Gradient description of capillary phenomena in multicomponent fluids

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KINEMATICS and dynamics of a multicomponent non-dissipative medium with free energy dependent on the constituent densities and their gradients is considered. Owing to a considerable idealisation of the model it is believed that its physical meaning can possibly be restricted to the limit case only — i.e., to the equilibrium equations. The equilibrium equations obtained are used for the investigations of two-phase equilibrium of multicomponent fluids. Expression for the surface tension is derived and equilibrium of the ideal solution with its saturated vapour is studied.

Rozpatruje się kinematykę i dynamikę wieloskładnikowego ośrodka niedysypatywnego o energii swobodnej, zależnej od gęstości poszczególnych składników oraz ich gradientów. Ze względu na znaczną idealizację modelu sens fizyczny przypisuje się głównie przypadkowi granicznemu — równaniom równowagi. Otrzymane równania równowagi wykorzystuje się do badania równowagi dwufazowej ośrodków wieloskładnikowych. Wyprowadza się m. in. wyrażenie na napięcie powierzchniowe oraz bada się równowagę roztworu idealnego z jego parą nasyconą.

Рассматриваются кинематика и динамика многокомпонентных недиссипативных сред со свободной энергией зависимой от плотностей компонентов от их градиентов. Ввиду далеко идущей идеализации модели, физической смысл, повидимому, свойствен лишь предельному случаю т. е. уравнениям равновесия. Полученные уравнения равновесия используются для исследования двухфазного равновесия многокомпонентных сред, и так, выводится выражение на поверхностное натяжение и исследуется равновесие идеального раствора с его насыщенным паром.

1. Introduction

IN PAPERS [1, 2] was described a simple model of a liquid with the elastic energy depending on the density gradient. The model was shown to allow for the existence of two-phase equilibrium with shearing stresses occurring in the transition zone and producing the effect of surface tension.

The model mentioned here was able to describe the behaviour of single-component substances only, thus giving the possibility of considering the surface phenomena on the interface between the "pure" (without admixtures) liquid and its saturated vapour. Both from the practical and cognitive points of view, much more interesting is the problem of surface effects in multicomponent systems involving such questions like action of surface-active substances or the interface tension at the interface of two media with limited solubility (of the liquid-liquid or liquid-gas type).

In this paper we shall propose and consider a certain more general gradient model for multicomponent substances, followed by an example of its realization in the case, in which the long-range interactions may be reduced to binary central interactions. The model will also be applied to the determination of surface tension of a low concentration

solution remaining in equilibrium with its saturated vapour, and to the evaluation of the proportionality factor in the Henry law.

The mathematical model proposed yields the complete system of equations of motion and constitutes a certain closed logical structure. From the physical viewpoint it represents a generalization of the elastic fluid model described in [2] to multicomponent media; both models are concerned with perfectly elastic substances in which all processes may be considered as reversible. Such an approach makes it possible to introduce the isothermal potentials and to consider the isothermal balance laws. In this manner, the relation of the theory considered here to the real behaviour of bodies is similar to the relation of the barotropic fluid theory to the real behaviour of viscous fluids, or of the theory of hyperelastic bodies to the viscoelastic character of real solids. However, its applicability to the description of real motions seems to be much more limited in comparison with the models mentioned above, since it would be rather difficult to indicate the definite substances or situations in which the processes accompanied by diffusion might be treated as reversible. On the other hand, as long as we are interested in the states of equilibrium, we may expect all the theories to lead to verifiable physical conclusions. The cognitive value of the present theory consists, in author's opinion, in the fact that it may be treated as a starting point for formulating the constitutive laws of more complicated models, taking account of dissipation and thermomechanical coupling. Having this in view. and also aiming at a better physical interpretation and trying to avoid the perils connected with the variational formalism (its application requires special care in the case of gradient theories), the formalism of non-linear mechanics will be applied in our considerations. However, in the present paper we shall be interested mainly in the final conclusions following solely from the conditions of equilibrium which might also be obtained by the virtual displacements technique, analogously to the numerous statical theories.

2. Kinematics

Let us consider the substance consisting of $n+1$ components distributed in a continuous and sufficiently smooth manner in a certain region of a three-dimensional Euclidean space. ϱ_α, $\alpha = 1, 2, ..., n$ denote the densities of individual components. Density of the medium will be called the value of ϱ,

$$(2.1) \qquad \qquad \varrho = \sum_{\alpha=0}^{n} \varrho_\alpha.$$

Following the example of GURTIN and VARGAS [4] let us moreover introduce the notions of mean velocity $\mathbf{v}$ and diffusion fluxes $\mathbf{h}_\alpha$. $\mathbf{v}_\alpha$ denote the velocities of individual components. Let us observe that theses magnitudes play here the role of primitive notions, the material coordinate systems of the components being not defined, though they have an immediate physical interpretation as mean velocities of molecules of the definite component α averaged over a sufficiently large domain to eliminate the Brownian components of the motion. Furthermore it is assumed that no chemical reactions occur in the medium,

i.e. in an arbitrary region D with immobile boundaries and at an arbitrary instant t, the equality holds true

$$(2.2) \qquad \frac{d}{dt} \int_D \varrho_\alpha dV = - \int_{\partial D} \varrho_\alpha \mathbf{n} \cdot \mathbf{v}_\alpha dS,$$

$\mathbf{n}$ being the unit vector normal to the boundary of the region. Velocity of the medium is defined by the formula

$$(2.3) \qquad \mathbf{v} \equiv \frac{\sum\limits_{\alpha=0}^{n} \mathbf{v}_\alpha \varrho_\alpha}{\varrho}.$$

Further notations [4] are the following:

$$(2.4) \qquad \mathbf{u}_\alpha \equiv \mathbf{v}_\alpha - \mathbf{v}, \quad \mathbf{h}_\alpha \equiv \varrho_\alpha \mathbf{u}_\alpha.$$

Let $a(\mathbf{x}, t)$ denote a certain scalar field, and $\mathbf{b}(\mathbf{x}, t)$ — a certain vector field. $\overset{\alpha}{a}$ and $\overset{\alpha}{\mathbf{b}}$ denote the convective derivatives with respect to the velocity field $\mathbf{v}_\alpha$,

$$(2.5) \qquad \overset{\alpha}{a} \equiv \frac{\partial a}{\partial t} + \mathbf{v}_\alpha \cdot \nabla a, \quad \overset{\alpha}{\mathbf{b}} \equiv \frac{\partial \mathbf{b}}{\partial t} + \mathbf{v}_\alpha \cdot \nabla \mathbf{b}.$$

Here ∇ is the gradient operation, and the dot denotes contraction of a pair of indices. Convective derivatives with respect to the velocity field $\mathbf{v}$ are defined in a similar manner; they will be called quasi-material derivatives and denoted by $\dot{a}, \dot{\mathbf{b}}$.

$$(2.6) \qquad \dot{a} \equiv \frac{\partial a}{\partial t} + \mathbf{v} \cdot \nabla a, \quad \dot{\mathbf{b}} \equiv \frac{\partial \mathbf{b}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{b}.$$

The convective derivatives obey the rules known for the one-component substances: the assumption (2.2) is thus equivalent to the relation

$$(2.7) \qquad \overset{\alpha}{\varrho_\alpha} = - \varrho_\alpha \nabla \cdot \mathbf{v}_\alpha.$$

We may also obtain (cf. [1])

$$(2.8) \qquad \overline{\nabla \varrho_\alpha}^{\alpha} = - \nabla \mathbf{v}_\alpha \cdot \nabla \varrho_\alpha - \nabla \varrho_\alpha (\nabla \cdot \mathbf{v}_\alpha) - \varrho_\alpha \nabla (\nabla \cdot \mathbf{v}_\alpha).$$

On using the definitions (2.1), (2.3) through (2.8), we easily obtain

$$(2.9) \qquad \begin{aligned} \dot{\varrho}_\alpha &= - \varrho_\alpha \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{h}_\alpha, \\ \dot{\varrho} &= - \varrho \nabla \cdot \mathbf{v}, \\ \overline{\nabla \varrho_\alpha}^{\,\cdot} &= - \nabla \mathbf{v} \cdot \nabla \varrho_\alpha - \varrho_\alpha \nabla (\nabla \cdot \mathbf{v}) - \nabla \varrho_\alpha (\nabla \cdot \mathbf{v}) - \nabla (\nabla \cdot \mathbf{h}_\alpha), \\ \overline{\nabla \varrho}^{\,\cdot} &= - \nabla \mathbf{v} \cdot \nabla \varrho - \nabla \varrho (\nabla \cdot \mathbf{v}) - \varrho \nabla (\nabla \cdot \mathbf{v}). \end{aligned}$$

