

A CRYSTAL STRUCTURE-BASED EIGENTRANSFORMATION AND ITS WORK-CONJUGATE MATERIAL STRESS

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Abstract

In the abstract of his 1970 paper, Eshelby stated: “*The force on a dislocation or point defect, as understood in solid-state physics, and the crack extension force of fracture mechanics are examples of quantities which measure the rate at which the total energy of a physical system varies as some kind of departure from uniformity within it changes its configuration.*” He then went on to demonstrate that the elastic energy-momentum tensor proves to be a useful tool in calculating such forces. The ‘forces’ turn out to be the appropriate traction vectors associated with the energy-momentum (stress) tensor. It is therefore natural and perhaps even fundamental to look for the ‘strain tensor’ that can be paired with the ‘stress tensor’ to form work. The ‘strain rate’ would then be that some kind of departure from uniformity within a physical system. In this paper, we examine the configurational changes brought about by atomic diffusion in a nonuniform alloy crystal. The transformation from a reference, single-parameter simple cubic cell to a six-parameter alloy crystal cell, called the eigentransformation, is identified as the needed kinematic tensor.

1. Introduction

We again quote Eshelby (1970) from the introduction of the same paper: “*In solid-state theory, theoretical metallurgy, fracture mechanics, and elsewhere, there are departures from uniformity in a material on various scales which, for want of a better term, we shall call defects. ... The configuration of the defects can be specified by a number, possibly infinite, of parameters.*” Here, the term defect is used to describe departures from uniformity in materials, and the geometric configurations of such defects are to be represented by a number of parameters. Toward the end of formulating a continuum theory, however, the possibly infinite number of parameters can be meaningfully converted into a finite number of field variables. In case atomic diffusion is the appropriate physical mechanism, a field of nonuniform molar concentrations becomes the defect of an alloy crystal. What is then the configuration, which is nothing but the time-geometry of the crystal, affected by this defect? In general, the composition of a crystal can vary from the stoichiometric value without altering the type of structure, although the edge lengths and interaxial angles may change slightly (Barrett, 1973). The transformation from a reference cell, which may be conveniently taken as a simple cubic cell, to a triclinic cell becomes the natural kinematic variable for describing the defect.

Eshelby continued in his introduction: “*Following the terminology of analytical mechanics and thermodynamics we call the rate of decrease of the total energy of the system with respect to a parameter the generalized force acting on that parameter, or, in simple cases, on the defect itself. ... It is always the total energy which is important, the energy of the system we concentrate*

our attention on, and which contains the defect, plus the energy of the environment with which it interacts, in our case some mechanical loading device. ... In thermodynamics the matter is handled by introducing enthalpy and Gibbs free energy, quantities which though nominally referring to the system under observation actually relate to the energy of the system plus the energy of its environment.” The concept conveyed in these statements, which are directly applicable to defects specified by parameters, can be straightforwardly extended to situations where defects are field variables. What is needed in this transition is an energy density per unit reference volume that is actually a function of the defect field. Such an energy density is constructed in this paper in terms of the molar Gibbs energy for zero stress and the strain energy density per unit stress-free volume. To convert the latter from per stress-free volume to per reference volume, three sets of kinematical variables are needed: an eigentransformation, which describes the defect field, a deformation gradient, which ties the reference configuration to the spatial configuration, and finally an elastic transformation. It should be noted that the mathematic structure of this scheme was first recognized by Epstein and Maugin (1990) as a way to obtain the energy-momentum tensor as the derivative of the energy density with respect to a kinematic tensor that we call eigentransformation. That the eigentransformation can actually be tied to the molar volume of a physical system, so that atomic diffusion and elastic deformation become coupled nonlinear phenomena in isotropic solids, appears to have been first recognized by Wu (2001). This result is now extended to anisotropic solids in this paper. We use the fact that the composition of a crystal can vary from the stoichiometric value without altering the type of structure, although the edge lengths and interaxial angles may change slightly (Barrett, 1973). Thus, the eigentransformation associated with an anisotropic crystal is in general fully populated, instead of showing a mere isotropic expansion.

