Pergamon

0021-8928(95)00087-9

J. Appl. Maths Mechs, Vol. 59, No. 5, pp. 745–752, 1995
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0021-8928/95 $24.00+0.00

A HYDRODYNAMIC DESCRIPTION OF A MULTICOMPONENT MULTIPHASE MIXTURE IN NARROW PORES AND THIN LAYERS†

O. Yu. DINARIYEV

Moscow

(*Received* 1 *June* 1994)

A hydrodynamic model of the isothermal processes in a multicomponent viscous mixture which interacts with fixed surfaces is constructed. In the steady case, the model reduces to a description using the Landau–de Gennes functional. Typical solutions of the equations for a mixture close to a surface or when there are phase transitions are analysed. Classical surface and capillary phenomena are matched with these solutions. Hence, the proposed model enables time-dependent viscous flows of a liquid and a gas in narrow pores and well-known static surface effects to be described simultaneously, namely, the anomalous properties of thin films and surface layers, and capillary condensation and wettability, which is one of the problems in the modern theory of capillary phenomena [1, 2].

1. We consider a multicomponent liquid or gaseous mixture which occupies a spatial domain D. We assume that the boundary ∂D is a piecewise-smooth surface which can be subdivided into two subsets: Γ_1, the piecewise-smooth boundary of the immobile solid phase which interacts with the mixture, and Γ_2, a piecewise-smooth impermeable surface which has no effect on the state of the mixture.

We assume that the Latin subscripts i, j, k take the values $1, \ldots, N$, where N is the number of components in the mixture, the Latin superscripts a, b, c take the values 1–3, corresponding to a certain fixed Cartesian system of coordinates x^a, the Greek superscripts α and β take the values 1–3 corresponding to a certain curvilinear system of coordinates y^α and the Latin superscripts A and B take the values 1 and 2; summation is carried out over repeated indices unless otherwise stated.

Let n_i be the molar density of the ith component in the mixture and let m_i be the corresponding molar mass. The thermodynamic properties of the mixture in bulk are completely defined by the free energy density [3, 4] $f = f(T, n_i)$, where T is the absolute temperature of the mixture. We recall that the relations

$$df = -sdT + \kappa_i dn_i, \quad f = -p + \kappa_i n_i \tag{1.1}$$

hold, where s is the entropy per unit volume, κ_i is the chemical potential of the ith component and p is the pressure.

Only isothermal processes are considered and the dependence of all thermodynamic and physicomechanical quantities on temperature will therefore henceforth be omitted. If $U = U(n_i)$, $V = V(x^a)$, $W = W(y^\alpha)$ are certain smooth functions, we shall use the notation

$$U_{,i} = \partial U / \partial n_i, \quad \partial_a V = \partial V / \partial x^a, \quad D_\alpha W = \partial W / \partial y^\alpha$$

In particular, according to (1.1), the following equality holds

$$f_{,i} = \kappa_i \tag{1.2}$$

If a mixture with certain densities n_{i0} undergoes separation into K phases with densities n_{il} and volume fractions of the phases s_l ($l = 1, \ldots, K$) then, neglecting surface effects, the mean free energy of the system of separated phases is equal to

$$f_m = \sum_{l=1}^{K} s_l f(n_{il}) \tag{1.3}$$

---

†*Prikl. Mat. Mekh.* Vol. 59, No. 5, pp. 776–783, 1995.

Here, the densities in the phases must satisfy the conditions for the conservation of the numbers of molecules of the components

$$n_{i0} = \sum_{l=1}^{K} s_l n_{il} \tag{1.4}$$

If the free energy of the homogeneous state $f_0 = f(n_{i0})$ is greater than f_m, then the homogeneous state is thermodynamically unstable with respect to its decomposition into phases. The heterogeneous state which ensures an absolute minimum of the functional (1.3) with respect to all virtual phase separations which satisfy Eq. (1.4) is thermodynamically stable. It can be shown in the standard way that the equalities [3, 4]

$$\kappa_i(n_{j1}) = \ldots = \kappa_i(n_{jK}) \tag{1.5}$$

$$p(n_{j1}) = \ldots = p(n_{jK}) \tag{1.6}$$

hold in the case of a stable state.

