THE DESCRIPTION OF A MULTICOMPONENT MIXTURE BY THE DENSITY FUNCTIONAL METHOD WHEN THERE ARE SURFACE PHASES PRESENT†

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The description of multicomponent mixtures, with an expression for the free energy or the entropy in the form of a density functional [1, 2], is extended to the case when the system contains surface phases, when the finite number of particles of the mixture can be linked with certain geometrical surfaces. Equations are obtained which define the static state and hydrodynamic flows for a mixture with an arbitrary number of volume and surface phases. © 2001 Elsevier Science Ltd. All rights reserved.

We previously considered [1, 2] the case of a continuous distribution of the components of a mixture in a volume. A description of the surface layers was possible in this case, strictly speaking, when the mean distance between molecules of the mixture is considerably less than the layer thickness. If this condition is not satisfied, the approach proposed in this paper must be used.

1. DESCRIPTION OF THE SURFACE PHASES IN CLASSICAL THERMODYNAMICS

We will consider surface phases arises in a layer of infinitesimal thickness that on a solid surface which is in contact with a multicomponent mixture (i.e. adsorption layers). The classical thermodynamic description of such systems enables a number of general relations to be established [3] for equilibrium states, ignoring the spatial arrangement of the phases. In particular, it is assumed that the properties of the surface are everywhere the same.

We briefly describe below some results of classical thermodynamics, which will be required later. The Latin subscripts i, j and k take values $1, \ldots, K$, corresponding to the numbers of the components of the mixture. Summation over repeated sub- or superscripts is understood.

For a homogeneous state in the volume, T_v is the absolute temperature, S_v is the entropy, U_v is the internal energy, N_{vi} is the number of particles of the component with number i in moles, and V is the volume of the mixture. Similarly, for a homogeneous state on the surface, T_s is the absolute temperature, S_s is the entropy, U_s is the internal energy, N_{si} is the number of particles of the component with number i in moles and A is the area of the surface corresponding to the state considered.

The following differential relations hold

$$T_v dS_v = dU_v - \varkappa_{vi} dN_{vi} + p_v dV$$

$$T_s dS_s = dU_s - \varkappa_{si} dN_{si} + p_s dA \tag{1.1}$$

Here $\varkappa_{vi}$ and $\varkappa_{si}$ are the chemical potentials of the component with number i for states in the volume and on the surface, respectively, p_v is the hydrostatic pressure, and p_s is the surface tension with the opposite sign. We postulate that the volume entropy $S_v = S_v(U_v, N_{vi}, V)$ and the surface entropy $S_s = S_s(U_s, N_{si}, A)$ are homogeneous first-order functions. This property, in conjunction with differential relations (1.1), leads to the equations

$$T_v S_v = U_v - \varkappa_{vi} N_{vi} + p_v V, \quad T_s S_s = U_s - \varkappa_{si} N_{si} + p_s A \tag{1.2}$$

Using the property of homogeneity, we can determine the values of the entropy per unit volume $s_v = S_v/V$ as a function of the energy density $u_v = U_v/V$ and of the volume densities of the components

$n_{vi} = N_{vi}/V$, and also the entropy per unit area $s_s = S_s/A$ as a function of the surface energy density $u_s = U_s/A$ and of the surface densities of the components $n_{si} = N_{si}/A$.

Here relations (1.1), (1.2) have the following analogies in terms of the volume and surface densities ($\sigma = v, s$)

$$T_\sigma ds_\sigma = du_\sigma - \varkappa_{\sigma i} dn_{\sigma i}, \quad T_\sigma s_\sigma = u_\sigma - \varkappa_{\sigma i} n_{\sigma i} + p_\sigma \tag{1.3}$$

