Geometrically nonlinear continuum thermomechanics with surface energies coupled to diffusion

A.T. McBride [a], A. Javili [a], P. Steinmann [a,*], S. Bargmann [b,1]

[a] Chair of Applied Mechanics, University of Erlangen-Nuremberg, Egerland-Str. 5, 91058 Erlangen, Germany
[b] Institute of Mechanics, Technical University of Dortmund, Leonhard-Euler-Str. 5, 44227 Dortmund, Germany

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ABSTRACT

Surfaces can have a significant influence on the overall response of a continuum body but are often neglected or accounted for in an ad hoc manner. This work is concerned with a nonlinear continuum thermomechanics formulation which accounts for surface structures and includes the effects of diffusion and viscoelasticity. The formulation is presented within a thermodynamically consistent framework and elucidates the nature of the coupling between the various fields, and the surface and the bulk. Conservation principles are used to determine the form of the constitutive relations and the evolution equations. Restrictions on the jump in the temperature and the chemical potential between the surface and the bulk are not a priori assumptions, rather they arise from the reduced dissipation inequality on the surface and are shown to be satisfiable without imposing the standard assumptions of thermal and chemical slavery. The nature of the constitutive relations is made clear via an example wherein the form of the Helmholtz energy is explicitly given.

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1. Introduction

Classical continuum mechanics based formulations are firmly established methodologies for describing the complex response of continua. Surfaces can have a significant influence on the overall response of the continuum body but are often neglected or accounted for in an ad hoc manner. The response of the surface can differ from that of the bulk due to factors such as oxidation and coating, which result in a surface composition distinct from the bulk, and the termination of interatomic bonds at the surface.

A phenomenological approach to capturing surface effects and describing scale-dependent phenomena at the nanoscale is to endow the surface and the bulk with their own Helmholtz (free) energies. The form of the Helmholtz energy for the surface (and indeed for the bulk) is assumed to be obtainable from experimental observation, fundamental reasoning, or direct numerical simulation at the micro-scale. Such a phenomenological approach was first adopted in the seminal work of Gibbs (1878) (see also Gibbs, 1906) who modelled phase interfaces as surfaces across which the material properties of the different bulk phases could exhibit discontinuities. The localised interaction of the distinct bulk phases was accounted for by endowing the interface with an energy.

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* Corresponding author. Tel.: +49 9131 85 28502; fax: +49 9131 85 28503.
E-mail addresses: andrew.mcbride@ltm.uni-erlangen.de (A.T. McBride), ali.javili@ltm.uni-erlangen.de (A. Javili),
paul.steinmann@ltm.uni-erlangen.de (P. Steinmann), swantje.bargmann@tu-dortmund.de (S. Bargmann).
[1] Tel.: +49 231 755 7902.

The first comprehensive, purely mechanical description of material surfaces which accounted for surface stress in an elastic media is due to Gurtin and Murdoch (1975). The kinematics and the balance laws for surfaces were described and the tensorial nature of surface tension was established. This work has been extended by Gurtin and co-workers to account for thermal effects (Angenent and Gurtin, 1989; Gurtin, 1988; Gurtin and Struthers, 1990).

A key extension of the theory of Gurtin and Murdoch (1975) is that of Gurtin and Voorhees (1993) on propagating interfaces within a solid undergoing infinitesimal deformations which accounts for mass transport. Central to the theory is a configurational interfacial balance which contains both the standard force and mass balances in the bulk phases and across the interface. Configurational forces (see Kienzler and Herrmann, 2000; Maugin, 1993, 1995; Steinmann, 2002a–c for an extensive overview) provide an elegant and powerful description of the role of surfaces separating distinct phases (Gurtin, 1995, 2000; Gurtin and Struthers, 1990; Gurtin and Voorhees, 1993; Maugin, 2010; Steinmann, 2008).

An alternative approach to develop general relations for the interface is to integrate the known equations for the bulk over the thickness of the interfacial layers (see e.g. Gogosov et al., 1983).

Daher and Maugin (1986a) use the elegant method of virtual power to derive the governing equations for an interface within a thermomechanical solid. This flexible approach is well suited to describing complex phenomena. For example, the work by Daher and Maugin (1987) applies the method to describe the challenging problem of deformable semiconductors with interfaces (see also Daher and Maugin, 1986b).

The work by Gurtin and Voorhees (1993) has been extended and applied to the modelling of various physical phenomena. Dolbow et al. (2004) consider the finite deformations that arise due to the chemically induced swelling of a hydrogel. Ji et al. (2006) extended this work to account for thermal effects.

The influence of surface effects on the overall response of a continuum structure increases as the scale of the structure decreases. Recent work applying the theory of Gurtin and Murdoch (1975) to describe the size-dependent response exhibited by materials at the nanoscale includes Duan et al. (2009), Miller and Shenoy (2000), Mitrushchenkov et al. (2010), She and Wang (2009), Wei et al. (2006), and Yvonnet et al. (2008). For a comprehensive overview of the motion of microscopic surfaces due to the coupling with a range of physical phenomena the reader is referred to Suo (1997). The surface stress induced by adsorption and the resulting effect on the mechanical response of nanoscale continua have been examined by Yi and Duan (2009). One key contribution of Yi and Duan was the elucidation of the relations between the macroscale interpretation of surface stress and the molecular-level description of adsorbate interactions.[2]

Surface tension generally plays a minor role in the overall response of a solid and is often neglected (see e.g. Miller and Shenoy, 2000). However, surface tension can be accommodated in the formulation presented here. Conceptually, our reference configuration is stress and deformation free. Surface tension, which should be present in all configurations, then acts to deform the reference configuration (see Javili and Steinmann, 2010a, for further details). Huang and Wang (2006) recognise this distinction explicitly and introduce a "fictitious, stress-free configuration" in addition to a stressed and deformed reference configuration. Furthermore, they demonstrate the role of surface effects for a range of constitutive models.

The contribution presented here constitutes a significant extension of the nonlinear continuum thermomechanics formulation by Javili and Steinmann (2010b) (see also Javili and Steinmann, 2009, 2010a for details of the numerical implementation of this formulation restricted to the purely mechanical setting and Javili and Steinmann (2011) for the thermomechanical case), which accounts for surface structures, to include the effects of diffusion and viscoelasticity. The focus here is on continuum domains where the external surface possesses its own energy; propagating interfaces, such as phase interfaces, will form the focus of a subsequent work. As such we restrict the presentation to non-propagating, coherent external surfaces. The surface is assumed to have negligible thickness and acts in a similar manner to a membrane "wrapped" around the bulk. Heat flux and species diffusion occur on the surface as well as in the bulk. The assumption of infinitesimal surface thickness restricts the flux vectors associated with the various surface quantities to be tangent to the surface.