In the special case when the free energy f is a convex function of the vector n_i, homogeneous states are always stable in bulk.

In order to describe the static states of a mixture, taking account of surface forces, we define the free energy F of a mixture in the form of the Landau–de Gennes functional

$$F = \int_D w\,dV + \int_{\Gamma_1} \omega\,dS + \int_D \rho\varphi\,dV \tag{1.7}$$

$$w = \frac{1}{2}\nu_{ij}\partial_a n_i \partial_a n_j + f$$

Here, $\nu_{ij} = \nu_{ij}(n_k)$ are the coefficients of a certain positive definite quadratic form, $\omega = \omega(n_i)$ is the surface energy of the interaction of the fluid with the rock, dV is a volume element, dS is an element of the surface ∂D, $\rho = m_i n_i$ is the total mass density and $\varphi = \varphi(x^a)$ is the gravitational potential. The absolute minimum of the functional (1.7) in the space of the distributions $n_i = n_i(x^a)$ which satisfy the supplementary conditions

$$\int_D n_i\,dV = N_i \tag{1.8}$$

where N_i is the specified number of molecules of the ith component, ensures a static state of the mixture.

We now calculate the variations of the functionals F and N_i

$$\begin{gathered}
\delta F = \int_D \Phi_i \delta n_i\,dV + \int_{\Gamma_1} \Gamma_{i1}\delta n_i\,dS + \int_{\Gamma_2} \Phi_{i2}\delta n_i\,dS \\
\delta N_i = \int_D \delta n_i\,dV, \quad \Phi_k = \frac{1}{2}\nu_{ij,k}\partial_a n_i \partial_a n_j - \nu_{ik,j}\partial_a n_i \partial_a n_j - \nu_{ik}\Delta n_i + f_{,k} + m_k\varphi \\
\Phi_{k1} = \omega_{,k} - \nu_{ki}\frac{\partial n_i}{\partial l}, \quad \Phi_{k2} = -\nu_{ki}\frac{\partial n_i}{\partial l}, \quad \Delta = \partial_a\partial_a
\end{gathered} \tag{1.9}$$

Here, l^a is an internal normal to ∂D.

The distribution $n_i = n_i(x^a)$ which minimizes the functional (1.7) subject to the supplementary conditions (1.8) must satisfy the differential relation

$$\delta F + \lambda_i \delta N_i = 0 \tag{1.10}$$

where λ_i are the Lagrangian multipliers. The necessary (but not necessarily sufficient) conditions imposed on the equilibrium state of the mixture follow from relations (1.10), when account is taken of (1.9), in the form of a system of elliptic equations and the corresponding boundary conditions

$$\Phi_i + \lambda_i = 0 \tag{1.11}$$

$$\Phi_{k1} = 0, \quad \Phi_{k2} = 0 \tag{1.12}$$

The Lagrangian multipliers must be chosen in such a way that conditions (1.8) are satisfied. If the distribution $n_i = n_i(x^a)$ is known then λ_i can be found from the condition (1.11)

$$\lambda_i = -\frac{1}{V(D)} \int_D \Phi_i dV \tag{1.13}$$

where $V(D)$ is the volume of the domain D. According to (1.2) and (1.9), $\lambda_i = -\kappa_i$ for a homogeneous state of a mixture when there are no gravitational forces.

On the basis of the theory which has been developed it is possible to calculate the stress tensor in a static state of the mixture. To do this, we assume that the volume D occupied by a mixture in a certain state (which need not be the equilibrium state) is deformed into another volume D' such that a certain new state is obtained which only differs from the old state to an infinitely small extent.

