

LINEARIZED HYDROGEN ELASTICITY

P. Sofronis

Department of Theoretical and Applied Mechanics
University of Illinois at Urbana-Champaign

July 1993

ABSTRACT

The general principles of the mechanics and thermodynamics of materials are used to describe the effects of interstitial mobile hydrogen on the mechanical behavior of metals and alloys. First the coupled general field equations accounting for hydrogen diffusion and nonlinear deformation are derived and then linearized for the case of small deformation. Linearization reveals that the Laplacian of the hydrostatic stress is related to the Laplacian of the hydrogen concentration in the lattice, and it is not zero, as has often been assumed in calculations involving stress driven diffusion of hydrogen under plane strain conditions. When the hydrogen is in equilibrium with the applied stress, that is, at steady state conditions of hydrogen transport, the linear elastic constitutive response of the solid accounting for the hydrogen effect can be described by the standard Hooke's law of infinitesimal elasticity in which the stiffness moduli are termed moduli at fixed solute chemical potential and are calculated in terms of the moduli at fixed solute composition, the nominal hydrogen concentration, and the material parameters of the system. These moduli at fixed solute chemical potential can be viewed as the corresponding counterparts of those characterizing the drained deformation at constant pressure of fluid-infiltrated porous geomaterials, or the isentropic deformation of thermoelastic materials. Next the linear transient field equations are solved in the case of a dislocation and a line force in an infinite medium under plane strain conditions by using analytic function theory. The range of validity of the solution to the linearized field equations for an isolated edge dislocation is investigated for specific materials. Lastly, the implications of the steady state constitutive behavior of the hydrogen/metal system on the fracture and dislocation behavior are discussed.

1. INTRODUCTION

The interaction of hydrogen with elastic deformation is a result of the lattice dilatation caused by hydrogen in solid solution with a metal or alloy. The study of this interaction recently (SIROIS, SOFRONIS and BIRNBAUM, 1992; SOFRONIS and BIRNBAUM, 1993) has increased significantly the understanding of the macroscopic mechanical behavior of materials in the presence of hydrogen. LARCHE and CAHN (1985) investigated the interaction of solute composition and stress in crystalline solids, but their analysis is not based on a consistent linearization scheme of the field equations. In most work to date, solutions for the hydrogen transport problem in an elastically deforming material were obtained, at least in the more sophisticated treatments, through a nonlinear equation for stress driven diffusion coupled with the linear elastic deformation of the lattice which, though, was treated as unaffected by hydrogen (LIU, 1970; VAN LEEUWEN, 1974; DUTTON et al., 1977). In addition, the study of the transient hydrogen diffusion under plane strain deformation was carried out on the basis that the term involving the Laplacian of the hydrostatic stress can be dropped from the diffusion equation accounting for drift. However, in the presence of hydrogen, total strain compatibility dictates a relationship between the local hydrostatic stress which is associated with the elastic dilatation and the hydrogen concentration which is directly related to the hydrogen induced strain in the lattice.

The purpose of this article is to devise a constitutive model for the linear behavior of the composite system made of a metal and interstitial hydrogen in solid solution. In particular, the aim is to derive a linear equation for the transient stress driven hydrogen diffusion coupled with the linear elastic deformation of the solid accounting for the hydrogen induced strains. The development of the model follows the work of CARLSON (1972) in linear thermoelasticity and that of RICE and CLEARY (1976) for fluid-saturated porous elastic solids. In Section 2, the

foundations of the linear theory are presented. The basic laws of mechanics and thermodynamics of materials are combined in Subsection 2.1 to describe the nonlinear deformation of a solid containing mobile hydrogen in solution and undergoing thermal straining. Constitutive laws for the nonlinear elastic material that satisfy the second law of thermodynamics are proposed in Subsection 2.2, and the resulting field equations are linearized in Subsection 2.3 (*linearized hydrogen elasticity*). In Subsection 2.4, the equations are specialized for the isotropic material case and, as an application, the moduli at fixed solute chemical potential are evaluated for the H/Ta, H/Nb and H/V systems at room temperature as functions of the nominal hydrogen concentration. In Section 3, the linearized hydrogen elasticity theory is used to set up and solve the boundary value problem for an edge dislocation and a line force in an infinite medium under plane strain conditions. The governing equations for general plane strain deformation are derived in Subsection 3.1 and a solution method in terms of complex potentials is presented in Subsection 3.2. In Subsection 3.3, the solution for an edge dislocation and a line force is found and, as an application, the transient hydrogen concentration and stress fields for an isolated edge dislocation are obtained. The implications of the current linearized hydrogen elasticity theory for understanding the hydrogen effect on dislocation plasticity and the hydrogen induced fracture in metals and alloys are discussed in Section 4.

2. FOUNDATIONS OF THE LINEAR THEORY OF THE CONSTITUTIVE BEHAVIOR OF THE HYDROGEN-METAL SYSTEM

2.1 Basic laws of mechanics and thermodynamics

A *body* is considered to be composed of a set of particles which at each instant of time t are assigned to unique points of a closed region \mathcal{G}_t of three-dimensional

Euclidean space. It is assumed that each point of \mathcal{G}_t is occupied by just one particle. The region \mathcal{G}_t is called the *configuration of the body at time t* or the *current configuration*. The configuration \mathcal{G}_0 occupied by the body at time $t=0$ is called the *reference configuration*. A particle of the body in configuration \mathcal{G}_0 is uniquely determined by the set of coordinates (X_1, X_2, X_3) , or the position vector \mathbf{X} , relative to a fixed Cartesian coordinate system. The motion of the body is described by the position vector \mathbf{x} of the particle \mathbf{X} in any subsequent time t in the form of $\mathbf{x} = \mathbf{x}(\mathbf{X}, t)$. Assume that the functions $x_1 = x_1(X_1, X_2, X_3, t)$, $x_2 = x_2(X_1, X_2, X_3, t)$, and $x_3 = x_3(X_1, X_2, X_3, t)$ are differentiable with respect to X_1, X_2, X_3 and t as many times as required. The coordinates X_i and x_i where $i = 1, 2, 3$ are termed *material* and *spatial* coordinates respectively. From now on, Cartesian vectors and tensors are denoted by bold-face roman letters (\mathbf{A} , \mathbf{a}) and their scalar components by the corresponding light-face italic letters (A_{ij} , a_i). When upper- or lower-case letters are used as indices, they are understood generally to range over 1, 2, and 3. Repetition of any subscript implies summation over the range. Mass is measured in units of atoms or moles although the concepts of this paper are continuum in character and treat matter as being indefinitely divisible. Atoms or moles are merely convenient units of mass.

Suppose that ϕ is any quantity which varies throughout the body in space and time. The conventional notation of the material time derivative $d\phi/dt$ or $\dot{\phi}$ is adopted for the rate of change of ϕ following a given particle, so that

$$\dot{\phi} = \frac{d\phi}{dt} = \frac{\partial \phi(\mathbf{X}, t)}{\partial t}, \quad (1)$$

where the differentiation is performed with \mathbf{X} held constant. The displacement vector of a typical particle from its position \mathbf{X} in the reference configuration \mathcal{G}_0 to its position \mathbf{x} at time t is

$$\mathbf{u}(\mathbf{X}, t) = \mathbf{x}(\mathbf{X}, t) - \mathbf{X}. \quad (2)$$

The velocity vector \mathbf{v} of a particle is the rate of change of its displacement and from eqs. (1) and (2)

$$\mathbf{v}(\mathbf{X}, t) = \dot{\mathbf{u}}(\mathbf{X}, t) = \frac{\partial \mathbf{u}(\mathbf{X}, t)}{\partial t} = \frac{\partial^2 \mathbf{x}(\mathbf{X}, t)}{\partial t^2}. \quad (3)$$

During motion the deformation of an infinitesimal element of the body is described by the deformation gradient tensor \mathbf{F} defined as

$$\mathbf{F} = \nabla \mathbf{x} = \mathbf{I} + \nabla \mathbf{u}, \quad (4)$$

where \mathbf{I} is the identity tensor and ∇ denotes the gradient operator. In component form

$$F_{ij} = x_{i,j} = \delta_{ij} + u_{i,j}, \quad (5)$$

where $(\cdot)_{,i} = \partial/\partial X_i$ and δ_{ij} is the Kronecker delta. It is assumed that the Jacobian $J = \det(F_{ij})$ exists at each point of the body during motion and that $J > 0$. The Green strain tensor is defined by

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^T \mathbf{F} - \mathbf{I}), \quad (6)$$

where the superscript T stands for tensor transpose. The rate at which the body shape changes is described by the deformation rate tensor

$$\mathbf{D} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^T), \quad (7)$$

which is the symmetric part of the velocity gradient $\nabla \mathbf{v}$, whose components are $v_{i,j}$ and $(\cdot)_{,i} = \partial(\cdot)/\partial x_i$.

Consider an arbitrary part \mathcal{P} of the body which occupies a region of volume V bounded by a surface S in the current configuration \mathcal{G}_t . The region occupied by \mathcal{P} in the reference configuration has a volume V_0 and is bounded by a surface S_0 . The region the part \mathcal{P} occupies at any instant of time contains the same material particles and is termed a *material region*. The material within \mathcal{P} is acted upon by external tractions \mathbf{T} and body forces \mathbf{b} measured per unit area and unit volume respectively in the current configuration \mathcal{G}_t . Let $\rho(\mathbf{x}, t)$ denote the density of the material

measured in moles per unit volume in \mathcal{G}_t and $\rho_0(\mathbf{X}, t)$ the respective density in \mathcal{G}_0 . Let σ denote the Cauchy stress tensor measured per unit area in \mathcal{G}_t . The balance of forces and moments are written as

$$\sigma_{ji,j} + b_i = \rho \ddot{u}_i, \quad (8)$$

$$\sigma_{ij} = \sigma_{ji} \quad (9)$$

respectively. If \mathbf{n} is the unit outward normal to the surface S , by using eqs. (8) and (9), $T_i = \sigma_{ij}n_j$ along S , and the divergence theorem one finds

$$\int_S T_i v_i dS + \int_{\mathcal{P}} b_i v_i dV = \dot{K} + \int_{\mathcal{P}} \sigma_{ij} D_{ij} dV, \quad (10)$$

where

$$K = \frac{1}{2} \int_{\mathcal{P}} \rho v_i v_i dV \quad (11)$$

is kinetic energy of the part \mathcal{P} and $\sigma_{ij}D_{ij}$ denotes the stress working rate per unit volume in the current configuration.

The presence of hydrogen in the lattice interstitial sites of the body is described by the concentration $N(\mathbf{x}, t)$ measured in hydrogen atoms per mole of the host material lattice in \mathcal{G}_t . Hydrogen is assumed to be mobile so that it can flow into or out of the region \mathcal{P} considered. The *chemical potential* $\mu(\mathbf{x}, t)$ of a hydrogen atom at any position \mathbf{x} within the stressed solid is defined to be the reversible work required to introduce the atom in the position \mathbf{x} under constant temperature T from its "standard state" at the same temperature, while the local strains, \mathbf{E} , are held fixed. Therefore, the rate of working in a hydrogen composition change at a rate \dot{N} under fixed temperature T and local strains \mathbf{E} , is given by

$$\dot{w} = \mu \dot{N}, \quad (12)$$

where w is measured in units of energy per lattice mole in \mathcal{G}_t . Equivalently, as will be seen in Subsection 2.2, the chemical potential is the increase in the Helmholtz free energy accompanying the placing of one hydrogen atom in the lattice. If \mathbf{j}

denotes the hydrogen flux vector, the amount of hydrogen that flows in the sense of the unit vector \mathbf{n} across a surface normal to \mathbf{n} per unit area in the current configuration per unit time is $\mathbf{j} \cdot \mathbf{n}$. Hydrogen mass conservation requires that the rate of change of total hydrogen inside \mathcal{P} be equal to the flux through the surface S :

$$\frac{d}{dt} \int_{\mathcal{P}} \rho N dV + \int_S j_i n_i ds = 0. \quad (13)$$

Application of the divergence theorem in eq. (13) and arbitrariness of the material region yield

$$\rho \dot{N} = -j_{i,i}. \quad (14)$$

If C denotes the hydrogen concentration measured in hydrogen atoms per unit volume in \mathcal{G}_t one can write

$$C = \rho N. \quad (15)$$

When the solution is dilute and the strains infinitesimal eq. (15) yields $\dot{C} = \rho \dot{N}$ thereby allowing eq. (14) to be recast into the standard form of Fick's second law for diffusion.

The heat input rate into the body consists of conduction through the surface S and distributed internal heat sources. If \mathbf{h} denotes the heat flux vector, the amount of energy that flows in the sense of the unit vector \mathbf{n} across a surface normal to \mathbf{n} per unit area in the current configuration per unit time is $\mathbf{h} \cdot \mathbf{n}$. The strength of the heat source is called the *heat supply* r and denotes energy per mole of material lattice in \mathcal{G}_t per unit time.

