

## Diffusion equations for a mixture of an elastic fluid and an elastic solid

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A MECHANICAL theory is formulated for the diffusion of an elastic fluid through an isotropic elastic solid. It is assumed that each point of the mixture is occupied simultaneously by both constituents in given proportions. The motion of each constituent is governed by the usual equations of motion and continuity. The mechanical properties of each component are specified by means of constitutive equations for the stresses. Diffusion effects are accounted for by means of a body force acting on each constituent which depends upon the composition, the elasticity of the solid and the relative motion of the substances in the mixture. This approach makes it possible to derive coupled diffusion equations for both constituents. Uncoupling of the equations is accomplished within the framework of a linearized theory by adopting particular motions for the mixture. The result is compared with classical diffusion equations derived by intuitive modifications to the empirical Fick's law.

Sformulowano teorię mechaniczną dla dyfuzji cieczy sprężystej przez izotropowe ciało stałe. Przyjęto, że w każdym punkcie mieszaniny występują jednocześnie obydwa składniki w odpowiednich proporcjach. Ruch każdego składnika rządzą zwykłymi równaniami ruchu i ciągłości. Własności mechaniczne poszczególnych składników wyspecyfikowane zostały przy pomocy równań konstytutywnych dla naprężeń. Efekty dyfuzji uwzględniono poprzez siłę masową działającą na każdy składnik, która zależy od kompozycji sprężystości ciała stałego i ruchu względnego substancji w mieszaninie. Stosując to podejście wyprowadzono sprzężone równania dyfuzji dla obydwu składników. Rozprężenia równań dokonano w ramach teorii zlinearyzowanej przez przypisanie poszczególnych ruchów mieszaninie. Wyniki porównano z klasycznymi równaniami dyfuzji wyprowadzonymi drogą intuicyjnych modyfikacji empirycznego prawa Ficka.

Сформулирована механическая теория диффузии упругой жидкости в изотропном твердом теле. Принимается, что в каждой точке смеси выступают оба компонента в соответствующих пропорциях. Движение каждого компонента описывается обыкновенными уравнениями движения и неразрывности. Механические свойства отдельных компонентов специфицированы при помощи определяющих уравнений для напряжений. Эффекты диффузии учтены через массовую силу действующую на каждый из компонентов, которая зависит от отношения упругости твердого тела и относительного движения субстанции в смеси. Применяя этот подход выведены сопряженные уравнения диффузии для обоих компонентов. Распрямление уравнений произведено в рамках линеаризованной теории через приписание отдельных движений смеси. Результаты сравнены с классическими уравнениями диффузии выведенными путем интуитивных модификаций эмпирического закона Фика.

### 1. Introduction

THE PROBLEM of diffusion of liquids and gases through stressed solids is an important one both in theory and practice. In a classical treatment [1–5] diffusion equations are derived by adding stress dependent terms to the first Fick's law of diffusion. More specifically, within a linear elastic theory, and no mechanical basis, it is proposed that in a gas-solid mixture at uniform total density, the following constitutive relation holds:

$$(1.1) \quad \rho \mathbf{v} = -D \nabla \rho + M^* \nabla \sigma,$$

where  $\rho$  is the density (concentration) of the gas,  $\mathbf{v}$  is its diffusion velocity,  $\sigma$  is the trace of the stress tensor, and  $D$ ,  $M^*$  are phenomenological coefficients which may depend on the densities (concentrations) and the temperature. For particular examples in references [1-5],  $D$  is considered as a constant,  $M^*$  is taken as a linear function of the density  $\rho$ , and temperature effects are assumed to be negligible. In that case, substitution of Eq. (1.1) into the equation of the conservation of mass of the gas and use of the well-known relation of linear elasticity

$$(1.2) \quad \nabla^2 \sigma = 0,$$

yield

$$(1.3) \quad \frac{\partial \rho}{\partial t} = DV^2 \rho - MV \rho \cdot \nabla \sigma.$$

One may note that Eq. (1.3) is in the form typically obtained for a hydrostatically-stressed solid [1-4], but is different from that of SHEWMON [5] and others [6, 7] which use the elastic potential  $V$  in the place of  $\sigma$ , thus retaining the  $\nabla^2 V$  term, in order to explain the interaction between particles and defects with no hydrostatic components. For example, a screw dislocation can interact with the tetragonal distortion of a point defect which produces shear stresses [6]. However, this might not be necessary for other types of defect distortions since STEHLE and SEEGER [8] have determined that screw dislocations have volume expansion due to a disregistry at the dislocation core. Since it is difficult to generalize the specific effects of the non-hydrostatic cases [9], we retain the hydrostatic first order term only recognizing that second order effects are possible.

In the present work we re-examine this problem by following the general theory of mixtures introduced by TRUESDELL and TOUPIN [10, Sects. 88, 158, 215, 295] and extended further by TRUESDELL [11, 12], ADKINS [13, 14] and GREEN and ADKINS [15]. The above authors reason that since the diffusion process involves the relative motion of the constituents of the mixture, a transfer of momentum between components is involved. For each constituent we assume that kinematic and mechanical quantities such as velocity, acceleration, density, stress and body force per unit mass may be assigned and that with the aid of these, equations of motion and of conservation of mass may be established. In the case of a mixture of two components, this procedure yields a system of four partial differential equations. Further, it is assumed that within the mixture, the properties of any given component are defined by means of constitutive equations relating the partial stress tensor, the deformation gradients, the density and the kinematic quantities, such as velocity gradients and acceleration gradients, for that component. To simplify the theory we assume here that, in particular, the stress components for the solid  $s_1$  depend upon the densities and the deformation gradient defined for  $s_1$ . The stress components for the fluid  $s_2$  depend on the densities and the elasticity of the solid through its deformation gradient. Of course the basic assumption for elastic fluids, i.e. that the fluid cannot support shearing stresses, is adopted here.

To account for diffusion phenomena it is assumed that the body force acting on a given component, and expressed per unit mass of that component can be subdivided into an extraneous body force, identical in character with that of single component systems, and a diffusive force. This diffusive force depends upon the composition of the mixture at the

point under consideration, upon the density gradient, upon the elasticity of the solid and upon the relative velocities of each constituent. The forms for the partial stresses and the diffusive force are restricted to satisfy the necessary conditions for invariance of the properties of the mixture under rigid body translations. Finally, we should point out that thermal effects are neglected in the present investigation.

## 2. Preliminaries

We consider an elastic solid  $s_1$  which is undergoing a continuous deformation and suppose that the region occupied by this solid is also permeated by a fluid  $s_2$  which is in motion relative to  $s_1$ . We assume that each point within the mixture is occupied simultaneously by  $s_1$  and  $s_2$ . The motion is referred to a fixed system of rectangular Cartesian axes. The motion  $\chi$  of a typical particle of  $s_1$  is described by the invertible transformation

$$(2.1) \quad \mathbf{x} = \chi(\mathbf{X}, t),$$

where  $\mathbf{x}$  and  $\mathbf{X}$  are the places of the particle in the present and the reference configuration, respectively, and  $t$  denotes time. Similarly, the motion  $\gamma$  of a typical particle of  $s_2$  is described by the invertible transformation

$$(2.2) \quad \mathbf{y} = \gamma(\mathbf{Y}, t),$$

where  $\mathbf{y}$  and  $\mathbf{Y}$  are the places of the particle in the present and the reference configuration, respectively. Since the particles under consideration occupy the same place at time  $t$ , we have  $\mathbf{x} = \mathbf{y}$ .

