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SYMMETRIZATION OF THE EQUATIONS OF DYNAMICS OF A CAPILLARY LIQUID

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A model of the motion of a nonisothermal capillary liquid in the presence of surfactants at low concentration is described. A symmetric form of the equations in the intensive variables temperature—chemical potential is derived based on fundamental principles of thermodynamics.

From the mechanical standpoint, capillary forces are internal forces and the problem of determining them is a problem in the rheology of a multiphase medium. The main difference between such a continuous medium and classical liquids is that in the phase mixing layer the stress tensor is anisotropic (Pascal's law is not satisfied). The thickness of the mixing layer is equal to several intermolecular distances and it remains virtually constant during the motion of the liquid. For this reason, it is natural to model this layer as an interphase surface Γ with distributed excess thermodynamic quantities ε (internal energy), η (entropy), and γ (concentration of surfactant molecules), making the assumption that the layer is an open thermodynamic system in contact with volume phases — a reservoir of heat and surfactant particles. This approach of Gibbs makes it possible to circumvent the complicated question of the structure and thickness of the phase mixing layer and to use more efficient thermodynamic methods [1].

The postulated principle of local thermodynamic equilibrium leads to the condition that the intensive parameters θ (absolute temperature) and ζ (the chemical potential of the surfactant), which are characteristics of the reservoir, are continuous. This condition makes it possible to extend the relations of equilibrium thermodynamics or thermostatics to nonstationary processes involved in the dynamics of an interphase boundary. Here the principle of minimum entropy production is very important. This principle must be used in order to construct the correct relation between the heat flux $\mathbf{q}$ and the flux of surfactant molecules $\mathbf{j}$ and the gradients of θ and ζ [2].

1. Thermodynamics of the Interphase Boundary. Consider a closed thermodynamic system consisting of two phases separated by a uniform interphase surface of area A. Let E be the total energy of the system, N be the number of surfactant molecules, S(E, N) be the entropy of the volume phases, and $A\eta(\varepsilon, \gamma)$ be the excess entropy of the surface. According to the principle of maximum total entropy $S(E - A\varepsilon, N - A\gamma) + A\eta(\varepsilon, \gamma) \to \max$ in the approximation $A\varepsilon \ll E$, $A\gamma \ll N$ (the reservoir is much larger than the system in contact with it)

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we obtain $\eta(\varepsilon, \gamma) - \varepsilon/\theta + \gamma\zeta/\theta \to \max$ [$1/\theta = \partial S(E, N)/\partial E$ and $\zeta/\theta = -\partial S(E, N)/\partial N$ are characteristics of the reservoir].

To find the equilibrium values of ε and γ it is convenient to introduce the function

$$\sigma(\theta, \zeta) = \min_{\varepsilon,\gamma}\{\varepsilon - \theta\eta(\varepsilon, \gamma) - \zeta\gamma\}. \tag{1.1}$$

Since θ is positive (as a consequence of the fact that there is no upper limit of the energy spectrum), the minimum is achieved for values of ε and γ for which the total entropy is maximum. According to the property of Legendre transformations, a concave function $\eta(\varepsilon, \gamma)$ satisfies the equation

$$\eta(\varepsilon, \gamma) = \min_{\theta,\zeta}\{[\varepsilon - \sigma(\theta, \gamma) - \zeta\gamma]/\theta\},$$

and from Eq. (1.1) there follow formulas for the equilibrium values:

$$\eta = -\sigma_\theta,\ \gamma = -\sigma_\zeta,\ \varepsilon = \sigma - \theta\sigma_\theta - \zeta\sigma_\zeta. \tag{1.2}$$

It is obvious that the function $\sigma(\theta, \zeta)$, as the lower limit of linear functions, is concave, so that the matrix of its second derivatives is negative-definite, i.e.,

$$\sigma_{\theta\theta} < 0,\ \sigma_{\zeta\zeta} < 0,\ \sigma_{\theta\theta}\sigma_{\zeta\zeta} > (\sigma_{\theta\zeta})^2. \tag{1.3}$$

For volume incompressible liquid phases, prescribing the specific entropy $s(e, c)$ as a concave function of its arguments e (specific internal energy) and c (specific surfactant concentration) makes it possible to introduce the thermodynamic Gibbs potential

$$f(\theta, \zeta) = \min_{e,c}\{e - \theta s(e, c) - \zeta c\}.$$

By analogy to Eqs. (1.2) and (1.3) we have

$$s = -f_\theta,\ c = -f_\zeta,\ e = f - \theta f_\theta - \zeta f_\zeta; \tag{1.4}$$

$$f_{\theta\theta} < 0,\ f_{\zeta\zeta} < 0,\ f_{\theta\theta}f_{\zeta\zeta} > (f_{\theta\zeta})^2. \tag{1.5}$$

In other words, the quantity $\sigma(\theta, \zeta)$ is equal to the excess surface denisty of the thermodynamic potential.

