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THERMAL EFFECTS IN THE DESCRIPTION OF A MULTICOMPONENT MIXTURE USING THE DENSITY FUNCTIONAL METHOD†

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The use of a model, based on an expression for the total entropy in the form of a functional with the temperature and density gradients of the components, is proposed to describe a multicomponent, multiphase system using continuous hydrodynamics (that is, within the framework of the approach of the continuum mechanics without discontinuities in the hydrodynamic quantities). It is proved that this model is consistent with the zeroth law of thermodynamics. Expressions for the stress tensor, the diffusion fluxes and the heat flux are found from the condition that the entropy production is non-negative. Compared with the classical Newton, Fick and Fourier laws, these expressions contain third-order spatial derivatives. The problem of a mixture between two parallel and impermeable walls at different temperatures is analysed. In this case, the system of dynamic equations reduces to a system of ordinary differential equations. It is shown that the number of free parameters, on which the solution depends, corresponds to the number of boundary and general integral conditions. © 1998 Elsevier Science Ltd. All rights reserved.

A hydrodynamic model has been proposed [1] which enables viscous flows and phase transitions in a multicomponent mixture to be jointly described without introducing discontinuities at the phase boundaries. An expression for the free energy in the form of a functional, which depends on the gradients of the molar densities of the components of the mixture, was the basis of the theory; static states of the mixture correspond to the critical points of this functional.

This approach is analogous to the Ginzburg–Landau method which is conventionally used in the theory of phase transitions of the second kind [2–5] (critical phenomena, superfluidity and superconductivity), and also to the density functional method in electronics and nuclear physics [6, 7]. This density functional method differs from the Ginzburg–Landau method in that the concept of an order parameter is not required. On the other hand, up to now the use of a density functional [6, 7] has been confined to the physics of single component Fermi systems.

It has been shown [1] that the use of a density functional in the case of multicomponent gas–liquid systems reproduces a number of classical surface and capillary effects. Unlike the traditional theory of surface forces [8], the concept of a disjoining pressure is not invoked in the construction of the hydrodynamics, but they are constructed using the conventional stress tensor, for which an explicit expression can be found.

An investigation carried out earlier [1] was restricted to the framework of isothermal processes. Below, the density functional method is extended to the case of non-trivial temperature fields.

1. EQUILIBRIUM STATES

Suppose a multicomponent mixture (gas or liquid) occupies a spatial domain D with a piecewise-smooth, impermeable boundary ∂D. The whole or a part of the boundary ∂D may correspond to the contact of the mixture with the solid phase. We shall assume that (a) the Latin indices i, j, k, l run from $1, \ldots, N$, where N is the number of components; (b) the Latin indices a, b, c have values of 1, 2, 3, which correspond to certain Cartesian coordinates x^a. Summation is carried out over repeated indices. Suppose T is the absolute temperature, n_i is the molar density of the ith component and m_i is the molar mass of the ith component. If $V = V(T, n_i)$, $W = W(x^a)$ are certain smooth functions, we shall use the notation $V_{,T} = \partial V/\partial T$, $V_{,i} = \partial V/\partial n_i$, $\partial_a W = \partial W/\partial x^a$.

In the case of states with a fixed temperature, the free energy of the mixture is given by the functional [1]

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$$F = \int_D \left(\frac{1}{2} \nu_{ij} \partial_a n_i \partial_a n_j + f \right) dV + \int_{\partial D} \omega dA \tag{1.1}$$

where $\nu_{ij} = \nu_{ij}(T, n_k)$ is a positive definite symmetric matrix, $f = f(T, n_i)$ is the free energy per unit volume, calculated for homogeneous states, ω is the surface interaction energy (which can be equal to zero), dV is a volume element and dA is an element of the surface ∂D.

