

## THERMODYNAMICALLY NON-EQUILIBRIUM BUBBLE MEDIUM

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UDC 532.5

*A model is developed for a thermodynamically locally-nonequilibrium two-temperature two-velocity bubble medium. The mathematical model is formulated in two stages. In the first stage, a quasiequilibrium model is deduced from the variational principle. In the second stage, locally non-equilibrium exchange terms are introduced into the equations obtained. From the general model thus formulated, one can obtain simpler equations (equations of the theories of long or short waves, etc.) using asymptotic and other methods.*

A model for a thermodynamically locally-nonequilibrium two-temperature two-velocity bubble medium is developed. The construction is performed in two stages.

Initially, a quasiequilibrium model, or more precisely, a model that is invariant with respect to reversal of time, is constructed on the basis of the variational principle. Similar equations were deduced in [1] (see also [2, 3]). However, in [1], the initial hypotheses are needlessly complicated, and, therefore, the final system turned out to be cumbersome and difficult to flow. Probably, this is the reason why the consideration in [1] is incomplete: for example, there are no energy-balance equations for individual components (a drawback of many models of heterogeneous media) and the energy conservation law for the system as a whole. As a result, it is difficult to correctly introduce terms that describe various locally nonequilibrium exchange processes. At the given stage of development of the theory of heterogeneous media, it is expedient to seek rational simplification of hypotheses to obtain a system with a most pronounced structure, so that it will be easier to perform an analysis of the characteristic features of the equations and their practical use, and to check them. (The simplest variant of a two-velocity system is constructed in Sec. 4.)

At the second stage, locally nonequilibrium exchange terms are introduced into the equations obtained. For this, an appropriate Onsager formalism, which is similar to the one described in [4], is postulated (see also [5, 6]). The two-stage construction of phenomenological models, i.e., a combination of the variational principle with subsequent use of an appropriate variant of Onsager formalism, seems to be most optimal methodically. Further, from such rather general models, more specific models (equations of the long- or short-wave theories, etc.) can be derived by asymptotic or other reasoning.

**1. Description of Thermodynamics.** We consider a two-component bubble liquid that includes: (a) a carrier component with density  $\rho_{(1)} = \text{const}$ , specific internal energy  $\epsilon_{(1)}$ , specific entropy  $s_{(1)}$ , and temperature  $T_{(1)}$ ; in this case, the differential Gibbs form is

$$d\epsilon_{(1)} = T_{(1)} ds_{(1)}; \quad (1.1)$$

(b) a bubble component, consisting of spherical bubbles of radius  $R$  with volumetric number density of the bubbles  $n$ ;  $\rho_{(2)}$  is the density of the gas (vapor) in a bubble,  $p_{(2)}$  is the pressure,  $\epsilon_{(2)}$  is the specific internal energy,  $s_{(2)}$  is the specific entropy, and  $T_{(2)}$  is the temperature; thus the differential Gibbs form for the gas is

\*Deceased.

$$D\varepsilon_{(2)} = T_{(2)}ds_{(2)} - p_{(2)}d(1/\rho_{(2)}). \quad (1.2)$$

The volumetric concentration of the bubbles is  $\alpha \equiv ((4/3)\pi R^3)n$ . The volumetric densities of the carrier and bubble components are  $\rho' \equiv (1 - \alpha)\rho_{(1)}$  and  $\rho'' \equiv \alpha\rho_{(2)}$ , respectively. It is assumed that the radius and concentration of the bubbles are small. The velocities of the components are denoted by  $v_{(i)} = (v_{(i)}^k)$ ,  $k = 1, 2, 3$ . It is convenient to introduce Galilean 4-dimensional velocity vectors  $v_{(i)}^\nu \equiv (1, v_{(i)}) = (1, v_{(i)}^1, v_{(i)}^2, v_{(i)}^3)$ , so that  $v_{(i)}^0 = 1$ . In addition, we assume that  $x^0 \equiv t$ . The Latin tensor indices take values 1 and 2, and the Greek tensor indices take values 0, 1, 2, and 3.

The motion of a spherical gas bubble at a velocity  $v_{(2)}$  in an incompressible medium having a velocity  $v_{(1)}$  gives rise to a perturbed flow in the medium. The kinetic energy of the flow is

$$k_{\text{per}} = \left(\frac{4}{3}\pi R^3\right)\rho_{(1)}\left(\frac{3}{2}\dot{R}^2 + \frac{w^2}{4}\right), \quad w \equiv v_{(1)} - v_{(2)}, \quad \dot{R} \equiv D_{(2)}R \equiv v_{(2)}^\nu \frac{\partial R}{\partial x^\nu} = \frac{\partial R}{\partial t} + v_{(2)}^k \frac{\partial R}{\partial x^k}.$$

If the bubbles interact weakly with one another (which is the case for small  $R$  and  $\alpha$ ), the volumetric density of the kinetic energy of the perturbed flow is

$$K_{\text{per}} = k_{\text{per}}n = \alpha\rho_{(1)}\left(\frac{3}{2}\dot{R}^2 + \frac{w^2}{4}\right). \quad (1.3)$$

Finally, the volumetric density of the surface-tension energy is

$$\varepsilon_{\text{surf}} = (4\pi R^2)n\sigma. \quad (1.4)$$

For simplicity, it is assumed that  $\sigma = \text{const}$ .

From the definitions it follows that

$$d\alpha = -\frac{1}{\rho_{(1)}}d\rho', \quad 3\frac{dR}{R} = -\frac{1}{\alpha\rho_{(1)}}d\rho' - \frac{dn}{n}, \quad \frac{d\rho_{(2)}}{\rho_{(2)}} = \frac{1}{\alpha\rho_{(1)}}d\rho' + \frac{1}{\alpha\rho_{(2)}}d\rho''.$$

Hence,  $3\dot{R}/R = -(1/\alpha\rho_{(1)})\dot{\rho}' - \dot{n}/n$ .