The inclusion of both diffusional, thermal and inelastic effects gives rise to a coupled response that is not well described in the literature, even for the bulk. One objective of this work is to elucidate the nature of the coupling for the bulk using a rigorous thermodynamic approach and then extend the result to the surface. The presentation draws on the work by Armero and Simo (1992) and Simo and Hughes (1998) for thermomechanical solids as well as that by Govindjee and Simo (1993) for coupling diffusion and deformation.

In summary, the key objectives and contributions of this work are as follows:

- to systematically derive the equations governing the response of a thermomechanical solid undergoing finite inelastic deformations with diffusion and extend these results to the surface;
- to explicitly derive the form of the constitutive relations for the bulk and suggest the form on the surface using logical thermodynamical arguments;
- to determine the admissible restrictions on the difference between the temperature, and the chemical potential, between the surface and the bulk, respectively, that arise as a consequence of the dissipation inequality as opposed to making a priori assumptions;
- to clarify the nature of the coupling between heat conduction, species diffusion, and finite inelastic deformation in the bulk by considering various forms of the Helmholtz energy.

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[2] An alternative methodology that utilises the Cauchy–Born hypothesis to capture surface effects is described in Park and Klein (2008), among others.

This paper is organised as follows. The notation and certain key concepts are introduced in Section 2. The equations governing the response of the bulk and the surface are derived from fundamental balance principles in Section 3. In particular, the conservation of solid and diffusing species mass, and the balance of linear and angular momentum are presented. Thereafter the balance of energy and entropy are detailed. A thermodynamic framework is then utilised to determine the form of the thermodynamically consistent constitutive relations in the bulk and on the surface. The nature of the coupling between the various fields (displacement, temperature and chemical potential) is made clear as is the nature of the coupling between the surface and the bulk. The section concludes by demonstrating two possible constraints between the temperature, and chemical potential, on the surface and in the bulk, respectively, that allow for a thermodynamically consistent formulation. The nature of the constitutive relations is made clear in Section 4 via an example wherein the form of the Helmholtz energy is explicitly given. We conclude and discuss further work in Section 5.

2. Preliminaries: notation and basic concepts

The purpose of this preliminary section is to summarise certain key concepts in nonlinear continuum mechanics and to introduce the notation adopted here. Detailed expositions on nonlinear continuum mechanics can be found in Ciarlet (1988), Truesdell and Noll (2004), among others. For further details concerning the continuum mechanics of deformable surfaces the reader is referred to Fosdick and Tang (2009), Gurtin and Murdoch (1975), Gurtin and Struthers (1990), Steinmann (2008), and the numerous references therein.[3]

2.1. Motion

We denote by the open set $\mathcal{B}_0 \subset \mathbb{R}^3$ the reference (initial) placement of a continuum body, as depicted in Fig. 1, with material particles labelled $\boldsymbol{X} \in \mathcal{B}_0$. The surface of $\mathcal{B}_0$, assumed smooth, is denoted as $\mathcal{S}_0 := \partial\mathcal{B}_0$ and the closure as $\overline{\mathcal{B}}_0 := \mathcal{B}_0 \cup \mathcal{S}_0$. The unit normal to $\mathcal{S}_0$ is denoted $\boldsymbol{N}$. Particles on the surface of the reference configuration $\mathcal{S}_0$ are labelled $\boldsymbol{X}|_{\mathcal{S}_0}$. Curves on the surface $\mathcal{S}_0$ are denoted $\mathcal{C}_0$.

Let $\mathbb{T} = [0,T] \subset \mathbb{R}_+$ denote the time domain. Here time simply provides a history parameter to order the sequence of events and quasi-static conditions are assumed henceforth. We denote by the orientation preserving map $\boldsymbol{\varphi} : \mathcal{B}_0 \times \mathbb{T} \to \mathbb{R}^3$, a smooth motion of the reference placement for a time $t \in \mathbb{T}$. The current placement of the body at time t associated with the motion $\boldsymbol{\varphi}$ is denoted $\mathcal{B}_t = \boldsymbol{\varphi}(\mathcal{B}_0(\boldsymbol{X}),t)$, with particles designated as $\boldsymbol{x} = \boldsymbol{\varphi}(\boldsymbol{X},t) \in \mathcal{B}_t$. The placement of particles on the surface of the current configuration, denoted $\boldsymbol{x}|_{\mathcal{S}_t}$, are obtained from those on the surface of the reference configuration $\boldsymbol{X}|_{\mathcal{S}_0}$ via the deformation map restricted to the surface. Here and henceforth, the subscripts t and 0 shall designate spatial and material quantities, respectively, unless specified otherwise.

Implicit in the statement that $\boldsymbol{x}|_{\mathcal{S}_t} = \boldsymbol{\varphi}(\boldsymbol{X}|_{\mathcal{S}_0},t)$ is the assumption that particles on the surface of the body $\mathcal{S}_0$ remain on the surface during a motion. This assumption, referred to as kinematic slavery (coherence), is made throughout this presentation.

The material velocity $\boldsymbol{V}(\boldsymbol{X},t)$ is defined by the conventional time derivative of the motion as $\boldsymbol{V}(\boldsymbol{X},t) = \partial\boldsymbol{\varphi}(\boldsymbol{X},t)/\partial t$. A spatial description of the motion can be obtained from the material description by transforming the independent variables from the material coordinates to the spatial coordinates. The spatial velocity field, denoted $\boldsymbol{v}(\boldsymbol{x},t)$, is obtained from the material velocity field as $\boldsymbol{v}(\boldsymbol{\varphi}(\boldsymbol{X},t),t) = \boldsymbol{V}(\boldsymbol{X},t)$.
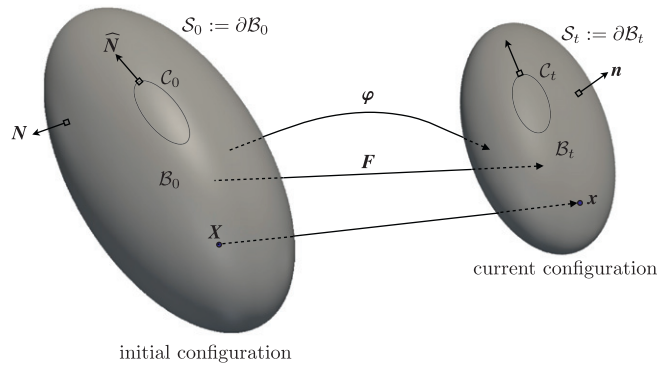
2.2. Control regions

The equations governing the coupled response of the bulk and the surface are obtained from the balances of solid and diffusing species mass, linear and angular momentum, and energy and entropy over a control region. These integral balance expressions are then localised at an arbitrary point on the surface $\mathcal{S}_0$ or in the bulk $\mathcal{B}_0$. The canonical control region considered here is one which possibly has, as part of its boundary, the surface $\mathcal{S}_0$ of the domain $\mathcal{B}_0$ and is denoted $\mathfrak{B}_0 \subset \overline{\mathcal{B}}_0$ with boundary $\partial\mathfrak{B}_0$ (see Fig. 2).

