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CROSS EFFECTS IN SOLID MEDIA WITH DIFFUSION

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Based on thermodynamics of irreversible processes, possible cross effects in isothermal diffusion in solids with internal surfaces are analyzed. Expressions for the fluxes of components and for the fluxes of a newly introduced thermodynamic parameter, specific area of internal surfaces per unit volume or mass of the medium, are obtained. An analysis of these relations and relations between the stresses and strains for various cases is given. In derivation of the governing relations, it was assumed that diffusion proceeds through interstitial sites.

Key words: *solids, diffusion, interfaces.*

Introduction. There are many papers on modeling diffusion in solids, considering the possibility of different diffusion mechanisms in different media. Two major mechanisms of diffusion in crystals are currently distinguished: substitutional diffusion, where atoms in crystals migrate only through vacant lattice sites, and interstitial diffusion, where the migrating atoms diffuse only through interstitial sites, the presence or absence of vacancies in this case being of minor importance.

The reported models were constructed to describe idealized situations, ignoring cross effects typical of solids or taking into account small deformations in the diffusion zone. For instance, in [1], solid-state diffusion in crystals proceeding by the substitutional or interstitial mechanism was analyzed for an isotropic incompressible medium with allowance for stresses and small deformations. Numerous particular models for diffusion in bodies with structural nonuniformities were reported in [2, 3]. Attempts were made to describe diffusion within the continuum-mechanics approach in [4]. In most of these works, problems of synthesis and processing of new materials were not considered, because these models disregard many phenomena observed in real crystals. In particular, this refers to diffusion in media with internal interfaces, such as grain and interphase boundaries. Available models for boundary diffusion based on Fisher's model [5] treat an individual boundary. For this reason, they do not describe multi-component diffusion or diffusion in nanostructured media. To describe properties of such media and physicochemical processes in them (generally, nonequilibrium ones), another approach is required.

In the present work, to construct a model for diffusion in a medium with a nonuniform internal structure, we use concepts borrowed from thermodynamics of irreversible processes [6] and introduce a new generalized thermodynamic parameter f_s, which is the specific area of internal interfaces per unit volume or mass of the medium. As is well known, introduction of new variables makes it possible to use the tools of the present-day mechanics of continuous media, i.e., the tools of thermomechanics of continuous media, to describe nonequilibrium processes. Among various available thermodynamic theories, the local-equilibrium theory seems to be most substantiated from the physical point of view; this model can easily be generalized to treat "fine" physical effects in simple media or analyze processes in structurally nonuniform media in a simple manner.

The description of interstitial diffusion, which is typical, for instance, for gas-phase diffusion into metals, is analogous to its description in hydrodynamics. The construction of a model for solid-state diffusion within the framework of mechanics of continuous media makes it possible to include many effects experimentally observed in solids. Substitutional diffusion treated within the framework of mechanics of continuous media requires special consideration.

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Note, at temperatures much lower than the melting point, there is almost no difference between the two diffusion mechanisms; in this case, the hydrodynamic model should be used.

1. General Relations. Cross Effects. We consider a multi-component thermodynamic system with internal interfaces. In this case, the local internal energy of the system u is a function of local entropy s, strain-tensor components ε_{ij}, mass concentrations of the reacting and migrating components C_k $(k = 1, 2, \dots, n)$) and the new parameter f_s:

$$u = u(s, \varepsilon_{ij}, C_k, f_s).$$

The Gibbs equation for such a system has the form

$$du = T\,ds + \sigma^e_{ij}\rho^{-1}\,d\varepsilon_{ij} + \sum_{k=1}^{n} g_k\,dC_k - g_f\,df_s, \tag{1}$$

where T is the temperature, σ^e_{ij} are the strain-tensor components calculated from elastic strains, g_k are the chemical potentials of the components, and g_f is the energy of the internal interfaces per unit mass or volume of the medium (depending on the definition of the parameter f_s).

Using the Gibbs energy $g = u - \rho^{-1}\varepsilon_{ij}\sigma^e_{ij} - Ts$, we can write (1) in the form

$$dg = -s\,dT - \varepsilon_{ij}\rho^{-1}\,d\sigma^e_{ij} + \sum_{k=1}^{n} g_k\,dC_k - g_f\,df_s. \tag{2}$$

This form of the Gibbs equation is more convenient for the description of the processes proceeding under the conditions $T = \text{const}$ and $\sigma^e_{ij} = \text{const}$. In the general case, like the potential g, the parameters s, ε_{ij}, g_k, and g_f are functions of the variables T, σ^e_{ij}, C_k, and f_s. Hence, we can write the following system of total differential equations:

$$ds = \Big(\frac{\partial s}{\partial T}\Big)\,dT + \sum_{(i,j)}\Big(\frac{\partial s}{\partial \sigma_{ij}}\Big)\,d\sigma^e_{ij} + \sum_{k=1}^{n}\Big(\frac{\partial s}{\partial C_k}\Big)\,dC_k + \Big(\frac{\partial s}{\partial f_s}\Big)\,df_s; \tag{3}$$

$$d\varepsilon_{ij} = \Big(\frac{\partial \varepsilon_{ij}}{\partial T}\Big)\,dT + \sum_{(\alpha,\beta)}\Big(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{\alpha\beta}}\Big)\,d\sigma^e_{\alpha\beta} + \sum_{k=1}^{n}\Big(\frac{\partial \varepsilon_{ij}}{\partial C_k}\Big)\,dC_k + \Big(\frac{\partial \varepsilon_{ij}}{\partial f_s}\Big)\,df_s; \tag{4}$$

$$dg_k = \Big(\frac{\partial g_k}{\partial T}\Big)\,dT + \sum_{(i,j)}\Big(\frac{\partial g_k}{\partial \sigma_{ij}}\Big)\,d\sigma^e_{ij} + \sum_{m=1}^{n}\Big(\frac{\partial g_k}{\partial C_m}\Big)\,dC_m + \Big(\frac{\partial g_k}{\partial f_s}\Big)\,df_s; \tag{5}$$

$$dg_f = \Big(\frac{\partial g_f}{\partial T}\Big)\,dT + \sum_{(i,j)}\Big(\frac{\partial g_f}{\partial \sigma_{ij}}\Big)\,d\sigma^e_{ij} + \sum_{k=1}^{n}\Big(\frac{\partial g_f}{\partial C_k}\Big)\,dC_k + \Big(\frac{\partial g_f}{\partial f_s}\Big)\,df_s. \tag{6}$$