Consider the situation when there are L_v homogeneous states in the volume and L_s homogeneous states on the surface. Quantities related to one of the homogeneous sates will be indicated by a superscript Latin capital letter – the number of the state. Neglecting the interface effect, we can write the following expressions for the total entropy, energy and numbers of particles of the system components

$$S_{tot} = \Sigma_A \, S_v^A + \Sigma_B S_s^B \tag{1.4}$$

$$U_{tot} = \Sigma_A \, U_v^A + \Sigma_B U_s^B, \quad N_{i\,tot} = \Sigma_A \, N_{vi}^A + \Sigma_B N_{si}^B \tag{1.5}$$

$$\left(\Sigma_A = \sum_{A=1}^{L_v}, \quad \Sigma_B = \sum_{B=1}^{L_s} \right)$$

A stable equilibrium multiphase state ensures an absolute maximum of functional (1.4) for specified values of the energy (the first relation of (1.5)), the number of particles of the components (the second relation of (1.5)), and also of the total volume and area

$$V_{tot} = \Sigma_A V^A, \quad A_{tot} = \Sigma_B A^B \tag{1.6}$$

The problem of finding the maximum of functional (1.4) with constraints (1.5) and (1.6) can be reduced to the problem of constructing a convex shell of a certain auxiliary function. We will describe this procedure.

For an arbitrary set of values of the energy U, the number of particles of the components N_i, the volume V, and the area A we determine the $(K + 2)$-dimensional vector with components

$$z_1 = U/N, ..., z_{n+1} = N_n/N, ..., z_{K+1} = V/N$$
$$z_{K+2} = A/N; \quad N = N_1 + N_2 + ... + N_K, n = 1, ..., (K - 1)$$

In view of the property of homogeneity of the entropy functions mentioned above, we can define the following auxiliary functions

$$h_v = h_v(z) = -S_v(U, N_i, V)/N$$

$$h_s = h_s(z) = -S_s(U, N_i, A)/N$$

$$h = h(z) = \min(h_s(z), \ h_v(z))$$

We will assume that the functions S_v and S_s are non-negative and vanish when $V = 0$ and when $A = 0$ respectively. This assumption agrees with the third law of thermodynamics.

Then, finding the maximum of functional (1.4) with constraints (1.5) and (1.6) is equivalent to the standard problem of convex analysis [4, 5] of constructing a convex shell of the function $h(z)$. The extreme points [4, 5] of this convex shell $h_*(z)$ correspond to stable homogeneous states, i.e. phases. The expansion of an arbitrary state z in a linear combination of extreme points

$$z = \sum_{A=1}^{L} \lambda^A z^A, \quad h_*(z) = \sum_{A=1}^{L} \lambda^A h(z^A); \quad \sum_{A=1}^{L} \lambda^A = 1, \quad \lambda^A \geqslant 0$$

is interpreted physically as the decomposition of a state of the mixture, described by the vector of the mean values of z, into phases z^A with corresponding molar fractions λ^A. One of the consequences of the well-known Carathéodory theorem [4, 5] on the number of extreme points is the following constraint on the number of phases

$$L = L_v + L_s \leqslant K + 3$$

We recall that there is a more restrictive constraint on the number of phases for the states of the mixture in the volume, namely, $L \leqslant K + 2$.

If an equilibrium heterogeneous state exists, the conditions for an extremum of functional (1.4) are the necessary conditions for thermodynamic equilibrium. Relations (1.3) enable us to formulate these conditions in the form of equality of the temperatures and chemical potentials in all the phases

$$T_v^A = T_s^B = T_*, \quad \varkappa_{vi}^A = \varkappa_{si}^B = \varkappa_{*i} \tag{1.7}$$

and also equality of the pressures for the volume phases and equality of the surface tensions for the surface phases

$$p_v^A = p_{v\,*}, \quad p_s^B = p_{s*} \tag{1.8}$$

Conditions (1.7) remain true if we take the interface effect into account. Conditions (1.8) are changed: interphase jumps in the pressure and surface tension, which depend on the curvature of the interface, appear in them.

2. THE DENSITY FUNCTIONAL METHOD IN STATICS

Suppose the mixture occupies a spatial region D with a smooth boundary ∂D. We will assume that ∂D coincides with the surface of the fixed and undeformed solid phase, on which it is possible for adsorption layers to form. If the characteristic thickness of the adsorption layer is much less than the characteristic radius of curvature of the surface ∂D and of the characteristic dimensions of the region D, we can assume that the layer is of infinitesimal thickness.