We define the orientable surface $\mathfrak{S}_0 := \mathcal{S}_0 \cap \partial\mathfrak{B}_0$ as the, possibly empty, intersection of the surface of the control region $\partial\mathfrak{B}_0$ with the surface of the reference configuration $\mathcal{S}_0$. The interior surface of the control region $\mathfrak{B}_0$ is denoted $\mathfrak{S}_0^\bullet := \partial\mathfrak{B}_0/\mathcal{S}_0$. The unit normal to the surface $\mathfrak{S}_0^\bullet$ is denoted $\boldsymbol{M}$. The boundary of $\mathfrak{S}_0$, a curve, is defined by $\mathfrak{C}_0 := \partial\mathfrak{S}_0$. The unit normal to the curve $\mathfrak{C}_0$ is denoted $\widehat{\boldsymbol{N}}$ and is tangent to the surface $\mathfrak{S}_0$.
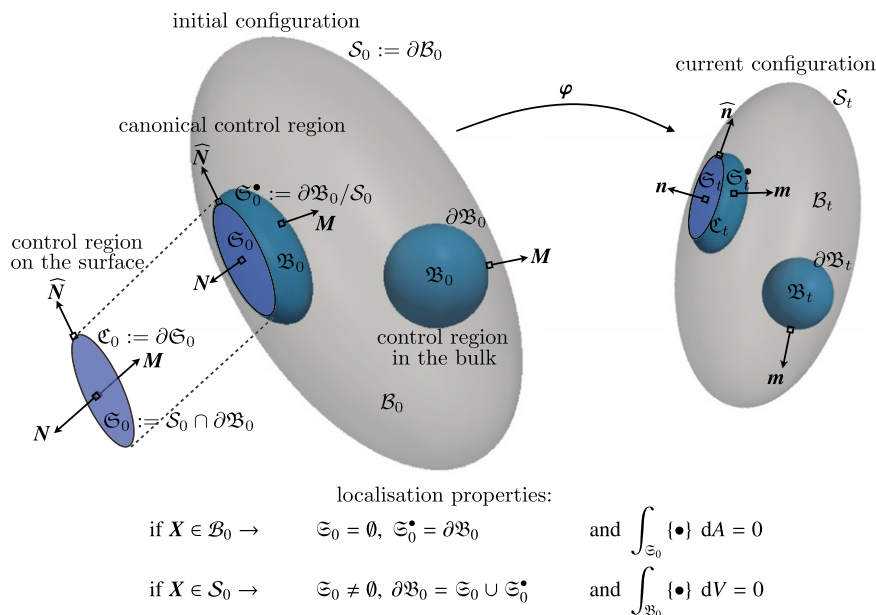
The region $\mathfrak{B}_0$ is mapped via the motion $\boldsymbol{\varphi}$ to the current configuration $\mathcal{B}_t$ as $\mathfrak{B}_t = \boldsymbol{\varphi}(\mathfrak{B}_0(\boldsymbol{X}),t) \subset \mathcal{B}_t$. The smooth surface of $\mathfrak{B}_t$ is denoted $\partial\mathfrak{B}_t = \mathfrak{S}_t \cup \mathfrak{S}_t^\bullet$ with outward unit normal $\boldsymbol{m}$. The spatial velocity is denoted $\boldsymbol{v}$ while the spatial velocity of the diffusing species is denoted $\boldsymbol{v}^\star$.

The preceding definition of the control region is reconciled with the more commonly adopted view of a control region as a domain completely within the bulk by specifying the surface $\mathfrak{S}_0$ to be an empty set when localising an integral

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[3] Direct notation is employed throughout. The scalar product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is denoted $\boldsymbol{a} \cdot \boldsymbol{b}$. The scalar product of two second-order tensors $\boldsymbol{A}$ and $\boldsymbol{B}$ is denoted $\boldsymbol{A} : \boldsymbol{B}$. The action of a second-order tensor $\boldsymbol{A}$ on a vector $\boldsymbol{b}$ is represented as $\boldsymbol{A} \cdot \boldsymbol{b}$, while the action of a fourth-order tensor $\mathbb{A}$ on a second-order tensor $\boldsymbol{B}$ is represented as $\mathbb{A} : \boldsymbol{B}$. The tensor product $\boldsymbol{a} \otimes \boldsymbol{b}$ of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is a second-order tensor defined by the relation $[\boldsymbol{a} \otimes \boldsymbol{b}] \cdot \boldsymbol{c} = [\boldsymbol{b} \cdot \boldsymbol{c}]\boldsymbol{a}$ $\forall$ vectors $\boldsymbol{c}$.

Fig. 1. The motion φ of the continuum body from the initial (reference) configuration $\overline{\mathcal{B}}_0$ to the current configuration $\overline{\mathcal{B}}_t$.

localisation properties:

$$\text{if } X \in \mathcal{B}_0 \rightarrow \qquad \mathfrak{S}_0 = \emptyset, \ \mathfrak{S}_0^\bullet = \partial \mathfrak{B}_0 \qquad \text{and} \int_{\mathfrak{S}_0} \{\bullet\} \ \mathrm{d}A = 0$$

$$\text{if } X \in \mathcal{S}_0 \rightarrow \qquad \mathfrak{S}_0 \neq \emptyset, \ \partial \mathfrak{B}_0 = \mathfrak{S}_0 \cup \mathfrak{S}_0^\bullet \qquad \text{and} \int_{\mathfrak{B}_0} \{\bullet\} \ \mathrm{d}V = 0$$

Fig. 2. The domains $\mathcal{B}_0$ and $\mathcal{B}_t$, and the canonical control region and its representation on the surface and in the bulk.

balance expression to an arbitrary point in the bulk. Critically, the equations governing the response of the bulk obtained by localising the integral balance equations over the canonical control region to a point in the bulk are identical to those obtained by localising the integral balance equations obtained from a conventional control region. The use of separate control regions on the surface and in the bulk is thus superfluous.