Here, the partial derivatives with respect to thermodynamic variables are taken for all other quantities being fixed. These equations take into account all direct processes and cross effects observed in composite media. For instance, the coefficient at the temperature differential in (3) includes the heat capacity under constant stress

$$c_\sigma = T\Big(\frac{\partial s}{\partial T}\Big)_{\hat\sigma, C_k, f_s} = -T\Big(\frac{\partial^2 g}{\partial T^2}\Big)_{\hat\sigma, C_k, f_s},$$

while Eq. (4) with $dT = 0$, $dC_k = 0$, and $df_s = 0$ yields the differential form of Hooke's law

$$d\varepsilon_{ij} = s_{ij\alpha\beta}\,d\sigma^e_{\alpha\beta}, \tag{7}$$

where

$$s_{ij\alpha\beta} = \Big(\frac{\partial \varepsilon_{ij}}{\partial \sigma^e_{\alpha\beta}}\Big)_{T, C_k, f_s} = -\rho\Big(\frac{\partial^2 g}{\partial \sigma^e_{ij}\,\partial \sigma^e_{\alpha\beta}}\Big)_{T, C_k, f_s}$$

are the elastic compliance coefficients, which form a fourth-rank tensor. If the temperature is not constant, then Eq. (4) yields the Duhamel–Neumann relations for an anisotropic medium:

$$d\varepsilon_{ij} = s_{ij\alpha\beta}\,d\sigma^e_{\alpha\beta} + \alpha^{(T)}_{ij}\,dT,$$

where

$$\alpha^{(T)}_{ij} = \Big(\frac{\partial \varepsilon_{ij}}{\partial T}\Big)_{C_k, f_s, \hat\sigma} = -\rho\Big(\frac{\partial^2 g}{\partial T\,\partial \sigma^e_{ij}}\Big)_{C_k, f_s}$$

are the linear thermal-expansion coefficients, which, in the general case, form a second-rank tensor. It follows from (2)–(4) that the variation of the strain-tensor components with temperature is described by the same coefficients as the variation of entropy caused by the variation of the strain-tensor components:

$$\alpha_{ij}^{(T)} = \Big(\frac{\partial \varepsilon_{ij}}{\partial T}\Big)_{C_k, f_s, \hat{\sigma}} = \rho\Big(\frac{\partial s}{\partial \sigma_{ij}^e}\Big)_{C_k, f_s, T}. \tag{8}$$

These coefficients describe the well-known cross effect observed in solids under heating or deformation (we will call them the direct effect and the inverse effect, respectively).

Similarly, if the chemical potential of the kth component varies as the stress-tensor components undergo changes, then the inverse effect, i.e., the variation of the strain-tensor components caused by the variation of the concentration of this component (due to diffusion or a physico-chemical transformation), is also observed:

$$\alpha_{ij}^{(k)} = \Big(\frac{\partial \varepsilon_{ij}}{\partial C_k}\Big)_{T, f_s, C_l, l\neq k, \hat{\sigma}} = -\rho\Big(\frac{\partial g_k}{\partial \sigma_{ij}^e}\Big)_{T, f_s, C_l}. \tag{9}$$

In thermodynamics, equations of the type (4) are known as generalized linearized nonequilibrium equations of state, and equations of the type (8) and (9) are known as the Maxwell relations. For the linear governing relations (3)–(6) to be satisfied, it is sufficient that the increment of the Gibbs energy relative to the equilibrium state be an expression that involves squared increments of the variables T, σ_{ij}^e, C_k, and f_s. Since the partial derivatives in (7)–(9) are taken with respect to local thermodynamic variables, which are functions of the independent coordinates x_i and time t, then taking the density outside the sign of the derivative is mathematically admissible.

2. Derivation of Relations for Irreversible Fluxes. Let us write several expressions that will be helpful in subsequent considerations.

The total system of equations of mechanics of a multi-species continuous medium, where volume solid-phase diffusion proceeds through interstitial sites, can be represented in the form [6–9]

$$\frac{d\rho}{dt} + \rho\nabla\cdot\boldsymbol{v} = 0; \tag{10}$$

$$\rho\,\frac{dC_k}{dt} + \nabla\cdot\boldsymbol{J}_k = \sigma_k; \tag{11}$$

$$\rho\,\frac{d\boldsymbol{v}}{dt} = \nabla\cdot\hat{\sigma} + \rho\boldsymbol{F} \equiv \nabla\cdot\hat{\sigma} + \rho\sum_{k=1}^{n} C_k\boldsymbol{F}_k; \tag{12}$$

$$\rho\,\frac{du}{dt} = -\nabla\cdot\boldsymbol{J}_T + \hat{\sigma}\cdot\cdot\nabla\boldsymbol{v} + \sum_{k=1}^{n}\boldsymbol{J}_k\cdot\boldsymbol{F}_k, \tag{13}$$

where $C_k = \rho_k/\rho$ and ρ_k are the partial densities of the components, $\boldsymbol{J}_k = \rho_k(\boldsymbol{v}_k - \boldsymbol{v})$ and σ_k are the diffusion mass flux and the sum of sources and sinks for the kth component, $\boldsymbol{v}$ is the velocity of the center of mass, given by the equation

$$\rho\boldsymbol{v} = \sum_{k=1}^{n}\rho_k\boldsymbol{v}_k,$$

$\boldsymbol{J}_T$ is the heat-flux density (its conductive part), $\boldsymbol{F}_k$ is the component of the external mass forces acting on the kth component, and $\nabla\cdot\boldsymbol{v} = \operatorname{div}\boldsymbol{v}$. If necessary, equations of angular-momentum and electric-charge balance should be added to system (10)–(13). In addition, system (10)–(13) should be supplemented by relations between irreversible fluxes and generalized thermodynamic forces causing these fluxes, and by the balance equation for the new parameter in the form

$$\frac{df_s}{dt} + \nabla\cdot\boldsymbol{J}_f = \sigma_f, \tag{14}$$

where $\boldsymbol{J}_f$ is the "diffusion" flux and the quantity σ_f describes the formation and accumulation of internal interfaces. As is known, the linear relations for the fluxes can be found from the entropy-balance equation, provided that entropy generation is nonnegative. To construct this equation, we write the Gibbs equation (1) in the form

$$\frac{ds}{dt} = \frac{1}{T}\,\frac{du}{dt} - \frac{\sigma_{ij}^e}{\rho T}\,\frac{d\varepsilon_{ij}}{dt} - \sum_{k=1}^{n}\frac{g_k}{T}\,\frac{dC_k}{dt} + \frac{g_f}{T}\,\frac{df_s}{dt} \tag{15}$$