The static states of the mixture are the critical points of the functional (1.1) and the thermodynamically stable equilibrium states are the absolute minimum points. Here, the functional (1.1) has to be varied in the class of states with a specified number of particles of the components

$$N_i = \int_D n_i dV \tag{1.2}$$

In the case of states with a temperature distribution $T = T(x^a)$, rather than constructing a theory on the basis of the free energy (1.1), it is natural to construct this theory on the basis of the entropy of the state of the mixture, for which we have the following expression

$$S = \int_D \vartheta dV + \int_{\partial D} s_* dA, \quad \vartheta = s - \frac{1}{2} \alpha \partial_a T \partial_a T - \alpha_i \partial_a T \partial_a n_i - \frac{1}{2} \alpha_{ij} \partial_a n_i \partial_a n_j \tag{1.3}$$

where $s = s(T, n)$ is the entropy per unit volume, calculated in the class of homogeneous states, $\alpha = \alpha(T, n_i) > 0$, $\alpha_{ij} = \alpha_{ij}(T, n_k)$ is a positive definite symmetric matrix and $s_* = s_*(T, n_i)$ is the surface entropy, which may be equal to zero on certain parts of the boundary ∂D. It is assumed that the matrix $(\alpha_{ij} - \alpha_i \alpha_j \alpha^{-1})$ is positive definite.

We assume that equilibrium states of the mixture correspond to the critical points of the functional (1.3) while the thermodynamically stable states correspond to the absolute minimum points. In this case, the states have to be varied for a fixed number of particles of the components (1.2) and, also, for a fixed internal energy of the mixture

$$U = \int_D (u + \rho\varphi) dV + \int_{\partial D} u_* dA \tag{1.4}$$

Here, $u = u(T, n_i)$ is the energy per unit volume, calculated in the class of homogeneous states, $u_* = u_*(T, n_i)$ is the surface energy, $\varphi = \varphi(x^a)$ is the gravitational potential and $\rho = m_i n_i$ is the mass density.

Remark 1. The expression for the internal energy functional (1.4) does not contain the gradients of the temperature and the particle densities although, at first glance, it would follow that an expression similar to (1.3) should be used. Formula (1.4) is a consequence of the assumption that the particle density and n_i the internal energy density u serve as the primary defining characteristics, while the temperature T is a secondary characteristic which is determined from the equation $u = u(T, n_i)$. Expression (1.4) is therefore associated with the determination of the local temperature. If it is assumed that n_i and ϑ are the primary characteristics and that the temperature is determined from the equation $\vartheta = s(T', n_i)$, then the gradients in the expression for the total entropy S disappear and appear in the expression for the total internal energy U. Here, the temperatures T and T', generally speaking, are connected by a differential relation and are only identical in the case of homogeneous states. The non-uniqueness in the determination of the local temperature in a theory with spatial derivatives means that a certain third effective temperature T_e, which differs from T and T' (see below), arises in the entropy production equation.

We will now calculate the variation of the functional (1.3)

$$\delta S = \int_D (\Phi_0 \delta T + \Phi_i \delta n_i + \int_{\partial D} (\Phi_{0*} \delta T + \Phi_{i*} \delta n_i) dA \tag{1.5}$$

$$\Phi_0 = s_{,T} + \frac{1}{2} \alpha_{,T} \partial_a T \partial_a T + \alpha_{,i} \partial_a T \partial_a n_i + \alpha \Delta T +$$

$$+ \alpha_{i,j} \partial_a n_j \partial_a n_i - \frac{1}{2} \alpha_{ij,T} \partial_a n_i \partial_a n_j + \alpha_i \Delta n_i$$

$$\Phi_i = s_{,i} - \frac{1}{2} \alpha_{,i} \partial_a T \partial_a T - \alpha_{j,i} \partial_a T \partial_a n_j +$$

$$+\alpha_{i,T}\partial_a T\partial_a T+\alpha_{i,j}\partial_a n_j\partial_a T-\frac{1}{2}\alpha_{jk,i}\partial_a n_j\partial_a n_k+$$

$$+\alpha_{ij,T}\partial_a T\partial_a n_j+\alpha_{ij,k}\partial_a n_k\partial_a n_j+\alpha_{ij}\Delta n_j$$

$$\Phi_{0*}=l_a(\alpha\partial_a T+\alpha_i\partial_a n_i)+s_{*,T},\quad \Phi_{i*}=l_a(\alpha_i\partial_a T+\alpha_{ij}\partial_a n_j)+s_{*,i}$$

Here, l_a is the inward normal to the boundary ∂D and $\Delta = \partial_a\partial_a$.