Let $n_i(x^a)$ be the old distribution and let $n_i'(x^a)$ be the new distribution. With each point of domain D with coordinates x^a it is possible to match a certain point of domain D' with coordinates

$$x'^a = x^a + u^a \tag{1.14}$$

where $u^a = u^a(x^b)$ is a small vector which is defined in such a manner that the total mass

$$m_i n_i(x^a) dV = m_i n_i'(x'^a) dV' \tag{1.15}$$

is conserved in each individual volume.

We now select an arbitrary subset $\Omega \subset D$ with a piecewise-smooth boundary which is deformed into a certain domain Ω' by the transformation (1.16). The free energies for the states in domains Ω, Ω' are calculated using formula (1.7)

$$F_\Omega = \int_\Omega (w + \rho\varphi) dV, \quad F_{\Omega'} = \int_{\Omega'} (w' + \rho'\varphi) dV'$$

The expression for the functional $F_{\Omega'}$ can be transformed into an integral over the domain Ω if formulae (1.14) is looked upon as a coordinate transformation. In this case, it is necessary to take account of equalities (1.15) and, also, the following relations, which hold with an accuracy up to the first order of smallness

$$dV' = (1 + \partial_a u^a) dV, \quad \frac{\partial n_1'}{\partial x'^a} = (\delta_a^b - \partial_a u^b) \frac{\partial n_i'}{\partial x'^b} \tag{1.16}$$

In the approximation which is linear with respect to u^a, we have

$$n_i'(x'^a) = n_i(x^a) + r_i(x^a) + q_i(x^a) \tag{1.17}$$

where r_i, q_i are quantities of the same order of smallness as u^a which satisfy the equalities

$$r_i(x^a) = -\partial_b u^b(x^a) n_i(x^a), \quad m_i q_i(x^a) = 0 \tag{1.18}$$

By using equalities (1.16)–(1.18) and integrating by parts, we obtain (k^a is the outward normal to $\partial\Omega$)

$$\Delta F = F_{\Omega'} - F_\Omega = W_1 + W_2 + W_3 + W_4 \tag{1.19}$$

$$W_C = \int_\Omega w_C dV, \quad C = 1,2,3, \quad W_4 = \int_{\partial\Omega} w_4 dS$$

$$w_1 = \sigma^{ab} \partial_a u^b, \quad w_2 = \rho u^a \partial_a \varphi, \quad w_3 = \Phi_i q_i$$

$$\sigma^{ab} = (-\Phi_k n_k + w + \rho\varphi) \delta^{ab} - \nu_{ij} \partial_a n_i \partial_b n_j$$

$$w_4 = \nu_{ij} \frac{\partial n_i}{\partial k} (r_j + q_j)$$

Following the ideas in [5], we shall interpret σ^{ab} as a static stress tensor, the quantity W_1 as the work of the surface forces, W_2 as the work of the gravitational forces and the sum $(W_3 + W_4)$ as the work of forces associated with mass transfer by diffusion.

The identity

$$\partial_a \sigma^{ab} = -n_k \partial_b \Phi_k + \rho \partial_b \varphi \tag{1.20}$$

holds.

The usual conditions of mechanical equilibrium

$$\partial_a \sigma^{ab} - \rho \partial_b \varphi = 0 \tag{1.21}$$

therefore hold in the thermodynamic equilibrium state when relations (1.11) are satisfied.

We shall now describe certain classical phenomena in a multicomponent mixture within the framework of the steady-state theory which has been developed.

The structure of the surface layer. Let a one-dimensional equilibrium distribution $n_i = n_i(x^1)$ exist when there are no gravitational forces ($\varphi = 0$). The equilibrium equations (1.11) reduce to the Hamiltonian form

$$\partial_1 n_i = \partial H / \partial p_i, \quad \partial_1 p_i = -\partial H / \partial n_i \tag{1.22}$$

$$p_i = \nu_{ij} \partial_1 n_j, \quad H = \frac{1}{2} \alpha_{ij} p_i p_j - f - \lambda_i n_i$$

where α_{ij} is a matrix which is the inverse of ν_{ij}. The Hamiltonian H, which is an integral of the dynamic system (1.22), is related to the stress tensor

$$H = -\sigma^{11}$$

in a simple manner.