**2. Variational Principle.** We assume that for particles of the carrier component, the Lagrangian coordinates are  $\xi(t, x) = (\xi^a)$ , and for the bubble component, they are  $\eta(t, x) = (\eta^a)$ . By the definition of Lagrangian coordinates, we have

$$D_{(1)}\xi^a = 0, \quad D_{(2)}\eta^a = 0, \quad D_{(i)} \equiv v_{(i)}^\nu \frac{\partial}{\partial x^\nu}. \quad (2.1)$$

We introduce the functional

$$J_1 \equiv \int_{t_0}^{t_1} \int_{R^3} \left\{ \rho' \frac{v_{(1)}^2}{2} + \rho'' \frac{v_{(2)}^2}{2} + K_{\text{per}} - \rho' \varepsilon_{(1)} - \rho'' \varepsilon_{(2)} - \varepsilon_{\text{surf}} \right\} dx dt.$$

We seek a stationary position  $J_1$  provided that equalities (1.1)–(1.4) and the following *conservation laws* are satisfied:

— for the mass of the carrier component

$$\mathbf{M}_{(1)} = 0, \quad \mathbf{M}_{(1)} \equiv \frac{\partial}{\partial x^\nu} [\rho' v_{(1)}^\nu]; \quad (2.2)$$

— for the mass of the bubble component

$$\mathbf{M}_{(2)} = 0, \quad \mathbf{M}_{(2)} \equiv \frac{\partial}{\partial x^\nu} [\rho'' v_{(2)}^\nu]; \quad (2.3)$$

— for the entropy of the carrier component

$$\mathbf{S}_{(1)} = 0, \quad \mathbf{S}_{(1)} \equiv \frac{\partial}{\partial x^\nu} [\rho' s_{(1)} v_{(1)}^\nu]; \quad (2.4)$$

— for the entropy of the bubble component

$$S_{(2)} = 0, \quad S_{(2)} \equiv \frac{\partial}{\partial x^\nu} [\rho'' s_{(2)} v_{(2)}^\nu]; \quad (2.5)$$

— for the number of bubbles

$$N = 0, \quad N \equiv \frac{\partial}{\partial x^\nu} [n v_{(2)}^\nu]. \quad (2.6)$$

Equations (2.1) define  $v_{(i)}^k$  via derivatives of the Lagrangian coordinates [7]. Using the Lagrange method, we replace  $J_1$  by the functional

$$J_2 \equiv \int_{t_0}^{t_1} \int_{R^3} \left\{ \rho' \frac{v_{(1)}^2}{2} + \rho'' \frac{v_{(2)}^2}{2} + K_{\text{per}} - \rho' \varepsilon_{(1)} - \rho'' \varepsilon_{(2)} - \varepsilon_{\text{surf}} \right. \\ \left. + \varphi' M_{(1)} + \varphi'' M_{(2)} + \psi' S_{(1)} + \psi'' S_{(2)} + \omega N \right\} dx dt.$$

Here  $\varphi'$ ,  $\varphi''$ ,  $\psi'$ ,  $\psi''$ , and  $\omega$  are the Lagrange multipliers. Since the addition of a divergent term does not affect the form of Euler equations,  $J_2$  can be replaced by the following functional, which is more convenient for calculations,

$$J \equiv \int_{t_0}^{t_1} \int_{R^3} L dx dt$$

$$\left[ L \equiv \rho' \frac{v_{(1)}^2}{2} + \rho'' \frac{v_{(2)}^2}{2} + K_{\text{per}} - \rho' \varepsilon_{(1)} - \rho'' \varepsilon_{(2)} - \varepsilon_{\text{surf}} - \rho' D_{(1)} \varphi' - \rho' s_{(1)} D_{(1)} \psi' - \rho'' D_{(2)} \varphi'' - \rho'' s_{(2)} D_{(2)} \psi'' - n D_{(2)} \omega \right].$$

The Lagrangian  $L$  is assumed to depend on  $\xi$ ,  $\eta$ ,  $\rho'$ ,  $\rho''$ ,  $s' \equiv \rho' s_{(1)}$ ,  $s'' \equiv \rho'' s_{(2)}$ ,  $n$ ,  $\varphi'$ ,  $\varphi''$ ,  $\psi'$ ,  $\psi''$ , and  $\omega$  and their derivatives. We denote  $E_{(\xi)\alpha} \equiv \delta L / \delta \xi^\alpha$ ,  $E_{(\eta)\alpha} \equiv \delta L / \delta \eta^\alpha$ ,  $E_{\rho'} \equiv \delta L / \delta \rho'$ ,  $E_{s'} \equiv \delta L / \delta s'$ , ..., where  $\delta L / \delta \xi^\alpha, \dots$  are variational derivatives.

By the Noether theorem, the invariance of  $L$  with respect to spatial shifts leads to the law of conservation of the total momentum  $J = 0$  [8], where

$$J^j = \{ \xi_j^\alpha E_{(\xi)\alpha} + \rho'_j E_{\rho'} + s'_j E_{s'} + \varphi'_j E_{\varphi'} + \psi'_j E_{\psi'} \} \\ + \{ \eta_j^\alpha E_{(\eta)\alpha} + \rho''_j E_{\rho''} + s''_j E_{s''} + n_j E_n + \varphi''_j E_{\varphi''} + \psi''_j E_{\psi''} + \omega_j E_\omega \}. \quad (2.7)$$

Here  $\xi_j^\alpha \equiv \partial \xi^\alpha / \partial x^j$ , etc. After calculations (taking into account the relations for the Lagrange multipliers obtained from the Euler equations) we obtain

$$J^j = 0, \quad J^j \equiv \frac{\partial}{\partial x^\nu} \left\{ \rho' v_{(1)}^\nu v_{(1)}^j + \rho'' v_{(2)}^\nu v_{(2)}^j + \frac{\alpha}{2} \rho_{(1)} w^\nu w^j + P \delta_j^\nu \right\}; \quad (2.8)$$

$$P \equiv \left( p_{(2)} - \frac{2\sigma}{R} \right) - \rho_{(1)} \left( R \dot{R} + \frac{3}{2} \dot{R}^2 - \frac{w^2}{4} \right), \quad \dot{R} = D_{(2)} R, \quad \ddot{R} = D_{(2)} \dot{R}, \quad w^\nu \equiv v_{(1)}^\nu - v_{(2)}^\nu. \quad (2.9)$$

Since, by definition,  $v_{(i)}^0 = 1$ , we have  $w^0 = 0$ .