For an equilibrium state of the mixture (which is not necessarily thermodynamically stable), the right-hand side of (1.5) vanishes when there are additional constraints on the variation following from (1.2) and (1.4). The differential relation

$$\delta S-\lambda_0\delta U+\lambda_i\delta N_i=0 \tag{1.6}$$

where λ_0, λ_i are Lagrange multipliers, must therefore be satisfied. When account is taken of (1.5), (1.2) and (1.4), relation (1.6) leads to a system of elliptic differential equations and boundary conditions

$$\Phi_0-\lambda_0 u_{,T}=0,\quad \Phi_i-\lambda_0(u_{,i}+m_i\varphi)+\lambda_i=0 \tag{1.7}$$

$$\Phi_{0*}\,|_{\partial D}=\lambda_0 u_{*,T},\quad \Phi_{i*}\,|_{\partial D}=\lambda_0 u_{*,i} \tag{1.8}$$

The Lagrange multipliers must be chosen such that conditions (1.2) and (1.4) and satisfied. If the distributions $T(x^a)$ and $n_i(x^a)$ are known, then, by (1.7), the Lagrange multipliers can be calculated using the formulae

$$\lambda_0=\int_D\Phi_0 dV/\int_D u_{,T}dV \tag{1.9}$$

$$\lambda_i=-\int_D(\Phi_i-\lambda_0(u_{,i}+m_i\varphi))dV/V(D) \tag{1.10}$$

where $V(D)$ is the volume of the domain D.

We recall that the thermodynamic relation [9]

$$du=Tds+\varkappa_i dn_i,\quad u=Ts+\varkappa_i n_i-p \tag{1.11}$$

holds, where $\varkappa_i$ is the chemical potential of the ith component and p is the hydrostatic pressure.

For a homogeneous state, when there are no gravitational forces, we obtain

$$\lambda_0=T^{-1},\quad \lambda_i=T^{-1}\varkappa_i \tag{1.12}$$

from (1.9) and (1.10).

We will now investigate the compatibility of the model with the well-known zeroth law of thermodynamics which states that, in the case of a thermodynamically stable equilibrium, the temperature is identical at all points of the system. We will consider relations (1.7) and (1.8) when t = const.

Suppose that β^{ij} is the inverse of the matrix α_{ij}, $\beta^{ij}\alpha_{jk}=\delta^i_k$. The $(N+1)$ equations of (1.7) contain N of the quantities Δn_i. On eliminating these quantities, we obtain the single equation

$$0=s_{,T}-\lambda_0 u_{,T}-\xi^i(s_{,i}-\lambda_0(u_{,i}+m_i\varphi)+\lambda_i)+\left(L_\xi\alpha_{ij}-\frac{1}{2}\alpha_{ij,T}\right)\partial_a n_i\partial_a n_j \tag{1.13}$$

where $\xi^i=\beta^{ij}\alpha_j$ and $L_\xi\alpha_{ij}$ is a Lie derivative [10] of the second rank tensor field α_{ij} in the N-dimensional space of the n_i along the vector field ξ^i. Since the gradients $\partial_a n_j$ at a point in the medium can be arbitrary, (1.13) splits into the two relations

$$s_{,T}-\lambda_0 u_{,T}-\xi^i(s_{,i}-\lambda_0(u_{,i}+m_i\varphi)+\lambda_i)=0 \tag{1.14}$$

$$L_\xi\alpha_{ij}-1/2\alpha_{ij,T}=0 \tag{1.15}$$

Conditions (1.14) and (1.15) are satisfied identically when account is taken of the first equality of (1.12), if

$$\alpha_i = 0, \quad \alpha_{ij,T} = 0 \tag{1.16}$$

On the other hand, if just one of conditions (1.16) is not satisfied, relation (1.14) leads to unnatural constraints on the thermodynamic functions $u = u(T, n_i)$, $s = s(T, n_i)$, since the parameter λ_0 is determined using (1.9) in a non-local manner and can take any value. Hence, starting from this instant, we shall assume that equalities (1.16) are satisfied.

A state with a constant temperature can satisfy the first of boundary conditions (1.8) only if the equality

$$u_{*,T} = Ts_{*,T} \tag{1.17}$$

holds.

Henceforth, we shall also assume that this equality is satisfied.

It turns out that conditions (1.16) and (1.17) are sufficient for the model to be compatible with the zeroth law of thermodynamics.

Lemma 1. For a specified distribution of the densities $n_i = n_i(x^a)$, the maximum of functional (1.3), subject to the additional condition (1.4), is attained at a certain constant temperature.

