

A ONE-DIMENSIONAL INTRODUCTION TO CHEMICAL STRAINS AND STRESSES WITH APPLICATIONS TO DIFFUSION IN CRACKED SOLIDS

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ABSTRACT

When a solid of nonuniform concentration is stressed, a flux of atoms is produced by not only just the concentration gradient but also a potential gradient. This latter effect is traditionally termed a stress-assisted diffusion by a chemical potential gradient. This potential depends, among other possible causes, the external load-induced stresses as well as those necessitated by a nonuniform concentration. A nonuniform concentration is accompanied by a state of eigentransformation, which, in view of its dependence on the associated molar volumes, may be called a chemical eigentransformation (or chemical strain for short). Chemical eigentransformations are, in general, incompatible and must be, in turn, accompanied by geometrically necessary elastic transformations. Such types of concentration-induced stresses are coupled to the ordinary load-affected stresses in the strain energy portion of the free energy. The derivative of the free energy with respect to the chemical eigentransformation is a generalized energy momentum tensor, which tends to the energy momentum tensor of Eshelby as the eigentransformation tends to the identity transformation. At the same time, the chemical potential deduced from the free energy is a functional of the load and concentration. It becomes a functional of only the load when the concentration is uniform. The diffusion promoted by such a load-induced potential are commonly known to be linearly coupled to the elastic field. The coupling disappears when the load-induced elastic field is quasi-static. Our coupled equations are built on the full nonlinear energy momentum tensor and the stress-assisted diffusion persists, as long as the elastic deformation is nonuniform.

A one-dimensional introduction to chemical strains and stresses is used in this paper to illustrate the roles of a generalized energy momentum tensor in chemical potentials and the associated bulk and surface diffusion. The general three-dimensional equations are used to demonstrate the effects of singularly nonuniform stress states on diffusion.

1 INTRODUCTION

The effect of a nonuniform elastic stress on diffusion is a flux of atoms driven by a stress potential V . In the context of linear elasticity, this potential is commonly taken to be the trace of the stress tensor σ_{kk} and the associated diffusion equation is

$$\frac{\partial c}{\partial t} = D \nabla \left[\nabla c + \frac{c \nabla V}{kT} \right], \quad (1)$$

where $c(x,y,z,t)$ is the concentration and all the symbols have the usual meaning. Applying the above to the situation where c is initially uniform everywhere, one reaches the conclusion that the solution for very short times is governed by

$$\frac{\partial c}{\partial t} = \frac{Dc}{kT} \nabla^2 V. \quad (2)$$

Since $\nabla^2 \sigma_{kk} = 0$, elastic stresses do not drive diffusion even if they are singularly nonuniform. It was shown in [1], however, that the stress potential V is actually more than just the trace of the

stress tensor. This is particularly true when the underlying solid is anisotropic [2]. In this paper the dependence of the stress potential on the energy momentum tensor, which is termed a chemical stress, is illustrated via a one-dimensional formalism. The general three-dimensional equation is then introduced to examine the effect of a singularly nonuniform stress field on crack-tip diffusion.

2 FORMULATION

Let B_Z be a mathematical one-dimensional reference body with reference points Z , $0 \leq Z \leq L$, where L is the total length. A one-dimensional material body is fabricated by placing $C^*(Z)$ mol/m of a mixture at Z ($C^*(Z)$ may be taken to be the total molar concentration at Z if the cross-sectional area of B_Z is 1 m^2). Since the molar length of such a one-dimensional material is a material property, the length, L , of the reference body and a prescribed $C^*(Z)$ define the length of the fabricated body. To fix ideas, consider a binary mixture defined by

$$C^* = C_1^* + C_2^*, \quad 1 = \mathbf{x}_1 + \mathbf{x}_2 \quad (3)$$

where \mathbf{x}_1 and \mathbf{x}_2 are mole fractions. Since the two mole fractions are not independent, we express them in terms of a single mole-fraction value \mathbf{x} as follows

$$\mathbf{x}_1 = \mathbf{x}, \quad \mathbf{x}_2 = 1 - \mathbf{x} \quad (4)$$

We denote the isothermal stress-free molar length by $\underline{\ell}(\mathbf{x})$. Then, $\lambda^* = C^* \underline{\ell}(\mathbf{x})$ is merely an eigen-stretch ratio such that an element dZ in B_Z is transformed into a stress-free element $dZ^{\text{SF}} = \lambda^* dZ$. Such a transformed state is usually redefined in terms of a conveniently chosen uniform state defined by

$$C_0^* = C_{10}^* + C_{20}^*, \quad 1 = \mathbf{x}_{10} + \mathbf{x}_{20}, \quad \lambda_0^* = C_0^* \underline{\ell}(\mathbf{x}_0), \quad \mathbf{x}_0 = \mathbf{x}_{10} = 1 - \mathbf{x}_{20} \quad (5)$$

The transformation from the mathematical reference body B_Z to a uniform material reference body B defined by eqn (5) is simply

$$dX = \lambda_0^* dZ \quad \text{and} \quad X = \lambda_0^* Z \quad (6)$$

For nonuniform states defined by $C_1^* = C_{10}^* + \Delta C_1^*$, $C_2^* = C_{20}^* + \Delta C_2^*$, the following identities apply:

$$\lambda^* = \lambda_0^* + \bar{\ell}_1(\mathbf{x}_0) \Delta C_1^* + \bar{\ell}_2(\mathbf{x}_0) \Delta C_2^* \quad (7)$$

$$\lambda^* = \lambda_0^* \left[1 + \bar{\ell}_1(\mathbf{x}_0) \frac{\Delta C_1^*}{\lambda_0^*} + \bar{\ell}_2(\mathbf{x}_0) \frac{\Delta C_2^*}{\lambda_0^*} \right] = \lambda_0^* \Lambda^* \quad (8)$$