and use Eqs. (11) and (13). In writing (1) and (15), we took into account that Eqs. (1)–(6) include only the stress-tensor components causing only "elastic" deformations, which are related, by definition [8], to the stress-tensor components by linear relations of the type (4). To describe irreversible-deformation processes, it is required to introduce some additional thermodynamic parameters; in the present work, such parameters are introduced using the variables C_k, f_s, etc. Simultaneously, Eqs. (12) and (13) involve the whole stress tensor. In thermodynamics, expressions for inelastic components of this tensor can be obtained similarly to the expressions for irreversible fluxes. For this reason, it makes sense to call the strain-tensor components given by relations (4) reversible and the components obtained from (15) under nonnegative entropy generation, irreversible. This classification is conventional since deformations induced by irreversible processes are most likely irreversible even if they are related to stresses by linear relations. In available dislocation theories of plasticity, the stresses are linearly related with, e.g., strains caused by dislocation origination and multiplication.

We represent the total tensor $\hat{\sigma}$ as the sum of its spherical and deviatoric components

$$\hat{\sigma} = -p\hat{\delta} + \hat{s} \tag{16}$$

($\hat{\delta}$ is the unit tensor, $p = -\sigma_{kk}/3$, and $s_{ij} = \sigma_{ij} - \sigma_{kk}/3$) and the pressure and deviator in the form

$$p = p^e + p^i, \qquad \hat{s} = \hat{s}^e + \hat{s}^i. \tag{17}$$

Here, the subscripts e and i refer to the elastic and irreversible processes, respectively. Then, using (16) and (17), from (11), (13) and (15), we obtain the following relation for entropy generation:

$$\sigma_s = -\boldsymbol{J}_T \cdot \Big(\frac{\nabla T}{T^2}\Big) - \sum_{k=1}^{n} \boldsymbol{J}_k \cdot \Big(\nabla\Big(\frac{g_k}{T}\Big) - \frac{\boldsymbol{F}_k}{T}\Big) - J_f \cdot \nabla\Big(\frac{g_f}{T}\Big) - \frac{1}{T}\sum_{i=1}^{r} \varphi_i A_i$$

$$- \frac{1}{T}\, g_f \sigma_f - \frac{p^i}{T} \nabla \cdot \boldsymbol{v} + \frac{1}{T}\, \hat{s}^i \cdot\cdot \nabla \boldsymbol{v} + \frac{1}{T}\Big[\hat{s}^e \cdot\cdot \nabla \boldsymbol{v} - \hat{s}^e \cdot\cdot \frac{d}{dt}\,\hat{\varepsilon}\Big] \geqslant 0. \tag{18}$$

Here $A_i = -\sum\limits_{k=1}^{n} g_k m_k \nu_{ki}$ is the affinity of the ith chemical reaction, m_k is the molar weight of the kth component, and ν_{ki} is the stoichiometric coefficient of the kth component in the ith reaction; the last bracketed term is nonzero only if the strain-rate tensor is asymmetric. For relation (18) to be satisfied, it suffices that the linear relations between the fluxes and the generalized driving thermodynamic forces, which are described by tensor quantities of identical structures, be fulfilled. For instance, if $\sigma_f = 0$ and $\sigma_k = 0$, then we have

$$p^i = -æ \nabla \cdot \boldsymbol{v}; \tag{19}$$

$$\hat{s} = C_{ij\alpha\beta} \nabla \boldsymbol{v}. \tag{20}$$

Relation (19) is the Newton viscosity law and relation (20) is the generalized Navier–Stokes law. Media that satisfy these relations are called viscous [8].

It follows from (4), (19), and (21) that there are three types of irreversible mechanical processes: 1) processes described by relations of the types (19) and (20), caused by viscosity of the medium; 2) processes caused by irreversible processes of various physicochemical nature [in this case, the components of the stress and strain tensors are related by linear relations of the type (4)]; 3) processes that are induced by asymmetry of the strain tensor and correspond to entropy generation in the brackets of (18). Note, if the sources and sinks for the components and for the new thermodynamic parameter are nonzero, then they enter relation (19) with their relaxation times (characteristic transformation times). For instance,

$$p^i = -æ \nabla \cdot \boldsymbol{v} - \sum_{j=1}^{r} L_j \,\frac{A_j}{T} - M\,\frac{g_f}{T},$$

where L_j and M are phenomenological coefficients. The expression for reaction rates is written in a similar manner.

Apparently, heat and mass transfer, physicochemical transformations, nucleation and multiplication of various lattice defects, and other irreversible processes described by relations (4) and (19) result in phenomena that are classified as plastic in mechanics of deformable solids and that can be describes with a great number of various theories involved.

In what follows, we consider diffusion-type irreversible transfer processes.

In the case with no external forces ($\boldsymbol{F} = 0$), the following equality is valid for the flux of a component (this equality follows from the nonnegativeness of entropy generation by irreversible processes described by vector quantities):

$$\boldsymbol{J}_k = -\sum_{l=1}^{n} L_{kl}\nabla\Big(\frac{g_l}{T}\Big) - L_{ks}\nabla\Big(\frac{g_f}{T}\Big) - L_{kT}\,\frac{\nabla T}{T^2}. \tag{21}$$

There is an similar relation for the flux of internal interfaces:

$$\boldsymbol{J}_f = -\sum_{l=1}^{n} L_{sl}\nabla\Big(\frac{g_l}{T}\Big) - L_{ss}\nabla\Big(\frac{g_f}{T}\Big) - L_{sT}\,\frac{\nabla T}{T^2}. \tag{22}$$

Generally speaking, in constructing a model for a particular medium, one can use, instead of (20)–(22), nonlinear relations and integrodifferential equations, whose limiting cases give generic laws that involve relaxation times of the fluxes of heat, mass, etc. It is obvious that, in each particular case, a special analysis of applicability of such laws is necessary. In generalization to the nonlinear region, condition (18) does not always hold and, to formulate the second law of thermodynamics, Prigogine's evolution criterion should be used [9].

We perform an analysis of the relations for irreversible fluxes (21) and (22) and for associated "elastic" deformations under the condition $T = \text{const}$. From here on, the subscript e is omitted.

