PMM *U.S.S.R.*,Vol.48,No.3,pp. 280-286,1984
Printed in Great Britain

0021-8928/84 $10.00+0.00

HYDRODYNAMICS OF SURFACE PHENOMENA*

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The hydrodynamics of the interface separating two media in contact, namely the liquid-liquid and liquid-gas interface, is investigated. The interface is modelled by a strong shock surface, with sources of mass, momentum and energy /1/. The influence of the interface on the motion of the volume phases is described using the characteristics of the surface phases such as the surface tension, surface density, velocity, temperature, energy, entropy, viscosity, etc. The parameters occur in the relations at the strong shock and characterize the internal sources of mass, momentum and energy.

The laws of conservation of mass, momentum and energy are derived for the surface phase consisting of N components, in the multivelocity approximation, when the velocity vector of every component is introduced and the complete equations of change of momentum are written out for each component. The kinetic energy of the surface phase is determined as the sum of the kinetic energies of every component. Such an approach is necessary when the velocities of separate components are comparable with the difference between the velocity of the component and the mean mass velocity of the mixture. The use of the conservation laws in the diffusion approximation in this case may give an incorrect result.

To use the equations obtained to describe the liquid solutions, the internal energy of every component, which must be defined when the equations are derived in the multivelocity approximation, is assumed to be a function of not only the parameters of the given component, but also of the densities of the other components.

The methods of the thermodynamics of irreversible processes are used to obtain the equations for the surface heat fluxes, the surface tensors of the viscous stresses, the frictional forces between the components of the surface phase, the chemical surface reaction rates, the tangential components of the momentum flux across the surface governed by the viscosity of the volume phases, and the mass transfer between the volume and the surface phases. The equations describing the mass flux components from the volume to the surface phases and vice versa describe the kinetics of the adsorption (desorption) processes in the case when the processes are essentially non-equilibrium.

In the case when the surface density, energy, viscosity, thermal conductivity and volume viscosity are all zero, the equations obtained reduce to those of /1/ describing the non-equilibrium phase transition.

Relations on the strong shock surface with external mass, momentum and energy sources were derived in /2/. The derivation of the equations of surface hydrodynamics in the diffusion approximation is analogous to that used in volume hydrodynamics, and is given in /3—6/. An extended bibliography covering this problem can be found in /7/.

The equations of surface hydrodynamics were derived in /7—9/ using the method of averaging the volume equations describing the processes in the interphase layer. In /7/ systems of equations were derived for the true, as well as for the redundant surface parameters. Generally speaking, the equations obtained differ from those of classical hydrodynamics. In /10/ a correction was obtained for the surface tension related to the mass flux across the interface separating two viscous media.

1. Kinematics of the interphase surface. Let us consider a system consisting of two media in contact, liquid-liquid and liquid-gas, which we shall call from now on the volume phases I and II. The interface separating them represents a layer of the order of 10—100 Å thick, and the characteristic parameters of the medium change across it form the values in one phase to those in the other phase. The mechanical and thermodynamic properties of the medium in the interphase layer differ substantially from those prevalent in the volume phases, therefore the interphase layer is regarded as a third, surface phase. We will assume that each phase has the same N components and we shall model the narrow interpahse layer by strong shock surface Σ_*.

**Prikl.Matem.Mekhan.*,48,3,388-396,1984

We shall write the aprametric equation of the interphase surface Σ_s in the form (the Latin superscripts i, j, k, take the values 1, 2, 3, and the Greek indices $\alpha, \beta - 1, 2)$ $x^i = x^i(\eta^\alpha, t)$. Here x^i is the fixed Cartesian coordinate system, K, and η^α is the curvilinear coordinate system K_s on the surface Σ_s . We shall choose the surface coordinates η^α for convenience in such a manner, that the relation $(\partial x^i/\partial t)|_{\eta^\alpha} = Dn^i$ holds. Here n^i are the components of the unit vector normal to the surface Σ_s,and directed towards the plane I, Dn^i are the components of the rate of displacement of the surface Σ_s in space /2/.

We shall assume that the surface velocity component normal to the surface $v_{asn} = D$ (here and henceforth $a = 1, 2, \ldots, N$). Here we can write that ($\mathbf{э}_\alpha = \partial\mathbf{r}/\partial\eta^\alpha$ are the coordinate vectors of the basis of the system, K_s, $v_{as}{}^\alpha$ are the velocity components of the surface phase elements in the system K_s, tangential to the surface Σ_s , repeated indices $\alpha, \beta, \gamma, \varepsilon, i, j, k, l$ denote summation),

$$\mathbf{v}_{as} = D\mathbf{n} + v^\alpha{}_{as}\mathbf{э}_\alpha \tag{1.1}$$

We also introduce the three-dimensional $K_s'(h, \eta^\alpha)$, coordinate system where h is the distance between the points of the space and the surface Σ_s with a plus (minus) sign if the point belongs to the phase I(II), and η^α are the coordinates of the projection of this point onto the surface Σ_s in the system K_s.