Velocity fields at the point  $\mathbf{x} = \mathbf{y}$  in  $s_1$  and  $s_2$  at time  $t$  are defined as

$$(2.3) \quad \mathbf{u} = \frac{D^{(1)}\mathbf{x}}{Dt} = \{u_i\}, \quad \mathbf{v} = \frac{D^{(2)}\mathbf{y}}{Dt} = \{v_i\},$$

where  $D^{(1)}/Dt$  denotes differentiation with respect to  $t$  holding  $\mathbf{X}$  fixed in the solid  $s_1$  and  $D^{(2)}/Dt$  denotes a similar operator for  $s_2$ , holding  $\mathbf{Y}$  fixed. The operators  $D^{(1)}/Dt$ ,  $D^{(2)}/Dt$  are given by

$$(2.4)^{(1)} \quad \frac{D^{(1)}}{Dt} = \frac{\partial}{\partial t} + u_m \frac{\partial}{\partial x_m}, \quad \frac{D^{(2)}}{Dt} = \frac{\partial}{\partial t} + v_m \frac{\partial}{\partial y_m}.$$

The deformation gradient  $\mathbf{F}$  of the motion  $\chi$  of the solid  $s_1$  is a second-order tensor field defined as

$$(2.5) \quad \mathbf{F} = \nabla \chi(\mathbf{X}, t).$$

We assume that at  $\mathbf{x} = \mathbf{y}$  and time  $t$  there exist partial stress tensors  $\mathbf{S}$  and  $\mathbf{T}$ , extraneous body force vectors  $\mathbf{g}_1$  and  $\mathbf{g}_2$ , and diffusive body force vectors  $\varrho_2/\varrho_1 \psi$  and  $-\psi$  for the constituents of the mixture  $s_1$  and  $s_2$ , respectively. The body forces are per unit mass and  $\varrho_1$  and  $\varrho_2$  are the densities of  $s_1$  and  $s_2$ , respectively. Then the equations of motion for each constituent become

$$(2.6) \quad \text{div} \mathbf{S} + \varrho_2 \psi + \varrho_1 \mathbf{g}_1 = \varrho_1 \frac{D^{(1)}\mathbf{u}}{Dt}, \quad \text{div} \mathbf{T} - \varrho_2 \psi + \varrho_2 \mathbf{g}_2 = \varrho_2 \frac{D^{(2)}\mathbf{v}}{Dt}.$$

In subsequent work we shall restrict attention to the case in which extraneous body forces are absent. Addition of the Eq. (2.6) eliminates the term  $\varrho_2 \psi$  and confirms the

<sup>(1)</sup> Summation convention is assumed over repeated indices.

fundamental fact that the diffusion forces arise from interactions between the solid and the fluid and that the mixture as a whole does not recognize their existence.

In the absence of chemical reactions between  $s_1$  and  $s_2$ , we have the equations of continuity for each constituent

$$(2.7) \quad \frac{\partial \rho_1}{\partial t} + \operatorname{div}(\rho_1 \mathbf{u}) = 0, \quad \frac{\partial \rho_2}{\partial t} + \operatorname{div}(\rho_2 \mathbf{v}) = 0.$$

We consider now motions of each constituent which differ from the motions defined by Eqs. (2.1), (2.2), (2.3) only by a superposed rigid-body rotation at time  $t$ . This is required in order to restrict the form of the constitutive relation by using the axiom of frame-indifference and any conditions imposed by material symmetry. A change of frame is a time-dependent mapping  $(\mathbf{x}, t)$  to  $(\mathbf{x}^*, t^*)$  such that

$$(2.8) \quad \mathbf{x}^* = \mathbf{c} + \mathbf{Q}(\mathbf{x} - \mathbf{0}), \quad t^* = t - t_0,$$

where  $\mathbf{c}$  is an arbitrary point function of  $t$ ,  $\mathbf{Q}$  is a time-dependent orthogonal linear transformation,  $\mathbf{0}$  is a fixed point in the space and  $t_0$  is an arbitrary constant. Then it follows that

$$(2.9) \quad \mathbf{F}^* = \mathbf{Q}\mathbf{F}, \quad \mathbf{u}^* - \mathbf{v}^* = \mathbf{Q}(\mathbf{u} - \mathbf{v}).$$

If the partial stresses  $\mathbf{S}^*$ ,  $\mathbf{T}^*$  and the diffusive force  $\psi^*$  associated with the motion (2.8) differ from  $\mathbf{S}$ ,  $\mathbf{T}$  and  $\psi$ , respectively, only by orientation, then the principle of frame indifference [11] implies that

$$(2.10) \quad \mathbf{S}^* = \mathbf{Q}\mathbf{S}\mathbf{Q}^T, \quad \mathbf{T}^* = \mathbf{Q}\mathbf{T}\mathbf{Q}^T, \quad \psi^* = \mathbf{Q}\psi,$$

where the symbol  $\mathbf{T}$  indicates transposition.

### 3. Constitutive assumptions

The system of Eqs. (2.6) and (2.7) is completed by the introduction of constitutive equations for the stresses  $\mathbf{S}$ ,  $\mathbf{T}$  and the diffusive force  $\psi$ . When  $s_1$  and  $s_2$  are separated they are specified by the constitutive equations

$$(3.1) \quad \mathbf{S} = \mathbf{S}(\mathbf{B}), \quad \mathbf{T} = \mathbf{g}(\rho_2),$$

where  $\mathbf{B} = \mathbf{F}\mathbf{F}^T$  is the left Cauchy-Green deformation tensor and  $\mathbf{g}$  and  $\mathbf{S}$  arbitrary tensor are functions. Relations (3.1) are deduced from a general functional relation for elastic materials by assuming that  $s_1$  is an elastic isotropic solid and  $s_2$  is an elastic isotropic fluid [16]. The axiom of frame indifference, as described by Eqs. (2.10), is applied to Eqs. (3.1) to give

$$(3.2) \quad \mathbf{S}(\mathbf{Q}\mathbf{B}\mathbf{Q}^T) = \mathbf{Q}\mathbf{S}(\mathbf{B})\mathbf{Q}^T, \quad \mathbf{g}(\rho_2) = \mathbf{Q}\mathbf{g}(\rho_2)\mathbf{Q}^T,$$

which indicate that  $\mathbf{S}$  is an isotropic function of its argument and  $\mathbf{g}$  is a second-order isotropic tensor. In view of Eqs. (3.2), Eq. (3.1) can be written in the usual canonical forms [16]:

$$(3.3) \quad \mathbf{S} = \beta_0 \mathbf{1} + \beta_1 \mathbf{B} + \beta_2 \mathbf{B}^2, \quad \mathbf{T} = -p(\rho_2) \mathbf{1},$$

where  $\beta_0, \beta_1, \beta_2$  are functions of the three principal invariants  $\mathbf{I}_B, \mathbf{II}_B, \mathbf{III}_B$ , of the tensor  $\mathbf{B}$  and are given by

$$(3.4) \quad \mathbf{I}_B = \operatorname{tr} \mathbf{B}, \quad \mathbf{II}_B = \frac{1}{2}[(\operatorname{tr} \mathbf{B})^2 - \operatorname{tr} \mathbf{B}^2], \quad \mathbf{III}_B = \det \mathbf{B}.$$

When  $s_1$  and  $s_2$  are flowing as a mixture we have to consider interaction terms occurring in the expressions for the partial stresses. Within the framework of a simplified theory we assume that the solid  $s_2$  will retain essentially the same character as defined by the constitutive Eq. (3.1)<sub>1</sub> with the modification that a dependence on the density of the fluid  $s_2$  is now allowable. The fluid  $s_2$  is assumed to retain its fundamental character of "not supporting shearing stresses" as in the constitutive Eq. (3.2)<sub>2</sub>; however, a dependence of the scalar-valued function  $p$  on the density of the solid and the elasticity of the solid through the left Cauchy-Green deformation tensor  $\mathbf{B}$  does result. Thus the constitutive equations for the partial stresses become

$$(3.5) \quad \mathbf{S} = \mathbf{S}(\mathbf{B}, \varrho_2), \quad \mathbf{T} = -p(\mathbf{B}, \varrho_2)\mathbf{1}.$$

Application of the principle of frame indifference and subsequent use of representation theorems for isotropic functions [16, 17], reduce Eqs. (3.5) to

$$(3.6) \quad \mathbf{S} = -\beta_0\mathbf{1} - \beta_1\mathbf{B} - \beta_2\mathbf{B}^2, \quad \mathbf{T} = -p\mathbf{1},$$

where  $\beta_0, \beta_1, \beta_2, p$  are scalar-valued functions of  $\varrho_1, \varrho_2, I_B$  and  $II_B$ , i.e. the densities and the first two principal invariants of  $\mathbf{B}$ .<sup>(2)</sup>

The diffusive force  $\psi$  may be regarded as a retarding effect exerted upon the motion of the fluid  $s_2$  due to the presence of the elastic solid  $s_1$ . It is natural to assume that it depends upon the elasticity of the solid through the deformation gradient  $\mathbf{F}$ , the densities and the density gradients, and the velocities of the constituents. Thus the constitutive equation for the diffusing force takes the form<sup>(3)</sup>

$$(3.7) \quad \psi = \psi(\mathbf{F}, \varrho_1 \mathbf{u}, \varrho_2 \mathbf{v}, \text{grad } \varrho_1, \text{grad } \varrho_2, \varrho_2).$$

The occurrence of  $\varrho_1 \mathbf{u}$  and  $\varrho_2 \mathbf{v}$  instead of  $\mathbf{u}$  and  $\mathbf{v}$  is more natural since on intuitive grounds, one could argue that "force depends on moments rather than velocities" or that interaction forces arise from momentum exchanges.