3. Diffusion and Stresses. For $dT = 0$ and $df_s = 0$, instead of (4) and (5), we have

$$d\varepsilon_{ij} = s_{ij\alpha\beta}\, d\sigma_{\alpha\beta} + \sum_{k=1}^{n} \alpha_{ij}^{(k)}\, dC_k; \tag{23}$$

$$dg_k = -\alpha_{ij}^{(k)} \rho^{-1}\, d\sigma_{ij} + \sum_{l=1}^{n} \beta_l^{(k)}\, dC_l. \tag{24}$$

The expressions for the coefficients $\beta_l^{(k)}$ are

$$\beta_l^{(k)} = \frac{\partial g_k}{\partial C_l} = \frac{RT}{m_k C_k}\, g_{kl}, \tag{25}$$

where $g_{kl} = \delta_{kl} + (C_k/C_l)\partial \ln\gamma_k/\partial \ln C_l$ are the thermodynamic multipliers resulting from the definition of chemical potentials of components for simple media [10, 11]

$$dg_k = (RT/m_k)\, d\ln(\gamma_k C_k).$$

Here γ_k is the coefficient of activity of the kth component in the solution or mixture (in the general case, γ_k is a complex function of all concentrations, and its form depends on the type of the solid solution or mixture), and m_k is the molar weight of the kth component. Equation (23) extends Hooke's law to the case of an anisotropic medium with diffusion. A similar generalization was reported in [12]. The second-rank tensor $\alpha_{ij}^{(k)}$ has the same structure as the tensor of thermal-expansion coefficients. In a particular case of an isotropic medium, Eq. (23) yields the well-known relations [1] written in the differential form

$$d\varepsilon_{ij} = \frac{1}{E}\,[(1+\nu)\, d\sigma_{ij} - \nu\delta_{ij}\, d\sigma_{kk}] + \delta_{ij}\sum_{k=1}^{n} \alpha_k\, dC_k, \tag{26}$$

where E is Young;s modulus, ν is Poisson's ratio, and α_k are the crystal-lattice thermal-expansion or dilatation coefficients. Summing (26) over all $i = j$, we obtain the equality

$$dV = \rho^{-1}\, d\varepsilon_{kk} = V_p\, dp + \sum_{k=1}^{n} V_k\, dC_k,$$

from which it follows that the change in the volume of the thermodynamic system of interest is caused by the change in pressure $dp = -d\sigma_{kk}/3$ ($V_p = -(1-2\nu)/(\rho E)$) and by the change in concentrations of the components ($V_k = 3\alpha_k/\rho$). Obviously, the following alternative form of relations (26) is possible:

$$d\sigma_{ij} = 2\mu\, d\varepsilon_{ij} + \delta_{ij}\Big[\lambda\, d\varepsilon_{kk} - 3K\sum_{k=1}^{n} \alpha_k\, dC_k\Big].$$

Here, λ and μ are the Lamé coefficients and $K = \lambda + 2\mu/3$ is the bulk compression modulus.

Relations (24) take into account the variation of chemical potentials of the components caused by the change in their concentrations and in the stress-tensor components. Using (24) and (21) with $dT = 0$ and $df_s = 0$ and taking into account definitions (9) and (25), we obtain:

$$\boldsymbol{J}_k = -\sum_{l=1}^{n} \frac{L_{kl}}{T} (\nabla g_l)_T \equiv -\sum_{l=1}^{n} \Big[\sum_{j=1}^{n-1} \frac{L_{kl}}{T} \beta_j^{(l)} \nabla C_j - \sum_{(i,j)} \frac{L_{kl}}{T} \frac{\alpha_{ij}^{(l)}}{\rho} \nabla \sigma_{ij}\Big] = -\rho \sum_{j=1}^{n-1} D_{kj} \nabla C_j + \sum_{(i,j)} B_{ij}^{(k)} \nabla \sigma_{ij}. \tag{27}$$

Here

$$D_{kj} = \frac{1}{T\rho} \sum_{l=1}^{n} L_{kl} \beta_j^{(l)} \tag{28}$$

are the partial diffusion coefficients and

$$B_{ij}^{(k)} = \sum_{l=1}^{n} \alpha_{ij}^{(l)} \frac{L_{kl}}{T\rho} \tag{29}$$

are the stress-induced transport coefficients. In writing (27), we took into account that, in a system composed of n components, only $n-1$ components are independent because $\sum\limits_{(k)} C_k = 1$. In addition, by definition, among a total of n fluxes, only $n-1$ fluxes are independent because $\sum\limits_{(k)} \boldsymbol{J}_k = 0$.

In the case of a binary system, we have only one relation for the flux

$$\boldsymbol{J}_1 = -\rho D_{11} \nabla C_1 + \sum_{(i,j)} B_{ij}^{(1)} \nabla \sigma_{ij}, \tag{30}$$

where

$$D_{11} = [L_{11}\beta_1^{(1)} + L_{12}\beta_1^{(2)}]/(\rho T); \tag{31}$$

$$B_{ij}^{(1)} = [L_{11}\alpha_{ij}^{(1)} + L_{12}\alpha_{ij}^{(2)}]/(\rho T). \tag{32}$$

In the diffusion theory, two types of approximations are usually considered. In the first case, it is assumed that the solution is ideal; then, $dg_k = (RT/m_k)\, d\ln C_k$ (i.e., $\gamma_k \equiv 1$), $g_{11} = 1$, $g_{12} = 0$, and the self-diffusion coefficient of component 1 can be obtained from (31):

$$D_{11} = L_{11}R/(m_1 C_1 \rho) = D_1^*. \tag{33}$$

In the second case, it is assumed that the solution is nonideal, but, unlike the diagonal coefficient L_{11}, the cross coefficient L_{12} can be neglected (this approximation can be justified by methods of statistical thermodynamics). Then, we have

$$D_{11} = L_{11}Rg_{11}/(m_1 C_1 \rho) = D_1^* g_{11}. \tag{34}$$

In a similar manner, we obtain

$$D_{22} = L_{22}Rg_{22}/(m_2 C_2 \rho) = D_2^* g_{22}.$$

Expressing the coefficient L_{11} from (33) and neglecting the coefficient L_{12}, we can represent the stress-induced transport coefficients (32) as

$$B_{ij}^{(1)} = \alpha_{ij}^{(1)} D_1^* m_1 C_1/(RT). \tag{35}$$

Apparently, similar approximations (for the ideal and nonideal solutions) are also valid for a multi-species medium.