At any time during the motion of the body the kinetic energy K of the continuum is only part of its energy. The remainder is called total internal energy U and is expressed in terms of the *specific internal energy* u , measured per mole of material lattice in \mathcal{G}_t , by

$$U = \int_{\mathcal{P}} \rho u dV. \quad (16)$$

The first law of thermodynamics requires conservation of energy in the body. That is, the material time derivative of $U+K$ is equal to the sum of the rate at which mechanical work is done by the body and surface forces, the rate at which energy enters into \mathcal{P} in the form of heat due to the internal heat supply r and surface flux \mathbf{h} , and the rate at which work is done on the body in the placing of the hydrogen atoms within \mathcal{P} . The mathematical formulation of the law is stated as

$$\dot{K} + \dot{U} = \int_S T_i v_i dS + \int_{\mathcal{P}} b_i v_i dV + \int_{\mathcal{P}} \rho r dV - \int_S h_i n_i dS + \int_{\mathcal{P}} \rho w dV. \quad (17)$$

Combining eqs. (10), (12) and (16), and using the divergence theorem, one finds

$$\int_{\mathcal{P}} (\rho \dot{u} - \sigma_{ij} D_{ij} - \rho r + h_{i,i} - \rho \mu \dot{N}) dV = 0. \quad (18)$$

Equation (18) is valid for arbitrary choice of the part \mathcal{P} within the continuous medium. Hence, the integrand must vanish at each particle of the solid:

$$\dot{u} = \frac{1}{\rho} \sigma_{ij} D_{ij} + \mu \dot{N} + r - \frac{1}{\rho} h_{i,i}. \quad (19)$$

The stress working rate per unit volume in \mathcal{G}_t can be expressed in terms of the second Piola-Kirchhoff stress \mathbf{S} ,

$$\mathbf{S} = J \mathbf{F}^{-1} \boldsymbol{\sigma} (\mathbf{F}^{-1})^T, \quad (20)$$

where the superscript -1 stands for tensor inverse, and the rate of change of the Green strain through

$$\sigma_{ij} D_{ij} = \frac{\rho}{\rho_0} S_{ij} \dot{E}_{ij}. \quad (21)$$

Substituting eq. (21) into eq. (19), one finds the final form of the energy equation expressing at each particle of the body the conservation of energy implied by the first law of thermodynamics

$$\dot{u} = \frac{1}{\rho_0} S_{ij} \dot{E}_{ij} + \mu \dot{N} + r - \frac{1}{\rho} h_{i,i}. \quad (22)$$

The second law of thermodynamics postulates that the total entropy production rate within \mathcal{P} is greater or equal to the sum of the entropy flux across the surface S and the rate at which entropy is supplied into the body by the internal heat sources. Therefore,

$$\frac{d}{dt} \int_V \rho s dV \geq \int_V \frac{\rho r}{T} dV - \int_S \frac{h_i n_i}{T} dS, \quad (23)$$

where $s(\mathbf{x}, t)$ is the entropy of the body measured in energy per lattice mole in \mathcal{G}_i per degree K. Since the material region \mathcal{P} is chosen arbitrarily, application of the divergence theorem to eq. (23) furnishes the local form of the second law:

$$Ts \geq r - \frac{1}{\rho} h_{i,i} + \frac{1}{\rho T} h_i T_{,i}. \quad (24)$$

On denoting the heat rate conducted in \mathcal{G}_i per lattice mole by

$$\dot{q} = r - \frac{1}{\rho} h_{i,i}, \quad (25)$$

ineq. (24) becomes

$$Ts \geq \dot{q} + \frac{1}{\rho T} h_i T_{,i}. \quad (26)$$

Lastly, introducing the *Helmholtz free energy* f measured per lattice mole in \mathcal{G}_i as

$$f = u - Ts \quad (27)$$

and using eq. (22) and ineq. (24), one arrives at the *local dissipation inequality*

$$\dot{f} - \frac{1}{\rho_0} S_{ij} \dot{E}_{ij} + s \dot{T} - \mu \dot{N} + \frac{1}{\rho T} h_i T_{,i} \leq 0. \quad (28)$$

2.2 Constitutive relations for elastic materials

A convenient starting point for the theory of *elastic materials* is to postulate a set of constitutive equations which provide at every particle X of the body the Helmholtz free energy f , the stress tensor S , the entropy s , the chemical potential μ ,

the hydrogen flux \mathbf{j} , and the heat flux \mathbf{h} as functions of the Green strain \mathbf{E} , the temperature T , the hydrogen concentration N , the gradient ∇T and possibly the gradient ∇N :

$$f = f\left(\frac{1}{\rho_0} \mathbf{E}, T, N\right), \quad (29a)$$

$$S_{ij} = \left. \frac{\partial f}{\partial \left(\frac{1}{\rho_0} E_{ij} \right)} \right|_{T, N}, \quad (29b)$$

$$s = -\left. \frac{\partial f}{\partial T} \right|_{E_{ij}, N}, \quad (29c)$$

$$\mu = \left. \frac{\partial f}{\partial N} \right|_{E_{ij}, N}, \quad (29d)$$

$$\mathbf{j} = -\frac{D\rho N}{kT} \nabla \mu, \quad (29e)$$

$$\mathbf{h} = \mathbf{h}\left(\frac{1}{\rho_0} \mathbf{E}, T, N, \nabla T, \nabla N\right), \quad (29f)$$

where D is the lattice diffusion constant that is assumed to be independent of stress and is measured in area per unit time and k is Boltzmann's constant. The forms of eqs. (29), as are written in terms of the Green strain tensor, obey the principle of material frame indifference (TRUESELL and NOLL, 1965).

The theory of elasticity based on eqs. (29a) and (29b) is usually referred to as *hyperelasticity* and the form of eq. (29b) is such that the second Piola-Kirchhoff stress \mathbf{S} is symmetric (cf. equations (20) and (9)). Equation (29c) agrees with the standard definition of the entropy, s , in terms of the Helmholtz free energy and definition (29d) is compatible with the use of the chemical potential in eq. (12). Equation (29e)

is valid at low hydrogen concentrations, at which there is no interaction between the diffusing hydrogen and the rate of diffusion depends only on hydrogen mobility. In addition, equation (29e) is consistent with the thermodynamics of diffusion, that chemical potential gradients motivate hydrogen diffusive fluxes such that $\mathbf{j} \cdot \nabla \mu < 0$.

It is noted here that the use of \mathbf{E} , T , N , ∇T , and ∇N , as the only independent variables in the constitutive equations (29) means that f , \mathbf{S} , s , μ , \mathbf{j} , and \mathbf{h} are completely determined when configurations \mathcal{G}_0 and \mathcal{G}_t , temperature and hydrogen concentration are specified. The rate at which the deformation is taking place or the rate at which the temperature and hydrogen composition change has no effect on stress, entropy, chemical potential, hydrogen and heat flux. Furthermore, the constitutive assumptions (29) are in accord with the second law of thermodynamics written in the form of the local dissipation ineq. (28). The discussion here concerns the postulate of COLEMAN and NOLL (1963) that any constitutive assumption should be such that the Clausius-Duhem inequality (23) holds for all admissible processes. Thus, at any given time t , a set of functions

$$\{\mathbf{E}, T, N, f, \mathbf{S}, s, \mu, \mathbf{j}, \mathbf{h}\}, \quad (30)$$

where $T > 0$, \mathbf{E} is the Green strain measure of the deformation of the body, and f , \mathbf{S} , s , μ , \mathbf{j} , and \mathbf{h} are defined by eqs. (29), which is compatible with the law of balance of linear momentum, eq. (8), the law of balance of energy, eq. (22), and the law of conservation of hydrogen mass, eq. (14), always satisfies ineq. (28). Indeed, substituting eq. (29a) into the local dissipation inequality (28), one obtains

$$\begin{aligned} & \left(\frac{\partial f}{\partial \left(\frac{1}{\rho_0} E_{ij} \right)} - S_{ij} \right) \frac{1}{\rho_0} \dot{E}_{ij} + \left(\frac{\partial f}{\partial T} + s \right) \dot{T} + \left(\frac{\partial f}{\partial N} - \mu \right) \dot{N} \\ & + \frac{\partial f}{\partial T_{,i}} \frac{dT_{,i}}{dt} + \frac{\partial f}{\partial N_{,i}} \frac{dN_{,i}}{dt} + \frac{1}{\rho T} h_i T_{,i} \leq 0, \end{aligned} \quad (31)$$

which in view of eqs. (29) and $\rho > 0$ reduces to

$$h_i T_{,i} \leq 0 \quad (32)$$

which is expected always to be true on physical grounds. Heat flows from regions of high temperature toward regions of low temperature.

Differentiating equation (29a) and using eqs. (29b, 29c and 29d), one finds

$$\dot{f} = \frac{1}{\rho_0} S_{ij} \dot{E}_{ij} - s \dot{T} + \mu \dot{N}, \quad (33)$$

$$S = S\left(\frac{1}{\rho_0} E, T, N\right), \quad (34)$$

$$s = s\left(\frac{1}{\rho_0} E, T, N\right), \quad (35)$$

$$\mu = \mu\left(\frac{1}{\rho_0} E, T, N\right). \quad (36)$$

Equations (27) and (33) combined yield

$$\dot{u} = \frac{1}{\rho_0} S_{ij} \dot{E}_{ij} + T \dot{s} + \mu \dot{N}. \quad (37)$$

Comparing eq. (37) with eq. (22) and using eq. (25), one finds

$$T \dot{s} = r - \frac{1}{\rho} h_{i,i} = \dot{q}. \quad (38)$$

Therefore an isentropic process is adiabatic as is always the case in linear thermoelasticity (CARLSON, 1972). Equation (38) indicates that diffusing hydrogen causes an entropy increase at the same rate that heat is generated in the body due to the formation of solution.

The *specific heat at constant volume* measured per mole of material lattice in G_i per degree K is defined to be a positive quantity such that

$$c_v = \frac{\partial u}{\partial T} \Big|_{E_{ij}, N} > 0, \quad (39)$$

where the form of the function u is given by eqs. (27) and (29a). Combining eq. (37) at constant E_{ij} and N with eq. (39) yields

$$c_v = T \frac{\partial s}{\partial T} \Big|_{E_{ij}, N}, \quad (40)$$

and therefore

$$\frac{\partial s}{\partial T} \Big|_{E_{ij}, N} > 0. \quad (41)$$

Equation (41) implies that eq. (35) is smoothly invertible in T and therefore eqs. (27) and (29a) provide

$$u = u\left(\frac{1}{\rho_0} E, s, N\right). \quad (42)$$

Combining eqs. (37) and (42) gives

$$S_{ij} = \left. \frac{\partial u}{\partial \left(\frac{1}{\rho_0} E_{ij} \right)} \right|_{s, N}, \quad (43)$$

$$T = \left. \frac{\partial u}{\partial s} \right|_{E_{ij}, C}, \quad (44)$$

$$\mu = \left. \frac{\partial u}{\partial N} \right|_{E_{ij}, s}. \quad (45)$$

Equations (33) and (37) indicate that the Helmholtz free energy is the portion of the internal energy u available for doing work and motivating hydrogen diffusion at constant temperature. Equations (29a), (33), (42), and (37) indicate that the Helmholtz

free energy f may be found by a Legendre transformation on the internal energy u which replaces the entropy s by the temperature T as independent thermodynamic variable. The condition stated by inequality (41) ensures the existence of the transformation.

Defining enthalpy h measured per mole of material lattice in \mathcal{G}_t such that

$$h = u - \frac{1}{\rho_0} S_{ij} E_{ij} \quad (46)$$

and using eq. (37), one obtains

$$\dot{h} = -\frac{1}{\rho_0} E_{ij} \dot{S}_{ij} + T \dot{s} + \mu \dot{N}. \quad (47)$$

From eqs. (42) and (43)

$$\mathbf{S} = \mathbf{S}\left(\frac{1}{\rho_0} \mathbf{E}, s, N\right) \quad (48)$$

and assuming that the Jacobian

$$\det \left(\begin{array}{|c|} \hline \frac{\partial S_{ij}}{\partial \left(\frac{1}{\rho_0} E_{kl} \right)} \\ \hline \end{array} \right|_{s,C} \neq 0, \quad (49)$$

one can invert eq. (48) so that $\mathbf{E}/\rho_0 = \mathbf{E}(\mathbf{S}, s, N)$. For a hyperelastic material the statement (49) is a consequence of the convexity of the strain energy density function. Then, equations (42) and (46) yield

$$h = h(\mathbf{S}, s, N) \quad (50)$$

and hence from eq. (47)

$$\frac{1}{\rho_0} E_{ij} = -\frac{\partial h}{\partial S_{ij}} \Big|_{s,N}, \quad (51)$$

$$T = \frac{\partial h}{\partial s} \Big|_{S_{ij}, N}, \quad (52)$$

$$\mu = \frac{\partial h}{\partial N} \Big|_{S_{ij}, s}. \quad (53)$$

Therefore, enthalpy h may be found by a Legendre transformation on the internal energy u which replaces E/ρ_0 by S as an independent thermodynamic variable. Equations (37) and (47) indicate that the enthalpy represents the portion of the internal energy corresponding to thermal conduction and hydrogen diffusion when the stress is held constant. Enthalpy is associated with the *specific heat at constant pressure* defined by

$$c_p = \frac{\partial h}{\partial T} \Big|_{S_{ij}, N} \quad (54)$$

and by eq. (47)

$$c_p = \frac{\partial h}{\partial T} \Big|_{S_{ij}, N} = T \frac{\partial s}{\partial T} \Big|_{S_{ij}, N}. \quad (55)$$

The Gibbs free energy, measured per lattice mole in \mathcal{G}_i , is defined by

$$g = u - \frac{1}{\rho_0} S_{ij} E_{ij} - Ts, \quad (56)$$

and with use of eq. (37)

$$\dot{g} = -\frac{1}{\rho_0} E_{ij} \dot{S}_{ij} - s \dot{T} + \mu \dot{N}. \quad (57)$$

Equations (42) and (44) imply

$$T = T(\frac{1}{\rho_0} E, s, N), \quad (58)$$

and with use of eqs. (41) and (49) equations (48) and (58) may be inverted to yield

$$\frac{1}{\rho_0} E = E(S, T, N), \quad (59)$$

$$s = s(S, T, N). \quad (60)$$

Substituting eqs. (59) and (60) into eqs. (42) and (56) yields

$$g = g(S, T, N), \quad (61)$$

which combined with eq. (57) furnishes

$$\frac{1}{\rho_0} E_{ij} = - \left. \frac{\partial g}{\partial S_{ij}} \right|_{T, N}, \quad (62)$$

$$s = - \left. \frac{\partial g}{\partial T} \right|_{S_{ij}, N}, \quad (63)$$

$$\mu = \left. \frac{\partial g}{\partial N} \right|_{S_{ij}, T}. \quad (64)$$

The Gibbs free energy g may be found by a Legendre transformation on the internal energy u which replaces E/ρ_0 and s by S and T respectively as independent thermodynamic variables. Equation (64) reveals another standard definition of the chemical potential of hydrogen in terms of the Gibbs free energy. That is, the chemical potential of an atom at position x of the stressed solid is equal to the change in the Gibbs free energy due to the introduction of a hydrogen atom in the position x under constant stress S and temperature T from its "standard state" at the same temperature and constant pressure.