Invariant considerations of isotropy and frame indifference allow one to assume the following special form for Eq. (3.7):

$$(3.8) \quad \psi = (\varphi_1\mathbf{1} + \varphi_2\mathbf{B} + \varphi_3\mathbf{B}^2)(\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) + (\varphi'_1\mathbf{1} + \varphi'_2\mathbf{B} + \varphi'_3\mathbf{B}^2)\text{grad } \varrho_1 + (\varphi''_1\mathbf{1} + \varphi''_2\mathbf{B} + \varphi''_3\mathbf{B}^2)\text{grad } \varrho_2,$$

where  $\varphi_\Gamma, \varphi'_\Gamma$  and  $\varphi''_\Gamma$ , ( $\Gamma = 1, 2, 3$ ), are scalar functions of the two principal invariants  $I_B, II_B$  and also depend on  $\varrho_1$  and  $\varrho_2$ . The representation (3.8) is appropriate for both isotropic (full isotropy under all orthogonal second order tensors, i.e. holohedral isotropy) and hemitropic (isotropy only under the proper orthogonal tensors, i.e. hemihedral isotropy) materials. Notice that the constitutive Eqs. (3.6) are also valid for isotropic and hemitropic materials. Thus, in the framework of the assumed constitutive equations, where the motions are also slow, the present theory is valid for both isotropic and hemitropic materials.

<sup>(2)</sup> For convenience in the analysis, in Sect. 3 and 4, the dependence of the various functions which occur in the theory on  $III_B$  is expressed as a dependence on  $\varrho_1$  through the continuity equations of the solid  $\varrho_1 = \varrho_0 \sqrt{III_B}$ .

<sup>(3)</sup> The case of small velocities and small density gradients is the one of interest in the subsequent analysis.

Further, we confine attention to the special case where  $\psi$  depends on the deformation tensor  $\mathbf{B}$  through its three principal invariants only. This is a generalization of the assumption of the classical approach that only normal stresses are important to diffusion. Then, Eq. (3.8) becomes

$$(3.9) \quad -\varrho_2 \psi = I_1(\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) + I_2 \text{grad } \varrho_1 + I_3 \text{grad } \varrho_2,$$

where  $I_1$ ,  $I_2$  and  $I_3$  are functions of  $I_B$ ,  $\Pi_B$ ,  $\varrho_1$  and  $\varrho_2$ .

#### 4. Diffusion equations — Non-linear theory

With the constitutive equations for the partial stresses and the diffusive force (3.6) and (3.10), we shall derive diffusion equations for the binary fluid-solid mixture using only the mechanical principles (2.6) and (2.7). We assume that the solid and the fluid are initially at rest (of course the solid could be under static deformation) with an equilibrium density  $\varrho_1$  for the solid independent of time and an equilibrium constant density  $\varrho_2$  for the fluid. During diffusion we assume that the densities become  $\varrho_1 + \sigma_1$ ,  $\varrho_2 + \sigma_2$  and that  $\sigma_1$ ,  $\sigma_2$  and the velocities  $\mathbf{u}$ ,  $\mathbf{v}$  of each component of the mixture and all their time and space derivatives are small quantities of the same order. Under these assumptions the field Eqs. (2.6) and (2.7) take the form

$$(4.1) \quad \frac{\partial \sigma_1}{\partial t} + \text{div}(\varrho_1 \mathbf{u}) = 0, \quad \frac{\partial \sigma_2}{\partial t} + \text{div}(\varrho_2 \mathbf{v}) = 0,$$

$$(4.2) \quad \text{div} \mathbf{S} + \varrho_2 \psi = \varrho_1 \frac{\partial \mathbf{u}}{\partial t}, \quad \text{div} \mathbf{T} - \varrho_2 \psi = \varrho_2 \frac{\partial \mathbf{v}}{\partial t}.$$

In the constitutive eqs. (3.6) and (3.9) we make a Taylor's expansion around the equilibrium point  $(\varrho_1, \varrho_2)$  and we neglect terms of order higher than the first. Then the expressions for the partial stresses and the diffusive force take the form

$$(4.3) \quad \begin{aligned} \mathbf{S} &= -[(\beta_0 + c_1 \sigma_1 + c_{12} \sigma_2) \mathbf{l} + (\beta_1 + c_1^* \sigma_1 + c_{12}^* \sigma_2) \mathbf{B} + (\beta_2 + c_1^{**} \sigma_1 + c_{12}^{**} \sigma_2) \mathbf{B}^2], \\ \mathbf{T} &= -[p + c_{21} \sigma_1 + c_2 \sigma_2] \mathbf{l}, \end{aligned}$$

$$-\varrho_2 \psi = I_1(\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) + I_2 \text{grad } \varrho_1 + (\bar{c}_1 \sigma_1 + \bar{c}_2 \sigma_2) \text{grad } \varrho_1 + I_2 \text{grad } \sigma_1 + I_3 \text{grad } \sigma_2,$$

where  $\beta_0$ ,  $\beta_1$ ,  $\beta_2$ ,  $c_1$ ,  $c_{12}$ ,  $c_1^*$ ,  $c_{12}^*$ ,  $c_1^{**}$ ,  $c_{12}^{**}$ ,  $p$ ,  $c_{21}$ ,  $c_2$ ,  $I_1$ ,  $I_2$ ,  $I_3$ ,  $\bar{c}_1$ , and  $\bar{c}_2$  are functions of the invariants  $I_B$ ,  $\Pi_B$  and also depend on the equilibrium densities  $\varrho_1$  and  $\varrho_2$ . Combining Eqs. (4.1), (4.2) and (4.3), we obtain

$$(4.4) \quad \begin{aligned} &\nabla^2(c_1 \sigma_1 + c_{12} \sigma_2) + \text{div} \{ \text{div} [(c_1^* \sigma_1 + c_{12}^* \sigma_2) \mathbf{B}] \} + \text{div} \{ \text{div} [(c_1^{**} \sigma_1 + c_{12}^{**} \sigma_2) \mathbf{B}^2] \} \\ &- I_1 \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) + I_2 \nabla^2 \sigma_1 + I_3 \nabla^2 \sigma_2 + \text{div} [(\bar{c}_1 \sigma_1 + \bar{c}_2 \sigma_2) \nabla \varrho_1] + \text{grad } I_1 \cdot (\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) \\ &\quad + \text{grad } I_2 \cdot \text{grad } \sigma_1 + \text{grad } I_3 \cdot \text{grad } \sigma_2 = \frac{\partial^2 \sigma_1}{\partial t^2}, \end{aligned}$$

$$\begin{aligned} &\nabla^2(c_{21} \sigma_1 + c_2 \sigma_2) + I_1 \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) - I_2 \nabla^2 \sigma_1 - I_3 \nabla^2 \sigma_2 - \text{div} [(\bar{c}_1 \sigma_1 + \bar{c}_2 \sigma_2) \nabla \varrho_1] \\ &\quad - \text{grad } I_1 \cdot (\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) - \text{grad } I_2 \cdot \text{grad } \sigma_1 - \text{grad } I_3 \cdot \text{grad } \sigma_2 = \frac{\partial^2 \sigma_2}{\partial t^2}. \end{aligned}$$

