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# A thermo-mechanically-coupled theory accounting for hydrogen diffusion and large elastic–viscoplastic deformations of metals

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## ABSTRACT

In this paper we develop a thermodynamically-consistent coupled-theory which accounts for diffusion of hydrogen, diffusion of heat, and large elastic–viscoplastic deformations of metals. The theory should be of utility in the analysis of hydrogen diffusion in elastic–plastically-deforming solids, an analysis which is an essential prerequisite for theoretical and numerical efforts aimed at modeling the integrity of structural components used for hydrogen gas storage and distribution.

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## 1. Introduction

Since the combustion of hydrogen produces only water as the combustion product, hydrogen is expected to play an increasingly important role as a “clean” fuel in the future.<sup>1</sup> However, hydrogen is a gas at ambient conditions, and the storage and distribution of hydrogen in its molecular or atomic form is a materials challenge (cf., e.g., Züttel et al., 2010). Atomic hydrogen, being the smallest of gaseous impurities, readily dissolves in and permeates through most materials. Hydrogen dissolution and permeation can be significant at high pressures which are expected to approach 100 MPa in some cases, and since hydrogen can embrittle materials it may affect the integrity of structural components used for hydrogen storage and distribution. Accordingly, it is important to understand and model the *coupled* diffusion–mechanics response of metallic components used to contain this gas, and this topic is receiving increasing attention because of its potential application to the development of the emerging technology of large-scale production, storage and distribution of hydrogen (cf., e.g., San Marchi et al., 2007; Dadfarnia et al., 2009, 2010).

The deleterious effects of hydrogen on the mechanical response of iron and steel are well-known (cf., e.g., Hirth, 1980). The precise

microscopic mechanisms by which hydrogen embrittles steels are still not very well understood or modeled. This topic continues to be the focus of intensive theoretical and experimental research (cf., e.g., Serebrinsky et al., 2004; Ramasubramaniam et al., 2008; Novak et al., 2010; Dadfarnia et al., 2010),<sup>2</sup> and is *not the focus of this paper*. Instead, our focus here is on the development of a continuum-level theory for the diffusion of hydrogen, coupled with the thermo–elastic–plastic response of materials, which, as emphasized by Birnbaum and Sofronis (1994), is an essential prerequisite to any attempt to address the issue of hydrogen-embrittlement-related failures in structural components.

It has long been observed that there is an asymmetry between the kinetics of absorption and the kinetics of evolution of hydrogen in steels, in that absorption proceeds with a larger apparent diffusivity than does evolution. This asymmetry in diffusivities is attributed to trapping of the hydrogen atoms at various microstructural “trapping sites,” which include interfaces between the matrix and various second-phase particles, grain boundaries, and dislocation cores. A widely-used micro-mechanical model for describing this asymmetry in diffusivities, is that of Oriani (1970). His model is

<sup>2</sup> As reviewed by Dadfarnia et al. (2010), research to date has identified the following two major mechanisms for hydrogen embrittlement: (i) hydrogen-enhanced decohesion—a mechanism induced by the segregation of hydrogen to microstructural interfaces such as grain-boundaries and particle/matrix interfaces, which leads to a reduction in the cohesive strength of the material; and (ii) hydrogen-enhanced localized plasticity—a mechanism induced by the segregation of hydrogen to dislocation cores, which leads to a reduction of the strength of barriers to dislocation motion, and thereby a reduction in the resistance to plastic flow.

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<sup>1</sup> Hydrogen is produced from water by electricity through an electrolyser, and the hydrogen so-produced is a “renewable” fuel only if it is produced directly from solar light, or indirectly from a renewable source, e.g., wind- or hydro-power (Züttel et al., 2010).

based on a crucial assumption regarding the effects of the microstructure on hydrogen transport and trapping. Oriani postulated that within a continuum-level material point, the microstructure affects the local distribution of hydrogen in a manner such that population of hydrogen in trapping sites is always in equilibrium with the population associated with normal lattice sites.

There is a long history of the study of species diffusion coupled to elasticity, and the status of mathematical modeling of the coupled diffusion–deformation interactions of interstitial (as well as substitutional) solutes in crystalline solids undergoing small elastic deformations, has been reviewed, in a classical paper, by Larché and Cahn (1985). One of the earliest papers which attempts to couple nonlinear diffusion of hydrogen with large elastoplastic deformation of metals is the seminal paper of Sofronis and McMeeking (1989), who formulated a theory which has Oriani's postulate of "local equilibrium" as one of its central ingredients. The theory of Sofronis and McMeeking was extended by Krom et al. (1999) to account for the effects of an increase in the number of trapping sites due to plastic deformation. This latter form of the theory, with minor modifications, is the one which is at present most often used to analyze the effects of interactions of hydrogen transport, elastic–plastic deformation, lattice-dilatation, and hydrogen-induced reduction of the resistance to plastic flow. A summary of this currently used coupled-theory may be found in Dadfarnia et al. (2009) and Miresmaeili et al. (2010), and references to the literature therein.

The purpose of this paper is to develop a thermo-mechanically-coupled theory accounting for hydrogen transport and large elastic–viscoplastic deformations within a modern continuum-mechanical framework. In doing so, we find that we cannot readily incorporate microstructural-level considerations of lattice and trapping sites and distinctions between lattice diffusivities and effective diffusivities. Although the experimental evidence of hydrogen-trapping is incontrovertible, we find Oriani's microstructural hypothesis to be of dubious validity and limited usefulness in formulating a consistent continuum-level coupled theory. Accordingly, in our continuum theory we do not attempt to explicitly incorporate microstructural considerations of lattice sites and trapping sites, and the attendant hypothesis of Oriani. Therefore the hydrogen diffusivity that we shall consider in our theory will de facto be an effective continuum-level diffusivity.

In formulating our theory, we limit our considerations to isotropic materials at low homologous temperatures,<sup>3</sup> and for these conditions we develop a reasonably general theory in Sections 2–8. We summarize the general theory in Section 9. In Section 10 we discuss a special set of constitutive equations which should be useful for applications. The specialized theory is similar in spirit to the theory of Sofronis–McMeeking, but has the following distinctive characteristics: (i) it is phrased entirely at the continuum-level; (ii) it is consistent with modern continuum thermodynamics; (iii) it is properly frame-indifferent; (iv) it uses modern  $\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$  kinematics to describe large elastic–plastic deformations; (v) it allows for thermally-activated rate-dependent plastic flow; and (vi) it is not restricted to isothermal conditions.

We emphasize that the purpose of this paper is only to report on the formulation of the theory. We leave a report concerning its numerical implementation and use for analysis of hydrogen transport, and the more difficult problem of hydrogen embrittlement, to future work.

## 2. Kinematics

Consider a macroscopically-homogeneous body  $B$  with the region of space it occupies in a fixed reference configuration, and de-

note by  $\mathbf{X}$  an arbitrary material point of  $B$ . A motion of  $B$  is then a smooth one-to-one mapping  $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$  with deformation gradient, velocity, and velocity gradient given by<sup>4</sup>

$$\mathbf{F} = \nabla \boldsymbol{\chi}, \quad \mathbf{v} = \dot{\boldsymbol{\chi}}, \quad \mathbf{L} = \text{grad } \mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}. \quad (2.1)$$

Following modern developments of large-deformation plasticity theory (cf., e.g., Anand and Gurtin, 2003; Gurtin and Anand, 2005), we base our theory on the Kröner (1960) decomposition

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p, \quad (2.2)$$

of the deformation gradient. Here, suppressing the argument  $t$ :

- (i)  $\mathbf{F}^e(\mathbf{X})$  represents the local deformation of material in an infinitesimal neighborhood of  $\mathbf{X}$  due to stretch and rotation of the microscopic lattice structure; and
- (ii)  $\mathbf{F}^p(\mathbf{X})$  represents the local deformation in an infinitesimal neighborhood of material at  $\mathbf{X}$  due to the motion of dislocations.

We refer to  $\mathbf{F}^e$  and  $\mathbf{F}^p$  as the elastic and plastic distortions, and we refer to the local space at  $\mathbf{X}$  represented by the range of  $\mathbf{F}^p(\mathbf{X})$ , as a local structural space.<sup>5</sup>

We assume that

$$J \stackrel{\text{def}}{=} \det \mathbf{F} > 0 \quad (2.3)$$

and hence, using (2.2),

$$J = J^e J^p, \quad \text{where } J^e \stackrel{\text{def}}{=} \det \mathbf{F}^e > 0 \quad \text{and} \quad J^p \stackrel{\text{def}}{=} \det \mathbf{F}^p > 0, \quad (2.4)$$

so that  $\mathbf{F}^e$  and  $\mathbf{F}^p$  are invertible.

The right polar decomposition of  $\mathbf{F}^e$  is given by

$$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e, \quad (2.5)$$

where  $\mathbf{R}^e$  is a rotation, while  $\mathbf{U}^e$  is a symmetric, positive-definite tensor with

$$\mathbf{U}^e = \sqrt{\mathbf{F}^{eT} \mathbf{F}^e}. \quad (2.6)$$

As is standard, we define

$$\mathbf{C}^e = \mathbf{U}^{e2} = \mathbf{F}^{eT} \mathbf{F}^e, \quad (2.7)$$

and refer to

$$\mathbf{E}^e = \frac{1}{2}(\mathbf{C}^e - \mathbf{1}), \quad (2.8)$$

as the elastic strain.

