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CONDITIONS ON THE LINE OF CONTACT OF THREE MEDIA*

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The paper deals with the derivation of general conditions obtaining at the line of contact between three media, a solid, liquid and gas, and uses these conditions to describe the capillary phenomena. A generalized Young's equation is obtained taking into account the tensor character of the surface stresses, linear tension in the wetting perimeter and the rate of displacement of the line of contact along the surface of the solid. The general conditions at the surfaces of strong shocks were derived in /1/ without concretizing the surface distribution of the physical parameters. Assigning the specific physical and mechanical characteristics (density, energy, elastic or viscosity properties, etc.) to the interface boundary separating two media, leads to the possibility of describing surface phenomena in terms of the conditions at the shocks /2,6/. In the course of constructing the mathematical models, linear objects with linear densities of various parameters were also considered. For example, the edge energy of crystals in /7/, energy of the wetting perimeter in /8/, linear density of the "string" in /9/, etc. The purpose of this paper is to obtain the general conditions at the line of contact between three media and to use them to describe the capillary phenomena.

1. Balancing equations. We shall denote the quantities referring to the three phases in contact with each other, i.e. the solid, liquid and gaseous phase, by the indices 1, 2 and 3. The double indices will denote the corresponding interfaces, and the lines of contact (wetting perimeters) will carry the index 0 . We shall use the following notation for brevity:

$$a_{12}+a_{13}+a_{23}=\sum_{\substack{i,j=1\\ i<j}}^{3} a_{ij}=\sum_{i,j=1}^{3}{}^{*} a_{ij}$$

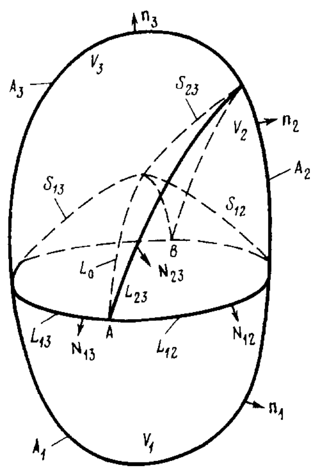

Fig.1

The following equations of mass balance (1.1), momentum (1.2), total energy (1.3) and entropy (1.4) hold for the material volume depicted in Fig.1:

$$\frac{d}{d\tau}\Big(\sum_{i=1}^{3}\int_{V_i}\rho_i dV+\sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\rho_{ij}dS+\int_{L_0}\rho_0 dL\Big)=0 \tag{1.1}$$

$$\frac{d}{d\tau}\Big(\sum_{i=1}^{3}\int_{V_i}\rho_i\mathbf{v}_i\,dV+\sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\rho_{ij}\mathbf{v}_{ij}\,dS+\int_{L_0}\rho_0\mathbf{v}_0\,dL\Big)= \tag{1.2}$$
$$\sum_{i=1}^{3}\int_{V_i}\rho_i\mathbf{F}_i\,dV+\sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\rho_{ij}\mathbf{F}_{ij}\,dS+\int_{L_0}\rho_0\mathbf{F}_0\,dL+$$
$$\sum_{i=1}^{3}\int_{A_i}\mathbf{n}_i\cdot\boldsymbol{\pi}_i\,dA+\sum_{i,j=1}^{3}{}^{*}\int_{L_{ij}}\mathbf{N}_{ij}\cdot\boldsymbol{\sigma}_{ij}\,dL+\sigma_0{}^{+}\mathbf{l}^{+}+\sigma_0{}^{-}\mathbf{l}^{-}$$

$$\frac{d}{d\tau}\Big(\sum_{i=1}^{3}\int_{V_i}\rho_i E_i\,dV+\sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\rho_{ij}E_{ij}\,dS+\int_{L_0}\rho_0 E_0\,dL\Big)=\sum_{i=1}^{3}\int_{V_i}\rho_i\mathbf{F}_i\cdot\mathbf{v}_i\,dV+\sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\rho_{ij}\mathbf{F}_{ij}\cdot\mathbf{v}_{ij}\,dS+\int_{L_0}\rho_0\mathbf{F}_0\cdot\mathbf{v}_0\,dL+ \tag{1.3}$$