In (2.7), separating terms that refer to the carrier medium, for the medium we obtain the momentum-balance equation that includes the a nondivergent term (this is actually a general method for determining the momentum of a carrier medium):

$$J_{(1)}^j = 0, \quad J_{(1)}^j \equiv \frac{\partial}{\partial x^\nu} \left\{ v_{(1)}^\nu \left[ \rho' v_{(1)}^j + \frac{\alpha}{2} \rho_{(1)} w^j \right] \right\} + \frac{\alpha}{2} \rho_{(1)} \left( w | \frac{\partial v_{(1)}}{\partial x^j} \right) + (1 - \alpha) \frac{\partial P}{\partial x^j}, \quad (2.10)$$

$[(a | b) \equiv \sum_i a^i b^i]$  is the scalar product of the vectors  $a, b \in R^3$ .

The momentum-balance equation for the bubble component is similarly constructed:

$$J_{(2)}^j = 0, \quad J_{(2)}^j \equiv \frac{\partial}{\partial x^\nu} \left\{ v_{(2)}^\nu \left[ \rho'' v_{(2)}^j - \frac{\alpha}{2} \rho_{(1)} w^j \right] \right\} - \frac{\alpha}{2} \rho_{(1)} \left( w \mid \frac{\partial v_{(1)}}{\partial x^j} \right) + \alpha \frac{\partial P}{\partial x^j}. \quad (2.11)$$

Obviously,  $J_{(1)}^j + J_{(2)}^j = J^j$ .

**Remark.** Because of the presence of the nondivergent term, it is not clear which relation can be correctly called the momentum-balance equation for the component. Apparently, the simple general method used above, which is based on the relationship between the definition of the momentum and invariance with respect to spatial shifts and on expression (2.7), which follows from the Noether theorem [8], gives the only correct definition. The same is true for the energy-balance equations (see below). The invariance with respect to the time shifts gives the law of conservation of the total energy  $\mathbf{E} = 0$ , where [cf. (2.7)]

$$-\mathbf{E} = \{ \xi_t^a E_{(\xi)a} + \dots + \psi_t^i E_{\psi^i} \} + \{ \eta_t^a E_{(\eta)a} + \dots + \omega_t E_\omega \}. \quad (2.12)$$

Here  $\xi_t^a \equiv \partial \xi^a / \partial t$ , etc. After calculations we obtain

$$\mathbf{E} = \frac{\partial}{\partial t} \left\{ \rho' \varepsilon_{(1)} + \rho'' \varepsilon_{(2)} + \varepsilon_{\text{surf}} + \rho' \frac{v_{(1)}^2}{2} + \rho'' \frac{v_{(2)}^2}{2} + K_{\text{per}} \right\} + \frac{\partial}{\partial x^k} \left\{ v_{(1)}^k \left[ \rho' \left( \varepsilon_{(1)} + \frac{v_{(1)}^2}{2} \right) + (1 - \alpha) P \right] \right. \\ \left. + \frac{\alpha}{2} \rho_{(1)} (v_{(1)} \mid w) w^k + v_{(2)}^k \left[ \rho'' \left( \varepsilon_{(2)} + \frac{v_{(2)}^2}{2} \right) + K_{\text{per}} + \varepsilon_{\text{surf}} + \alpha P \right] \right\}. \quad (2.13)$$

Separating terms in (2.12) that refer to the carrier component, we obtain the following energy-balance equation for this component:

$$\mathbf{E}_{(1)} = 0, \quad (2.14)$$

$$\mathbf{E}_{(1)} \equiv \frac{\partial}{\partial x^\nu} \left\{ v_{(1)}^\nu \left[ \rho' \left( \varepsilon_{(1)} + \frac{v_{(1)}^2}{2} \right) + \frac{\alpha}{2} \rho_{(1)} (v_{(1)} \mid w) \right] \right\} - \frac{\alpha}{2} \rho_{(1)} \left( w \mid \frac{\partial v_{(1)}}{\partial t} \right) + v_{(1)}^j (1 - \alpha) \frac{\partial P}{\partial x^j}.$$

**3. Final System.** Thus, the variational principle with the functional  $J$  leads to Eq. (2.2)–(2.6), (2.8)–(2.11), (2.13), and (2.14). The final system is conveniently written as

$$\mathbf{M} = 0, \quad \mathbf{J}^j = 0, \quad \mathbf{E} = 0; \quad (3.1a)$$

$$\mathbf{M}_{(1)} = 0, \quad \mathbf{J}_{(1)}^j = 0, \quad \mathbf{E}_{(1)} = 0; \quad (3.1b)$$

$$\mathbf{N} = 0; \quad (3.1c)$$

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 - \frac{w^2}{4} = \frac{1}{\rho_{(1)}} \left( p_{(2)} - \frac{2\sigma}{R} - P \right), \quad (3.1d)$$

where  $\mathbf{M} = \mathbf{M}_{(1)} + \mathbf{M}_{(2)} \equiv (\partial / \partial x^\nu) \{ \rho' v_{(1)}^\nu + \rho'' v_{(2)}^\nu \}$ .