Due to the interpretation of $\mathbf{v}_\alpha$ assumed, a natural definition of acceleration $\mathbf{a}_\alpha$ of the component α is

$$(2.10) \qquad a_\alpha \equiv \overset{\alpha}{\mathbf{v}}.$$

Equations (2.5), (2.6) yield now

(2.11) $\dot{\mathbf{v}}_\alpha = \mathbf{a}_\alpha - \mathbf{u}_\alpha \cdot \nabla \mathbf{u}_\alpha - \mathbf{u}_\alpha \cdot \nabla \mathbf{v}.$

Let the field $\mathbf{v}(\mathbf{x}, t)$ satisfy in a certain region $(\mathbf{x}, t)$ the Lipschitz condition with respect to $\mathbf{x}$. The trajectory of an arbitrary point carried by the field

(2.12) $$\frac{\partial \mathbf{x}}{\partial t} = \mathbf{v}(\mathbf{x}, t)$$

has the property that through each point $(\mathbf{x}, t)$ passes exactly one integral curve [5]. Each selected surface may, at a certain instant t_0, be treated as the position of (exactly one) quasi-material surface $S(t)$ (i.e. the surface conveyed by the field $\mathbf{v}$) and such that for each of its points $\mathbf{x}$ its normal velocity U is equal to the normal component of the velocity field

$$U(\mathbf{x}) = \mathbf{v}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{x}).$$

Here $\mathbf{x} \in S(t_0)$, and $\mathbf{n}(\mathbf{x})$ is the unit normal vector. Fulfilment of the Lipschitz condition ensures the preservation of the topological properties of the quasi-material surface in motion, and hence we may consider closed quasi-material surfaces. The mobile regions bounded by quasi-material surfaces will be called the quasi-material regions. In the case of one-component media the Eq. (2.12) defines the trajectory of a material point, while the notions of quasi-material surfaces and regions are then reduced to the known notions of material surfaces and regions.

If D were a certain time-variable region bounded by the moving surface ∂D, it would be easy to determine from the Eq. (2.2)

$$\frac{d}{dt} \int_D \varrho_\alpha dV = - \int_{\partial D} \varrho_\alpha \mathbf{n} (\mathbf{v}_\alpha - U\mathbf{n}) dS$$

but for D being a quasi-material region $\mathbf{n} \cdot (U\mathbf{n}) = \mathbf{n} \cdot \mathbf{v}$ and

(2.13) $$\frac{d}{dt} \int_D \varrho_\alpha dV = \int_{\partial D} \mathbf{n} \cdot \mathbf{h}_\alpha dS.$$

Performing the summation in (2.13) over all α and taking into account that $\sum_{\alpha=0}^{n} \mathbf{h}_\alpha = 0$ we obtain, as it could be expected,

(2.14) $$\frac{d}{dt} \int_D \varrho dV = 0.$$

It follows that if μ is the density with respect to the measure of ϱ, the formula known from the kinematics of one-component media holds true:

(2.15) $$\frac{d}{dt} \int_D \varrho \mu dV = \int_D \varrho \dot{\mu} dV.$$

3. Simple multicomponent medium

Our considerations are aimed at the derivation of equations of the gradient theory in which the free energy density depends on all densities and their gradients. To make the derivations as clear as possible let us first tackle the simpler problem of a simple multicomponent medium, i.e. such medium in which the free energy is independent of the density gradients; the derivations will then be generalized (disregarding those which are identical in both cases).

Let us consider the function of density of free energy, $w = \overline{w}(\varrho, \varrho_1, ..., \varrho_n)$, satisfying for each quasi-material region (at constant temperature) and for each set of velocity fields $\mathbf{v}_0, \mathbf{v}_1, ..., \mathbf{v}_n$ the following equation of balance (valid only for isothermal transformations)

$$(3.1) \quad \frac{d}{dt} \int_V \varrho \overline{w} \, dV = \int_{\partial V} \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{v} \, dS - \int_{\partial V} \sum_{\alpha=0}^{n} \mathbf{n} \cdot (\mathbf{h}_\alpha e_\alpha) \, dS - \int_{\partial V} \sum_{\alpha=0}^{n} \mathbf{n} \cdot \left(\mathbf{h}_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \right) dS$$

$$+ \int_V \sum_{\alpha=0}^{n} \mathbf{r}_\alpha \cdot \mathbf{v}_\alpha \varrho_\alpha \, dV - \frac{d}{dt} \int_V \sum_{\alpha=0}^{n} \varrho_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \, dV;$$

$\mathbf{T}$ is the stress tensor, the first right-hand integral represents the work done by contact forces, the second and third right-hand terms represent the energy convection due to the mass exchange of the components across the boundaries of the quasi-material region. The kinetic energy convection is singled out in the third term, while the second term contains the magnitudes e_α characterizing the energy exchange caused by the changes of concentrations of the components. Further terms represent: the work done by body forces acting on individual components ($\mathbf{r}_\alpha$ are body force densities), and the change of kinetic energy. It is easily observed that the approach applied differs from that used by GURTIN and VARGAS [4] who did not consider the body forces (together with the inertia forces) separately for each of the components, but globally. The set of independent variables consists of $\varrho_\alpha, \mathbf{h}_\alpha, (\alpha = 1, ..., n), \mathbf{v}$ and ϱ, what evidently is equivalent to taking $\mathbf{v}_i, \varrho_i, (i = 0, 1, ..., n)$ as the independent variables. Suitable selection of the set of independent variables is important from the point of view of simplicity of further transformations as also their physical interpretation. Including here the magnitudes $\mathbf{v}$ and ϱ yields, in a natural manner, the notion of stress tensor, while $\mathbf{h}_\alpha$ yield the relative chemical potentials.

The right-hand side of the Eq. (3.1) contains, however, both $\mathbf{v}, \varrho$, and $\mathbf{h}_\alpha, \mathbf{v}_\alpha, \varrho_\alpha$, in particular for $\alpha = 0$. Before approaching the further transformations we must eliminate all the dependent variables. First of all let us observe that

$$(3.2) \quad \mathbf{h}_0 = -\sum_{\alpha=1}^{n} \mathbf{h}_\alpha,$$

and hence

$$(3.3) \quad \sum_{\alpha=0}^{n} \mathbf{h}_\alpha e_\alpha = \sum_{\alpha=1}^{n} \mathbf{h}_\alpha (e_\alpha - e_0),$$

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as also

$$(3.4) \qquad \sum_{\alpha=0}^{n} \mathbf{r}_\alpha \cdot \mathbf{v}_\alpha \varrho_\alpha = \sum_{\alpha=0}^{n} \mathbf{r}_\alpha (\mathbf{h}_\alpha - \varrho_\alpha \mathbf{v}) = \sum_{\alpha=1}^{n} (\mathbf{r}_\alpha - \mathbf{r}_0) \cdot \mathbf{h}_\alpha + \mathbf{v} \sum_{\alpha=0}^{n} \mathbf{r}_\alpha \varrho_\alpha.$$

Variation of the kinetic energy may be represented in the form

$$(3.5) \qquad \frac{d}{dt} \int_V \sum_{\alpha=0}^{n} \varrho \left(\frac{\varrho_\alpha}{\varrho} \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \right) dV = \int_V \varrho \sum_{\alpha=0}^{n} \overline{\left(\frac{\varrho_\alpha}{\varrho} \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \right)^{\boldsymbol{\cdot}}} \, dV.$$

Differentiating with respect to time and using the Eqs. (2.5), (2.6), (2.10), (2.9) and (3.2), we obtain the identity

$$(3.6) \qquad \sum_{\alpha=0}^{n} \varrho \overline{\left(\frac{\varrho_\alpha}{\varrho} \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \right)^{\boldsymbol{\cdot}}} = - \sum_{\alpha=0}^{n} \nabla \cdot \left(\mathbf{h}_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \right) + \sum_{\alpha=1}^{n} (\mathbf{a}_\alpha - \mathbf{a}_0) \cdot \mathbf{h}_\alpha + \mathbf{v} \sum_{\alpha=0}^{n} \mathbf{a}_\alpha \varrho_\alpha,$$

and so

$$(3.7) \qquad - \int_{\partial V} \left[\sum_{\alpha=0}^{n} \mathbf{h}_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \, dS - \frac{d}{dt} \sum_{\alpha=0}^{n} \int_V \varrho_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} \right] dV$$

$$= - \int_V \left[\sum_{\alpha=1}^{n} (\mathbf{a}_\alpha - \mathbf{a}_0) \cdot \mathbf{h}_\alpha + \mathbf{v} \cdot \sum_{\alpha=0}^{n} \mathbf{a}_\alpha \varrho_\alpha \right] dV.$$