Eshelby concluded his introduction in the quoted paper with the admission: *“The writer should perhaps admit that this tensor has become an obsession with him since he first noticed its connection with the force on a defect, and no doubt it appears at some points in the argument where one could get along without.”* This writer must admit that finding the work-conjugate tensor of the energy-momentum tensor has also become an obsession with him ever since he seemed to have understood the implication of this so-called materials stress. The result presented in this paper is but one specific case that can only be applied to atomic diffusion in nonuniform crystals. Eigentransformations for other physical systems must be built upon specific physical mechanisms. It appears, however, that once a mechanism is identified and properly formulated, one just could not get along without the knowledge of the associated energy-momentum tensor in studying the evolution of the underlying mechanism.

2. Kinematics

Kinematics deals with the time-geometry of motions of bodies. It is not in any way concerned with the causes of motions. Let \mathbf{X} denote the coordinates of points in a continuum in some reference configuration $V(\mathbf{X})$ that is just a region of the ambient Euclidean space. The coordinate of the place occupied by \mathbf{X} at time t is given by

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

and $v(\mathbf{x})$ is the spatial configuration, another region of the Euclidean space, taken up by $V(\mathbf{X})$ at time t . The velocity of the point \mathbf{X} is denoted by

$$\dot{\mathbf{y}}(\mathbf{X}, t) = \frac{\partial}{\partial t} \mathbf{y}(\mathbf{X}, t). \quad (2.2)$$

The spatial configuration $v(\mathbf{x})$ is customarily referred to as the **deforming body**, and the above velocity the **motion velocity** when the transformation $\mathbf{X} \rightarrow \mathbf{x}$ is caused by Newtonian body forces and surface tractions. The transformation may also be the result of **eigentransformations** brought about by such nonelastic strains as thermal expansion, phase transformation, initial strains, plastic and misfit strains (Mura, 1982). For such cases, the above velocity may be referred to as the **configurational velocity**, even though the function $\mathbf{y}(\mathbf{X}, t)$ is the so-called total deformation that consists of the generally incompatible eigentransformation and an accompanying elastic transformation. This observation is however not pursued further in this paper. In the most general case, of course, the effects of Newtonian forces and eigentransformations are coupled. The deformation gradient \mathbf{F} or the Jacobian matrix, and the associated Jacobian J are

$$\mathbf{F} = \nabla \mathbf{y}(\mathbf{X}, t), \quad J = \det \mathbf{F}. \quad (2.3)$$

The transformation of volumes between reference and spatial coordinates is given by

$$dv(\mathbf{x}) = JdV(\mathbf{X}). \quad (2.4)$$

The eigentransformations studied in this paper are the result of nonuniform composition in a \mathcal{C} -component system. Let a single-phase mixture of \mathcal{C} components be defined by \mathcal{C} molar concentrations C_i [mol/m³], so that the total molar concentration (or simply molar density) C and the associated mole fractions $\mathbf{x}_i = C_i/C$ satisfy

$$C = \sum_{i=1}^{\mathcal{C}} C_i, \quad 1 = \sum_{i=1}^{\mathcal{C}} \mathbf{x}_i. \quad (2.5)$$

The use of \mathbf{x}_i for mole fractions is a historical one that is commonly found in chemical treatment of mixtures and should not cause any confusion with the three components of the spatial coordinate representation \mathbf{x} . In fact, we will follow the practice of Sandler (1999) and use $\underline{\mathbf{x}}$ to represent the first $\mathcal{C}-1$ mole fractions for short, as only $\mathcal{C}-1$ of the mole fractions are independent by the second of (2.5). The \mathcal{C} components are the components of a triclinic system of edge lengths a , b , and c (along the corresponding crystal axes); and interaxial angles α , β and γ . We shall use $\mathbf{p} \equiv (a, b, c; \alpha, \beta, \gamma)$ to denote the six crystal lattice parameters for short. It is known that a composition of an alloy can vary from the stoichiometric value without altering the type of structure, although the crystal parameters generally change somewhat with composition. Thus, if a simple cubic cell in the reference configuration $V(\mathbf{X})$ is filled with the \mathcal{C} components in accordance with the local molar concentrations $C_i(\mathbf{X}, t)$, the cell by itself will develop into a stress-free crystal cell, of which the lattice parameters may be determined by the local composition, i.e.,

$$p = p(\underline{\mathbf{x}}(\mathbf{X}, t)) = (a, b, c; \alpha, \beta, \gamma)(\underline{\mathbf{x}}(\mathbf{X}, t)). \quad (2.6)$$

Let \mathbf{e}_I ($I = 1, 2, 3$) be the fixed unit vectors in \mathbf{X} , and \mathbf{a}_α ($\alpha = 1, 2, 3$) the three edge vectors of the stress-free crystal cell. The mapping that takes \mathbf{e}_I to \mathbf{a}_α is a linear transformation that will be denoted by \mathbf{F}^* in the development to follow. One convenient representation for \mathbf{F}^* would be $\mathbf{a}_\alpha = F_{\alpha I}^* \mathbf{e}_I$. While there is not a unique way to define \mathbf{F}^* , it suffices to say that \mathbf{F}^* is a function of the lattice parameters, which, in turn, are functions of the mole fractions that are actually functions of position and time in a nonuniform system.