Proof. Suppose that, for a specified value of U, T_0 is the temperature value such that, when $T = T_0$, equality (1.4) is satisfied. For brevity, we shall label quantities calculated when $T = T_0$ with an additional zero subscript. We now take some arbitrary temperature distribution $T = T(x^a)$ which satisfies (1.4). It is obvious that

$$S - S_0 \leqslant \int_D (s - s_0)dV + \int_{\partial D} (s_* - s_{*0})dA \tag{1.18}$$

where the equality sign is only attained when $T = \text{const}$. Furthermore, the equality

$$0 = \int_D (u - u_0)dV + \int_{\partial D} (u_* - u_{*0})dA \tag{1.19}$$

holds.

Note that, since $u_{.T} > 0$, $u_{*.T} > 0$, the dependence of the functions s and s_* on the temperature T can be replaced by a dependence on the quantities u and u_*, respectively.

We will now calculate the second derivatives

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

By virtue of this, the equalities

$$s - s_0 = T_0^{-1}(u - u_0) + a \tag{1.20}$$

$$s_* - s_{*0} = T_0^{-1}(u_* - u_{*0}) + a_* \tag{1.21}$$

hold, where $a \leqslant 0$, $a_* \leqslant 0$ and the equality sign is only achieved when $T = T_0$ at a given point. On substituting expressions (1.20) and (1.21) into the right-hand side of (1.18) and using (1.19), we obtain the proof of the lemma.

Lemma 1 in fact proves that the problem of determining the maximum of the functional (1.3), subject to the additional conditions (1.2) and (1.4), is equivalent to the problem of minimizing the functions (1.1), subject to the additional conditions (1.2), which was considered earlier [1]. Here, $\nu_{ij} = T\alpha_{ij}$, $f = u - T_s$, $\omega = u_* - Ts_*$. Therefore, as far as stable equilibrium states are concerned, the results of the theory which is being developed here are identical with the results following from the isothermal model [1].

Remark 2. An analysis of the proof of Lemma 1 shows this proof still holds if $\alpha = 0$. Models, in which the entropy functional is altogether independent of the temperature gradient are therefore permissible.

2. DYNAMIC EQUATIONS

We will now consider the situation when the volume occupied by a mixture in a certain state (not necessarily an equilibrium state) is deformed into some other volume, which only differs infinitesimally from the original. Suppose that $T(x^a)$, $n_i'(x^a)$ is the initial state of the mixture, $T'(x^a)$, $n_i'(x^a)$ is the new state, and $\delta T(x^a) = T'(x^a) - T(x^a)$, $\delta n_i(x^a) = n_i'(x^a) - n_i(x^a)$. It is possible to associate a point in the final state with the coordinates

$$x^{a'} = x^a + u^a \tag{2.1}$$

where $u^a = u^a(x^b)$ is a small displacement vector, with each point x^a of the volume occupied by the mixture in the initial state. If the displacements characterize the mean mass motion, then the total mass

$$m_i n_i (x^a) dV = m_i n_i' (x^a) dV' \tag{2.2}$$

is conserved in each individual volume.

We now select an arbitrary domain $\Omega \subset D$ with a piecewise-smooth boundary which is deformed into a certain domain Ω' by means of transformation (2.1). We assume that the boundary of the domain Ω does not intersect the boundary ∂D: $\partial\Omega \subset D$. Using formula (1.3), it is possible to calculate the entropy in the initial and final states

$$S_\Omega = \int_\Omega \vartheta dV, \quad S'_{\Omega'} = \int_{\Omega'} \vartheta' dV'$$

The expression for the functional $S'_{\Omega'}$ can be transformed to an integral over the domain Ω' if formula (2.1) is interpreted as a transformation of the coordinates. In this case, it is necessary to take account of equality (2.2) as well as the following relations, which hold, apart from terms in second-order infinitesimals

$$dV' = (1 + \partial_a u^a) dV, \quad \frac{\partial}{\partial x^{a'}} = (\delta_a^b - \partial_a u^b) \frac{\partial}{\partial x^b} \tag{2.3}$$

We use the notation $\delta_* T(x^a) = T'(x^{a'}) - T(x^a)$, $\delta_* n_i(x^a) = n_i'(x^{a'}) - n_i(x^a)$. The representation

$$\delta_* n_i (x^a) = r_i (x^a) + \nu_i (x^a) \tag{2.4}$$

holds, where r_i, ν_i are quantities of the same order of infinitesimals as u^a, and the equality

$$r_i (x^a) = -\partial_b u^b (x^a) n_i (x^a) \tag{2.5}$$

is satisfied.