Now the surface integrals in the Eq. (3.1) are transformed into volume integrals, the Eqs. (3.3), (3.4), (3.7) are used, and account is taken of the fact that the Eq. (3.1) should hold true for each quasi-material region; then we obtain for every set of fields $\mathbf{v}, \mathbf{h}_\alpha$ ($\alpha = 1, \ldots, n$)

$$(3.8) \qquad \varrho \left(\frac{\partial \bar{w}}{\partial \varrho} \dot{\varrho} + \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \dot{\varrho}_\alpha \right) = \nabla \cdot (\mathbf{T} \cdot \mathbf{v}) - \nabla \cdot \left(\sum_{\alpha=1}^{n} \mathbf{h}_\alpha \bar{e}_\alpha \right)$$

$$+ \sum_{\alpha=1}^{n} - \bar{\mathbf{r}}_\alpha \cdot \mathbf{h}_\alpha + \mathbf{v} \cdot \sum_{\alpha=0}^{n} \mathbf{r}_\alpha \varrho_\alpha - \sum_{\alpha=1}^{n} \bar{\mathbf{a}}_\alpha \cdot \mathbf{h}_\alpha - \mathbf{v} \sum_{\alpha=0}^{n} \mathbf{a}_\alpha \varrho_\alpha.$$

Here $\bar{\mathbf{r}}_\alpha \equiv \mathbf{r}_\alpha - \mathbf{r}_0$; $\bar{\mathbf{a}}_\alpha \equiv \mathbf{a}_\alpha - \mathbf{a}_0$; $\bar{e}_\alpha \equiv e_\alpha - e_0$. On using the Eqs. $(2.9)_1$, $(2.9)_2$ and performing the differentiation we obtain

$$(3.9) \qquad - \varrho \left(\frac{\partial \bar{w}}{\partial \varrho} \varrho \nabla \cdot \mathbf{v} + \nabla \cdot \mathbf{v} \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \varrho_\alpha + \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \nabla \cdot \mathbf{h}_\alpha \right) = (\nabla \cdot \mathbf{T}) \cdot \mathbf{v}$$

$$+ \mathbf{T} : \nabla \mathbf{v} - \sum_{\alpha=1}^{n} \nabla \cdot \mathbf{h}_\alpha \bar{e}_\alpha - \sum_{\alpha=1}^{n} \mathbf{h}_\alpha \cdot \nabla \bar{e}_\alpha + \sum_{\alpha=1}^{n} \bar{\mathbf{r}}_\alpha \cdot \mathbf{h}_\alpha - \sum_{\alpha=1}^{n} \bar{\mathbf{a}}_\alpha \cdot \mathbf{h}_\alpha + \mathbf{v} \cdot \sum_{\alpha=0}^{n} \varrho_\alpha (\mathbf{r}_\alpha - \mathbf{a}_\alpha).$$

Similarly to the Eq. (3.8), also the Eq. (3.9) must be satisfied for each set of fields $\mathbf{v}, \mathbf{h}_\alpha$ ($\alpha = 1, \ldots, n$), though a well grounded doubt may arise whether each such set can be realized, provided the function $w = \bar{w}(\varrho, \varrho_1, \ldots, \varrho_n)$ and the density fields ϱ, ϱ_α ($\alpha = 1, \ldots, n$) are prescribed. The positive answer is ensured by the presence of terms $\mathbf{r}_\alpha$, provided the latter can be arbitrary. Thus let us assume the possibility of applying in-

dependent body forces to each of the components (if we assumed two different particles to react identically to all possible force field configurations, then they would be indiscernible and thus they should belong to the same component). This implies that the Eq. (3.9) may be split into four independent equations

$$\left[\nabla \cdot \mathbf{T} + \sum_{\alpha=0}^{n} \varrho_\alpha (\mathbf{r}_\alpha - \mathbf{a}_\alpha)\right] \cdot \mathbf{v} = 0,$$

$$\sum_{\alpha=1}^{n} (-\nabla \bar{e}_\alpha + \bar{\mathbf{r}}_\alpha - \bar{\mathbf{a}}_\alpha) \cdot \mathbf{h}_\alpha = 0,$$

(3.10)

$$\left[\mathbf{T} + \varrho \left(\frac{\partial \bar{w}}{\partial \varrho} \varrho + \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \varrho_\alpha\right) \mathbf{1}\right] : \nabla \mathbf{v} = 0,$$

$$\sum_{\alpha=1}^{n} \left(\varrho \frac{\partial \bar{w}}{\partial \varrho_\alpha} - \bar{e}_\alpha\right) \nabla \cdot \mathbf{h}_\alpha = 0,$$

which, owing to the independence of $\mathbf{v}$, $\mathbf{h}_\alpha$, $\nabla \mathbf{v}$, $\nabla \mathbf{h}_\alpha$, yield the following $2n+2$ relations

$$\nabla \cdot \mathbf{T} + \sum_{\alpha=0}^{n} \varrho_\alpha \mathbf{r}_\alpha = \sum_{\alpha=0}^{n} \varrho_\alpha \mathbf{a}_\alpha, \quad -\nabla \bar{e}_\alpha + \bar{\mathbf{r}}_\alpha = \bar{\mathbf{a}}_\alpha,$$

(3.11)

$$\mathbf{T} = -\mathbf{1}\varrho \left(\frac{\partial \bar{w}}{\partial \varrho} \varrho + \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \varrho_\alpha\right), \quad \bar{e}_\alpha = \varrho \frac{\partial \bar{w}}{\partial \varrho_\alpha}.$$

Substituting now $(3.11)_3$ into $(3.11)_1$ and $(3.11)_4$ into $(3.11)_2$ we obtain $n+1$ vector differential equations representing one of the possible forms of the system of equations of motion of the simple multicomponent liquid.

(3.12)

$$-\nabla \left[\varrho \left(\frac{\partial \bar{w}}{\partial \varrho} \varrho + \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \varrho_\alpha\right)\right] + \sum_{\alpha=0}^{n} \varrho_\alpha \mathbf{r}_\alpha = \sum_{\alpha=0}^{n} \varrho_\alpha \mathbf{a}_\alpha,$$

$$-\nabla \left(\varrho \frac{\partial \bar{w}}{\partial \varrho_\alpha}\right) + \bar{\mathbf{r}}_\alpha = \bar{\mathbf{a}}_\alpha.$$

Equations (3.12) together with (2.7) yield the complete set of $4n+4$ equations of the simple multicomponent liquid.

The former considerations were based on the assumption that w is a function $\bar{w}(\varrho, \varrho_\alpha)$ of the variables ϱ, ϱ_α ($\alpha = 1, \ldots, n$) what enabled us to introduce the stress tensor (in the case considered it was reduced to pressure); using the objective magnitudes $\mathbf{h}_\alpha$ was also convenient. In further considerations it will be more convenient, however, to pass to the variables ϱ_i ($i = 0, 1, \ldots, n$). Let us write

$$w = \hat{w}(\varrho_0, \ldots, \varrho_n).$$

It may easily be shown that

(3.13)
$$\frac{\partial \bar{w}}{\partial \varrho} \varrho + \sum_{\alpha=1}^{n} \frac{\partial \bar{w}}{\partial \varrho_\alpha} \varrho_\alpha = \sum_{i=0}^{n} \frac{\partial \hat{w}}{\partial \varrho_i} \varrho_i, \quad \frac{\partial \bar{w}}{\partial \varrho_\alpha} = \frac{\partial \hat{w}}{\partial \varrho_i} - \frac{\partial \hat{w}}{\partial \varrho_0}.$$

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Using the Eq. (3.13) and the definitions of **r** and **a**$_\alpha$ we may rewrite the Eq. (3.12) in the form

(3.14)
$$-\nabla\left(\varrho\sum_{i=0}^{n}\frac{\partial\hat{w}}{\partial\varrho_i}\varrho_i\right)+\sum_{i=0}^{n}\varrho_i\mathbf{r}_i = \sum_{i=0}^{n}\varrho_i\mathbf{a}_i,$$

$$-\nabla\left[\varrho\left(\frac{\partial\hat{w}}{\partial\varrho_i}-\frac{\partial\hat{w}}{\partial\varrho_0}\right)\right]+\mathbf{r}_i-\mathbf{r}_0 = \mathbf{a}_i-\mathbf{a}_0.$$

On multiplying each of the Eqs. (3.14)$_2$ by ϱ_i, adding and subtracting from their sum the Eq. (3.14)$_1$, and dividing by ϱ we obtain

(3.15)
$$-\nabla\left(\varrho\frac{\partial\hat{w}}{\partial\varrho_0}\right)-\sum_{i=0}^{n}\frac{\partial\hat{w}}{\partial\varrho_i}\nabla\varrho_i+\mathbf{r}_0 = \mathbf{a}_0.$$

Equations (3.15) are now substituted in (3.14)$_2$ and multiplied with ϱ_i to yield a system symmetric with respect to ϱ_i and consisting of $n+1$ vectorial equations of motion

(3.16)
$$-\varrho_i\nabla\left(\frac{\partial(\varrho\hat{w})}{\partial\varrho_i}\right)+\varrho_i\mathbf{r}_i = \varrho_i\mathbf{a}_i$$

for each $i = 0, 1, ..., n$.