In the case of a two-component isotropic medium, from (30), (34), and (35), we have

$$B_{ij}^{(1)} = \alpha_1 D_1^* m_1 C_1 \delta_{ij}/(RT)$$

and

$$\boldsymbol{J}_1 = -\rho D_1^* g_{11} \nabla C_1 + \alpha_1 (D_1^* m_1 C_1/(RT)) \nabla \sigma_{kk}. \tag{36}$$

With $dT = 0$, $df_s = 0$, and $\boldsymbol{F} = 0$, the total system of equations of mechanics of an "elastic" continuous medium for interrelated mass-transfer and deformation processes acquires the form

$$\frac{d\rho}{dt} + \rho \nabla \cdot \boldsymbol{v} = 0, \qquad \rho \frac{dC_1}{dt} + \nabla \cdot \boldsymbol{J}_1 = \sigma_1, \qquad \rho \frac{d\boldsymbol{v}}{dt} = \nabla \cdot \hat{\sigma}, \qquad \rho \frac{du}{dt} = \hat{\sigma} \cdot \cdot \nabla \boldsymbol{v}. \tag{37}$$

This system should be closed by the relation for the mass flux (36), the linear relations between the components of the stress and strain tensors in the form (26), and the mass-balance equation $C_2 + C_1 = 1$. System (37) (derived with no restrictions imposed on the value of strains) can be simplified in the case of small deformations and low velocities and accelerations, for which the following relations are valid [8]:

$$\nabla \cdot \boldsymbol{v} = 0, \quad \frac{d\rho}{dt} = 0, \quad \varepsilon_{ij} = \frac{1}{2}\Big(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\Big), \quad \frac{d\boldsymbol{v}}{dt} \approx \frac{\partial^2 \boldsymbol{u}}{\partial t^2}$$

(i.e., for an incompressible medium). Here $\boldsymbol{u}$ is the displacement vector. In this case, from the "total" system (37), we obtain the system of mass-elasticity equations [1] for a two-component mixture (solid solution)

$$\rho\,\frac{\partial^2 \boldsymbol{u}}{\partial t^2} = \nabla \cdot \hat{\sigma}; \tag{38}$$

$$\frac{\partial C_1}{\partial t} = \nabla \cdot [D_1^* g_{11} \nabla C_1] - \frac{\alpha_1 D_1^* m_1}{RT\rho} \nabla \cdot (C_1 \nabla \sigma_{kk}) + \rho^{-1} \sigma_1; \tag{39}$$

$$d\sigma_{ij} = 2\mu\, d\varepsilon_{ij} + \delta_{ij}[\lambda d\varepsilon_{kk} - 3K(\alpha_1 - \alpha_2)\, dC_1], \tag{40}$$

where the strains are given by the Cauchy relations.

The system of mass-elasticity equations can be alternatively derived using expansion of the local Gibbs energy in powers of low stresses [4] and concentrations or expansion of free Helmholtz energy in powers of small deformations and concentrations [1].

In particular problems, for instance, in problems considered in [1], in view of the fact that the propagation velocity of mechanical disturbances is much (by two to five orders of magnitude) greater than the velocity of substance transport by means of diffusion, it is a common practice to disregard inertial forces in the equation of motion (38) and pass to analyzing quasistatic problems. Another assumption adopted almost in all available papers (see [1–3]) is the smallness of the second term in the transport equation (39). Nevertheless, under the conditions of an intense mechanical loading generating large stress gradients, the transfer of the substance under the action of $\nabla\sigma_{kk}$ prevails over the diffusion transport or, at least, is comparable with it. In this case, neglecting inertial forces in (38) and the term related to stresses in (39) becomes inadequate. From the mathematical point of view, weak perturbations induced by the terms ignored in available publications are singular. Problems based on models of the types (37), (36), (26) or (38)–(40) require a special study.

In contrast to the statement put forward in [1], the transfer of the substance under the action of the parameter $\nabla\sigma_{kk}$ more closely resembles barodiffusion than thermal expansion. This conclusion is confirmed by an analysis of the equation for the flux of the second component. By definition of the diffusion fluxes,

$$\boldsymbol{J}_2 = -\boldsymbol{J}_1 = -\rho D_1^* g_{11} \nabla C_2 - \alpha_1 (D_1^* m_1 (1 - C_2)/(RT)) \nabla \sigma_{kk}.$$

Hence, the mixing rate of one component in a binary system increases under the action of the stress gradient, while the mixing rate of the other component decreases, as it also occurs in the hydrodynamic model of diffusion [6, 13].

For the case of an isotropic medium, simple procedures for estimating the coefficients α_k are available [14].

Very likely, the phenomenon of abnormally fast solid-phase mixing of the substance experimentally observed under intense mechanical actions and also some rapid regimes of solid-phase transformations under specific conditions (see, e.g., [15]) can be attributed to the transfer of the substance under the action of stress gradients.

4. Diffusion in a Medium with Internal Interfaces. We consider a hydrodynamic system with $dT = 0$ and $d\sigma_{ij} = 0$ but assume now that the variation of the area of internal interfaces cannot be ignored. Then, it follows from (5) and (6) that

$$\begin{gathered} dg_k = \sum_{m=1}^{n} \Big(\frac{\partial g_k}{\partial C_m}\Big)_{T,\hat{\sigma},f_s,C_l,l\neq m} dC_m + \Big(\frac{\partial g_k}{\partial f_s}\Big)_{T,\hat{\sigma},C_m} df_s, \quad k = 1, 2, \ldots, n, \\ dg_f = \sum_{k=1}^{n} \Big(\frac{\partial g_f}{\partial C_k}\Big)_{T,\hat{\sigma},f_s,C_l,l\neq k} dC_k + \Big(\frac{\partial g_f}{\partial f_s}\Big)_{T,\hat{\sigma},C_k} df_s. \end{gathered} \tag{41}$$

Similarly to (8) and (9), we write

$$\gamma_s^{(k)} = \frac{\partial g_k}{\partial f_s} = -\frac{\partial g_f}{\partial C_k} = \Big(\frac{\partial^2 g}{\partial f_s\, \partial C_k}\Big)_{T,\hat{\sigma}}.$$

It follows from this equality that the change in the chemical potential of the kth component due to the change in the area of internal interfaces equals the change in the energy of these interfaces due to the variation of the concentration of this component, which allows one to significantly reduce the number of coefficients required to describe the state of the thermodynamic system. We introduce an additional parameter

$$\Omega = \Big(\frac{\partial g_f}{\partial f_s}\Big)_{C_k} = \Big(\frac{\partial^2 g}{\partial f_s^2}\Big)_{C_k,\hat{\sigma},T}$$

that describes the variation of surface energy due to the variation of surface curvature. The partial derivatives of chemical potentials with respect to concentrations of the components are known. With the adopted notation, system (41) becomes

$$dg_k = \sum_{j=1}^{n} \beta_j^{(k)}\, dC_j + \gamma_s^{(k)}\, df_s, \quad dg_f = -\sum_{k=1}^{n} \gamma_s^{(k)}\, dC_k + \Omega\, df_s. \tag{42}$$