In the case of mean mass motion, the displacement field must satisfy the differential equation

$$\partial_a (u^a \rho) = -m_i \delta n_i \tag{2.6}$$

as a consequence of (2.2) and the first of relations (2.3).

Remark 3. Using Eq. (2.6) for the mean mass motion, it is possible to formulate the problem of determining the displacement field for specified initial and final particle density distributions of the components. The solution of this problem is known to be non-unique, since Eq. (2.6) is invariant under the substitution $u^a \to u^a + \rho^{-1} \varepsilon_{abc} \partial_b b_c$, where b_a is an arbitrary smooth vector field.

Using Eqs (2.1) and (2.3)–(2.5) and integrating by parts, we find an expression for the change in entropy

$$\delta S_\Omega = S'_{\Omega'} - S_\Omega = \int_\Omega dV (-\partial_a u^b \Sigma^{ab} + \Phi_k \nu_k + \Phi_0 \delta_* T) - \tag{2.7}$$

$$- \int_{\partial\Omega} k_a (\alpha \partial_a T \delta_* T + \alpha_{ij} \partial_a n_i \delta_* n_j) dA$$

$$\Sigma^{ab} = (\Phi_i n_i - \vartheta) \delta^{ab} - \alpha \partial_b T \partial_a T - \alpha_{ij} \partial_b n_i \partial_a n_j$$

where k_a is the outward normal to $\partial\Omega$. We will now consider the special case when the displacement field $u^a(x^b)$ vanishes in a sufficiently small neighbourhood of the boundary $\partial\Omega$. Expression (2.7) can then be rewritten in the form

$$\delta S_\Omega = \int_\Omega dV u^b (\partial_a \Sigma^{ab} - n_k \partial_b \Phi_k + \partial_b T \Phi_0) +$$
$$+ \int_\Omega dV (\Phi_0 \delta T + \Phi_k \delta n_k) - \int_{\partial\Omega} k_a (\alpha \partial_a T \delta T + \alpha_{ij} \partial_a n_i \delta n_j) dA \tag{2.8}$$

The constraint on the displacements (2.6) was not used in deriving expression (2.7) and, accordingly, expression (2.8). The values of $u^a(x^b)$ at the internal points of the domain Ω are therefore arbitrary. The identity

$$\partial_a \Sigma^{ab} - n_k \partial_b \Phi_k + \partial_b T \Phi_0 = 0 \tag{2.9}$$

follows from this.

We select the usual laws of conservation of the number of particles of each components, the momentum and energy [11, 12] as the system of equations defining the dynamics of the medium

$$\partial_t n_i + \partial_a I_i^a = 0 \tag{2.10}$$

$$\rho(\partial_t + v^b \partial_b) v^a = \partial_b p^{ab} - \rho \partial_a \varphi \tag{2.11}$$

$$\rho(\partial_t + v^b \partial_b)(\rho^{-1} u + \varphi) = p^{ab} \partial_a v^b - \partial_a q^a \tag{2.12}$$

Here, I_i^a is the flux of particles of the ith component, $\upsilon^a = \rho_a^{-1} m_i I_i^a$ is the mean mass velocity, p^{ab} is the stress tensor, q^a is the heat flux and ∂_t is the partial derivative with respect to time t. For the closure of the hydrodynamic model it is necessary to specify the expressions for the diffusion fluxes $Q_i^a = I_i^a \upsilon^a - n_i \upsilon^a$, the stress tensor and the heat flux. We shall seek these expressions starting from the condition that the entropy production is non-negative for the mixture as a whole.

In the dynamical problem, we adopt the no-slip and impermeability boundary conditions

$$v^a \big|_{\partial D} = 0, \quad l_a Q_i^a \big|_{\partial D} = 0 \tag{2.13}$$

and, also, the condition, imposed on the dynamics of the surface energy,

$$\partial_t u_* = (q_{\text{ex}}^a - q^a) l_a \tag{2.14}$$

where q_{ex}^a is the influx of energy to the system. The boundary conditions, which are extended by conditions (1.8) to the non-equilibrium case, will be formulated later.