In the case of simple one-component media in which $w = \int[p(\varrho)/\varrho^2]d\varrho$ (cf. [2]), the Eq. (3.16) is reduced to the known equation

(3.17)
$$-\nabla P+\varrho\mathbf{r} = \varrho\mathbf{a}.$$

The magnitudes $\dfrac{\partial(\varrho\hat{w})}{\partial\varrho} = \mu_i$ will here be called chemical potentials. Usually, in chemical thermodynamics, the name of chemical potentials is attributed to the magnitudes $\mu_i^* \equiv \partial G(n_i, V)/\partial n_i$ (cf. [5, 6]), with $G(n_i, V)$ denoting the Gibbs free energy for the system containing n_i ($i = 0, 1, ..., n$) mols of individual components and occupying the volume V. It may be shown that in a homogeneous system

(3.18)
$$\mu_i = \frac{\mu_i^*}{M_i}.$$

Here M_i is the gram-molecular weight of the n-th component.

If the density of free Helmholtz energy is represented as a function of specific volume $v = 1/\varrho$ and concentration c_α

$$w = w^*(v, c_\alpha) \quad (\alpha = 1, ..., n)$$

with $c_\alpha \equiv \varrho_\alpha/\varrho$, then the following relation may be established:

(3.19)
$$-\frac{\partial w^*}{\partial v} = \varrho\sum_{i=0}^{n}\frac{\partial\hat{w}}{\partial\varrho_i}\varrho_i.$$

The left-hand side of that equation coincides with the definition of pressure in chemical thermodynamics; it may also be found from the Eqs. (3.11)$_1$, (3.13)$_1$ that the right-hand side equals $-\dfrac{1}{3}\mathrm{tr}\mathbf{T} = P$ and thus represents pressure in the mechanical sense. This

implies that, in absence of body forces, the Eq. (3.14) yields the following known equations of equilibrium

$$(3.20) \qquad\qquad \nabla P = 0, \qquad \nabla \mu'_\alpha = 0,$$

in which $\mu'_\alpha \equiv \mu_\alpha - \mu_0$ is the reduced chemical potential (cf. [4] where this magnitude is denoted by μ_α).

The problem of physical interpretation of the equations of motion was discussed earlier and so let us now observe that in passing to the equilibrium equations we have obtained the results possessing unquestionable physical meaning.

4. Gradient theory

In the previous chapter we have demonstrated the method of derivation of the complete set of equations of motion under the assumption that the density of free energy w is independent of the density gradients of the individual components. Let us now repeat the reasoning for the case in which such dependence exists. Assume that

$$(4.1) \qquad\qquad w = \overline{w}(\varrho, \varrho_1, ..., \varrho_n, \nabla\varrho, \nabla\varrho_1, ..., \nabla\varrho_n)$$

and that the following isothermal balance law holds true for each quasi-material region and for each velocity field

$$(4.2) \quad \frac{d}{dt}\int_V \varrho\overline{w}\,dV = \int_{\partial V} \mathbf{n}\cdot\mathbf{T}\cdot\mathbf{v}\,dS + \int_{\partial V}\mathbf{n}\cdot\mathbf{Q}(\nabla\cdot\mathbf{v})\,dS - \int_{\partial V}\sum_{\alpha=0}^n \mathbf{n}\cdot(\mathbf{h}_\alpha e_\alpha)\,dS$$

$$- \int_{\partial V}\sum_{\alpha=0}^n \mathbf{n}\cdot\mathbf{h}_\alpha\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}\,dS + \int_{\partial V}\sum_{\alpha=0}^n \mathbf{n}\cdot\mathbf{q}_\alpha(\nabla\cdot\mathbf{h}_\alpha)\,dS + \int_V \sum_{\alpha=0}^n \varrho_\alpha\mathbf{r}_\alpha\cdot\mathbf{v}_\alpha\,dV$$

$$- \frac{d}{dt}\int_V \sum_{\alpha=0}^n \varrho_\alpha\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}\,dV.$$

Generalized contact forces $\mathbf{Q}$ and $\mathbf{q}_\alpha$ are introduced here; they perform work on the fields $\nabla\mathbf{v}$ and $\nabla\mathbf{h}_\alpha$, like in the papers [2, 8] and other sources dealing with gradient theories; their physical meaning does not immediately result from the Eq. (4.2), however from the considerations to follow it will be clear that by putting them equal to zero we would obtain (contrary to our assumption) the function $\overline{w}$ to be independent of the variables $\nabla\varrho, \nabla\varrho_\alpha$. Introduction of those magnitudes proves then to be necessary in order to keep the theory non-trivial.

The left-hand side of the Eq. (4.2) may be written as

$$(4.3) \quad \frac{d}{dt}\int_V \varrho\overline{w}\,dV = \int_V \varrho\left(\frac{\partial\overline{w}}{\partial\varrho}\dot{\varrho} + \sum_{\alpha=1}^n \frac{\partial\overline{w}}{\partial\varrho_\alpha}\dot{\varrho}_\alpha + \frac{\partial\overline{w}}{\partial(\nabla\varrho)}\cdot\overline{\nabla\varrho} + \sum_{\alpha=1}^n \frac{\partial\overline{w}}{\partial(\nabla\varrho_\alpha)}\cdot\overline{\nabla\varrho_\alpha}\right)dV.$$

The further procedure is similar to that used in the preceding section, i.e. we apply the formulae (2.9) to the left-hand side as presented by the Eq. (4.2) and change the surface integrals appearing at the right-hand side into volume integrals; the magnitudes $\overline{\mathbf{r}}_\alpha$, $\overline{\mathbf{a}}_\alpha$ and

$\overline{\mathbf{q}}_\alpha \equiv \mathbf{q}_0 - \mathbf{q}_0$ are introduced. Since the Eq. (4.2) holds true for every quasi-material region and every velocity field, we finally obtain

$$\nabla \cdot \mathbf{T} + \sum_{\alpha=0}^n \varrho_\alpha \mathbf{r}_\alpha = \sum_{\alpha=0}^n \varrho_\alpha \mathbf{a}_\alpha,$$

$$T = -\left[\varrho^2 \frac{\partial \overline{w}}{\partial \varrho} + \varrho \sum_{\alpha=1}^n \frac{\partial \overline{w}}{\partial \varrho_\alpha} \varrho_\alpha + \varrho \frac{\partial \overline{w}}{\partial (\nabla \varrho)} \cdot \nabla \varrho + \varrho \sum_{\alpha=1}^n \frac{\partial w}{\partial (\nabla \varrho_\alpha)} \cdot \nabla \varrho + \nabla \cdot \mathbf{Q} \right] \mathbf{1}$$

$$- \varrho \frac{\partial \overline{w}}{\partial (\nabla \varrho)} \otimes \nabla \varrho - \varrho \sum_{\alpha=1}^n \frac{\partial \overline{w}}{\partial (\nabla \varrho_\alpha)} \otimes \nabla \varrho_\alpha,$$

(4.4)
$$\mathbf{Q} = -\varrho^2 \frac{\partial \overline{w}}{\partial (\nabla \varrho)} - \varrho \sum_{\alpha=1}^n \frac{\partial \overline{w}}{\partial (\nabla \varrho_\alpha)} \varrho_\alpha,$$

and

$$-\nabla \overline{e}_\alpha + \overline{\mathbf{r}}_\alpha = \overline{\mathbf{a}}_\alpha, \quad \overline{e}_\alpha = \varrho \frac{\partial \overline{w}}{\partial \varrho_\alpha} + \nabla \cdot \overline{\mathbf{q}}_\alpha, \quad \overline{\mathbf{q}}_\alpha = -\varrho \frac{\partial \overline{w}}{\partial (\nabla \varrho_\alpha)},$$

valid for each $\alpha = 1, 2, ..., n$.