In sum, the governing equations for a nonlinear elastic material can be stated as follows:

(i) kinematical relations

$$\mathbf{F} = \nabla \mathbf{x} = \mathbf{I} + \nabla \mathbf{u}, \quad (65a)$$

$$\mathbf{E} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}). \quad (65b)$$

(ii) Dynamical equilibrium equations in terms of the Cauchy stress

$$\sigma_{ji,j} + b_i = \rho \ddot{u}_i, \quad (65c)$$

$$\sigma_{ij} = \sigma_{ji}. \quad (65d)$$

(iii) Energy equation

$$T\dot{s} = r - \frac{1}{\rho} h_{i,i} = \dot{q}. \quad (65e)$$

(iv) Constitutive relations in terms of the Helmholtz free energy potential

$$f = f\left(\frac{1}{\rho_0} \mathbf{E}, T, N\right), \quad (65f)$$

$$S = S\left(\frac{1}{\rho_0} \mathbf{E}, T, N\right), \quad (65g)$$

$$s = s\left(\frac{1}{\rho_0} \mathbf{E}, T, N\right), \quad (65h)$$

$$\mu = \mu\left(\frac{1}{\rho_0} \mathbf{E}, T, N\right). \quad (65i)$$

$$\mathbf{j} = -\frac{D\rho N}{kT} \nabla \mu \quad (65j)$$

$$\mathbf{h} = \mathbf{h}\left(\frac{1}{\rho_0} \mathbf{E}, T, N, \nabla T, \nabla N\right), \quad (65k)$$

$$S_{ij} = \left. \frac{\partial f}{\partial \left(\frac{1}{\rho_0} E_{ij} \right)} \right|_{T,N}, \quad (65l)$$

$$s = -\left. \frac{\partial f}{\partial T} \right|_{E_{ij},N}, \quad (65m)$$

$$\mu = \left. \frac{\partial f}{\partial N} \right|_{E_{ij},N}. \quad (65n)$$

Alternatively, part (iv) may be replaced by

(v) the Gibbs free energy potential

$$g = g(\mathbf{S}, T, N), \quad (65o)$$

$$\frac{1}{\rho_0} E_{ij} = -\left. \frac{\partial g}{\partial S_{ij}} \right|_{T,N}, \quad (65p)$$

$$s = -\left. \frac{\partial g}{\partial T} \right|_{S_{ij},N}, \quad (65q)$$

$$\mu = \left. \frac{\partial g}{\partial N} \right|_{S_{ij},T}. \quad (65r)$$

2.3 Linear theory for elastic materials

The linearized governing equations for an elastic material are obtained by assuming that the displacement gradient and its rate of change are small; the temperature and concentration fields are nearly equal to given uniform fields T_0 and N_0 called respectively the *reference temperature* and the *nominal concentration*; the temperature rate, the temperature gradient, the concentration rate, and the concentration gradient are small. Thus, it is assumed that the magnitude of $|u_{i,j}|$, $|\dot{u}_{i,j}|$, $|T - T_0|$, $|\dot{T}|$, $|N - N_0|$, and $|\dot{N}|$, are of $O(\epsilon)$, where ϵ can be made infinitesimally small. Under these conditions the derivatives $(\cdot)_{,i}$ and $(\cdot)_{,I}$ are equal to first order and it is immaterial whether gradients are formed by differentiating with respect to material or spatial coordinates. Hence, equations (65a) and (65b) furnish

$$F_{ij} = \delta_{ij} + O(\epsilon), \quad (66)$$

$$E_{ij} = \epsilon_{ij} + O(\epsilon^2), \quad (67)$$

where

$$\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \quad (68)$$

are the components of the strain tensor of infinitesimal elasticity. Consequently, equation (67) yields

$$\dot{E}_{ij} = \dot{\epsilon}_{ij} + O(\epsilon^2). \quad (69)$$

By eqs. (65g) and (67)

$$\mathbf{S} = \mathbf{S}\left(\frac{1}{\rho_0} \boldsymbol{\epsilon}, T, N\right), \quad (70)$$

and then by eqs. (20), (66) and (70)

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}\left(\frac{1}{\rho_0} \boldsymbol{\epsilon}, T, N\right) = \mathbf{S}\left(\frac{1}{\rho_0} \boldsymbol{\epsilon}, T, N\right) \quad (71)$$

to $O(1)$. The body is assumed to be stress free in the reference configuration, that is, there are no *residual stresses* at time $t = 0$. In addition, the corresponding hydrogen concentration and temperature fields in \mathcal{G}_0 are assumed uniform throughout the body and equal to the *reference temperature* T_0 and the *nominal concentration* N_0 respectively. By eq. (71) the condition for zero residual stress is

$$\boldsymbol{\sigma}(\boldsymbol{\epsilon} = 0, T_0, N_0) = 0. \quad (72)$$

Expanding the stress $\boldsymbol{\sigma}$, as given by eq. (71), in a Taylor series about $\boldsymbol{\epsilon} = 0$, $T = T_0$, and $N = N_0$, and using eq. (72), one finds to $O(\epsilon)$

$$\sigma_{ij}\left(\frac{1}{\rho_0} \boldsymbol{\epsilon}_{kl}, T, N\right) = C_{ijkl} \boldsymbol{\epsilon}_{kl} + M_{ij}(T - T_0) + L_{ij}(N - N_0), \quad (73)$$

where

$$C_{ijkl} = \left. \frac{\partial \sigma_{ij}\left(\frac{1}{\rho_0} \boldsymbol{\epsilon}_{mn}, T, N\right)}{\partial \epsilon_{kl}} \right|_{\begin{array}{l} \epsilon_{ij}=0 \\ T=T_0 \\ N=N_0 \end{array}} \quad (74)$$

are the components of the fourth order *isothermal stiffness tensor*, or *stiffness tensor at fixed solute composition*,

$$M_{ij} = \left. \frac{\partial \sigma_{ij} \left(\frac{1}{\rho_0} \epsilon_{mn}, T, N \right)}{\partial T} \right|_{\begin{array}{l} \epsilon_{ij}=0 \\ T=T_0 \\ N=N_0 \end{array}} \quad (75)$$

are the components of the *stress-temperature tensor*, and

$$L_{ij} = \left. \frac{\partial \sigma_{ij} \left(\frac{1}{\rho_0} \epsilon_{mn}, T, N \right)}{\partial N} \right|_{\begin{array}{l} \epsilon_{ij}=0 \\ T=T_0 \\ N=N_0 \end{array}} \quad (76)$$

are the components of the *stress-hydrogen tensor*. Definition (74) along with eqs. (71) and (65l) imply symmetry of the isothermal elasticity tensor. Symmetry of the stress-temperature and stress-hydrogen tensors results from the symmetry of the stress tensor σ and definitions (75) and (76).

Next, the linearized form of the energy eq. (65e) is derived. By eqs. (65h) and (67)

$$\dot{s} = \left. \frac{\partial s \left(\frac{1}{\rho_0} \epsilon_{mn}, T, N \right)}{\partial \left(\frac{1}{\rho_0} \epsilon_{ij} \right)} \right|_{T,N} \left. \frac{1}{\rho_0} \dot{\epsilon}_{ij} + \frac{\partial s \left(\frac{1}{\rho_0} \epsilon_{mn}, T, N \right)}{\partial T} \right|_{\epsilon_{ij},N} \left. \dot{T} + \frac{\partial s \left(\frac{1}{\rho_0} \epsilon_{mn}, T, N \right)}{\partial N} \right|_{\epsilon_{ij},T} \dot{N}. \quad (77)$$

Expanding the derivatives in Taylor series about $\epsilon = 0$, $T = T_0$, and $N = N_0$, one finds

$$\left. \frac{\partial s}{\partial \left(\frac{1}{\rho_0} \epsilon_{ij} \right)} \right|_{T,N} = \left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial \left(\frac{1}{\rho_0} \epsilon_{ij} \right)} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} + o(1), \quad (78)$$

$$\left. \frac{\partial s}{\partial T} \right|_{\epsilon_{ij}, N} = \left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial T} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} + o(1), \quad (79)$$

$$\left. \frac{\partial s}{\partial N} \right|_{\epsilon_{ij}, T} = \left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial N} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} + o(1). \quad (80)$$

Upon differentiation, equations (65l) and (65m) yield the Maxwell relation

$$\left. \frac{\partial s}{\partial \left(\frac{1}{\rho_0} E_{ij} \right)} \right. = - \left. \frac{\partial S_{ij}}{\partial T} \right. \quad (81)$$

Expanding both sides of eq. (81) in Taylor series about $\epsilon=0$, $T=T_0$, and $N=N_0$, and using eqs. (67) and (71), one finds to $O(1)$

$$\left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial \left(\frac{1}{\rho_0} \epsilon_{ij} \right)} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} = - \left. \frac{\partial \sigma_{ij}(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial T} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} . \quad (82)$$

Then combining eqs. (75) and (82), one finds

$$\left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial \left(\frac{1}{\rho_0} \epsilon_{ij} \right)} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} = -M_{ij} . \quad (83)$$

Using eq. (65h) to expand the right hand side of eq. (40) in a Taylor series about $\epsilon = 0$, $T = T_0$, and $N = N_0$, and making use of eq. (67), one finds to $O(1)$.

$$\left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial T} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} = \frac{c_v}{T_0} . \quad (84)$$

Substituting eqs. (80), (83) and (84) into eq. (77) gives

$$\dot{s} = -\frac{1}{\rho_0} M_{ij} \dot{\epsilon}_{ij} + \frac{c_v}{T_0} \dot{T} + \left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial N} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} \dot{N} . \quad (85)$$

to $O(\epsilon)$. Equations (65m) and (65n) upon differentiation yield the following Maxwell relation

$$\frac{\partial s}{\partial N} = -\frac{\partial \mu}{\partial T} \quad (86)$$

where the forms of s and μ are given by eqs. (65h) and (65i).

Expanding both sides of eq. (86) about $\epsilon = 0$, $T = T_0$, and $N = N_0$ gives

$$\left. \frac{\partial s(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial N} \right|_{\begin{array}{l} \epsilon_{ij}=0 \\ T=T_0 \\ N=N_0 \end{array}} = - \left. \frac{\partial \mu(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial T} \right|_{\begin{array}{l} \epsilon_{ij}=0 \\ T=T_0 \\ N=N_0 \end{array}} \quad (87)$$

to $O(1)$, and substituting into eq. (85) implies

$$T\dot{s} = -\frac{T_0}{\rho_0} M_{ij} \dot{\epsilon}_{ij} + c_v \dot{T} - T_0 \left. \frac{\partial \mu(\frac{1}{\rho_0} \epsilon_{mn}, T, N)}{\partial T} \right|_{\begin{array}{l} \epsilon_{ij}=0 \\ T=T_0 \\ N=N_0 \end{array}} \dot{N} \quad (88)$$

to $O(\epsilon)$.

Inverting the constitutive relation (73) yields

$$\epsilon_{ij} = K_{ijkl} \sigma_{kl} + A_{ij}(T - T_0) + \rho_0 H_{ij}(N - N_0), \quad (89)$$

where

$$\mathbf{K} = \mathbf{C}^{-1}, \quad (90)$$

$$\mathbf{A} = -\mathbf{K}\mathbf{M}, \quad (91)$$

$$\rho_0 \mathbf{H} = -\mathbf{K}\mathbf{L} \quad (92)$$

are called the *isothermal compliance tensor* or the *compliance tensor at fixed solute composition*, the *thermal expansion tensor* and the *hydrogen expansion tensor* respectively. Then from the linearized constitutive eq. (89)

$$H_{ij} = \frac{\partial}{\partial N} \left(\frac{1}{\rho_0} \epsilon_{ij} \right) \Bigg|_{\sigma_{ij}=0, T=T_0} \quad (93)$$

to $O(1)$. Equations (65p) and (65r) combined yield the Maxwell relation

$$\frac{\partial \mu}{\partial S_{ij}} \Bigg|_{T,N} = - \frac{\partial}{\partial N} \left(\frac{1}{\rho_0} E_{ij} \right) \Bigg|_{S_{ij}, T}, \quad (94)$$

which with use of eqs. (67) and (71) becomes

$$\frac{\partial \mu}{\partial \sigma_{ij}} \Bigg|_{T,N} = - \frac{\partial}{\partial N} \left(\frac{1}{\rho_0} \epsilon_{ij} \right) \Bigg|_{\sigma_{ij}, T}. \quad (95)$$

Equations (93) and (95) can be used to evaluate $\partial \mu / \partial \sigma_{ij}$ to $O(1)$ as a function of stress σ at constant temperature T and hydrogen concentration N :

$$\frac{\partial \mu}{\partial \sigma_{ij}} \Bigg|_{T,N} = -H_{ij}. \quad (96)$$

Integrating eq. (96) while keeping the temperature and the hydrogen concentration constant yields to $O(\epsilon)$

$$\mu(\sigma_{ij}, T, N) = \mu(-p\delta_{ij}, T, N) - H_{ij}\sigma_{ij} - pH_{kk}, \quad (97)$$

where $-p\delta_{ij}$ denotes a stress state of pure hydrostatic pressure p at which for an *interstitial solid solution* (LARCHE and CAHN, 1985)

$$\frac{\partial \mu}{\partial N} = \beta \frac{kT}{N}, \quad (98)$$

where β is a constant equal to unity when the solution is ideal. Integrating eq. (98) for an ideal solution yields

$$\mu(-p\delta_{ij}, T, N) = \mu_0 + kT \ln \left(\frac{N}{N_0} \right), \quad (99)$$

where μ_0 is the chemical potential of hydrogen for the "standard state" at the same pressure and hydrogen concentration equal to the nominal N_0 . Substituting eq. (99) into eq. (97) gives to $O(\epsilon)$

$$\mu(\sigma_{ij}, T, N) = \mu_0 + kT \ln\left(\frac{N}{N_0}\right) - H_{ij}\sigma_{ij} - pH_{kk}, \quad (100)$$

which in conjunction with eq. (73) yields to $O(1)$

$$\frac{\partial \mu}{\partial T} \Big|_{\epsilon_{ij}, N} = k \ln\left(\frac{N}{N_0}\right) - H_{ij}M_{ij}, \quad (101)$$

where the hydrogen expansion tensor H has been evaluated at the reference temperature T_0 and zero stress through eq. (93), and the stress σ has been evaluated by linearization about $\epsilon = 0$ as indicated by eq. (73). Under those circumstances eq. (101) gives to $O(1)$

$$\left. \frac{\partial \mu\left(\frac{1}{\rho_0}\epsilon_{ij}, T, N\right)}{\partial T} \right|_{\substack{\epsilon_{ij}=0 \\ T=T_0 \\ N=N_0}} = -H_{ij}M_{ij}, \quad (102)$$

and substituting into eq. (88) one finds to $O(\epsilon)$

$$T\dot{s} = -\frac{T_0}{\rho_0}M_{ij}\dot{\epsilon}_{ij} + c_v\dot{T} + T_0H_{ij}M_{ij}\dot{N}. \quad (103)$$