Conceptually, the process of localising an integral expression over a control region to a point on the surface is as follows. Firstly, as depicted in Fig. 2, the volume of the control region is decreased to zero in a manner such that the surfaces $\mathfrak{S}_0$ and $\mathfrak{S}_0^\bullet$ coincide and $N \cdot M = -1$ on $\mathfrak{S}_0$. Hence all terms involving integrals over the volume $\mathfrak{B}_0$ in the integral expression vanish. The remaining terms are then localised to a point on the surface in the standard manner and the relationship $\widehat{N} \cdot N = 0$ holds. The process of localising an expression over a control region to a point on the surface is in agreement with the assumption that the surface has zero thickness and can be viewed as a membrane.

When localising an integral expression over a control region to a point in the bulk, the surface $\mathfrak{S}_0$ is, by definition, empty and all integrals over $\mathfrak{S}_0$ vanish.

The integral form of the balance equations typically include terms due to convective or physical fluxes, or both, of a quantity over the internal surface $\mathfrak{S}_0^\bullet \subseteq \partial \mathfrak{B}_0$. We denote by $\{\bullet\}_0$ the material flux vector associated with the aforementioned quantity. The contribution of the flux vector to the integral balance expression will generally be of the form $\int_{\mathfrak{S}_0^\bullet} \{\bullet\}_0 \cdot M \ \mathrm{d}A$. This integral expression when localised to a point on the surface $\mathcal{S}_0$ becomes $-\{\bullet\}_0 \cdot N$. When the integral expression is localised to a point in the bulk, the divergence theorem will be used to convert the area integral over $\partial \mathfrak{B}_0$ to a volume integral over $\mathfrak{B}_0$. Neumann boundary conditions on the flux act on the exterior of the surface $\mathfrak{S}_0$. The prescribed flux is denoted $\{\widehat{\bullet}\}_0^p$. The contribution of the prescribed term to the integral expression of the balance equations is of the form $\int_{\mathfrak{S}_0} \{\widehat{\bullet}\}_0^p \ \mathrm{d}A$ which when localised to a

point on the surface $\mathcal{S}_0$ becomes $\{\hat{\bullet}\}_0^{\mathrm{p}}$. There is thus generally a term of the form $[\{\hat{\bullet}\}_0^{\mathrm{p}}-\{\bullet\}_0 \cdot \boldsymbol{N}]$ present when the balance equations are localised to a point on the surface. This term represents the net flux due to a prescribed flux acting from the exterior and the flux from the bulk in the interior. Additional details of the localisation procedure in the bulk and on the surface are given in Sections 3.2.1 and 3.2.2, respectively.

2.3. Tensors and vectors

A second-order tensor field on the surface $\mathcal{S}_t$, arbitrarily denoted $\boldsymbol{S}(\boldsymbol{x}|_{\mathcal{S}_t})$, is a linear transformation from the tangent space at $\boldsymbol{x}|_{\mathcal{S}_t}$ (the space of all vectors which are orthogonal to the surface normal vector $\boldsymbol{n}$) to $\mathbb{R}^3$. This definition is made compatible with the standard definition of a second-order tensor as a linear transformation from $\mathbb{R}^3$ to $\mathbb{R}^3$ by requiring that the transformation of the surface normal vector by $\boldsymbol{S}$ is precisely the zero vector (see e.g. Gurtin et al., 1998). Thus, the so-called superficial second-order tensor associated with $\boldsymbol{S}$ is denoted by $\widehat{\boldsymbol{S}} : \mathbb{R}^3 \to \mathbb{R}^3$ and satisfies the property that $\widehat{\boldsymbol{S}} \cdot \boldsymbol{n} = \boldsymbol{0}$. One important example of a superficial second-order tensor is the spatial projection

$$\mathbb{P}_t := \boldsymbol{i} - \boldsymbol{n} \otimes \boldsymbol{n} \tag{1}$$

which maps an arbitrary vector in $\mathbb{R}^3$ tangent to the surface with normal $\boldsymbol{n}$. The tensor $\boldsymbol{i}$ is the ordinary second-order mixed-variant unit tensor of the three-dimensional embedding Euclidean space in the spatial configuration. A superficial second-order tensor may be further classified as tangential or normal, denoted $\widehat{\boldsymbol{S}}_{\|}$ and $\widehat{\boldsymbol{S}}_{\perp}$, respectively, according to the definitions (Gurtin et al., 1998):

$$\widehat{\boldsymbol{S}} = \widehat{\boldsymbol{S}}_{\|} \Rightarrow \boldsymbol{n} \cdot \widehat{\boldsymbol{S}} \cdot \boldsymbol{s} = 0 \qquad \forall \boldsymbol{s} \text{ (tangential superficial second-order tensor),}$$

$$\widehat{\boldsymbol{S}} = \widehat{\boldsymbol{S}}_{\perp} \Rightarrow \mathbb{P}_t \cdot \widehat{\boldsymbol{S}} \cdot \boldsymbol{s} = \boldsymbol{0} \qquad \forall \boldsymbol{s} \text{ (normal superficial second-order tensor),}$$

where $\boldsymbol{s} \in \mathbb{R}^3$ is an arbitrary vector.

An arbitrary vector located at the surface, denoted $\{\hat{\bullet}\}$, can be decomposed into parts tangential and normal to the surface, denoted $\{\hat{\bullet}\}_{\|}$ and $\{\hat{\bullet}\}_{\perp}$, respectively, as $\{\hat{\bullet}\} = \{\hat{\bullet}\}_{\|} + \{\hat{\bullet}\}_{\perp}$.

2.4. Deformation

The invertible linear tangent map $\boldsymbol{F} : T\mathcal{B}_0 \to T\mathcal{B}_t$ (that is, the deformation gradient) maps a line element $\mathrm{d}\boldsymbol{X} \in T\mathcal{B}_0$ in the reference configuration to a line element $\mathrm{d}\boldsymbol{x} \in T\mathcal{B}_t$ in the current configuration and is defined as the derivative of the motion with respect to the reference placement; that is,

$$\boldsymbol{F}(\boldsymbol{X},t) = \text{Grad } \boldsymbol{\varphi}(\boldsymbol{X},t),$$

where $\text{Grad}\{\bullet\} := \partial\{\bullet\}/\partial\boldsymbol{X}$ is the gradient operator with respect to the reference placement. The notation $T\{\bullet\}$ denotes the tangent space to $\{\bullet\}$. The action of the gradient operator with respect to the current placement is denoted $\text{grad}\{\bullet\} := \partial\{\bullet\}/\partial\boldsymbol{x}$. The Jacobian determinant of the deformation gradient is denoted $J(\boldsymbol{X},t) := \det(\boldsymbol{F}(\boldsymbol{X},t)) > 0$. The inverse of the deformation gradient is denoted $\boldsymbol{f} := \boldsymbol{F}^{-1}$ with an associated inverse Jacobian determinant $j := \det \boldsymbol{f} = 1/J > 0$. The condition on the motion that $J(\boldsymbol{X},t) > 0$ implies that the motion is invertible and hence $\boldsymbol{v} = \boldsymbol{V} \circ \boldsymbol{\varphi}^{-1}$, where $f \circ g$ denotes the composition of two functions f and g, respectively. The Jacobian determinants are (invertible) volume maps that relate the spatial and material volume elements, $\mathrm{d}v$ and $\mathrm{d}V$, respectively, as

$$\mathrm{d}v = J \, \mathrm{d}V \quad \text{and} \quad \mathrm{d}V = j \, \mathrm{d}v. \tag{2}$$