Equations (3.1) lead to the law of conservation of the total entropy:

$$\mathbf{S} = 0, \quad \mathbf{S} \equiv \mathbf{S}_{(1)} + \mathbf{S}_{(2)} \equiv \frac{\partial}{\partial x^\nu} \{ \rho' s_{(1)} v_{(1)}^\nu + \rho'' s_{(2)} v_{(2)}^\nu \}. \quad (3.2)$$

The following relations are valid:

$$\mathbf{E}_{(1)} = \left( \varepsilon_{(1)} - T_{(1)} s_{(1)} - \frac{v_{(1)}^2}{2} \right) \mathbf{M}_{(1)} + v_{(1)}^j \mathbf{J}_{(1)}^j + T_{(1)} \mathbf{S}_{(1)}; \quad (3.3)$$

$$\mathbf{E}_{(2)} = \frac{1}{\rho_{(1)}} P \mathbf{M}_{(1)} + \left( \gamma_{(2)} - \frac{v_{(2)}^2}{2} \right) \mathbf{M}_{(2)} + v_{(2)}^j \mathbf{J}_{(2)}^j + T_{(2)} \mathbf{S}_{(2)} + \zeta \mathbf{N}. \quad (3.4)$$

Here  $\mathbf{E}_{(2)} \equiv \mathbf{E} - \mathbf{E}_{(1)}$ ;

$$\gamma_{(2)} \equiv \varepsilon_{(2)} - T_{(2)} s_{(2)} + p_{(2)} / \rho_{(2)}; \quad (3.5)$$

$$\zeta \equiv \frac{1}{n} \left\{ \alpha \left( P - p_{(2)} - \rho_{(1)} \frac{w^2}{2} \right) + K_{\text{per}} + \varepsilon_{\text{surf}} \right\}. \quad (3.6)$$

Relations (3.3) and (3.4) lead to the fundamental equality

$$\mathbf{E} = \left( \gamma_{(1)} - \frac{v_{(1)}^2}{2} \right) \mathbf{M}_{(1)} + v_{(1)}^j \mathbf{J}_{(1)}^j + T_{(1)} \mathbf{S}_{(1)} + \left( \gamma_{(2)} - \frac{v_{(2)}^2}{2} \right) \mathbf{M}_{(2)} + v_{(2)}^j \mathbf{J}_{(2)}^j + T_{(2)} \mathbf{S}_{(2)} + \zeta \mathbf{N}; \quad (3.7)$$

$$\gamma_{(1)} \equiv \varepsilon_{(1)} - T_{(1)} s_{(1)} + P / \rho_{(1)}. \quad (3.8)$$

Relation (3.7) is a representation of the second law of thermodynamics for the bubble medium considered (see also [8]). In the derivation of (3.4), the Rayleigh equation (3.1d) was assumed to be identically satisfied, i.e., it was regarded as a definition of  $P$ . We note that  $\gamma_{(1)}$  and  $\gamma_{(2)}$ , defined by expressions (3.8) and (3.5), are in essence the specific thermodynamic Gibbs potentials. Relations (3.3) and (3.4) lead to a second fundamental relation, which supplements (3.7):

$$\begin{aligned} \mathbf{S} = & -\frac{1}{T_{(2)}} \left\{ \Gamma_{(2)} - \frac{v_{(2)}^2}{2} \right\} \mathbf{M} - \frac{1}{T_{(2)}} v_{(2)}^j \mathbf{J}^j + \frac{1}{T_{(2)}} \mathbf{E} - \left\{ \frac{1}{T_{(1)}} \left( \Gamma_{(1)} - \frac{v_{(1)}^2}{2} \right) \right. \\ & \left. - \frac{1}{T_{(2)}} \left( \Gamma_{(2)} - \frac{v_{(2)}^2}{2} \right) \right\} \mathbf{M}_{(1)} - \left\{ \frac{1}{T_{(1)}} v_{(1)}^j - \frac{1}{T_{(2)}} v_{(2)}^j \right\} \mathbf{J}_{(1)}^j + \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\} \mathbf{E}_{(1)} - \frac{\zeta}{T_{(2)}} \mathbf{N}. \end{aligned} \quad (3.9)$$

Here

$$\Gamma_{(1)} \equiv \varepsilon_{(1)} - T_{(1)} s_{(1)} + \frac{T_{(1)}}{T_{(2)}} \frac{P}{\rho_{(1)}}, \quad \Gamma_{(2)} \equiv \gamma_{(2)}. \quad (3.10)$$

Relation (3.9) implies, in particular, that if equalities (3.1) are valid, the closing conservation law (3.2) is obeyed.

For  $T_{(1)} = T_{(2)}$ , we have  $\Gamma_{(1)} = \gamma_{(1)}$ . In the general case of a two-temperature medium [ $T_{(1)} \neq T_{(2)}$ ], there is an important difference between  $\Gamma_{(1)}$  and  $\gamma_{(1)}$ .

**4. Simplified System.** If  $w$  is small, we have  $w^2/4 \ll (3/2)\dot{R}^2$  and, instead of (1.3), we can write

$$K_{\text{per}} \equiv \alpha \rho_{(1)} \frac{3}{2} \dot{R}^2. \quad (4.1)$$

As a result, we come to the system

$$\mathbf{M} = 0, \quad \mathbf{J}^j = 0, \quad \mathbf{E} = 0; \quad (4.2a)$$

$$\mathbf{M}_{(1)} = 0, \quad \mathbf{J}_{(1)}^j = 0, \quad \mathbf{E}_{(1)} = 0; \quad (4.2b)$$

$$\mathbf{N} = 0; \quad (4.2c)$$

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho_{(1)}} \left( p_{(2)} - \frac{2\sigma}{R} - P \right), \quad (4.2d)$$

where

$$\mathbf{J}^j \equiv \frac{\partial}{\partial x^\nu} \{ \rho' v_{(1)}^\nu v_{(1)}^j + \rho'' v_{(2)}^\nu v_{(2)}^j + P \delta_j^\nu \};$$