By (2.1)<sub>3</sub> and (2.2),

$$\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e-1}, \quad (2.9)$$

with

$$\mathbf{L}^e = \dot{\mathbf{F}}^e \mathbf{F}^{e-1}, \quad \mathbf{L}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p-1}. \quad (2.10)$$

The elastic and inelastic stretching and spin tensors are defined through

$$\left. \begin{aligned} \mathbf{D}^e &= \text{sym } \mathbf{L}^e, & \mathbf{W}^e &= \text{skw } \mathbf{L}^e, \\ \mathbf{D}^p &= \text{sym } \mathbf{L}^p, & \mathbf{W}^p &= \text{skw } \mathbf{L}^p, \end{aligned} \right\} \quad (2.11)$$

<sup>3</sup> That is for absolute temperatures  $\vartheta \leq 0.35\vartheta_m$ , where  $\vartheta_m$  is the melting temperature of the material.

<sup>4</sup> Notation: We use standard notation of modern continuum mechanics (Gurtin et al., 2010). Specifically:  $\nabla$  and  $\text{Div}$  denote the gradient and divergence with respect to the material point  $\mathbf{X}$  in the reference configuration;  $\text{grad}$  and  $\text{div}$  denote these operators with respect to the point  $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$  in the deformed body; a superposed dot denotes the material time-derivative. Throughout, we write  $\mathbf{F}^{e-1} = (\mathbf{F}^e)^{-1}$ ,  $\mathbf{F}^{e-T} = (\mathbf{F}^e)^{-T}$ , etc. We write  $\text{tr } \mathbf{A}$ ,  $\text{sym } \mathbf{A}$ ,  $\text{skw } \mathbf{A}$ ,  $\mathbf{A}_0$ , and  $\text{sym}_0 \mathbf{A}$  respectively, for the trace, symmetric, skew, deviatoric, and symmetric-deviatoric parts of a tensor  $\mathbf{A}$ . Also, the inner product of tensors  $\mathbf{A}$  and  $\mathbf{B}$  is denoted by  $\mathbf{A} : \mathbf{B}$ , and the magnitude of  $\mathbf{A}$  by  $|\mathbf{A}| = \sqrt{\mathbf{A} : \mathbf{A}}$ .

<sup>5</sup> Also sometimes referred to as the intermediate or relaxed local space at  $\mathbf{X}$ .

so that  $\mathbf{L}^e = \mathbf{D}^e + \mathbf{W}^e$  and  $\mathbf{L}^p = \mathbf{D}^p + \mathbf{W}^p$ .

We make two basic kinematical assumptions concerning plastic flow:

- (i) First, we make the standard assumption that *plastic flow is incompressible*, so that

$$J^p = \det \mathbf{F}^p = 1 \quad \text{and} \quad \text{tr} \mathbf{L}^p = \text{tr} \mathbf{D}^p = 0. \quad (2.12)$$

Hence, using (2.4)

$$J = J^e. \quad (2.13)$$

- (ii) Second, from the outset we constrain the theory by limiting our discussion to circumstances under which the material may be idealized as isotropic (cf. Appendix A). For isotropic elastic–viscoplastic theories utilizing the Kröner decomposition, it is widely assumed that the plastic flow is *irrotational*, in the sense that<sup>6</sup>

$$\mathbf{W}^p = \mathbf{0}. \quad (2.14)$$

Then, trivially,  $\mathbf{L}^p \equiv \mathbf{D}^p$  and

$$\dot{\mathbf{F}}^p = \mathbf{D}^p \mathbf{F}^p. \quad (2.15)$$

Let

$$d^p \stackrel{\text{def}}{=} |\mathbf{D}^p|, \quad (2.16)$$

denote a *scalar plastic flow rate*. Then, whenever  $d^p \neq 0$ ,

$$\mathbf{N}^p = \frac{\mathbf{D}^p}{d^p}, \quad \text{with} \quad \text{tr} \mathbf{N}^p = 0, \quad (2.17)$$

defines the *plastic flow direction*.

### 3. Frame-indifference

A *change in frame*, at each fixed time  $t$ , is a transformation—defined by a rotation  $\mathbf{Q}(t)$  and a spatial point  $\mathbf{y}(t)$ —which transforms *spatial points*  $\mathbf{x}$  to spatial points

$$\mathbf{x}^* = \mathcal{F}(\mathbf{x}), \quad (3.1)$$

$$= \mathbf{y}(t) + \mathbf{Q}(t)(\mathbf{x} - \mathbf{o}), \quad (3.2)$$

with  $\mathbf{o}$  a fixed spatial origin, and the function  $\mathcal{F}$  represents a rigid mapping of the observed space into itself. By (3.2) the transformation law for the motion  $\mathbf{x} = \chi(\mathbf{X}, t)$  has the form

$$\chi^*(\mathbf{X}, t) = \mathbf{y}(t) + \mathbf{Q}(t)(\chi(\mathbf{X}, t) - \mathbf{o}). \quad (3.3)$$

Hence the deformation gradient  $\mathbf{F}$  transforms according to

$$\mathbf{F}^* = \mathbf{Q}\mathbf{F}. \quad (3.4)$$

The reference configuration and the intermediate structural space are independent of the choice of such changes in frame; thus

$$\mathbf{F}^p \text{ is invariant under a change in frame.} \quad (3.5)$$

This observation (2.2) and (3.4) yield the transformation law

$$\mathbf{F}^{e*} = \mathbf{Q}\mathbf{F}^e. \quad (3.6)$$

Also, by (2.10)<sub>2</sub>

$$\mathbf{L}^p \text{ is invariant,} \quad (3.7)$$

and, by (2.10)<sub>1</sub>,  $\mathbf{L}^{e*} = \mathbf{Q}\mathbf{L}^e\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top$ , and hence

$$\mathbf{D}^{e*} = \mathbf{Q}\mathbf{D}^e\mathbf{Q}^\top, \quad \mathbf{W}^{e*} = \mathbf{Q}\mathbf{W}^e\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top. \quad (3.8)$$

Further, by (2.5),

$$\mathbf{F}^{e*} = \mathbf{Q}\mathbf{R}^e\mathbf{U}^e,$$

and we may conclude from the uniqueness of the polar decomposition that

$$\mathbf{R}^{e*} = \mathbf{Q}\mathbf{R}^e, \quad \text{and} \quad \mathbf{U}^e \text{ is invariant,} \quad (3.9)$$

and hence also that

$$\mathbf{C}^e \text{ and } \mathbf{E}^e \text{ are invariant.} \quad (3.10)$$

### 4. Balance of forces and moments

Throughout, we denote by  $P$  an arbitrary *part* (subregion) of the reference body  $B$  with  $\mathbf{n}_R$  the outward unit normal on the boundary  $\partial P$  of  $P$ .

Since time scales associated with species diffusion are usually considerably longer than those associated with wave propagation, we neglect all inertial effects. Then standard considerations of balance of forces and moments, when expressed referentially, give:

- (a) There exists a stress tensor  $\mathbf{T}_R$ , called the Piola stress, such that the surface traction on an element of the surface  $\partial P$  of  $P$ , is given by

$$\mathbf{t}_R(\mathbf{n}_R) = \mathbf{T}_R \mathbf{n}_R. \quad (4.1)$$

- (b)  $\mathbf{T}_R$  satisfies the macroscopic force balance

$$\text{Div} \mathbf{T}_R + \mathbf{b}_R = \mathbf{0}, \quad (4.2)$$

where  $\mathbf{b}_R$  is an external body force per unit reference volume, which, consistent with neglect of inertial effects, is taken to be time-independent.

- (c)  $\mathbf{T}_R$  obeys the symmetry condition

$$\mathbf{T}_R \mathbf{F}^\top = \mathbf{F} \mathbf{T}_R^\top, \quad (4.3)$$

which represents a balance of moments.

Further, under a change in frame  $\mathbf{T}_R$  transforms as

$$\mathbf{T}_R^* = \mathbf{Q}\mathbf{T}_R. \quad (4.4)$$

Finally, as is standard, the Piola stress  $\mathbf{T}_R$  is related to the standard symmetric Cauchy stress  $\mathbf{T}$  in the deformed body by

$$\mathbf{T}_R = J\mathbf{T}\mathbf{F}^{-\top}, \quad (4.5)$$

so that

$$\mathbf{T} = J^{-1}\mathbf{T}_R\mathbf{F}^\top; \quad (4.6)$$

and, as is also standard, under a change in frame,  $\mathbf{T}$  transforms as

$$\mathbf{T}^* = \mathbf{Q}\mathbf{T}\mathbf{Q}^\top. \quad (4.7)$$

### 5. Balance law for the diffusing species

Let  $C(\mathbf{X}, t)$  denote the *total number of moles of hydrogen atoms per unit reference volume*. Changes in  $C$  in a part  $P$  are brought about by the diffusion across its boundary  $\partial P$ . The diffusion is characterized by a *flux*  $\mathbf{j}_R(\mathbf{X}, t)$ , the number of moles of hydrogen measured per unit area per unit time, so that

$$-\int_{\partial P} \mathbf{j}_R \cdot \mathbf{n}_R da_R$$

represents the number of moles of hydrogen atoms entering  $P$  across  $\partial P$  per unit time.

<sup>6</sup> This assumption is adopted here solely on pragmatic grounds: when discussing finite deformations for isotropic materials the theory without plastic spin is far simpler than one with plastic spin.