The right Cauchy–Green tensor, a measure of the stretch, is defined by $\boldsymbol{C} := \boldsymbol{F}^t \cdot \boldsymbol{F}$.

The non-invertible, linear surface tangent map $\widehat{\boldsymbol{F}} : T\mathcal{S}_0 \to T\mathcal{S}_t$ (that is, the surface deformation gradient) maps tangential line elements on the surface of the reference configuration $\mathrm{d}\widehat{\boldsymbol{X}} \in \mathcal{S}_0$ to tangential line elements on the surface of the current configuration $\mathrm{d}\widehat{\boldsymbol{x}} \in \mathcal{S}_t$. Although the linear surface tangent map is non-invertible, due to rank deficiency, it does possess an inverse, denoted $\widehat{\boldsymbol{f}}$, in the following generalised sense:

$$\widehat{\boldsymbol{F}} \cdot \widehat{\boldsymbol{f}} = \widehat{\boldsymbol{i}} \quad \text{and} \quad \widehat{\boldsymbol{f}} \cdot \widehat{\boldsymbol{F}} = \widehat{\boldsymbol{I}},$$

where $\widehat{\boldsymbol{i}}$ and $\widehat{\boldsymbol{I}}$ are the mixed-variant surface unit tensors defined by

$$\widehat{\boldsymbol{i}} = \mathbb{P}_t = \boldsymbol{i} - \boldsymbol{n} \otimes \boldsymbol{n} \quad \text{and} \quad \widehat{\boldsymbol{I}} = \mathbb{P}_0 = \boldsymbol{I} - \boldsymbol{N} \otimes \boldsymbol{N},$$

and $\boldsymbol{I}$ is the ordinary second-order mixed-variant unit tensor of the three-dimensional embedding Euclidean space in the material configuration. From Eq. (1) it is clear that $\widehat{\boldsymbol{i}}$ and $\widehat{\boldsymbol{I}}$ are simply the spatial and material projections, $\mathbb{P}_t$ and $\mathbb{P}_0$, onto the surfaces with normals $\boldsymbol{n}$ and $\boldsymbol{N}$, respectively. It is obvious that as the projection tensors depend on the surface normal, so do the surface unit tensors. The right Cauchy–Green tensor on the surface, a measure of the surface stretch, is defined by $\widehat{\boldsymbol{C}} := \widehat{\boldsymbol{F}}^t \cdot \widehat{\boldsymbol{F}}$.

The surface deformation gradient $\widehat{\boldsymbol{F}}$ and its generalised inverse $\widehat{\boldsymbol{f}}$ are computed as the surface gradients of the surface deformation and its inverse, respectively. That is,

$$\widehat{\boldsymbol{F}} := \widehat{\text{Grad}}\,\widehat{\boldsymbol{\varphi}}(\boldsymbol{X}|_{\mathcal{S}_0},t) \quad \text{and} \quad \widehat{\boldsymbol{f}} := \widehat{\text{grad}}\,\widehat{\boldsymbol{\varphi}}^{-1}(\boldsymbol{x}|_{\mathcal{S}_t},t),$$

where

$$\widehat{\text{Grad}}\{\widehat{\bullet}\} := \text{Grad}\{\widehat{\bullet}\} \cdot \widehat{\boldsymbol{I}} \quad \text{and} \quad \widehat{\text{grad}}\{\widehat{\bullet}\} := \text{grad}\{\widehat{\bullet}\} \cdot \widehat{\boldsymbol{i}}$$

are simply the projections of the standard gradient operators onto the surface; thus $\widehat{\boldsymbol{F}} = \boldsymbol{F} \cdot \widehat{\boldsymbol{I}}$. The Jacobian determinant of the surface deformation gradient is denoted by $\widehat{J}(\boldsymbol{X}|_{\mathcal{S}_0},t) := \widehat{\det}(\widehat{\boldsymbol{F}}(\boldsymbol{X}|_{\mathcal{S}_0},t)) > 0$, and its inverse by $\widehat{j}(\boldsymbol{x},t) := \widehat{\det}(\widehat{\boldsymbol{f}}(\boldsymbol{x}|_{\mathcal{S}_t},t)) > 0$, and are defined in Gurtin and Struthers (1990), Steinmann (2008), among others. The surface Jacobian determinant $\widehat{J}$ relates the surface area elements $\mathrm{d}A \in \mathcal{S}_0$ and $\mathrm{d}a \in \mathcal{S}_t$ as

$$\mathrm{d}a = \widehat{J}\,\mathrm{d}A \quad \text{and} \quad \mathrm{d}A = \widehat{j}\,\mathrm{d}a. \tag{3}$$

Nanson's formula relates oriented surface area elements $\mathrm{d}\boldsymbol{A} \in T\mathcal{S}_0$ and $\mathrm{d}\boldsymbol{a} \in T\mathcal{S}_t$ as follows:

$$\boldsymbol{n}\,\mathrm{d}a = [\text{cof}\,\boldsymbol{F}] \cdot \boldsymbol{N}\,\mathrm{d}A \quad \text{and} \quad \boldsymbol{N}\,\mathrm{d}A = [\text{cof}\,\boldsymbol{f}] \cdot \boldsymbol{n}\,\mathrm{d}a, \tag{4}$$

where the cofactor of an arbitrary second-order tensor $\{\bullet\}$ is defined by: $\text{cof}(\bullet) := \det(\bullet)\{\bullet\}^{-t}$. Similarly, the surface Nanson's formula (Steinmann, 2008) relates oriented line elements $\mathrm{d}\widehat{\boldsymbol{L}} \in T\mathcal{C}_0$ and $\mathrm{d}\widehat{\boldsymbol{l}} \in T\mathcal{C}_t$ as follows:

$$\widehat{\boldsymbol{n}}\,\mathrm{d}l = [\widehat{\text{cof}}\,\widehat{\boldsymbol{F}}] \cdot \widehat{\boldsymbol{N}}\,\mathrm{d}L \quad \text{and} \quad \widehat{\boldsymbol{N}}\,\mathrm{d}L = [\widehat{\text{cof}}\,\widehat{\boldsymbol{f}}] \cdot \widehat{\boldsymbol{n}}\,\mathrm{d}l, \tag{5}$$

where the surface cofactor is defined by: $\widehat{\text{cof}}(\widehat{\bullet}) := \widehat{\det}(\widehat{\bullet})\{\widehat{\bullet}\}^{-t}$.

