DESCRIPTION OF SURFACE PHENOMENA IN ELASTICALLY POLARIZED SOLIDS

Yu. Z. Povstenko

UDC 539.3

Spatial orientation of point defects can occur during surface formation in a solid. The average tensor of elastic dipoles [1], on whose orientation the dia- and paraelasticity are based [1, 2], can be viewed from the point of view of the mechanics of a continuous medium as a tensor state parameter, i.e., an analog of the usual scalar concentration of dissolved substance. The idea that scalar quantities (concentration and the chemical potential) are inadequate for describing deformation of solids in the diffusion theory, but corresponding tensors must be introduced, is stated in [3, 4] (see also [5, 6]). As state parameters of a nonideal solid solution, the temperature T, the entropy s, stress tensor σ, deformation e, chemical potential φ, and concentration c, for which a coupled system of equations is obtained in [3, 4], are chosen.

The purpose of this paper is to construct a two-dimensional analog of the system of equations indicated taking into account the specifics of surface phenomena, modeling the thin near-surface layer by a surface having intrinsic state parameters.

1. Balance Equations. For the material volume illustrated in the figure, the following equations are valid: conservation of mass

$$\frac{\partial}{\partial t}\left(\int_{V_1}\rho_1 dV_1+\int_{V_2}\rho_2 dV_2+\int_{\Sigma}\rho d\Sigma\right)=0; \tag{1.1}$$

conservation of the defect density tensor

$$\frac{\partial}{\partial t}\left(\int_{V_1}\mathbf{P}_1 dV_1+\int_{V_2}\mathbf{P}_2 dV_2+\int_{\Sigma}\mathbf{P}\,d\Sigma\right)=0; \tag{1.2}$$

momentum tensor

$$\frac{\partial}{\partial t}\left(\int_{V_1}\rho_1\mathbf{v}_1 dV_1+\int_{V_2}\rho_2\mathbf{v}_2 dV_2+\int_{\Sigma}\rho\mathbf{v}\,d\Sigma\right)=\int_{V_1}\rho_1\mathbf{F}_1 dV_1+ \\ +\int_{V_2}\rho_2\mathbf{F}_2 dV_2+\int_{\Sigma}\rho\mathbf{F}\,d\Sigma+\int_{A_1}\mathbf{n}_1\cdot\boldsymbol{\sigma}_1 dA_1+\int_{A_2}\mathbf{n}_2\cdot\boldsymbol{\sigma}_2 dA_2+\int_{\Gamma}\mathbf{N}\cdot\boldsymbol{\sigma}d\Gamma; \tag{1.3}$$

total energy

$$\frac{\partial}{\partial t}\left(\int_{V_1}\rho_1 E_1 dV_1+\int_{V_2}\rho_2 E_2 dV_2+\int_{\Sigma}\rho E\,d\Sigma\right)=\int_{V_1}\rho_1\mathbf{F}_1\cdot\mathbf{v}_1 dV_1+ \\ +\int_{V_2}\rho_2\mathbf{F}_2\cdot\mathbf{v}_2 dV_2+\int_{\Sigma}\rho\,\mathbf{F}\cdot\mathbf{v}\,d\Sigma+\int_{A_1}\mathbf{n}_1\cdot\boldsymbol{\sigma}_1\cdot\mathbf{v}_1 dA_1+\int_{A_2}\mathbf{n}_2\cdot\boldsymbol{\sigma}_2\cdot\mathbf{v}_2 dA_2+ \\ +\int_{\Gamma}\mathbf{N}\cdot\boldsymbol{\sigma}\cdot\mathbf{v}\,d\Gamma-\int_{A_1}\mathbf{n}_1\cdot\mathbf{q}_1 dA_1-\int_{A_2}\mathbf{n}_2\cdot\mathbf{q}_2 dA_2-\int_{\Gamma}\mathbf{N}\cdot\mathbf{q}\,d\Gamma; \tag{1.4}$$

entropy

$$\frac{\partial}{\partial t}\left(\int_{V_1}\rho_1 s_1 dV_1+\int_{V_2}\rho_2 s_2 dV_2+\int_{\Sigma}\rho s\,d\Sigma\right)=\int_{V_1}\eta_1 dV_1+\int_{V_2}\eta_2 dV_2+\int_{\Sigma}\eta\,d\Sigma-\int_{A_1}\mathbf{n}_1\cdot\mathbf{J}_1^{(s)}dA_1-\int_{A_2}\mathbf{n}_2\cdot\mathbf{J}_2^{(s)}dA_2-\int_{\Gamma}\mathbf{N}\cdot\mathbf{J}^{(s)}d\Gamma, \tag{1.5}$$