The coupled Eqs. (4.4) describe the diffusion process of an elastic fluid through the most general non-linear elastic isotropic or hemitropic solid, the mixture undergoing uniformly slow motions. If we further adopt a Helmholtz representation for the vector  $\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}$ , then  $\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}$  is eliminated from Eqs. (4.4) and we obtain

$$\begin{aligned}
 & \nabla^2(c_1 \sigma_1 + c_{12} \sigma_2) + \operatorname{div} \{ \operatorname{div} [(c_1^* \sigma_1 + c_{12}^* \sigma_2) \mathbf{B}] \} + \operatorname{div} \{ \operatorname{div} [(c_1^{**} \sigma_1 + c_{12}^{**} \sigma_2) \mathbf{B}^2] \} \\
 & - \mathbf{I}_1 \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) + \mathbf{I}_2 \nabla^2 \sigma_1 + \mathbf{I}_3 \nabla^2 \sigma_2 + \operatorname{div} [(\tilde{c}_1 \sigma_1 + \tilde{c}_2 \sigma_2) \nabla \varrho_1] + \operatorname{grad} \mathbf{I}_2 \cdot \operatorname{grad} \sigma_1 \\
 (4.5)_1 \quad & + \operatorname{grad} \mathbf{I}_3 \cdot \operatorname{grad} \sigma_2 + \frac{1}{4\pi} \operatorname{grad} \left\{ \int \int \int_{\Omega} \frac{1}{r} \frac{\partial}{\partial t} [\sigma_1(\xi, \eta, \zeta) - \sigma_2(\xi, \eta, \zeta)] d\xi d\eta d\zeta \right\} \\
 & \operatorname{grad} \mathbf{I}_1 + \operatorname{curl} \mathbf{a} \cdot \operatorname{grad} \mathbf{I}_1 = \frac{\partial^2 \sigma_1}{\partial t^2},
 \end{aligned}$$

$$\begin{aligned}
 & \nabla^2(c_{21} \sigma_1 + c_2 \sigma_2) + \mathbf{I}_1 \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) - \mathbf{I}_2 \nabla^2 \sigma_1 - \mathbf{I}_3 \nabla^2 \sigma_2 - \operatorname{div} [(\tilde{c}_1 \sigma_1 + \tilde{c}_2 \sigma_2) \nabla \varrho_1] \\
 (4.5)_2 \quad & - \operatorname{grad} \mathbf{I}_2 \cdot \operatorname{grad} \sigma_1 - \operatorname{grad} \mathbf{I}_3 \cdot \operatorname{grad} \sigma_2 - \frac{1}{4\pi} \left\{ \int \int \int_{\Omega} \frac{1}{r} \frac{\partial}{\partial t} [\sigma_1(\xi, \eta, \zeta) \right. \\
 & \left. - \sigma_2(\xi, \eta, \zeta)] d\xi d\eta d\zeta \right\} \cdot \operatorname{grad} \mathbf{I}_1 - \operatorname{curl} \mathbf{a} \cdot \operatorname{grad} \mathbf{I}_1 = \frac{\partial^2 \sigma_2}{\partial t^2},
 \end{aligned}$$

where  $r^2 = (x - \xi)^2 + (y - \eta)^2 + (z - \zeta)^2$ ,  $\mathbf{a}$  is an arbitrary vector and  $\Omega$  denotes the part of the space occupied by the mixture.

Performing some of the differential operations in Eqs. (4.5) and rearranging terms, we deduce the final form of the coupled diffusion equations for a binary system of a non-linear elastic solid and an elastic fluid which reads

$$\begin{aligned}
 & Y_1 \nabla^2 \sigma_1 + Y_2 \nabla^2 \sigma_2 + Y_3 \sigma_1 + Y_4 \sigma_2 + \boldsymbol{\omega}_1 \cdot \operatorname{grad} \sigma_1 + \boldsymbol{\omega}_2 \cdot \operatorname{grad} \sigma_2 + \mathbf{I}_1 \left( \frac{\partial \sigma_2}{\partial t} - \frac{\partial \sigma_1}{\partial t} \right) \\
 & + \operatorname{div} \{ \operatorname{div} [(c_1^* \sigma_1 + c_{12}^* \sigma_2) \mathbf{B}] \} + \operatorname{div} \{ \operatorname{div} [(c_1^{**} \sigma_1 + c_{12}^{**} \sigma_2) \mathbf{B}^2] \} + \frac{1}{4\pi} \operatorname{grad} \left\{ \int \int \int_{\Omega} \frac{1}{r} \frac{\partial}{\partial t} \right. \\
 & \left. \times [\sigma_1(\xi, \eta, \zeta) - \sigma_2(\xi, \eta, \zeta)] d\xi d\eta d\zeta \right\} \cdot \operatorname{grad} \mathbf{I}_1 + \operatorname{curl} \mathbf{a} \cdot \operatorname{grad} \mathbf{I}_1 = \frac{\partial^2 \sigma_1}{\partial t^2}, \\
 (4.6) \quad & Y_1 \nabla^2 \sigma_1 + Y_2 \nabla^2 \sigma_2 + Y_3 \sigma_1 + Y_4 \sigma_2 + \boldsymbol{\omega}_1 \cdot \operatorname{grad} \sigma_1 + \boldsymbol{\omega}_2 \cdot \operatorname{grad} \sigma_2 + \mathbf{I}_1 \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) \\
 & - \frac{1}{4\pi} \operatorname{grad} \left\{ \int \int \int_{\Omega} \frac{1}{r} \frac{\partial}{\partial t} [\sigma_1(\xi, \eta, \zeta) - \sigma_2(\xi, \eta, \zeta)] d\xi d\eta d\zeta \right\} \cdot \operatorname{grad} \mathbf{I}_1 \\
 & - \operatorname{curl} \mathbf{a} \cdot \operatorname{grad} \mathbf{I}_1 = \frac{\partial^2 \sigma_2}{\partial t^2},
 \end{aligned}$$

where  $Y_{\Gamma, \Gamma'}$ ;  $\{\Gamma, \Gamma'\} = 1, 2, 3, 4$  and  $\boldsymbol{\omega}_{\Gamma, \Gamma'}$ ;  $\{\Gamma, \Gamma'\} = 1, 2$  are correspondingly scalar and vector functions of  $\mathbf{I}_B, \mathbf{II}_B, \varrho_1$  and  $\varrho_2$ , and they are given by the relations  $Y_{1,1'} = c_{1,21} \pm \mathbf{I}_2$ ;  $Y_{2,2'} = c_{12,2} \pm \mathbf{I}_3$ ;  $Y_{3,3'} = \nabla^2 c_{1,21} \pm (\tilde{c}_1 / \mathbf{I}_2) \nabla^2 p \pm \operatorname{grad} p \cdot \operatorname{grad} (\tilde{c}_1 / \mathbf{I}_2)$ ;  $Y_{4,4'} = \nabla^2 c_{12,2} \pm (\tilde{c}_2 / \mathbf{I}_2) \nabla^2 p \pm \operatorname{grad} p \cdot \operatorname{grad} (\tilde{c}_2 / \mathbf{I}_2)$ ;  $\boldsymbol{\omega}_{1,1'} = \operatorname{grad} (2c_{1,21} \pm \mathbf{I}_2) \pm (\tilde{c}_1 / \mathbf{I}_2) \operatorname{grad} p$ ;  $\boldsymbol{\omega}_{2,2'} = \operatorname{grad} (2c_{12,2} \pm \mathbf{I}_3) \pm c_2 / \mathbf{I}_2$ .

To simplify further the theory, we omit the last two terms of the left hand side of both Eqs. (4.6)<sub>1,2</sub> by arguing either that we adopt very slow motions with velocities that may differ considerably from point to point in the space, or that we assume special cases where the function  $I_1$  is constant.