Thus the rate of change of hydrogen in  $P$  is given by

$$\frac{d}{dt} \int_P C d\nu_R = - \int_{\partial P} \mathbf{j}_R \cdot \mathbf{n}_R da_R \quad (5.1)$$

for every part  $P$ . Bringing the time derivative in (5.1) inside the integral and using the divergence theorem on the integral over  $\partial P$ , we find that

$$\int_P (\dot{C} + \text{Div } \mathbf{j}_R) d\nu_R = 0. \quad (5.2)$$

Since  $P$  is arbitrary, this leads to the following local balance law for  $C$ ,

$$\dot{C} = -\text{Div } \mathbf{j}_R. \quad (5.3)$$

## 6. Balance of energy. Entropy imbalance

Our discussion of thermodynamics follows Gurtin et al. (2010, Section 64), and involves the following fields:

$\varepsilon_R$	the internal energy density per unit reference volume
$\eta_R$	the entropy density per unit reference volume
$\mathbf{q}_R$	the heat flux per unit reference area
$q_R$	the external heat supply per unit reference volume
$\vartheta$	the absolute temperature ( $\vartheta > 0$ )
$\mu$	the chemical potential

Consider a material region  $P$ . Then, consistent with our omission of inertial effects, we neglect kinetic energy, and take the balance law for energy as

$$\begin{aligned} \frac{d}{dt} \int_P \varepsilon_R d\nu_R &= \int_{\partial P} (\mathbf{T}_R \mathbf{n}_R) \cdot \dot{\boldsymbol{\chi}} da_R + \int_P \mathbf{b}_R \cdot \dot{\boldsymbol{\chi}} d\nu_R - \int_{\partial P} \mathbf{q}_R \cdot \mathbf{n}_R da_R \\ &\quad + \int_P q_R d\nu_R - \int_{\partial P} \mu \mathbf{j}_R \cdot \mathbf{n}_R da_R, \end{aligned} \quad (6.1)$$

where the last term in (6.1) represents the flux of energy carried into  $P$  by the flux  $\mathbf{j}_R$  of hydrogen atoms (Gurtin, 1996). Applying the divergence theorem to the terms in (6.1) involving integrals over the boundary  $\partial P$  of  $P$ , we obtain

$$\begin{aligned} \int_P (\dot{\varepsilon}_R - (\text{Div } \mathbf{T}_R + \mathbf{b}_R) \cdot \dot{\boldsymbol{\chi}} - \mathbf{T}_R : \dot{\mathbf{F}} + \text{Div } \mathbf{q}_R - q_R + \mu \text{Div } \mathbf{j}_R \\ + \mathbf{j}_R \cdot \nabla \mu) d\nu_R = 0, \end{aligned} \quad (6.2)$$

which upon use of the balance laws (4.2) and (5.3), and using the fact that (6.2) must hold for all parts  $P$ , gives the local form of the energy balance as

$$\dot{\varepsilon}_R = \mathbf{T}_R : \dot{\mathbf{F}} + \mu \dot{C} - \text{Div } \mathbf{q}_R + q_R - \mathbf{j}_R \cdot \nabla \mu. \quad (6.3)$$

Also, the second law takes the form of an entropy imbalance

$$\frac{d}{dt} \int_P \eta_R d\nu_R \geq - \int_{\partial P} \frac{\mathbf{q}_R \cdot \mathbf{n}_R}{\vartheta} da_R + \int_P \frac{q_R}{\vartheta} d\nu_R, \quad (6.4)$$

in which case the local entropy imbalance has the form

$$\dot{\eta}_R \geq -\text{Div} \left( \frac{\mathbf{q}_R}{\vartheta} \right) + \frac{q_R}{\vartheta}. \quad (6.5)$$

Then, in view of the local energy balance (6.3),

$$\begin{aligned} -\text{Div} \left( \frac{\mathbf{q}_R}{\vartheta} \right) + \frac{q_R}{\vartheta} &= \frac{1}{\vartheta} (-\text{Div } \mathbf{q}_R + q_R) + \frac{1}{\vartheta^2} \mathbf{q}_R \cdot \nabla \vartheta, \\ &= \frac{1}{\vartheta} \left( \dot{\varepsilon}_R - \mathbf{T}_R : \dot{\mathbf{F}} - \mu \dot{C} + \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla \vartheta + \mathbf{j}_R \cdot \nabla \mu \right), \end{aligned}$$

and this with the local entropy imbalance (6.5) implies that

$$(\dot{\varepsilon}_R - \vartheta \dot{\eta}_R) - \mathbf{T}_R : \dot{\mathbf{F}} - \mu \dot{C} + \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla \vartheta + \mathbf{j}_R \cdot \nabla \mu \leq 0. \quad (6.6)$$

Introducing the Helmholtz free energy

$$\psi_R = \varepsilon_R - \vartheta \eta_R, \quad (6.7)$$

(6.6) yields the following local free-energy imbalance

$$\dot{\psi}_R + \eta_R \dot{\vartheta} - \mathbf{T}_R : \dot{\mathbf{F}} - \mu \dot{C} + \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla \vartheta + \mathbf{j}_R \cdot \nabla \mu \leq 0. \quad (6.8)$$

The term  $\mathbf{T}_R : \dot{\mathbf{F}}$  in (6.8) represents the stress–power per unit reference volume. Using (2.2), (4.5) and (2.10)<sub>2</sub> the stress–power may be written as

$$\begin{aligned} \mathbf{T}_R : \dot{\mathbf{F}} &= \mathbf{T}_R : (\dot{\mathbf{F}}^e \mathbf{F}^p + \mathbf{F}^e \dot{\mathbf{F}}^p), \\ &= (\mathbf{T}_R \mathbf{F}^{pT}) : \dot{\mathbf{F}}^e + (\mathbf{F}^{eT} \mathbf{T}_R) : \dot{\mathbf{F}}^p, \\ &= (\mathbf{J} \mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-T}) : (\mathbf{F}^{eT} \dot{\mathbf{F}}^e) + (\mathbf{C}^e \mathbf{J} \mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-T}) : \mathbf{L}^p. \end{aligned} \quad (6.9)$$

In view of (6.9), we introduce two new stress measures:

- The elastic second Piola stress,

$$\mathbf{T}^e \stackrel{\text{def}}{=} \mathbf{J} \mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-T}, \quad (6.10)$$

which is *symmetric* on account of the symmetry of the Cauchy stress  $\mathbf{T}$ .

- The Mandel stress,

$$\mathbf{M}^e \stackrel{\text{def}}{=} \mathbf{C}^e \mathbf{T}^e, \quad (6.11)$$

which in general is *not symmetric*.

Note that on account of the transformation rule (3.6) for  $\mathbf{F}^e$ , and the transformation rule (4.7), the elastic second Piola stress and the Mandel stress are invariant under a change in frame,

$$\mathbf{T}^{e*} = \mathbf{T}^e \quad \text{and} \quad \mathbf{M}^{e*} = \mathbf{M}^e. \quad (6.12)$$

Further, from (2.7) and (2.8)

$$\dot{\mathbf{E}}^e = \frac{1}{2} \dot{\mathbf{C}}^e = \frac{1}{2} (\dot{\mathbf{F}}^{eT} \mathbf{F}^e + \mathbf{F}^{eT} \dot{\mathbf{F}}^e). \quad (6.13)$$

Thus, using the definitions (6.10) and (6.11) and the relation (6.13), the stress–power (6.9) may be written as

$$\mathbf{T}_R : \dot{\mathbf{F}} = \underbrace{\mathbf{T}^e : \dot{\mathbf{E}}^e}_{\text{elastic power}} + \underbrace{\mathbf{M}^e : \mathbf{L}^p}_{\text{plastic power}}. \quad (6.14)$$

**Remark 1.** The Mandel stress  $\mathbf{M}^e$  is plastic-power conjugate to the tensor  $\mathbf{L}^p$ , with both tensors defined in the intermediate structural space. Using the definitions (6.10) and (6.11) for elastic second Piola stress and the Mandel stress, respectively, the plastic power per unit reference volume may be written as

$$\mathbf{M}^e : \mathbf{L}^p = (\mathbf{J} \mathbf{T}) : (\mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e-1}), \quad (6.15)$$

which shows that the Kirchhoff stress ( $\mathbf{J} \mathbf{T}$ ) is plastic power conjugate to the *elastic push-forward* ( $\mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e-1}$ ) of  $\mathbf{L}^p$  to the deformed body.

Further, use of the assumptions (2.12) and (2.14) concerning plastic flow gives

$$\mathbf{T}_R : \dot{\mathbf{F}} = \mathbf{T}^e : \dot{\mathbf{E}}^e + \mathbf{M}_0^e : \mathbf{D}^p. \quad (6.16)$$

Using (6.16) in (6.8) allows us to write the free energy imbalance in the following useful form,

$$\dot{\psi}_R + \eta_R \dot{\vartheta} - \mathbf{T}^e : \dot{\mathbf{E}}^e - \mu \dot{C} - \mathbf{M}_0^e : \mathbf{D}^p + \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla \vartheta + \mathbf{j}_R \cdot \nabla \mu \leq 0. \quad (6.17)$$

Finally, note that  $\psi_R$ ,  $\eta_R$ ,  $\vartheta$ , and  $C$  are invariant under a change in frame since they are scalar fields, and on account of the



transformation rules discussed in Section 3, and the transformation rules (6.12), the fields

$$\mathbf{E}^e, \mathbf{D}^p, \mathbf{T}^e, \text{ and } \mathbf{M}^e, \tag{6.18}$$

are also invariant, as are the fields

$$\mathbf{q}_R, \nabla\vartheta, \mathbf{j}_R, \text{ and } \nabla\mu, \tag{6.19}$$

since they are referential vector fields.