Inserting now the Eq. $(4.4)_2$ and $(4.4)_3$ into $(4.4)_1$ and passing from the variables ϱ, ϱ_α, $\nabla \varrho, \nabla \varrho_\alpha$ $(\alpha = 1, ..., n)$ to $\varrho_i, \nabla \varrho_i$ $(i = 0, 1, ..., n)$, multiplying the Eq. $(4.4)_4$ by ϱ_i and summing from 1 to n, and subtracting the result from $(4.4)_1$ we obtain, like before, the expression for $\mathbf{a}_0$ to be substituted into Eq. $(4.4)_4$. The further procedure is also similar and yields

(4.5)
$$-\varrho_i \nabla \left(\frac{\partial (\varrho \hat{w})}{\partial \varrho_i} \right) + \varrho_i \nabla \left(\nabla \cdot \frac{\partial (\varrho \hat{w})}{\partial (\nabla \varrho_i)} \right) + \varrho_i \mathbf{r}_i = \varrho_i \mathbf{a}_i, \quad i = 0, 1, ..., n.$$

Here $\hat{w}(\varrho_0, \varrho_1, ..., \varrho_n, \nabla \varrho_0, \nabla \varrho_1, ..., \nabla \varrho_n) = \overline{w}(\varrho, \varrho_1, ..., \varrho_n, \nabla \varrho, \nabla \varrho_1, ..., \nabla \varrho_n) = w$.

Thus the system of equations of motion of the gradient theory (4.4), being a generalization of the Eqs. (3.11), is reduced to a more compact form (4.5), symmetric with respect to the variables $\varrho_i, \nabla \varrho_i$ and constituting a counterpart of the system (3.16). The equations (4.4) or (4.5) yield, together with the Eqs. (2.7), the complete set of equations of the gradient theory.

The value of $\mathbf{T}$ expressed in terms of the variables $\varrho_i, \nabla \varrho_i$ has the form

(4.6)
$$\mathbf{T} = -\left[\sum_{i=0}^n \frac{\partial (\varrho \hat{w})}{\partial \varrho_i} \varrho_i - \varrho \hat{w} - \sum_{i=0}^n \varrho_i \nabla \cdot \left(\frac{\partial (\varrho \hat{w})}{\partial (\nabla \varrho_i)} \right) \right] \mathbf{1} - \sum_{i=0}^n \frac{\partial (\varrho \hat{w})}{\partial (\nabla \varrho_i)} \otimes \nabla \varrho_i.$$

From that equation it is easily found that the tensor $\mathbf{T}$ is symmetric in isotropic materials. Symmetry of the first term is obvious and we have to investigate the second term. Since in isotropic materials w may depend on $\nabla \varrho_i$ exclusively through the invariants, we can write

(4.7)
$$w = \overline{\overline{w}}(\varrho_i, I_{ik}).$$

Here $I_{ik} = \nabla\varrho_i \cdot \nabla\varrho_k$; I_{ik} form a triangular matrix due to the identity $I_{ik} = I_{kl}$. Then we have

$$(4.8) \quad \sum_{i=0}^{n} \frac{\partial(\varrho\hat{w})}{\partial(\nabla\varrho_i)} \otimes \nabla\varrho_i = \varrho \sum_{i=0}^{n} \frac{\partial\hat{w}}{\partial(\nabla\varrho_i)} \otimes \nabla\varrho_i = \varrho \sum_{i=0}^{n} \sum_{j,k=0}^{n} \left(\frac{\partial\bar{\bar{w}}}{\partial I_{jk}} \frac{\partial I_{jk}}{\partial(\nabla\varrho_i)} \otimes \nabla\varrho_i \right)$$

$$= \varrho \sum_{i=0}^{n} \sum_{j,k=0}^{n} \left[\frac{\partial\bar{\bar{w}}}{\partial I_{jk}} (\delta_{ik}\nabla\varrho_j + \delta_{ij}\nabla\varrho_k) \otimes \nabla\varrho_i \right] = 2\varrho \sum_{i,l=0}^{n} \frac{\partial\bar{\bar{w}}}{\partial I_{il}} (\nabla\varrho_l \otimes \nabla\varrho_i)$$

$$= \varrho \sum_{i,l=0}^{n} \frac{\partial\bar{\bar{w}}}{\partial I_{il}} (\nabla\varrho_l \otimes \nabla\varrho_i + \nabla\varrho_i \otimes \nabla\varrho_l).$$

Here δ_{ij} is the Kronecker delta. In this form, the symmetry of the expression is also obvious.

Everything what was established with respect to the physical interpretation of the model discussed here applies to the Eqs. (4.4), (4.5) as well. Therefore it should be expected that the equations of equilibrium obtained from the Eqs. (4.5) (in absence of body forces) and written in the form

$$(4.9) \quad -\nabla\left(\frac{\partial(\varrho\hat{w})}{\partial\varrho_i}\right) + \nabla\left(\nabla \cdot \frac{\partial(\varrho\hat{w})}{\partial(\nabla\varrho_i)}\right) = 0$$

represent an adequate description to a certain class of physical systems. It should also be expected that once the Eqs. (4.9) are satisfied, the formula (4.9) will describe real stresses sufficiently well.

In [2] it was proved that in the case of a one-component medium, fulfilment of the Eq. (4.9) did not have to imply the uniform density distribution. It is not difficult to construct the examples which may be used to demonstrate the same property with respect to a higher number of components. Examining the form of the Eq. (4.6) we may easily observe that, if the form of w allows for non-trivial solution of the system (4.9), the tensor **T** need not necessarily be a spherical tensor in the state of equilibrium of a multicomponent gradient medium (similarly to the conclusion of [2] concerning one-component media), contrary to the case of a simple multicomponent medium considered in the preceding section in which the tensor **T** was always reduced to pressure.

5. Surface tension in multicomponent media

Let us consider the one-dimensional case in which the form of w allows for the existence of solution with non-uniform distribution of density $\varrho_\alpha = \varrho_\alpha(x)$, corresponding to the existence of a single phase transition in a multicomponent medium. Let the values of ϱ_α at $x \to \pm\infty$ tend asymptotically to certain finite limits (different, in general, for $+\infty$ and $-\infty$), the derivatives $\partial\varrho_\alpha/\partial x$, $\partial^2\varrho_\alpha/\partial x^2$ tending at infinity to zero. Such conditions may correspond e.g. to the equilibrium of two liquids of finite solubility, or to the solution being in equilibrium with its saturated vapour.

Let us use the Eq. (4.4)$_1$ which at equilibrium takes the form

$$(5.1) \quad \nabla \cdot \mathbf{T} = 0,$$

T being defined by the Eq. (4.6). From the conditions at infinity we obtain, similarly to [2], the relations

$$(5.2) \qquad\qquad \mathbf{T}_\infty = \mathbf{T}_{-\infty} = -\mathbf{1}P_\infty.$$

Let us apply the "force" definition of surface tension σ,

$$(5.3) \qquad\qquad \sigma = \int\limits_{-\infty}^{\infty} \left(T_{yy} - \frac{1}{3}\, \mathrm{tr}\,\mathbf{T}_\infty \right) dx$$

(cf. [9, 2]) in which y is an arbitrary direction perpendicular to x. Integration of the Eq. (4.9) yields in the one-dimensional case

$$(5.4) \qquad\qquad -\frac{\partial(\varrho\hat{w})}{\partial\varrho_i} + \left(\frac{\partial(\varrho\hat{w})}{\partial(\varrho_i')}\right)' = k_i \equiv \frac{\partial(\varrho\hat{w})}{\partial\varrho_i}\bigg|_{\pm\infty}.$$

Primes denote differentiation in x. Introduce the notation

$$(5.5) \qquad\qquad A_i \equiv \frac{\partial(\varrho\hat{w})}{\partial(\varrho_i')}.$$

On multiplying the Eq. (5.4) with ϱ_i' and summing over all values of i we obtain

$$(5.6) \quad -\sum_{i=0}^{n}\frac{\partial(\varrho\hat{w})}{\partial\varrho_i}\varrho_i' + \sum_{i=0}^{n}A_i'\varrho_i' - \sum_{i=0}^{n}k_i\varrho_i' = -\sum_{i=0}^{n}\frac{\partial(\varrho\hat{w})}{\partial\varrho_i}\varrho_i' - \sum_{i=0}^{n}A_i\varrho_i''$$

$$+ \sum_{i=0}^{n}[(A_i\varrho_i')' - k_i\varrho_i] = -(\varrho\hat{w})' + \left[\sum_{i=0}^{n}A_i\varrho_i'\right]' - \left[\sum_{i=0}^{n}k_i\varrho_i\right]' = 0$$

whence

$$(5.7) \qquad\qquad -\varrho\hat{w} + \sum_{i=0}^{n}A_i\varrho_i' = \sum_{i=0}^{n}k_i\varrho_i + k,$$

k is the integration constant.