$$\begin{aligned} \mathbf{E} = & \frac{\partial}{\partial t} \left\{ \rho' \varepsilon_{(1)} + \rho'' \varepsilon_{(2)} + \varepsilon_{\text{surf}} + \rho' \frac{v_{(1)}^2}{2} + \rho'' \frac{v_{(2)}^2}{2} + K_{\text{per}} \right\} + \frac{\partial}{\partial x^k} \left\{ v_{(1)}^k \left[ \rho' \left( \varepsilon_{(1)} + \frac{v_{(1)}^2}{2} \right) \right. \right. \\ & \left. \left. + (1 - \alpha) P \right] + v_{(2)}^k \left[ \rho'' \left( \varepsilon_{(2)} + \frac{v_{(2)}^2}{2} \right) + K_{\text{per}} + \varepsilon_{\text{surf}} + \alpha P \right] \right\}; \end{aligned}$$

$K_{\text{per}}$  is defined by formula (4.1);

$$J_{(1)}^j \equiv \frac{\partial}{\partial x^\nu} (\rho' v_{(1)}^\nu v_{(1)}^j) + (1 - \alpha) \frac{\partial P}{\partial x^j}; \quad E_{(1)} \equiv \frac{\partial}{\partial x^\nu} \left\{ v_{(1)}^\nu \rho' \left( \varepsilon_{(1)} + \frac{v_{(1)}^2}{2} \right) \right\} + v_{(1)}^j (1 - \alpha) \frac{\partial P}{\partial x^j}.$$

Equations (4.2) lead to the closing conservation law

$$\mathbf{S} = 0. \quad (4.3)$$

Here and below,  $\mathbf{M}_{(i)}$ ,  $\mathbf{M}$ ,  $\mathbf{S}_{(i)}$ , and  $\mathbf{S}$  have the same meaning as in Sec. 3.

The following relations, which are similar to (3.3) and (3.4), are valid:

$$\mathbf{E}_{(1)} = \left( \varepsilon_{(1)} - T_{(1)} s_{(1)} - \frac{v_{(1)}^2}{2} \right) \mathbf{M}_{(1)} + v_{(1)}^j \mathbf{J}_{(1)}^j + T_{(1)} \mathbf{S}_{(1)}; \quad (4.4)$$

$$\mathbf{E}_{(2)} = \frac{1}{\rho_{(1)}} P \mathbf{M}_{(1)} + \left( \gamma_{(2)} - \frac{v_{(2)}^2}{2} \right) \mathbf{M}_{(2)} + v_{(2)}^j \mathbf{J}_{(2)}^j + T_{(2)} \mathbf{S}_{(2)} + \zeta \mathbf{N}. \quad (4.5)$$

Here  $\gamma_{(2)}$  is defined by formula (3.5);  $\mathbf{E}_{(2)} \equiv \mathbf{E} - \mathbf{E}_{(1)}$ ;

$$\zeta \equiv \frac{1}{n} \{ \alpha (P - p_{(2)}) + K_{\text{per}} + \varepsilon_{\text{surf}} \} \quad (4.6)$$

[cf. (3.6) and (4.6)];  $K_{\text{per}}$  is taken according to (4.1). As in Sec. 3, it is assumed that the Rayleigh equation (4.2d) is identically satisfied. Relations (4.4) and (4.5) lead to

$$\begin{aligned} \mathbf{S} = & -\frac{1}{T_{(2)}} \left\{ \Gamma_{(2)} - \frac{v_{(2)}^2}{2} \right\} \mathbf{M} - \left\{ \frac{1}{T_{(2)}} v_{(2)}^j \right\} \mathbf{J}^j + \left\{ \frac{1}{T_{(2)}} \right\} \mathbf{E} - \left\{ \frac{1}{T_{(1)}} \left( \Gamma_{(1)} - \frac{v_{(1)}^2}{2} \right) \right. \\ & \left. - \frac{1}{T_{(2)}} \left( \Gamma_{(2)} - \frac{v_{(2)}^2}{2} \right) \right\} \mathbf{M}_{(1)} - \left\{ \frac{1}{T_{(1)}} v_{(1)}^j - \frac{1}{T_{(2)}} v_{(2)}^j \right\} \mathbf{J}_{(1)}^j + \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\} \mathbf{E}_{(1)} - \frac{\zeta}{T_{(2)}} \mathbf{N}. \end{aligned} \quad (4.7)$$

Here  $\Gamma_{(i)}$  is obtained from (3.10). Comparison of (3.9) and (4.7) shows that these expressions coincide with accuracy up to the definition of  $\zeta$ . When expressions of the form (3.9) coincide, we deal with *structural isomorphism* of the systems. Thus, systems (3.1), (3.2) and (4.2), (4.3) are structurally isomorphic with accuracy up to the definition of  $\zeta$ . Structurally isomorphic systems have many similar thermodynamic properties (see also Secs. 5–9).

**5. Onsager Formalism.** When the temperatures and some other characteristics of the components are not equal, local thermodynamic nonequilibrium takes place and locally nonequilibrium exchange processes occur. In a first approximation, they can be described phenomenologically using Onsager formalism, which is based on relations that are similar to (4.7). For the class of exchange processes of interest, we give the axiomatics of Onsager formalism in a similar manner as was done in [4] for diffusion processes (see also [5, 6]). We assume that at a point  $(t, x)$ , the state of the physical system considered is specified by the set of parameters  $(u_\alpha) \equiv u$ ,  $\alpha = 1, \dots, m$  and the dynamics of “reversible” processes is described by the differential equations

$$\mathbf{L}^\beta[u] = 0, \quad \beta = 1, \dots, m. \quad (5.1)$$

“Reversibility” means that system (5.1) is invariant with respect to reversal of time, i.e., the transformation  $t \rightarrow -t$ . It is assumed that each of Eqs. (5.1) represents a law of conservation or balance of mass, momentum, and energy (and generally, other important physical quantities, for example, angular momentum) for the system as a whole and its individual components. A corollary of (5.1) in this case is the differential law of conservation of the total entropy

$$\mathbf{S} = 0. \quad (5.2)$$

It is assumed that the following relation, which is similar to (4.7), holds:

$$q_\beta \mathbf{L}^\beta[u] = \mathbf{S}. \quad (5.3)$$

Here  $q_\beta$  depend on  $u^\alpha$  and, possibly, on the derivatives  $\partial u \equiv u_\nu^\alpha \equiv \partial u^\alpha / \partial x^\nu$ . The quantities  $q_\beta$  are called *integrating factors*.