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$$\sum_{i=1}^{3}\int_{A_i} \mathbf{n}_i\cdot\boldsymbol{\pi}_i\cdot\mathbf{v}_i\,dA + \sum_{i,j=1}^{3}{}^{*}\int_{L_{ij}} \mathbf{N}_{ij}\cdot\boldsymbol{\sigma}_{ij}\cdot\mathbf{v}_{ij}\,dL +$$
$$\sigma_0{}^{+}\mathbf{l}^{+}\cdot\mathbf{v}_0{}^{+} + \sigma_0{}^{-}\mathbf{l}^{-}\cdot\mathbf{v}_0{}^{-} - \sum_{i=1}^{3}\int_{A_i} \mathbf{q}_i\cdot\mathbf{n}_i\,dA - \sum_{i,j=1}^{3}{}^{*}\int_{L_{ij}} \mathbf{q}_{ij}\cdot\mathbf{N}_{ij}\,dL - \mathbf{q}_0{}^{+}\cdot\mathbf{l}^{+} - \mathbf{q}_0{}^{-}\cdot\mathbf{l}^{-}$$

$$\frac{d}{d\tau}\Big(\sum_{i=1}^{3}\int_{V_i}\rho_i s_i\,dV + \sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\rho_{ij}s_{ij}\,dS + \int_{L_0}\rho_0 s_0\,dL\Big) = \tag{1.4}$$
$$\sum_{i=1}^{3}\int_{V_i}\eta_i\,dV + \sum_{i,j=1}^{3}{}^{*}\int_{S_{ij}}\eta_{ij}\,dS + \int_{L_0}\eta_0\,dL -$$
$$\sum_{i=1}^{3}\int_{A_i}\frac{1}{T_i}\mathbf{q}_i\cdot\mathbf{n}_i\,dA - \sum_{i,j=1}^{3}{}^{*}\int_{L_{ij}}\frac{1}{T_{ij}}\mathbf{q}_{ij}\cdot\mathbf{N}_{ij}\,dL - \frac{1}{T_0^{+}}\mathbf{q}_0{}^{+}\cdot\mathbf{l}^{+} - \frac{1}{T_0^{-}}\mathbf{q}_0{}^{-}\cdot\mathbf{l}^{-}$$

Here ρ is density, $\mathbf{v}$ is velocity, $\mathbf{F}$ is the external mass forces density, $\boldsymbol{\pi}$ is the three-dimensional stress tensor, $\boldsymbol{\sigma}$ is the two-dimensional stress tensor, σ_0 is the linear tension u and s are the densities of internal energy and entropy, $E = {}^1/_2 v^2 + u$, $\mathbf{q}$ is the heat flux, η is work done by entropy, T is absolute temperature, τ is time, $\mathbf{n}$ in the outward normal to the surface, $\mathbf{N}_{ij}$ is the outward normal to the contour L_{ij} tangent to the corresponding surface and $\mathbf{l}$ is the tangent to the wetting perimeter. The plus and minus indices denote the values of the quantities at the points A and B respectively (see Fig.1).

Passing to the limit by means of contracting the volume to a point on the line L_0 is analogous to the passage to the limit in the course of obtaining the conditions at a shock surface /1,4/, and leads to the following equations:

$$\frac{d\rho_0}{d\tau} + \rho_0\nabla_0\cdot\mathbf{v}_0 = \sum_{i,j=1}^{3}{}^{*} m_{ij} \tag{1.5}$$

$$\rho_0\frac{d\mathbf{v}_0}{d\tau} = \rho_0\mathbf{F}_0 + \frac{d(\sigma_0\mathbf{l})}{dl} + \sum_{i,j=1}^{3}{}^{*}[\mathbf{N}_{ij}{}^{0}\cdot\boldsymbol{\sigma}_{ij} + m_{ij}(\mathbf{v}_{ij} - \mathbf{v}_0)] \tag{1.6}$$

$$\rho_0\frac{dE_0}{d\tau} = \rho_0\mathbf{F}_0\cdot\mathbf{v}_0 - \nabla_0\cdot\mathbf{q}_0 + \frac{d}{dl}(\sigma_0\mathbf{l}\cdot\mathbf{v}_0) + \sum_{i,j=1}^{3}{}^{*}[\mathbf{N}_{ij}{}^{\circ}\cdot\boldsymbol{\sigma}_{ij}\cdot\mathbf{v}_{ij} - \mathbf{q}_{ij}\cdot\mathbf{N}_{ij}{}^{\circ} + m_{ij}(E_{ij} - E_0)] \tag{1.7}$$