where ρ is the density; $\mathbf{P}=\rho\mathbf{c}$, defect density tensor; $\mathbf{v}$, velocity; $\mathbf{F}$, vector of mass forces; σ_1 and σ_2, three-dimensional stress tensors; $\boldsymbol{\sigma}$, a two-dimensional stress tensor on the surface; $E = u + (1/2)v^2$; u, internal energy density; $\mathbf{q}$, heat flux vector; s, η, $J^{(S)}$, density, formation, and flux of entropy; t, time; $\mathbf{n}$, external

---

Lvov. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 117-121, January-February, 1983. Original article submitted December 15, 1981.

0021-8944/83/2401-0102$07.50

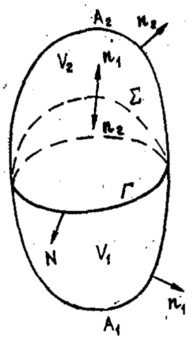

Fig. 1

normal to the surface; N, outer normal to the contour Γ, tangent to the surface Σ (see Fig. 1). The indices 1 and 2 indicate quantities relating to the two media in contact; quantities without indices are characteristics of the surface.

The transition in Eqs. (1.1)-(1.5) to the limit with the volume V contracted to a point on the surface Σ [7, 8] assuming that the velocities on the surface are equal leads to the local equations

$$d\rho/dt + \rho\nabla_\Sigma\cdot\mathbf{v} = 0; \tag{1.6}$$

$$\rho d\mathbf{c}/dt = -\nabla_\Sigma\cdot\mathbf{J} + \mathbf{n}_1\cdot\mathbf{J}_1 + \mathbf{n}_2\cdot\mathbf{J}_2; \tag{1.7}$$

$$\rho d\mathbf{v}/dt = \rho\mathbf{F} + \nabla_\Sigma\cdot\boldsymbol{\sigma} - \mathbf{n}_1\cdot\boldsymbol{\sigma}_1 - \mathbf{n}_2\cdot\boldsymbol{\sigma}_2; \tag{1.8}$$

$$\rho dE/dt = \rho\mathbf{F}\cdot\mathbf{v} - \nabla_\Sigma\cdot\mathbf{q} + \nabla_\Sigma\cdot(\boldsymbol{\sigma}\cdot\mathbf{v}) + \mathbf{n}_1\cdot\mathbf{q}_1 + \mathbf{n}_2\cdot\mathbf{q}_2 - \mathbf{n}_1\cdot\boldsymbol{\sigma}_1\cdot\mathbf{v}_1 - \mathbf{n}_2\cdot\boldsymbol{\sigma}_2\cdot\mathbf{v}_2; \tag{1.9}$$

$$\rho ds/dt = \eta - \nabla_\Sigma\cdot\mathbf{J}^{(s)} + \mathbf{n}_1\cdot\mathbf{J}_1^{(s)} + \mathbf{n}_2\cdot\mathbf{J}_2^{(s)}, \tag{1.10}$$

where $\mathbf{J} = \mathbf{w}\mathbf{P}$ is the rank 3 defect flux tensor; w is the diffusion velocity; ∇_Σ is the surface nabla operator.

The conservation of internal energy follows from Eqs. (1.8) and (1.9)

$$\rho du/dt = -\nabla_\Sigma\cdot\mathbf{q} + (\nabla_\Sigma\mathbf{v}) : \boldsymbol{\sigma} + \mathbf{n}_1\cdot\mathbf{q}_1 + \mathbf{n}_2\cdot\mathbf{q}_2. \tag{1.11}$$

2. Condition of Local Equilibrium. Following [3, 4] and using as a basis the principle of local autonomy of the surface phase [9], we shall write the condition for local equilibrium in the form

$$du = Tds + \rho^{-1}\boldsymbol{\sigma} : d\mathbf{e} + \boldsymbol{\varphi} : d\mathbf{c}. \tag{2.1}$$