#### Example

To illustrate the theory we study in detail the steady-state absorption of liquids in solids. This kind of problem arises, for example, in the swelling of rubber and plastics by solvents. We assume that the solid is a Mooney-material (for example natural rubber) for which the constitutive equation is given by [16]

$$(4.7) \quad \mathbf{S} = -\tilde{p}\mathbf{1} + \mu \left( \frac{1}{2} + \gamma \right) \mathbf{B} - \mu \left( \frac{1}{2} - \gamma \right) \mathbf{B}^{-1},$$

where the scalar  $\tilde{p}$  is an indeterminate pressure function of the spatial coordinates, and  $\mu$  and  $\gamma$ , which satisfy the inequalities  $\mu > 0$  and  $-\frac{1}{2} \leq \gamma \leq \frac{1}{2}$ , depend on the density  $\varrho_2$ . Because such a type of material is incompressible ( $\det \mathbf{B} = 1$ ), the density of the solid remains constant during any process of deformation or diffusion. In this example we confine attention to the case where only small quantities of fluid are absorbed by the solid, in which case the coefficients  $\mu$  and  $\gamma$  are constants and do not depend on the density of the fluid.

For simplicity we consider a homogeneous deformation field, namely a pure extension, with principal directions parallel to the coordinates  $\{X_i\}$ . Thus, the deformation is described by

$$(4.8) \quad x_1 = \lambda_1 X_1, \quad x_2 = \lambda_2 X_2, \quad x_3 = \lambda_3 X_3,$$

where  $\lambda_1, \lambda_2, \lambda_3$  are constants satisfying the incompressibility condition

$$(4.9) \quad \lambda_1 \lambda_2 \lambda_3 = 1.$$

The tensors  $\mathbf{B}$  and  $\mathbf{B}^{-1}$  are found as

$$(4.10) \quad \mathbf{B} = \begin{bmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{bmatrix}, \quad \mathbf{B}^{-1} = \begin{bmatrix} 1/\lambda_1^2 & 0 & 0 \\ 0 & 1/\lambda_2^2 & 0 \\ 0 & 0 & 1/\lambda_3^2 \end{bmatrix},$$

and the principal invariants of  $\mathbf{B}$  are constants given by

$$(4.11) \quad I_B = \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \quad II_B = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_1^2 \lambda_3^2, \quad III_B = \lambda_1^2 \lambda_2^2 \lambda_3^2 = 1.$$

Thus, under the above assumptions the coefficients  $c_1, c_{12}, c_1^*, c_{12}^*, c_{12}^{**}, c_{12}^{***}, c_{21}, I_2$  and  $\tilde{c}_1$  become zero and  $c_2, I_1$  and  $I_3$  become constants dependent on the numbers  $\varrho_1$  and  $\varrho_2$ . The equilibrium equations indicate that the pressures  $\tilde{p}$  and  $p$  are also constants. It then follows that Eq. (4.6)<sub>1</sub> is trivial in an assumed steady-state situation, while Eq. (4.6)<sub>2</sub> takes the form

$$(4.12) \quad \nabla^2 \sigma_2 = 0,$$

which is recognized as the steady-state diffusion equation of Fick.



In the previous example, if the solid is a general compressible non-linear elastic material, its constitutive equation is given by Eq. (3.3)<sub>1</sub> with the coefficients  $\beta_r$ ;  $r = 0, 1, -1$  dependent on  $\varrho_1, \varrho_2, \mathbf{I}_B$  and  $\Pi_B$ . In this case  $\lambda_1, \lambda_2$  and  $\lambda_3$  in Eqs. (4.8) depend on the motion which is not easily specified. The deformation tensor  $\mathbf{B}$  is therefore difficult to determine. However, in cases of engineering interest Eqs. (4.10) may be used in Eqs. (4.6) as a first approximation. Then the coefficients in Eqs. (4.3) and the equilibrium densities become constants and the diffusion Eqs. (4.6) for a steady state become

$$\begin{aligned}
 (4.13) \quad & Y_1 \nabla^2 \sigma_1 + Y_2 \nabla^2 \sigma_2 + c_{11}^* \left( \lambda_1^2 \frac{\partial^2 \sigma_1}{\partial x^2} + \lambda_2^2 \frac{\partial^2 \sigma_1}{\partial y^2} + \lambda_3^2 \frac{\partial^2 \sigma_1}{\partial z^2} \right) + c_{12}^* \left( \lambda_1^2 \frac{\partial^2 \sigma_2}{\partial x^2} \right. \\
 & \left. + \lambda_2^2 \frac{\partial^2 \sigma_2}{\partial y^2} + \lambda_3^2 \frac{\partial^2 \sigma_2}{\partial z^2} \right) + c_{11}^{**} \left( \frac{1}{\lambda_1^2} \frac{\partial^2 \sigma_1}{\partial x^2} + \frac{1}{\lambda_2^2} \frac{\partial^2 \sigma_1}{\partial y^2} + \frac{1}{\lambda_3^2} \frac{\partial^2 \sigma_1}{\partial z^2} \right) \\
 & \left. + c_{12}^{**} \left( \frac{1}{\lambda_1^2} \frac{\partial^2 \sigma_2}{\partial x^2} + \frac{1}{\lambda_2^2} \frac{\partial^2 \sigma_2}{\partial y^2} + \frac{1}{\lambda_3^2} \frac{\partial^2 \sigma_2}{\partial z^2} \right) = 0, \right. \\
 & Y_1 \cdot \nabla^2 \sigma_1 + Y_2 \cdot \nabla^2 \sigma_2 = 0,
 \end{aligned}$$

where  $Y_1, Y_2, c_{11}^*, c_{12}^*$  and  $c_{11}^{**}, c_{12}^{**}$  are constants dependent on  $\varrho_2$  and  $\lambda_1, \lambda_2, \lambda_3$ . The system (4.13) is not difficult to solve. In the special case in which  $\lambda_1 = \lambda_2 = \lambda_3$ , Eqs. (4.13) yield

$$(4.14) \quad \nabla^2 \sigma]_2 = 0,$$

which is the classical result of Fick's law for a steady-state situation. The same relation for the same problem was derived by a different approach by ADKINS [14].

**5. Diffusion equations — Linear theory**

In the present section we derive a simplified diffusion law by linearizing the constitutive equations for the partial stresses and the diffusive force. The theory concerns the flow of a fluid through a solid which, when separated, follow an elastic and a linear elastic isotropic behavior, correspondingly.

Within the framework of a linear theory, the constitutive equations (3.6) and (3.10) for the partial stresses and the diffusive force take the form

$$\begin{aligned}
 (5.1) \quad & \mathbf{S} = -\alpha(\varrho_2)\mathbf{I} - \lambda(\varrho_2)\text{tr}\mathbf{e}\mathbf{l} - \mu(\varrho_2)\mathbf{e}, \\
 & \mathbf{T} = -\beta(\varrho_2)\mathbf{I} - p(\varrho_2)\text{tr}\mathbf{e}\mathbf{l}, \\
 & -\varrho_2 \boldsymbol{\Psi} = \mathbf{I}_1(\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) + \mathbf{I}_2 \nabla \varrho_r + \mathbf{I}_3 \nabla \varrho_2,
 \end{aligned}$$

where  $\mathbf{I}_r = \gamma_r(\varrho_2) + \delta_r(\varrho_2)\text{tr}\mathbf{e}$ ,  $r = 1, 2, 3$  and  $\mathbf{e}$  is the small deformation tensor.

We again assume that the solid and the fluid are initially at rest with equilibrium densities  $\varrho_1$  and  $\varrho_2$ . During diffusion the densities become  $\varrho_1 + \sigma_1$  and  $\varrho_2 + \sigma_2$ . We further assume that  $\sigma_1, \sigma_2$ , the velocities  $\mathbf{u}, \mathbf{v}$  and all their time and space derivatives, are small quantities of the same order and that in the fundamental equations terms of order higher than the first are negligible. Thus the field equations are given again by Eqs. (4.1) and (4.2).