The following relation /11/ holds for any tensor function $A_s(\eta^\alpha, t)$ defined on the surface Σ_s:

$$\frac{d}{dt}\int\limits_{\Sigma_s(t)} A_s\,d\Sigma = \int\limits_{\Sigma_s(t)} \left[\frac{\partial A_s}{\partial t}\bigg|_{\eta^\alpha} + \nabla_{s\alpha}A_s v_s{}^\alpha - 2HA_sD\right] d\Sigma \tag{1.2}$$

Here $\Sigma_s(t)$ is the liquid surface bound to the particles of the surface phase, $\nabla_{s\alpha}$ is the covariant derivative on the surface, $H = a^{\alpha\beta}b_{\alpha\beta}/2$ is the mean curvature of the surface, and $a^{\alpha\beta}$ $(b_{\alpha\beta})$ is the first (second) fundamental quadratic form of the surface. We see that (1.2) holds equally well for the characteristics of every component.

The following formulas hold at any point of the surface Σ_s :

$$\begin{gathered}\frac{\partial\mathbf{n}}{\partial t}\bigg|_{\eta^\alpha} = -\mathbf{э}_\alpha a^{\alpha\beta}\nabla_{s\beta}D, \quad \nabla_{s\alpha}\mathbf{n} = -b_\alpha{}^\beta\mathbf{э}_\beta \\ \frac{\partial\mathbf{э}_\alpha}{\partial t}\bigg|_{\eta^\alpha} = \mathbf{n}\nabla_{s\alpha}D - \mathbf{э}_\beta D b_\alpha{}^\beta\end{gathered} \tag{1.3}$$

Moreover, the partial time derivatives of the surface parameters will be taken everywhere at fixed values of the coordinates η^α, and denoted by $\partial/\partial t$.

2. Basic thermodynamic relations.

We shall assume that the volume and surface phases represent an N-component mixture. We denote by $\rho_a^{\mathrm{I(II)}}$ (ρ_{as}), $U_a^{\mathrm{I(II)}}$ (U_{as}), $S_a^{\mathrm{I(II)}}$ (S_{as}) the density, internal energy and entropy per unit mass of the a-th component in the volume (on the surface) respectively. The indices s, I and II denote the parameters corresponding to the surface and volume phases I and II respectively. Further, whenever the parameters of the volume phases need not be distinguished from each other, the indices I and II will be omitted. The temperature of all components is assumed to be the same within each phase, but the temperatures of the volume phases T^{I} and T^{II} at the interface as well as the temperature of the surface phase T_s do, generally, differ from each other.

In the case of multicomponent mixtures, except for the mixture of perfect gases, the internal energy of every component is a function of not only the thermodynamic parameters of this component, but also of the thermodynamic parameters of the other components in the mixture /12/

We shall assume that the internal energy of the a-th component in the volume phase U_a (in the surface phase U_{as}) depends on the entropy of the a-th component in the volume S_a (surface entropy S_{as}) and on the volume densities of all components ρ_b, $b = 1, 2, \ldots, N$ (surface densities ρ_{bs}, $b = 1, 2 \ldots, N$)

$$U_a = U_a(S_a, \rho_b), \; U_{as} = U_{as}(S_{as}, \rho_{bs}) \tag{2.1}$$

We will write Gibbs identity for the a-th component in the volume and surface phases in the form (summation over a and b is carried out everywhere from 1 to N)

$$dU_a = T\,dS_a + \sum_b \frac{\partial U_a}{\partial\rho_b}\,d\rho_b, \quad T = \frac{\partial U_a}{\partial S_a} \tag{2.2}$$

$$dU_{as} = T_s\,dS_{as} + \sum_b \frac{\partial U_{as}}{\partial\rho_{bs}}\,d\rho_{bs}, \quad T_s = \frac{\partial U_{as}}{\partial S_{as}} \tag{2.3}$$

We note that, in general, the surface phase is not "autonomous", i.e. the internal surface energy can depend not only on the surface, but also on the volume parameters /13–14/, e.g. on the density of the components in the volume phases and on the geometry (e.g. the curvature) of the surface /15/.