The equations of state are defined by the equation

$$T = (\partial u/\partial s)_{\mathbf{e},\mathbf{c}},\ \boldsymbol{\sigma} = \rho(\partial u/\partial\mathbf{e})_{s,\mathbf{c}},\ \boldsymbol{\varphi} = (\partial u/\partial\mathbf{c})_{s,\mathbf{e}}. \tag{2.2}$$

If we introduce the grand potential density

$$\omega = u - Ts - \boldsymbol{\varphi} : \mathbf{c},$$

then instead of Eqs. (2.1) and (2.2) we obtain

$$d\omega = -sdT + \rho^{-1}\boldsymbol{\sigma} : d\mathbf{e} - \mathbf{c} : d\boldsymbol{\varphi}; \tag{2.3}$$

$$s = -(\partial\omega/\partial T)_{\mathbf{e},\boldsymbol{\varphi}},\ \boldsymbol{\sigma} = \rho(\partial\omega/\partial\mathbf{e})_{T,\boldsymbol{\varphi}},\ \mathbf{c} = -(\partial\omega/\partial\boldsymbol{\varphi})_{T,\mathbf{e}}. \tag{2.4}$$

In the theory of surface phenomena, the densities calculated per unit surface area are usually used: $u^* = \rho u$, $\omega^* = \rho\omega$, $s^* = \rho s$. Then Eqs. (2.1)-(2.4) are rewritten in the form

$$du^* = Tds^* + (\boldsymbol{\sigma} - \omega^*\mathbf{a}) : d\mathbf{e} + \boldsymbol{\varphi} : d\mathbf{P}; \tag{2.5}$$

$$T = \left(\frac{\partial u^*}{\partial s^*}\right)_{\mathbf{e},\mathbf{P}},\ \boldsymbol{\varphi} = \left(\frac{\partial u^*}{\partial\mathbf{P}}\right)_{s^*,\mathbf{e}},\ \boldsymbol{\sigma} = \omega^*\mathbf{a} + \left(\frac{\partial u^*}{\partial\mathbf{e}}\right)_{s^*,\mathbf{P}}; \tag{2.6}$$

$$d\omega^* = -s^*dT + (\boldsymbol{\sigma} - \omega^*\mathbf{a}) : d\mathbf{e} - \mathbf{P} : d\boldsymbol{\varphi}; \tag{2.7}$$

$$s^* = -(\partial\omega^*/\partial T)_{\mathbf{e},\boldsymbol{\varphi}},\ \mathbf{P} = -(\partial\omega^*/\partial\boldsymbol{\varphi})_{T,\mathbf{e}},\ \boldsymbol{\sigma} = \omega^*\mathbf{a} + (\partial\omega^*/\partial\mathbf{e})_{T,\boldsymbol{\varphi}}, \tag{2.8}$$

where a is the metric tensor on the surface Σ.

The equations of state for the stress tensor (2.6) and (2.8), coupling the surface stress tensor with the surface density of the grand potential, have the form of the Herring equation [10] and, in particular, emphasize the important role of the quantity ω^* in studying surface phenomena in solid solutions.

We shall expand the density of the grand potential ω^* in a series with respect to the natural variables in the vicinity of the equilibrium state (indicated by the index 0), retaining quadratic terms:

$$\omega^* = \omega_0^* - \frac{\rho_0 C}{2T_0}\Theta^2 - \beta K\Theta\,\mathrm{tr}\,\mathbf{e} - \rho_0\xi\Theta\,\mathrm{tr}\,\mathbf{\Phi} + \tag{2.9}$$

$$+\frac{\lambda}{2}(\mathrm{tr}\,\mathbf{e})^2 - \frac{\rho_0 D}{2}(\mathrm{tr}\,\mathbf{\Phi})^2 - \gamma K(\mathrm{tr}\,\mathbf{e})(\mathrm{tr}\,\mathbf{\Phi}) + \mu\mathbf{e}:\mathbf{e} - \rho_0\nu\mathbf{\Phi}:\mathbf{\Phi} + 2\zeta\,\mathbf{e}:\mathbf{\Phi}.$$