Here and below the Latin subscripts a, b and c take the values 1, 2, 3, corresponding to Cartesian coordinates in the space x^a; the Greek superscripts α, β and γ, take the values 1 and 2, corresponding to curvilinear coordinates on the surface y^α, $\partial_a = \partial/\partial x^a$ and ∇_α is the covariant derivative on the surface corresponding to the induced metric. Summation over repeated sub- or superscripts is implied. We will use the following notation for the derivatives for the functions g, which depend on the absolute temperature T and on the molar densities of the components n_i,

$$g_{,T} = \frac{\partial g}{\partial T}, \quad g_{,i} = \frac{\partial g}{\partial n_i}$$

We will take the expression for the total energy of the mixture in the form

$$S_{\text{tot}} = \int_D \vartheta_v \, dV + \int_{\partial D} \vartheta_s \, dA \tag{2.1}$$

$$\vartheta_v = s_v - \frac{1}{2}\alpha \partial_a T_v \partial_a T_v - \frac{1}{2}\alpha_{ij}\partial_a n_i \partial_a n_j$$

$$\vartheta_s = s_s - \frac{1}{2}\beta g^{\alpha\beta}\nabla_\alpha T_s \nabla_\beta T_s - \frac{1}{2}\beta_{ij}g^{\alpha\beta}\nabla_\alpha n_{si}\nabla_\beta n_{sj}$$

The entropy densities s_v and s_s are assumed to be functions of T_v, n_{vi} and T_s, n_{si} respectively, $\alpha = \alpha(T_v, n_{vi}) > 0$, $\beta = \beta(T_s, n_{si}) > 0$, $\alpha_{ij} = \alpha_{ij}(n_{vk})$ and $\beta_{ij} = \beta_{ij}(n_{sk})$ are positive-definite symmetrical matrices and $g_{\alpha\beta}$ is the metric on the surface ∂D.

The case when expression (2.1) contains only the first term was investigated previously in [2]. The second term is introduced to describe the surface phases, taking into account the interface structure, by analogy with the first term.

Remark. Expression (2.1) contains no terms having products of the temperature gradients and the density gradients, and the coefficients α_{ij} and β_{ij} are independent of the temperature. This ensures that theory is compatible with the zeroth law of thermodynamics [2], i.e. with the condition that the temperature should be the same in all parts of the system for equilibrium states.

We will also employ the usual expressions for the total internal energy and the numbers of particles of the components

$$U_{\text{tot}} = \int_D (u_v + \rho_v \varphi)dV + \int_{\partial D} (u_s + \rho_s \varphi)dA \tag{2.2}$$

$$N_{i\,\text{tot}} = \int_D n_{vi}dV + \int_{\partial D} n_{si}dA \tag{2.3}$$

In expression (2.2) $\varphi = \varphi(x^a)$ is the gravitational potential, $\rho = m_i n_{vi}$, $\rho_s = m_i n_{si}$ are the mass densities and m_i is the mass of a mole of the component with number i.

Varying functional (2.1) we obtain the expression

$$\delta S_{\text{tot}} = \int_D (\Phi_{v0}\,\delta T_v + \Phi_{vi}\delta n_{vi})dV + \int_{\partial D} (\chi_0\,\delta T_v + \chi_i\delta n_{vi} + \Phi_{s0}\delta T_s + \Phi_{si}\delta n_{si})dA \tag{2.4}$$

$$\Phi_{v0} = s_{v,T} + \frac{1}{2}\alpha_{,T}\partial_a T_v\,\partial_a T_v + \alpha_{,i}\partial_a T_v\partial_a n_{vi} + \alpha\Delta T_v$$

$$\Phi_{vi} = s_{v,i} - \frac{1}{2}\alpha_{,i}\partial_a T_v\partial_a T_v - \frac{1}{2}\alpha_{jk,i}\partial_a n_{vj}\partial_a n_{vk} + \alpha_{ij,k}\partial_a n_{vk}\partial_a n_{vj} + \alpha_{ij}\Delta n_{vj}$$

$$\chi_0 = l_a\alpha\partial_a T_v\,, \quad \chi_i = l_a\alpha_{ij}\partial_a n_{vj}$$

$$\Phi_{s0} = s_{s,T} + \frac{1}{2}\beta_{,T}g^{\alpha\beta}\nabla_\alpha T_s\nabla_\beta T_s + \beta_{,i}g^{\alpha\beta}\nabla_\alpha T_s\nabla_\beta n_{si} + \beta\Delta_s T_s$$

$$\Phi_{si} = s_{s,i} - \frac{1}{2}\beta_{,i}g^{\alpha\beta}\nabla_\alpha T_s\nabla_\beta T_s - \frac{1}{2}\beta_{jk,i}g^{\alpha\beta}\nabla_\alpha n_{sj}\nabla_\beta n_{sk} +$$

$$+ \beta_{ij,k}g^{\alpha\beta}\nabla_\alpha n_{sk}\nabla_\beta n_{sj} + \beta_{ij}\Delta_s n_{sj}$$

Here l_a is the inward normal to the boundary ∂D and $\Delta_v = \partial_a\partial_a$, $\Delta_s = g^{\alpha\beta}\nabla_\alpha\nabla_\beta$.