The final form of the energy equation is obtained from eq. (65e) with use of eq. (103). Thus, taking into account that for deformations with infinitesimal strains, $\rho = \rho_0$, one finds to $O(\epsilon)$

$$\dot{q} + \frac{T_0}{\rho_0}M_{ij}\dot{\epsilon}_{ij} - T_0H_{ij}M_{ij}\dot{N} = c_v\dot{T}. \quad (104)$$

In the case of *linear thermoelasticity*, that is, in the absence of hydrogen in the present analysis, the energy equation (103) can be integrated under isentropic conditions of heat conduction through the body to yield the temperature drop during adiabatic straining as

$$T - T_0 = \frac{T_0}{\rho_0 c_v} M_{ij} \epsilon_{ij}. \quad (105)$$

Substituting this result into eq. (73) yields

$$\sigma = C^s \epsilon, \quad (106)$$

where C^s is called the *isentropic stiffness tensor* and is given by

$$C_{ijkl}^s = C_{ijkl} + T_0 \frac{M_{ij} M_{kl}}{\rho_0 c_v}. \quad (107)$$

A similar situation arises in the case of *linearized hydrogen elasticity*, that is, when hydrogen diffuses through the material while the reference temperature T_0 remains constant in time and uniform throughout the body. By linearizing the second term in the right hand side of eq. (100) about $T = T_0$ and $N = N_0$, one obtains to $O(\epsilon)$ the complete linearized form of the chemical potential, μ , about $\sigma = 0$, $T = T_0$, and $N = N_0$ as

$$\mu(\sigma_{ij}, T, N) = \mu_0 + \frac{kT_0}{N_0} (N - N_0) - H_{ij} \sigma_{ij} - p H_{kk}, \quad (108)$$

and consequently

$$\nabla \mu = \frac{kT_0}{N_0} \nabla N - H_{ij} \nabla \sigma_{ij} \quad (109)$$

to $O(\epsilon)$.

Linearizing eq. (65j), one finds to $O(\epsilon)$

$$\mathbf{j} = -\frac{D \rho_0 N_0}{kT_0} \nabla \mu, \quad (110)$$

where $\nabla\mu$ is given by eq. (109). The *steady state or equilibrium concentration* of hydrogen can be found from eq. (109) by setting $\nabla\mu = 0$ which follows from eq. (110) when $j=0$. Under those conditions, integration of eq. (109) from $N=N_0$ at $\sigma=0$ gives to $O(\epsilon)$ the local hydrogen concentration in terms of the corresponding stress as

$$N - N_0 = \frac{H_j \sigma_j}{kT_0} N_0. \quad (111)$$

Substituting this result into eq. (89), one finds that the linear constitutive behavior of a material at uniform constant temperature T_0 containing interstitial hydrogen *in equilibrium with local stress* is described to $O(\epsilon)$ in the standard form of Hooke's law by

$$\epsilon = K^\mu \sigma \quad (112)$$

with the hydrogen effect being accounted for, through a hydrogen dependent compliance tensor K^μ given by

$$K_{ijkl}^\mu = K_{ijkl} + \rho_0 N_0 \frac{H_{ij} H_{kl}}{kT_0}. \quad (113)$$

Tensor K^μ is called the *compliance tensor at fixed solute chemical potential*.

It is worth noting that in the case of *linear thermoelasticity* the constitutive law at any reference temperatures T_0 is expressed in terms of the corresponding *isothermal stiffness tensor* C and the *stress-temperature tensor* M through eq. (73) from which the term $L_{ij}(N - N_0)$ due to hydrogen has been dropped. In particular, if the heat conduction in the body happens isentropically, the constitutive law (73) for the linear thermoelasticity can be stated solely in terms of the *isentropic stiffness tensor* C^* . Isentropic conditions are usually met at deformations of short duration where there is insufficient time for heat exchange among the particles of the body and between the body and the surroundings. In the case of *linearized hydrogen elasticity* the constitutive law is expressed at any nominal hydrogen concentration

N_0 in terms of the *stiffness tensor at fixed solute composition*, $\mathbf{K} = \mathbf{C}^{-1}$, and the *hydrogen expansion tensor* \mathbf{H} through eq. (89) in which the term $A_{ij}(T - T_0)$ due to temperature is set equal to zero in view of $T = T_0$ throughout the body at all times. In particular, at steady state, that is, after sufficient time has passed and the diffused hydrogen has neutralized the local chemical potential gradients by relaxing to the concentrations given by eq. (111), the constitutive law (89) for the linearized hydrogen elasticity can be written solely in terms of the *compliance tensor at fixed solute chemical potential* \mathbf{K}^μ . Note that unlike the isentropic conditions in linear thermoelasticity, which are prevalent during fast straining, the corresponding isochemical potential conditions in linearized hydrogen elasticity are achieved practically after an infinitely long time of hydrogen diffusion. Notice also the direct analogy between the coupled diffusion and deformation in fluid-infiltrated geomaterials (RICE and CLEARY, 1976) and the linearized hydrogen elasticity. The "*undrained deformation*" and the associated "*undrained moduli*" at constant fluid mass content m correspond to the deformation at constant hydrogen solute concentration N_0 and the related moduli defined by eq. (74) at fixed solute composition. In both fluid-infiltrated and hydrogen containing solids the conditions for undrained deformation and deformation at fixed solute composition respectively are obtained during fast straining. "*Drained deformation*" at constant pore pressure p and the related "*drained moduli*" correspond to equilibrium situations at fixed solute chemical potential potential μ and the associated moduli defined by eq. (113). Both drained and fixed solute chemical potential deformations are the case when the straining is slow.

Solution of the energy equation (104) yields the simultaneous evolution in time of the temperature and hydrogen concentration fields T and N respectively. The solution can be facilitated by observing that term $\rho_0 T_0 H_{ij} M_{ij} \dot{N}$ can be neglected when compared to term $T_0 M_{ij} \dot{\epsilon}_{ij}$ if the strain rates induced by the dissolved hydrogen

are much less than those caused by the applied loads. In particular, this is true in the case of isotropic elasticity of dilute solutions, when $\Delta v \dot{C} \ll \dot{\epsilon}_{kk}$, where Δv is the dilatation of the host lattice per hydrogen atom. Hence, as in linear thermoelasticity (CARLSON, 1972), the terms $\rho_0 T_0 H_{ij} M_{ij} \dot{N}$ and $T_0 M_{ij} \dot{\epsilon}_{ij}$ may be neglected in comparison to $\rho_0 \dot{q}$ and $\rho_0 c_v \dot{T}$. As a result, the system of governing equations becomes uncoupled in the sense that the temperature field can be found independently by solving the energy equation (104) in the form

$$\rho_0 r - h_{i,i} = \rho_0 c_v \dot{T}, \quad (114)$$

where the divergence of the heat flux, when treated as unaffected by hydrogen, can be linearized and written in terms of the conductivity tensor in the standard form of the Fourier heat conduction law (CARLSON, 1972). The evolution of the hydrogen concentration field can then be found by combining eqs. (14), (109) and (110) to establish the standard diffusion equation in which the hydrogen concentration and stress fields are coupled. In the rest of this paper the discussion focuses on the static linearized hydrogen elasticity, where it is assumed that hydrogen diffuses into the material, while the body's temperature T_0 is uniform and does not change with time.

Linearizing eq. (15) about $N = N_0$ and $\rho = \rho_0$, gives

$$C = \rho_0 N \quad (115)$$

to $O(1)$. Then, one may summarize the governing equations of linearized hydrogen elasticity at nominal hydrogen concentration C_0 and reference temperature T_0 as follows:

(i) strain-displacement relations

$$\epsilon_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}) \quad (116a)$$

(ii) Equilibrium equations

$$\sigma_{ji,j} + b_i = 0, \quad (116b)$$

$$\sigma_{ij} = \sigma_{ji} \quad (116c)$$

(iii) Stress-strain relationship

$$\epsilon_{ij} = K_{ijkl}\sigma_{kl} + H_{ij}(C - C_0), \quad (116d)$$

where C_0 is the nominal hydrogen concentration equal to $\rho_0 N_0$ by eq. (115), and the linear form of the *hydrogen expansion tensor* is given by

$$H_{ij} = \left(\frac{\partial \epsilon_{ij}}{\partial C} \right) \Bigg|_{\substack{\sigma_{ij}=0 \\ T=T_0}}. \quad (116e)$$

At *steady state* constitutive law (116d) can be cast into

$$\epsilon = \mathbf{K}^\mu \boldsymbol{\sigma}, \quad (116f)$$

where \mathbf{K}^μ is the *compliance tensor at fixed solute chemical potential* given in component form by

$$K_{ijkl}^\mu = K_{ijkl} + C_0 \frac{H_{ij} H_{kl}}{kT_0}. \quad (116g)$$

(iv) With use of eq. (14) the linearized transient hydrogen diffusion law is written as

$$\dot{C} = -\nabla \cdot \mathbf{j}, \quad (116h)$$

where

$$\mathbf{j} = -D \nabla C + \frac{DC_0}{kT_0} H_{ij} \nabla \sigma_{ij} \quad (116i)$$

by combining eqs. (109) and (110). At *steady state*, solution to eqs. (116h) and (116i) gives the hydrogen concentration in equilibrium with local stress as

$$C - C_0 = \frac{H_{ij} \sigma_{ij}}{kT_0} C_0, \quad (116j)$$

where the concentration C_0 at zero stress has been used as a boundary condition.

2.4 Isotropic linearized hydrogen elasticity

Assume that n_H hydrogen moles are introduced in a stress free region of n_M host metal moles with the local hydrogen concentration thus being $c = n_H/n_M$ hydrogen atoms per host metal atom. The solution of hydrogen into a stress free metal lattice is characterized by a volume dilatation Δv of the host lattice per hydrogen atom (PEISL, 1978; HIRTH, 1980). Volume change Δv is directly related to the partial molar volume of hydrogen by

$$V_H = \Delta v N_A, \quad (117)$$

where N_A is Avogadro's number. For dilute solutions, $c \ll 1$, the concentrations C , c , and N are related by

$$C = \frac{c}{\Omega} = \frac{N}{V_M}, \quad (118)$$

where $\Omega = V_M/N_A$ and $V_M = 1/\rho_0$ are the mean atomic and molar volumes of the host metal lattice. The local unconstrained volume dilatation of the lattice volume $V = n_M V_M$ is $\Delta V = n_H N_A \Delta v$, (SOFRONIS and BIRNBAUM, 1993). Hence, the corresponding unconstrained dilatational strain is

$$e^H = c \frac{\Delta v}{\Omega}, \quad (119)$$

and setting

$$\lambda = \frac{\Delta v}{\Omega}, \quad (120)$$

one may write with use of eq. (118) the local hydrogen induced strain *at zero stress* as

$$\epsilon_{ij}^H = \frac{1}{3} \lambda c \delta_{ij} = \frac{1}{3} \lambda \Omega C \delta_{ij}. \quad (121)$$

The strain tensor ϵ^H is often referred as the hydrogen induced transformation strain in the treatment of the hydrogen mechanical effect (SOFRONIS and BIRNBAUM, 1993). Introducing eq. (121) into eq. (116e) yields the hydrogen expansion tensor as

$$H_{ij} = \frac{1}{3} \lambda \Omega \delta_{ij}. \quad (122)$$

Substitution of eq. (122) into eq. (116d) furnishes

$$\varepsilon_{ij} = K_{ijkl} \sigma_{kl} + \frac{1}{3} \lambda \Omega (C - C_0) \delta_{ij}, \quad (123)$$

and for isotropic material eq. (123) becomes

$$\varepsilon_{ij} = \frac{1+v}{E} \sigma_{ij} - \frac{v}{E} \sigma_{kk} \delta_{ij} + \frac{1}{3} \lambda \Omega (C - C_0) \delta_{ij}, \quad (124)$$

where E is the Young's modulus and v is the Poisson's ratio at fixed solute composition C_0 and zero external applied stress. Inserting eq. (124) into the compatibility conditions (SOKOLNIKOFF, 1956)

$$\varepsilon_{ij,kl} + \varepsilon_{kl,ij} - \varepsilon_{ik,jl} + \varepsilon_{jl,ik} = 0 \quad (125)$$

and using the eqs. (116b) and (116c) in the absence of body forces, one obtains the following six independent compatibility equations written in terms of σ_{ij} and C :

$$\sigma_{ij,kk} + \frac{1}{1+v} \sigma_{mm,ij} = -\frac{1}{3} \lambda \Omega \left(\frac{E}{1+v} C_{,ij} + \frac{E}{1-v} C_{,kk} \delta_{ij} \right). \quad (126)$$

Contraction on i, j results in a relationship between the Laplacian, $\nabla^2() = ()_{,ii}$, of the hydrostatic stress σ_{kk} and the Laplacian of the hydrogen concentration C :

$$\nabla^2 \sigma_{kk} = -\frac{2}{3} \frac{E}{1-v} \lambda \Omega \nabla^2 C. \quad (127)$$

The equation for the transient hydrogen diffusion is found by combining eqs. (116h), (116i) and (122):

$$\dot{C} = D \nabla^2 C - \frac{DC_0}{3kT_0} \lambda \Omega \nabla^2 \sigma_{kk}, \quad (128)$$

and by replacing $\nabla^2 \sigma_{kk}$ by $\nabla^2 C$ from eq. (127) to get

$$\dot{C} = D_{eff} \nabla^2 C, \quad (129)$$

where the effective diffusion constant D_{eff} is given by

$$D_{eff} = D \left(1 + \frac{2}{9} \frac{C_0}{kT_0} \frac{E}{1-v} \lambda^2 \Omega^2 \right). \quad (130)$$

Next, the Young's modulus E^μ , Poisson's ratio v^μ , and shear modulus G^μ at fixed solute chemical potential will be evaluated in terms of the corresponding moduli E , v , and G at fixed solute composition. Since the hydrogen expansion tensor is purely hydrostatic for crystals of cubic symmetry or for an isotropic solid, any moduli defined in terms of the deviatoric stresses and strains are the same regardless of whether they are defined under fixed solute composition or fixed solute chemical potential. Hence, for isotropic hydrogen elasticity the shear modulus must satisfy

$$G^\mu = G, \quad (131)$$

and combining eq. (116g) when the material is isotropic with eqs. (122) and (131), one finds

$$E^\mu = \frac{E}{1 + \xi \lambda^2 E}, \quad (132)$$

$$v^\mu = \frac{v - \xi \lambda^2 E}{1 + \xi \lambda^2 E}, \quad (133)$$

where

$$\xi = \frac{c_0 \Omega}{9kT_0}, \quad (134)$$

and c_0 is the nominal concentration measured in hydrogen atoms per metal atom.