We will now study the equilibrium process of the change in the area A of the interphase boundary. Taking into account the condition $d\varepsilon - \theta d\eta - \zeta d\gamma = 0$ at the point of the minimum gives the basic thermodynamic identity

$$\sigma dA = (\varepsilon - \theta\eta - \zeta\gamma)dA = d(A\varepsilon) - \theta d(A\eta) - \zeta d(A\gamma).$$

Therefore the function $\sigma(\theta, \zeta)$ is the surface tension and the stressed state Γ is described by the surface tensor σG_Γ ($G_\Gamma = G - \mathbf{n} \otimes \mathbf{n}$ is the metric tensor of the surface Γ, G is the metric tensor of the space, $\mathbf{n}$ is the normal to Γ, and $\otimes$ designates a tensor product).

The condition $\sigma > 0$ is necessary in order for the interphase boundary, which can only be stretched, to be stable. In the opposite case, the liquids in contact with one another will dissolve within one another. The excess quantities η, γ, and ε are not necessarily positive (the class of surfactants also includes inactive substances, which strive to penetrate into the region of phase mixing), so that the signs of σ_θ and σ_ζ can be arbitrary. The conditions (1.3) are more fundamental, since they are based on the principle of maximum entropy. At first glance the inequality $\sigma_{\theta\theta} < 0$ contradicts the anomalous thermocapillary effect, connected with the experimental observation that $\sigma(\theta)$ is minimum on the interface of water solutions of some alcohols and air [3]. In reality, there is no contradiction here, since the thermodynamic state of solutions having the same temperature is not determined: it is necessary to introduce the chemical potential of alcohol. In the experiments the complicated dependence $\sigma(\theta, \zeta(\theta))$ was actually measured; this dependence has a minimum, if ζ decreases as θ increases, which determines the intense process of transfer of surfactant molecules out of the mixing layer into the volume with a corresponding increase in σ.

2. Equations of Motion. Assume that the temperature and low concentration of surfactant molecules have no effect on the dynamical characteristics of the solvent, i.e., the density ρ and the viscosity μ are piecewise-constant with a surface of discontinuity Γ.

We write the classical laws of conservation of momentum, mass, energy, and number of surfactant molecules in the diffusion approximation:

$$\rho\dot{\mathbf{v}} = \rho\mathbf{g} - \nabla p + \mu\Delta\mathbf{v},\ \operatorname{div}\mathbf{v} = 0; \tag{2.1}$$

$$\rho\dot{e} = 2\mu D : D - \operatorname{div}\mathbf{q},\ \rho\dot{c} = -\operatorname{div}\mathbf{j}. \tag{2.2}$$

Here v is the velocity, p is the pressure, D is the strain-rate tensor, **g** is the mass density of external forces, and a dot designates a total time derivative. We introduce the pressure tensor $P = pG - 2\mu D$. Then the laws of conservation of momentum, energy, and number of surfactant molecules on Γ will assume the form

$$[P\cdot\mathbf{n}] = \operatorname{div}_\Gamma(\sigma G_\Gamma); \tag{2.3}$$

$$\dot{\varepsilon} + \varepsilon\operatorname{div}_\Gamma\mathbf{v} = \sigma\operatorname{div}_\Gamma\mathbf{v} - [\mathbf{q}\cdot\mathbf{n}],\ \dot{\gamma} + \gamma\operatorname{div}_\Gamma\mathbf{v} = -[\mathbf{j}\cdot\mathbf{n}]. \tag{2.4}$$