We calculate the time derivative of the total entropy from expression (2.7), which was obtained earlier, and Eq. (2.10) by putting $u^a = \upsilon^a dt$

$$\frac{dS}{dt} = \int_D dV(-\partial_a v^b \Sigma^{ab} - \Phi_k \partial_a Q_k^a + \Phi_0(\partial_t + v^b \partial_b) T) + \int_{\partial D} l_a (\Phi_{0*} \partial_t T + \Phi_{i*} \partial_t n_i) dA \tag{2.15}$$

The temperature derivative with respect to time can be eliminated by using Eqs (2.12) and (2.14). On carrying out this procedure and taking condition (2.13) into account, we reduce expression (2.15) to the form

$$\frac{dS}{dt} = \int_D \sigma dV + \int_{\partial D} (\Phi_{0*} u_{*,T}^{-1} q_{\text{ex}}^a l_a + (\Psi_0 - \Phi_{0*} u_{*,T}^{-1}) q^a l_a + (\Phi_{i*} - u_{*,i} \Phi_{0*} u_{*,T}^{-1}) \partial_t n_i) dA \tag{2.16}$$

$$\sigma = \partial_a v^b \tau^{ab} \Psi_0 + Q_i^a \partial_a \Psi_i + q^a \partial_a \Psi_0, \quad \tau^{ab} = p^{ab} - \sigma^{ab}, \quad \sigma^{ab} = \Psi_0^{-1} \Sigma^{ab} + (u - u_{,i} n_i) \delta^{ab}$$

$$\Psi_0 = \Phi_0 u_{,T}^{-1}, \quad \Psi_i = \Phi_i - \Phi_0 u_{,T}^{-1} u_{,i}$$

The quantity Ψ_0 has the dimensions of inverse temperature. The equality $T = \Psi_0^{-1}$ holds in the case of a homogeneous state or in the case when $\alpha = 0$. The quantity Ψ_0^{-1} can therefore be considered as one of the definitions for the local temperature (see Remark 1).

We now use the notation $T_e = \Psi_0^{-1}$ and extend boundary conditions (1.8) to the non-equilibrium case

$$(\Phi_{0*} - T_e^{-1} u_{*,T})\big|_{\partial D} = 0, \quad (\Phi_{i*} - T_e^{-1} u_{*,i})\big|_{\partial D} = 0 \tag{2.17}$$

Use of boundary conditions (2.17) reduces Eq. (2.16) to the usual form which describes the entropy production [12]

$$\frac{dS}{dt} - \int_{\partial D} T_e^{-1} q_{\text{ex}}^a l_a dA = \int_D \sigma dV \tag{2.18}$$

In order to make the analogy with the theory without spatial gradients clearer, we note that we have the equality $\Psi_i = -T^{-1}\varkappa_i$ in the case of a homogeneous state or in the case when $\alpha = 0$ and $\alpha_{ij} = 0$. The quantity $\psi_i = -T^{-1}\varkappa_i$ can therefore be considered as a generalization of the quantity $-T^{-1}\varkappa_i$. The tensors σ^{ab} and τ^{ab} can naturally be interpreted as the static and viscous stress tensors, respectively. For a homogeneous state or in the case when $\alpha = 0$ and $\alpha_{ij} = 0$, the tensor σ^{ab} reduces to the expression $(-p\delta^{ab})$.

We shall construct the transport laws, that is, expressions for the viscous stresses τ^{ab}, the diffusion fluxes Q_i^a and the heat flux q^a in accordance with the requirement that the right-hand side of (2.18) is non-negative. This constraint on the transport laws is quite weak, so that a set of models exists which satisfy the condition of non-decreasing entropy production. We will now adopt these transport laws which, in the limit when the coefficients α, α_{ij} vanish, become the classical Newton, Fick and Fourier laws. In this case, it should be borne in mind that the expression for the diffusion fluxes must be consistent with the identity $m_i Q_i^a = 0$.

