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CHEMICAL POTENTIAL TENSOR FOR A TWO-PHASE CONTINUOUS MEDIUM MODEL

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Relations for jumps of thermodynamic variables with allowance for inertial terms are derived under conditions of thermal equilibrium and in the absence of dissipation on the interphase surface. The notion of the chemical potential tensor is generalized for this case within the framework of the elastic continuous medium model. A thermodynamically well-posed definition of the chemical potential tensor is proposed for a class of two-phase models of deformable solids.

Key words: *chemical potential tensor, two-phase model of deformable solids.*

Introduction. Numerous experimental investigations show that almost all materials experience phase transitions under thermomechanical actions. In the macroscopic theory of continuous media, the origination of regions of the new phase is interpreted as the emergence of an interphase boundary, which is a discontinuity surface for certain thermodynamic potentials of the medium and their derivatives. These discontinuities have been well studied for the case of thermal and mechanical equilibrium of the liquid (gas) phases. One difficulty in studying phase transformations in solids is the necessity of using a tensor set of variables for the description of the state of materials, e.g., the stress and strain tensors. In contrast to the classical case of equilibrium of the liquid (gas) phases, one has to avoid the traditional concepts of some quantities, in particular, one has to take into account the tensor character of the chemical potential on discontinuity surfaces. It was Gibbs who showed long ago [1] that a soluble solid in the state of mechanical and chemical equilibrium with its solutions at different pressures should obey the conditions of identical chemical potentials in contacting phases, and the equilibrium conditions derived by Gibbs show that the introduced chemical potential of the motionless component depends on the choice of the spatial direction: position of the solid-body boundary. Though Gibbs did not clearly stipulate the necessity of introducing the notion of the chemical potential tensor, this notion is naturally introduced in the theory of heterogeneous phase equilibrium of single-component substances [2], and the corresponding approach is commonly called the theory of the local chemical potential.

On the other hand, formation of one or several phases is a consequence of physical and chemical transformations in the material and can proceed in the entire volume of the body. The directed character of these transformations in materials depends on their mechanical state determined by defining the stress tensor as a function of spatial coordinates and time. Beginning from 1960s, this made chemists consider the chemical potential as a tensor object, regardless of availability of the selected surface; the corresponding approach is commonly called the theory of the absolute chemical potential [3]. The main difficulty in determining the chemical potential tensor is the fact that, if the chemical potential is a tensor, then the thermodynamically conjugate quantity (number of moles) is also a tensor. From the thermodynamic definition of the chemical potential, however, it follows that the number of moles is an obviously scalar quantity. Rusanov [3] suggested that the change in the number of moles could be attributed a directed character; the resultant anisotropy of the chemical potential tensor is determined by anisotropy of the stress tensor.

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In the theories of the local and absolute chemical potentials, the problem of defining the chemical potential tensor was considered in the quasi-static approximation. It is shown in Sec. 1 of the present paper that the definition of the chemical potential tensor introduced in the theory of heterogeneous phase equilibrium [2] should be corrected if inertial terms are taken into account in deriving relations on the interface under conditions of thermal equilibrium and in the absence of dissipation. For the elastic continuous medium model, the correlation between the corrected definition of the chemical potential tensor and the corresponding definition in the theory of the absolute chemical potential is demonstrated in Sec 2. In a particular case of mechanical equilibrium, both definitions yield the known condition of continuity of the normal component of the chemical potential tensor [2, 4]. A thermodynamically well-posed variant of introduction of the chemical potential tensor for the class of two-phase models of deformable solids with arbitrary strains is described in Secs. 3–5.

1. Relations on the Interphase Surface. It is well known [4] that the following relations for the jumps in quantities in Eulerian variables are valid for the interphase surface (interface) moving with a velocity L relative to the observation point:

$$[\rho(L - v_n)] = 0; \tag{1}$$

$$[\rho(L - v_n)v^i] + [\sigma_{ik}]n_k = 0; \tag{2}$$

$$[\rho(L - v_n)(u + |\boldsymbol{v}|^2/2)] + [\sigma_{ik}v^i]n_k = [J_k^{(q)}]n_k; \tag{3}$$

$$[\rho(L - v_n)s] = [J_k^{(q)}/T]n_k - R; \tag{4}$$

$$[\rho(L - v_n)F_k^i] + [\rho v^i F_k^l]n_l = 0. \tag{5}$$

Here ρ is the density, σ_{ik} is the stress tensor, v^i are the velocity components, $v_n = v^k n_k$, where n_k are the components of the external (relative to one of the phases) unit normal to the discontinuity surface with respect to the observation point, u and s are the specific internal energy and entropy, $J_k^{(q)}$ are the components of the heat-flux vector, R is the entropy production on the jump, $F_k^i = \partial x^i/\partial \xi^k$ determines the strain gradient, and relation (5) indicates the absence of a singular source of strain incompatibility. The symbol $[f] = f|_+ - f|_-$ indicates a jump in a quantity f on the sides of the discontinuity surface.