We want to expand the constitutive Eqs. (5.1) around the equilibrium point. The method followed here is based on physical grounds, but results in identical forms for the diffusion equations as the perturbation technique which is discussed elsewhere [19]. Thus, in the

constitutive Eqs. (5.1), we allow an arbitrary dependence of the response coefficients on  $\sigma_1$ , i.e. the deviation from the equilibrium density of the solid, and we subject them to a Taylor's expansion around the equilibrium point  $(\varrho_1, \varrho_2)$ , keeping the infinitesimal strain tensor  $\mathbf{e}$  fixed at its equilibrium value. The arbitrary dependence of the response coefficients on  $\sigma_1$  takes also care of the changes of  $\text{tr} \mathbf{e}$ , through the continuity equation of the solid. This is sufficient for a diffusion theory in consistency with previous assumptions that only normal stresses are significant in a diffusion process. Thus we obtain

(5.2)

$$\begin{aligned} \mathbf{S} &= -[\alpha(\varrho_2) + c_1 \sigma_1 + c_{12} \sigma_2] \mathbf{l} - [\lambda(\varrho_2) + c_1^* \sigma_1 + c_{12}^* \sigma_2] \text{tr} \mathbf{e} \mathbf{l} - [\mu(\varrho_2) + c_{11}^{**} \sigma_1 + c_{12}^{**} \sigma_2] \mathbf{e}, \\ \mathbf{T} &= -[\beta(\varrho_2) + c_{21} \sigma_1 + c_2 \sigma_2] \mathbf{l} - [p(\varrho_2) + c_{21}^* \sigma_1 + c_2^* \sigma_2] \text{tr} \mathbf{e} \mathbf{l}, \\ -\varrho_2 \psi &= \mathbf{I}_1(\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) + (\mathbf{I}_2 + c_3 \sigma_1 + c_4 \sigma_2) \nabla \varrho_1 + \mathbf{I}_2 \nabla \sigma_1 + \mathbf{I}_3 \nabla \sigma_2, \end{aligned}$$

where  $\alpha, \lambda, \mu, \beta, p, \mathbf{I}_1, \mathbf{I}_2, \mathbf{I}_3$  and  $c_1, c_{12}, c_1^*, c_{12}^*, c_{11}^{**}, c_{12}^{**}, c_{21}, c_2, c_{21}^*, c_2^*, c_3, c_4$  are constants dependent on the number  $\varrho_2$ .

We next insert Eqs. (5.2) into Eqs. (4.2). To the resultant equations we apply the div operator and we also use the mass balance (4.1) and the well-known relation of linear elasticity

$$(5.3) \quad \nabla^2 \text{tr} \mathbf{e} = 0,$$

which it can be easily shown to hold here. Thus we obtain

$$\begin{aligned} &c_1 \nabla^2 \sigma_1 + c_{12} \nabla^2 \sigma_2 + 2c_{11}^* \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_1 + c_{11}^* \text{tr} \mathbf{e} \nabla^2 \sigma_1 + 2c_{12}^* \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_2 + c_{12}^* \text{tr} \mathbf{e} \nabla^2 \sigma_2 \\ &+ \nabla \cdot \{ \nabla \cdot [(c_{11}^{**} \sigma_1 + c_{12}^{**} \sigma_2) \mathbf{e}] \} - (\gamma_1 + \delta_1 \text{tr} \mathbf{e}) \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) + \delta_1 \nabla \text{tr} \mathbf{e} \cdot (\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) \\ &\quad - c_3 \varrho_0 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_1 - c_4 \varrho_0 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_2 + \delta_2 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_1 + (\gamma_2 + \delta_2 \text{tr} \mathbf{e}) \nabla^2 \sigma_1 \\ &\quad + \delta_3 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_2 + (\gamma_3 + \delta_3 \text{tr} \mathbf{e}) \nabla^2 \sigma_2 = \frac{\partial^2 \sigma_1}{\partial t^2}, \end{aligned} \quad (5.4)$$

$$\begin{aligned} &c_{21} \nabla^2 \sigma_1 + c_2 \nabla^2 \sigma_2 + 2c_{21}^* \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_1 + c_{21}^* \text{tr} \mathbf{e} \nabla^2 \sigma_1 + 2c_2^* \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_2 + c_2^* \text{tr} \mathbf{e} \nabla^2 \sigma_2 \\ &+ (\gamma_1 + \delta_1 \text{tr} \mathbf{e}) \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) - \delta_1 \nabla \text{tr} \mathbf{e} \cdot (\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v}) + c_3 \varrho_0 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_1 \\ &\quad + c_4 \varrho_0 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_2 - \delta_2 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_1 - (\gamma_2 + \delta_2 \text{tr} \mathbf{e}) \nabla^2 \sigma_1 - \delta_3 \nabla \text{tr} \mathbf{e} \cdot \nabla \sigma_2 \\ &\quad - (\gamma_3 + \delta_3 \text{tr} \mathbf{e}) \nabla^2 \sigma_2 = \frac{\partial^2 \sigma_2}{\partial t^2}. \end{aligned}$$

If we consider only the cases where either the gradients of the velocities are large in comparison with the velocities or the coefficient  $\delta_1(\varrho_2)$  is zero, then we can omit the term  $\delta_1 \nabla \text{tr} \mathbf{e} \cdot (\varrho_1 \mathbf{u} - \varrho_2 \mathbf{v})$ . Then by collecting terms appropriately in Eqs. (5.4) we have

$$\begin{aligned} &\nabla^2 (\bar{c}_{11} \sigma_1 + \bar{c}_{12} \sigma_2) + \nabla \text{tr} \mathbf{e} \cdot \nabla (\bar{c}_{11}^* \sigma_1 + \bar{c}_{12}^* \sigma_2) + \text{tr} \mathbf{e} \nabla^2 (\bar{c}_{11}^{**} \sigma_1 + \bar{c}_{12}^{**} \sigma_2) \\ &+ \nabla \cdot \{ \nabla \cdot [(c_{11}^{**} \sigma_1 + c_{12}^{**} \sigma_2) \mathbf{e}] \} - (\gamma_1 + \delta_1 \text{tr} \mathbf{e}) \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) = \frac{\partial^2 \sigma_1}{\partial t^2}, \\ (5.5) \quad &\nabla^2 (\bar{c}_{21} \sigma_1 + \bar{c}_2 \sigma_2) + \nabla \text{tr} \mathbf{e} \cdot \nabla (\bar{c}_{21}^* \sigma_1 + \bar{c}_2^* \sigma_2) + \text{tr} \mathbf{e} \nabla^2 (\bar{c}_{21}^{**} \sigma_1 + \bar{c}_2^{**} \sigma_2) \\ &+ (\gamma_1 + \delta_1 \text{tr} \mathbf{e}) \left( \frac{\partial \sigma_1}{\partial t} - \frac{\partial \sigma_2}{\partial t} \right) = \frac{\partial^2 \sigma_2}{\partial t^2}, \end{aligned}$$

where

$$\begin{aligned} \bar{c}_{1,21} &= c_{1,21} \pm \gamma_2, & \bar{c}_{12,2} &= c_{12,2} \pm \gamma_3, & \bar{c}_{1,21}^* &= 2c_{1,21}^* \mp \varrho_0 c_3 \pm \delta_2, \\ \bar{c}_{12,2}^* &= 2c_{12,2}^* \mp \varrho_0 c_4 \pm \delta_3, & \bar{c}_{1,21}^{**} &= c_{1,21}^* \pm \delta_2 & \text{and} & \bar{c}_{12,2}^{**} &= c_{12,2}^* \pm \delta_3. \end{aligned}$$

The system of the coupled partial differential Eqs. (5.5) describes, in a general linear theory of very slow motions, the diffusion of a perfect fluid through an elastic solid. It is remarkable that besides the presence of deformation dependent terms, inertia terms appear on the right hand side of Eqs. (5.5). Thus, Eqs. (5.5) have the form of the telegrapher's equations rather than those associated with the classical Fick's law [18].