2.5. Reynolds's transport theorem

The governing equations derived in Section 3 are constructed from balance principles over a spatial control region $\mathfrak{B}_t$ (that is, a material control region mapped by the deformation $\boldsymbol{\varphi}$ to the current configuration $\mathcal{B}_t$), as depicted in Fig. 2. Two forms of flux over the boundary of the spatial control region are accounted for: (1) convective flux due to the motion of the control region and (2) physical flux due to the motion of the diffusing species. A key ingredient when manipulating the integral balance equations is a modified form of Reynolds's transport theorem.

We define by $\widehat{\boldsymbol{v}} := \mathbb{P}_t \cdot \boldsymbol{v}$ the surface velocity; a surface tangent vector. The notation $\widehat{\boldsymbol{v}}$ does not denote the (bulk) velocity evaluated at the surface $\mathcal{S}_t$, i.e. $\widehat{\boldsymbol{v}} \neq \boldsymbol{v}|_{\mathcal{S}_t}$, rather it is the projection of the bulk velocity $\boldsymbol{v}$ onto the surface with normal $\boldsymbol{n}$.

Spatial scalar quantities in the bulk $\{\bullet\}(\boldsymbol{x},t)$ and on the surface $\{\widehat{\bullet}\}(\boldsymbol{x}|_{\mathcal{S}_t},t)$ are denoted $\{\bullet\}_t$ and $\{\widehat{\bullet}\}_t$, respectively.

The material time derivative of an integral over a spatial control region $\mathfrak{B}_t \subset \overline{\mathcal{B}}_t$ is given by a modified form of Reynolds's transport theorem as

$$\mathrm{D}_t \int_{\mathfrak{B}_t} \{\bullet\}_t\,\mathrm{d}v + \mathrm{D}_t \int_{\mathfrak{S}_t} \{\widehat{\bullet}\}_t\,\mathrm{d}a = \int_{\mathfrak{B}_t} \mathrm{d}_t\{\bullet\}_t\,\mathrm{d}v + \int_{\mathfrak{S}_t^\bullet} \{\bullet\}_t \boldsymbol{v} \cdot \boldsymbol{m}\,\mathrm{d}a + \int_{\mathfrak{S}_t} \mathrm{d}_t\{\widehat{\bullet}\}_t\,\mathrm{d}a + \int_{\mathfrak{C}_t} \{\widehat{\bullet}\}_t \widehat{\boldsymbol{v}} \cdot \widehat{\boldsymbol{n}}\,\mathrm{d}l. \tag{6}$$

Here $\mathrm{D}_t\{\bullet\}$ and $\mathrm{d}_t\{\bullet\}$ denote the material and spatial time derivatives of a scalar $\{\bullet\}$, respectively. The modified form of Reynolds's transport theorem given in Eq. (6) simplifies to the standard form (see, for example, Malvern, 1969) if the control region is completely within the bulk as $\mathfrak{S}_t = \emptyset$ and hence $\mathfrak{S}_t^\bullet = \partial\mathfrak{B}_t$. With this assumption the second term on the left-hand side and the third and fourth terms on the right-hand side of Eq. (6) disappear. The resulting (bulk) Reynolds's transport theorem equates the material rate of change of the integral of a spatial quantity $\{\bullet\}_t$ in the bulk to the integral of the instantaneous rate of change of the quantity in the bulk and changes due to the convective flux of the quantity over the surface $\partial\mathfrak{B}_t$.

Consider the case now where $\mathfrak{S}_t \neq \emptyset$. The second term on the left-hand side of Eq. (6) represents the contribution due to the material rate of change of an integral of a surface quantity $\{\widehat{\bullet}\}_t$. The third and fourth terms on the right-hand side account for the instantaneous rate of change of the integral of the spatial quantity $\{\widehat{\bullet}\}_t$ over the surface, and changes due to the convective flux of the quantity over the curve $\mathfrak{C}_t$, respectively.

It proves inconvenient to separate the transport theorem into individual surface and bulk parts due to the coupling between the surface and the bulk; in addition to the convective flux over the boundary $\mathfrak{C}_t$ there is a net flux through the surface $\mathfrak{S}_0$ due to the bulk contribution and the prescribed external Neumann boundary conditions. Furthermore, utilising a single expression for Reynolds's transport theorem, specialised in accordance with the notion of the canonical control region in the bulk and on the surface, greatly simplifies the presentation.

The divergence theorem relates the integral of a quantity over the boundary of a region to an integral over the region itself. The exact form of the divergence theorem depends on the type of boundary. If the boundary is the surface bounding a volume (e.g. as in the second term on the right-hand side of Eq. (6) if $\mathfrak{S}_t = \emptyset$ and hence $\mathfrak{S}_t^\bullet = \partial\mathfrak{B}_t$) then the divergence theorem is standard (see e.g. Malvern, 1969). If the boundary is the curve bounding an area (e.g. as in the fourth term on the right-hand side of Eq. (6)) then the divergence theorem is non-standard and its form depends on the nature of the flux vector. For the most general case where the flux vector on the surface is not a tangent vector an additional term involving the surface curvature is present. We denote by $\boldsymbol{s}$ and $\widehat{\boldsymbol{s}}$ arbitrary flux vectors in the bulk and on the surface, respectively,

and do not constrain $\widehat{\boldsymbol{s}}$ to be a tangent vector. The divergence theorems for the bulk and the surface are then given by Steinmann (2008) as

$$\int_{\mathfrak{B}_t} \text{div}\ \boldsymbol{s}\ \mathrm{d}v = \int_{\partial\mathfrak{B}_t} \boldsymbol{s} \cdot \boldsymbol{m}\ \mathrm{d}a, \tag{7}$$

$$\int_{\mathfrak{S}_t} \widehat{\text{div}}\ \widehat{\boldsymbol{s}}\ \mathrm{d}a = \int_{\mathfrak{C}_t} \widehat{\boldsymbol{s}} \cdot \widehat{\boldsymbol{n}}\ \mathrm{d}l - \int_{\mathfrak{S}_t} \underbrace{[-\widehat{\text{div}}\ \boldsymbol{n}]}_{\kappa} \widehat{\boldsymbol{s}} \cdot \boldsymbol{n}\ \mathrm{d}a, \tag{8}$$

where κ is twice the mean surface curvature, and the surface divergence operator is defined by: $\widehat{\text{div}}\{\bullet\} := \widehat{\text{grad}}\{\bullet\} : \widehat{\boldsymbol{i}}$.