Let us consider a phase transition for which $[T] = 0$ and $R = 0$. In this case, Eq. (1) yields

$$\rho(L - v_n) = m = \text{const}.$$

To calculate the jumps in the product of quantities in (2)–(5), we use the formula

$$[ab] = [a]b|_- + [b]a|_+. \tag{6}$$

Then, Eq. (2) is written in the form

$$[\sigma_{ik}]n_k = -m[v^i]. \tag{7}$$

Multiplying Eq. (5) by n_i and summing in terms of i, we obtain $L[\rho F_k^i]n_i = 0$, which means that the components $S_k = \rho F_k^l n_l$ of the vector $\boldsymbol{S}$ on the discontinuity surface are continuous. Then, the jump of the strain gradient is

$$[F_k^i] = h^i S_k, \qquad h^i = -[v^i]/m. \tag{8}$$

Let us consider relations (3) and (4). Eliminating the normal component of the heat-flux vector from these equations, we obtain

$$m[(f + |\boldsymbol{v}|^2/2)] + [\sigma_{ik}v^i]n_k = 0, \tag{9}$$

where $f = u - Ts$ is the density of free energy of the continuous medium. Using Eq. (6), we write the second jump in Eq. (9) as follows:

$$[\sigma_{ik}v^i]n_k = [\sigma_{ik}n_k]v^i|_- + [v^i]n_k\sigma_{ik}|_+. \tag{10}$$

Applying formula (7) to the first term in Eq. (10), we obtain

$$[\sigma_{ik}v^i]n_k = -m[|\boldsymbol{v}|^2] + [v^i](n_k\sigma_{ik}|_+ + mv^i|_+).$$

The velocity jump is determined from Eq. (8):

$$[v^i] = -m[F^i_k]S_k/|\boldsymbol{S}|^2. \tag{11}$$

By means of direct calculations, we can verify that

$$[v^i](n_k\sigma_{ik}|_+ + mv^i|_+) = -m\{[F^i_kS_kn_l\sigma_{li}] + m[F^i_kS_kv^i]\}/|\boldsymbol{S}|^2.$$

Then, relation (9) becomes

$$m[f] - m\{[|\boldsymbol{v}|^2]/2 + m[F^i_kS_kv^i]/|\boldsymbol{S}|^2 + [F^i_kS_kn_l\sigma_{li}]/|\boldsymbol{S}|^2\} = 0. \tag{12}$$

Since

$$[|\boldsymbol{v}|^2]/2 = [v^k]v^k|_+ - [v^k][v^k]/2,$$

$$m[F^i_kS_kv^i]/|\boldsymbol{S}|^2 = -[v^k]v^k|_+ + mS_k[v^i]F^i_k|_-/|\boldsymbol{S}|^2,$$

the sum of the two first terms in braces in Eq. (12) with allowance for Eq. (11) is

$$[|\boldsymbol{v}|^2]/2 + m[F^i_kS_kv^i]/|\boldsymbol{S}|^2 = -m^2[F^i_kS_kF^i_mS_m]/(2|\boldsymbol{S}|^4). \tag{13}$$

Summarizing all calculations, we finally obtain

$$m[f] - m[F^i_kS_kn_l\sigma_{li}]/|\boldsymbol{S}|^2 + m^3[F^i_kS_kF^i_mS_m]/(2|\boldsymbol{S}|^4) = 0. \tag{14}$$

Relation (14) is an analog of Gibbs' classical condition of phase equilibrium [1] with allowance for dynamics of the medium. The condition of continuity of the normal component of the Eulerian chemical potential tensor in equilibrium arises if the last term in Eq. (14) is ignored, which corresponds to the formal transition $m \to 0$. Indeed, neglecting the last term and using the definition of quantities in Eq. (14), we obtain

$$m\{[u - Ts - F^i_kF^j_kn_jn_l\sigma_{li}/(\rho F^i_kF^j_kn_in_j)]\} = 0. \tag{15}$$

Since $F^i_kF^j_k = g^{ij}$, Eq. (15) is equivalent to

$$m\{[u - Ts - g^{ij}n_jn_l\sigma_{li}/(\rho g^{ij}n_in_j)]\} = 0. \tag{16}$$

We introduce the tensors

$$\mu_{ik} = -\sigma_{ik}/\rho + \delta_{ik}(u - Ts), \qquad M^j_i = g^{jk}\mu_{ik}/(g^{pq}n_pn_q). \tag{17}$$

The tensor μ^j_k coincides with Bowen's symmetric chemical potential tensor [5]; then, it follows from here and from Eq. (16) that the normal component of the tensor M^j_i is continuous:

$$m[n_iM^j_in_j] = 0. \tag{18}$$

This relation shows that the condition of continuity of the normal component of the chemical potential tensor under equilibrium conditions arises as a requirement of vanishing of the leading term in the expansion with respect to the small parameter m.