3. Laws of conservation of mass, momentum and energy in the volume phases.

Using the methods of the thermodynamics of irreversible processes, we can write the set of equations for a multicomponent system the internal energies of whose components satisfy the Gibbs identities (2.2) in the multivelocity approximation /12/

$$
\begin{aligned}
&\frac{\partial\rho_a}{\partial t}+\operatorname{div}\rho_a\mathbf{v}_a=\varkappa_a,\quad \sum_a\varkappa_a=0 \qquad (3.1)\\
&\frac{\partial}{\partial t}\rho_a v_a{}^i+\nabla_k\rho_a v_a{}^i v_a{}^k=R_a{}^i+\rho_a f_a{}^i\\
&\sum_a\frac{\partial}{\partial t}\left(\rho_a U_a+\rho_a\frac{v_a{}^2}{2}\right)=-\operatorname{div}\Big[\sum_a\rho_a\mathbf{v}_a\left(U_a+\frac{v_a{}^2}{2}+\frac{p_a}{\rho_a}\right)+\\
&\qquad \mathbf{q}-\sum_a\tau_{aik}v_a{}^i\text{э}^k\Big]+\sum_a\rho_a\mathbf{f}_a\mathbf{v}_a,\quad p_a=\sum_b\rho_a\rho_b\frac{\partial U_b}{\partial\rho_a}\\
&\mathbf{R}_a=-\nabla p_a-\sum_b\left(\rho_a\frac{\partial U_a}{\partial\rho_b}\nabla\rho_b-\rho_b\frac{\partial U_b}{\partial\rho_a}\nabla\rho_a\right)+\nabla_i\tau_a{}^{ij}\text{э}_j+\varkappa_a\mathbf{v}_a-\\
&\qquad \sum_b L_{ab}(\mathbf{v}_b-\mathbf{v}_1)\\
&\sum_a\mathbf{R}_a=-\nabla p+\sum_a\nabla_i\tau_a{}^{ij}\text{э}_j,\quad p=\sum_a p_a\\
&\qquad \mathbf{q}=-L\nabla T,\ L>0,\quad \tau_a{}^{ij}=L_a^{ijkl}\nabla_k v_{al},\\
&\qquad \varkappa_a=\sum_b\varphi_{ab}\left[\xi^1-\xi^b-\frac{(\mathbf{v}_b-\mathbf{v}_1)^2}{2}\right],\quad \xi^a=U_a-TS_a+\frac{p_a}{\rho_a}
\end{aligned}
$$

Here $\mathbf{v}_a$ is the velocity of motion of the *a*-th component, $\mathbf{f}_a$ is the external force acting on the unit mass of the *a*-th component, $\mathbf{q}$ is the heat flux, τ_{aik} is the viscous stress tensor of the *a*-th component, $\varkappa_a$ is the mass change of the *a*-th component per unit volume per unit time, and L_{ab}, L, φ_{ab}, $L_a{}^{ijkl}$ are the kinetic coefficients.

In the case when the internal energy and entropy of the unit mass of the mixture can be given by the formulas $U=\sum\limits_a c_aU_a$, $S=\sum\limits_a c_aS_a$ $(c_a=\rho_a/\rho)$, the quantities ξ^a represent the chemical potentials of the mixture, i.e. $\xi^a=(\partial U/\partial c_a)_{S,\,\rho,\,c_b,\,b\neq a}$.

4. Integral equations of mass and momentum change.

Let us consider, at some instant *t*, an arbitrary control volume *V* bounded by the surface Σ, containing within it a part of the interphase surface Σ_{sl} encircled by a closed contour *l*. Let us choose a point *M* on the surface Σ_{sl} and construct at *M* the basis vectors of the coordinate system K_s', $\mathbf{n}(M)$, $\text{э}_\alpha(M)$. We shall also consider a liquid volume $V_a(t)$ and liquid surface $\Sigma_{asl}(t)$ of the *a*-th component, which are identical at the given instant *t* with the control volume *V* and surface Σ_{sl} respectively.

Let us write the equations of change of mass and momentum projected on the direction of the vectors $\text{э}_\alpha(M)$ for each component, and equations of change of momentum for the mixture projected on the direction of the vector $\mathbf{n}(M)$ (all equations are written in the fixed *K* coordinate system)

$$
\begin{aligned}
&\frac{d}{dt}\Big(\int\limits_{V_a(t)}\rho_a\,d\tau+\int\limits_{\Sigma_{asl}(t)}\rho_{as}\,d\Sigma\Big)=\int\limits_V\varkappa_a\,d\tau+\int\limits_{\Sigma_{sl}}\varkappa_{as}\,d\Sigma,\quad\sum_a\varkappa_{as}=0 \qquad (4.1)\\
&\text{э}_\alpha\frac{d}{dt}\Big(\int\limits_{V_a(t)}\rho_a\mathbf{v}_a\,d\tau+\int\limits_{\Sigma_{asl}(t)}\rho_{as}\mathbf{v}_{as}\,d\Sigma\Big)=\int\limits_V R_{a\alpha}\,d\tau+\int\limits_{\Sigma_{sl}}R_{as\alpha}\,d\Sigma+\\
&\qquad\int\limits_V\rho_a f_{a\alpha}\,d\tau+\int\limits_{\Sigma_{sl}}\rho_{as}f_{as\alpha}\,d\Sigma\\
&\mathbf{n}\sum_a\frac{d}{dt}\Big(\int\limits_{V_a(t)}\rho_a\mathbf{v}_a\,d\tau+\int\limits_{\Sigma_{asl}(t)}\rho_{as}\mathbf{v}_{as}\,d\Sigma\Big)=\sum_a\Big(\int\limits_V R_{an}\,d\tau+\\
&\qquad\int\limits_{\Sigma_{sl}}R_{asn}\,d\Sigma+\int\limits_V\rho_a f_{an}\,d\tau+\int\limits_{\Sigma_{sl}}\rho_{as}f_{asn}\,d\Sigma\Big)
\end{aligned}
$$