The brackets designate the operation of calculating a jump

$$[f](\mathbf{x}) = \lim_{z\to 0}\operatorname{sgn} z\{f(\mathbf{x} + z\mathbf{n}) - f(\mathbf{x} - z\mathbf{n})\},$$

and $\nabla_\Gamma = G_\Gamma\cdot\nabla$ is a surface gradient. The dynamical condition (2.3) at equilibrium transforms into Laplace's law $[p] = \sigma k$ ($k = -\operatorname{div}_\Gamma\mathbf{n}$ is the sum of the principle curvatures of Γ). For $v = 0$ and $\sigma = \mathrm{const}$ this follows from the chain of equalities

$$\operatorname{div}_\Gamma G_\Gamma = \operatorname{div}_\Gamma(G - \mathbf{n}\otimes\mathbf{n}) = -\mathbf{n}\operatorname{div}_\Gamma\mathbf{n} - \mathbf{n}\cdot\nabla_\Gamma\mathbf{n} = k\mathbf{n},$$

because the tensor $\nabla_\Gamma\mathbf{n}$ does not have normal components.

Assume that there are no phase transitions (Γ is a Lagrangian surface) and the principle of local thermodynamic equilibrium is satisfied. Then

$$\dot{\mathbf{x}} = \mathbf{v},\ [\mathbf{v}] = \mathbf{0},\ [\theta] = 0,\ [\zeta] = 0 \text{ on } \Gamma. \tag{2.5}$$

We will describe transport processes by means of Onsager's principle (a particular variant of the principle of minimum entropy production), i.e., we assume [2] that

$$\mathbf{q} = L_{11}\nabla(1/\theta) + L_{12}\nabla(-\zeta/\theta),\ \mathbf{j} = L_{21}\nabla(1/\theta) + L_{22}\nabla(-\zeta/\theta), \tag{2.6}$$

the matrix of kinematic coefficients (L_{ij}) is symmetric and positive-definite.

For simplicity transport processes along Γ are neglected in Eq. (2.4): there are no excess thermal conductivity and diffusion coefficients. These quantities are extremely small and cannot be reliably measured experimentally. Apparently, only the diffusion of undissolved surfactants along Γ can appreciably affect the motion and this can be taken into account by adding to the right side of the last equation in Eqs. (2.4) the term $-\operatorname{div}_\Gamma \times \mathbf{j}_\Gamma$, $\mathbf{j}_\Gamma = -L_\Gamma\nabla_\Gamma(\zeta/\theta)$. In all other cases the effect of surface diffusion is explained by diffusion in the volume and does not require introducing into the model additional difficult to measure quantities on the basis of the principle of local thermodynamic equilibrium.

3. Transfer to Intensive Variables. The conservation laws (2.2) and (2.4) lead to the equations of entropy production in the volume $\rho\dot{s} = \Phi - \operatorname{div}\mathbf{h}$ and at the surface $\dot{\eta} + \eta \times \operatorname{div}_\Gamma\mathbf{v} = -[\mathbf{h}\cdot\mathbf{n}]$, where $\Phi = 2\pi D{:}D/\theta + \mathbf{q}\cdot\nabla(1/\theta) + \mathbf{j}\cdot\nabla(-\zeta/\theta)$ is the dissipation function and $\mathbf{h} = (\mathbf{q} - \zeta\mathbf{j})/\theta$ is the entropy flux vector. From Eq. (2.6) there follow the representations

$$-\mathbf{h} = K_{11}\nabla\theta + K_{12}\nabla\zeta,\ -\mathbf{j} = K_{21}\nabla\theta + K_{22}\nabla\zeta, \tag{3.1}$$

$K_{11} = (L_{11} - 2\zeta L_{12} + \zeta^2 L_{22})/\theta^3$, $K_{12} = K_{21} = (L_{12} - \zeta L_{22})/\theta^2$, $K_{22} = L_{22}/\theta$, i.e., the matrix K_{ij} is symmetric and positive-definite. Now the laws of conservation of energy and number of surfactant molecules, substituting Eqs. (1.2) and (1.4), can be written as

$$\rho(-f_\theta)^\cdot = \Phi - \operatorname{div}\mathbf{h},\ \rho(-f_\zeta)^\cdot = -\operatorname{div}\mathbf{j}; \tag{3.2}$$

$$(\sigma_\theta)^\cdot + \sigma_\theta\operatorname{div}_\Gamma\mathbf{v} = [\mathbf{h}\cdot\mathbf{n}],\ (\sigma_\zeta)^\cdot + \sigma_\zeta\operatorname{div}_\Gamma\mathbf{v} = [\mathbf{j}\cdot\mathbf{n}]. \tag{3.3}$$

Thus, based on Eqs. (1.3) and (1.5), the system of equations (3.1)-(3.3) in the variables (θ, ζ) has a symmetric dissipative structure.