### 7. Constitutive theory

#### 7.1. Energetic constitutive equations

Guided by the free-energy imbalance (6.17) we first consider the following set of constitutive equations for the free energy  $\psi_R$ , the stress  $\mathbf{T}^e$ , the entropy  $\eta_R$ , and the chemical potential  $\mu$ :

$$\left. \begin{aligned} \psi_R &= \bar{\psi}_R(\mathbf{\Lambda}), \\ \mathbf{T}^e &= \bar{\mathbf{T}}^e(\mathbf{\Lambda}), \\ \eta_R &= \bar{\eta}_R(\mathbf{\Lambda}), \\ \mu &= \bar{\mu}(\mathbf{\Lambda}), \end{aligned} \right\} \tag{7.1}$$

where  $\mathbf{\Lambda}$  denotes the list

$$\mathbf{\Lambda} = (\mathbf{E}^e, \vartheta, C). \tag{7.2}$$

Substituting the constitutive equations (7.1) into the free-energy imbalance (6.17), we find that it may then be written as

$$\left( \frac{\partial \bar{\psi}_R}{\partial \mathbf{E}^e} - \bar{\mathbf{T}}^e \right) : \dot{\mathbf{E}}^e + \left( \frac{\partial \bar{\psi}_R}{\partial \vartheta} + \bar{\eta}_R \right) \dot{\vartheta} + \left( \frac{\partial \bar{\psi}_R}{\partial C} - \bar{\mu} \right) \dot{C} - \mathbf{M}_0^e : \mathbf{D}^p + \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla\vartheta + \mathbf{j}_R \cdot \nabla\mu \leq 0. \tag{7.3}$$

This inequality is to hold for all values of  $\mathbf{\Lambda}$ . Since  $\dot{\mathbf{E}}^e$ ,  $\dot{\vartheta}$  and  $\dot{C}$  appear linearly, their ‘‘coefficients’’ must vanish, for otherwise  $\dot{\mathbf{E}}^e$ ,  $\dot{\vartheta}$ , and  $\dot{C}$  may be chosen to violate (7.3). We are therefore led to the thermodynamic restriction that the free energy determines the stress  $\mathbf{T}^e$ , the entropy  $\eta$ , and the chemical potential  $\mu$  through the ‘‘state relations’’

$$\left. \begin{aligned} \mathbf{T}^e &= \frac{\partial \bar{\psi}_R(\mathbf{\Lambda})}{\partial \mathbf{E}^e}, \\ \eta_R &= -\frac{\partial \bar{\psi}_R(\mathbf{\Lambda})}{\partial \vartheta}, \\ \mu &= \frac{\partial \bar{\psi}_R(\mathbf{\Lambda})}{\partial C}, \end{aligned} \right\} \tag{7.4}$$

and we are left with the following reduced dissipation inequality

$$\mathbf{M}_0^e : \mathbf{D}^p - \frac{1}{\vartheta} \mathbf{q}_R \cdot \nabla\vartheta - \mathbf{j}_R \cdot \nabla\mu \geq 0. \tag{7.5}$$

#### 7.2. Dissipative constitutive equations

Let

$$\dot{\bar{e}}^p \stackrel{\text{def}}{=} \sqrt{(2/3)d^p} = \sqrt{(2/3)|\mathbf{D}^p|} \geq 0, \tag{7.6}$$

define an *equivalent tensile plastic strain rate*.<sup>7</sup> Then, as is traditional, we define an *equivalent tensile plastic strain* by

$$\bar{e}^p(\mathbf{X}, t) \stackrel{\text{def}}{=} \int_0^t \dot{\bar{e}}^p(\mathbf{X}, \zeta) d\zeta, \quad \bar{e}^p(\mathbf{X}, 0) = 0, \tag{7.7}$$

and use it as a scalar *hardening variable* to account for the strain-hardening characteristics typically observed during plastic deformation.

<sup>7</sup> The quantity  $\dot{\bar{e}}^p$  defined in (7.6) is not a material time derivative of  $\bar{e}^p$ . This notation for the equivalent tensile plastic strain rate is traditional, and is a slight abuse of our notational convention that an overset dot represent a material time derivative.

Since  $\bar{e}^p$  is a scalar field it is invariant under a change in frame.

Next, guided by the dissipation inequality (7.5), and experience with existing plasticity theories, we assume that the plastic stretching is given in terms of the Mandel stress deviator, the temperature, the equivalent tensile plastic strain  $\bar{e}^p$ , and the hydrogen content  $C$ :

$$\mathbf{D}^p = \bar{\mathbf{D}}^p(\mathbf{M}_0^e, \vartheta, \bar{e}^p, C). \tag{7.8}$$

To the constitutive equation (7.8), we append a Fourier-type relation for the heat flux, and a Fick-type relation for the flux of the diffusing species,<sup>8</sup>

$$\left. \begin{aligned} \mathbf{q}_R &= -\mathbf{K}(\tilde{\mathbf{\Lambda}}) \nabla\vartheta, \\ \mathbf{j}_R &= -\mathbf{M}(\tilde{\mathbf{\Lambda}}) \nabla\mu, \end{aligned} \right\} \tag{7.9}$$

where  $\mathbf{K}$  is a *thermal conductivity tensor*, and  $\mathbf{M}$  is a *mobility tensor*, and where

$$\tilde{\mathbf{\Lambda}} = (\mathbf{E}^e, \vartheta, \bar{e}^p, C). \tag{7.10}$$

Using (7.8), (7.9), (2.16), (2.17) and (7.6), the dissipation inequality (7.5) may be written as

$$\sqrt{3/2}(\mathbf{M}_0^e : \mathbf{N}^p) \dot{\bar{e}}^p + \frac{1}{\vartheta} \nabla\vartheta \cdot \mathbf{K} \nabla\vartheta + \nabla\mu \cdot \mathbf{M} \nabla\mu \geq 0. \tag{7.11}$$

Henceforth, we define

$$\bar{\sigma} \stackrel{\text{def}}{=} \sqrt{3/2}(\mathbf{M}_0^e : \mathbf{N}^p) \tag{7.12}$$

as the *equivalent tensile stress* which is power conjugate to the equivalent tensile plastic strain rate. We also assume that the material is *strongly dissipative* in the sense that

$$\bar{\sigma} \dot{\bar{e}}^p > 0 \quad \text{for } \dot{\bar{e}}^p > 0, \tag{7.13}$$

$$\nabla\vartheta \cdot \mathbf{K}(\tilde{\mathbf{\Lambda}}) \nabla\vartheta > 0 \quad \text{for } \nabla\vartheta \neq \mathbf{0}, \tag{7.14}$$

$$\nabla\mu \cdot \mathbf{M}(\tilde{\mathbf{\Lambda}}) \nabla\mu > 0 \quad \text{for } \nabla\mu \neq \mathbf{0}. \tag{7.15}$$

Thus, note that the thermal conductivity tensor  $\mathbf{K}$  and the mobility tensor  $\mathbf{M}$  are positive-definite.

Also note that on account of the transformation rules listed in the paragraph containing (6.18) and (6.19), the constitutive Eqs. (7.1), (7.8) and (7.9) are frame-indifferent.

#### 7.3. Further consequences of thermodynamics

In view of (7.1) and (7.4), we have the *first Gibbs relation*,

$$\dot{\psi}_R = \mathbf{T}^e : \dot{\mathbf{E}}^e - \eta_R \dot{\vartheta} + \mu \dot{C}, \tag{7.16}$$

which, with (6.7), yields the *second Gibbs relation*

$$\dot{e}_R = \vartheta \dot{\eta}_R + \mathbf{T}^e : \dot{\mathbf{E}}^e + \mu \dot{C}. \tag{7.17}$$

Using balance of energy (6.3), the stress-power relation (6.16), the second Gibbs relation (7.17), the constitutive equations (7.1)<sub>2,3</sub> and (7.8), and equations (7.13) through (7.15), we arrive at the *entropy balance*

$$\vartheta \dot{\eta}_R = -\text{Div } \mathbf{q}_R + q_R + \bar{\sigma} \dot{\bar{e}}^p + \nabla\mu \cdot \mathbf{M} \nabla\mu. \tag{7.18}$$

Granted the thermodynamically-restricted constitutive relations (7.4), this balance is equivalent to the balance of energy.