$$\rho_0\frac{ds_0}{d\tau} = -\nabla_0\cdot\frac{\mathbf{q}_0}{T_0} + \eta_0 + \sum_{i,j=1}^{3}{}^{*}\Big[-\frac{1}{T_{ij}}\mathbf{q}_{ij}\cdot\mathbf{N}_{ij}{}^{\circ} + m_{ij}(s_{ij} - s_0)\Big] \tag{1.8}$$
$$\Big(\nabla_0 \equiv \mathbf{l}\frac{d}{dl},\quad m_{ij} = -\rho_{ij}(\mathbf{v}_{ij} - \mathbf{v}_0)\cdot\mathbf{N}_{ij}{}^{\circ}\Big)$$

where $\mathbf{N}_{ij}{}^{\circ}$ is the inward normal to L_0, tangent to the surfaces S_{ij}, $i < j$. Equations (1.6) and (1.7) yield the internal energy balance

$$\rho_0\frac{du_0}{d\tau} = -\nabla_0\cdot\mathbf{q}_0 + \sigma_0\nabla_0\cdot\mathbf{v}_0 + \sum_{i,j=1}^{3}{}^{*}[-\mathbf{q}_{ij}\cdot\mathbf{N}_{ij}{}^{\circ} + \mathbf{N}_{ij}{}^{\circ}\cdot\boldsymbol{\sigma}_{ij}\cdot(\mathbf{v}_{ij} - \mathbf{v}_0) + m_{ij}(E_{ij} - u_0 - \mathbf{v}_{ij}\cdot\mathbf{v}_0 + {}^1/_2 v_0{}^2)] \tag{1.9}$$

2. Principle of local equilibrium. The principle of local equilibrium was used in "two-dimensional" form in many papers in the studies of surface phenomena in continuous media e.g. /4,5,10/. In what follows, we shall postulate the validity of the "one-dimensional" relation

$$du_0 = T_0 ds_0 + \gamma_0 d(1/\rho_0),\ \gamma_0 = \sigma_0 - \sigma_0{}^{*} \tag{2.1}$$

where $\sigma_0{}^{*}$ is the viscous component of the linear tension. Using the principle of local equilibrium, we can obtain the following expression for the appearance of entropy:

$$\eta_0 = \mathbf{q}_0\cdot\nabla_0\frac{1}{T_0} + \frac{\sigma_0{}^{*}}{T_0}\nabla_0\cdot\mathbf{v}_0 + T_0^{-1}\sum_{i,j=1}^{3}{}^{*}\{\mathbf{N}_{ij}{}^{\circ}\cdot\boldsymbol{\sigma}_{ij}\cdot(\mathbf{v}_{ij} - \mathbf{v}_0) + \tag{2.2}$$
$$T_0(T_{ij}^{-1} - T_0^{-1})\,\mathbf{q}_{ij}\cdot\mathbf{N}_{ij}{}^{\circ} +$$
$$m_{ij}[E_{ij} - u_0 - \mathbf{v}_0\cdot\mathbf{v}_{ij} + {}^1/_2 v_0{}^2 + \gamma_0/\rho_0 + T_0(s_0 - s_{ij})]\}$$

In the present paper we shall not write out the complete system of linear phenomenological relations between the thermodynamic forces and flows, instead we shall adopt the simplest relationships

$$\mathbf{q}_0 = -\lambda_0 \nabla_0 T_0 \tag{2.3}$$

$$\sigma_0^* = \zeta_0 \nabla_0 \cdot \mathbf{v}_0 \tag{2.4}$$

where λ_0 is the heat conductivity coefficient and ζ_0 is the viscosity coefficient. Using the formulas (2.1) and (2.4), we can write the equations of state

$$T_0 = \left(\frac{\partial u_0}{\partial s_0}\right)_{\rho_0}, \quad \sigma_0 = -\rho_0^2 \left(\frac{\partial u_0}{\partial \rho_0}\right)_{s_0} + \zeta_0 \nabla_0 \cdot \mathbf{v}_0 \tag{2.5}$$

Using the Maxwell relations connecting the thermodynamic potentials /11/ and the formulas (1.8), (2.3), we arrive to the generalized equation of heat conductivity

$$\lambda_0 \nabla_0^2 T_0 = \rho_0 C_0 \frac{dT_0}{d\tau} - T_0 B_0 \beta_0 \rho_0^{-1} \frac{d\rho_0}{d\tau} - \Phi_0 \tag{2.6}$$

$$\Phi_0 = T_0 \left\{ \eta_0 - \mathbf{q}_0 \cdot \nabla_0 \frac{1}{T_0} + \sum_{i,j=1}^{*} [-T_{ij}^{-1} \mathbf{q}_{ij} \cdot \mathbf{N}_{ij}^0 + m_{ij}(s_{ij} - s_0)] \right\}$$

where C_0 is the heat capacity, B_0 is the isothermal modulus of linear elasticity and β_0 is the isobaric coefficient of linear expansion. In this manner we have obtained the equations of continuity (1.5), motion (1.6), state (2.5) and heat conductivity (2.6) for a linear object modelling the region of contact of three media (wetting perimeter).