Using relations (21) and (22) for the fluxes and assuming that

$$g_j = g_j(C_1, C_2, \ldots, C_{n-1}, f_s), \quad g_f = g_f(C_1, C_2, \ldots, C_{n-1}, f_s),$$

in a close analogy with (27), with the help of (42), we obtain

$$\boldsymbol{J}_k = -\rho \sum_{i=1}^{n-1} D_{ki} \nabla C_i - \rho D_{ks} \nabla f_s, \quad \boldsymbol{J}_f = -\sum_{j=0}^{n-1} D_{sj} \nabla C_j - D_{ss} \nabla f_s, \tag{43}$$

where

$$D_{ki} = \sum_{j=1}^{n} \frac{L_{kj}}{T\rho}\, \frac{\partial g_j}{\partial C_i} + \frac{L_{ks}}{T\rho}\, \frac{\partial g_s}{\partial C_i} = \frac{1}{T\rho}\Big(\sum_{j=1}^{n} L_{kj}\, \frac{RT}{m_j C_j}\, g_{ji} - L_{ks}\gamma_s^{(i)}\Big),$$

$$D_{ks} = \sum_{j=1}^{n} \frac{L_{kj}}{T\rho}\, \frac{\partial g_j}{\partial f_s} + \frac{L_{ks}}{T\rho}\, \frac{\partial g_s}{\partial f_s} = \frac{1}{T\rho}\Big(\sum_{j=1}^{n} L_{kj}\gamma_s^{(j)} + L_{ks}\Omega\Big),$$

$$D_{sj} = \sum_{k=1}^{n} \frac{L_{sk}}{T}\, \frac{\partial g_k}{\partial C_j} + \frac{L_{ss}}{T}\, \frac{\partial g_f}{\partial C_j} = \frac{1}{T}\Big(\sum_{k=1}^{n} L_{sk}\, \frac{RT}{m_k C_k}\, g_{kj} - L_{ss}\gamma_s^{(j)}\Big), \tag{44}$$

$$D_{ss} = \sum_{k=1}^{n} \frac{L_{sk}}{T}\, \frac{\partial g_k}{\partial f_s} + \frac{L_{ss}}{T}\, \frac{\partial g_f}{\partial f_s} = \frac{1}{T}\Big(\sum_{k=1}^{n} L_{sk}\gamma_s^{(k)} + L_{ss}\Omega\Big).$$

Although the matrix of the Onsager coefficients is symmetric, the matrix of diffusion coefficients can be devoid of this property.

In their physical meaning, the coefficients D_{ki} are partial diffusion coefficients in the bulk of a polycrystalline system. Their values differ from the partial diffusion coefficients in the bulk of a single crystal (28). In what follows, we mark these coefficients with the superscripts "zero." The difference between D_{ki} and D_{ki}^0, also observed experimentally [5], is caused by the effect of internal interfaces or, more precisely, by the effect of internal energy accumulated in the form of interfacial energy.

The coefficients D_{ks} are the diffusivities along grain and interphase boundaries; as is well known, these coefficients are much greater than volume diffusivity. Their values directly depend on the total energy of internal interfaces.

The coefficients D_{sj} can be called the coefficients of interface migration due to gradients of concentrations of migrating species, and the coefficients D_{ss} can be called the coefficients of migration of internal interfaces due to their nonuniform distribution in the polycrystal.

As the analysis of numerous data on diffusion in complex media shows, all coefficients introduced for a polycrystalline system are experimentally measurable quantities; apparently, they can be estimated on the basis of the simplest problems [5] for an individual interface.

We consider two approximations traditionally used in the theory of diffusion in solids.

If the solution is ideal, then for the partial diffusion coefficients D_{ki} and for the coefficients of interface migration D_{sj} we have:

$$D_{ki} = \frac{1}{\rho}\Big(\frac{L_{ki}R}{C_i m_i} - \frac{L_{ks}}{T}\,\gamma_s^{(i)}\Big), \quad D_{sj} = \frac{L_{sj}R}{C_j m_j} - \frac{L_{ss}}{T}\,\gamma_s^{(j)}.$$

The other coefficients remain unchanged.

If the solution is non-ideal but the cross coefficients L_{ij} are small compared to the diagonal coefficients L_{ii} and, therefore, can be neglected, then, from (44), we obtain:

$$D_{ki} = L_{kk}\beta_i^{(k)}/(T\rho) - L_{ks}\gamma_s^{(i)}/(T\rho), \qquad D_{ks} = [L_{kk}\gamma_s^{(k)} + L_{ks}\Omega]/(T\rho).$$

The other coefficients remain unchanged. Taking into account that we have

$$L_{kk}\beta_i^{(k)}/(\rho T) = D_{ki}^0 = D_k^* g_{ki}, \qquad L_{kk} = m_k C_k \rho D_k^*/R$$

in the case of a nonideal solution (D_k^* is the self-diffusion coefficient of the kth component), we write

$$D_{ki} = D_k^* g_{ki} - L_{ks}\gamma_s^{(i)}/(T\rho), \qquad D_{ks} = D_k^*\gamma_s^{(k)} C_k m_k/(RT\rho) + L_{ks}\Omega/(T\rho). \tag{45}$$

Let us examine interstitial diffusion in a binary system. Taking into account that $C_1+C_2 = 1$ and $\boldsymbol{J}_1+\boldsymbol{J}_2 = 0$, from (43), we obtain the following system for the fluxes:

$$\boldsymbol{J}_1 = -\rho D_{11}\nabla C_1 - \rho D_{1s}\nabla f_s, \qquad \boldsymbol{J}_f = -D_{s1}\nabla C_1 - D_{ss}\nabla f_s.$$