Allowance for dynamics of the medium is responsible for an additional contribution (proportional to m^3) in the energy condition (14) on the discontinuity, as compared to the equilibrium situation. This makes us modify the definition of the chemical potential tensor proposed in the theory of the local chemical potential [4]. As this definition is based on the use of the discontinuity condition (18), its formal generalization for the discontinuity (14) yields the condition of continuity of the normal component of the following tensor X^j_i:

$$\begin{gathered} m[n_iX^j_in_j] = 0, \qquad X^j_i = g^{jk}x_{ik}/(g^{pq}n_pn_q), \\ x_{ik} = -\sigma_{ik}/\rho + \delta_{ik}(u - Ts) + m^2g^{ik}/(2\rho^2g^{pq}n_pn_q). \end{gathered} \tag{19}$$

We will further show how it is possible to introduce the chemical potential tensor within the framework of the elastic continuous medium model.

2. Chemical Potential of an Elastic Medium. The volume density of energy E_{el} of an elastic medium is a function of specific entropy s, components of the mass flux $j^k = \rho v^k$, and components of the metric tensor g_{ij} characterizing the medium strain. Let us write the expression for the total differential of energy:

$$dE_{\mathrm{el}} = \mu_j^i \, dg_{ij} + T \, d(\rho s) + v^k \, dj^k. \tag{20}$$

Here, we used Gibbs' identity $T = \partial E_{\mathrm{el}}/\partial \rho s$ and the fact that the derivative of energy with respect to momentum is the velocity of motion. On the other hand, the energy equals $E_{\mathrm{el}} = |\boldsymbol{j}|^2/(2\rho) + \rho u$, where $u = u(s, g_{ij})$ is the specific internal energy, and

$$dE_{\mathrm{el}} = \rho \frac{\partial u}{\partial g_{ij}} \, dg_{ij} + \rho T \, ds + d\rho \Big(u - Ts - \frac{|\boldsymbol{v}|^2}{2} \Big) + v^k \, dj^k. \tag{21}$$

The law of conservation of mass $\rho = \rho_0 \sqrt{\det \|g_{ij}\|}$ yields $d\rho = \rho g^{ij} \, dg^{ij}/2$, where g^{ij} are the components of the inverse metric tensor. As we consider a model of an elastic continuous medium, the equation of state is given by the relation [6]

$$\rho \frac{\partial u}{\partial g_{ij}} = -\frac{1}{2} \sigma_{jk} g^{ki}.$$

Combining it with Eq. (21), we obtain

$$dE_{\mathrm{el}} = (1/2) g^{ik} (-\sigma_{jk} + \rho \delta_{jk} (u - Ts - |\boldsymbol{v}|^2)/2) \, dg_{ij} + T \, d(\rho s) + v^k \, dj^k. \tag{22}$$

A comparison of Eqs. (22) and (20) yields the following expression for μ_j^i:

$$\mu_j^i = g^{ik} \rho \mu_{jk}/2, \qquad \mu_{jk} = (-\sigma_{jk}/\rho + \delta_{jk}(u - Ts - |\boldsymbol{v}|^2/2)). \tag{23}$$

It is seen from here that Eq. (23) coincides with Eq. (17) in equilibrium, i.e., for $\boldsymbol{v} = 0$. Therefore, the tensor μ_{ik} in Eq. (23) is the chemical potential tensor introduced regardless of the presence or absence of the selected surface, and its anisotropy is completely determined by anisotropy of the stress tensor. If the mechanical state of the medium is isotropic and equilibrium, i.e., $\sigma_{ik} = -\delta_{ik} p$ and $\boldsymbol{v} = 0$, then we have

$$\mu_{ik} = \delta_{ik}(u + p/\rho - Ts) = \delta_{ik} \psi.$$

The quantity ψ determines the specific thermodynamic potential. It is known that the chemical potential can be treated, with accuracy to a constant, as a specific thermodynamic potential. Hence, in the mechanically isotropic equilibrium state, all eigenvalues of the tensor μ_{ik} are identical and are determined by a scalar quantity, which is commonly called the chemical potential.

Though the chemical potential tensors defined by relations (17) and (23) coincide in the limiting case of mechanical equilibrium, it is not reasonable to consider Eq. (23) as a generalization of the definition of the chemical potential tensor to the dynamic case, because the jump of the normal component (23) on the phase surface does not coincide with the jump (19).

A possible way out of this situation is to consider an elastic material with an emerging new phase as a two-phase continuous medium. Formation of the new phase can be represented as an elementary excitation with a pulse $\boldsymbol{p}$ in the first phase. We pass to a reference system K_0, where the velocity of the first phase equals zero, and its pulse is $\boldsymbol{p}$. The values of the energy E in the coordinate system fitted to the observation point are related to its values in the system K_0 by the following conversion formulas known from mechanics:

$$E = |\boldsymbol{j}|^2/(2\rho) + j^k p^k/\rho + \rho u. \tag{24}$$

The energy u is considered as a function of the metric tensor g_{ij} and specific entropy s. Further calculations are similar to those performed at the beginning of the present Section; therefore, we omit them and find that E satisfies the thermodynamic relation

$$dE = (1/2) \rho g^{ik} (-\sigma_{jk}/\rho + \delta_{jk}(u - Ts - |\boldsymbol{v}|^2/2) - v^k p^k/\rho) \, dg_{ij} + T \, d(\rho s) + (v^k + p^k/\rho) \, dj^k.$$