The surface divergence is simply the contraction of the surface gradient operator with the spatial projection tensor. Note that if $\widehat{\boldsymbol{s}}$ is a tangent vector then, by definition, the term involving the surface curvature in Eq. (8) is zero. For this reason, the curvature term will not directly enter into the formulation presented here as the surface flux vectors are tangent vectors.

3. Governing equations

The objective of this section is to derive the equations governing the response of a continuum due to the contributions from the bulk and the surface. The governing equations are systematically derived by considering the conservation of several key properties, namely solid mass, diffusing species mass, linear and angular momentum, internal energy and entropy over a spatial control region. The integral form of the governing balance equations are stated in a manner that allows them to be localised to a point in the bulk or on the surface by applying the procedures discussed in Section 2 and elaborated upon further in this section. The Clausius–Duhem form of the second law of thermodynamics and the resulting local dissipation inequality provide the form of the constitutive relations for the bulk and for the surface. The restrictions that arise from the reduced dissipation inequality stipulate the thermodynamically consistent form of the remaining constitutive relations. The possible thermodynamically admissible constraints between the surface and bulk temperatures, and the surface and bulk chemical potentials are then discussed. The section concludes with the derivation of the temperature evolution equations in the bulk and on the surface.

3.1. Conservation of solid mass

Consider the material and spatial control regions, denoted $\mathfrak{B}_0$ and $\mathfrak{B}_t$, respectively, as shown in Fig. 2. The bulk densities of the solid in the reference and current configurations are denoted ρ_0 (kg/m^3) and ρ_t (kg/m^3), respectively. Furthermore, the solid surface densities in the reference and current configurations are denoted $\widehat{\rho}_0$ (kg/m^2) and $\widehat{\rho}_t$ (kg/m^2), respectively.

As stated in Section 2, material particles $\boldsymbol{X}|_{\mathcal{S}_0}$ on the surface of the domain $\mathcal{S}_0$ are mapped to particles $\boldsymbol{x}|_{\mathcal{S}_t}$ on the surface $\mathcal{S}_t$. There is thus no solid mass exchange between the surface and the bulk.

The global statement of conservation of solid mass over the control region reads

$$\int_{\mathfrak{B}_0} \rho_0\ \mathrm{d}V + \int_{\mathfrak{S}_0} \widehat{\rho}_0\ \mathrm{d}A = \int_{\mathfrak{B}_t} \rho_t\ \mathrm{d}v + \int_{\mathfrak{S}_t} \widehat{\rho}_t\ \mathrm{d}a. \tag{9}$$

Firstly, consider the localisation of Eq. (9) at a point in the bulk $\mathcal{B}_0$. It follows that, using the kinematic slavery assumption, $\mathfrak{S}_0 = \mathfrak{S}_t = \emptyset$. Using Eq. (2)$_1$ to change the limits of integration on the right-hand side of Eq. (9) to the reference configuration and applying the standard localisation theorem renders the familiar local form for the conservation of solid mass (see e.g. Malvern, 1969) as

$$J\rho_t = \rho_0 \quad \text{or} \quad \rho_t = j\rho_0. \tag{10}$$

The localisation process is valid for an arbitrary region $\mathfrak{B}_0 \subset \mathcal{B}_0$ and hence Eq. (10) holds throughout the domain $\mathcal{B}_0$.

Alternatively, consider the localisation of Eq. (9) at a point on the surface $\mathcal{S}_0$. Using Eq. (3)$_1$ to change the limits of integration in Eq. (9) to the reference configuration and applying the localisation theorem renders the non-standard local form for the conservation of solid mass on the surface as

$$\widehat{J}\widehat{\rho}_t = \widehat{\rho}_0 \quad \text{or} \quad \widehat{\rho}_t = \widehat{j}\widehat{\rho}_0. \tag{11}$$

As in the bulk, the localisation process is valid for an arbitrary surface $\mathfrak{S}_0 \subset \mathcal{S}_0$ and hence Eq. (11) holds everywhere on the surface $\mathcal{S}_0$.

Due to the assumption of kinematic slavery, the localised expression for the conservation of solid mass in the bulk (Eq. (10)) is, formally, identical to that on the surface (Eq. (11)).

3.2. Conservation of diffusing species mass

The mass of the diffusing species per unit volume of the (deformed) solid is denoted $\rho_t^\star$ (kg/m^3). The concentration of the diffusing species per unit volume of the (deformed) solid, denoted c_t (mol/m^3), is related to the diffusing species

density $\rho_t^\star$ via the inverse of the diffusing species molar mass c (mol/kg) as

$$c_t = c\rho_t^\star \quad (\text{mol/m}^3) = (\text{mol/kg}) \cdot (\text{kg/m}^3).$$

The related quantities on the surface are the mass of the diffusing species per unit area of the (deformed) surface $\widehat{\rho}_t^\star$ (kg/m²). The concentration of the diffusing species per unit area of the (deformed) surface $\mathfrak{S}_t$, denoted $\widehat{c}_t$ (mol/m²), is related to the diffusing species surface density $\widehat{\rho}_t^\star$ via the inverse of the diffusing species surface molar mass $\widehat{c}$ (mol/kg) as

$$\widehat{c}_t = \widehat{c}\widehat{\rho}_t^\star \quad (\text{mol/m}^2) = (\text{mol/kg}) \cdot (\text{kg/m}^2).$$