Here $\mathbf{v}_{as}$ is the velocity of the *a*-th component of the surface phase, $\mathbf{f}_{as}$ is the external force per unit mass of the *a*-th component at the surface, $\mathbf{R}_{as}$ is the force acting on the *a*-th component at the surface from the direction of the *a*-th and other components of the surface phase and $\varkappa_{as}$ is the change in mass of the *a*-th component per unit surface area per unit time.

The subscripts n and α denote the projections of the vectors on the h and η^α axes.

5. Differential equations describing the change in mass, momentum, energy and entropy on the interphase surface. Applying to the integral equations (4.1) the procedure of deriving relations at the shock at the point M given in the monograph /2/, and taking the equations (1.2), (1.3) into account, we obtain the following differential equations describing the change of mass and momentum at the interphase surface ($\{F\} = F^{\mathrm{I}} - F^{\mathrm{II}}$, $v_{ans} = D$) :

$$\frac{\partial}{\partial t}\rho_{as} + \nabla_{s\alpha}\rho_{as}v_{as}^{\alpha} - 2H\rho_{as}D = -\{j_a\} + \varkappa_{as}, \quad \sum_a \varkappa_{as} = 0, \tag{5.1}$$

$$j_a = \rho_a(v_{an} - D)$$

$$\frac{\partial}{\partial t}\rho_{as}v_{as}^{\alpha} + \nabla_{s\beta}\rho_{as}v_{as}^{\beta}v_{as}^{\alpha} - \rho_{as}Dv_{as}^{\beta}b_{\beta}^{\alpha} - \rho_{as}Da^{\alpha\beta}\nabla_{s\beta}D - 2H\rho_{as}v_{as}^{\alpha}D = \tag{5.2}$$
$$\{\tau_{an}^{\alpha}\} - \{j_a v_a{}^{\alpha}\} + R_{as}^{\alpha} + \rho_{as}f_{as}^{\alpha}, \quad \tau_{an}^{\alpha} = \tau_{aj}^{\alpha}n^j$$

$$\sum_a \Big[\frac{\partial}{\partial t}\rho_{as}D + \nabla_{s\alpha}\rho_{as}Dv_{as}^{\alpha} + \rho_{as}v_{as}^{\alpha}\nabla_{s\alpha}D + \rho_{as}v_{as}^{\alpha}v_{as}^{\beta}b_{\alpha\beta} - \tag{5.3}$$
$$2H\rho_{as}D^2\Big] = \Big\{-p + \sum_a \tau_{ann}\Big\} + 2H\alpha + \sum_a \tau_{as}^{\alpha\beta}b_{\alpha\beta} -$$
$$\sum_a \{j_a v_{an}\} + \sum_a \rho_{as}f_{asn}, \quad p = \sum_a p_a, \quad \tau_{ann} = \tau_{aij}n^i n^j$$

The following assumptions were made in deriving (5.1)–(5.3):

$$\lim_{V\to 0}\int_V R_a{}^{\alpha}\,d\tau = \int_{\Sigma_{sl}} \{\tau_{an}^{\alpha}\}\,d\Sigma \tag{5.4}$$

$$\lim_{V\to 0}\sum_a \int_V R_{an}\,d\tau = \int_{\Sigma_{sl}} \Big\{-p + \sum_a \tau_{ann}\Big\}\,d\Sigma \tag{5.5}$$

$$\sum_a \mathbf{R}_{as} = \nabla_{s\beta}P_s^{\alpha\beta}\text{э}_{\alpha}, \quad P_s^{\alpha\beta} = \alpha a^{\alpha\beta} + \sum_a \tau_{as}^{\alpha\beta}, \tag{5.6}$$
$$\alpha = -\sum_a \alpha_a, \quad \alpha_a = \sum_b \rho_{as}\rho_{bs}\frac{\partial U_{bs}}{\partial \rho_{as}}$$

