon m})^{2}}{2T_{\epsilon m}} + \frac{U_{\epsilon(ji)}}{T_{\epsilon i}} - \frac{U_{\epsilon(ji)}}{T_{\epsilon m}} - \frac{\xi_{\epsilon ik}}{T_{\epsilon i}} + \frac{\xi_{\epsilon mk}}{T_{\epsilon m}}$$
(15)

 $J_{ikn} = \rho_k (v_{kn} - v_{nsi}), \quad J_{ni} = \rho (v_n - v_{nsi}), \quad J_{kn} = \rho_k (v_{kn} - v_n), \quad d_i \varepsilon_{si} / dt = \partial \varepsilon_{si} / dt + v_{si}^{\alpha} \nabla_{\alpha} \varepsilon_{si}, \quad w = U + p / \rho$ $\tau_{ni} = t_{ni} + p \mathbf{n}, \quad e_{si\alpha\beta} = \frac{1}{2} (\nabla_{\alpha} v_{si\beta} + \nabla_{\beta} v_{si\alpha}), \quad E_{i\alpha\beta} = e_{si\alpha\beta} - b_{\alpha\beta} v_{nsi}, \quad E_i = E_{i\alpha\beta} a^{\alpha\beta}$ $E_{i\alpha\beta}^* = E_{i\alpha\beta} - \frac{1}{2} E_{i\alpha\beta}, \quad \pi_i = \frac{1}{2} \pi_i^{\alpha\beta} a_{\alpha\beta}, \quad \pi_i^{*\alpha\beta} = \pi_i^{\alpha\beta} - \pi_i a^{\alpha\beta}$

Here, w is the enthalpy of the three-dimensional phases, τ_{ni} is the viscous stress on the surface of phase i, and $X_{s(ij)}^{k}$ are obtained from $X_{s(ji)}^{k}$ by replacing $v_{s(ji)}$ and $U_{s(jj)}$, respectively.

In deriving Eq. (15), we have used the relation

$$\sum_{k=1}^{n} \rho_{sik} \, d\xi_{sik} = -\rho_{si} S_{si} \, dT_{si} - \varepsilon_{si} \, d\alpha_i$$

which is the surface analog of the usual Gibbs-Duhem equation [17].

We define the entropy production $\sigma_{\mathbf{S}}$ on the interface as follows:

$$\sigma_{s} = \sum_{i=1}^{m} \varepsilon_{si} \pi_{i} \frac{E_{i}}{T_{si}} + \sum_{i=1}^{m} \varepsilon_{si} \pi_{i} \frac{E_{i}^{*} \alpha_{\beta}}{T_{si}} \frac{E_{i\alpha\beta}^{*}}{T_{si}} + \sum_{i=1}^{m} q_{si}^{\alpha} \nabla_{\alpha} \frac{1}{T_{si}} - \sum_{i=1}^{n} \frac{1}{T_{si}} \sum_{i=1}^{m} \frac{1}{T_{si}} \frac{1}{T_{si}} \frac{1}{T_{si}} \sum_{i=1}^{m-1} \frac{1}{T_{si}} \sum_{i=1}^{m-1}$$

 $\mathbf{\tau}_{ni} = \mathbf{n} \mathbf{\tau}_{nni} + \mathbf{\tau}_{n\tau i}, \quad \mathbf{v} = \mathbf{n} \boldsymbol{v}_n + \mathbf{v}_{\tau}, \quad \mathbf{v}_{si} = \mathbf{n} \boldsymbol{v}_{sni} + \mathbf{v}_{\tau si}, \quad \mathbf{F}_{s(ji)} = \mathbf{n} \boldsymbol{F}_{ns(ji)} + \mathbf{e}^{\alpha} \boldsymbol{F}_{\alpha s(ji)}$

We shall attribute the remaining terms on the right-hand side of Eq. (15) to the reversible flow of entropy to the interface.

The expression (16) for the entropy production is a sum of binary products of thermodynamic fluxes and the conjugate thermodynamic forces.

The transport coefficients L_{ij} in the linear expressions for the thermodynamic fluxes are related through the forces by the Onsager-Casimir reciprocity relations [18]

 $L_{ij} = e_i e_j L_{ji}$

where e_i , $e_j = 1$ if the thermodynamic forces with the numbers i and j belong to type α (i.e., are even functions of the velocities of the microscopic particles), and e_i , $e_j = -1$ if the forces are of type β (i.e., they are odd functions of the velocities).

Because they are cumbersome, we do not here give the linear expressions for fluxes in terms of the forces. Below, we list (write out) the thermodynamic fluxes and forces.