**Remark.** In [9], we considered the classical situation in which  $q_\beta \equiv q$  depended on  $u$  only. In this case, it was required that the mapping  $u \rightarrow q(u)$  be locally one-to-one, i.e., the equation  $q(u) = q$  should be uniquely solvable locally and the inverse mapping  $u(q)$  should be defined locally. If  $q = q(u, \partial u)$ , then, apparently, a certain analog of the condition of unique solvability will also be useful here, but it is not clear how it should be exactly formulated.

Furthermore, it is assumed that the system of conservation laws and/or balance equations (5.1) is an Onsager system in the sense of [4], i.e., the set of integrating factors  $(q_1, \dots, q_m)$  can be written as a set  $(z_1, \dots, z_k)$ , where, for all orthogonal transformations of space  $R^3$  that form the group  $O(3)$ , each  $z_i$  is transformed by a tensor rule, i.e., it represents a certain  $O(3)$  tensor (scalar, vector, ...). Thus, for (4.2), the set of integrating factors [see (4.7)] includes five  $O(3)$  scalars:  $-(1/T_{(2)})\{\Gamma_{(2)} - v_{(2)}^2/2\}$ ,  $1/T_{(2)}$ ,  $-\{(1/T_{(1)})(\Gamma_{(1)} - v_{(1)}^2/2) - (1/T_{(2)})(\Gamma_{(2)} - v_{(2)}^2/2)\}$ ,  $\{1/T_{(1)} - 1/T_{(2)}\}$ , and  $-\zeta/T_{(2)}$  and two vectors:  $-(1/T_{(2)})v_{(2)}^j$  and  $-\{(1/T_{(1)})v_{(1)}^j - (1/T_{(2)})v_{(2)}^j\}$ .

The introduction of terms that describe locally nonequilibrium exchange processes within the framework of Onsager formalism is performed as follows. Equations (5.1) are replaced by the equations

$$\mathbf{L}^\beta[u] = A^{\beta\gamma} q_\gamma. \quad (5.4)$$

Multiplying (5.4) by  $q_\beta$  and taking into account (5.3), instead of (5.2) we obtain

$$\mathbf{S} = \Theta, \quad \Theta \equiv A^{\beta\gamma} q_\beta q_\gamma \geq 0. \quad (5.5)$$

The matrix  $A \equiv [A^{\beta\gamma}]$  will be called an *Onsager matrix*. It should have the following properties:

(a) *symmetry*:  $A^{\beta\gamma} = A^{\gamma\beta}$ ,

(b) *dissipativity*:  $A \geq 0$ ,

(c)  $\Theta$  is a *Galilean invariant* because we are interested in equations that are invariant with respect to a Galilean group.

Along with the general conditions (a)–(c), additional restrictions on  $A^{\beta\gamma}$  can result from the specificity of the physical system considered or from the requirements of simplicity. For example, for elementary exchange processes, the matrix  $A$  usually has rank 1 (see Secs. 6–9). If  $q_\gamma$  are scalars (Galilean invariants), the matrix  $A$  can be diagonal and the right sides of (5.4) correspond (for each  $\beta$ ) to a specific elementary process. Generally this is not the case.

Let us consider the equations of Secs. 3 and 4. Assuming that the total masses, momentum, and energy are conserved, we examine the equations

$$\mathbf{M} = 0, \quad \mathbf{J}^j = 0, \quad \mathbf{E} = 0; \quad (5.6)$$

$$\mathbf{M}_{(1)} = \mathbf{m}_{(1)}, \quad \mathbf{J}_{(1)}^j = \mathbf{f}_{(1)}^j, \quad \mathbf{E}_{(1)} = \mathbf{h}_{(1)}; \quad (5.7)$$

$$\mathbf{N} = \mathbf{l}, \quad (5.8)$$

where  $\mathbf{m}_{(1)}$ ,  $\mathbf{f}_{(1)}^j$ ,  $\mathbf{h}_{(1)}$ , and  $\mathbf{l}$  have an Onsager structure that is similar to the right side of (5.4).

Like (5.7), we write  $\mathbf{M}_{(2)} = \mathbf{m}_{(2)}$ , where, according to (5.6),  $\mathbf{m}_{(1)} + \mathbf{m}_{(2)} = 0$  (and the same for the remaining relations), i.e.,  $\mathbf{E}_{(2)} = \mathbf{h}_{(2)}$  and  $\mathbf{E}_{(2)} \equiv \mathbf{E} - \mathbf{E}_{(1)}$ . Therefore,  $\mathbf{h}_{(1)} + \mathbf{h}_{(2)} = 0$ , and  $\mathbf{m}_{(1)}$ ,  $\mathbf{m}_{(2)}$ ,  $\mathbf{h}_{(1)}$ , and  $\mathbf{h}_{(2)}$  have an Onsager structure (5.4), i.e., they are linearly expressed in terms of the integrating factors  $q_\gamma$ .