Relation (5.4) follows from the assumption that the projections of the quantities ∇p_a, $\rho_a(\partial U_a/\partial\rho_b)\cdot\nabla\rho_b$ tangential to the shock, and the force of friction proportional to the difference in velocities, occurring in the expression for $\mathbf{R}_{a\tau}$ in (3.1), are finite. Relation (5.5) follows from the definition of R_{an} in (3.1). The first relation of (5.6) means that the sum of all internal forces $\mathbf{R}_{as}$, acting on the surface components is equal to the surface gradient of the surface stress tensor of the mixture $P_s^{\alpha\beta}$. The second equation of (5.6) represents the assumption that the tensor $P_s^{\alpha\beta}$ can be represented by the sum $\alpha a^{\alpha\beta}$ and the viscous surface stress tensor, the latter, in turn, being the sum of the viscous stress tensor components, and α is the surface tension. Using (1.3) we obtain from (5.6)

$$\sum_a R_{asn} = 2H\alpha + \sum_a \tau_{as}^{\alpha\beta}b_{\alpha\beta}$$

The equations of motion (5.2) and (5.3) together yield the kinetic-energy theorem

$$\sum_a \Big[\frac{\partial}{\partial t}\rho_{as}\frac{v_{as}^2}{2} + \nabla_{s\alpha}\rho_{as}\frac{v_{as}^2}{2}v_{as}^{\alpha} - 2H\rho_{as}\frac{v_{as}^2}{2}D\Big] = \tag{5.7}$$
$$\sum_a \Big[\Big\{-j_a\Big(\mathbf{v}_a\mathbf{v}_{as} - \frac{v_{as}^2}{2}\Big) + \tau_{an}\mathbf{v}_{as} - p\mathbf{D}\Big\} + R_{as}^{\alpha}v_{as\alpha} + 2\alpha HD +$$
$$\tau_{as}^{\alpha\beta}b_{\alpha\beta}D - \varkappa_{as}\frac{v_{as}^2}{2} + \rho_{as}\mathbf{f}_{as}\mathbf{v}_{as}\Big], \quad \tau_{an} = \tau_{ann}\mathbf{n} + \tau_{an}^{\alpha}\text{э}_{\alpha}$$

Following /16/, we shall make the following **fundamental assumptions**:

1°. We shall assume that the energy-change equation of the surface phase has the form ($\mathbf{q}_s$ is the surface heat flux)

$$\sum_a \Big[\frac{\partial}{\partial t}E_{as} + \nabla_{as}E_{as}v_{as}^{\alpha} - 2HE_{as}D\Big] = \sum_a \Big[-\Big\{j_a\Big(U_a + \frac{v_a{}^2}{2}\Big) + \tag{5.8}$$
$$p_a v_{an} - \tau_{an}\mathbf{v}_a\Big\} - \nabla_{s\alpha}(\alpha_a v_{as}^{\alpha} - \tau_{as}^{\alpha\beta}v_{as\beta}) + \rho_{as}\mathbf{f}_{as}\mathbf{v}_{as}\Big] -$$
$$\{q_n\} - \nabla_{s\alpha}q_s^{\alpha}, \quad E_{as} = \rho_{as}\Big(U_{as} + \frac{v_{as}^2}{2}\Big)$$

2°. We shall assume that the change in entropy caused by the influx of heat and entropy and also due to the deformation of the interface during its motion, has the form

$$- \nabla_{s\alpha}\rho_{as}S_{as}v_{as}^{\alpha} + 2H\rho_{as}S_{as}D - \left\{\sum_a j_a S_a + \frac{q_n}{T}\right\} - \nabla_{s\alpha}\frac{q_s{}^{\alpha}}{T_s}$$

Subtracting (5.7) from (5.8) and taking the Gibbs identity (2.3) into account, we obtain the equation describing the change in surface entropy (σ_s is a dissipative function)

$$\sum_a \left[\frac{\partial}{\partial t}\rho_{as}S_{as} + \nabla_{s\alpha}\rho_{as}S_{as}v_{as}^{\alpha} - 2H\rho_{as}S_{as}D\right] = \tag{5.9}$$

$$-\left\{\sum_a j_a S_a + \frac{q_n}{T}\right\} - \nabla_{s\alpha}\frac{q_s{}^{\alpha}}{T_s} + \sigma_s$$

$$\sigma_s = q_s{}^{\alpha}\nabla_{s\alpha}\frac{1}{T_s} + \sum_a \frac{\varkappa_{as}}{T_s}\left[\xi_s{}^1 - \xi_s{}^a - \frac{(\mathbf{v}_{as} - \mathbf{v}_{1s})^2}{2}\right] + \tag{5.10}$$

$$\sum_a \frac{\tau_{as}^{\alpha\beta}}{T_s} e_{as\alpha\beta} + \sum_a \frac{1}{T_s}\Bigg[R_{as}^{\alpha} + \nabla_s{}^{\alpha}\alpha_a - \nabla_{s\beta}\tau_{as}^{\alpha\beta} - \varkappa_{as}v_{as}^{\alpha} +$$