Consequently, multiplying the Eq. (5.4) by ϱ_i and summing over all i, and then substituting together with the Eq. (5.7) in the Eq. (4.6) we obtain

$$(5.8) \qquad\qquad \mathbf{T} = -\left[k - \sum_{i=0}^{n}A_i\varrho_i'\right]\mathbf{1} - \sum_{i=0}^{n}A_i\varrho_i'(\mathbf{e}_x\otimes\mathbf{e}_x),$$

where $\mathbf{e}_x$ is the unit direction vector of the x-axis. From the conditions at infinity $k = P_\infty$, whence

$$(5.9) \qquad\qquad T_{yy} = -P_\infty + \sum_{i=0}^{n}A_i\varrho_i'.$$

Since

$$(5.10) \qquad\qquad \sum_{i=0}^{n}A_i\varrho_i' = 2\sum_{i,j=0}^{n}\frac{\partial(\varrho\bar{\bar{w}})}{\partial I_{ij}}\,\varrho_i'\varrho_j',$$

inserting (5.9) into the Eq. (5.3) we have

(5.11)
$$\sigma = \int\limits_{-\infty}^{\infty} \sum_{i,j=0}^{n} \Phi_{ij}\varrho_i'\varrho_j' dx,$$

where Φ_{ij} is the symmetric matrix constructed in the following way:

$$\Phi_{ij} = \frac{\partial(\varrho\overline{\overline{w}})}{\partial I_{ij}} \quad \text{for} \quad i \neq j, \quad \Phi_{ij} = 2\frac{\partial(\varrho\overline{\overline{w}})}{\partial I_{ij}} \quad \text{for} \quad i = j.$$

In the case of a one-component medium and under the additional assumption that $\Phi_{11} \equiv \Phi_3 = \text{const}$, the Eq. (5.11) is reduced to that derived in [2], i.e.

$$\sigma = \Phi_3 \int\limits_{-\infty}^{\infty} \varrho'^2 dx.$$

It was derived under much more specific assumptions which are thus shown to be not necessary.

6. Simple nonlocal interactions

In this section we shall demonstrate a certain realization of the theory derived in Sec. 4 which, under rather general assumptions concerning the non-local interactions, may substantially be simplified. These considerations will clarify the physical interpretation of the gradient theory which may be considered as an approximate description of nonlocal interactions.

From the expression for the free energy $w = \hat{w}(\varrho_i, \nabla\varrho_i)$ we may separate the term $w_0 = w_0(\varrho_i)$ defined as the value of $\hat{w}(\varrho_i, \nabla\varrho_i)$ at $\nabla\varrho_i = 0$ for every i, and it may be written formally that

(6.1)
$$w = w_0(\varrho_i) + w_1(\varrho_i, \nabla\varrho_i), \quad i = 0, 1, ..., n.$$

In considering various physical systems the interactions are divided into long-range and short-range types, and in spite of a rather conventional character of that division it has a definite physical meaning with respect to certain definite systems. In our case the short-range interactions will be considered as such interactions which do not contribute to w_1.

In other words, the free energy connected with those interactions remains independent of the density gradients. All the remaining interactions will be considered as long-range ones. Our next assumption is the possibility of representing the free energy w in the form $w = w' + w''$, w' being the result of short-range interactions, while w'' — due to long-range interactions. Since w_1, according to the definition, does not depend on the short-range interactions, we have

(6.2)
$$w = w_0' + w_0'' + w_1$$

with $w_0' + w_0'' = w_0$ and $w_0' = w'$.

In [2] the long-range interactions were assumed to be central and expressible in terms of potentials (e.g. the Lennard-Jones type potential). This approach may easily be gen-

eralized to the case of many components. The density of force $\mathbf{f}_i$ resulting from the long-range interactions and applied to the component i at point $\mathbf{x}$ may be expressed in the form

$$(6.3) \qquad \mathbf{f}_i = \varrho_i(\mathbf{x}) \int \sum_{j=0}^{n} \varrho_j(\mathbf{y}) \psi_{ij}(R) \frac{\mathbf{R}}{R} dV_y.$$

Here $\mathbf{R} = \mathbf{y} - \mathbf{x}$, $R = |\mathbf{R}|$, and the functions ψ_{ij} are assumed to be bounded, symmetric in their indices and have bounded supports, the integration being performed over a certain ball of radius R_1 containing supports of all the functions ψ_{ij}. Under certain assumptions concerning the smoothness of ϱ_j they can be expanded into series in the neighbourhood of the point $\mathbf{x}$. Performing now the integration of consecutive terms and confining ourselves to the first five terms of the expansion we obtain, similarly to [2], the result

$$(6.4) \qquad \mathbf{f}_i(\mathbf{x}) = \varrho_i(\mathbf{x}) \sum_{j=0}^{n} [\psi_{ij}^{(1)} \nabla \varrho_j(\mathbf{x}) + \psi_{ij}^{(3)} \nabla \Delta \varrho_j(\mathbf{x})].$$

Here

$$(6.5) \qquad \begin{aligned} \psi_{ij}^{(1)} &= \frac{4\pi}{3} \int_{0}^{R_1} \psi_{ij}(R) R^3 dR, \\[2mm] \psi_{ij}^{(3)} &= \frac{2\pi}{15} \int_{0}^{R^1} \psi_{ij}(R) R^5 dR. \end{aligned}$$

On the other hand, according to the Eqs. (4.5), (6.1), (6.2) we should have

$$(6.6) \qquad \mathbf{f}_i(\mathbf{x}) = -\varrho_i \nabla \left(\frac{\partial(\varrho w_0'')}{\partial \varrho_i} \right) - \varrho_i \nabla \left(\frac{\partial(\varrho w_1)}{\partial \varrho_i} \right) + \varrho_i \nabla \left(\nabla \cdot \frac{\partial(\varrho w_1)}{\partial(\nabla \varrho_i)} \right).$$

It is easily verified that the Eq. (6.6) yields the Eq. (6.4) provided

$$(6.7) \qquad w_0'' = \sum_{ij=0}^{n} A_{ij} \frac{\varrho_i \varrho_j}{\varrho}, \qquad w_1 = \sum_{ij=0}^{n} B_{ij} \frac{\nabla \varrho_i \cdot \nabla \varrho_i}{\varrho}.$$

Here

$$A_{ij} = A_{ji}, \quad A_{ij} = \psi_{ij}^{(1)} \quad \text{for} \quad i \neq j, \quad A_{ij} = \frac{1}{2} \psi_{ij}^{(1)} \quad \text{for} \quad i = j;$$

$$B_{ij} = B_{ji}, \quad B_{ij} = \psi_{ij}^{(2)} \quad \text{for} \quad i \neq j, \quad B_{ij} = \frac{1}{2} \psi_{ij}^{(2)} \quad \text{for} \quad i = j.$$

By means of the Eq. (6.2) we finally obtain

$$(6.8) \qquad \hat{w}(\varrho_i, \nabla \varrho_i) = w_0(\varrho_i) + \frac{1}{\varrho} \sum_{ij=0}^{n} \psi_{ij}^{(3)} \left(\nabla \varrho_i \cdot \nabla \varrho_j - \frac{1}{2} \sum_{i,m=0}^{n} \nabla \varrho_i \cdot \nabla \varrho_m \delta_{ijlm} \right).$$

The equation (4.9) takes then the form

$$(6.9) \qquad -\nabla \left(\frac{\partial(\varrho w_0)}{\partial \varrho_i} \right) + \sum_{k=0}^{n} \psi_{ik}^{(3)} \nabla \Delta \varrho_k = 0,$$

while for σ we obtain

$$(6.10) \qquad \sigma = \sum_{ij=0}^{n} \psi_{ij}^{(3)} \int_{-\infty}^{\infty} \varrho_i' \varrho_j' dx.$$

In the considerations to follow the notion of pressure P will be understood as

$$(6.11) \qquad P = \varrho \sum_{i=0}^{n} \frac{\partial w_0}{\partial \varrho_i} \varrho_i,$$

which is not, in general, equal to $-\dfrac{1}{3}\,\mathrm{tr}\,\mathbf{T}$ and coincides with the latter expression only in the case in which $\nabla \varrho_i = 0$ for every i. Similarly, the potential μ_i will be understood as

$$(6.12) \qquad \mu_i = \frac{\partial(\varrho w_0)}{\partial \varrho_i}.$$

Magnitudes defined in this manner coincide with the classical ones. Using such notations the Eq. (6.9) may be written in the form

$$(6.13) \qquad -\nabla \mu_i + \sum_{k=0}^{n} \psi_{ik}^{(3)} \nabla \Delta \varrho_k = 0$$

and by multiplying the Eq. (6.9) by ϱ_i and summing over i we obtain

$$(6.14) \qquad -\nabla P + \sum_{i,k=0}^{n} \psi_{ik}^{(3)} \varrho_i \nabla \Delta \varrho_k = 0$$

The equations obtained (6.13) constitute one of the possible realizations of the general equations of equilibrium (4.9) corresponding to the form of interactions assumed in this section, while the Eq. (6.14) is the counterpart of the Eq. $(4.4)_1$ (with substitutions of the Eqs. $(4.4)_2$ and $(4.4)_3$) for the case of equilibrium and vanishing body forces.