Equations (5.6)–(5.8) lead to

$$\mathbf{S} = \Theta; \quad (5.9)$$

$$\begin{aligned} \Theta = & -\left\{ \frac{1}{T_{(1)}} \left( \Gamma_{(1)} - \frac{v_{(1)}^2}{2} \right) - \frac{1}{T_{(2)}} \left( \Gamma_{(2)} - \frac{v_{(2)}^2}{2} \right) \right\} \mathbf{m}_{(1)} \\ & - \left\{ \frac{v_{(1)}^j}{T_{(1)}} - \frac{v_{(2)}^j}{T_{(2)}} \right\} \mathbf{f}_{(1)}^j + \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\} \mathbf{h}_{(1)} - \frac{\zeta}{T_{(2)}} \mathbf{l}. \end{aligned} \quad (5.10)$$

We consider various elementary processes.

**6. Heat Exchange.** Let  $m_{(1)} = 0$ ,  $f_{(1)}^j = 0$ , and  $l = 0$ . By virtue of the symmetry conditions (a) (see Sec. 5), there is only the possibility  $h_{(1)} \sim \{1/T_{(1)} - 1/T_{(2)}\}$ , so that

$$h_{(1)} \equiv -na\Delta T, \quad \Delta T \equiv T_{(1)} - T_{(2)}. \quad (6.1)$$

The Onsager matrix is a diagonal matrix and, according to (5.9) and (5.10), we have

$$\Theta = \frac{na}{T_{(1)}T_{(2)}} (\Delta T)^2, \quad (\Theta \geq 0) \Leftrightarrow a \geq 0. \quad (6.2)$$

**7. Friction between the Components.** In the derivation of expression (1.3) for  $K_{per}$ , it was assumed that the flow in a neighborhood of a bubble is potential. Therefore, it is physically meaningless to introduce friction between the components in the model of Sec. 3. However, it is possible to consider a class of models for different types of local flows, and the following will be valid if the structure of the integrating factors, i.e., the structure of (5.9) and (5.10), remains unchanged.

Linear friction is characterized by the conditions  $m_{(1)} = 0$ ,  $l = 0$ , and

$$f_{(1)}^j \equiv -n\lambda(v_{(1)}^j - v_{(2)}^j) \equiv -n\lambda w^j. \quad (7.1a)$$

Assuming that  $v \equiv (1 - \alpha)v_{(1)} + \alpha v_{(2)}$ ,  $\alpha \equiv \rho''/\rho$ ,  $1 - \alpha \equiv \rho'/\rho$ ,  $\rho \equiv \rho' + \rho''$ , and  $1/T \equiv \alpha/T_{(1)} + (1 - \alpha)/T_{(2)}$ , we have

$$\left\{ -\frac{v_{(1)}}{T_{(1)}} + \frac{v_{(2)}}{T_{(2)}} \right\} = -\frac{1}{T}w - \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\}v. \quad (7.2)$$

Let

$$h_{(1)} \equiv -n\lambda(v | w). \quad (7.1b)$$

Taking into account (7.2), we obtain

$$f_{(1)}^j = n\lambda T \left\{ -\frac{v_{(1)}^j}{T_{(1)}} + \frac{v_{(2)}^j}{T_{(2)}} \right\} + n\lambda T v^j \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\},$$

$$h_{(1)} = n\lambda T v^j \left\{ -\frac{v_{(1)}^j}{T_{(1)}} + \frac{v_{(2)}^j}{T_{(2)}} \right\} + n\lambda T v^2 \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\}.$$

Thus, the Onsager matrix is symmetric and has rank 1 but it is not a diagonal matrix. Next, we find that

$$\Theta = n\lambda w^2/T, \quad (\Theta \geq 0) \Rightarrow (\lambda \geq 0). \quad (7.3)$$

To what extent does the expression (7.1b) for  $h$  uniquely defined? Let

$$h_{(1)} \equiv -n\lambda(v | w) + h_0. \quad (7.4)$$

From (7.1a) and (7.4) and the symmetry condition we obtain

$$h_0 = z \left\{ \frac{1}{T_{(1)}} - \frac{1}{T_{(2)}} \right\}; \quad (7.5)$$

$$\Theta = \frac{n\lambda}{T} w^2 + \frac{z}{(T_{(1)}T_{(2)})^2} \Delta T^2. \quad (7.6)$$

Comparison of (7.4)–(7.6) with (6.1), (6.2), (7.1b), and (7.3) shows that for  $z \neq 0$ , expressions (7.1a), (7.4), and (7.5) describe two elementary processes, friction and heat exchange, and the Onsager matrix has rank 2.

**8. Formation of New Bubbles.** If  $l$  new bubbles that appeared are of the same sort as those considered, i.e., if they have the same mass, velocity, etc., then, accordingly, the mass, momentum, and

energy of the bubble component increase and those of the carrier medium decrease. Since the total mass, momentum, and energy are thus conserved in this case, Eqs. (5.6) remain valid and, hence,

$$\mathbf{m}_{(1)} = -\mu \mathbf{l}, \quad \mu \equiv \frac{4}{3} \pi R^3 \rho_{(2)}; \quad (8.1a)$$

$$\mathbf{f}_{(1)}^j = \mu v_{(2)}^j \mathbf{l}; \quad (8.1b)$$

$$\mathbf{h}_{(1)} = -A \mathbf{l}; \quad (8.1c)$$

$$\mathbf{N} = \mathbf{l}, \quad (8.1d)$$

where, for the simplified model of Sec. 4, we have  $A = (\varepsilon_2 + v_{(2)}^2/2)\mu + (4/3)\pi R^3 \rho_{(1)}(3/2)\dot{R}^2 + 4\pi R^2 \sigma$ .