In an effort to uncouple Eqs. (5.5), in order to give a simple usable diffusion law, we neglect the inertia terms [18]. We confine attention to the special case in which

$$(5.6) \quad \nabla \cdot [(c_1^{**}\sigma_1 + c_{12}^{**}\sigma_2)\mathbf{e}] = \nabla \times \boldsymbol{\omega},$$

where  $\boldsymbol{\omega}$  is an arbitrary vector. The situation where  $c_1^{**} = c_{12}^{**} = 0$  is described in Eq. (5.6) by letting  $\boldsymbol{\omega}$  be a constant. Physically, Eq. (5.6) means that we allow influence of the deformation on the diffusion process only through the principal invariants of the strain tensor. This is also the basic assumption of the classical theories [1-9].

It then follows that for some motions

$$(5.7) \quad (\bar{c}_1 + \bar{c}_{21})\sigma_1 + (\bar{c}_2 + \bar{c}_{12})\sigma_2 = (\bar{c}_1^* + \bar{c}_{21}^*)\sigma_1 + (\bar{c}_2^* + \bar{c}_{12}^*)\sigma_2 \\ = (\bar{c}_1^{**} + \bar{c}_{21}^{**})\sigma_1 + (\bar{c}_2^{**} + \bar{c}_{12}^{**})\sigma_2 = 0.$$

If, in particular,

$$(5.8) \quad \bar{c}_1 = K\bar{c}_1^*, \quad \bar{c}_{12} = K\bar{c}_{12}^*, \quad \bar{c}_2 = K\bar{c}_2^*, \quad \bar{c}_{21} = K\bar{c}_{21}^*, \quad \bar{c}_1^{**} = K^*\bar{c}_1^*, \\ \bar{c}_{12}^{**} = K^*\bar{c}_{12}^*, \quad \bar{c}_2^{**} = K^*\bar{c}_2^*, \quad \bar{c}_{21}^{**} = K^*\bar{c}_{21}^*,$$

where  $K$  and  $K^*$  are constants, then Eqs. (5.5) give

$$(5.9) \quad \left[ K(\bar{c}_1^*\bar{c}_2^* - \bar{c}_{12}^*\bar{c}_{21}^*)\nabla^2 + (\bar{c}_1^*\bar{c}_2^* - \bar{c}_{12}^*\bar{c}_{21}^*)\nabla \text{tr} \mathbf{e} \cdot \nabla + K^*(\bar{c}_1^*\bar{c}_2^* - \bar{c}_{12}^*\bar{c}_{21}^*)\text{tr} \mathbf{e} \nabla^2 \right. \\ \left. - \{(\gamma_1 + \delta_1 \text{tr} \mathbf{e})(\bar{c}_1^* + \bar{c}_2^* + \bar{c}_{12}^* + \bar{c}_{21}^*)\} \frac{\partial}{\partial t} \right]_{\sigma_2}^{\sigma_1} = 0.$$

Introducing a series expansion for  $1/\gamma_1 + \delta_1 \text{tr} \mathbf{e}$  we obtain

$$(5.10) \quad \frac{\partial}{\partial t} - \tilde{K}\nabla^2 - \tilde{L}\nabla \text{tr} \mathbf{e} \cdot \nabla - \tilde{F}\text{tr} \mathbf{e} \nabla^2 \Big|_{\sigma_2}^{\sigma_1} = 0,$$

where  $\tilde{K}$ ,  $\tilde{L}$  and  $\tilde{F}$  are constants dependent on  $\varrho_2$  and related in an obvious way with  $K$ ,  $K^*$ ,  $\gamma_1$ ,  $\delta_1$ ,  $\bar{c}_1^*$ ,  $\bar{c}_2^*$ ,  $\bar{c}_{12}^*$  and  $\bar{c}_{21}^*$ . This is the diffusion law for both constituents under the assumptions of the proposed simplified theory.

Using a relation between the first invariants of the stress and strain tensor deduced from Eq. (5.1)<sub>1</sub>, i.e.

$$(5.11) \quad \text{tr} \mathbf{e} = -3\alpha/3\lambda + \mu - \text{tr} \mathbf{S}/3\lambda + \mu = -3\alpha/3\lambda + \mu - \sigma/3\lambda + \mu,$$

(5.10) yields

$$(5.12) \quad \frac{\partial \varrho}{\partial t} = D\nabla^2 \varrho - M\nabla \sigma \cdot \nabla \varrho + N\sigma \nabla^2 \varrho,$$

where the constants  $D$ ,  $M$ ,  $N$  are given by

$$D = \tilde{K} - 3\alpha\tilde{F}/3\lambda + \mu, \quad M = \tilde{L}/3\lambda + \mu, \quad N = -\tilde{F}/3\lambda + \mu,$$

and  $\sigma$  is the trace of the stress for the solid and  $\rho$  represents the density of either the fluid or the solid. We require the constant  $D$  to be positive and we allow at the present time any sign for the constants  $M$  and  $N$  depending on the deformation state and the relative size of the atomic radius of the constituents.

Formula (5.12) is the most simple expression for a diffusion law within the framework of the proposed theory. A direct comparison with the semi-empirical formula (1.3) indicates the presence of the additional term  $N\sigma\nabla^2\rho$ . Equation (5.12) may be rewritten as

$$(5.13) \quad \frac{\partial \rho}{\partial t} = D^* \nabla^2 \rho - M \nabla \sigma \cdot \nabla \rho, \quad D^* = D + N\sigma.$$

Thus Eq. (5.13) has the form of Eq. (1.3) with the diffusivity coefficient replaced now by an "effective diffusion coefficient" linearly dependent on the trace of the stress tensor.

Here, we should point out that our theory differs from the usual fluid-solid mixture theories (e.g. [20-22]) because of the special constitutive structure we introduced. This simplified structure, with the aid of some approximations and specializations, allows one to obtain practical and easy-to-use results which, in addition, turn out to be generalizations of previous Fick type theories [1-5]. Also, linear mixture theories usually neglect the cross effect of stress-diffusion and thus, terms such as the  $M \nabla \sigma \cdot \nabla \rho$  of Eq. (5.13) do not appear in those theories [20-22].

## 6. Ramifications to classical diffusion interpretations

The normal way to explain stress effects on diffusion is to invoke an additional exponential term or terms associated with vacancies. For self-diffusion or substitutional diffusion,  $D_s$  is normally given as [5]

$$(6.1) \quad D_s = a_0^2 \nu \exp[-(E_{fv} + E_{mv})/RT] \exp(-P\Delta v/RT),$$

where  $a_0$  is the lattice parameter,  $\nu$  is the Debye frequency,  $E_{fv}$ ,  $E_{mv}$  refer to formation and migration energies of vacancies,  $P$  is the hydrostatic pressure and  $\Delta v$  the activation volume. In these vacancy-controlled mechanisms, it is easy to envision  $\Delta v$  as associated with a relaxation of the surrounding atoms into the vacancy. Physically, this would reflect that as the hydrostatic pressure increases, the vacancy concentration decreases to relieve the pressure hence, a decrease in diffusivity results.

For interstitial diffusion, it is much more difficult to rationalize effects of stress (pressure) by such mechanisms since vacancies are not normally thought to be involved. In order to explain such effects as well as other anomalous diffusion data, the concept of migration by interstitial-vacancy pairs has been invoked [23]. It is assumed that the binding energy between an interstitial and a vacancy is sufficient to make interstitial-vacancy pairs contribute to the mechanism of diffusion at high temperature. The interstitial diffusivity,  $D_i$ , is given as

$$(6.2) \quad D_i = D_0 \exp(-E_{mi}/RT) + 6(\nu_1/\nu_2) D_{0p} \exp[(B - E_{fv} - E_{mp})/RT],$$

where  $D_0$ ,  $D_{0p}$  are the pre-exponential terms for the interstitial and the pair;  $\nu_1$  and  $\nu_2$  are the vibrational frequencies of the two configurations;  $E_{mi}$  and  $E_{mp}$  are migration energies of the interstitial and the pair;  $B$  is the binding energy and  $E_{fv}$  is the formation energy of the vacancy.