Thus, all the equilibrium one-dimensional distributions are described by the methods of symplectic geometry [6].

In order to describe the structure of the surface layer it is sufficient to solve problem (1.22) in the half-line $x^1 \geqslant 0$ subject to the following boundary conditions: the equality (see (1.12))

$$p_i = \omega_{,i} \tag{1.23}$$

holds when $x^1 = 0$ and, when $x^1 \to +\infty$, the state of the mixture tends to a certain homogeneous distribution $n_i \to n_{i0}$. We note that $\lambda_i = -\kappa_i(n_{j0})$ in this case.

If a homogeneous state n_{i0} is thermodynamically state in bulk, the expression $(-f - \lambda_i n_i)$ reaches a local minimum at this point. The trajectories of the Hamiltonian system (1.22), which converge when $x^1 \to +\infty$ to the point $n_i = n_{i0}$, $p_i = 0$, occupy a certain N-dimensional manifold M_1 in the $(2N - 1)$-dimensional hyperspace

$$H = -f(n_{i0}) - \lambda_i n_{i0} \tag{1.24}$$

On the other hand, in this case the N-dimensional Lagrangian manifold (1.23) intersects the hyperspace (1.24) over the $(N - 1)$-dimensional submanifold M_2. In the general case, the intersection of M_1 and M_2 is zero-dimensional, that is, it corresponds to one or several required trajectories. The model which has been proposed therefore enables one, in principle, to describe the structure of a layer close to a surface interacting with a mixture.

Note that, according to (1.1) and (1.24), the Hamiltonian H, which is constant on the required trajectory, is equal to the hydrostatic pressure in the homogeneous state n_{i0}. At the same time, close to the wall it may differ from the corresponding hydrostatic pressure (the disjoining pressure effect [1]).

The structure of a straight interphase boundary. Suppose it is required to find a solution of system (1.22) which tends to the homogeneous state n_{i1} when $x^1 \to -\infty$ and to the homogeneous state n_{i2} when $x^1 \to +\infty$, where both homogeneous states are stable in bulk. It is immediately obvious that

$$\lambda_i = -\kappa_i(n_{j1}) = -\kappa_i(n_{j2}) \tag{1.25}$$

and equality of the chemical potentials in the phases (see (1.5)) is therefore a necessary condition for a solution to exist. Moreover, if a solution exists, the Hamiltonian is constant along the trajectories and equal to the hydrostatic pressure in phase 1 and 2. Consequently, a further necessary condition for a solution to exist (see (1.6)) is obtained.

Now let conditions (1.5) and (1.6) be satisfied. Trajectories which tend to the point $n_i = n_{i1}, p_i = 0$ (to the point $n_i = n_{i2}, p_i = 0$ respectively) when $x^1 \to -\infty$ ($x^1 \to +\infty$) occupy a certain N-dimensional submanifold $M_1(M_2)$ in the hyperspace (1.25). In the general case, the intersection of M_1 and M_2 is one-dimensional, that is, it consists of one or several trajectories.

It may be concluded that the static theory, based on the functional (1.7), reproduces the classical phase equilibrium conditions (1.5) and (1.6) and enables one to describe the fine structure of an interphase boundary. If a solution $n_i(x^1)$ is found, then it is possible to calculate the surface tension

$$\sigma = \int_{-\infty}^{+\infty} (w - H + \lambda_i n_i) dx^1 = \int_{-\infty}^{+\infty} \nu_{ij} \partial_1 n_i \partial_1 n_j dx^1 \tag{1.26}$$

If the substitution

$$\nu_{ij} \to \varepsilon \nu_{ij}, \quad f \to \varepsilon^{-1} f \tag{1.27}$$

is made in the equation of the theory, where ε is a small, dimensionless, positive parameter, then, as an analysis of the equations shows, the distribution $n_i(\varepsilon^{-1}x^1 + a)$, where a is an arbitrary constant with the dimensions of length, will be a new solution. The magnitude of the surface tension (1.26) does not change in this case.