The conditions for an extremum of functional (2.1) for specified values of the quantities (2.2) and (2.3) has the form

$$\delta S_{\text{tot}} - \lambda_0\delta U_{\text{tot}} + \lambda_i\delta N_{i\,\text{tot}} = 0 \tag{2.5}$$

where λ_0 and λ_i are Lagrange multipliers. Substituting expression (2.4) into (2.5) we obtain the equalities

$$\Phi_{\sigma0} - \lambda_0 u_{\sigma,T} = 0, \quad \Phi_{\sigma i} - \lambda_0(u_{\sigma,i} + m_i\varphi) + \lambda_i = 0; \quad \sigma = v, s \tag{2.6}$$

$$\chi_0 = 0, \qquad \chi_i = 0 \tag{2.7}$$

Relations (2.7) are the boundary conditions for Eqs (2.6) when $\sigma = v$.

The physical meaning of the Lagrange multipliers was discussed previously in [2]. For a homogeneous state in a volume in which there are no gravitational forces, we have the relations $\lambda_0 = T_v^{-1}$, $\lambda_1 = T_v^{-1}\chi_{vi}$. In exactly the same way, for a homogeneous state on the surface when there are no gravitational forces the following equations hold: $\lambda_0 = T_s^{-1}$, $\lambda_1 = T_s^{-1}\chi_{si}$.

Expression (2.1) is compatible with the zeroth law of thermodynamics, which asserts that for thermodynamic equilibrium the temperature in all parts of the system is the same. The following lemma confirms this.

Lemma. For a specified density distribution in the volume $n_{vi} = n_{vi}(x^a)$ and on the surface $n_{si} = n_{si}(y^\alpha)$ the maximum of functional (2.1), with additional condition (2.2), is reached at a certain temperature, which is the same at all points of the mixture.

Proof. For a specified value of u_{tot} a temperature T_0 exists such that Eq. (2.2) is satisfied when $T_v = T_s = T_0$. This is a consequence of the monotonic temperature dependence of the functions u_v and u_s

$$u_{v,T} > 0, \quad u_{s,T} > 0 \tag{2.8}$$

For brevity, we will denote quantities calculated when $T_v = T_s = T_0$ by an additional zero subscript. We will take a certain arbitrary temperature distribution $T_v = T_v(x^a)$, $T_s = T_s(y^\alpha)$, which satisfies Eq. (2.2). It is obvious that

$$S - S_0 \leqslant \int_D (s_v - s_{v0})dV + \int_{\partial D} (s_s - s_{s0})dA \tag{2.9}$$

where the equality sign only applies when $T_v = T_s = T_0$. In addition, the following equality holds

$$0 = \int_D (u_v - u_{v0})dV + \int_{\partial D} (u_s - u_{s0})dA \tag{2.10}$$

Note that, by virtue of inequalities (2.8), the following inequalities hold

$$\left(\frac{\partial^2 s_\sigma}{\partial u_\sigma^2}\right)_{n_i} = -T_\sigma^{-2} u_{\sigma,T}^{-1} < 0; \quad \sigma = v, s$$

We therefore have the relations

$$s_\sigma - s_{\sigma 0} = T_0^{-1}(u_\sigma - u_{\sigma 0}) + a_\sigma; \quad \sigma = v, s \tag{2.11}$$

where $a_v \leq 0$, $a_s \leq 0$, and the equality signs only apply when $T_v = T_0$ and $T_s = T_0$ respectively at the given point. Substituting (2.11) into the right-hand side of inequality (2.9) and using (2.10) we obtain the assertion of the lemma.

It was shown in [1] the Eqs (2.6) when $\sigma = v$ describe, in particular, the interface structure in a volume. We will show, using a simple example, how Eqs (2.6) describe the interface structure on a surface when $\sigma = s$.