We introduce the tensors z_{ik} and Z_i^j, assuming that

$$z_{ik} = -\sigma_{ik}/\rho + \delta_{ik}(u - Ts - |\boldsymbol{v}|^2/2 - v^s p^s/\rho), \qquad Z_i^j = g^{jk} z_{ki}/(g^{pq} n_p n_q). \tag{25}$$

Under conditions of mechanical equilibrium, we have $\boldsymbol{v} = 0$ and $z_{ik} = x_{ik}$. We choose the components p^k of the pulse $\boldsymbol{p}$ in the form

$$p^i = m g^{ik} n_k/(g^{pq} n_p n_q).$$

Combining Eqs. (25) and (13) yields $[n_i Z_i^j n_j] = [n_i X_i^j n_j] = 0$. Thus, the normal component of the tensor Z_i^j is continuous, and z_{ik} is a "candidate" for the chemical potential tensor. It was shown above that x_{ik} [see Eq. (19)] can also be considered as a chemical potential tensor. Nevertheless, the local values of z_{ik} and x_{ik} do not coincide in the general case: only their static contribution coincides.

The fact of ambiguous introduction of thermodynamic potentials is already known in the scientific literature [6]. It turns out that this fact can be useful for correcting the equations of state of the continuous medium. In particular, such a correction in [6, § 31] allows one to change the equation of state of the nonlinear elasticity theory so that it becomes rigorously convex without changing the smooth solutions of the elasticity theory and to bring the system of conservation laws to a symmetric hyperbolic form.

In the case of formation of a new phase considered here, this process should be modeled within the framework of the formal description of mechanics of heterogeneous media. Deriving only balance equations of conservation in a very generic form does not present particular interest for mechanics of mixtures, because particular applications of these equations are associated with the use of certain hypotheses on phase interaction. Below, we will show how the chosen hypothesis determines the structure of the chemical potential tensor that appears in the theory.

3. Governing Equations. First, we write the balance equations of conservation for a two-phase continuous medium. Such a medium obeys the law of conservation of mass

$$\frac{\partial \rho}{\partial t} + \frac{\partial j^k}{\partial x^k} = 0, \tag{26}$$

where the mass flux equals the sum of mass fluxes associated with each phase: $j^k = \rho_1 v_1^k + \rho_2 v_2^k$. The coefficients ρ_1 and ρ_2 are the densities of the phases, and their sum equals the density of the material: $\rho = \rho_1 + \rho_2$.

The law of conservation of momentum is described by the equation

$$\frac{\partial j^i}{\partial t} + \frac{\partial \Pi^{ik}}{\partial x^k} = 0, \tag{27}$$

where $\Pi^{ik} = \rho_1 v_1^i v_1^k + \rho_2 v_2^i v_2^k - \sigma^{ik}$ is the momentum-flux density tensor. The equation of conservation for the energy E and entropy s is written in the divergent form as

$$\frac{\partial E}{\partial t} + \frac{\partial Q^k}{\partial x^k} = 0; \tag{28}$$

$$\frac{\partial \rho s}{\partial t} + \frac{\partial J^k}{\partial x^k} = D, \qquad D \geq 0, \tag{29}$$

where Q^k and J^k are the components of the energy-flux vector and the entropy-flux vector, and D is a dissipative function.

The equations formulated above should be supplemented by the equation for the second phase velocity v_2^k and for the quantity characterizing material strains. The equation for the velocity v_2^k is written in the form

$$\frac{\partial v_2^k}{\partial t} + v_2^i \frac{\partial v_2^k}{\partial x^i} = I^k. \tag{30}$$

In the right side of Eq. (30), we introduced a source for the second phase. It is shown below that the structure of this source is determined by the requirement of representing the dissipative function as a bilinear form of thermodynamic forces and fluxes.

To characterize the strain of the continuous medium, we can introduce the strain tensor g_{ij}. If we consider each phase separately, the strain tensor within the framework of the classical model of an elastic medium is determined via the distortion p_i^α:

$$g_{ij} = p_i^\alpha p_j^\alpha, \qquad p_i^\alpha = \frac{\partial \xi^\alpha}{\partial x^i}, \qquad \frac{d\xi^\alpha}{dt} = \frac{\partial \xi^\alpha}{\partial t} + v^k \frac{\partial \xi^\alpha}{\partial x^k} = 0.$$

This yields the equation for the classical distortion in the form

$$\frac{\partial p_i^\alpha}{\partial t} + \frac{\partial}{\partial x^i}\, v^k p_k^\alpha = 0. \tag{31}$$

In the general case, one should take into account the relative motion of the phases to describe the heterogeneous structure of the medium. The use of this fact in particular models is associated with additional hypotheses on the mutual deformation and motion of the phases. A possible approach to this problem is indicated, e.g., in [7]: the authors proposed to introduce the external strain-rate tensor characterizing displacement of particles of a selected volume and the true strain-rate tensor taking into account the structure of the components of the mixture.