Next, the internal energy density is given by

$$e_R = \bar{e}_R(\mathbf{\Lambda}) \stackrel{\text{def}}{=} \bar{\psi}_R(\mathbf{\Lambda}) + \vartheta \bar{\eta}_R(\mathbf{\Lambda}), \tag{7.19}$$

and, as is standard, the *specific heat* is defined by

<sup>8</sup> We ignore any cross-coupling Soret-type effects, such as a temperature gradient directly affecting the species flux.

$$c \stackrel{\text{def}}{=} \frac{\partial \bar{\epsilon}(\Lambda)}{\partial \vartheta}. \tag{7.20}$$

Hence, from (7.19)

$$c = \left( \frac{\partial \bar{\psi}(\Lambda)}{\partial \vartheta} + \bar{\eta}(\Lambda) + \vartheta \frac{\partial \bar{\eta}(\Lambda)}{\partial \vartheta} \right), \tag{7.21}$$

and use of (7.4) gives

$$c = -\vartheta \frac{\partial^2 \bar{\psi}(\Lambda)}{\partial \vartheta^2}. \tag{7.22}$$

Next, from (7.4) and (7.22),

$$\begin{aligned} \vartheta \dot{\eta}_R &= -\vartheta \frac{\partial^2 \bar{\psi}(\Lambda)}{\partial \vartheta \partial \mathbf{E}^e} : \dot{\mathbf{E}}^e + c \dot{\vartheta} - \vartheta \frac{\partial^2 \bar{\psi}(\Lambda)}{\partial \vartheta \partial C} \dot{C} \\ &= -\vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{\mathbf{E}}^e + c \dot{\vartheta} - \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{C}. \end{aligned} \tag{7.23}$$

Then, using (7.22) and (7.23) in (7.18) gives the following partial differential equation for the temperature

$$c \dot{\vartheta} = -\text{Div} \mathbf{q}_R + q_R + \bar{\sigma} \dot{\bar{e}}^p + \nabla \mu \cdot \mathbf{M} \nabla \mu + \vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{\mathbf{E}}^e + \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{C}. \tag{7.24}$$

### 8. Isotropy

Henceforth we restrict attention to isotropic materials. The Appendix A, makes precise our notion of an isotropic material. In this case,

- (†) the response functions  $\bar{\psi}_R$ ,  $\bar{\mathbf{T}}^e$ ,  $\bar{\eta}_R$ ,  $\bar{\mu}$ , and  $\bar{\mathbf{D}}^p$  must also each be isotropic.
- (‡) the thermal conductivity and the mobility tensors have the representations

$$\mathbf{K}(\tilde{\Lambda}) = \kappa(\tilde{\Lambda}) \mathbf{1}, \quad \text{with } \kappa(\tilde{\Lambda}) > 0, \tag{8.1}$$

a scalar thermal conductivity, and

$$\mathbf{M}(\tilde{\Lambda}) = m(\tilde{\Lambda}) \mathbf{1}, \quad \text{with } m(\tilde{\Lambda}) > 0, \tag{8.2}$$

a scalar mobility, and where  $\tilde{\Lambda}$  now represents the list

$$\tilde{\Lambda} = (\mathcal{I}_{\mathbf{E}^e}, \vartheta, \bar{e}^p, C), \tag{8.3}$$

with

$$\mathcal{I}_{\mathbf{E}^e} = (I_1(\mathbf{E}^e), I_2(\mathbf{E}^e), I_3(\mathbf{E}^e))$$

the list of principal invariants of  $\mathbf{E}^e$ .

#### 8.1. Isotropic free energy

An immediate consequence of the isotropy of the free energy is that the free energy function has the representation

$$\bar{\psi}_R(\mathbf{E}^e, \vartheta, C) = \bar{\psi}_R(\mathcal{I}_{\mathbf{E}^e}, \vartheta, C). \tag{8.4}$$

Thus, from (7.4)<sub>1</sub>, it follows that

$$\mathbf{T}^e = \bar{\mathbf{T}}^e(\mathcal{I}_{\mathbf{E}^e}, \vartheta, C) = \frac{\partial \bar{\psi}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, C)}{\partial \mathbf{E}^e}, \tag{8.5}$$

and that  $\bar{\mathbf{T}}^e$  is an isotropic function of  $\mathbf{E}^e$  (and hence also of  $\mathbf{C}^e$ ). Then since the Mandel stress is defined by (cf. (6.11)),

$$\mathbf{M}^e = \mathbf{C}^e \mathbf{T}^e,$$

we find that  $\mathbf{T}^e$  and  $\mathbf{C}^e$  commute,

$$\mathbf{C}^e \mathbf{T}^e = \mathbf{T}^e \mathbf{C}^e, \tag{8.6}$$

and hence that the Mandel stress  $\mathbf{M}^e$  is symmetric.

#### 8.2. Plastic flow rule for isotropic materials

Recall the constitutive Eq. (7.8), along with (7.6), (2.16) and (2.17) for the plastic stretching  $\mathbf{D}^p$ ,

$$\begin{aligned} \mathbf{D}^p &= \bar{\mathbf{D}}^p(\mathbf{M}_0^e, \vartheta, \bar{e}^p, C) \\ &= \sqrt{3/2} \dot{\bar{e}}^p(\mathbf{M}_0^e, \vartheta, \bar{e}^p, C) \bar{\mathbf{N}}^p(\mathbf{M}_0^e, \vartheta, \bar{e}^p, C). \end{aligned} \tag{8.7}$$

Guided by (7.11), we henceforth adopt the classical **codirectionality hypothesis**, which asserts that the direction of plastic flow  $\bar{\mathbf{N}}^p$  is parallel to and points in the same direction as  $\mathbf{M}_0^e$ ,

$$\bar{\mathbf{N}}^p = \frac{\mathbf{M}_0^e}{|\mathbf{M}_0^e|}. \tag{8.8}$$

Further, note that on account of the isotropy of  $\bar{\mathbf{D}}^p$ , the equivalent tensile plastic strain rate function  $\dot{\bar{e}}^p(\mathbf{M}^e, \vartheta, \bar{e}^p, C)$  is also isotropic, and has the representation

$$\dot{\bar{e}}^p = \hat{\bar{e}}^p(\mathcal{I}_{\mathbf{M}_0^e}, \vartheta, \bar{e}^p, C) \geq 0, \tag{8.9}$$

where  $\mathcal{I}_{\mathbf{M}_0^e}$  is the list of principal invariants of  $\mathbf{M}_0^e$ .

A further consequence of (8.8) is that from the definition (7.12) for the equivalent tensile stress we have

$$\bar{\sigma} = \sqrt{3/2}(\mathbf{M}_0^e : \mathbf{N}^p) = \sqrt{3/2}|\mathbf{M}_0^e|. \tag{8.10}$$

Further, in accordance with prior experience, we henceforth neglect any dependence on  $\det \mathbf{M}_0^e$  in the expression (8.9) for viscoplastic flow. Then, using (7.12), (7.6) and (8.8), the plastic stretching  $\mathbf{D}^p$  in (8.7) may be written as

$$\mathbf{D}^p = \dot{\bar{e}}^p(3\mathbf{M}_0^e/2\bar{\sigma}) \quad \text{with} \quad \dot{\bar{e}}^p = \hat{\bar{e}}^p(\bar{\sigma}, \vartheta, \bar{e}^p, C) \geq 0. \tag{8.11}$$

### 9. Summary

In this section we summarize our isotropic chemo-thermo-mechanically-coupled theory. The theory relates the following basic fields:

$\mathbf{x} = \chi(\mathbf{X}, t)$	motion
$\mathbf{F} = \nabla \chi, J = \det \mathbf{F} > 0$	deformation gradient
$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$	multiplicative decomposition of $\mathbf{F}$
$\mathbf{F}^e, J^e = \det \mathbf{F}^e > 0$	elastic distortion
$\mathbf{F}^p, J^p = \det \mathbf{F}^p = 1$	plastic distortion
$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e$	polar decomposition of $\mathbf{F}^e$
$\mathbf{C}^e = \mathbf{F}^{eT} \mathbf{F}^e = \mathbf{U}^{e2}$	elastic right Cauchy–Green tensor
$\mathbf{E}^e = \frac{1}{2}(\mathbf{C}^e - \mathbf{1})$	elastic strain tensor
$\mathbf{T} = \mathbf{T}^T$	Cauchy stress
$\mathbf{T}^e = J \mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-T}$	elastic second Piola stress
$\mathbf{T}_R = J \mathbf{T} \mathbf{F}^{-T}$	Piola stress
$\psi_R$	free energy density per unit reference volume
$\eta_R$	entropy density per unit reference volume
$\vartheta > 0$	absolute temperature
$\nabla \vartheta$	referential temperature gradient
$\mathbf{q}_R$	referential heat flux vector
$C$	number of moles of hydrogen atoms per unit reference volume
$\mu$	chemical potential
$\nabla \mu$	referential gradient of chemical potential
$\mathbf{j}_R$	referential species flux vector

9.1. Constitutive equations

1. Free energy

$$\psi_R = \tilde{\psi}_R(\mathcal{I}_{E^e}, \vartheta, C), \tag{9.1}$$

where  $\mathcal{I}_{E^e}$  represents a list of the principal invariants of the elastic strain  $E^e$ .

2. Elastic second Piola stress. Mandel stress

The elastic second Piola stress is given by

$$\mathbf{T}^e = \frac{\partial \tilde{\psi}_R(\mathcal{I}_{E^e}, \vartheta, C)}{\partial E^e}, \tag{9.2}$$

and the Mandel stress is given by

$$\mathbf{M}^e = \mathbf{C}^e \mathbf{T}^e, \tag{9.3}$$

which, on account of the isotropy of  $\tilde{\psi}_R$ , is symmetric. Also, the equivalent tensile stress is defined by

$$\bar{\sigma} \stackrel{\text{def}}{=} \sqrt{(3/2)|\mathbf{M}_0^e|}. \tag{9.4}$$

3. Entropy. Chemical potential

The partial derivatives of the free energy

$$\left. \begin{aligned} \eta_R &= -\frac{\partial \tilde{\psi}_R(\mathcal{I}_{E^e}, \vartheta, C)}{\partial \vartheta}, \\ \mu &= \frac{\partial \tilde{\psi}_R(\mathcal{I}_{E^e}, \vartheta, C)}{\partial C}, \end{aligned} \right\} \tag{9.5}$$

respectively, represent the entropy and the chemical potential.