We will consider the one-dimensional case (which corresponds to a cylindrical surface ∂D) without gravitational forces. Suppose y is the corresponding spatial coordinate. By the lemma, we can assume $T_s = $ const. The change in surface densities is described by the group of equations (2.6) with $\sigma = s$

$$\Phi_{si} - \lambda_0 u_{s,i} + \lambda_i = 0 \tag{2.12}$$

$$\Phi_{si} = s_{s,i} - \frac{1}{2}\beta_{jk,i}\partial_y n_{sj}\partial_y n_{sk} + \beta_{ij,k}\partial_y n_{sk}\partial_y n_{sj} + \beta_{ij}\partial_y^2 n_{sj}$$

This is a system of K equations in K unknown $n_{si} = n_{si}(y)$. It can be interpreted as a system of Lagrange equations for the Lagrangian

$$L = \frac{1}{2}\beta_{ij}\partial_y n_{si}\partial_y n_{sj} - s_s + \lambda_0 u_s - \lambda_i n_{si}$$

In particular, we have the integral

$$J = \frac{1}{2}\beta_{ij}\partial_y n_{si}\partial_y n_{sj} + s_s - \lambda_0 u_s + \lambda_i n_{si}$$

If there are several singular points of system (2.12) on the surface $J = $ const, solutions $n_{si} = n_{si}(y)$ can exist which converge to singular points as $y \to \pm\infty$. These solutions describe the interface structure for coexisting phases corresponding to the singular points.

Hence, the one-dimensional problem of the interface structure on a surface is formally completely analogous to the corresponding one-dimensional problem in a volume [1]. For non-one-dimensional problems (for example, for surfaces which differ from cylindrical) the multiphase states on a surface may have qualitatively new geometrical properties. The problem must be investigated by methods of the theory of elliptical systems of differential equations on two-dimensional surfaces.

3. THE DENSITY FUNCTIONAL METHOD IN DYNAMICS

We will take as the equations of the dynamics of a mixture the usual hydrodynamic equations of the conservation of the components, momentum and energy. In the volume the system of these equations has the form

$$\partial_t n_{vi} + \partial_a I_{vi}^a = 0$$

$$\partial_t(\rho_v v_v^a) + \partial_b \Pi_v^{ab} = -\rho_v \partial_a \varphi \tag{3.1}$$

$$\partial_t(K_v + u_v) + \partial_a Q_v^a = -\rho_v v_v^a \partial_a \varphi$$

Here I_{vi}^a is the flux of the i-th component, $v_v^a = \rho_v^{-1} m_i I_{vi}^a$ is the mean mass velocity, Π_v^{ab} is the momentum flux, $K_v = \frac{1}{2}\rho_v v_v^a v_v^a$ is the kinetic energy of a particle of the medium and Q_v^a is the energy flux.

In order to write the hydrodynamic equations on the surface we will introduce three-dimensional basis vectors $e_\alpha^a = \partial x^a / \partial y^\alpha$ corresponding to the system of coordinates on the surface y^α. The set of three-dimensional vectors e_α^a and the vector of the inward normal to the surface l^a form a basis in three-dimensional space at each point of the surface. The Greek subscripts in the set e_α^a can be raised and lowered using the metric tensor $g_{\alpha\beta}$. By definition, the set of vectors e_α^a satisfies the relations

$$e_\alpha^a e_\beta^a = g_{\alpha\beta}, \quad g^{\alpha\beta} e_\alpha^a e_\beta^b + l_a l_b = \delta^{ab}$$

For an adsorbed layer the equations of conservation of the components, momentum and energy have the form

$$\partial_t n_{si} + \nabla_\alpha I_{si}^\alpha + l_a I_{vi}^a = 0 \tag{3.2}$$

$$\partial_t (\rho_s v_s^a) + \nabla_\beta \Pi_s^{a\beta} + l_b \Pi_v^{ab} = -\rho_s \partial_a \varphi + R^a \tag{3.3}$$

$$\partial_t (K_s + u_s) + \nabla_\alpha Q_s^\alpha + l_a Q_v^a = \varepsilon + (-\rho_s \partial_a \varphi + R^a) v_s^a \tag{3.4}$$

Here I_{si}^α is the flux of the component with number i, $v_s^\alpha = \rho_s^{-1} m_i I_{si}^\alpha$ is the mass velocity in the layer in curvilinear coordinates, $v_s^a = v_s^\alpha e_\alpha^a$ is the mass velocity in Cartesian coordinates, $K_s = \frac{1}{2}\rho_s v_s^a v_s^a$ is the kinetic energy of a particle of the layer, $\Pi_s^{\alpha\beta}$ is the momentum flux in the layer, R^a is the force arising from the action of the solid phase, Q_s^α is the energy flux in the layer and ε is the heat-exchange parameter of the adsorption layer with the rigid body.