The idea of calculating strain characteristics via the velocity field can be used in formulating the transport equations in the two-phase model. We assume that the characteristic of strain of a two-phase medium is chosen to be the distortion matrix P_i^α determined as the solution of the differential equation of the type (31):

$$\frac{\partial P_i^\alpha}{\partial t} + \frac{\partial}{\partial x^i}\, u^k P_k^\alpha = 0. \tag{32}$$

Here, the velocity components u^k along which P_i^α is transferred are unknown. It directly follows from Eq. (32) that the solution P_i^α is generated by a certain vector field η^α: $P_i^\alpha = \partial\eta^\alpha/\partial x^i$. Nevertheless, η^α cannot be identified with the Lagrangian coordinate of any phase of the mixture, because the components u^k are to be determined. The constraints imposed on u^k are related to the kinematic and thermodynamic well-posedness of the relations obtained. A natural kinematic requirement is satisfaction of the law of conservation of mass (26). In the classical elastic medium model, the integrated form of this law is $\rho = \rho_0 |\det \|P_i^\alpha\||$. If we differentiate this relation with the use of Eq. (32) and compare the result with Eq. (26), we find that the components u^k are determined via the mass flux as follows:

$$u^k = j^k/\rho.$$

Hence, the velocity $\boldsymbol{u}$ coincides with the mean-mass velocity of the mixture. In the general case, $\boldsymbol{u}$ can differ from the mean-mass velocity, but this case is outside the scope of the present paper.

4. Dissipative Function of a Two-Phase Medium. Let us pass to the reference system K_0, where the velocity v_2^k equals zero. In this reference system, the medium moves with the velocity $w^k = v_1^k - v_2^k$. The values of the mass and energy fluxes in the observation-point-fitted coordinate system are related to their values in the system K_0 by the following conversion formulas known from mechanics:

$$j^k = \rho v_2^k + j_0^k, \qquad j_0^k = \rho_1 w^k, \qquad E = \rho|\boldsymbol{v}_2|^2/2 + j_0^k v_2^k + E_0. \tag{33}$$

The energy E_0 is considered as a function of distortions P_i^α, specific entropy s, and j_0^k and satisfies the thermodynamic relation

$$dE_0 = \mu_i^\alpha\, dP_i^\alpha + T\, d(\rho s) + w^k\, dj_0^k, \tag{34}$$

written in the form

$$\frac{\partial E_0}{\partial t} = \mu_i^\alpha \frac{\partial P_i^\alpha}{\partial t} + T\frac{\partial \rho s}{\partial t} + w^k \frac{\partial j_0^k}{\partial t}.$$

We perform further calculations as follows. We substitute E from Eq. (33) into the equation of conservation of energy (28); the derivative $\partial E_0/\partial t$ is expressed in accordance with Eq. (34) in which the derivative $\partial\rho s/\partial t$ is eliminated with the help of Eq. (29). Then, Eq. (28) is reduced to

$$\mu_i^\alpha \frac{\partial P_i^\alpha}{\partial t} + T\Big(D - \frac{\partial J^k}{\partial x^k}\Big) + w^k \frac{\partial j_0^k}{\partial t} + \frac{\partial}{\partial t}\Big(\frac{\rho|\boldsymbol{v}_2|^2}{2} + j_0^k v_2^k\Big) = -\frac{\partial Q^k}{\partial x^k}.$$

From here, we find

$$D = \frac{\partial}{\partial x^k}\Big(J^k - \frac{Q^k}{T}\Big) - \frac{1}{T^2}\frac{\partial T}{\partial x^k}\frac{\partial Q}{\partial x^k} - \frac{1}{T}\mu_i^\alpha \frac{\partial P_i^\alpha}{\partial t} - \frac{1}{T} w^k \frac{\partial j_0^k}{\partial t} - \frac{1}{T}\frac{\partial}{\partial t}\Big(\frac{\rho|\boldsymbol{v}_2|^2}{2} + j_0^k v_2^k\Big). \tag{35}$$