Here D_{11} is the volume diffusivity, D_{1s} is the diffusivity over grain boundaries, D_{s1} is the diffusivity of the boundary for a varied concentration of component 1, and D_{ss} is the diffusivity of internal interfaces under the action of their own curvature. Assuming that $\nabla\cdot\boldsymbol{v} = 0$ ($d\rho/dt = 0$) and using the balance equations (11) and (14), we obtain the system of differential equations

$$\frac{\partial C_1}{\partial t} = \nabla\cdot[D_{11}\nabla C_1 + D_{1s}\nabla f_s] + \sigma_1\rho^{-1}, \qquad \frac{\partial f_s}{\partial t} = \nabla\cdot[D_{s1}\nabla C_1 + D_{ss}\nabla f_s] + \sigma_f, \tag{46}$$

where

$$\begin{gathered} D_{11} = D_1^* g_{11} - L_{1s}\gamma_s^{(1)}/(T\rho), \qquad D_{1s} = D_1^*\gamma_s^{(1)} C_1 m_1/(RT) + L_{1s}\Omega/(T\rho), \\ D_{s1} = R\Big(\frac{L_{s1}g_{11}}{m_1C_1} + \frac{L_{s2}g_{21}}{m_2C_2}\Big) - \frac{L_{ss}}{T}\,\gamma_s^{(1)}, \qquad D_{ss} = \frac{1}{T}\,(L_{s1}\gamma_s^{(1)} + L_{s2}\gamma_s^{(2)} + L_{ss}\Omega). \end{gathered} \tag{47}$$

A system of equations similar to (46) arises in the description of substitutional diffusion in a binary system under conditions of a nonequilibrium vacancy concentration and also in the description of interstitial diffusion in a ternary system. The methods of solving such systems can be used to analyze diffusion in media with internal interfaces. For constant diffusion coefficients, there exist exact analytical solutions of the simplest boundary problems for system (46). These solutions, in particular, show that distributions of concentrations of the diffusing species and the internal-interface areas can be nonmonotonic for some proportions between the diffusion coefficients, and the positions of the extrema of the parameters C_1 and f_s can be noncoincident.

5. Diffusion in a Structurally Nonuniform Medium with Allowance for Stresses and Strains. Let the thermodynamic system be under isothermal conditions, but $d\sigma_{ij} \neq 0$, $df_s \neq 0$, and $dC_k \neq 0$. Then, it follows from (4)–(6) that

$$\begin{gathered} d\varepsilon_{ij} = s_{ij\alpha\beta}\,d\sigma_{\alpha\beta} + \sum_{k=1}^{n}\alpha_{ij}^{(k)}\,dC_k + \Big(\frac{\partial\varepsilon_{ij}}{\partial f_s}\Big)_{\hat{\sigma},C_k} df_s, \\ dg_k = -\alpha_{ij}^{(k)}\rho^{-1}\,d\sigma_{ij} + \sum_{j=1}^{n}\beta_j^{(k)}\,dC_j + \gamma_s^{(k)}\,df_s, \\ dg_f = \Big(\frac{\partial g_f}{\partial\sigma_{ij}}\Big)_{C_k,f_s} d\sigma_{ij} - \sum_{k=1}^{n}\gamma_s^{(k)}\,dC_k + \Omega\,df_s. \end{gathered} \tag{48}$$

The new coefficients describe the interaction between the internal-stress field and the field of internal interfaces. The change in the strain-tensor components due to variation of the specific area of internal interfaces

$(\partial\varepsilon_{ij}/\partial f_s)$ is described by the same coefficients that describe the change in the energy of internal interfaces due to variation of the internal-stress field $(\partial g_s/\partial\sigma_{ij})$. Similarly to (9), we have

$$\alpha_{ij}^{(s)} = \Big(\frac{\partial\varepsilon_{ij}}{\partial f_s}\Big)_{\hat\sigma, C_k} = -\rho\Big(\frac{\partial^2 g}{\partial f_s\,\partial\sigma_{ij}}\Big)_{C_k} = -\rho\Big(\frac{\partial^2 g}{\partial\sigma_{ij}\,\partial f_s}\Big)_{C_k} = \rho\Big(\frac{\partial g_f}{\partial\sigma_{ij}}\Big)_{C_k, f_s}. \qquad (49)$$

Using (21), for a constant temperature, we can write

$$\boldsymbol{J}_k = -\sum_{l=1}^{n}\frac{L_{kl}}{T}\Big[\frac{\partial g_l}{\partial\sigma_{ij}}\nabla\sigma_{ij} + \sum_{m=1}^{n-1}\frac{\partial g_l}{\partial C_m}\nabla C_m + \frac{\partial g_l}{\partial f_s}\nabla f_s\Big]$$

$$-\frac{L_{ks}}{T}\Big[\frac{\partial g_f}{\partial\sigma_{ij}}\nabla\sigma_{ij} + \sum_{m=1}^{n-1}\frac{\partial g_f}{\partial C_m}\nabla C_m + \frac{\partial g_f}{\partial f_s}\nabla f_s\Big] = -\rho\sum_{m=1}^{n-1}D_{km}\nabla C_m - \rho D_{ks}\nabla f_s + B_{ij}^{(k)}\nabla\sigma_{ij}, \qquad (50)$$

where the partial diffusion coefficients D_{km} and the surface-diffusion coefficients D_{ks} are the same as in (44), whereas the stress-induced transport coefficients have the form

$$B_{ij}^{(k)} = \sum_{l=1}^{n}\frac{L_{kl}}{T\rho}\,\alpha_{ij}^{(l)} - \frac{L_{ks}}{T\rho}\,\alpha_{ij}^{(s)},$$

i.e., they differ from (29).

Using (22), for the flux of interfaces, we obtain

$$\boldsymbol{J}_f = -\sum_{m=1}^{n-1}D_{sm}\nabla C_m - D_{ss}\nabla f_s + B_{ij}^{(s)}\nabla\sigma_{ij}. \qquad (51)$$

The interface-migration coefficients D_{sm} and D_{ss} can be found by formulas (44), and $B_{ij}^{(s)}$ are the coefficients of interface migration under the action of the stress gradient, which depend on the previously defined parameters $\alpha_{ij}^{(k)}$ [see (9)] and $\alpha_{ij}^{(s)}$ [see (49)]:

$$B_{ij}^{(s)} = \sum_{k=1}^{n}\frac{L_{sk}}{T\rho}\,\alpha_{ij}^{(k)} - \frac{L_{ss}}{T\rho}\,\alpha_{ij}^{(s)}.$$

For an isotropic medium, we have

$$B_{ij}^{(k)} = \Big(\sum_{l=1}^{n}\frac{L_{kl}}{T\rho}\,\alpha_k - \frac{L_{ks}}{T\rho}\,\alpha_s\Big)\delta_{ij} = B_k\delta_{ij}, \qquad B_{ij}^{(s)} = \Big(\sum_{l=1}^{n}\frac{L_{sl}}{T\rho}\,\alpha_l - \frac{L_{ss}}{T\rho}\,\alpha_s\Big)\delta_{ij} = B_s\delta_{ij}.$$

In this case, the last terms in the right sides of Eqs. (50) and (51) acquire the forms $B_k\nabla\sigma_{kk}$ and $B_s\nabla\sigma_{kk}$, respectively.