In order to abbreviate the notation, we will now agree that the subscripts A, B and C take the values $0, \ldots, N$ and, by definition, we put $Q_0^a = q^a$, $a_{*0} = 0$, $a_{*i} = m$. In accordance with the preceding remarks, we assume that

$$\tau^{ab} = \left(\eta_V - \frac{2}{3}\eta_S\right)\delta^{ab}\partial_c v^c + \eta_S(\partial_a v^b + \partial_b v^a) \tag{2.19}$$

$$Q_A^a = \mu_{AB}\partial_a \Psi_B \tag{2.20}$$

Here, η_V, η_S are the positive coefficients of the bulk and shear viscosity respectively and μ_{AB} is a symmetric matrix which satisfies the additional conditions: (a) $a_{*A}\mu_{AB} = 0$; (b) $\mu_{AB}b_A b_B > 0$ for any non-zero vector b_A not collinear with the vector a_{*A}. The requirement that the matrix μ_{AB} should be symmetric is associated with the time-reversibility of the processes at the microscopic level (the Onsager relations). The coefficients η_V, η_S, μ_{AB} may depend on T, n_i.

We will now prove that the dynamic theory (2.10)–(2.12), (2.19), (2.20) is consistent with the equilibrium theory constructed in Section 1.

Lemma 2. The system of equilibrium equations (1.7) is equivalent to the system of hydrodynamic equations when there are no fluxes

$$\partial_b \sigma^{ab} - \rho\partial_a\varphi = 0 \tag{2.21}$$

$$Q_A^a = 0 \tag{2.22}$$

Proof. Suppose Eqs (1.7) are satisfied. Then, $\Psi_0 = \lambda_0$, $\Psi_i = \lambda_0 m_i\varphi - \lambda_i$. Substitution into formula (2.20) immediately gives Eqs (2.22). Furthermore, we have, by definition

$$\partial_b \sigma^{ab} = \lambda_0^{-1}\partial_b \Sigma^{ab} + u_{,T}\partial_a T - n_i \partial_a u_{,i} \tag{2.23}$$

We now use identity (2.9). Equation (2.23) then becomes

$$\partial_b \sigma^{ab} = \lambda_0^{-1}(n_i\partial_a\Phi_i - \partial_a T\Phi_0) + u_{,T}\partial_a T - n_i\partial_a u_{,i} \tag{2.24}$$

Substituting the expressions for Φ_A from Eqs (1.7) into this equation we obtain (2.21).

On the other hand, suppose Eqs (2.21) and (2.22) are satisfied. Then, by using formula (2.20), we immediately obtain $\Psi_0 = \lambda_0$, $\Psi_i = \lambda_0 m_i\psi - \lambda_i$, where λ_A are certain constants and ψ is an unknown function of the coordinates. Hence, in order to obtain the system of equations (1.7), we only need to prove that the function ψ is identical, apart from a constant term, with the gravitational potential φ. We again make use of Eq. (2.22). On substituting the expressions

$$\Phi_0 = \lambda_0 u_{,T}, \quad \Phi_i = \lambda_0 (u_{,i} + m_i \psi) - \lambda_i$$

into it and using (2.21), we obtain that $\partial_a \varphi = \partial_a \psi$, as was to be proved.

Since the condition that the entropy production should not be negative defines the model uniquely, it is of interest to establish which transport laws are consistent with the equilibrium theory in Section 1. An analysis of the proof of Lemma 2 shows that the equivalence of Eqs (2.22) and the relations

$$\partial_a (\Psi_A - a_{*A}(a_{*B}\Psi_B)(a_{*C}a_{*C})^{-1}) = 0$$

is a sufficient condition.

3. THE HEAT FLUX BETWEEN TWO PARALLEL AND IMPERMEABLE WALLS

We will now consider the problem of the steady state of a multicomponent mixture situated between two impermeable walls, one of which is heated to a temperature T_1 while the other is heated to a temperature T_2. We neglect gravitational forces. In this case, all the functions depend on a single coordinate, and it is therefore convenient to introduce the notation: $x = x^1$, $D = d/dx$. The mixture is located in the domain $x_1 \leqslant x \leqslant x_2$. There are no diffusion fluxes and hence

$$Q_A^a = q\delta_1^a \delta_{A0} \tag{3.1}$$

where q is the unknown heat flux. The solution of Eqs (2.20) with right-hand side (3.1) gives

$$D\Psi_A = q\xi_A + a_{*A}\psi \tag{3.2}$$

where $\xi_A = \xi_A(T, n_i)$ are certain known functions and $\psi = \psi(x)$ is an arbitrary function.

The condition of mechanical equilibrium

$$D\sigma^{xx} = 0 \tag{3.3}$$

holds.