$$\sum_b \left(\rho_{as}\frac{\partial U_{as}}{\partial \rho_{bs}}\nabla_s{}^{\alpha}\rho_{bs} - \rho_{bs}\frac{\partial U_{bs}}{\partial \rho_{as}}\nabla_s{}^{\alpha}\rho_{as}\right)\Bigg](v_{1s\alpha} - v_{as\alpha}) +$$

$$\sum_a \left\{\frac{\tau_{an}^{\alpha}}{T_s}(v_{a\alpha} - v_{as\alpha})\right\} + \left\{q_n\left(\frac{1}{T} - \frac{1}{T_s}\right)\right\} + \sum_a \left\{\frac{j_a}{T_s}\Psi^a\right\}$$

$$\xi_s{}^a = U_{as} + \frac{\alpha_a}{\rho_{as}} - T_s S_{as}, \quad e_{as\alpha\beta} = \nabla_{s\beta}v_{as\alpha} - b_{\alpha\beta}D$$

$$\Psi^a = \xi_s{}^a - \xi^a - \frac{(\mathbf{v}_a - \mathbf{v}_{as})^2}{2} + \frac{\tau_{ann}}{\rho_a} + S_a(T_s - T)$$

We note that the first four sums appearing in expression (5.10) for the increase in entropy σ_s, are connected with the irreversible surface processes, and the last three sums with the irreversible interaction between the surface and the volume phases.

Just as in the volume phases, the quantities $\xi_s{}^a$ are the chemical potentials of the mixture, with

$$U_s = \sum_a c_{as}U_{as}, \quad S_s = \sum_a c_{as}S_{as}, \quad \xi_s{}^a = \left(\frac{\partial U_s}{\partial c_{as}}\right)_{S_s,\,\rho,\,c_{bs},\,b\neq a},$$

$$c_{as} = \frac{\rho_{as}}{\rho_s}$$

When the chemical reactions at the surface proceed in such a manner that we have groups of components reacting with each other and not reacting with the components of the other groups, the second term on the right hand side of (5.10) and the corresponding kinetic relations, will change.

Let us assume that for the shocks in question, the mass and heat flux towards the shock, and the viscous friction of the surface phase against the volume phase are determined by the difference in the values of the corresponding parameters of the volume and surface phases occurring in the dissipative function, and the surface characteristics such as surface heat flux, rate of change of mass $\varkappa_{as}$, viscous stress tensor and the forces $R_{as}{}^{\alpha}$, are determined by the corresponding parameters just as in the case of the volume parameters. Let us write the linear relation connecting the generalized thermodynamic fluxes and forces (for brevity, we shall take into account the effects acting across the phases only in the formulas $q_n^{\mathrm{I(II)}}$ and j_a)

$$\mathbf{q}_s = -L_s\nabla_s T_s, \; L_s > 0; \; \tau_{as}^{\alpha\beta} = L_{as}^{\alpha\beta\varepsilon\gamma}e_{as\varepsilon\gamma} \tag{5.11}$$

$$\varkappa_{as} = \sum_b \varphi_{abs}\left[\xi_s{}^1 - \xi_s{}^b - \frac{(\mathbf{v}_{bs} - \mathbf{v}_{1s})^2}{2}\right]$$

$$R_{as}^{\alpha} = -\nabla_s{}^{\alpha}\alpha_a + \nabla_{s\beta}\tau_{as}^{\alpha\beta} + \varkappa_{as}v_{as}^{\alpha} - \sum_b \Bigg(\rho_{as}\frac{\partial U_{as}}{\partial \rho_{bs}}\nabla_s{}^{\alpha}\rho_{bs} -$$

$$\rho_{bs}\frac{\partial U_{bs}}{\partial \rho_{as}}\nabla_s{}^{\alpha}\rho_{as}\Bigg) - \sum_b L_{abs}(v_{bs}{}^{\alpha} - v_{1s}{}^{\alpha})$$

$$\tau_{an}^{\mathrm{I}} = k_a{}^{\mathrm{I}}(\mathbf{v}_a{}^{\mathrm{I}} - \mathbf{v}_{as}), \quad \tau_{an}^{\mathrm{II}} = -k_a^{\mathrm{II}}(\mathbf{v}_a^{\mathrm{II}} - \mathbf{v}_{as}) \tag{5.12}$$

$$q_n{}^{\mathrm{I}} = \zeta_1{}^{\mathrm{I}}\left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T_s}\right) + \sum_a \zeta_{a2}^{\mathrm{I}}\Psi^{a\mathrm{I}} \tag{5.13}$$

$$q_n^{\mathrm{II}} = \zeta_1^{\mathrm{II}}\left(\frac{1}{T^{\mathrm{II}}} - \frac{1}{T_s}\right) + \sum_a \zeta_{a2}^{\mathrm{II}}\Psi^{a\mathrm{II}}$$

$$j_a{}^{\mathrm{I}} = \sum_b \chi_{ab}^{\mathrm{I}}\Psi^{b\mathrm{I}} + \chi_a{}^{\mathrm{I}}\left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T_s}\right) \quad -j_a^{\mathrm{II}} = \sum_b \chi_{ab}^{\mathrm{II}}\Psi^{b\mathrm{II}} + \chi_a^{\mathrm{II}}\left(\frac{1}{T^{\mathrm{II}}} - \frac{1}{T_s}\right) \tag{5.14}$$