The bulk modulus B^μ at fixed solute chemical potential is then given by

$$\frac{1}{B^\mu} = \frac{1}{B} + 9\xi \lambda^2, \quad (135)$$

where B is the bulk modulus at fixed solute composition. Equation (133) indicates that the Poisson's ratio at fixed solute chemical potential becomes non-positive when

$$c_0 \geq \frac{9\nu kT_0}{E\Omega\lambda^2}. \quad (136)$$

Equations (131), (132), (133), and (135) are identical with eqs. (5.6) in the work of LARCHE and CAHN (1985). However, the hydrogen concentration to be used in the formulae (5.6) of LARCHE and CAHN (1985) is not predicted by their theory. On the contrary, in this work, the hydrogen concentration to be used in the evaluation of the moduli at fixed solute chemical potential is the concentration about which the linearization of the field equations has been carried out. So for a system that is in contact with a chemical reservoir, the composition at equilibrium under zero stress is not only "usually a good choice" as LARCHE and CAHN (1985) maintain, but in fact, it is the right choice since it constitutes the physical basis for the linearization. Inserting eq. (122) into (116j) yields the steady state equilibrium concentration $C - C_0$ in terms of the hydrostatic stress σ_{kk} :

$$C - C_0 = \frac{\lambda\Omega C_0 \sigma_{kk}}{3kT_0}. \quad (137)$$

Using eqs. (132), (133), (134), and (118), one may write eq. (130) for the effective diffusion constant in terms of the Poisson's ratios at fixed solute composition and chemical potential as

$$D_{eff} = D \frac{(1+\nu)(1-\nu^\mu)}{(1-\nu)(1+\nu^\mu)}. \quad (138)$$

Equations (129) and (138) describe the stress and concentration driven non-steady state hydrogen diffusion at given nominal concentration C_0 . The stress effect has been absorbed into the effective diffusion constant, D_{eff} , and therefore, existing solutions for hydrogen transient diffusion according to Fick's second law can be used where the normal lattice diffusion constant, D , is replaced by D_{eff} . Consequently, the linearized hydrogen isotropic elasticity problem is uncoupled in the sense that the solution for the hydrogen concentration can be found directly in

terms of the diffusion constant D and the Poisson's ratios ν and ν^u at fixed solute concentration and fixed solute chemical potential respectively. The hydrogen concentration field changes during straining and large concentration gradients may develop after long diffusion times. In that case, a new updated concentration C_0 may be needed in order for the linearization conditions to continue to be valid. A new average reference concentration can be calculated from eq. (137) which provides a new Poisson's ratio, ν^u , and in turn a new effective diffusion constant, D_{eff} , which, as a result of its calculation, is stress dependent. Therefore, after long diffusion times, the transient hydrogen diffusion equation depends implicitly on the applied stress through the updating of the reference concentration.

Application: H/Ta, H/Nb, H/V and H/Fe systems

The Young's modulus and Poisson's ratio for the hydrogen free material were taken to be the moduli E and ν at fixed solute composition. This approximation is fairly reliable in the case of dilute solutions. Thus, E was taken equal to 189.35 GPa, 87.1 GPa, 128.8 GPa, 200GPa and ν equal to 0.339, 0.415, 0.352, 0.300 respectively for Ta, Nb, V, and Fe. The data for the Nb system are from the work of MAZZOLAI and BIRNBAUM (1985a, 1985b); those for Ta and V are from HIRTH and LOTHE (1982); and those for Fe from the METALS HANDBOOK (1985). The atomic volume Ω for Ta, Nb, and V was calculated $0.18 \cdot 10^{-28} m^3 / atom$ from the lattice parameter $a = 3.301 \text{ \AA}$, and that for Fe was calculated $0.12 \cdot 10^{-28} m^3 / atom$ from the magnitude of the dislocation's Burgers vector $b = 2.5 \text{ \AA}^\circ$ (METALS HANDBOOK, 1985). The ratio of volume expansion per hydrogen atom to volume of the host lattice atom is $\lambda = 0.155, 0.174, 0.190$ correspondingly for the H/TA, H/Nb and H/V systems (PEISL, 1978); and $\lambda = 0.276$ for the Fe/H system a value which corresponds to a partial molar volume of hydrogen in solution of $2 cm^3 / mole$ (HIRTH, 1980).

In Fig. 1, Young's modulus E^μ , Poisson's ratio ν^μ and Bulk modulus B^μ at fixed solute chemical potential, as given by eqs. (132), (133) and (135) respectively, are plotted against nominal hydrogen concentration c_0 for the H/Ta, H/Nb and H/V systems at $T = 300K$. In the same figure the effective diffusion constant D_{eff} as given by eq. (138) is plotted too. The elastic moduli E^μ, B^μ are normalized respectively by the moduli E, B at fixed solute composition and the effective diffusion constant, D_{eff} , is normalized by the normal lattice diffusion constant D . The ratio D_{eff} / D is greater than unity because of the stress effect on the diffusion of hydrogen. The moduli E^μ, ν^μ, B^μ decrease with hydrogen concentration and the implications of this behavior to the dislocation plasticity and fracture of the materials are discussed in Section 4. The minimum nominal concentration c_0 at which the parameter ν^μ becomes negative at temperature 300K is calculated from eq. (136) to be 0.154, 0.326, 0.201 and 0.061 for solute hydrogen in Ta, Nb, V, and Fe respectively. Therefore, a negative Poisson's ratio at fixed solute chemical potential may, indeed, be the case in the Ta, Nb and V systems, but it is definitely impossible for the Fe system where the hydrogen solubility is very small, that is, of the order of 4 hydrogen atoms per 10^8 Fe atoms in equilibrium with gas at one atmosphere pressure (JOHNSON, 1974).

3. SINGULAR SOLUTION FOR EDGE DISLOCATION AND LINE FORCE

3.1 Governing equations for plane strain deformation

Throughout this section Greek indices are used for the range 1, 2 and a repeated Greek index implies summation over the range. In plane strain deformation, parallel to the x_1, x_2 -plane, the component u_3 of the displacement vector vanishes and the components u_1 and u_2 are functions of the coordinates x_1

and x_2 but not of x_3 . As a result, the kinematic constraint $\varepsilon_{3j} = 0$ in conjunction with constitutive eq. (124) requires

$$\sigma_{33} = v\sigma_{yy} - \frac{E}{3}\lambda\Omega(C - C_0), \quad \sigma_{31} = \sigma_{32} = 0, \quad (139)$$

and hence

$$\sigma_{kk} = (v+1)\sigma_{yy} - \frac{E}{3}\lambda\Omega(C - C_0). \quad (140)$$

Then, the constitutive eq. (124) can be written as

$$2G\varepsilon_{\alpha\beta} = \sigma_{\alpha\beta} - v\sigma_{yy}\delta_{\alpha\beta} + \frac{E}{3}\lambda\Omega(C - C_0)\delta_{\alpha\beta}. \quad (141)$$

The equilibrium eqs. (116b) in the absence of body forces are written as

$$\sigma_{11,1} + \sigma_{12,2} = 0, \quad (142)$$

$$\sigma_{12,1} + \sigma_{22,2} = 0, \quad (143)$$

and with use of eq. (140) for the hydrostatic stress the compatibility condition (127) becomes

$$\nabla^2\sigma_{yy} = -\frac{E}{3(1-v)}\lambda\Omega\nabla^2C. \quad (144)$$

Lastly, combining eqs. (137), (132), (133), and (134) one finds that at steady state, i.e at time $t=\infty$, the in-plane hydrostatic stress σ_{yy} is related to the corresponding equilibrium concentration by

$$\sigma_{yy} = \frac{E}{3(v-v^\mu)}\lambda\Omega(C - C_0). \quad (145)$$

If σ_{11} , σ_{22} , σ_{12} , and C are chosen as the independent field variables the governing equations are described by the the set of eqs. (139) through (144) along with the transient diffusion eq. (129) which, as was discussed in Section 2.4, can be solved directly under appropriate boundary and initial conditions.

In order to solve for the stresses σ_{11} , σ_{22} , and σ_{12} , following RICE and CLEARY (1976) one may define

$$4 \operatorname{Re}[\Phi(z, t)] = \sigma_{yy} + \frac{E}{3(1-v)} \lambda \Omega (C - C_0), \quad (146)$$

where $\Phi(z, t)$ is an analytic complex function of the complex variable $z = x_1 + ix_2$ with $i = \sqrt{-1}$. Re means 'real part of', and as is indicated by eq. (146) the function $\Phi(z, t)$ is in general time dependent. It may be assumed that immediately after the introduction of the edge dislocation into the perfect crystal ($t = 0^+$) the classical elasticity solution based on the moduli v , E , and G at fixed solute composition C_0 applies. Similarly, the classical elasticity solution based on the moduli v^μ , E^μ , and G^μ at fixed solute chemical potential applies at steady state ($t = \infty$). Therefore eq. (146) yields

$$(\sigma_{yy})_{0^+} = 4 \operatorname{Re}[\Phi(z, 0^+)], \quad (147)$$

and in conjunction with eq. (145)

$$(\sigma_{yy})_\infty = 4 \frac{1-v}{1-v^\mu} \operatorname{Re}[\Phi(z, \infty)]. \quad (148)$$

If the function $\Phi(z, t)$ is time independent it should satisfy $\Phi(z, 0^+) = \Phi(z, \infty)$. In that case eqs. (147) and (148) indicate that traction boundary value problems are excluded since in these problems the solution for the stresses does not depend on the elastic moduli. Furthermore, eqs. (147) and (148) indicate that in order for $\Phi(z, 0^+) = \Phi(z, \infty)$ the solution for σ_{yy} should be inversely proportional to a factor $1-v^e$ so that

$$\sigma_{yy} = 4 \frac{1-v}{1-v^e} \operatorname{Re}[\Phi(z, t)], \quad (149)$$

where v^e is an effective Poisson's ratio such that $v^e = v$ at $t = 0^+$ and $v^e = v^\mu$ at $t = \infty$. This is, as RICE and CLEARY (1976) observe, exactly the feature of some basic singular elasticity solutions, such as the classical plane strain solutions for an isolated edge dislocation and an isolated line force, which has led us to extract their counterparts in linear isotropic hydrogen elasticity.

3.2 Plane strain solution in terms of complex potentials

Following the corresponding formalism in classical elasticity (MUSKHELISHVILI, 1953), one can express the solution to the plane strain governing equations for the stresses and displacements in terms of two analytic functions, complex potentials $\Phi(z,t)$ and $\Psi(z,t)$ of the complex variable $z = x_1 + ix_2$. By considering z and its complex conjugate $\bar{z} = x_1 - ix_2$ as the pair of independent variables, one may write the hydrogen concentration $C(x_1, x_2, t)$, which is not an analytic function, as $C(z, \bar{z}, t)$. By setting

$$\sigma = \frac{\sigma_{11} + \sigma_{22}}{2} \quad \text{and} \quad \tau = \frac{\sigma_{22} - \sigma_{11}}{2} + i\sigma_{12}, \quad (150)$$

equilibrium eqs. (142) and (143) become

$$\frac{\partial \tau}{\partial \bar{z}} = \frac{\partial \sigma}{\partial z}. \quad (151)$$

By eqs. (146) and (150)

$$\sigma = 2 \operatorname{Re}[\Phi(z,t)] - \frac{E}{6(1-\nu)} \lambda \Omega (C(z, \bar{z}, t) - C_0), \quad (152)$$

and upon differentiation

$$\frac{\partial \sigma}{\partial z} = \frac{\partial \Phi(z,t)}{\partial z} - \frac{E}{6(1-\nu)} \lambda \Omega \frac{\partial (C(z, \bar{z}, t) - C_0)}{\partial z}. \quad (153)$$

Inserting this result into eq. (151) and integrating yields

$$\tau = \bar{z} \frac{\partial \Phi(z,t)}{\partial z} + \Psi(z,t) - \frac{E}{6(1-\nu)} \lambda \Omega \int_{f(z,t)}^{\bar{z}} \frac{\partial [C(z, \zeta, t) - C_0]}{\partial z} d\zeta, \quad (154)$$

where the lower limit of integration $f(z,t)$ is an arbitrary analytic function to be chosen accordingly with the boundary conditions of the problem, and the analytic function $\Psi(z,t)$ is an arbitrary function of integration.