If we start out solely from the definitions, we obtain

$$\sigma^{xx} = \Psi_0^{-1}\left(\Psi_i n_i - s - \frac{1}{2}\alpha DTDT - \frac{1}{2}\alpha_{ij} Dn_i Dn_j + \Psi_0 u\right)$$

$$D\sigma^{xx} = \Psi_0^{-1}(n_i D\Psi_i + n_i u_{,i} D\Psi_0 - D\Psi_0 \sigma^{xx})$$

From these expressions and, also, from Eqs (3.2) and (3.3), it is possible to calculate the function ψ

$$\psi = q\rho^{-1}((\sigma^{xx} - n_i u_{,i})\xi_0 - n_i \xi_i)$$

Consequently, it can be assumed that ψ is an unknown function of the quantitites T, n_i, DT, Dn_i, Ψ_A. Next, we immediately derive the equations

$$D^2 T = \alpha^{-1}\left(u_{,T}\Psi_0 - s_{,T} - \frac{1}{2}\alpha_{,T} DT^2 - \alpha_{,i} DTDn_i\right) \tag{3.4}$$

$$D^2 n_i = \beta^{il}\left(-\Psi_l + \Psi_0 u_{,l} + s_{,l} - \frac{1}{2}\alpha_{jk,l} Dn_j Dn_k + \alpha_{lj,k} Dn_k Dn_j\right) \tag{3.5}$$

from the definitions of the quantities Ψ_A.

The problem of the state of the mixture between the impermeable walls reduces to the system of ordinary differential equations (3.2), (3.4), (3.5). By making the trivial substitution $\zeta_0 = DT$, $\zeta_i = Dn_i$, it is possible to transform this system into a system of 3 $(N + 1)$ first-order ordinary differential equations in the 3 $(N + 1)$ unknown functions T, n_i, ζ_A, Ψ_A, which depend on the x coordinate. The general solution of this system depends on $3N + 4$ free parameters (we recall that the equations contain the parameter q). To determine these parameters, there are 2 $(N + 1)$ boundary conditions on the walls (2.17),

N conditions (1.2) which fix the numbers of particles of each of the components, and also two conditions which take account of the temperature of the walls

$$\Psi_0\big|_{x=x_1} = T_1^{-1}, \quad \Psi_0\big|_{x=x_2} = T_2^{-1} \tag{3.6}$$

The problem of a mixture between walls has therefore been correctly formulated. In the case of real mixtures, there is no possibility of obtaining an explicit analytical solution and the above formulation can be used either to find a numerical solution or for a qualitative investigation.

Remark 4. When formulating boundary conditions (3.6) we again encounter the non-uniqueness of the determination of the temperature in models with spatial derivatives. At first glance, we should put $T|_{x=x_1} = T_1$, $T|_{x=x_2} = T_2$. However, only conditions (3.6) ensure the continuity of the entropy flux $(T_e^{-1}q^a)$. Otherwise, if one uses a model with $\alpha = 0$ (see Remark 2), T_e is identical with T.

4. DISCUSSION OF THE RESULTS

It has been shown above that a theory based on a functional of the entropy (1.3) with spatial derivatives consistently describes the equilibrium and non-equilibrium states of a mixture using continuous hydrodynamics, since the presence of higher spatial derivatives enables one to describe multiphase states without introducing density discontinuities [1]. Actually, the higher spatial derivatives usually become essential just at the interface, and, in the remaining situations, the theory with $\alpha = 0$, $\alpha_{ij} = 0$ works quite well in describing the mixture behaviour. The advantage of a continuous approach over an approach with discontinuity surfaces is well known in the continuum mechanics: in the first case it is possible to solve a single system of equations for the whole mixture while, in the second case, it is necessary to introduce interfaces (the location of which is specified "a priori" to some extent) and the different equations are solved for each phase.

The system of dynamic equations (2.10)–(2.12) has an evolutionary form and it is therefore possible to attempt to apply the general theory of such equations [13] to this system. On the one hand, according to the definition of a dynamic model, it has a Lyapunov function, as which we can take the entropy with a positive sign. This simplifies the analysis. On the other hand, system (2.10)–(2.12) apparently does not fall into the class of equations for which theorems on the existence and uniqueness of the solution have been proved, especially as system (2.10)–(2.12) contains a "Navier–Stokes" part with all the well-known difficulties, and, in the general case, it is not known whether the solution is unique (different equilibrium multiphase states with the same numbers of particles of the components can exist at the specified temperature).

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