4. Flow rule

The evolution equation for  $F^p$  is

$$\dot{F}^p = \mathbf{D}^p F^p, \tag{9.6}$$

where  $\mathbf{D}^p$  is given by

$$\mathbf{D}^p = \dot{\bar{e}}^p (3\mathbf{M}_0^e/2\bar{\sigma}), \tag{9.7}$$

with  $\dot{\bar{e}}^p$  given by a constitutive equation

$$\dot{\bar{e}}^p = \hat{\bar{e}}^p(\bar{\sigma}, \vartheta, \bar{e}^p, C) \geq 0, \tag{9.8}$$

where

$$\bar{e}^p(\mathbf{X}, t) = \int_0^t \dot{\bar{e}}^p(\mathbf{X}, \zeta) d\zeta \quad \text{with} \quad \bar{e}^p(\mathbf{X}, 0) = 0, \tag{9.9}$$

is the equivalent tensile plastic strain.

5. Fourier's law

The heat flux  $\mathbf{q}_R$  is presumed to obey Fourier's law,

$$\mathbf{q}_R = -\kappa \nabla \vartheta, \tag{9.10}$$

with  $\kappa(\mathcal{I}_{E^e}, \vartheta, \bar{e}^p, C) > 0$  the thermal conductivity.

6. Fick's law

The species flux  $\mathbf{j}_R$  is presumed to obey Fick's law

$$\mathbf{j}_R = -m \nabla \mu, \tag{9.11}$$

with  $m(\mathcal{I}_{E^e}, \vartheta, \bar{e}^p, C) > 0$  the species mobility.

9.2. Governing partial differential equations

The governing partial differential equations consist of:

1. The local force balance (4.2), viz.

$$\text{Div} \mathbf{T}_R + \mathbf{b}_R = \mathbf{0}, \tag{9.12}$$

where  $\mathbf{T}_R = \mathbf{J} \mathbf{T} F^{-T}$  is the Piola stress, with  $\mathbf{T} = J^{-1}(\mathbf{F}^e \mathbf{T}^e \mathbf{F}^{eT})$  and  $\mathbf{T}^e$  given by (9.2), and  $\mathbf{b}_R$  is the non-inertial body force.

2. The local balance of energy (7.24), which, together with (9.10) and (9.11), gives the following partial differential equation for the temperature

$$c \dot{\vartheta} = \text{Div}(\kappa \nabla \vartheta) + q_R + \bar{\sigma} \dot{\bar{e}}^p + m |\nabla \mu|^2 + \vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{E}^e + \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{C}, \tag{9.13}$$

in which

$$c = -\vartheta \frac{\partial^2 \tilde{\psi}(\mathcal{I}_{E^e}, \vartheta, C)}{\partial \vartheta^2} \tag{9.14}$$

is the specific heat.

3. The local balance equation for the concentration of hydrogen atoms (5.3), together with (9.11), gives

$$\dot{C} = \text{Div}(m \nabla \mu). \tag{9.15}$$

10. Specialization of the constitutive equations

The theory presented thus far is quite general. We now introduce special constitutive equations appropriate for situations in which the elastic strains are small, the temperature is close to fixed reference temperature  $\vartheta_0$ , and the concentration  $C$  close to a reference concentration  $C_0$ . Since the precise nature of the various coupling effects has not been completely elucidated in the existing literature, the special constitutive equations listed below should provide a suitable beginning for analysis and future refinement.

10.1. Free energy

We consider a separable free energy of the form

$$\begin{aligned} \tilde{\psi}_R(E^e, \vartheta, C) &= G |E^e|^2 + \frac{1}{2} \left( K - \frac{2}{3} G \right) (\text{tr} E^e)^2 - (3K\alpha)(\vartheta - \vartheta_0)(\text{tr} E^e) \\ &\quad + c(\vartheta - \vartheta_0) - c\vartheta \ln \left( \frac{\vartheta}{\vartheta_0} \right) - (3K\beta)(C - C_0)(\text{tr} E^e) \\ &\quad + \mu_0 C + R\vartheta C (\ln \tilde{C} - 1). \end{aligned} \tag{10.1}$$

Here,  $G$  is the shear modulus,  $K$  the bulk modulus,  $\alpha$  the coefficient of thermal expansion,  $c$  the specific heat,  $\beta$  the coefficient of chemical expansion,  $\mu_0$  a reference chemical potential, and  $R$  the gas constant. The last two terms in (10.1) represent a classical entropic contribution of a dilute ideal interstitial solid solution to the free energy density, where, with  $\mathcal{M}_M$  denoting the molar mass of the host metal (kg/mol) and  $\rho_M$  its mass density (kg/m<sup>3</sup>),

$$N_M \stackrel{\text{def}}{=} \frac{\rho_M}{\mathcal{M}_M} \tag{10.2}$$

is the number of moles of host metal atoms per unit reference volume, and

$$\tilde{C} \stackrel{\text{def}}{=} \frac{C}{N_M}, \tag{10.3}$$

a normalized hydrogen concentration, represents the mole fraction of hydrogen for a dilute solution.

Then, by (9.2) and (9.5), the elastic second Piola stress, the entropy, and the chemical potential are given by

$$\begin{aligned} \mathbf{T}^e &= 2GE_0^e + K(\text{tr} E^e) \mathbf{1} - 3K\alpha(\vartheta - \vartheta_0) \mathbf{1} - 3K\beta(C - C_0) \mathbf{1}, \\ \eta_R &= c \ln \left( \frac{\vartheta}{\vartheta_0} \right) + 3K\alpha(\text{tr} E^e) - RC(\ln \tilde{C} - 1), \\ \mu &= \mu_0 + R\vartheta \ln \tilde{C} - (3K\beta)(\text{tr} E^e). \end{aligned} \tag{10.4}$$

The inverted form of the stress relation (10.4)<sub>1</sub> is

$$E^e = \frac{1}{2G} \left( \mathbf{T}^e - \frac{(3K - 2G)}{9K} (\text{tr} \mathbf{T}^e) \mathbf{1} \right) + \alpha(\vartheta - \vartheta_0) \mathbf{1} + \beta(C - C_0) \mathbf{1}, \tag{10.5}$$



which gives

$$\text{tr}\mathbf{E}^e = \frac{1}{3K}(\text{tr}\mathbf{T}^e) + 3\alpha(\vartheta - \vartheta_0) + 3\beta(C - C_0). \quad (10.6)$$

The last term in (10.6) justifies our terminology for  $\beta$  as a coefficient of chemical expansion. It is related to the partial molar volume of the gas,  $\bar{V}_H$ , used in the hydrogen literature (Hirth, 1980) through<sup>9</sup>

$$\beta = \frac{1}{3}\bar{V}_H. \quad (10.7)$$

### 10.2. Plastic flow rate. Hardening/softening

Next, we consider the flow function (9.8) which specifies the equivalent tensile plastic strain rate. First we introduce two scalar valued resistances  $S_*$  and  $S_a$  with dimensions of stress. We assume that  $S_*$  – a thermally-activatable resistance – is a constant, while

$$S_a = \hat{S}_a(\bar{\epsilon}^p, \vartheta, \tilde{C})$$

is an athermal resistance which depends on the equivalent tensile plastic strain  $\bar{\epsilon}^p$ , the temperature  $\vartheta$ , and the normalized hydrogen concentration  $\tilde{C}$ . The athermal resistance  $S_a$  accounts for strain hardening/softening characteristics of the material.

Restricting our attention to temperatures less than  $0.35 \vartheta_m$ , where  $\vartheta_m$  is the melting temperature of the material, as a specific expression for  $\dot{\bar{\epsilon}}^p$ , we choose a thermally-activated relation of the form (cf., e.g., Kocks et al., 1975)

$$\dot{\bar{\epsilon}}^p = \begin{cases} 0 & \text{if } \bar{\sigma} \leq S_a, \\ \dot{\epsilon}_0 \exp\left[\frac{-\Delta F}{R\vartheta} \left(1 - \left(\frac{\bar{\sigma} - S_a}{S_*}\right)^p\right)^q\right] & \text{if } \bar{\sigma} > S_a. \end{cases} \quad (10.8)$$

Here  $\Delta F$  is an activation energy required to overcome obstacles to plastic flow without the aid of an applied stress, the constants  $p$  and  $q$  are taken to lie in the ranges

$$0 \leq p \leq 1 \quad \text{and} \quad 1 \leq q \leq 2, \quad (10.9)$$

and the pre-exponential reference tensile strain rate  $\dot{\epsilon}_0$  has a typical value of  $\approx 10^6$  to  $10^7$ /s. For non-zero plastic strain rate, (10.8) may be inverted to give the following strength relation,

$$\bar{\sigma} = S_a(\bar{\epsilon}^p, \vartheta, \tilde{C}) + S_* \times Z(\vartheta, \dot{\bar{\epsilon}}^p), \quad (10.10)$$

with

$$Z \stackrel{\text{def}}{=} \left(1 - \left(\frac{\vartheta}{\vartheta_c}\right)^{1/q}\right)^{1/p} \quad \text{and} \quad \vartheta_c \stackrel{\text{def}}{=} \frac{\Delta F}{R \ln(\dot{\epsilon}_0/\dot{\bar{\epsilon}}^p)}. \quad (10.11)$$

The thermally-activated rate-relation (10.8) is valid only for temperatures  $\vartheta < \vartheta_c$ , where  $\vartheta_c$  depends on the strain rate (cf. (10.11)<sub>2</sub>). A model of this type is widely-used to describe the variation of the plastic flow strength of metal alloys over a wide range of strain rates ( $\approx 10^{-4}$  to  $\approx 10^4$ ), and also a wide range of temperatures (77 K to  $\vartheta_c$ ) (cf., e.g., Stout and Follansbee, 1986; Follansbee and Kocks, 1988; Follansbee et al., 1990; Kothari and Anand, 1998; Balasubramanian and Anand, 2002; Guo and Nemat-Nasser, 2006).