Unless the stress-free crystal cells are identical they cannot be stacked together to form stress-free crystals. To form crystals from nonuniform stress-free cells additional elastic deformation, \mathbf{F}^e , must be imposed on all the cells and the final product is a crystal with residual stress, but without the influence of Newtonian body and surface forces. Such a crystalline body is termed a **free body** by Mura (1982). The result of applying \mathbf{F}^* to a differential element $d\mathbf{X}$ in $V(\mathbf{X})$ is another differential element, which will be denoted by $d\mathbf{X}^{\text{SF}}$, a stress-free element, i.e.,

$$d\mathbf{X}^{\text{SF}} = \mathbf{F}^* d\mathbf{X}, \quad dV^{\text{SF}} = \det \mathbf{F}^* dV = J^* dV. \quad (2.7)$$

The transformation \mathbf{F}^* is in general incompatible in the sense that the first of the above cannot be integrated to obtain \mathbf{X}^{SF} as single-valued functions of \mathbf{X} . The solid body, which occupies $V(\mathbf{X})$, is therefore forced to deform into a new configuration that occupies $v(\mathbf{x})$ in a spatial reference coordinate system \mathbf{x} . The associated transformation is the deformation gradient $\mathbf{F} = \partial \mathbf{x} / \partial \mathbf{X}$. Finally, the combination of \mathbf{F} and \mathbf{F}^* is termed the elastic transformation $\mathbf{F}^e = \mathbf{F} \mathbf{F}^{*-1}$. We have

$$d\mathbf{x} = \mathbf{F} d\mathbf{X}, \quad dv = J dV, \quad J = \det \mathbf{F} \quad (2.8)$$

$$d\mathbf{x} = \mathbf{F}^e d\mathbf{X}^{\text{SF}}, \quad dv = J^e dV^{\text{SF}}, \quad J^e = \det \mathbf{F}^e = J / J^* \quad (2.9)$$

which, together with (2.7), complete the needed three-frame kinematics illustrated in Fig. 1.

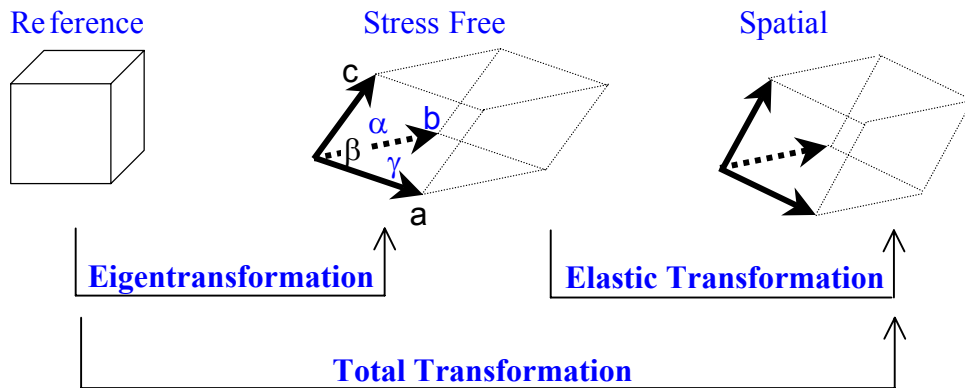


Fig.1. The three-frame kinematics

In terms of the volume elements dV , dV^{SF} and dv , the three sets of densities are:

$$C = \sum_{i=1}^{\mathcal{E}} C_i(\mathbf{X}, t), \quad C^{\text{SF}} = \sum_{i=1}^{\mathcal{E}} C_i^{\text{SF}}(\mathbf{X}, t), \quad c = \sum_{i=1}^{\mathcal{E}} c_i(\mathbf{x}, t). \quad (2.10)$$