The surface thermodynamic fluxes are

(16)

$$e_{si}\pi_{i}, \quad d_{m}\varepsilon_{si}/dt, \quad \varkappa_{sik}, \quad \overset{h}{m_{s(ji)}}, \quad \overset{h}{m_{s(ij)}}, \quad \sum_{j=1}^{m} q_{s(ji)} - \alpha_{i} \frac{d_{i}\varepsilon_{si}}{dt}, \quad q_{si}^{\alpha}, \quad I_{si}^{\alpha}, \quad \varepsilon_{si}\pi_{i}^{\alpha}$$

$$\sum_{j=1}^{m} F_{s(ji)}^{\alpha}, \quad \sum_{j=1}^{m} F_{ns(ji)}, \quad \varepsilon_{si}(q_{n}^{\nu} + w^{\nu}J_{ni}^{\nu}), \quad \varepsilon_{si}J_{ikn}^{\nu}, \quad \varepsilon_{si}\tau_{nni}^{\nu}, \quad \varepsilon_{si}\tau_{n\tau i}^{\nu}$$

$$(17)$$

The surface thermodynamic forces are

$$\frac{E_{i}}{T_{si}}, \quad \frac{\alpha_{m}-\alpha_{i}}{T_{sm}}, \quad \frac{\xi_{sin}-\xi_{sih}}{T_{si}}, \quad X_{s(ji)}^{h}, \quad -X_{s(ij)}^{h}, \quad \frac{1}{T_{si}} - \frac{1}{T_{sm}}, \quad \nabla_{\alpha} \frac{1}{T_{si}}$$

$$\nabla_{\alpha} \frac{\xi_{smn}-\xi_{sih}}{T_{si}}, \quad \frac{E_{i\alpha\beta}^{*}}{T_{si}}, \quad \frac{\upsilon_{nsm}-\upsilon_{nsi}}{T_{sm}}, \quad \frac{\upsilon_{sm}^{\alpha}-\upsilon_{si}^{\alpha}}{T_{sm}}$$

$$\frac{1}{T_{v}} - \frac{1}{T_{si}}, \quad \frac{\xi_{sih}}{T_{si}} - \frac{\xi_{h}^{v}}{T_{v}} - \frac{(v^{v}-v_{si})^{2}}{2T_{si}}, \quad \frac{\upsilon_{n}^{v}-\upsilon_{sni}}{T_{si}}, \quad \frac{V_{\tau}^{v}-v_{\tau si}}{T_{si}}$$
(18)

Here, v = 1 for the first three-dimensional phase and v = 2 for the second.

In the surface thermodynamic forces (18), the first, ninth, tenth, 11th, 14th, and 15th are of type β and the remaining of type α .

We shall assume that the interface and the three-dimensional phases are isotropic; then in accordance with Curie's principle [18], the thermodynamic fluxes will depend on the thermodynamic forces of the same tensor dimension. Isotropy of the interface is understood in the sense that the physical properties of the interface do not depend on the direction in the tangential plane. Curie's principle in the two-dimensional case takes the form that the linear expressions for the fluxes in terms of the forces can contain only quantities having the same transformation properties with respect to an arbitrary orthogonal transformation of the surface coordinate system. Further, in the two-dimensional case the fluxes depend on the forces and the fundamental tensor $a_{\alpha\beta}$ of the surface.

We now discuss the thermodynamic fluxes (17) and the forces (18). The quantities $\epsilon_{si}\pi_{i}$, which depend on the scalar forces (18), and $\epsilon_{si}\pi_{i}^{*\alpha\beta}$, which depend on the tensor forces (18), characterize the viscous two-dimensional stresses in phase i; the quantities χ_{sih} , $m_{s(ij)}^{k}$, $m_{s(ij)}^{k}$, which characterize the production rate of component k of phase i due to the chemical reactions and the two-dimensional phase transitions, depend on all the scalar forces (18); the quantities $q_{s(ji)}$, which characterize the heat transfer between the two-dimensional phases, also depend on all the scalar forces. The rate of change of the area occupied by phase i, $d_m \epsilon_{si}/dt$, also depends only on the scalar forces. The surface heat flux vectors q_{Si}^{α} and diffusion flux vectors I_{Sik}^{α} depend on all the vector thermodynamic forces (18). The quantities $\epsilon_{si}(q_n + wJ_{ni})$ characterize the irreversible heat flux from the volume to the surface, and $\epsilon_{si}J_{ikn}$ characterize the mass transfer between the interface and the volume. The quantities $\epsilon_{si}\tau_{ni}$ and $\epsilon_{si}\tau_{ni}$ and $F_{sij}(j)$ and $F_{s(ji)}$ characterize the frictional forces in the three-dimensional phases acting on the interface in the normal and tangential directions, respectively. Finally, $F_{ns}(ji)$ and $F_{s(ji)}$ characterize the force of the interaction between the two-dimensional phases due to their being in disequilibrium.

In the case of an arbitrary nonisotropic interface, the dependences of the fluxes on the forces become much more complicated, and each flux component will depend on all components of the thermodynamic forces.

The above equations of motion of films of surface-active substances must be solved simultaneously with the equations of motion of the three-dimensional phases, which have the usual form [18].

Under some special assumptions, the two-dimensional equations simplify appreciably and take the form of the boundary conditions on a liquid interface that are well known in hydrodynamics. We note finally that comparison of the theory developed here with experiment [1] is at present impossible due to the absence of quantitative experimental results. However, the equations derived here show what quantities and connections between them should be investigated in an experiment. We note also that it is of interest to derive the equations of motion of films of surface-active substances with concentrated incompressible islands of condensation of molecules.

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