Let us consider two last contributions in Eq. (35). The derivatives of ρ with respect to time are eliminated with the help of Eq. (26), and the derivative of j_0^k is expressed in terms of the derivatives of ρ and j^k, in accordance with Eqs. (33) and (27). As a result, we obtain

$$-\frac{1}{T}\,w^k\,\frac{\partial j_0^k}{\partial t}-\frac{1}{T}\,\frac{\partial}{\partial t}\Big(\frac{\rho|\boldsymbol{v}_2|^2}{2}+j_0^k v_2^k\Big)=\frac{\partial}{\partial x^k}\,\frac{1}{T}\Big(\frac{j^k|\boldsymbol{v}_2|^2}{2}+\rho_1 v_1^k v_1^i w^i\Big)$$
$$+\frac{1}{T^2}\,\frac{\partial T}{\partial x^k}\Big(\frac{j^k|\boldsymbol{v}_2|^2}{2}+\rho_1 v_1^k v_1^i w^i\Big)-\frac{1}{T}\,j^k\,\frac{\partial}{\partial x^k}\Big(\frac{|\boldsymbol{v}_2|^2}{2}-v_1^i v_2^i\Big)$$
$$-\frac{1}{T}\,\frac{\partial v_1^k}{\partial x^k}\,(\rho_1 v_1^k v_1^i+\rho_2 v_2^k v_2^i)-\frac{1}{T}\,v_1^k\,\frac{\partial \sigma_k^i}{\partial x^i}+\frac{\rho_2}{T}\,w^k\,\frac{\partial v_2^k}{\partial t}.$$

Using Eq. (32), we find the convolution $\mu_i^\alpha\,\partial P_i^\alpha/\partial t$:

$$-\frac{1}{T}\,\mu_i^\alpha\,\frac{\partial P_i^\alpha}{\partial t}=\frac{\partial}{\partial x^k}\Big(\frac{1}{T}\,u^k\mu_i^\alpha P_i^\alpha\Big)+\frac{1}{T^2}\,\frac{\partial T}{\partial x^k}\,u^k\mu_i^\alpha P_i^\alpha+\frac{1}{T}\,\frac{\partial u^k}{\partial x^i}\,(\mu_i^\alpha P_k^\alpha-\delta_{ik}\mu_s^\alpha P_s^\alpha)-\frac{1}{T}\,P_i^\alpha u^k\,\frac{\partial \mu_i^\alpha}{\partial x^k}.$$

We identify the pressure p and the deviatoric contribution in the stress tensor, assuming that $\sigma_k^i=\tau_k^i-\delta_k^i p$. Then, we obtain

$$\frac{v_1^k}{T}\,\frac{\partial \sigma_k^i}{\partial x^i}=\frac{\partial}{\partial x^i}\Big(\frac{1}{T}\,v_1^k\tau_k^i\Big)+\frac{1}{T^2}\,\frac{\partial T}{\partial x^i}\,v_1^k\tau_k^i-\frac{1}{T}\,\tau_k^i\,\frac{\partial v_1^k}{\partial x^i}-\frac{1}{T}\,v_1^k\,\frac{\partial p}{\partial x^k}.$$

Summing up the resultant relations, we obtain the following expression for the dissipative function:

$$D=\frac{\partial}{\partial x^k}\Big(J^k+\frac{1}{T}\Big(-Q^k+\frac{j^k|\boldsymbol{v}_2|^2}{2}+\rho_1 v_1^k v_1^i w^i+u^k\mu_i^\alpha P_i^\alpha-v_1^i\tau_k^i\Big)\Big)$$
$$+\frac{1}{T^2}\,\frac{\partial T}{\partial x^k}\Big(-Q^k+\frac{j^k|\boldsymbol{v}_2|^2}{2}+\rho_1 v_1^k v_1^i w^i+u^k\mu_i^\alpha P_i^\alpha-v_1^i\tau_i^k\Big)$$
$$+\frac{1}{T}\,v_1^k\,\frac{\partial p}{\partial x^k}-\frac{u^k}{T}\,P_i^\alpha\frac{\partial \mu_i^\alpha}{\partial x^k}+\frac{1}{T}\,\frac{\partial u^k}{\partial x^i}\,(\mu_i^\alpha P_k^\alpha-\delta_{ik}\mu_s^\alpha P_s^\alpha)$$
$$-\frac{1}{T}j^k\,\frac{\partial}{\partial x^k}\Big(\frac{|\boldsymbol{v}_2|^2}{2}-v_1^i v_2^i\Big)-\frac{1}{T}\,\frac{\partial v_1^k}{\partial x^k}\,(\rho_1 v_1^k v_1^i+\rho_2 v_2^k v_2^i)+\frac{\tau_k^i}{T}\,\frac{\partial v_1^k}{\partial x^i}+\frac{\rho_2}{T}\,w^k\,\frac{\partial v_2^k}{\partial t}. \tag{36}$$

We introduce p by the formula

$$E_0+p=\mu_i^\alpha P_i^\alpha/3+\rho_1|\boldsymbol{w}|^2+T\rho s. \tag{37}$$

Differentiating Eq. (37) and using Eq. (34), we obtain the expression for the differentials of thermodynamic parameters

$$dp=(1/3)P_i^\alpha\,d\mu_i^\alpha-(2/3)\mu_i^\alpha\,dP_i^\alpha+\rho s\,dT+j_0^k\,dw^k. \tag{38}$$