An analogous construction can be suggested for modeling phase transitions; in particular, Stefan's problem of thermal diffusion can be symmetrized. Here it must be assumed that there exists a section where $s(e, c)$ is linear and which, under a Legendre transformation, will correspond to the line of corner points of the graph of the function $f(\theta, \zeta)$, which will result in discontinuity of the extensive thermodynamic variables s, c, and e, represented by the formulas (1.4). This line in the plane (θ, ζ) determines the dependence of the temperature of the phase transition on the chemical potential ζ and not on the impurity concentration.

The equations of equilibrium gas dynamics and the theory of elasticity are symmetrized in [4] based on the second law of thermodynamics. The relation between the symmetrization of the equations of thermomechanics of continuous media and the principles of the minimum thermodynamic potential and entropy production was pointed out in [5], where instead of (θ, ζ) the variables $(1/\theta, -\zeta/\theta)$ were employed. We note that the requirement that the thermodynamic functions and the dissipation potentials be convex is very important and apparently necessary in order to construct the correct mathematical models of the mechanics of a continuous medium.

4. Examples. The model of the motion of a capillary liquid (2.1), (2.3), (2.5), and (3.1)-(3.3) requires prescribing the matrix of transfer coefficients K_{ij} and two concave functions $f(\theta, \zeta)$, $\sigma(\theta, \zeta)$. Comparing Eqs. (2.6) and (3.1) with Fourier's law $\mathbf{q} = -\chi\nabla\theta$ and Fick's law $\mathbf{j} = -\lambda\nabla\zeta$ (χ, λ are the thermal conductivity and diffusion coefficient), we obtain

$$K_{11} = (\varkappa + \alpha\zeta)/\theta,\ K_{12} = K_{21} = -\alpha,\ K_{22} = \lambda.$$

For f and σ we can use the functions

$$\begin{aligned} f(\theta, \zeta) &= -\theta\{a \log(\theta/\theta_0) + c_0 \exp(\zeta/\theta)\}, \\ \sigma(\theta, \zeta) &= \sigma_0(\theta) - \gamma_\infty\theta \log\{1 + \exp(\zeta/\theta)\}, \end{aligned} \tag{4.1}$$

where the positive quantities a (specific heat capacity), θ_0, and c_0 depend on the phase of the solvent, $\sigma_0(\theta)$ is the surface tension of a clean interphase boundary, and γ_∞ is the maximum concentration of the surfactant on Γ. The equalities (1.2) and (1.4) lead to the expressions

$$s = a\{\log(\theta/\theta_0) + 1\} + c_0(1 - \zeta/\theta)\exp(\zeta/\theta), \quad c = c_0 \exp(\zeta/\theta),$$
$$e = a\theta, \quad \eta = -\sigma_0'(\theta) - \gamma_\infty\{(\zeta/\theta)\exp(\zeta/\theta)/[1 + \exp(\zeta/\theta)] -$$
$$- \log[1 + \exp(\zeta/\theta)]\}, \quad \gamma = \gamma_\infty \exp(\zeta/\theta)/[1 + \exp(\zeta/\theta)], \quad \varepsilon = \sigma_0(\theta) - \theta\sigma_0'(\theta),$$

and from the conditions (2.5) there follows Langmuir's adsorption formula

$$\gamma = \gamma_\infty c/(c_0 + c),\ [c/c_0] = 0 \text{ on } \Gamma.$$

The relations (4.1) correspond to the expressions for the specific and surface entropy

$$s(e, c) = a\{\log(e/a\theta_0) + 1\} + c\{1 - \log(c/c_0)\},$$
$$\eta(\varepsilon, \gamma) = \eta_0(\varepsilon) + \gamma_\infty \log\{\gamma_\infty/(\gamma_\infty - \gamma)\} - \gamma \log\{\gamma/(\gamma_\infty - \gamma)\},$$

i.e., they transform into one another under a Legendre transformation.

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