It is possible to compare the present theory and the above classical interpretations to experimental data by reducing Eq. (5.13). Equation (5.13) gives

$$(6.3) \quad D^*/D - 1 = N\sigma/D.$$

Having in mind the values of  $N$  and  $D$  from Eq. (5.12) and assuming that  $\alpha$ , appropriately normalized, is small compared to the other constants, which is physically well justified, we obtain

$$(6.4) \quad N/D \simeq -F/(3\lambda + \mu)\tilde{K} = -1/(3\lambda + \mu)\tilde{K}^*,$$

where  $\tilde{K}^*$  is a new constant. We further approximate the values of the functions  $\lambda$  and  $\mu$  at equilibrium, with the Lamé constants of the elastic solid ( $-\lambda$  is equal to the first Lamé constant and  $-\mu$  is equal to twice the second Lamé constant). Finally, Lamé constants may be reduced to Young's modulus,  $E$ , and Poisson's ratio,  $\nu$ , so that Eqs. (6.3) and (6.4) may give

$$(6.5) \quad \frac{D^*}{D} - 1 \simeq \frac{\sigma}{\tilde{K}^*} \left( \frac{1-2\nu}{E} \right).$$

This very interesting result implies that stress-affected diffusivity only varies from system to system by a constant,  $\tilde{K}^*$ , except for a small temperature dependency of  $\nu$ ,  $E$ . It is now possible to compare Eq. (6.5) to Eqs. (6.1) and (6.2) with experimental data taken as a function of stress and temperature.

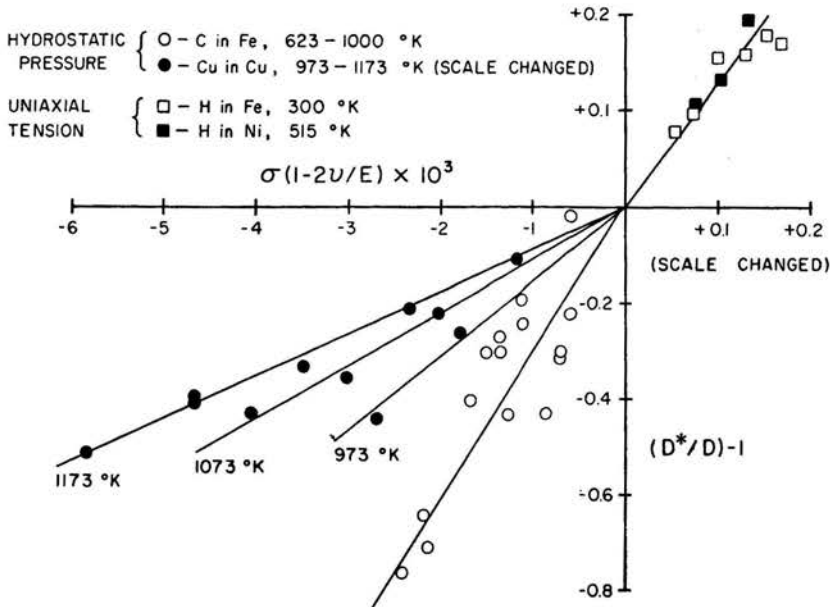


FIG. 1.

A considerable body of diffusion data has been reduced in Fig. 1 for both interstitials in tension and hydrostatic stress fields, as well as the pressure effect on self-diffusion. If one first examines the self-diffusion data of Cu in Cu, one is struck by the remarkable straight lines when  $\sigma(1-2\nu)/E$  is plotted versus  $(D^*/D) - 1$ . Of course, Eq. (6.5) is lacking

in that the constant  $\tilde{K}^*$  must be a function of temperature. This simply reflects that the effect of pressure on the vacancy concentration, as indicated in Eq. (6.1), undoubtedly is involved and exhibits the well-known temperature dependency. In this respect, the present theory would not make interpretation of substitutional or self-diffusion any simpler but would add an additional dimension.

On the other hand, if one examines the interstitial diffusion data of H and C in Fe and Ni, one sees little temperature dependence in Fig. 1. It should be pointed out that the scatter was inherent at any particular temperature. Thus, over an even larger temperature range than the self-diffusion case, the data for both interstitials indicate a temperature-independent constant,  $\tilde{K}^*$ , in Eq. (6.5). This would imply that the arguments leading to Eq. (6.2) are either invalid or of secondary importance. It further suggests a much simpler interpretation of stress effects on interstitial diffusion via Eq. (6.5).

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### References

1. J. C. M. LI, R. A. ORIANI and L. D. DARKEN, *The thermodynamics of stressed solids*, Z. Phys. Chem., **49**, 271–290, 1966.
2. R. A. ORIANI, *Hydrogen in metals*, In *fundamental aspects of stress corrosion cracking*, Nat. Assoc. Corros. Engineers, Houston, Texas, 32–50, 1969.
3. H. W. LIU, *Stress-corrosion cracking and the interaction between crack-tip stress field and solute atoms*, ASME, H. Basic Engr., 633–630, 1970.
4. H. P. VAN LEEUWEN, *A quantitative model of hydrogen induced grain boundary cracking*, J. of Corrosion., NACA, **29**, 197–204, 1973.
5. P. G. SHEWMON, *Diffusion in solids*, McGraw-Hill, New York, 23, 1963.
6. A. COCHARDT, G. SCHOEK and H. WIEDERSICH, *Interaction between dislocations and interstitial atoms in body-centered cubic metals*, Acta Met., **3**, 533–537, 1955.
7. R. BULLOUGH and R. C. NEWMAN, *The interaction of vacancies with dislocations*, Phil. Mag., **7**, 529–531, 1962.
8. H. STEHLE and A. SEEGER, Z. Phys., *Electronentheoretische Untersuchungen über Fehlstellen in Metallen*, III., **146**, 217–241, 1956.
9. A. G. McLELLAN, *The chemical potential in thermodynamic systems under non-hydrostatic stresses*, Proc. Roy. Soc., A307, 1–13, 1968.
10. C. TRUESDELL and R. TOUPIN, *The classical fields theories*, In: Flugge's Handbuch der Physik, Band I/1, Springer-Verlag, Berlin-Göttingen-Heidelberg 1960.
11. C. TRUESDELL, *Celebrazioni Archimede del secolo XX*, Siracusa, III simposio di meccanica e Matematica Applicata, 161, 1961.
12. C. TRUESDELL, *Mechanical basis of diffusion*, J. Chem. Phys., **27**, 2336–2344, 1962.
13. J. E. ADKINS, *Non-linear diffusion I*, Phil. Trans. R. Soc. A255, 607–633, 1963.
14. J. E. ADKINS, *Non-linear diffusion III*, Phil. Trans. R. Soc. A258, 301–316, 1964.
15. A. E. GREEN and J. E. ADKINS, *A contribution to the theory of non-linear diffusion*, Arch. Rational Mech. Anal., **15**, 235–246, 1964.

16. C. TRUESDELL and W. NOLL, *The non-linear field theories of mechanics*, In: Flugge's Handbuch der Physik, Band III/3, Springer-Verlag, Berlin-Heidelberg-New York 1965.
17. A. J. M. SPENCER, *Theory of invariants*, In: Continuum Physics I, Edited by A. C. Eringen, Academic Press, 1971.
18. S. SADLER and J. DAHLER, *Non-stationary diffusion*, The Phys. of Fluids, 7, 11, 1743-1746, 1964,
19. E. C. AIFANTIS, *Thermomechanical modeling for gaseous diffusion in thermoelastic stress fields*, Ph. D. Thesis, University of Minnesota, Minneapolis, Minnesota 1975.
20. R. M. BOWEN and J. C. WIESE, *Diffusion in mixtures of elastic materials*, Int. J. Engr. Sci., 7, 689-722, 1969.
21. N. T. DUNWOODY, *A thermomechanical theory of diffusion in solid-fluid mixtures*, Arch. Rat. Mech. Anal., 38, 348-371, 1970.
22. R. M. BOWEN, *Continuum theory of mixtures*, Ballistic Res. Lab. Contract Rep. No. 45, 1971b.
23. C. G. HOMAN, *Diffusion of carbon in alpha iron*, Acta Met., 12, 1071-1079, 1964.

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