It is convenient to rewrite the three equations (3.3) in space in terms of the tangential and normal components. To do this we will represent the momentum flux and the external force in the form

$$\Pi_s^{a\beta} = \pi^{\alpha\beta} e_\alpha^a + \xi^\beta l_a, \quad R^a = r^\alpha e_\alpha^a + \zeta l_a \tag{3.5}$$

$$\pi^{\alpha\beta} = \Pi_s^{a\beta} e^{\alpha a}, \quad \xi^\beta = \Pi_s^{a\beta} l_a, \quad r^\alpha = R^a e^{\alpha a}, \quad \zeta = R^a l_a$$

Substituting relations (3.5) into (3.3) and using the equality $\nabla_\beta e_\alpha^a = -b_{\alpha\beta} l^a$, where $b_{\alpha\beta} = \partial_\beta l^a e_\alpha^a$ is the second fundamental form of the surface, we obtain

$$\partial_t (\rho_s v_s^\alpha) + \nabla_\beta \pi^{\alpha\beta} + \xi^\beta b_\beta^\alpha + l_b e^{\alpha a} \Pi_v^{ab} = -g^{\alpha\beta} \rho_s \nabla_\beta \varphi + r^\alpha \tag{3.6}$$

$$\nabla_\beta \xi^\beta - \eta^{\alpha\beta} b_{\alpha\beta} + l_a l_b \Pi_v^{ab} = -\rho_s l_a \partial_a \varphi + \zeta$$

The last equation can be regarded as a definition of the quantity ζ – the normal reaction of the rigid body, if all the remaining quantities are known. This equation will therefore not be used henceforth.

In Eqs (3.1)–(3.3) we will introduce, in the usual way, diffusion fluxes, the stress tensor and the heat flux vector respectively

$$Q_{vi}^a = I_{vi}^a - n_{vi} v_v^a, \quad p_v^{ab} = -\Pi_v^{ab} + \rho_v v_v^a v_v^b$$

$$q_v^a = Q_v^a - (K_v + u_v) v_v^a + p_v^{ab} v_v^b$$

These equations can then be converted to the form

$$\partial_t n_{vi} = -\partial_a (n_{vi} v_v^a + Q_{vi}^a) \tag{3.7}$$

$$\rho_v (\partial_t + v_v^b \partial_b) v_v^a = \partial_b p_v^{ab} - \rho_v \partial_a \varphi \tag{3.8}$$

$$\partial_t u_v = p_v^{ab} \partial_a v_v^b - \partial_a (q_v^a + u_v v^a) \tag{3.9}$$

Similarly, for the surface phases we introduce diffusion fluxes, the stress tensor and the heat flux vector, respectively

$$Q_{si}^\alpha = I_{si}^\alpha - n_s \nu_s^{\ \alpha}, \quad p_s^{\alpha\beta} = -\pi^{\alpha\beta} + \rho_s \nu_s^{\ \alpha} \nu_s^{\ \beta}$$

$$q_s^a = Q_s^a - (K_s + u_s)\nu_s^{\ a} + p_s^{ab}\nu_s^{\ b}$$

Equations (3.2), (3.6) and (3.4) can then be converted to the form

$$\partial_t n_{si} = -\nabla_\alpha (n_{si}\nu_s^{\ a} + Q_{si}^\alpha) = -l_a (n_{\nu i}\nu_\nu^{\ a} + Q_{\nu i}^a) \tag{3.10}$$

$$\rho_s(\partial_t + \nu_s^{\ \beta}\nabla_\beta)\nu_s^{\ \alpha} = \nabla_\beta p_s^{\alpha\beta} - \xi^\beta b_\beta^\alpha - l_b e^{\alpha a}\Pi_\nu^{ab} - g^{\alpha\beta}\rho_s\nabla_\beta\varphi + r^\alpha \tag{3.11}$$

$$\partial_t u_s = p_s^{\alpha\beta}\nabla_\alpha \nu_{s\beta} + \xi^\alpha \nu_s^{\ \beta} b_{\alpha\beta} - $$

$$-\nabla_\alpha(q_s^\alpha + u_s\nu_s^{\ \alpha}) + l_a(\nu_{s\alpha}e^{ab}\Pi_\nu^{ba} - Q_\nu^a) + \varepsilon \tag{3.12}$$