The kinetic coefficients in (5.11)—(5.14) can depend, generally speaking, on the local state parameters of the surface phase, such as temperature, density, component concentration, etc. The kinetic equations (5.11), (5.12) can be generalized by including the effects acting across the phases. The kinetic equations (5.11) for $\mathbf{q}_s, \varkappa_{as}, \tau_{as}^{\alpha\beta}, \mathbf{R}_{as}$ are analogous to the corresponding equations for the volume parameters, and have the same physical sense. The kinetic equations (5.12)—(5.14) refer to the change in mass, momentum and energy between the interface and the volume phases.

Equations (5.12) describe the viscous interaction between the volume phases and the interface, and follow from the fact that the modelling of the motion along the surface where the velocity distribution across the narrow interphase layer was not homogeneous, involved the surface velocities of the components as the mean characteristics. Such a modelling is analogous to introducing a frictional force between the gas and the particles dispersed in it, proportional to the difference between the velocity of the particles and the oncoming flow. We can obtain from (5.12) the relation expressing the equality of the tangential velocity components at the boundary between the phases in contact with each other, and this is the boundary condition commonly used in hydrodynamics.

Formulas (5.13) for $q_{n\mathrm{I(II)}}$ represent an expression for the irreversible heat flux between the volume phases and the interface. The flux is proportional, as expected, to the temperature difference between the volume and surface phases. We note that the temperatures at the interface between two phases may differ from each other and from the surface temperature due to the presence of a considerable temperature gradient within the normally narrow interphase layer. The temperature gradient may be caused by an anomalously low thermal conductivity of the interphase layer, by considerable mass and heat fluxes, etc.

Equations (5.14) describe the kinetics of the adsorption-desorption type processes in the case when the essential non-equilibrium character of the process represents the generalization of the conditions of phase equilibrium (equality of the chemical potentials of the phase components) which follow from (5.14) in the case of thermodynamic equilibrium. From (5.14) it follows that the adsorption-desorption process is caused not only by the difference in the chemical potentials, but also by the difference in phase temperatures.

Equations (5.1)—(5.3), (5.8) and (5.11)—(5.14) together with the equations in the volume phases I, II (3.1) represent a system for determining the motion of the surface and volume phases. Special attention must be given to the structure of the system of equations obtained. On one hand, the equations (5.1)—(5.3), (5.8) and (5.11)—(5.14) represent the boundary conditions connecting the parameters of two volume phases at the shock. On the other hand, they represent a system of equations for determining the surface phase parameters when the distribution of the volume parameters at the interphase surface is known. In this case additional initial and boundary conditions for the surface parameters must generally speaking be obtained, in order to solve the equations uniquely. The boundary conditions are specified on the lines situated on the surface in question. In general, the distribution of the characteristics of the surface and volume phases and the position of the interphase surface must be found by solving simultaneously the system of equation in the volume and at the interphase surface, with specified necessary boundary and initial conditions for the volume, as well as the surface parameters.

In the special case when the surface density, energy, entropy, viscosity, thermal conductivity and volume viscosities can all be neglected, the dissipative function σ_s is identical with the dissipative function given in /1/. A suitable choice of the coefficients reduces the kinetic equations for j_a and q_n to the kinetic equations of /1/.

REFERENCES

1. GOGOSOV V.V., NALETOVA V.A., CHYONG ZA BIN' and SHAPOSHNIKOVA G.A., On non-equilibrium phase transitions. In: Modern Problems of Mechanics. Pt.2, Moscow, Iz-vo MGU, 1984.
2. SEDOV L.I., Mechanics od continua. Vol.1, Moscow, NAUKA, 1976.
3. SCRIVEN L.E., Dynamics of a fluid interface. Equation of motion for Newtonian surface fluids. Chem. Engng Sci., Vol.12, 1960.
4. BEDEAUX D., ALBANO M.A. and MAZUR P., Boundary conditions and non-equilibrium thermodynamics. Physica, Vol.82A, No.3, 1976.
5. KOVAC J., Non-equilibrium thermodynamics of interfacial systems. Physica, Vol.86A, No.1, 1977.
6. NAPOLITANO L.G., Thermodynamics and dynamics of surface phases. Acta Astronautica, Vol.6, No.9, 1979.
7. GOGOSOV V.V., NALETOVA V.A., CHYONG ZA BIN' and SHAPOSHNIKOVA G.A., Laws of conservation of mass, momentum and energy at the interphase surface for the real and redundant surface parameters. Izv. Akad. Nauk SSSR, MZhG, No.6, 1983.
8. SLATTERY J.C., General balance equation for a phase interface. Industr. and Engng Chem. Fundamentals, Vol.6, No.1, 1967.
9. GUDRICH F.CH., Surface viscosity as the redundant capillary property of transport. In: Modern Theory of Capillarity. Leningrad, Khimiya, 1980.