This allows us to write the contributions in Eq. (36) as follows:

$$\frac{1}{T}\,v_1^k\,\frac{\partial p}{\partial x^k}-\frac{u^k}{T}\,P_i^\alpha\,\frac{\partial \mu_i^\alpha}{\partial x^k}=-\frac{\partial}{\partial x^k}\Big(\frac{2}{3}\,\frac{v_1^k}{T}\,\mu_i^\alpha P_i^\alpha\Big)+\frac{\partial v_1^k}{\partial x^k}\,\frac{2}{3T}\,\mu_i^\alpha P_i^\alpha$$
$$-\frac{2}{3T^2}\,\frac{\partial T}{\partial x^k}\,v_1^k\mu_i^\alpha P_i^\alpha+\frac{1}{T}\,(v_1^k-u^k)P_i^\alpha\,\frac{\partial \mu_i^\alpha}{\partial x^k}+\frac{1}{T}\,\rho s v_1^k\,\frac{\partial T}{\partial x^k}+j_0^i\,\frac{\partial w^i}{\partial x^k}\,v_1^k. \tag{39}$$

Then, the dissipative function (36) becomes

$$D=\frac{\partial}{\partial x^k}\Big(J^k+\frac{1}{T}\Big(-Q^k+\frac{j^k|\boldsymbol{v}_2|^2}{2}+\rho_1 v_1^k v_1^i w^i+u^k\mu_i^\alpha P_i^\alpha-\frac{2}{3}\,v_1^k\mu_i^\alpha P_i^\alpha-v_1^i\tau_k^i\Big)\Big)$$
$$+\frac{1}{T^2}\,\frac{\partial T}{\partial x^k}\Big(-Q^k+\frac{j^k|\boldsymbol{v}_2|^2}{2}+\rho_1 v_1^k v_1^i w^i+u^k\mu_i^\alpha P_i^\alpha-\frac{2}{3}\,v_1^k\mu_i^\alpha P_i^\alpha-v_1^i\tau_i^k+\rho s T v_1^k\Big)$$
$$+\frac{1}{T}\,(v_1^k-u^k)P_i^\alpha\,\frac{\partial \mu_i^\alpha}{\partial x^k}+\frac{1}{T}\,\frac{\partial u^k}{\partial x^i}\,(\mu_i^\alpha P_k^\alpha-\delta_{ik}\mu_s^\alpha P_s^\alpha)+\frac{\tau_k^i}{T}\,\frac{\partial v_1^k}{\partial x^i}+\frac{2}{3T}\,\frac{\partial v_1^k}{\partial x^k}\,\mu_i^\alpha P_i^\alpha$$
$$+\frac{1}{T}\,j_0^i\,\frac{\partial w^i}{\partial x^k}\,v_1^k-\frac{1}{T}\,j^k\,\frac{\partial}{\partial x^k}\Big(\frac{|\boldsymbol{v}_2|^2}{2}-v_1^i v_2^i\Big)-\frac{1}{T}\,\frac{\partial v_1^k}{\partial x^k}\,(\rho_1 v_1^k v_1^i+\rho_2 v_2^k v_2^i)+\frac{\rho_2}{T}\,w^k\,\frac{\partial v_2^k}{\partial t}. \tag{40}$$

After simple calculations, we obtain

$$j_0^i\,\frac{\partial w^i}{\partial x^k}\,v_1^k - j^k\,\frac{\partial}{\partial x^k}\Big(\frac{|\boldsymbol{v}_2|^2}{2} - v_1^i v_2^i\Big) - \frac{\partial v_1^k}{\partial x^k}\,(\rho_1 v_1^k v_1^i + \rho_2 v_2^k v_2^i) = \rho_2 v_2^k w^i\,\frac{\partial v_2^i}{\partial x^k}.$$

This term is grouped with the last contribution in Eq. (40) to the expression

$$\frac{\rho_2}{T}\,w^k\Big(\frac{\partial v_2^k}{\partial t} + v_2^i\,\frac{\partial v_2^k}{\partial x^i}\Big).$$

In accordance with the standard scheme of nonequilibrium thermodynamics, the dissipative function should be presented as a bilinear form of thermodynamic forces and fluxes [8]. For this purpose, we present the source in Eq. (30) as

$$I^k = \frac{1}{\rho}\,\frac{\partial \Gamma_q^k}{\partial x^q} - \frac{P_i^\alpha}{\rho}\,\frac{\partial \mu_i^\alpha}{\partial x^k},$$

where the functions Γ_q^k are to be determined. Since $(v_1^k - u^k) = w^k\rho_2/\rho$, we obtain

$$\frac{w^k\rho_2}{T}\Big(\frac{\partial v_2^k}{\partial t} + v_2^i\,\frac{\partial v_2^k}{\partial x^i}\Big) + \frac{v_1^k - u^k}{T}\,P_i^\alpha\,\frac{\partial \mu_i^\alpha}{\partial x^k} = \frac{w^k\rho_2}{T\rho}\,\frac{\partial \Gamma_q^k}{\partial x^q}$$

$$= \frac{\partial}{\partial x^i}\Big(\frac{w^k\rho_2}{T\rho}\,\Gamma_q^k\Big) + \frac{\rho_2}{\rho T^2}\,\frac{\partial T}{\partial x^q}\,\Gamma_q^k w^k - \frac{\Gamma_q^k}{T}\,\frac{\partial}{\partial x^q}\Big(\frac{w^k\rho_2}{\rho}\Big).$$