3. Connection with the Young's equation. The best known relations of the theory of capillar phenomena are the Laplace equation /12/ and the Young's equation /13/ (in the notation adopted here)

$$2H\sigma_{13} = -n \cdot (\boldsymbol{\pi}_1 - \boldsymbol{\pi}_3) \cdot n, \quad \sigma_{23} \cos\theta = \sigma_{13} - \sigma_{12} \tag{3.1}$$

Here σ_{ij} denote the surface tensions, H is the mean surface curvature and θ is the edge angle (angle between $\mathbf{N}_{12}^0$ and $\mathbf{N}_{23}^0$). The effect of the linear tension σ_0 on the edge angle under the conditions of axial symmetry was taken into account in /8,14/:

$$\sigma_{23} \cos\theta = \sigma_{13} - \sigma_{12} - (\sigma_0 \cos\varphi)/R \tag{3.2}$$

where R is the radius of the base of the liquid drop and φ is the angle of inclination of the surface S_{13} at the line of three-phase contact (the case $\varphi = 0$ was dealt with in /8/).

At present it is generally accepted that for the solid body surfaces the tensors σ_{12} and σ_{13} cannot, in general, be reduced to the scalar surface tensions $\boldsymbol{\sigma}_{12}$ and $\boldsymbol{\sigma}_{13}$. The corresponding generalization of the Laplace formula (first formula of (3.1)) is known and given in /10,15/. The equation (1.6) represents a generalization of the Young's equation (second formula of (3.1)). In the case $m_{ij} = 0$, $\mathbf{N}_{12}^0 = -\mathbf{N}_{13}^0 = \mathbf{t}$ we project the equation (1.6) onto the coordinate axes $\mathbf{t}, \mathbf{l}$ and $\mathbf{n}$. Taking the Serret-Frenet formula /16/ into account, we obtain

$$\begin{aligned} \rho_0 a_0^t &= \rho_0 F_0^t + \sigma_{12}^{tt} - \sigma_{13}^{tt} + \sigma_{23}\cos\theta + \sigma_0 \varkappa \cos\varphi \\ \rho_0 a_0^l &= \rho_0 F_0^l + \sigma_{12}^{tl} - \sigma_{13}^{tl} + d\sigma_0/dl \\ \rho_0 a_0^n &= \rho_0 F_0^n + \sigma_{23}\sin\theta - \sigma_0 \varkappa \sin\varphi \end{aligned} \tag{3.3}$$

Here φ is the angle between the principal normal to the wetting perimeter and the $\mathbf{t}$-axis, $\varkappa$ is the curvature of the line of contact, and $\mathbf{a}_0 = d\mathbf{v}_0/d\tau$. We assume in (3.3) that on the surface S_{23} the surface stress tensor $\boldsymbol{\sigma}_{23}$ can be reduced to surface tension σ_{23}, i.e. that the surface viscosity effects can be neglected.

A drop lying on a plane surface or spreading along it, may deviate from its axial symmetry by virtue of the tensor character of $\boldsymbol{\sigma}_{12}$ and $\boldsymbol{\sigma}_{13}$. The linear tension gradient allows us to describe the known, Marangoni-type effects, connected with the surface tension gradient.

4. Possible applications of the theory. The results obtained above sharpen the conditions of equilibrium between thin films and volume phases /17,18/, and between two-dimensional phases /19,20/. They can be used to develop further the theory of seeding the condensed phase /21/ and the capillary theory of flotation /22/ based on the analysis of the situation prevailing at the line separating three media, using the concept of linear tension. At present there exists a large amount of accumulated experimental material relating to the dependence of the wetting angle on the rate of motion of the perimeter, and concerning, in particular, the "advancing" and "receding" edge angles. In the survey /23/ of experiments and suggested mechanisms the need for seeking new representations is manifest. The dynamic characteristics entering the equation (1.6) describe only one of such mechanisms.

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