Differentiation of expression (2.9) leads to the specific form of the equations of state

$$s = \frac{C}{T_0}\Theta + \frac{\beta K}{\rho_0}\mathrm{tr}\,\mathbf{e} + \xi\,\mathrm{tr}\,\mathbf{\Phi},\ \mathbf{c} = 2\nu\,\mathbf{\Phi} - \frac{2\zeta}{\rho_0}\mathbf{e} + \Big(D\,\mathrm{tr}\,\mathbf{\Phi} + \tag{2.10}$$

$$+\xi\Theta + \frac{\gamma K}{\rho_0}\mathrm{tr}\,\mathbf{e}\Big)\mathbf{a},\ \boldsymbol{\sigma} = 2\mu\mathbf{e} + 2\zeta\,\mathbf{\Phi} + \left(\omega_0^* - \beta K\Theta - \gamma K\,\mathrm{tr}\,\mathbf{\Phi} + \lambda\,\mathrm{tr}\,\mathbf{e}\right)\mathbf{a},$$

where $\Theta = T - T_0$; $\Phi = \varphi - \varphi_0$; λ, μ, K are the two-dimensional coefficients of elasticity; C is the heat capacity; β is the coefficient of thermal expansion; γ is the coefficient of diffusive expansion; D and ν are coefficients characterizing the mass content; ζ and ξ describe the cross effects between diffusion deformation and heat conduction, respectively.

In the expansion (2.9) and in equations of state (2.10), for the surface stress tensor σ, a constant term ω_0^*, which is important in studying surface phenomena, is included. The need to include terms of this kind was emphasized in [11].

3. Formation of Entropy and the System of Equations. Simultaneous analysis [12] of the conditions of local equilibrium and the conservation equations specifies the expression for the flow and generation of entropy (compare with [13]):

$$\mathbf{J}^{(s)} = \frac{\mathbf{q} - \mathbf{J}:\boldsymbol{\varphi}}{T},\quad \eta = \left(\nabla_\Sigma\frac{1}{T}\right)\cdot\mathbf{q} - \left(\nabla_\Sigma\frac{\boldsymbol{\varphi}}{T}\right):\mathbf{J} + \mathbf{n}_1\cdot\mathbf{q}_1\left(\frac{1}{T} - \frac{1}{T_1}\right) +$$

$$+\mathbf{n}_2\cdot\mathbf{q}_2\left(\frac{1}{T} - \frac{1}{T_2}\right) - \mathbf{n}_1\cdot\mathbf{J}_1:\left(\frac{\boldsymbol{\varphi}}{T} - \frac{\boldsymbol{\varphi}_1}{T_1}\right) - \mathbf{n}_2\cdot\mathbf{J}_2:\left(\frac{\boldsymbol{\varphi}}{T} - \frac{\boldsymbol{\varphi}_2}{T_2}\right).$$

The phenomenological equations, including Curie's principle and symmetry of phenomenological coefficients $L_{12} = L_{21}$, $M_{12} = M_{21}$, are written in the form

$$\mathbf{q} = L_q\nabla_\Sigma/T,\ \mathbf{J} = -L_J\nabla_\Sigma\ \boldsymbol{\varphi}/T, \tag{3.1}$$

$$\mathbf{n}_1\cdot\mathbf{q}_1 = L_{11}(1/T - 1/T_1) + L_{12}(1/T - 1/T_2),\ \mathbf{n}_2\cdot\mathbf{q}_2 =$$

$$= L_{12}(1/T - 1/T_1) + L_{22}(1/T - 1/T_2),\ \mathbf{n}_1\cdot\mathbf{J}_1 = -M_{11}(\boldsymbol{\varphi}/T -$$

$$-\boldsymbol{\varphi}_1/T_1) - M_{12}(\boldsymbol{\varphi}/T - \boldsymbol{\varphi}_2/T_2),\ \mathbf{n}_2\cdot\mathbf{J}_2 = -M_{12}(\boldsymbol{\varphi}/T - \boldsymbol{\varphi}_1/T_1) - M_{22}(\boldsymbol{\varphi}/T - \boldsymbol{\varphi}_2/T_2).$$