The case presented obviously does not exhaust all the possibilities and it should be expected that the class of interactions which can be, in a good approximation, described by the equations derived in Sec. 4 is much wider.

7. Low concentration solution; surface tension and Henry law

In this section we shall apply the Eqs. (6.13) and (6.14) to the investigation of the problems of phase equilibrium and surface tension in a two-component solution of low concentration. Assume that for a certain substance A we know the one-dimensional, two-phase solution $\varrho_{0A}(x)$ of the equation

$$(7.1) \qquad -\nabla P(\varrho_A) + \psi_A^{(3)} \nabla \Delta \varrho_A = 0.$$

Let us investigate the changes in $\varrho_{0A}(x)$ and the form of $\varrho_B(x)$ produced by introducing such an amount of the component B to the system that its equivalent asymptotic concentration (i.e. the concentration measured far enough from the transition zone) reaches the value of ϱ_B $(\varrho_B \ll \varrho_A)$.

The two-component equilibrium will be governed by the two Eqs. (6.13) or, what is equivalent, by one of the Eqs. (6.13) together with the Eq. (6.14).

It is known from experiments that in perfect solutions the chemical potential of the solvent is expressed by the formula

$$(7.2) \qquad \mu_A = \mu_0 + \frac{RT}{M_A} \ln\left(\frac{\varrho_A/M_A}{\varrho_A/M_A + \varrho_B/M_B}\right),$$

μ_0 denoting the chemical potential of pure solvent [7]. For a pure substance we have $w = \int (P/\varrho^2)d\varrho$, and hence

$$(7.3) \qquad \mu_0 = \int \frac{\partial P_0(\varrho_{0A})}{\partial \varrho_{0A}} \frac{1}{\varrho_{0A}} d\varrho_{0A}.$$

Index 0 is used to denote all values referring to the pure solvent. As the second equation let us consider the Eq. (6.14). Thus we have

$$(7.4) \qquad -\frac{\partial P_0}{\partial \varrho_A} \frac{1}{\varrho_A} \varrho_A' - \frac{RT}{M_A}\left[\ln\left(\frac{\varrho_A/M_A}{\varrho_A/M_A+\varrho_B/M_B}\right)\right]' + \psi_A^{(3)}\varrho_A''' + \psi_{AB}^{(3)}\varrho_B''' = 0,$$

$$-\frac{\partial P(\varrho_A, \varrho_B)}{\partial \varrho_A} \varrho_A' - \frac{\partial P(\varrho_A, \varrho_B)}{\partial \varrho_B} \varrho_B' + \psi_A^{(3)}\varrho_A\varrho_A''' + \psi_{AB}^{(3)}(\varrho_A\varrho_B''' + \varrho_A'''\varrho_B) + \psi_B^{(3)}\varrho_B\varrho_B''' = 0.$$

Function $\varrho_A = \varrho_A(x)$ may be represented as

$$(7.5) \qquad \varrho_A(x) = \varrho_0(x) + \varrho^*(x).$$

Here $\varrho_0(x)$ is the solution of the Eq. (7.1) under the conditions

$$\lim_{x \to \pm\infty} \varrho_0', \varrho_0'' = 0.$$

As it was mentioned before, ϱ_B may be assumed as small in comparison with ϱ_A; in what follows we shall consider ϱ_B and ϱ^* together with their derivatives to be small enough to disregard their products. A more accurate analysis (omitted here) requires the equations to be written in dimensionless variables; it is fairly easy owing to the fact that the theory contains certain characteristic lengths (e.g. the magnitude l introduced in [2]) which facilitates the introduction of derivatives evaluated with respect to dimensionless variables x/l instead of x.

Disregarding therefore the expressions mentioned above and taking into account that $\varrho_0(x)$ satisfies the Eq. (7.1) we obtain after integration

$$(7.6) \qquad -\left(\frac{\partial P_0}{\partial \varrho_0} \frac{1}{\varrho_0}\right) \varrho^* + \frac{RT}{\varrho_0 M_B} \varrho_B + \psi_A^{(3)}\varrho^{*''} + \psi_{AB}^{(3)}\varrho_B'' = k_1,$$

$$-\frac{\partial P_0}{\partial \varrho_0} \varrho^* - \varphi(\varrho_0)\varrho_B + \psi_A^{(3)}(\varrho_0\varrho^{*''} + \varrho_0'\varrho^* - \varrho_0'\varrho^*) + \psi_{AB}^{(3)}(\varrho_0\varrho_B'' + \varrho_0''\varrho_B - \varrho_0'\varrho_B') = k_2,$$

Here $P(\varrho_0)$, ϱ_0, ϱ_0'', ϱ_0'' are known functions of x, and $\varphi(\varrho_0)$ is a known function of its argument defined as

$$(7.7) \qquad \varphi(\varrho_0) \equiv \left.\frac{\partial P(\varrho_A, \varrho_B)}{\partial \varrho_B}\right|_{\substack{\varrho_B=0 \\ \varrho_A=0}},$$

while k_1, k_2 are integration constants. Multiplying the Eq. $(7.6)_1$ by ϱ_0 and subtracting from the Eq. $(7.6)_2$ we obtain

$$(7.8) \qquad -\left(\varphi(\varrho_0)+\frac{RT}{M_B}\right)\varrho_B+\psi_A^{(3)}(\varrho_0''\varrho^*-\varrho_0'\varrho^{*\prime})+\psi_{AB}^{(3)}(\varrho_0''\varrho_B-\varrho_0'\varrho_B') = k_2-\varrho_0 k_1$$

Let us introduce the notation

$$(7.9) \qquad \theta \equiv -\psi_B^{(3)}(\varrho_0''\varrho^*-\varrho_0'\varrho^{*\prime})-\psi_{AB}^{(3)}(\varrho_0''\varrho_B-\varrho_0'\varrho_B')$$

whence

$$(7.10) \qquad \frac{\theta'}{\varrho_0'} = -\frac{\varrho_0'''}{\varrho_0'}\psi_A^{(3)}\varrho^*+(\psi_{A}^{(3)}\varrho^{*\prime\prime}+\psi_{AB}^{(3)}\varrho_B'')-\frac{\varrho_0'''}{\varrho_0'}\psi_{AB}^{(3)}\varrho_B.$$

However, from the the Eq. (7.1) written in one-dimensional form we have

$$(7.11) \qquad \frac{\varrho_0'''}{\varrho_0'}\psi_A^{(3)} = \frac{\partial P_0}{\partial \varrho_0}\frac{1}{\varrho_0}.$$

Substitution of the Eq. (7.11) in the Eq. (7.10) and then in the Eq. $(7.6)_1$ yields

$$(7.12) \qquad \frac{RT}{\varrho_0 M_B}\varrho_B+\frac{\theta'}{\varrho_0'}+\frac{\partial P_0}{\partial \varrho_0}\frac{1}{\varrho_0}\frac{\psi_{AB}^{(3)}}{\psi_A^{(3)}}\varrho_B = k_1.$$

The Eqs. (7.8) and (7.12) may be written as

$$(7.13) \qquad \begin{aligned} \left(\varphi(\varrho_0)+\frac{RT}{M_B}\right)\varrho_B+\theta &= k_1\varrho_0-k_2, \\ \frac{\varrho_0'}{\varrho_0}\left(\frac{\psi_{AB}^{(3)}}{\psi_A^{(3)}}\cdot\frac{\partial P_0}{\partial \varrho_0}+\frac{RT}{M_B}\right)\varrho_B+\theta' &= k_1\varrho_0'. \end{aligned}$$

Of interest are such solutions which at $x \to \pm \infty$ yield the density distributions asymptotically tending to certain constant values, and thus we shall seek the solution of the Eqs. (7.1) under the conditions $\varrho^{*\prime}, \varrho_B', \varrho^{*\prime\prime}, \varrho_B'' \to 0$ at $x \to \pm\infty$, since also $\varrho_0', \varrho_0'' \to 0$ at $x \to \pm\infty$; hence

$$(7.14) \qquad \lim_{x\to\pm\infty} \theta, \theta' = 0.$$

The Eq. $(7.13)_1$ is now differentiated, inserted into $(7.13)_2$ and divided by ϱ_B to yield

$$(7.15) \qquad \frac{\dfrac{\varrho_0'}{\varrho_0}\left(\dfrac{\psi_{AB}^{(3)}}{\psi_A^{(3)}}\dfrac{\partial P_0}{\partial \varrho_0}+\dfrac{RT}{M_B}\right)-\left(\varphi(\varrho_0)+\dfrac{RT}{M_B}\right)'}{\left(\varphi(\varrho_0)+\dfrac{RT}{M_B}\right)}-\frac{\varrho_B'}{\varrho_B} = 0.$$

To simplify the considerations let us assume that $\varrho_{0(\infty)} > \varrho_{0(-\infty)}$ and so we shall be interested in the distribution of ϱ_B at a fixed density $\varrho_{B(\infty)}$ of the component B in the liquid phase. Solution of the Eq. (7.15) leads to

$$(7.16) \qquad \varrho_B = \varrho_{B(\infty)}\left(\frac{\varphi(\varrho_0)_{(\infty)}+\dfrac{RT}{M_B}}{\varphi(\varrho_0)+\dfrac{RT}{M_B}}\right)\exp\left(-\int_{\varrho_0}^{\varrho_{0(\infty)}}\frac{1}{\varrho_0}\frac{\dfrac{\psi_{AB}^{(3)}}{\psi_A^{(3)}}\dfrac{\partial P_0}{\partial \varrho_0}+\dfrac{RT}{M_B}}{\varphi(\varrho_0)+\dfrac{RT}{M_B}}d\varrho_0\right).$$

The functions $\partial P_0/\partial\varrho_0$, $\varphi(\varrho_0)$, $\varrho_0(x)$ being known, we can determine the function $\varrho_B(x)$ effectively.