The expressions for the displacements u_1 and u_2 are obtained as follows: Constitutive eqs. (141) combined with eqs. (150) yield

$$\frac{\varepsilon_{11} + \varepsilon_{22}}{2} = \frac{1}{2G} \left[(1 - 2\nu)\sigma + \frac{E}{3} \lambda \Omega (C - C_0) \right], \quad (155)$$

$$\frac{\varepsilon_{22} - \varepsilon_{11}}{2} + i\varepsilon_{12} = \frac{\tau}{2G}. \quad (156)$$

Using the strain-displacement relations (116a), one can easily show that

$$\frac{\varepsilon_{11} + \varepsilon_{22}}{2} = \operatorname{Re} \left[\frac{\partial(u_1 - iu_2)}{\partial\bar{z}} \right], \quad (157)$$

$$\frac{\varepsilon_{22} - \varepsilon_{11}}{2} + i\varepsilon_{12} = - \frac{\partial(u_1 - iu_2)}{\partial z}. \quad (158)$$

Inserting eqs. (152) and (154) into eqs. (155) and (156) respectively and combining the result with eqs. (157) and (158), one finds by integration that

$$2\mu(u_1 - iu_2) = (3 - 4\nu)\bar{\varphi}(\bar{z}, t) - \bar{z}\Phi(z, t) - \psi(z, t) + \frac{E}{6(1-\nu)} \lambda \Omega \int_{f(z,t)}^{\bar{z}} [C(z, \zeta, t) - C_0] d\zeta, \quad (159)$$

where

$$\frac{\partial\varphi(z, t)}{\partial z} = \Phi(z, t) \quad (160)$$

and

$$\frac{\partial\psi(z, t)}{\partial z} = \Psi(z, t) - \frac{E}{6(1-\nu)} \lambda \Omega [C(z, f(z, t), t) - C_0] \frac{\partial f(z, t)}{\partial z}. \quad (161)$$

The resultant force $F_1 + iF_2$ exerted through any segment, defined by the arc length s_0 and s of its ends, of a contour in the x_1, x_2 plane can be found by integrating the traction vector $T_1 + iT_2$. Thus

$$-i(F_1 - iF_2) = -i \int_{s_0}^s (T_1 - iT_2) ds = \int_{s_0}^s (\sigma d\bar{z} + \tau dz). \quad (162)$$

Since the integrand $\sigma d\bar{z} + \tau dz$ is a perfect differential, the integral of eq. (162) can be calculated in any simply connected region containing no singularities to be

$$-i(F_1 - iF_2) = \bar{z}\Phi(z, t) + \bar{\varphi}(\bar{z}, t) + \psi(z, t) - \frac{E}{6(1-\nu)} \lambda \Omega \int_{f(z,t)}^{\bar{z}} [C(z, \zeta, t) - C_0] d\zeta. \quad (163)$$

3.3 Edge dislocation and point force

Consider a stress free infinite solid with a uniform hydrogen composition C_0 . The linear elastic constitutive behavior of the material is characterized by the isotropic moduli E , ν and G at fixed solute concentration C_0 . At time $t=0$ an edge dislocation with Burgers vector $b = b_1 + i b_2$ is suddenly introduced, but quasi-statically, and a point force $P = P_1 + iP_2$, which is also turned on at the same time, acts at the origin. The dislocation and force are to be maintained at all times $t > 0$. As a result, there exist chemical potential gradients which motivate hydrogen diffusion. Eventually, at $t = \infty$, the material is characterized by the moduli E^μ , ν^μ , and $G^\mu = G$ at fixed solute chemical potential and the hydrogen concentration field C assumes its steady state value

$$(C - C_0)_\infty = \frac{12(\nu - \nu^\mu)(1 - \nu)}{E(1 - \nu^\mu)} \frac{1}{\lambda\Omega} \operatorname{Re}[\Phi(z, \infty)], \quad (164)$$

which is found by combining eqs. (145) and (148). In these two limit cases, i.e at $t=0$ and $t=\infty$, the classical elasticity solution applies and the corresponding complex potentials $\Phi(z)$ and $\Psi(z)$ are well known and given by

$$\Phi(z) = \frac{1}{1 - \nu^e} \frac{\mathcal{D}}{z}, \quad (165)$$

$$\Psi(z) = \frac{-2G\bar{b} + (3 - 4\nu^e)i\bar{P}}{8\pi i(1 - \nu^e)} \frac{1}{z}, \quad (166)$$

where

$$\mathcal{D} = \frac{2Gb - iP}{8\pi i}, \quad (167)$$

$\nu^e = \nu$ at $t = 0^+$ and $\nu^e = \nu^\mu$ at $t = \infty$. In addition, the in-plane hydrostatic stress in these two limit cases is given by

$$\sigma_{yy} = 4 \frac{\mathcal{D}}{1 - \nu^e} \operatorname{Re}\left[\frac{1}{z}\right]. \quad (168)$$

By comparing eqs. (149) and (168), one deduces that at $t=0^+$ and $t=\infty$ the function $\Phi(z,t)$ should be of the form

$$\Phi(z,t) = \frac{1}{1-v} \frac{\mathcal{D}}{z}, \quad (169)$$

and therefore condition $\Phi(z,0^+) = \Phi(z,\infty)$ is satisfied. Next a solution is found which verifies that function $\Phi(z,t)$ is time independent.

Substituting eq. (169) into the boundary condition (164), one finds

$$(C - C_0)_\infty = \frac{6(v - v^\mu)}{E(1-v^\mu)} \frac{1}{\lambda\Omega} \left(\frac{\mathcal{D}}{z} + \frac{\bar{\mathcal{D}}}{\bar{z}} \right). \quad (170)$$

Also

$$(C - C_0)_{0^+} = 0 \quad (171)$$

at $t=0^+$. The solution to the transient hydrogen diffusion eq. (129) subject to conditions (170) and (171) is given by

$$C - C_0 = \frac{6(v - v^\mu)}{E(1-v^\mu)} \frac{1}{\lambda\Omega} \left(\frac{\mathcal{D}}{z} + \frac{\bar{\mathcal{D}}}{\bar{z}} \right) \exp \left(-\frac{z\bar{z}}{4D_{eff}t} \right). \quad (172)$$

Notice that as the distance from the origin increases the hydrogen concentration C , calculated from eq. (172), tends to the nominal concentration C_0 which prevails far away from the dislocation core where the lattice is essentially unstressed. Solution (172) is compatible with dislocation cores which exhibit an infinite capacity to accommodate hydrogen on the tensile side and an infinite ability of the compressive side to provide hydrogen. The latter implies negative hydrogen concentrations in the region of compressive hydrostatic stress. This result, which is discussed in detail in the next section, is related directly to the linearized theory used to characterize the hydrogen diffusion.

In order to use eqs. (159) and (163) the integral

$$\begin{aligned}
I &= \int_{z_0}^{\bar{z}} \left(\frac{\mathcal{D}}{z} + \frac{\bar{\mathcal{D}}}{\zeta} \right) \exp \left(-\frac{z\zeta}{4D_{eff}t} \right) d\zeta \\
&= \frac{4\mathcal{D}D_{eff}t}{z^2} \left[\exp \left(-\frac{zz_0}{4D_{eff}t} \right) - \exp \left(-\frac{z\bar{z}}{4D_{eff}t} \right) \right] + \bar{\mathcal{D}} \log \left(\frac{\bar{z}}{z_0} \right) + \int_{z_0}^{\bar{z}} \left[\exp \left(-\frac{z\zeta}{4D_{eff}t} \right) - 1 \right] \frac{\bar{\mathcal{D}}}{\zeta} d\zeta
\end{aligned} \quad (173)$$

is needed where the function $f(z,t)$ has been replaced by the real constant z_0 . It will be seen that $z_0 = 0$ in order for the transient solution to agree with the classical elasticity solution at $t = 0^+$, eq. (171), and $t = \infty$, eq. (170). In that case eq. (173) indicates that I diverges at the origin and generates a jump in $u_1 + iu_2$ and $F_1 + iF_2$ as in the classical elasticity. Notice also that this jump in I is independent of time. Thus, as RICE and CLEARY (1976) observe, only the integral's contribution which generates a function with a branch cut associated with a jump in the displacement and force will be considered. Hence

$$I = \frac{4\mathcal{D}D_{eff}t}{z^2} \left[1 - \exp \left(-\frac{z\bar{z}}{4D_{eff}t} \right) \right] + \bar{\mathcal{D}} \log \bar{z} + \int_0^{\bar{z}} \left[\exp \left(-\frac{z\zeta}{4D_{eff}t} \right) - 1 \right] \frac{\bar{\mathcal{D}}}{\zeta} d\zeta. \quad (174)$$

Next, it is proposed that

$$\varphi(z,t) = A(t) \log z \quad \text{and} \quad \psi(z,t) = B(t) \log z \quad (175)$$

so that the jump conditions generated by eqs. (174) and (175) when using them in eqs. (159) and (163) take the forms

$$2G\bar{b} = (3 - 4v)(-2\pi i)\bar{A}(t) - 2\pi iB(t) - 2\pi i \frac{v - v^\mu}{(1-v)(1-v^\mu)} \bar{\mathcal{D}}, \quad (176)$$

$$i\bar{P} = -2\pi i\bar{A}(t) + 2\pi iB(t) + 2\pi i \frac{v - v^\mu}{(1-v)(1-v^\mu)} \bar{\mathcal{D}}. \quad (177)$$

The solution to the system of eqs. (176) and (177) is time independent, i.e.

$$A(t) = A = \frac{\mathcal{D}}{1-v} \quad \text{and} \quad B(t) = B = \frac{-2G\bar{b} + (3-4v^\mu)i\bar{P}}{8\pi i(1-v^\mu)}. \quad (178)$$

Substituting this result into eqs. (175) and using eqs. (160) and (161) with $f(z,t) = 0$, one finds

$$\Phi(z,t) = \frac{1 - \nu}{z} \frac{\mathcal{D}}{1 - \nu^\mu}, \quad (179)$$

in agreement with eq. (169) at time $t=0$ and $t=\infty$, and

$$\Psi(z,t) = \frac{-2G\bar{b} + (3 - 4\nu^\mu)i\bar{P}}{8\pi i(1 - \nu^\mu)} \frac{1}{z}. \quad (180)$$

So the complex potentials $\Phi(z,t)$ and $\Psi(z,t)$ for the transient stress field are correspondingly the complex potential $\Phi(z)$ at time $t=0^+$, i.e. at fixed solute composition, and the complex potential $\Psi(z)$ at time $t=\infty$, i.e. at fixed solute chemical potential. The time dependent stress field may now be obtained from eqs. (152) and (154). For this purpose the integral $\int_{z_0}^z \frac{\partial [C(z,\zeta,t) - C_0]}{\partial z} d\zeta$ is needed, and in fact with use of eq. (172)

$$\int_{z_0}^z \frac{\partial [C(z,\zeta,t) - C_0]}{\partial z} d\zeta = \frac{6(\nu - \nu^\mu)}{E(1 - \nu^\mu)} \frac{1}{\lambda\Omega} \left\{ \begin{aligned} & \frac{8\mathcal{D}D_{eff}t}{z^3} \left[\exp\left(-\frac{z\bar{z}}{4D_{eff}t}\right) - \exp\left(-\frac{zz_0}{4D_{eff}t}\right) \right] \\ & + \frac{\mathcal{D}}{z^2} \left[\bar{z} \exp\left(-\frac{z\bar{z}}{4D_{eff}t}\right) - z_0 \exp\left(-\frac{zz_0}{4D_{eff}t}\right) \right] \\ & + \frac{\bar{\mathcal{D}}}{z} \left[\exp\left(-\frac{z\bar{z}}{4D_{eff}t}\right) - \exp\left(-\frac{zz_0}{4D_{eff}t}\right) \right] \end{aligned} \right\}. \quad (181)$$

By imposing the known elasticity solution at $t=0^+$ and $t=\infty$ in eq. (154), one deduces $z_0 = 0$, as has already been mentioned, and hence

$$\int_{z_0}^z \frac{\partial [C(z, \zeta, t) - C_0]}{\partial z} d\zeta = \frac{6(v - v^\mu)}{E(1 - v^\mu)} \frac{1}{\lambda \Omega} \left\{ \begin{aligned} & \frac{8\mathcal{D}D_{eff}t}{z^3} \left[\exp\left(-\frac{z\bar{z}}{4D_{eff}t}\right) - 1 \right] \\ & + \frac{\mathcal{D}}{z^2} \bar{z} \exp\left(-\frac{z\bar{z}}{4D_{eff}t}\right) \\ & + \frac{\bar{\mathcal{D}}}{z} \left[\exp\left(-\frac{z\bar{z}}{4D_{eff}t}\right) - 1 \right] \end{aligned} \right\}. \quad (182)$$

Application: an isolated edge dislocation

In the case of an isolated edge dislocation with Burgers vector \mathbf{b} parallel to the x_1 axis, as is shown in Fig. 2, $P = 0$ and $\mathcal{D} = Gb/4\pi i$. Then the linearized transient hydrogen concentration field is given by eq. (172) as

$$\frac{C}{C_0} = 1 - \frac{3}{2\pi} \frac{(v - v^\mu)}{(1 + v)(1 - v^\mu)} \frac{b}{c_0 \lambda} \frac{\sin \theta}{r} \exp\left(-\frac{r^2}{4D_{eff}t}\right), \quad (183)$$

and at $t = \infty$, i.e at steady state,

$$\frac{C}{C_0} = 1 - \frac{3}{2\pi} \frac{(v - v^\mu)}{(1 + v)(1 - v^\mu)} \frac{b}{c_0 \lambda} \frac{\sin \theta}{r}. \quad (184)$$

One may check the result of eq. (184) by calculating the steady state hydrogen concentration directly from the non-linear form (100) for the chemical potential of hydrogen. Substituting the result of eq. (122) for the hydrogen expansion tensor into eq. (100) and imposing the condition $\nabla \mu = 0$ for neutral chemical potential, one finds

$$\frac{\nabla C}{C} = \frac{\lambda \Omega \nabla \sigma_{kk}}{3kT_0}. \quad (185)$$

By observing that at regions far away from the dislocation core the unstressed lattice, $\sigma = 0$, is characterized by hydrogen concentrations at the nominal level C_0 , one may integrate eq. (185) to find

$$\frac{C}{C_0} = \exp\left(\frac{\lambda\Omega\sigma_{kk}}{3kT_0}\right) \quad (186)$$

at $t = \infty$. Substituting into eq. (186) the value for σ_{kk} as calculated from the classical elasticity solution for the dislocation stress field with use of the moduli at fixed solute chemical potential yields the nonlinear steady state solution as

$$\frac{C}{C_0} = \exp\left(-\frac{3}{2\pi} \frac{(v - v^\mu)}{(1+v)(1-v^\mu)} \frac{b}{c_0\lambda} \frac{\sin\theta}{r}\right). \quad (187)$$

This Boltzmann type of approximation (HIRTH and CARNAHAN, 1978) predicts infinite solute concentration in the tensile side of the dislocation core and zero in the compressive. Comparing eqs. (184) and (187) one verifies that when the distance r from the dislocation core is large the linearized solution (184) for the hydrogen concentration at steady state is equal to the first two terms in the Taylor series expansion of the concentration as is given by eq. (187). This result indicates that the linearized solution is fairly accurate at regions remote from the core where the hydrogen concentration does not deviate markedly from the nominal value. Consequently the linearized solution (184) is not expected to represent the hydrogen concentration field close to the core because the linearization condition of small $C - C_0$ is not met. In fact, as has already been discussed, eq. (184) predicts for $0 < \theta < \pi$ negative hydrogen concentrations within a circular region whose cutoff radius increases with time. At steady state this radius is maximum and given by

$$\frac{r_0}{b} = \frac{3(v - v^\mu)\sin\theta}{2\pi c_0\lambda(1+v)(1-v^\mu)}. \quad (188)$$

The cutoff radius r_0 at $\theta = \pi/2$ defines a circular region in which the linearized solution (183) fails to be valid at least in the compressive side of the dislocation. It should be mentioned though that neither is the nonlinear solution (187) valid close to the core, where a Fermi-Dirac form (HIRTH and CARNAHAN, 1978) is more appropriate than the Boltzmann approximation of eq. (187). In Fig. 3, the steady state hydrogen concentration C / C_0 , as given by eqs. (184) and (187) in the H/Ta system, is plotted against the normalized distance r / b at $\theta = 3\pi/2$, (see Fig. 2), at temperature 300K and nominal hydrogen concentration of 0.1H/Ta. Concentrations predicted by the linearized solution (184) are in agreement with those of the nonlinear solution (187) only when $r / b > 6$. The same result is also valid in the case of Nb/H and V/H systems. The linearized solution fails to predict the hydrogen concentration very close to the dislocation core because of the prevailing severe concentration gradients which render the linearization of the field equations invalid. Therefore the proposed linearized solution (184) is only a far field solution.