To close the system of dynamic equations (3.7)–(3.12) it is necessary to specify expressions for the quantities

$$Q_{\nu i}^a, \quad p_\nu^{ab}, \quad q_\nu^a, \quad Q_{si}^\alpha, \quad p_s^{\alpha\beta}, \quad q_s^a, \quad \xi^\alpha$$

i.e. to specify material relations. The standard requirement which the material relations must satisfy is the condition that the production of entropy should be non-negative, i.e. the condition that the change in entropy, after subtracting the contribution of heat exchange with the surroundings, is non-negative.

We will assume that boundary conditions (2.7) are also satisfied in the dynamic theory. Then, the derivative with respect to time of the entropy functional (2.1) can be evaluated using Eqs (3.7), (3.9), (3.10) and (3.12). The result is the expression

$$\frac{dS}{dt} = \int_D (\Psi_{\nu 0}(p_\nu^{ab}\partial_a\nu_\nu^{\ b} - \partial_a(q_\nu^a + \nu_\nu^{\ a}u_\nu)) + \Psi_{\nu i}(-\partial_a(n_\nu \nu_\nu^{\ a} + Q_{\nu i}^a))dV +$$

$$+ \int_{\partial D} (\Psi_{s0}(p_s^{\alpha\beta}\nabla_\alpha\nu_{s\beta} + \xi^\alpha\nu_s^{\ \beta}b_{\alpha\beta} - \nabla_\alpha(q_s^\alpha + \nu_s^{\ \alpha}u_s) + l_a(\nu_{s\alpha}e^{ab}\Pi_\nu^{ba} - Q_\nu^a) + \varepsilon) +$$

$$+ \Psi_{si}(-\nabla_\alpha(n_s\nu_s^{\ \alpha} + Q_{si}^\alpha) - l_a(n_\nu\nu_\nu^{\ a} + Q_{\nu i}^a)))dA \tag{3.13}$$

where we have used the notation

$$\Psi_{\nu 0} = \Phi_{\nu 0}u_{\nu,T}^{-1}, \quad \Psi_{\nu i} = \Phi_{\nu i} - \Phi_{\nu 0}u_{\nu,T}^{-1}u_{\nu,i}$$

$$\Psi_{s0} = \Phi_{s0}u_{s,T}^{-1}, \quad \Psi_{si} = \Phi_{si} - \Phi_{s0}u_{s,T}^{-1}u_{s,i}$$

To simply expression (3.13) we will introduce the following auxiliary quantities

$$\Sigma_\nu^{ab} = -\alpha\partial_a T_\nu \partial_b T_\nu - \alpha_{ij}\partial_a n_{\nu i}\partial_b n_{\nu j} + \delta_{ab}(\vartheta_\nu + \Psi_{\nu 0}u_\nu + \Psi_{\nu i}n_{\nu i})$$

$$\Sigma_{s\alpha\beta} = -\alpha\nabla_\alpha T_s\nabla_\beta T_s - \alpha_{ij}\nabla_\alpha n_{si}\nabla_\beta n_{sj} + g_{\alpha\beta}(\vartheta_s + \Psi_{s0}u_s + \Psi_{si}n_{si})$$

These quantities satisfy the identities

$$\Sigma_{\nu,b}^{ab} - u_\nu \partial_a\Psi_{\nu 0} - n_{\nu i}\partial_a\Psi_{\nu i} = 0 \tag{3.14}$$

$$g^{\gamma\beta}\nabla_\gamma\Sigma_{s\alpha\beta} - u_s\nabla_\alpha\Psi_{s0} - n_{si}\nabla_\alpha\Psi_{si} = 0 \tag{3.15}$$