Using Eqs. (1.7) and (1.11), after linearizing and neglecting the coupling effects in the equations of the process (3.1), we obtain a system of equations consisting of the following equations of motion (1.8), generalizing the well-known Laplace equation [14] for liquids, relating the jump in pressure to the surface tension; the equations of state (2.10); equation of heat conduction

$$\Lambda\Delta_\Sigma\Theta = \rho_0 C\frac{\partial\Theta}{\partial t} + T_0\beta K\frac{\partial\,\mathrm{tr}\,\mathbf{e}}{\partial t} + \rho_0 T_0\xi\frac{\partial\,\mathrm{tr}\,\mathbf{\Phi}}{\partial t} - \mathbf{n}_1\cdot\mathbf{q}_1 - \mathbf{n}_2\cdot\mathbf{q}_2;$$

diffusion equation

$$\mathrm{M}\Delta_\Sigma\mathbf{\Phi} = \rho_0 D\frac{\partial\,\mathrm{tr}\,\mathbf{\Phi}}{\partial t}\mathbf{a} + 2\rho_0\nu\frac{\partial\mathbf{\Phi}}{\partial t} - 2\zeta\frac{\partial\mathbf{e}}{\partial t} + \rho_0\xi\frac{\partial\Theta}{\partial t}\mathbf{a} + \gamma K\frac{\partial\,\mathrm{tr}\,\mathbf{e}}{\partial t}\mathbf{a} - \mathbf{n}_1\cdot\mathbf{J}_1 - \mathbf{n}_2\cdot\mathbf{J}_2;$$

conditions for the type of exchange according to Newton's law

$$\mathbf{n}_i\cdot\mathbf{q}_i = \alpha_i(\Theta_i - \Theta),\ \mathbf{n}_i\cdot\mathbf{J}_i = \varepsilon_i(\mathbf{\Phi}_i - \mathbf{\Phi}),\ i = 1,\ 2;$$

kinematic

$$\mathbf{v}_1 = \mathbf{v}_2 = \mathbf{v}$$

and geometric conditions

$$\mathbf{e} = (\nabla_\Sigma\mathbf{u})^s_{\parallel}, \tag{3.2}$$

where Λ is the coefficient of thermal conductivity; M, coefficient of mass conductivity; α, heat-transfer coefficient; ε, mass transfer coefficient; **u**, displacement vector; the superscript s in Eq. (3.2) indicates the symmetric part, while the subscript ∥ indicates the fact that the surface component of the spatial tensor $\nabla_{\Sigma}\mathbf{u}$ is taken.

Thus, a closed system of equations is obtained, describing surface phenomena in elastically polarizing solids, which, in particular, can be viewed as generalized boundary conditions for the spatial system of equations proposed in [3, 4].

LITERATURE CITED

1. O. V. Temnov, "Dia- and paraelastic polarization in solids," in: Research on Elasticity and Plasticity [in Russian], Leningrad State Univ. (1974).
2. E. Krener, General Continuum Theory of Dislocations and Internal Stresses [Russian translation], Mir, Moscow (1965).
3. Ya. S. Podstrigach, "Differential equations of diffusion theory of deformations of a solid," Dokl. Akad. Nauk Ukr. SSR, No. 3 (1963).
4. Ya. S. Podstrigach, "Diffusion theory of inelastic metals," Zh. Prikl. Mekh. Tekh. Fiz., No. 2 (1965).
5. B. Stuke, "Allgemeine Rahmengleichungen der Kontinuumsdynamik," Phys. Lett., 21, No. 6 (1966).
6. B. Stuke, "Tensorielle chemische potential: eine notwendige erweiterung der Gibbs'schen Thermodynamik," Z. Naturforschung, 30a, No. 11 (1975).
7. L. I. Sedov, Two-Dimensional Problems in Gas Dynamics and Aerodynamics [in Russian], Nauka, Moscow (1966).
8. J. M. Delhaye, "Jump conditions and entropy sources in two-phase systems. Local instant formulation," Int. J. Multiphase Flow, 1, No. 3 (1974).
9. R. Ghez, "A generalized Gibbsian surface," Surface Sci., 4, No. 2 (1966).
10. C. Herring, "Surface tension as a motivation for sintering," in: The Physics of Powder Metallurgy, McGraw-Hill, New York (1951).
11. L. I. Sedov, Mechanics of a Continuous Medium [in Russian], Vols. 1, 2, Nauka, Moscow (1970).
12. I. D'Yarmati, Nonequilibrium Thermodynamics [Russian translation], Mir, Moscow (1974).
13. J. Kovac, "Nonequilibrium theromodynamics of interfacial systems," Physica, A86, No. 1 (1977).
14. L. D. Landau and E. M. Lifshitz, Mechanics of Continuous Media [in Russian], Gostekhizdat, Moscow (1954).