The transient stress field is determined by observing that when $P = 0$ and $\mathcal{D} = Gb/4\pi i$ the complex potentials of eqs. (179) and (180) take the form

$$\Phi(z, t) = \frac{1 - \mathcal{D}}{1 - v^{\mu}} z \quad \text{and} \quad \Psi(z, t) = -\frac{1 - \mathcal{D}}{1 - v^{\mu}} \frac{\mathcal{D}}{z}. \quad (189)$$

Substituting eqs. (172), (182) and (189) into eqs. (152) and (154) and using

$$\frac{\sigma_{rr} + \sigma_{\theta\theta}}{2} = \sigma \quad \text{and} \quad \frac{\sigma_{\theta\theta} - \sigma_{rr}}{2} + i\sigma_{r\theta} = \tau \exp(2i\theta), \quad (190)$$

one finds

$$\sigma_{rr} = \frac{\mu b}{2\pi(1-v)(1-v^{\mu})} \left\{ -(1-v^{\mu}) - (v - v^{\mu}) \frac{4D_{eff}t}{r^2} \left[\exp\left(-\frac{r^2}{4D_{eff}t}\right) - 1 \right] \right\} \frac{\sin\theta}{r}, \quad (191)$$

$$\sigma_{\theta\theta} = \frac{\mu b}{2\pi(1-\nu)(1-\nu^\mu)} \left\{ -(1-\nu^\mu) - (\nu - \nu^\mu) \left[\frac{2 \exp\left(-\frac{r^2}{4D_{eff}t}\right) +}{\frac{4D_{eff}t}{r^2} \left(\exp\left(-\frac{r^2}{4D_{eff}t}\right) - 1 \right)} \right] \right\} \frac{\sin \theta}{r}, \quad (192)$$

$$\sigma_{r\theta} = \frac{\mu b}{2\pi(1-\nu)(1-\nu^\mu)} \left\{ (1-\nu^\mu) + (\nu - \nu^\mu) \frac{4D_{eff}t}{r^2} \left[\exp\left(-\frac{r^2}{4D_{eff}t}\right) - 1 \right] \right\} \frac{\cos \theta}{r}. \quad (193)$$

4. IMPLICATIONS FOR DISLOCATION PLASTICITY AND FRACTURE

Using the constitutive description of the hydrogen/metal system in conjunction with standard linear elasticity results for lattice defect interactions, one may draw some important conclusions about the hydrogen effect on the deformation of materials under fixed solute chemical potential conditions of hydrogen diffusion (RICE, 1992a).

The interaction force between two parallel edge dislocations is proportional to $G/(1-\nu)$. It has been found that the Poisson's ratio ν^μ at fixed solute chemical potential is less than the Poisson's ratio ν at fixed solute composition. Therefore the interaction between two edge dislocation becomes smaller when the hydrogen in solution reaches equilibrium with the applied stress. This result has also been found by SOFRONIS and BIRNBAUM (1993) who modeled the interaction between two edge dislocations numerically. It should be mentioned that weakening of the interaction between edge dislocations is the physical basis of the hydrogen enhanced localized plasticity (HELP) model of hydrogen embrittlement (SIROIS, SOFRONIS and BIRNBAUM, 1992; SIROIS and BIRNBAUM, 1992; BIRNBAUM and SOFRONIS, 1993).

The energy per unit length of an edge dislocation is proportional to $G/(1-\nu)$ and that of a screw dislocation is proportional to G . It is very likely that the Poisson's ratio ν^H at fixed solute chemical potential may become negative, locally, close to the dislocation core where large hydrogen accumulation is predicted. As a consequence, segments of edge dislocations become energetically more favorable than those of screw dislocations since the energy of an edge dislocation is less than the energy of a screw dislocation. Therefore hydrogen may limit the ability of dislocations to cross slip. ULMER and ALTSTETTER (1991) suggested this effect as a possible mechanism of hydrogen induced cracking by proposing that hydrogen provides a force which tends to maintain the dislocations in the edge configuration, making relaxation of the pile up stress field by screw dislocation cross slip more difficult.

The Griffith theory of brittle fracture and the new theory of RICE (1992b) for dislocation nucleation from a crack tip suggest that the critical stress intensity factor, squared, is proportional to $G/(1-\nu)$ multiplied either by the surface energy, $2\gamma_s$, or by the unstable stacking energy γ_u . Therefore, at equilibrium conditions, hydrogen through its Poisson's ratio effect can trigger dislocation injection at a crack tip or can cause a crack to propagate.

4. CLOSURE

A linearized hydrogen elasticity theory has been developed which describes the coupling of the lattice hydrogen diffusion and the linear elastic deformation of a solid containing interstitial hydrogen in solid solution.

The linearized hydrogen diffusion is governed by the standard Fick's law where the normal lattice diffusion constant has been replaced by an effective diffusion constant in order to account for the drift due to hydrostatic stress. The effective diffusion constant depends only on the nominal hydrogen concentration

and reference temperature, the hydrogen and solvent material parameters, and does not depend on stress. Therefore the existing diffusion solutions for various specimen geometries can be used to study hydrogen diffusion under stress at given nominal solute concentration. As an example, the coupled transient field equations were solved analytically in the case of hydrogen diffusing towards the tension side of the core of an isolated edge dislocation in an infinite medium under plane strain deformation conditions.

The constitutive response of the solid solution at fixed solute chemical potential was found to resemble that of a fluid-infiltrated porous material during drained deformation at constant pore pressure or the thermoelastic response of a solid under isentropic straining. The linear elastic moduli at fixed solute chemical potential have been calculated as functions of the nominal hydrogen concentration in terms of the moduli at fixed solute nominal composition, the reference temperature, and the material parameters of the system. Therefore at steady state conditions of hydrogen migration, when the gradients of the solute chemical potential have been neutralized, the hydrogen effect on the linear elastic constitutive behavior is depicted in and modeled through the constitutive moduli. The implications of this result are important in understanding the hydrogen effect on dislocation plasticity and fracture of metals and alloys. Thus, using the linear elastic results for the dislocation stress fields, one deduces that hydrogen causes material softening by reducing the interaction between edge dislocation, enhances the planarity of slip by reducing the strain energy of an edge dislocation relative to the strain energy of a screw dislocation, decreases the intensity of the loads required to cause a crack to propagate, and assists the dislocation injection ahead of a crack tip according to RICE's (1992b) new theory for dislocation nucleation. These effects are in excellent agreement with the hydrogen enhanced localized plasticity model of hydrogen embrittlement proposed by BIRNBAUM and his co-workers (1992, 1993).

ACKNOWLEDGEMENTS

The author is indebted to Professor J. R. RICE for suggesting the topic of this paper and for the helpful correspondence during the development of this research. He is also grateful to Professor H. K. BIRNBAUM for providing invaluable advice during the course of this work and to Professor D. E. CARLSON for the helpful discussions on the theory of thermoelasticity. In addition, the research was supported by the Department of Energy through contract DEFGO2-91ER45439 with the Materials Research Laboratory at the University of Illinois at Urbana-Champaign.

REFERENCES

- BIRNBAUM, H. K. and SOFRONIS, P. (1993) *Mat. Sci. Eng.*, submitted.
- CARLSON, D. E. (1972) *Mechanics of Solids*, Vol. II, p. 297 (edited by C. Truesdell), Springer-Verlag Berlin, Heidelberg.
- COLEMAN, B. D. and NOLL, W. (1963) *Arch. Rational Mech. Anal.* **13**, 167.
- DUTTON, R., NUTTALL, K, PULS, M. P. and SIMPSON, L. A. (1977) *Met. Trans.* **8A**, 1553.
- HIRTH, J. P. (1980) *Met. Trans.* **11A**, 861.
- HIRTH, J. P. and CARNAHAN, B. (1978) *Acta Metall.* **26**, 1795.
- HIRTH, J. P. and LOTHE, J. (1982) *Theory of Dislocations*, John Wiley & Sons, Inc.
- JOHNSON, H. H. (1974) *Hydrogen in Metals*, p. 35, (edited by I. M. Bernstein and A. W. Thompson), ASM, Ohio.
- LARCHE, F. C. and CAHN, J. W. (1985) *Acta Metall.* **33**, 331.
- LIU, H. W. (1970) *J. Basic Eng.*, Trans. ASME, **92**, 633.
- MAZZOLAI, F. M. and BIRNBAUM, H. K. (1985a) *J. Phys. F: Met. Phys.* **15**, 507.
- MAZZOLAI, F. M. and BIRNBAUM, H. K. (1985b) *J. Phys. F: Met. Phys.* **15**, 525.
- METALS HANDBOOK (1985) (edited by H.E. Boyer and T. L. GALL), ASM, Ohio.
- MUSKHELISHVILI, N. I. (1953) *Some Basic Problems in the Mathematical Theory of Elasticity*, translated from the Russian by J. R. M. Radok, Noordhoff, Groningen, Netherlands.
- PEISL, H. (1978) *Hydrogen in Metals, Topics in Applied Physics*, Vol. 28, p. 53, (edited by G. Alefeld and J. Volkl), Springer-Verlag Berlin, Heidelberg.
- RICE, J. R. (1992a) Private communication.
- RICE, J. R. (1992b) *J. Mech. Phys. Solids*, **40**, 239.
- RICE, J. R. and CLEARY, M. P. (1976) *Rev. Geophys. Space Phys.* **14**, 227.
- SIROIS, E. and BIRNBAUM, H. K. (1992) *Acta Metall.* **40**, 1377.

- SIROIS, E., SOFRONIS, P. and BIRNBAUM, H. K. (1992) *Fundamental Aspects of Stress Corrosion Cracking* (Proc. of Parkins Symposium), p. 173 (edited by S. M. Bruemmer, E. I. Meletis, R. H. Jones, W. W. Gerberich, F. P. Ford, and R. W. Staehle), The Minerals, Metals and Materials Society.
- SOFRONIS, P. and BIRNBAUM, H. K. (1993) To be published.
- SOKOLNIKOFF, I. S. (1956) *Mathematical Theory of Elasticity*, McGraw-Hill, New York.
- TRUESELL, C. and NOLL, W. (1965) *Handbuch der Physik*. Vol. III/3, p. 297 (edited by S. Flugge), Springer-Verlag Berlin, Heidelberg, New York.
- VAN LEEUWEN, H. P. (1974) *Eng. Fract. Mech.* **6**, 141.
- ULMER, D. G. and ALTSTETTER, C. J. (1991) *Acta Metall.* **39**, 1237.

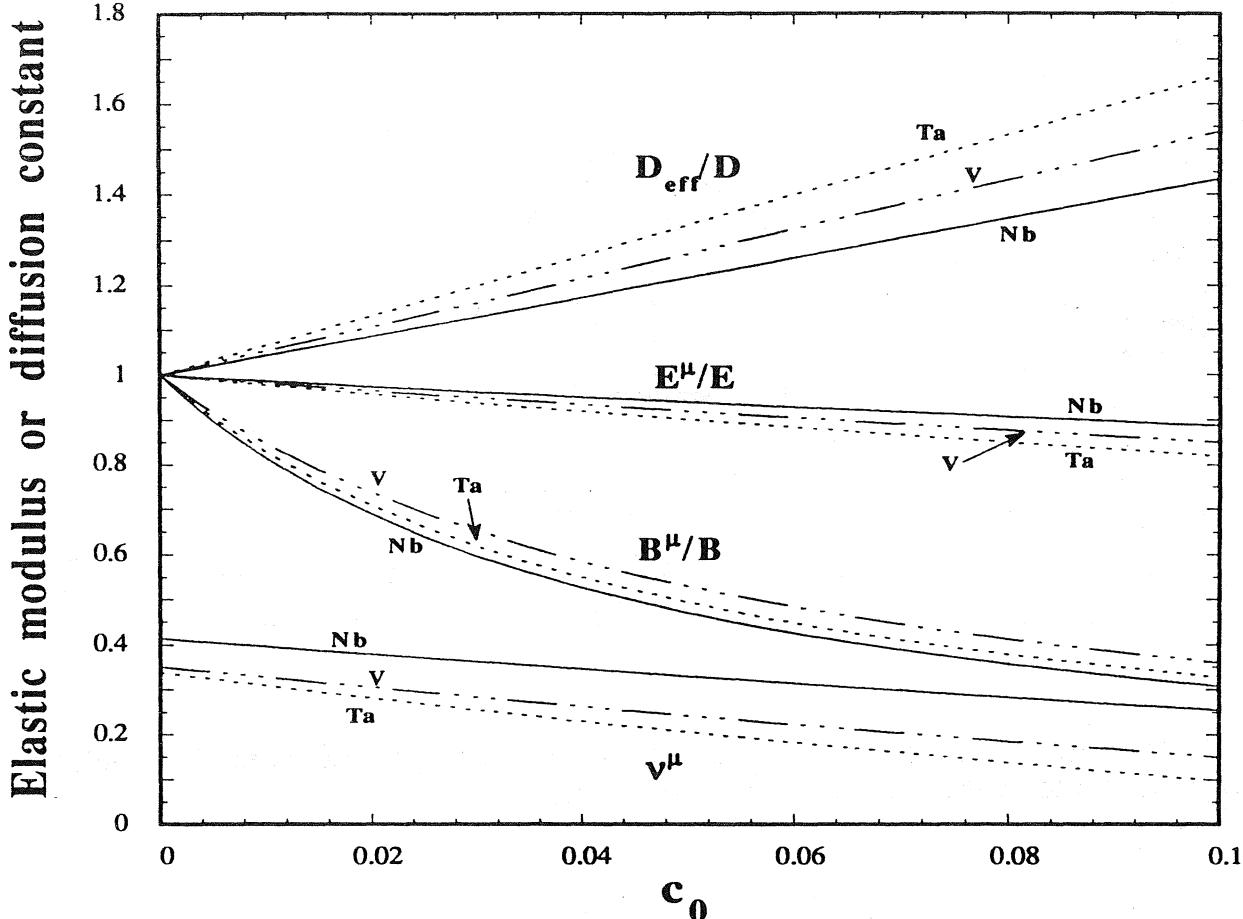


Fig. 1. Plot of Young's modulus E^{μ}/E , bulk modulus B^{μ}/B , and Poisson's ratio v^{μ} at fixed solute chemical potential; and of effective diffusion constant D_{eff}/D vs nominal hydrogen concentration c_0 in the Ta/H, Nb/H and V/H systems at temperature 300K. Nominal concentration c_0 is measured in hydrogen atoms per metal atom. Constants E and B are Young's and bulk modulus for the hydrogen free material respectively, and D is the normal lattice diffusion constant.