Neglecting the cross coefficients L_{kl}, which are small compared to the diagonal coefficients L_{kk}, and expressing L_{kk} in terms of the self-diffusion coefficient of the kth component, we describe diffusion in a nonideal isotropic solid solution using the following relations for the transport coefficients [see (45)], the coefficients D_{sj} and D_{ss} [see (44)], and the parameters

$$B_k = \frac{D_k^* m_k C_k}{RT}\,\alpha_k - \frac{L_{ks}}{T\rho}\,\alpha_s, \qquad B_s = -\sum_{k=1}^{n}\frac{L_{sk}}{T\rho}\,\alpha_k + \frac{L_{ss}}{T\rho}\,\alpha_s.$$

We consider the case of a binary system in an isotropic medium. Equation (48) acquires the form

$$d\varepsilon_{ij} = [(1+\nu)\,d\sigma_{ij} - \nu\delta_{ij}\,d\sigma_{kk}]/E + \delta_{ij}[(\alpha_1-\alpha_2)\,dC_1 + \alpha_s\,df_s]. \qquad (52)$$

The equation for the flux of component 1 and for the flux of interfaces includes terms of three types

$$\boldsymbol{J}_1 = -\rho D_{11}\nabla C_1 - \rho D_{1s}\nabla f_s + B_1\nabla\sigma_{kk}, \qquad \boldsymbol{J}_f = D_{s1}\nabla C_1 - D_{ss}\nabla f_s + B_s\nabla\sigma_{kk}$$

with six transport coefficients [see (47)]; here,

$$B_1 = D_1^* m_1 C_1\alpha_1/(RT) - L_{1s}\alpha_s/(T\rho), \qquad B_s = (L_{s1}\alpha_1 + L_{s2}\alpha_2)/(T\rho) - L_{ss}\alpha_s/(T\rho).$$

Neglecting the cross coefficients $L_{1s} = L_{s1}$ and $L_{2s} = L_{s2}$, which are small compared to the diagonal coefficients (although this statement lacks sufficient substantiation), we can appreciably simplify the expressions for the transport coefficients:

$$D_{11} = D_1^* g_{11}, \quad D_{1s} = D_1^* \gamma_s^{(1)} C_1 m_1/(RT), \quad D_{s1} = -L_{ss}\gamma_s^{(1)}/T, \quad D_{ss} = L_{ss}\Omega/T,$$

$$B_1 = D_1^* m_1 C_1 \alpha_1/(RT), \qquad B_s = -L_{ss}\alpha_s/(T\rho).$$

Considering the volume- and surface-diffusion coefficients to be known, we can represent the system of equations for the fluxes as

$$\boldsymbol{J}_1 = -\rho D_1^* g_{11} \nabla C_1 - \rho D_{1s} \nabla f_s + \frac{D_1^* m_1 C_1}{RT}\, \alpha_1 \nabla \sigma_{kk}, \qquad \boldsymbol{J}_f = \frac{D_{ss} RT}{\Omega C_1 m_1} \nabla C_1 - D_{ss} \nabla f_s + \frac{D_{ss}\alpha_s}{\Omega\rho} \nabla \sigma_{kk}. \tag{53}$$

These equations yield rather obvious conclusions: the interfaces migrate in the direction opposite to the direction of the diffusion flux of component 1 and, since $D_{1s}/D_1^* \gg 1$, diffusion of interfaces under the action of the concentration gradient prevails over the diffusion under the action of the parameter ∇f. The flux of interfaces can be represented as

$$\boldsymbol{J}_f = -D_{s1} \nabla C_1 + \frac{\Omega D_{s1} D_1^*}{D_{1s} RT}\, C_1 m_1 \nabla f_s + \frac{D_1^* \alpha_s}{RT\rho}\, C_1 m_1 \,\frac{D_{s1}}{D_{1s}}\, \nabla \sigma_{kk}, \tag{54}$$

which is more convenient, because the denominator does not contain the concentration.

As in the case of cross processes (such as diffusion, thermal conductivity, barodiffusion, thermodiffusion, heat transfer via diffusion, and heat transfer under the action of a pressure gradient) in liquids, to describe six transfer processes in the case under consideration, we need only three independent coefficients.

System (37) should be supplemented by Eqs. (52)–(54) and by the balance equation (14). In the case of small deformations, we obtain system (38) and

$$\frac{\partial C_1}{\partial t} = -\nabla \cdot (\rho^{-1} \boldsymbol{J}_1) + \sigma_1 \rho^{-1}, \qquad \frac{\partial f_s}{\partial t} = -\nabla \cdot \boldsymbol{J}_f + \sigma_f,$$

where the fluxes are calculated by the formulas (53) and (54), and, instead of (40), the following equality is valid:

$$d\sigma_{ij} = 2\mu\, d\varepsilon_{ij} + \delta_{ij}[\lambda\, d\varepsilon_{kk} - 3K(\alpha_1 - \alpha_2)\, dC_1 - 3K\alpha_s\, df_s].$$

Similarly to [1, 2], we can easily show, based on the problems of saturation of bodies of various shapes with impurities, that, in the case of slow diffusion and with no external mechanical action exerted on the system, the effect of internal stresses on the transport processes can be treated if the effective diffusion coefficients are considered to be variable quantities, provided that the following condition of smallness of the dimensionless coefficient (similar to the connectivity coefficient in the theory of thermoelasticity) is valid:

$$\omega = \frac{(3K\alpha_1)^2}{\lambda + 2\mu}\, \frac{m_1}{\rho RT}.$$

Under a high-intensity external mechanical action or in the case of a substantially nonuniform stress field, it seems that the terms proportional to $\nabla \sigma_{kk}$ will prevail in Eqs. (53) and (54). Such problems need a special consideration.

Conclusions. Thus, the present paper extends the model of mechanics of continuous media to the case of anisotropic media with volume and interfacial diffusion. Expressions are obtained for the fluxes of components and for the fluxes of internal interfaces. It is shown that, to describe the direct and cross processes in a binary isotropic medium with internal interfaces, three coefficient are sufficient, which can be calculated or found independently. It is shown that interstitial diffusion in a binary isotropic medium with allowance for stresses can be described similarly to diffusion, barodiffusion, and other processes in liquid media. Diffusion in media with dislocations, vacancies, or lattice imperfections such as voids or cracks can be treated similarly.

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