We will now consider the case of a one-component ($N = 1$) and assume that ν_{11} = const. For simplicity, we put $z = n_1, z_1 = n_{11}, z_2 = n_{12}, \nu = \nu_{11}, \lambda = \lambda_1, z_2 > z_1$. The equilibrium equation has the integral (see (1.26))

$$\tfrac{1}{2}\nu(\partial_1 z)^2 - f - \lambda z = \beta = -f(z_1) - \lambda z_1$$

The expression for $\partial_1 z$

$$\partial_1 z = (2\nu^{-1} U)^{1/2}, \quad U(z) = f + \lambda z + \beta$$

is easily found.

A solution of the problem which has been formulated exists if the function $U(z)$ is positive in the interval from z_1 to z_2 and vanishes at the boundary points together with its first derivatives. On substituting the expression for $\partial_1 z$ into (1.26), we obtain

$$\sigma = (2\nu)^{1/2} \int_{z_1}^{z_2} (U(z))^{1/2} dz$$

The relation can be considered as a connection between the surface tension σ and the phenomenological parameter ν.

The structure of a thin curved interphase boundary. We will consider the situation when there is an interphase domain which separates states n_{i1} and n_{i2}, which are thermodynamically stable in bulk. The substitution (1.27) can be made. Then, in the limit as $\varepsilon \to 0$, the interphase region degenerates into a certain smooth surface P. Let γ^a be a normal to the surface P which is directed from phase 1 to phase 2 and let ζ^A be coordinates on the surface P. The surface P and the normal γ^a are then specified by certain equations

$$x^a = X^a(\zeta^A), \quad \gamma^a = \gamma^a(\zeta^A)$$

For small values of ε, we introduce, in the neighbourhood of P, the curvilinear coordinates y^α by the formulae

$$x^a = X^a(y^A) + \gamma^a(y^A)\varepsilon y^3$$

A distribution density in the form

$$n_i = n_i^0(y^\alpha) + \varepsilon n_i^1(y^\alpha) + \dots$$

can be sought in the region of phase separation in accordance with the results on the structure of a straight interphase boundary when solving the equilibrium equations (1.3).

By analogy with this, the phase characteristics must be expanded in series

$$n_{iC} = n_{iC}^0 + \varepsilon n_{iC}^1 + \ldots, \qquad C = 1,2$$

We rewrite the differential operators in Eqs (1.11) in the curvilinear coordinates y^α. If we confine ourselves to the lowest two orders in the expansion with respect to ε then, instead of (1.13), it is sufficient to consider the system of equations

$$\frac{1}{2}\nu_{ij,k} D_3 n_i D_3 n_j - D_3(\nu_{ik} D_3 n_i) - \varepsilon\beta\nu_{ik} D_3 n_i + f_{,k} + \varepsilon\lambda_k = 0, \quad \lambda_i = \varepsilon^{-1}\lambda_i^0 + \lambda_i^1 + \ldots \tag{1.28}$$

Here, $\beta = \beta(\zeta^A) = g^{AB}b_{AB}$, $g_{AB} = D_A X^a D_B X^a$ is the first fundamental form of the surface P and $b_{AB} = D_A X^a D_\beta \gamma^a$ is the second fundamental form of the surface P [7].

Analysis of the system of equations (1.28) when $y^3 \to \pm\infty$ leads, as earlier, to the equalities $\varepsilon\lambda_i = -f_{,i}(n_{i1}) = -f_{,i}(n_{i2})$ which hold in the lowest two orders with respect to ε. This again gives the conditions of phase equilibrium (1.5). When this is taken into account, from (1.28) and (1.1) we derive the relation

$$p(n_{i1}) - p(n_{i2}) + \beta \int_{-\infty}^{+\infty} \nu_{ij} D_3 n_i D_3 n_j dy^3 = 0$$

If the definition (1.26) is used, the Laplace relation for the capillary pressure jump [8]

$$p(n_{i1}) - p(n_{i2}) + \beta\sigma = 0$$

is reproduced with the framework of the theory being developed.