There are also the identities:

$$J^* = dV^{\text{SF}} / dV = C / C^{\text{SF}}(\mathbf{X}, t) = C_i(\mathbf{X}, t) / C_i^{\text{SF}}(\mathbf{X}, t), \quad (2.11)$$

$$J = dv / dV = C / c(\mathbf{x}, t) = C_i(\mathbf{X}, t) / c_i(\mathbf{x}, t), \quad (2.12)$$

$$J^e = dv / dV^{\text{SF}} = C^{\text{SF}}(\mathbf{X}, t) / c(\mathbf{x}, t) = C_i^{\text{SF}}(\mathbf{X}, t) / c_i(\mathbf{x}, t), \quad (2.13)$$

$$x_i = c_i / c = C_i / C = C_i^{\text{SF}} / C^{\text{SF}} \quad (i = 1 \text{ to } \mathcal{E}). \quad (2.14)$$

We conclude this section by defining the following convenient symbols for a number of inverse quantities:

$$\mathbf{f} \equiv \mathbf{F}^{-1}, \quad j \equiv 1/J; \quad \mathbf{f}^* \equiv \mathbf{F}^{*-1}, \quad j^* \equiv 1/J^*; \quad \mathbf{f}^e \equiv \mathbf{F}^{e-1}, \quad j^e \equiv 1/J^e. \quad (2.15)$$

3. The Helmholtz Free Energy

The desired Helmholtz free energy per unit volume of $V(\mathbf{X})$ is

$$\mathbf{A}(\mathbf{F}, T, C_1, \dots, C_{\mathcal{E}}) = \mathbf{C}\underline{\mathbf{A}}(\mathbf{F}, T, \underline{\mathbf{x}}) = \mathbf{C}\underline{\mathbf{G}}(\mathbf{S}, T, \underline{\mathbf{x}}) + \mathbf{S} \cdot \mathbf{F} \quad \text{and} \quad \mathbf{F} = \mathbf{F}^e \mathbf{F}^* \quad (3.1)$$

where T is the temperature, $\underline{\mathbf{A}}(\mathbf{F}, T, \underline{\mathbf{x}})$ the molar Helmholtz energy, $\underline{\mathbf{G}}(\mathbf{S}, T, \underline{\mathbf{x}})$ the molar Gibbs energy and \mathbf{S} the Piola stress. The following conditions and substitutions are used:

$$\underline{\mathbf{A}}(\mathbf{I}, T_0, \underline{\mathbf{x}}_0) = 0, \quad (3.2)$$

$$\underline{\mathbf{A}}(\mathbf{F}^*, T, \underline{\mathbf{x}}) = \underline{\mathbf{G}}^{\text{SF}}(T, \underline{\mathbf{x}}) \equiv \underline{\mathbf{G}}(\mathbf{S}, T, \underline{\mathbf{x}})|_{\mathbf{S}=0}, \quad (3.3)$$

$$\begin{aligned} \underline{\mathbf{A}}(\mathbf{F}^e \mathbf{F}^*, T, \underline{\mathbf{x}}) &= \underline{\mathbf{A}}(\mathbf{F}^*, T, \underline{\mathbf{x}}) + \frac{C^{\text{SF}}}{C^{\text{SF}}} [\underline{\mathbf{A}}(\mathbf{F}^e \mathbf{F}^*, T, \underline{\mathbf{x}}) - \underline{\mathbf{A}}(\mathbf{F}^*, T, \underline{\mathbf{x}})] \\ &= \underline{\mathbf{A}}(\mathbf{F}^*, T, \underline{\mathbf{x}}) + \frac{1}{C^{\text{SF}}} W^{\text{SF}}(\mathbf{F}^e, T) \end{aligned} \quad (3.4)$$

The condition (3.2) sets the uniform state as a reference, (3.3) follows from the fact that \mathbf{F}^* is the stress-free eigentransformation at temperature T and composition $\underline{\mathbf{x}}$, and the definition of W^{SF} indicates that it is just the strain energy density per unit stress-free volume and $W^{\text{SF}}(\mathbf{I}, T, \underline{\mathbf{x}}) = 0$. Using the above properties, we obtain from (3.1)

$$A(\mathbf{F}, T, C_1, \dots, C_\ell) = C \underline{A}(\mathbf{F}^e \mathbf{F}^*, T, \underline{\mathbf{x}}) = C [\underline{A}(\mathbf{F}^*, T, \underline{\mathbf{x}}) + \frac{1}{C^{\text{SF}}} W^{\text{SF}}(\mathbf{F}^e, T)], \text{ or} \quad (3.5)$$