A variety of specific expressions for the dependence of  $S_a$  on  $\bar{\epsilon}^p$  have been proposed in the literature, and the simplest of these allows for a separable power-law dependence of  $S_a$  on  $\bar{\epsilon}^p$  of the form

$$S_a(\bar{\epsilon}^p, \vartheta, \tilde{C}) = \phi(\tilde{C}, \vartheta) \left(1 + \frac{\bar{\epsilon}^p}{\epsilon_0}\right)^n, \quad (10.12)$$

with  $\epsilon_0$  and  $n$  constants. The dependence of the factor  $\phi(\tilde{C}, \vartheta)$  on  $\tilde{C}$  and  $\vartheta$  remains to be fully explored, but for isothermal conditions see

<sup>9</sup> For example, for  $\alpha$ -Fe at 293 K,  $\bar{V}_H = 2.0 \times 10^{-6}$  m<sup>3</sup>/mol (Hirth, 1980), and hence  $\beta = 6.67 \times 10^{-7}$  m<sup>3</sup>/mol.

a specific form suggested by Sofronis et al. (2001) and Liang et al. (2003). The specific form introduced by these authors is intended to represent a continuum-level description of the decrease in flow resistance due to an increase in the hydrogen concentration—a form that they introduced in order to account for a microstructural mechanism widely known as hydrogen-enhanced localized plasticity (cf., e.g., Birnbaum and Sofronis, 1994).

### 10.3. Heat flux

From (9.10), we have that the heat flux is given by

$$\mathbf{q}_R = -\kappa \nabla \vartheta, \quad (10.13)$$

with  $\kappa(\mathcal{I}_{E^e}, \vartheta, \bar{\epsilon}^p, \tilde{C}) > 0$  the thermal conductivity. At this point in time the dependence of the thermal conductivity on the variables  $(\mathcal{I}_{E^e}, \bar{\epsilon}^p, \tilde{C})$  is not well understood; if one ignores such dependence then  $\kappa(\vartheta) > 0$  is a temperature-dependent thermal conductivity which is tabulated for many metals.

### 10.4. Species flux

From (9.11) we have that the species flux is given by

$$\mathbf{j}_R = -m \nabla \mu, \quad (10.14)$$

with  $m(\mathcal{I}_{E^e}, \vartheta, \bar{\epsilon}^p, \tilde{C}) > 0$  the species mobility. Thus, with the chemical potential  $\mu$  given by (10.4), we may write (10.14) as

$$\mathbf{j}_R = -\frac{m(\mathcal{I}_{E^e}, \vartheta, \bar{\epsilon}^p, \tilde{C})R\vartheta}{C} \left( \nabla C - \frac{C}{R\vartheta} (3K\beta) \nabla(\text{tr}\mathbf{E}^e) \right). \quad (10.15)$$

Defining a diffusivity  $D$  by

$$D(\mathcal{I}_{E^e}, \vartheta, \bar{\epsilon}^p, \tilde{C}) \stackrel{\text{def}}{=} m(\mathcal{I}_{E^e}, \vartheta, \bar{\epsilon}^p, \tilde{C}) \times \frac{R\vartheta}{C}, \quad (10.16)$$

(10.15) may be written as

$$\mathbf{j}_R = -D \nabla C + \frac{DC}{R\vartheta} (3K\beta) \nabla(\text{tr}\mathbf{E}^e). \quad (10.17)$$

As for the thermal conductivity, the dependence of the effective diffusivity  $D$  on the variables  $(\mathcal{I}_{E^e}, \bar{\epsilon}^p, \tilde{C})$  is not well understood; if one ignores such dependence, then  $D(\vartheta) > 0$  is a temperature-dependent effective diffusivity which is experimentally measurable.

## 11. Governing partial differential equations for the specialized constitutive equations. Boundary conditions

The governing partial differential equations consist of:

1. The local force balance (9.12), viz.

$$\text{Div}\mathbf{T}_R + \mathbf{b}_R = \mathbf{0}, \quad (11.1)$$

where  $\mathbf{T}_R = J\mathbf{T}\mathbf{F}^{-T}$  is the Piola stress, with  $\mathbf{T} = J^{-1}(\mathbf{F}^e \mathbf{T}^e \mathbf{F}^{eT})$  and  $\mathbf{T}^e$  given by (10.4)<sub>1</sub>, and  $\mathbf{b}_R$  is the non-inertial body force.

2. The local balance equation for the hydrogen concentration (5.3), together with (10.17), gives the following partial differential equation for  $C$ :

$$\dot{C} = \text{Div}(D \nabla C) - \text{Div} \left( \frac{DC}{R\vartheta} (3K\beta) \nabla(\text{tr}\mathbf{E}^e) \right). \quad (11.2)$$

3. The local balance of energy (9.13), which, together with (10.4)<sub>3</sub> and (10.16), gives the following partial differential equation for the temperature

$$c\dot{\vartheta} = \text{Div}(\kappa \nabla \vartheta) + q_R + \bar{\sigma} \dot{\bar{\epsilon}}^p + \frac{DC}{R\vartheta} |\nabla \mu|^2 + \vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{\mathbf{E}}^e + \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{C}. \quad (11.3)$$

We also need initial and boundary conditions to complete the theory. Let  $S_1$  and  $S_2$  be complementary subsurfaces of the boundary  $\partial B$  of the body  $B$  in the sense  $\partial B = S_1 \cup S_2$  and  $S_1 \cap S_2 = \emptyset$ . Similarly let  $S_c$  and  $S_{j_R}$  be complementary subsurfaces of the boundary:  $\partial B = S_c \cup S_{j_R}$  and  $S_c \cap S_{j_R} = \emptyset$ , and finally, let  $S_\vartheta$  and  $S_{q_R}$  be complementary subsurfaces of the boundary:  $\partial B = S_\vartheta \cup S_{q_R}$  and  $S_\vartheta \cap S_{q_R} = \emptyset$ . Then for a time interval  $t \in [0, T]$  we consider a pair of simple boundary conditions in which the motion is specified on  $S_1$  and the surface traction on  $S_2$ :

$$\begin{cases} \boldsymbol{\chi} = \check{\boldsymbol{\chi}} & \text{on } S_1 \times [0, T], \\ \mathbf{T}_R \mathbf{n}_R = \check{\mathbf{t}}_R & \text{on } S_2 \times [0, T]; \end{cases} \quad (11.4)$$

another pair of boundary conditions in which the concentration is specified on  $S_c$  and the species flux on  $S_{j_R}$

$$\begin{cases} C = \check{C} & \text{on } S_c \times [0, T], \\ \mathbf{j}_R \cdot \mathbf{n}_R = \check{j}_R & \text{on } S_{j_R} \times [0, T]; \end{cases} \quad (11.5)$$

and a final pair of boundary conditions in which the temperature is specified on  $S_\vartheta$  and the heat flux on  $S_{q_R}$

$$\begin{cases} \vartheta = \check{\vartheta} & \text{on } S_\vartheta \times [0, T], \\ \mathbf{q} \cdot \mathbf{n}_R = \check{q}_R & \text{on } S_{q_R} \times [0, T]; \end{cases} \quad (11.6)$$

with  $\check{\boldsymbol{\chi}}, \check{\mathbf{t}}_R, \check{\vartheta}, \check{q}_R, \check{C}$ , and  $\check{j}_R$  prescribed functions of  $\mathbf{X}$  and  $t$ . To these boundary conditions we append the initial data

$$\begin{aligned} \boldsymbol{\chi}(\mathbf{X}, 0) &= \boldsymbol{\chi}_0(\mathbf{X}), \quad C(\mathbf{X}, 0) = C_0(\mathbf{X}), \quad \text{and} \\ \vartheta(\mathbf{X}, 0) &= \vartheta_0(\mathbf{X}) \quad \text{in } B. \end{aligned} \quad (11.7)$$

The coupled set of Eqs. (11.1), (11.2) and (11.3), together with (11.4), (11.5), (11.6) and (11.7), yield an initial boundary-value problem for the motion  $\boldsymbol{\chi}(\mathbf{X}, t)$ , the chemical species concentration  $C(\mathbf{X}, t)$ , and the temperature  $\vartheta(\mathbf{X}, t)$ .