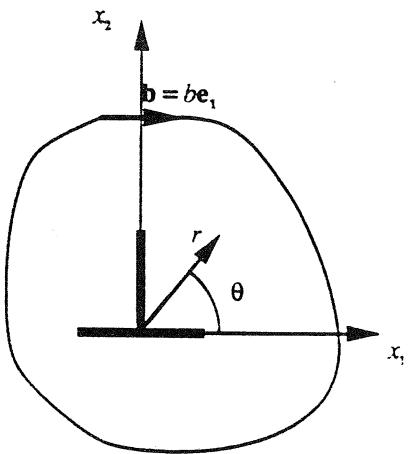


Fig. 2. An edge dislocation at the origin of the coordinates in the plane. Parameter b is the magnitude of the dislocation's Burgers vector.

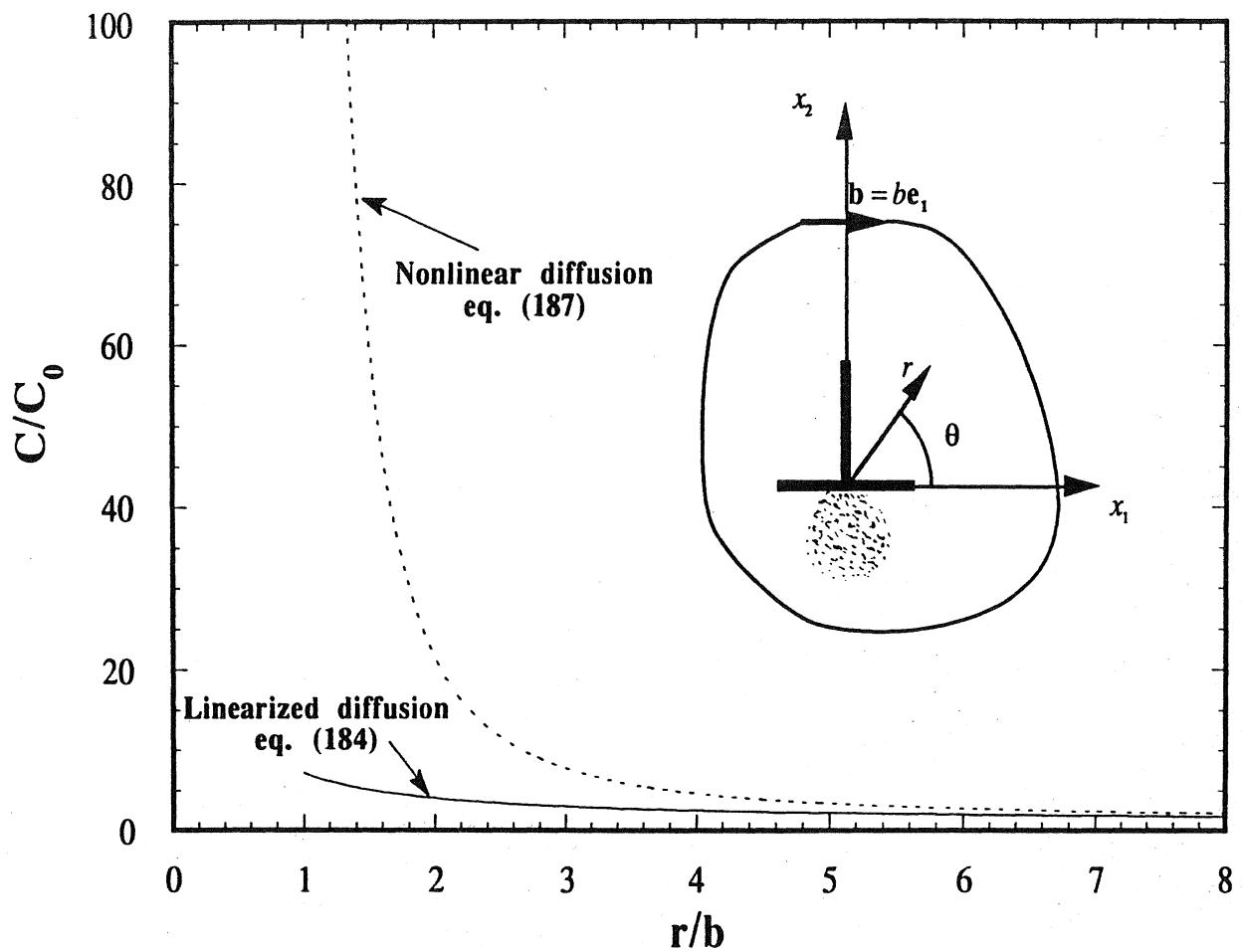
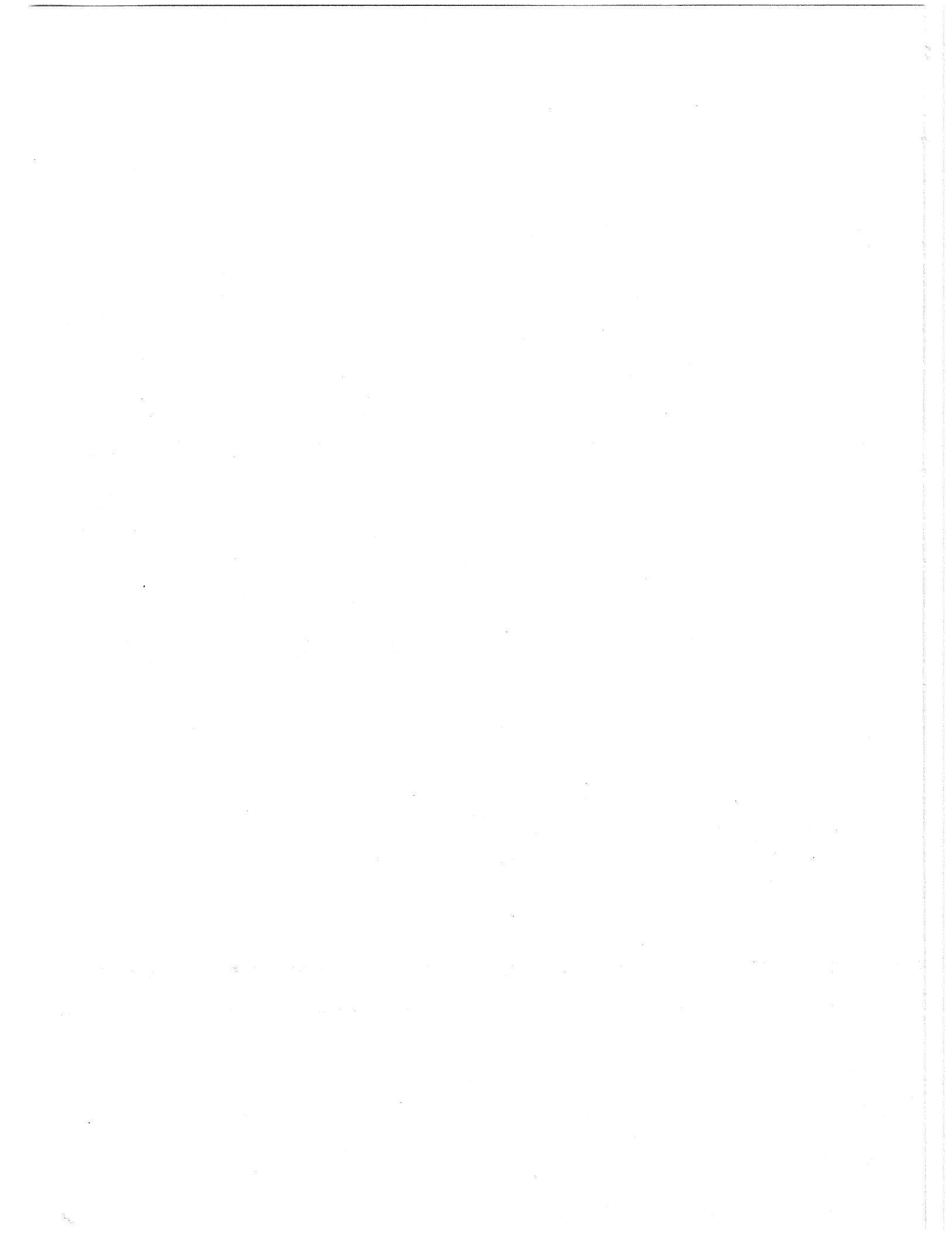


Fig. 3. Plot of the steady state hydrogen concentration c_0/c at an edge dislocation with Burgers vector magnitude b in the H/Ta system vs normalized distance r/b at $\theta = 3\pi/2$, temperature 300K, and nominal hydrogen concentration of 0.1 H/Ta.



List of Recent TAM Reports

No.	Authors	Title	Date
490	Dasgupta, A.	An experimental investigation of homogeneous fatigue damage in a random short-fiber composite under combined tension-torsion loading	Dec. 1988
491	Lee, H.-I., and D. S. Stewart	Calculation of linear detonation instability--Part I: One-dimensional instability of plane detonation	Dec. 1988
492	Weaver, R. L.	Diffusivity of ultrasound in polycrystals	Feb. 1989
493	Shawki, T. G., R. J. Clifton, and Y. Kadioglu	Calculation of the viscoplastic response of polycrystals from slip theory for FCC single crystals	Mar. 1989
494	Toro, J. R.	Existence of weak solutions to the thick plate problem with various boundary conditions	Apr. 1989
495	Stewart, D. S., and B. W. Asay	Discrete modeling of beds of propellant exposed to strong stimulus	Apr. 1991
496	Klein, R., and D. S. Stewart	The relation between curvature, rate state dependence, and detonation velocity	Apr. 1991
497	Powers, J. M., and D. S. Stewart	Approximate solutions for oblique detonations in the hypersonic limit	Apr. 1991
498	Davidson, M. T., K. L. Kuster, K. W. Quinn, N. A. Sluz, and G. Stojkovich	Twenty-fifth student symposium on engineering mechanics, M. E. Clark, coord. (1988)	Feb. 1992
499	Cardenas, H. E., W. C. Crone, D. J. Scott, G. G. Stewart, and B. F. Tatting	Twenty-sixth student symposium on engineering mechanics, M. E. Clark, coord. (1989)	Mar. 1992
500	Juister, C. E., D. W. Newport, C. S. Payne, J. M. Peters, M. P. Thomas, and J. C. Trovillion	Twenty-seventh student symposium on engineering mechanics, M. E. Clark, coord. (1990)	Apr. 1992
701	Bernard, R. T., D. W. Claxon, J. A. Jones, V. R. Nitzsche, and M. T. Stadtherr	Twenty-eighth student symposium on engineering mechanics, M. E. Clark, coord. (1991)	Apr. 1992
702	Greening, L. E., P. J. Joyce, S. G. Martensen, M. D. Morley, J. M. Ockers, M. D. Taylor, and P. J. Walsh	Twenty-ninth student symposium on engineering mechanics, J. W. Phillips, coord. (1992)	May 1992
703	Kuah, H. T., and D. N. Riahi	Instabilities and transition to chaos in plane wakes	Nov. 1992
704	Stewart, D. S., K. Prasad, and B. W. Asay	Simplified modeling of transition to detonation in porous energetic materials	Nov. 1992
705	Stewart, D. S., and J. B. Bdzil	Asymptotics and multi-scale simulation in a numerical combustion laboratory	Jan. 1993
706	Hsia, K. J., Y.-B. Xin, and L. Lin	Numerical simulation of semi-crystalline Nylon 6: Elastic constants of crystalline and amorphous parts	Jan. 1993
707	Hsia, K. J., and J. Q. Huang	Curvature effects on compressive failure strength of long fiber composite laminates	Jan. 1993
708	Jog, C. S., R. B. Haber, and M. P. Bendsoe	Topology design with optimized, self-adaptive materials	Mar. 1993
709	Barkey, M. E., D. F. Socie, and K. J. Hsia	A yield surface approach to the estimation of notch strains for proportional and nonproportional cyclic loading	Apr. 1993
710	Feldsien, T. M., A. D. Friend, G. S. Gehner, T. D. McCoy, K. V. Remmert, D. L. Riedl, P. L. Scheiberle, and J. W. Wu	Thirtieth student symposium on engineering mechanics, J. W. Phillips, coord. (1993)	Apr. 1993
711	Weaver, R. L.	Anderson localization in the time domain: Numerical studies of waves in two-dimensional disordered media	Apr. 1993
712	Cherukuri, H. P., and T. G. Shawki	An energy-based localization theory	Apr. 1993
713	Manring, N. D., and R. E. Johnson	Modeling a variable-displacement pump	June 1993
714	Birnbaum, H. K., and P. Sofronis	Hydrogen-enhanced localized plasticity—A mechanism for hydrogen-related fracture	July 1993
715	Balachandar, S., and M. R. Malik	Inviscid instability of streamwise corner flow	July 1993
716	Sofronis, P.	Linearized hydrogen elasticity	July 1993