We impose the following additional boundary conditions on the surface ∂D

$$\Psi_{\nu 0} = \Psi_{s0}, \quad \Psi_{\nu i} = \Psi_{si} \tag{3.16}$$

Then, using integration by parts and taking relations (3.14)–(3.16) into account, expression (3.13) can be converted as follows:

$$\frac{dS}{dt} = \int_{\partial D} T_e^{-1}\varepsilon dA + \int_D \sigma_v \, dV + \int_{\partial D} \sigma_s dA \tag{3.17}$$

$$\sigma_v = \Psi_{v0}\tau_v^{ab}\partial_a\nu_v^b + \partial_a\Psi_{v0}q_v^a + \partial_a\Psi_{vi}Q_{vi}^a$$

$$\sigma_s = \Psi_{s0}\tau_s^{\alpha\beta}\nabla_\alpha\nu_{s\beta} + \Psi_{s0}\xi^\alpha\nu_s^\beta b_{\alpha\beta} + \nabla_\alpha\Psi_{s0}q_s^\alpha + \nabla_\alpha\Psi_{si}Q_{si}^\alpha + \Psi_{s0}l_a C^a$$

$$\tau_v^{ab} = p_v^{ab} - \Psi_{v0}^{-1}\Sigma_v^{ab}, \quad \tau_s^{\alpha\beta} = p_s^{\alpha\beta} - \Psi_{s0}^{-1}\Sigma_s^{\alpha\beta}$$

$$C^a = \nu_s^b\rho_v\nu_v^b\nu_v^a - K_v\nu_v^a + \tau_v^{ab}\nu_v^b - p_v^{ab}\nu_s^b$$

$$T_e = \Psi_{v0}^{-1}$$

The expression for the change in entropy (3.17) has a canonical form, used in the thermodynamics of irreversible processes. The first term on the right-hand side of Eq. (3.17) represents the change in entropy due to the influx of heat. The quantity T_e has the meaning of the generalized temperature. The reasons why this quantity differs from the temperature T_v were discussed previously in [2]. In the isothermal case all the definitions of the temperatures are identical: $T_v = T_s = T_e$. The quantities σ_v and σ_s represent the production of entropy in the volume and on the surface respectively. The condition for the second and third terms on the right-hand side of Eq. (3.17) to be non-negative imposes considerable limitations on the material relations, although it does not fix them uniquely.

We will present one of the versions corresponding to the classical Newton–Fick–Fourier laws

$$\tau_v^{ab} = (\eta_v - \tfrac{2}{3}\mu_v)\delta^{ab}\partial_c\nu_v^c + \mu_v(\partial_a\nu_v^b + \partial_b\nu_v^a)$$

$$\tau_{s\alpha\beta} = (\eta_s - \tfrac{2}{3}\mu_s)g_{\alpha\beta}\nabla_\gamma\nu_s^\gamma + \mu_s(\nabla_\alpha\nu_{s\beta} + \nabla_\beta\nu_{s\alpha})$$

$$q_v^a = M_v^{0B}\partial_a\Psi_{vB}, \quad Q_{vi}^a = M_v^{iB}\partial_a\Psi_{vB} \tag{3.18}$$

$$q_s^\alpha = g^{\alpha\beta}M_s^{0B}\nabla_\beta\Psi_{sB}, \quad Q_{si}^\alpha = g^{\alpha\beta}M_s^{iB}\nabla_\beta\Psi_{sB}$$

$$\xi_\alpha = \nu\nu_s^\beta b_{\alpha\beta}$$

$$l_a C^a = 0$$

Here η_v, μ_v, η_s, μ_s, ν are non-negative dissipative coefficients and M_v^{AB}, M_s^{AB} $(A, B = 0, \ldots, K)$ are non-negative symmetrical matrices, which satisfy the additional conditions $m_i M_v^{iB} = 0$, $m_i M_s^{iB} = 0$. Expressions (3.18), apart from the last one, represent a set of material relations which close the hydrodynamic problem. The last equation of (3.18) is an additional boundary condition, which relates the velocity field in the volume and on the surface. We emphasize that, in the theory considered, there is no no-slip condition, since the possibility of adsorption and desorption presupposes a non-zero mean-mass velocity on ∂D.

The hydrodynamic model constructed corresponds to the static theory developed in Section 2: the stationary solutions of the hydrodynamic equations are identical with the solutions of the equilibrium equations (2.6). The proof of this assertion is completely analogous to the proofs presented previously in [1, 2].

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