10. GOGOSOV V.V., NALETOVA V.A., CHYONG ZA BIN' and SHAPOSHNIKOVA G.A., Relations at the interface between media, when there is mass transfer and inhomogeneity of the defining parameters along the surface. Dokl. Akad. Nauk SSSR, Vol.268, No.3, 1983.
11. MOECKEL G.P., Thermodynamics of an interface. Arch. Rational Mech. Analysis, Vol.57, No.3, 1974.
12. GREEN A.E. and NAGHDI P.M., On basic equations for mixtures. Quart. J. Mech. and Appl. Math., Vol.22, pt.4, 1969.
13. DEFAY R. and PRIGOGINE I., Surface tension and adsorption. N.Y.: Wiley, 1966.
14. DEFAY R., PRIGOGINE I. and SANFELD A., Surface thermodynamics, J. Colloid. and Interface Sci., Vol.58, No.3, 1977.
15. ONO S. and KONDO S., Molecular Theory of Surface Tension in Liquids. Moscow, Izd-vo inostr. lit. 1963.
16. GOGOSOV V.V., NALETOVA V.A. and SHAPOSHNIKOVA G.A., On the construction of models of polarizable disperse and multicomponent media. PMM Vol.43, No.3, 1979.

Translated by L.K.

PMM U.S.S.R.,Vol.48,No.3,pp.286-291,1984.
Printed in Great Britain

0021-8928/84 $10.00+0.00

MODELS OF POLARIZABLE CONTINUA WITH INTERNAL MECHANICAL MOMENTS*

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General methods of constructing models of continua are used to obtain a closed system of equations for a polarizable continuum with internal mechanical moments, and the distribution of small perturbations in such a medium studied.

1. Consider a system of N material points with masses m_ν and radius vectors $\mathbf{r}_\nu$, whose motion relative to the inertial frame of reference is described by the following Lagrange equations:

$$\frac{d}{dt}\frac{\partial L}{\partial \mathbf{r}_\nu^{\cdot}}-\frac{\partial L}{\partial \mathbf{r}_\nu}=\mathbf{f}_\nu \tag{1.1}$$

Here L is the Lagrangian of the system of material points, $\mathbf{f}_\nu$ is the external force vector acting on the ν-th point, and t is the time.

Let the Lagrangian be invariant with respect to translation and rotation of the frame of reference, and to the translation of the initial instant of time. We shall also assume in accordance with the Galileo's principle of relativity, that the dependence of the Lagrangian on the velocities $\mathbf{r}_\nu^{\cdot}$ has the following form (here and henceforth the summation over ν is carried out from $\nu=1$ to $\nu=N$):

$$L=\frac{1}{2}\sum m_\nu \mathbf{r}_\nu^{\cdot 2}-U(t,\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{1.2}$$

(In this case the passage to another inertial frame of reference changes the Lagrangian by a total derivative of some function). Then the laws of conservation of momentum $\mathbf{\Pi}$, angular momentum $\mathbf{K}$, energy ε and mass momentum of the system $\mathbf{G}$ all hold in the closed system (i.e. when $\mathbf{f}_\nu=0$).

Taking into account the external forces, we obtain from (1.1) the following balance equations:

$$\begin{gathered}\frac{d\mathbf{\Pi}}{dt}=\sum \mathbf{f}_\nu,\quad \frac{d\mathbf{E}}{dt}=\sum \mathbf{f}_\nu\cdot\mathbf{r}_\nu^{\cdot}\\ \frac{d\mathbf{K}}{dt}=\sum \mathbf{r}_\nu\times\mathbf{f}_\nu,\quad \frac{d\mathbf{G}}{dt}=-t\sum \mathbf{f}_\nu\\ \mathbf{\Pi}\equiv\sum m_\nu\mathbf{r}_\nu^{\cdot},\quad \mathbf{K}\equiv\sum \mathbf{r}_\nu\times m_\nu\mathbf{r}_\nu^{\cdot}\\ \mathbf{E}\equiv\sum\frac{1}{2}m_\nu\mathbf{r}_\nu^{\cdot 2}+U,\quad G\equiv\sum(m_\nu\mathbf{r}_\nu-tm_\nu\mathbf{r}_\nu^{\cdot})\end{gathered} \tag{1.3}$$

The existence of ten balance equations (1.3) is justified by the corresponding symmetry of the Lagrangian L, noted above, with respect to the complete ten-parametric group of the

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*Prikl.Matem.Mekhan.,48,3,397-403,1984