$$\Lambda^* = 1 + \bar{\ell}_1(\mathbf{x}_0) \frac{\Delta C_1^*}{\lambda_0^*} + \bar{\ell}_2(\mathbf{x}_0) \frac{\Delta C_2^*}{\lambda_0^*} = 1 + \bar{\ell}_1(\mathbf{x}_0) \Delta C_1 + \bar{\ell}_2(\mathbf{x}_0) \Delta C_2 \quad (9)$$

where $\bar{\ell}_i$ are the partial molar length and $\Delta C_i = C_i - C_{i0}$ the nonuniform concentration variables defined per unit length of the uniform state and are expressed in X . They are respectively defined by

$$\bar{\ell}_i = \frac{\partial}{\partial C_i} \left[C(\bar{\ell}(\mathbf{x})) \right] \Big|_{C_0, C_2}, \quad \Delta C_i = \frac{\Delta C_i^*}{\lambda_0^*}. \quad (10)$$

The eigen-stretch ratio Λ^* , which relates dZ^{SF} to dX , is now clearly defined. Since the eigen-stretch ratio depends only on the composition of the mixture, it may be referred to as a chemical stretch ratio. If we use $\mathbf{x} = \mathbf{x}(X)$ to define the spatial position of the one-dimensional body, then the total stretch ratio $\Lambda(X)$, elastic stretch ratio $\Lambda^e(X)$ and $\Lambda^*(X)$ are related by

$$\frac{dx}{dX} = \Lambda, \quad \frac{dZ^{\text{SF}}}{dX} = \Lambda^*, \quad \frac{dx}{dZ^{\text{SF}}} = \Lambda^e = \frac{\Lambda}{\Lambda^*}, \quad (11)$$

which will be used to define the free energy.

Let $A(\Lambda, C_1, C_2)$ be the Helmholtz free energy per unit length of the material reference body B in X. We have

$$\begin{aligned} A(\Lambda, C_1, C_2) &= C \underline{A}(\Lambda^e \Lambda^*, \mathbf{x}) \\ &= C \left[\underline{A}(\Lambda^*, \mathbf{x}) + \frac{\Lambda^*}{C} W^{\text{SF}}(\Lambda^e) \right] \\ &= C \underline{A}(\Lambda^*, \mathbf{x}) + \Lambda^* W^{\text{SF}}(\Lambda / \Lambda^*) \\ &= C \underline{G}(\sigma, \mathbf{x})_{\sigma=0} + \Lambda^* W^{\text{SF}}(\Lambda / \Lambda^*) \\ &= C \underline{G}^{\text{SF}}(\mathbf{x}) + \Lambda^* W^{\text{SF}}(\Lambda / \Lambda^*) \\ &= C \underline{G}^{\text{SF}}(\mathbf{x}) + W(\Lambda, \Lambda^*) \end{aligned} \quad (12)$$

where \underline{A} is the molar Helmholtz energy, W^{SF} the strain energy per unit length of stress-free material, G^{SF} the stress-free molar Gibbs energy, and W the strain energy per unit length of the uniform material body, all defined for isothermal conditions. It follows from the thermodynamic identity

$$\dot{A} = \frac{\partial A}{\partial \Lambda} \dot{\Lambda} + \frac{\partial A}{\partial C_1} \dot{C}_1 + \frac{\partial A}{\partial C_2} \dot{C}_2 = \sigma \dot{\Lambda} + \mu_1 \dot{C}_1 + \mu_2 \dot{C}_2 \quad (13)$$

that

$$\begin{aligned} \mu_i &= \bar{G}_i^{\text{SF}} + \left[W^{\text{SF}} - (\Lambda^e - 1)\sigma - \sigma \right] \frac{\partial \Lambda^*}{\partial C_i} \\ &= \bar{G}_i^{\text{SF}} + \left[W^{\text{SF}} - (\Lambda^e - 1)\sigma - \sigma \right] \bar{\ell}_i(\mathbf{x}_0) \quad (i=1 \text{ and } 2) \end{aligned} \quad (14)$$

which is the full chemical potential that must be used in studying stress-assisted diffusion. It is noted that the quantity associated with the partial molar length is the energy momentum tensor in one dimension. In this sense it may be referred to as a chemical stress, which may be split into two parts, a complimentary energy density portion and a stress term, i.e.

$$\left[W^{\text{SF}} - \Lambda^e \sigma \right] = \left[W^{\text{SF}} - (\Lambda^e - 1)\sigma \right] - \sigma = \text{complimentary energy density} - \sigma. \quad (15)$$

The one-dimensional stress-assisted diffusion is, therefore, governed by

$$\frac{\partial c}{\partial t} = D \nabla \left[\nabla c + \frac{c}{kT} \nabla \left\{ \left[W^{SF} - (\Lambda^e - 1) \sigma \right] - \sigma \right\} \right]. \quad (16)$$

The three-dimensional counterpart of the above is

$$\frac{\partial c}{\partial t} = D \nabla \left[\nabla c + \frac{c}{kT} \nabla \left(W^{SF} - \sigma_{kk} \right) \right] \quad (17)$$

which is to be compared with eqn (1). It is noted that the diffusion is now dependent on the nonuniform elastic stress even though $\nabla^2 \sigma_{kk} = 0$. The diffusion around a crack tip is examined in this paper via the use of this equation.

References

- [1] Wu, C. H., The role of Eshelby stress ion composition-generated and stress-assisted diffusion. *J. Mech. Phys. Solids*, 49, 1771-1794, 2001.
- [2] Wu, C. H., A crystal structure-based eigentransformation and its work-conjugate material stress. *EUROMECH COLLOQUIUM 445*, University of Kaiserslautern, May 21-24, 2003.