2. We will now consider the dynamic processes in a multicomponent mixture. In order to describe the isothermal hydrodynamics of a multicomponent mixture it is natural to use the conservation equations for the components and the equation of the momenta for the medium as a whole [5]

$$\partial_t n_i + \partial_a I_i^a = 0 \tag{2.1}$$

$$\rho(\partial_t \upsilon^a + \upsilon^b \partial_b \upsilon^a) = \partial_b p^{ab} - \rho\partial_a \varphi \tag{2.2}$$

Here, I_i^a is the flow of molecules of the ith component in the mixture, $\upsilon^a = \rho^{-1} m_i I_i^a$ is the mean mass velocity, p^{ab} is the stress tensor and ∂_t is a derivative with respect to time.

To construct a closed hydrodynamic model it is necessary to give expressions for the stress tensor p^{ab} and for the diffusion fluxes $Q_i^a = I_i^a - n_i \upsilon^a$.

It is convenient to define the dynamic stress tensor as the sum of the static stress tensor σ^{ab} (Section 1) and the viscous stress tensor τ^{ab}.

$$p^{ab} = \sigma^{ab} + \tau^{ab}$$

$$\tau^{ab} = \eta\delta^{ab}\partial_c \upsilon^c + \mu\left(\partial_a \upsilon^b + \partial_b \upsilon^a - \frac{2}{3}\delta^{ab}\partial_c \upsilon^c\right)$$

where $\eta > 0$ is the bulk viscosity of the mixture and $\mu > 0$ is the shear viscosity of the mixture. We shall impose the no-slip boundary conditions

$$\upsilon^a\big|_{\partial D} = 0 \tag{2.3}$$

which are conventional in the theory of a viscous fluid, on the velocity υ^a.

In the case of the diffusion fluxes we shall require that the no-flow boundary condition is satisfied on the boundary ∂D

$$Q_i^a l^a = 0 \tag{2.4}$$

We shall also assume that the boundary conditions (1.12) are satisfied.

We introduce the notation $Q_i = \partial_a Q_i^a$ and define the total energy of the system, E, as the sum of the kinetic energy of the mean mass flow and the free energy (1.7)

$$E = \frac{1}{2} \int_D \rho \upsilon^a \upsilon^a dV + F \tag{2.5}$$

We will now calculate the time derivative of expression (2.5) To do this, we put

$$u^a = \upsilon^a dt, \qquad q_i = -Q_i dt$$

in formulae (1.14) and (1.17) and use formula (1.19). Then, when account is taken of Eqs (2.1) and (2.2) and the boundary conditions (1.14) and (2.3), we obtain

$$\frac{dE}{dt} = E_1 + E_2, \quad E_1 = -\int_D \tau^{ab} \partial_a \upsilon^b dV, \quad E_2 = -\int_D \Phi_i Q_i dV$$

We will determine the quantities λ_i using formulae (1.13) and then determine the quantities $\Psi_i = (\Phi_i + \lambda_i)$, $S_i = (\Psi_i - m_i m_j \Psi_j (m_k m_k)^{-1})$. According to (2.4), the expression for E_2 can be transformed to the form

$$E_2 = -\int_D S_i Q_i dV \tag{2.6}$$

We now define the diffusion fluxes by means of the implicit formula

$$Q_i = \delta S_i \tag{2.7}$$

in which δ is a certain positive quantity. With this definition, $dE/dt \leqslant 0$ according to (2.6) and the dynamic model which has been constructed turns out to be stable. The implicit definition (2.7) is sufficient to solve the dynamical equations. The diffusion fluxes can be found in explicit form from the solution of the Neumann problem

$$Q_i^a = \partial_a \chi_i, \quad \Delta \chi_i = Q_i, \quad \partial \chi / \partial l \big|_{\partial D} = 0$$

The set of steady solutions of the hydrodynamic equations (2.1) and (2.2) for which there is no mass transfer ($\upsilon^a = 0$) are identical with the set of solutions of problem (1.11), (1.12).