**Remark.** From the expression (10.4)<sub>3</sub> for the chemical potential, we note that

$$\begin{aligned} \dot{\mu} &= \frac{R\vartheta}{C} \dot{C} + R \ln \tilde{C} \dot{\vartheta} - (3K\beta) \text{tr} \dot{\mathbf{E}}^e \\ \Rightarrow \dot{C} &= \frac{C}{R\vartheta} (\dot{\mu} + (3K\beta) \text{tr} \dot{\mathbf{E}}^e - R \ln \tilde{C} \dot{\vartheta}). \end{aligned} \quad (11.8)$$

Using (11.8)<sub>2</sub>, one may alternatively write the balance Eq. (9.15) for  $C$  as a balance for the chemical potential:

$$\dot{\mu} = \left( \frac{R\vartheta}{C} \right) \text{Div}(m \nabla \mu) - (3K\beta) \text{tr} \dot{\mathbf{E}}^e + R \ln \tilde{C} \dot{\vartheta}. \quad (11.9)$$

In applications it may be advantageous to use the balance Eq. (11.9) for the chemical potential  $\mu$ , rather than the balance Eq. (11.2) for  $C$ . In this case, with  $S_\mu$  and  $S_j$  complementary subsurfaces of the boundary  $\partial B$ , the boundary conditions (11.5) are replaced by boundary conditions

$$\begin{cases} \mu = \check{\mu} & \text{on } S_\mu \times [0, T], \\ -m(\nabla \mu) \cdot \mathbf{n}_R = \check{j} & \text{on } S_j \times [0, T], \end{cases} \quad (11.10)$$

with  $\check{\mu}$ , and  $\check{j}$  prescribed functions of  $\mathbf{X}$  and  $t$ , and initial data  $\mu(\mathbf{X}, 0) = \mu_0(\mathbf{X})$  in  $B$ . (11.11)

**12. Concluding remarks**

We have developed a continuum-level theory which couples transient hydrogen diffusion, heat diffusion, and large thermo-elastic–viscoplastic deformations, and accounts for hydrogen-induced lattice dilatation and hydrogen-induced softening of the plastic flow resistance of the material. This theory should aid the

macroscale modeling of the failure of metallic components due to hydrogen embrittlement.

Although our study has been motivated by the application of hydrogen in metals, the theory itself is not limited to such an application, and is quite general. It should be applicable to a wide variety of other situations in which one needs to account for the coupled effects of elastic–viscoplastic deformation, transient heat conduction, and interstitial diffusion of a gaseous species.

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**Appendix A. Isotropy**

The following definitions help to make precise our notion of an isotropic material (cf., Anand and Gurtin, 2003):

- (i)  $\text{Orth}^+$  = the group of all rotations (the proper orthogonal group);
- (ii) the symmetry group  $G_R$ , is the group of all rotations of the reference configuration that leaves the response of the material unaltered;
- (iii) the symmetry group  $G_t$  at each time  $t$ , is the group of all rotations of the intermediate structural space that leaves the response of the material unaltered.

We now discuss the manner in which the basic fields transform under such transformations, granted the physically natural requirement of invariance of the stress-power (6.16), or equivalently, the requirement that

$$\mathbf{T}^e : \dot{\mathbf{E}}^e, \quad \text{and} \quad \mathbf{M}_0^e : \mathbf{D}^p \quad \text{be invariant.} \quad (A.1)$$

*A.1. Isotropy of the reference configuration*

Let  $\mathbf{Q}$  be a time-independent rotation of the reference configuration. Then  $\mathbf{F} \rightarrow \mathbf{F}\mathbf{Q}$ , and hence

$$\mathbf{F}^p \rightarrow \mathbf{F}^p \mathbf{Q}, \quad \text{and} \quad \mathbf{F}^e \text{ is invariant, and hence } \mathbf{E}^e \text{ is invariant,} \quad (A.2)$$

so that, by (2.8) and (2.10)

$\dot{\mathbf{E}}^e$  and  $\mathbf{D}^p$  are invariant.

We may therefore use (A.1) to conclude that

$$\mathbf{T}^e \text{ and } \mathbf{M}^e \text{ are invariant.} \quad (A.3)$$

Thus

- the constitutive equations (7.1) and (7.8) are unaffected by such rotations of the reference configuration.

Turning our attention next to the constitutive equation (7.9)<sub>1</sub> for the heat flux, a standard result from the theory of finite thermo-elasticity is that under a symmetry transformation  $\mathbf{Q}$  for the reference configuration, the temperature gradient  $\nabla \vartheta$  and the heat flux  $\mathbf{q}_R$  transform as (cf. Gurtin et al. (2010), Section 57.8)

$$\nabla \vartheta \rightarrow \mathbf{Q}^T \nabla \vartheta, \quad \mathbf{q}_R \rightarrow \mathbf{Q}^T \mathbf{q}_R.$$

Hence, from (7.8)<sub>1</sub> the thermal conductivity tensor  $\mathbf{K}$  must obey

$$\mathbf{K}(\tilde{\Lambda}) = \mathbf{Q}^T \mathbf{K}(\tilde{\Lambda}) \mathbf{Q} \quad \text{for all rotations } \mathbf{Q} \in \mathcal{G}_R. \quad (\text{A.4})$$

By an analogous argument, the mobility tensor  $\mathbf{M}$  must obey

$$\mathbf{M}(\tilde{\Lambda}) = \mathbf{Q}^T \mathbf{M}(\tilde{\Lambda}) \mathbf{Q} \quad \text{for all rotations } \mathbf{Q} \in \mathcal{G}_R. \quad (\text{A.5})$$

We refer to the material as *initially isotropic* (and to the reference configuration as undistorted) if

$$\mathcal{G}_R = \text{Orth}^+ \quad (\text{A.6})$$

so that the response of the material is invariant under arbitrary rotations of the reference space. Henceforth

- we restrict attention to materials that are initially isotropic.

In this case, the thermal conductivity and the mobility tensors have the representations

$$\mathbf{K}(\tilde{\Lambda}) = \kappa(\tilde{\Lambda}) \mathbf{1}, \quad \text{with } \kappa(\tilde{\Lambda}) > 0 \quad (\text{A.7})$$

a scalar thermal conductivity, and

$$\mathbf{M}(\tilde{\Lambda}) = m(\tilde{\Lambda}) \mathbf{1}, \quad \text{with } m(\tilde{\Lambda}) > 0. \quad (\text{A.8})$$

a scalar mobility.

## A.2. Isotropy of the intermediate structural space

Next, let  $\mathbf{Q}$  a *time-independent rotation of the intermediate space*, be a symmetry transformation. Then  $\mathbf{F}$  is unaltered by such a rotation, and hence

$$\mathbf{F}^e \rightarrow \mathbf{F}^e \mathbf{Q} \quad \text{and} \quad \mathbf{F}^p \rightarrow \mathbf{Q}^T \mathbf{F}^p, \quad (\text{A.9})$$

and also

$$\mathbf{E}^e \rightarrow \mathbf{Q}^T \mathbf{E}^e \mathbf{Q}, \quad \dot{\mathbf{E}}^e \rightarrow \mathbf{Q}^T \dot{\mathbf{E}}^e \mathbf{Q}, \quad \mathbf{D}^p \rightarrow \mathbf{Q}^T \mathbf{D}^p \mathbf{Q}. \quad (\text{A.10})$$

Then (A.10) and (A.1) yield the transformation laws

$$\mathbf{T}^e \rightarrow \mathbf{Q}^T \mathbf{T}^e \mathbf{Q}, \quad \mathbf{M}^e \rightarrow \mathbf{Q}^T \mathbf{M}^e \mathbf{Q}. \quad (\text{A.11})$$

Thus, with reference to the constitutive equations (7.1) and (7.8), together with (8.1) and (8.2) we conclude that

$$\left. \begin{aligned} \bar{\psi}_R(\Lambda) &= \bar{\psi}_R(\mathbf{Q}^T \Lambda \mathbf{Q}), \\ \mathbf{Q}^T \bar{\mathbf{T}}^e(\Lambda) \mathbf{Q} &= \bar{\mathbf{T}}^e(\mathbf{Q}^T \Lambda \mathbf{Q}), \\ \bar{\eta}_R(\Lambda) &= \bar{\eta}_R(\mathbf{Q}^T \Lambda \mathbf{Q}), \\ \bar{\mu}(\Lambda) &= \bar{\mu}(\mathbf{Q}^T \Lambda \mathbf{Q}), \\ \mathbf{Q}^T \bar{\mathbf{D}}^p(\mathbf{M}_0^e, \vartheta, \bar{e}^p, C) \mathbf{Q} &= \bar{\mathbf{D}}^p(\mathbf{Q}^T \mathbf{M}_0^e \mathbf{Q}, \vartheta, \bar{e}^p, C), \\ \kappa(\tilde{\Lambda}) &= \kappa(\mathbf{Q}^T \tilde{\Lambda} \mathbf{Q}), \\ m(\tilde{\Lambda}) &= m(\mathbf{Q}^T \tilde{\Lambda} \mathbf{Q}), \end{aligned} \right\} \quad (\text{A.12})$$

with

$$\mathbf{Q}^T \Lambda \mathbf{Q} = (\mathbf{Q}^T \mathbf{E}^e \mathbf{Q}, \vartheta, C) \quad \text{and} \quad \mathbf{Q}^T \tilde{\Lambda} \mathbf{Q} = (\mathbf{Q}^T \mathbf{E}^e \mathbf{Q}, \vartheta, \bar{e}^p, C),$$

must hold for all rotations  $\mathbf{Q}$  in the *symmetry group*  $\mathcal{G}_I$  at each time  $t$ .

We refer to the material as one which is *continually isotropic*, if in addition to the referential isotropy discussed in the previous subsection,

$$\mathcal{G}_I = \text{Orth}^+, \quad (\text{A.13})$$

so that the response of the material is also invariant under arbitrary rotations of the intermediate space at each time  $t$ . Henceforth

- we restrict attention to materials that are not only initially, but also continually, isotropic.

In this case, the response functions  $\bar{\psi}_R$ ,  $\bar{\mathbf{T}}^e$ ,  $\bar{\eta}_R$ ,  $\bar{\mu}$ ,  $\bar{\mathbf{D}}^p$ ,  $\kappa$ , and  $m$  must also each be *isotropic*.

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