According to (5.4),  $\mathbf{l}$  has an Onsager structure ( $\mathbf{l} = A^\gamma q_\gamma$ ), where  $q_\gamma$  are integrating factors. Relation (8.1) and the symmetry conditions of the Onsager matrix yield

$$\mathbf{l} = -\zeta \Delta K; \quad (8.2)$$

$$\Delta K = \left[ \frac{\Delta e}{T_{(1)}} - \Delta s + \frac{1}{T_{(2)}} P \Delta \frac{1}{\rho} \right] - \frac{1}{T_{(1)}} \frac{w^2}{2}, \quad (8.3)$$

where  $\Delta e \equiv e_{(1)} - e_{(2)}$ ,  $\Delta s \equiv s_{(1)} - s_{(2)}$ ,  $\Delta(1/\rho) = 1/\rho_{(1)} - 1/\rho_{(2)}$ ,  $e_{(1)} \equiv \varepsilon_{(1)}$ , and  $e_{(2)} \equiv \varepsilon_{(2)} + (K_{\text{per}} + \varepsilon_{\text{surf}})/\rho''$ .

Obviously,  $e_{(2)}$  can be treated as the total "internal" energy calculated with allowance for the perturbations produced by the bubbles and the surface-tension energy.

It is of interest to compare (8.3) with the classical differential Gibbs form for equilibrium thermodynamics:

$$T ds = d\varepsilon + P d(1/\rho).$$

Hence,

$$\left[ \frac{d\varepsilon}{T} - ds + \frac{1}{T} P d \frac{1}{\rho} \right] = 0. \quad (8.4)$$

The expressions in square brackets in (8.3) and (8.4) are similarly constructed with a correction in (8.3) for the final differences and two-temperature nature. As before, the dissipativity condition gives  $\zeta \geq 0$ .

Apparently,  $\zeta$  depends greatly on the sign of  $\Delta K$ . In the simplest variant it is possible to set

$$\zeta \equiv \begin{cases} \zeta_+ > 0, & \text{if } \Delta K > 0, \\ 0, & \text{if } \Delta K \leq 0. \end{cases}$$

If  $\Delta K < 0$  and  $\zeta > 0$ , bubbles of the sort considered disappear (turn out to be thermodynamically unstable). Actually, this most likely means that such bubbles collapse. A fuller and more correct description of this phenomenon is possible in a phenomenological model that includes several different sorts of bubbles and in the rest is constructed similarly to the model described here.

According to the model of Sec. 3, for  $\mathbf{l}$  we have a more cumbersome expression but it is generally constructed in a similar manner as (8.2) and (8.3).

**9. Evaporation and Condensation.** Up to this point, the principles of Onsager formalism coupled to simple and natural physical reasoning uniquely determine the exchange terms for the elementary process in Eqs. (5.7) and (5.8) with accuracy up to one non-negative factor (in principle, the latter cannot be determined at the phenomenological level of reasoning and should be determined from experiments). In the case of evaporation, the situation is different. Here, generally speaking, it is possible to adopt different hypotheses to specify the elementary process, and it is difficult to tell beforehand which of them is most exact. Below, we formulated the simplest hypothesis that only the mass of the bubble changes in the process considered, and the remaining characteristics vary insignificantly (the *quasistationarity* hypothesis). More specifically, the hypothesis is as follows [cf. (8.1)]:

$$\mathbf{M}_{(1)} = \mathbf{m}_{(1)}, \quad \mathbf{M}_{(2)} = \mathbf{m}_{(2)} = -\mathbf{m}_{(1)}; \quad (9.1a)$$

$$\mathbf{f}_{(1)}^j = -v_{(2)}^j \mathbf{m}_{(2)} = v_{(2)}^j \mathbf{m}_{(1)}; \quad (9.1b)$$

$$\mathbf{h}_{(1)} = \left( \varepsilon_{(2)} + \frac{v_{(2)}^j}{2} \right) \mathbf{m}_{(1)}; \quad (9.1c)$$

$$\mathbf{N} = 0. \quad (9.1d)$$

Here  $\mathbf{m}_{(1)}$  has an Onsager structure (5.4), where  $q_\gamma$  are integrating factors which enter (5.10) [or (3.9) and (4.7) for the total and simplified systems, respectively]. The symmetry condition for the Onsager matrix leads to the expression

$$\mathbf{m}_{(1)} = -n\alpha\Delta G, \quad (9.2)$$

where

$$\Delta G \equiv \frac{1}{T_{(1)}} \left( \Delta\varepsilon - \frac{w^2}{2} \right) - \Delta s + \frac{1}{T_{(2)}} \left( \frac{P}{\rho_{(1)}} - \frac{P}{\rho_{(2)}} \right), \quad \Delta\varepsilon \equiv \varepsilon_{(1)} - \varepsilon_{(2)}, \quad \Delta s \equiv s_{(1)} - s_{(2)}.$$

Apparently,  $\alpha$  depends significantly on the sign of  $\Delta G$ .

In the one-temperature ( $T_{(1)} \sim T_{(2)} \sim T$ ) and one-velocity ( $w \sim 0$ ) limit  $\gamma_{(1)} \sim \varepsilon_{(1)} - Ts_{(1)} + P/\rho_{(1)}$ , and  $\gamma_{(2)} \sim \varepsilon_{(2)} - Ts_{(2)} + P/\rho_{(2)}$ , relation (9.2) leads to the following natural expression for the rate of phase transition:  $\mathbf{m} \sim -n\alpha\Delta\gamma/T$ , where  $\Delta\gamma \equiv \gamma_{(1)} - \gamma_{(2)}$ .

From (5.9), (5.10), (9.1), and (9.2) it follows that  $\Theta = n\alpha(\Delta G)^2$  and  $\Theta \geq 0 \Leftrightarrow \alpha \geq 0$ . For the simplified model of Sec. 4 we also use expressions (9.1) and (9.2).

Certainly, in this Section, as in Sec. 8, it is assumed that the carrier medium and the bubbles are formed by the same substance, which can exist in two states — a liquid state (the carrier medium) and a vapor state (the bubbles), so that evaporation and condensation are treated as phase transitions.

This work was supported by the Russian Foundation for Fundamental Research (Grant No. 96-01-01641).

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