We choose the flux J^k in the form

$$J^k = \frac{1}{T}\Big(Q^k - \frac{j^k|\boldsymbol{v}_2|^2}{2} - \rho_1 v_1^k v_1^i w^i - u^k\mu_i^\alpha P_i^\alpha + \frac{2}{3}\,v_1^k\mu_i^\alpha P_i^\alpha + v_1^i\tau_k^i - \frac{\rho_2}{\rho}\,\Gamma_k^q w^q\Big).$$

In the approximation of linear relations, we assume that

$$J^k - \rho s v_1^k = -\lambda\,\frac{\partial T}{\partial x^k}, \qquad \lambda \geq 0.$$

As a result, relation (40) is written as

$$D = \frac{\lambda}{T}\,\frac{\partial T}{\partial x^k}\,\frac{\partial T}{\partial x^k} + \frac{1}{T}\,\frac{\partial v_1^k}{\partial x_i}\Big(\mu_i^\alpha P_k^\alpha - \frac{1}{3}\,\delta_{ik}\mu_s^\alpha P_s^\alpha + \tau_{ik}\Big) + \frac{1}{T}\,(\mu_i^\alpha P_k^\alpha - \delta_{ik}\mu_s^\alpha P_s^\alpha - \Gamma_i^k)\,\frac{\partial}{\partial x_i}\Big(\frac{\rho_2 w^k}{\rho}\Big).$$

In such a form, the dissipative function is presented as a bilinear form of thermodynamic forces and fluxes: $D(X) = X^i Y_i$ and $\partial D/\partial X^i = Y^i$.

5. Chemical Potential of a Two-Phase Dissipation-Free Medium. Further detalization of the relations obtained is associated with choosing the energy E_0 and the dissipative function D. Let E_0 be prescribed, and the dissipative function be zero. This yields the following relations:

$$\tau_{ik} = -\mu_i^\alpha P_k^\alpha + (1/3)\delta_{ik}\mu_s^\alpha P_s^\alpha, \qquad \Gamma_i^k = \mu_i^\alpha P_k^\alpha - \delta_{ik}\mu_s^\alpha P_s^\alpha.$$

The convolution $\mu_s^\alpha P_s^\alpha$ is calculated in accordance to Eq. (37); then, we have

$$\mu_i^\alpha P_k^\alpha = -\sigma_{ik} + \delta_{ik}(E_0 - \rho T s - \rho_1|\boldsymbol{w}|^2). \tag{41}$$

We introduce the chemical potential tensor μ_j^i of a two-phase dissipation-free medium via μ_i^α. For this purpose, we require satisfaction of the equality $\mu_j^i\,dG_{ij} = \mu_i^\alpha\,dP_i^\alpha$, where $G_{ij} = P_i^\alpha P_j^\alpha$, which is equivalent to the transition from the kinematic set of variables P_i^α to g_{ij} in the energy E_0 (34). This yields $\mu_j^\alpha = 2\mu_j^i P_i^\alpha$.

We introduce the matrix Q_α^s inverse to P_i^α: $P_i^\alpha Q_\alpha^s = \delta_i^s$; then, Eq. (41) yields

$$\mu_i^\alpha = Q_\alpha^k(-\sigma_{ik} + \delta_{ik}(E_0 - \rho T s - \rho_1|\boldsymbol{w}|^2))$$

and the chemical potential tensor μ_j^i of the two-phase medium

$$\mu_j^i = (1/2)G^{ik}(-\sigma_{jk} + \delta_{jk}(E_0 - \rho T s - \rho_1|\boldsymbol{w}|^2)).$$

Anisotropy of the tensor μ_j^i is determined by anisotropy of the stress tensor, but an important factor for a two-phase medium is the relative motion of the phases.

In a particular case, E_0 depends on the tensor g_{ij} via its determinant g, which corresponds to a two-phase liquid. During calculations, one can easily find that μ^i_j has the following structure: $\mu^i_j = \rho\mu g^{ij}/2$, where μ is a certain scalar function. Then, the thermodynamic relations (34) and (38) are reduced to

$$dE_0 = \mu\, d\rho + T\, d(\rho s) + w^k\, dj^k_0, \qquad dp = \rho\, d\mu + \rho s\, dT + j^k_0\, dw^k.$$

These formulas for thermodynamic quantities coincide, in particular, with the corresponding formulas for the model of superfluid helium [9], and the function μ has the meaning of a chemical potential that determines the source (30) for the second phase: $I^k = -\partial\mu/\partial x^k$.

Conclusions. The scheme of the classical formalism of nonequilibrium thermodynamics is generalized in the present paper to construct two-phase models of deformable solids, which makes it possible to suggest a thermodynamically well-posed definition of the chemical potential tensor. A particular choice of the model is determined by specifying interaction between the phases and the dissipative function.

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