Complicated form of the expression makes the discussion of the Eq. (7.16) rather difficult although the value of ϱ'_B may be determined comparatively easily to yield the following condition of extremum of the function

$$\frac{\partial\varphi}{\partial\varrho_0} = \frac{1}{\varrho_0}\left(\frac{\psi^{(3)}_{AB}}{\psi^{(3)}_A}\frac{\partial P_0}{\partial\varrho_0} + \frac{RT}{M_B}\right).$$

It is seen that $\varrho_B(x)$ is not necessarily monotone and may assume extremal values in the transition zone what may, e.g. in the case of a maximum, correspond to the known effect of higher concentration of surface-active substances in the sub-surface zone.

From the Eqs. $(7.13)_1$ and (7.16) θ is calculated,

(7.17) $$\theta = k_1\varrho_0 - k_2 - \varrho_{B(\infty)}\left(\varphi(\varrho_0)_{(\infty)} + \frac{RT}{M_B}\right)F(\varrho_0),$$

with the notation

$$F(\varrho_0) \equiv \exp\left[-\int_{\varrho_0}^{\varrho_0(\infty)}\frac{1}{\varrho_0}\frac{\dfrac{\psi^{(3)}_{AB}}{\psi^{(3)}_A}\dfrac{\partial P_0}{\partial\varrho_0} + \dfrac{RT}{M_B}}{d\varrho_0\varphi(\varrho_0) + \dfrac{RT}{M_B}}\,d\varrho_0\right].$$

From the Eq. (7.16) we may determine $\varrho_{B(-\infty)}$ as a function of $\varrho_{B(\infty)}$ and then, taking the limit $x \to \pm\infty$ in Eq. $(7.18)_1$, two equations are obtained enabling us to determine k_1 and k_2.

Let us now observe that substitution of the Eq. (7.5) into (6.10) yields

(7.18) $$\sigma = \int_{-\infty}^{\infty}[\psi^{(3)}_A(\varrho'^2_0 + 2\varrho'_0\varrho^{*'} + (\varrho^{*'})^2) + 2\psi^{(3)}_{AB}(\varrho'_0\varrho'_B + \varrho^{*'}\varrho'_B) + \psi^{(3)}_B(\varrho'_B)']dx,$$

or, the terms involving the products of derivatives of ϱ^* and ϱ_B being disregarded, the formula is found

(7.19) $$\sigma = \sigma_0 + 2\int_{-\infty}^{\infty}(\psi^{(3)}_{A_1}\varrho'_0\varrho^{*'} + \psi^{(3)}_{AB}\varrho'_0\varrho'_B)dx,$$

σ_0 denoting the surface tension of pure solvent.

Let us now observe that

(7.20) $$\int_{-\infty}^{\infty}\theta dx = \int_{-\infty}^{\infty}\varrho'_0(\psi^{(3)}_{A_1}\varrho^{*'} + \psi^{(3)}_{AB}\varrho'_B)dx - \int_{-\infty}^{\infty}\varrho''_0(\psi^{(3)}_{A_1}\varrho^* + \psi^{(3)}_{AB}\varrho_B)dx.$$

Integrating the second right-hand integral by parts and bearing in mind that $\varrho'_0 \to 0$ at $x \to \pm\infty$, we obtain

(7.21) $$\int_{-\infty}^{\infty}\theta dx = 2\int_{-\infty}^{\infty}(\psi^{(3)}_A\varrho'_0\varrho^{*'} + \psi^{(3)}_{AB}\varrho'_0\varrho'_B)dx$$

and thus

$$(7.22) \qquad \sigma = \sigma_0 + \int_{-\infty}^{\infty} \theta \, dx.$$

The value of θ from the Eq. (7.17) and the values of k_1, k_2 evaluated by the method described before are now inserted into this formula to yield

$$(7.23) \qquad \sigma = \sigma_0 + \varrho_{B(\infty)}\left(\varphi(\varrho_0)_{(\infty)} + \frac{RT}{M_B}\right) \times$$

$$\times \int_{-\infty}^{\infty}\left[\frac{(\varrho_0 - \varrho_{0(-\infty)}) + (\varrho_{0(\infty)} - \varrho_0)F(\varrho_0)_{(-\infty)}}{\varrho_{0(\infty)} - \varrho_{0(-\infty)}} - F(\varrho_0)\right] dx.$$

The surface tension is expressed here as a linear function of $\varrho_{B(\infty)}$ at low concentrations of the component B in the solution. Linearity of that relationship is an obvious result of linearization of the initial set of equations, the essential feature of the result consisting in the fact, that the corresponding coefficient of proportionality is expressed in terms of known (at least formally) magnitudes and material functions.

It should also be stressed here that tha Eq. (7.16) leads directly to the Henry law which is usually expressed in the form

$$C_B = kP_B$$

with C_B denoting the concentration of component B in the solution, and P_B — its partial pressure in the gaseous phase as determined from the Dalton law. Also here the mere fact of obtaining the Henry law is not surprising, the law being practically postulated earlier by assuming the chemical potential in the form of (7.2) another fact is important here: the proportionality coefficient k may effectively be determined from the Eq. (7.16).

8. Conclusions

All the equations derived within the framework of the model considered, gradient terms being disregarded, reduce in the case of equilibrium to known, classical relations. The asymptotic values of concentration at $x \to \pm\infty$ coincide with those obtained by the methods used in thermodynamics of solutions. The advantage of the model proposed over other methods consists in the fact that it creates the possibility of considering spatial distributions of components within the transition zones and, consequently, of determining e.g. the surface tensions. A certain drawback of the method is due to the necessity of knowing the values of certain material constants and functions, which were not known so far; more than that, the values can not be determined by means of the known experimental techniques within the entire region of their arguments, i.e. at certain values of the arguments they must be evaluated by extrapolation or by theoretical methods of statistical mechanics.

In the case of a single component the model is reduced to that described in [2], and in that case of practical value may be not only the equations of equilibrium but also the

equations of motion which can be utilized in all cases in which the viscosity and thermal coupling are neglegible, like e.g. in barotropic liquids.

In the case of two components, the equations of motion derived may easily be generalized by introducing the terms due to viscosity and assuming that the dissipation connected with diffusion depends on the diffusion flux only through the modulus h_1, since in this case $h_1 = -h_0$.

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References

1. A. BLINOWSKI, *On the surface behaviour of gradient-sensitive liquids*, Arch. Mech., **25**, 2, 259–268, 1973.
2. A. BLINOWSKI, *On the order of magnitude of the gradient-of-density dependent part of an elastic potential in liquids*, Arch. Mech., **25**, 5, 833–849, 1973.
3. A. BLINOWSKI, *Droplets and layers in the gradient model of capillary liquids*, Arch. Mech. [printing].
4. M. E. GURTIN, A. S. VARGAS, *On the classical theory of reacting fluid mixtures*, Arch. Rat. Mech. Analysis, **43**, 3, 179–197, 1971.
5. I. G. PETROVSKIĬ, *Lectures on the theory of ordinary differential equations* [in Russian], Nauka, Moskwa 1964.
6. J. H. HILDEBRANDT, R. L. SCOTT, *Regular solutions*, Prentice-Hall, Englewood Cliffs, NJ 1962.
7. K. ZALEWSKI, *Lectures on phenomenological and statistical thermodynamics* [in Polish], PWN, Warszawa 1969.
8. R. D. MINDLIN, *Second gradient of strain and surface tension in linear elasticity*, Int. J. Solids Structures, **1**, 417–438, 1965.
9. A. N. RUSANOV, *Phase equilibria and surface phenomena* [in Russian], Himia, Leningrad 1967.

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