$$A(\mathbf{F}, T, C_1, \dots, C_\ell) = C \underline{G}(\mathbf{0}, T, \underline{\mathbf{x}}) + \frac{C}{C^{\text{SF}}} W^{\text{SF}}(\mathbf{F}^e, T, \underline{\mathbf{x}}) = C \underline{G}^{\text{SF}}(T, \underline{\mathbf{x}}) + J^* W^{\text{SF}}(\mathbf{F}^e, T), \quad (3.6)$$

where the dependence of W^{SF} on concentration has been ignored, as it is usually negligible. Before proceeding, we note that

$$J^* = J^*(\underline{\mathbf{x}}(\mathbf{X}, t)), \quad \mathbf{F}^e = \mathbf{F}(\mathbf{F}^*)^{-1} \quad \text{and} \quad \mathbf{F}^* = \mathbf{F}^*(\underline{\mathbf{x}}(\mathbf{X}, t)). \quad (3.7)$$

It is also noted that the very last term of (3.6) may be interpreted as the strain energy density per unit volume in $V(\mathbf{X})$, i.e.,

$$W(\mathbf{F}, t) = J^* W^{\text{SF}}(\mathbf{F}^e, T). \quad (3.8)$$

With the last two equations in mind and for isothermal conditions, we have from (3.6)

$$\begin{aligned} \dot{A}(\mathbf{F}, T, C_1, \dots, C_\ell) &= \frac{\partial A}{\partial \mathbf{F}} \cdot \dot{\mathbf{F}} + \sum_i \frac{\partial A}{\partial C_i} \cdot \dot{C}_i \\ &= \frac{\partial W}{\partial \mathbf{F}} \cdot \dot{\mathbf{F}} + \sum_i \frac{\partial}{\partial C_i} [C \underline{G}^{\text{SF}}(T, \underline{\mathbf{x}}) + J^* W^{\text{SF}}(\mathbf{F}^e, T)] \cdot \dot{C}_i \\ &= \frac{\partial W}{\partial \mathbf{F}} \cdot \dot{\mathbf{F}} + \sum_i \left\{ \bar{G}_i^{\text{SF}}(T, \underline{\mathbf{x}}) + \frac{\partial}{\partial C_i} [J^* W^{\text{SF}}(\mathbf{F}^e, T)] \right\} \cdot \dot{C}_i \\ &= \mathbf{S} \cdot \dot{\mathbf{F}} + \sum_i \mu_i \cdot \dot{C}_i \end{aligned} \quad (3.9)$$

In the above equation, the Piola stress \mathbf{S} and chemical potential μ_i are given by

$$\mathbf{S} = \frac{\partial A}{\partial \mathbf{F}} = \frac{\partial W}{\partial \mathbf{F}} = J^* \mathbf{S}^e(\mathbf{f}^*)^T, \quad \mathbf{S}^e \equiv \frac{\partial W^{\text{SF}}}{\partial \mathbf{F}^e}, \quad \mathbf{f}^* = (\mathbf{F}^*)^{-1} \quad (3.10)$$

$$\mu_i = \bar{G}_i^{\text{SF}}(T, \underline{\mathbf{x}}) + J^* \mathbf{C}^e \cdot \left[\frac{\partial \mathbf{F}^*}{\partial C_i}(\mathbf{f}^*)^T \right] = \bar{G}_i^{\text{SF}}(T, \underline{\mathbf{x}}) + \mathbf{C} \cdot \left[\mathbf{f}^* \frac{\partial \mathbf{F}^*}{\partial C_i} \right] \quad (3.11)$$

where \mathbf{C}^e and \mathbf{C} are the generalized materials or configurational stresses given by

$$\mathbf{C}^e = W^{\text{SF}} \mathbf{1} - (\mathbf{F}^e)^T \mathbf{S}^e, \quad \mathbf{C} = W \mathbf{1} - (\mathbf{F})^T \mathbf{S}. \quad (3.12)$$

It is now clear that the above tensors are needed in defining the chemical potentials, but the chemical potentials themselves are not tensors (Truskinovskiy, 1983).

4. Conclusions

The use of a simple cubic lattice as a common reference framework is found to be most convenient in describing nonuniform anisotropic crystal structures via the introduction of an eigentransformation. This practice is expected to be most useful in the treatment of bicrystal interfaces. The known phenomena of finite elastic deformation and atomic diffusion can now be seamlessly merged into a unified theory.

5. Acknowledgement

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6. References

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