Actually, if conditions (1.11) and (1.12) are satisfied and $\upsilon^a = 0$, then the conditions of mechanical equilibrium (1.21) are satisfied and Eqs (2.1) and (2.2) are obviously satisfied.

On the other hand, let the conditions of mechanical equilibrium be satisfied and suppose $Q_i = 0$. Then, $\Psi_i = m_i h$, where $h = m_i \Psi_i (m_k m_k)^{-1}$. Using identity (1.20), we obtain $\partial_a h = 0$ from which the equality $h = 0$ follows, when account is taken of (1.13).

3. Thus, a hydrodynamic model of a multicomponent liquid or gas has been constructed which describes phenomena in narrow pores and thin layers using the methods of mechanics of continuous media. In the case of steady equilibrium states, the model is equivalent to a description based on the functional (1.7) which adequately reproduces the structure of the surface layers and the interphase regions. The dynamical equations describe non-linear processes of relaxation to equilibrium states. Unlike the conventional hydrodynamics of a multicomponent viscous mixture, the mean mass transfer equations are of a higher order with respect to the spatial derivatives, while the diffusive transfer equations have the form of reaction–diffusion equations.

Note that the consistency with the steady-state theory of Section 1 establishes the hydrodynamic model in a non-unique manner. Thus, instead of the material relation (2.7), the expression

$$Q_i^a = -D_{ij} \partial_a S_i \tag{3.1}$$

can be postulated, where the symmetric matrix D_{ij} satisfies the supplementary conditions: (a) $m_i D_{ij} = 0$, (b) $D_{ij} a_i a_j \geqslant 0$ for any vector a_i from the $(N - 1)$-dimensional subspace $m_i a_i = 0$. Formula (3.1) corresponds to the classic approach in the sense that it leads to the conventional diffusion equations

[9] when $\nu_{ij} = 0$. However, when $\nu_{ij} \neq 0$, the differential equations for the concentrations, which are of the fourth order in the spatial derivatives, follow from formulae (3.1). The hydrodynamic model proposed in Section 2 is minimal from the point of view of the order of the equations and the number of phenomenological coefficients.

REFERENCES

1. DERYAGIN B. V., CHURAYEV N. V. and MULLER V. M., *Surface Forces.* Nauka, Moscow, 1985.
2. EVANS R., Phase equilibria and adsorption of fluids confined in narrow pores. *Lecture Notes in Physics*, Vol. 386, pp. 62–76. Springer, Berlin, 1991.
3. LANDAU L. D. and LIFSHITS Ye. M., *Theoretical Physics*, Vol. 5. *Statistical Physics*, Part 1. Nauka, Moscow, 1976.
4. PRIGOZHIN I. and DEFEI R., *Chemical Thermodynamics*. Nauka, Novosibirsk, 1996.
5. SEDOV L. I., *Mechanics of a Continuous Medium*, Vol. 1. Nauka, Moscow, 1973.
6. ARNOL'D V. I. and GIVENTAL' A. B., Symplectic geometry. In *Results of Science and Technology. Current Problems in Mathematics. Main Trends*, Vol. 4, pp. 5–139. The All-Union Institute for Scientific and Technical Information (VINITI), 1985.
7. STERNBERG S., *Lectures on Differential Geometry*. Mir, Moscow, 1970.
8. FINN R., *Equilibrium Capillary Surfaces. Mathematical Theory*. Mir, Moscow, 1989.
9. DE GROOT S. and MAZUR P., *Non-equilibrium Thermodynamics*. Mir, Moscow, 1964.

Translated by E.L.S.