Consider a spatial control region $\mathfrak{B}_t \subset \overline{\mathcal{B}}_t$ as shown in Figs. 2 and 3. The global statement of conservation of diffusing species mass over $\mathfrak{B}_t$ reads

$$\int_{\mathfrak{B}_t} \mathrm{d}_t c_t \, \mathrm{d}v + \int_{\mathfrak{S}_t} \mathrm{d}_t \widehat{c}_t \, \mathrm{d}a = - \int_{\mathfrak{S}_t^\bullet} c_t \boldsymbol{v}^\star \cdot \boldsymbol{m} \, \mathrm{d}a + \int_{\mathfrak{B}_t} w \, \mathrm{d}v - \int_{\mathfrak{C}_t} \widehat{c}_t \widehat{\boldsymbol{v}}^\star \cdot \widehat{\boldsymbol{n}} \, \mathrm{d}l + \int_{\mathfrak{S}_t} \widehat{w}^{\mathrm{p}} \, \mathrm{d}a, \tag{12}$$

where $\boldsymbol{v}^\star$ and $\widehat{\boldsymbol{v}}^\star$ are the spatial velocities of the diffusing species in the bulk and on the surface, respectively, and $\boldsymbol{v}$ and $\widehat{\boldsymbol{v}} := \mathbb{P}_t \cdot \boldsymbol{v}$ are the spatial velocities of the bulk and surface, respectively. Bulk sources of species generation are denoted w (mol/m³s), and $\widehat{w}^{\mathrm{p}}$ (mol/m²s) denotes the prescribed diffusional flux on the exterior of the surface. The quantities $c_t \boldsymbol{v}^\star$ and $\widehat{c}_t \widehat{\boldsymbol{v}}^\star$ represent the physical species fluxes over the boundaries $\mathfrak{S}_t^\bullet$ and $\mathfrak{C}_t$, respectively. Neumann type boundary conditions on the concentration flux enter as surface balance equations; a non-standard feature of the model that will be elaborated on subsequently. The preceding statement of conservation of diffusing species mass can be expressed, using the modified version of Reynolds's transport theorem given in Eq. (6), as

$$\mathrm{D}_t \int_{\mathfrak{B}_t} c_t \, \mathrm{d}v + \mathrm{D}_t \int_{\mathfrak{S}_t} \widehat{c}_t \, \mathrm{d}a = - \int_{\mathfrak{S}_t^\bullet} \underbrace{c_t[\boldsymbol{v}^\star - \boldsymbol{v}]}_{\boldsymbol{w}} \cdot \boldsymbol{m} \, \mathrm{d}a + \int_{\mathfrak{B}_t} w \, \mathrm{d}v - \int_{\mathfrak{C}_t} \underbrace{\widehat{c}_t[\widehat{\boldsymbol{v}}^\star - \widehat{\boldsymbol{v}}]}_{\widehat{\boldsymbol{w}}} \cdot \widehat{\boldsymbol{n}} \, \mathrm{d}l + \int_{\mathfrak{S}_t} \widehat{w}^{\mathrm{p}} \, \mathrm{d}a, \tag{13}$$

where $\boldsymbol{w}$ (mol/m²s) and $\widehat{\boldsymbol{w}}$ (mol/ms) are the (net) spatial diffusional flux vectors in the bulk and on the surface, respectively. We note once again that the surface diffusional flux vector $\widehat{\boldsymbol{w}}$ is a tangent vector.

The Piola transforms (pull-backs) of the (net) diffusional flux vectors in the bulk and on the surface in the spatial configuration to the corresponding quantities $\boldsymbol{W}$ and $\widehat{\boldsymbol{W}}$ in the reference configuration, respectively, are

$$\boldsymbol{W} = J\boldsymbol{w} \cdot \boldsymbol{f}^t \quad \text{or, equivalently,} \quad \boldsymbol{W} = \boldsymbol{w} \cdot \mathrm{cof}\, \boldsymbol{F}, \tag{14}$$

$$\widehat{\boldsymbol{W}} = \widehat{J}\widehat{\boldsymbol{w}} \cdot \widehat{\boldsymbol{f}}^t \quad \text{or, equivalently,} \quad \widehat{\boldsymbol{W}} = \widehat{\boldsymbol{w}} \cdot \widehat{\mathrm{cof}\, \widehat{\boldsymbol{F}}}. \tag{15}$$

The bulk and surface concentrations of the diffusing species expressed in the current and reference configurations, c_t and c_0, and $\widehat{c}_t$ and $\widehat{c}_0$, respectively, are related via the Piola transformations as

$$c_0 = Jc_t \quad \text{and} \quad \widehat{c}_0 = \widehat{J}\widehat{c}_t. \tag{16}$$

By transforming the limits of integration in Eq. (13) to the reference configuration using Eqs. (2) and (3) and Nanson's equations (4) and (5), and using the relations given in Eq. (14)–(16) one obtains the material expression for the balance of
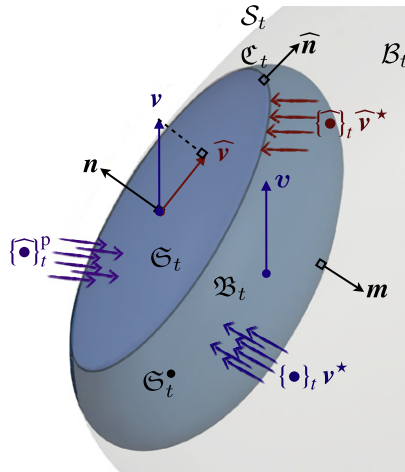
Fig. 3. A portion of the domain $\mathcal{B}_t$ and the spatial control region $\mathfrak{B}_t$. The physical flux vector associated with an arbitrary scalar spatial quantity in the bulk $\{\bullet\}_t$ is denoted $\{\bullet\}_t \boldsymbol{v}^\star$. The physical tangent flux vector associated with an arbitrary scalar spatial quantity on the surface $\{\widehat{\bullet}\}_t$ is denoted $\{\widehat{\bullet}\}_t \widehat{\boldsymbol{v}}^\star$. The velocity of the bulk is denoted $\boldsymbol{v}$, while the surface velocity is defined by $\widehat{\boldsymbol{v}} := \mathbb{P}_t \cdot \boldsymbol{v}$. The flux vectors due to convection of the bulk and the surface are denoted $\{\bullet\}_t \boldsymbol{v}$ and $\{\widehat{\bullet}\}_t \widehat{\boldsymbol{v}}$, respectively.

diffusing species mass as

$$D_t \int_{\mathfrak{B}_t} c_t \, dv + D_t \int_{\mathfrak{S}_t} \widehat{c}_t \, da = D_t \int_{\mathfrak{B}_0} \underbrace{c_t J}_{c_0} \, dV + D_t \int_{\mathfrak{S}_0} \underbrace{\widehat{c}_t \widehat{J}}_{\widehat{c}_0} \, dA = -\int_{\mathfrak{S}_0^{\bullet}} \boldsymbol{W} \cdot \boldsymbol{M} \, dA + \int_{\mathfrak{B}_0} W \, dV - \int_{\mathfrak{C}_0} \widehat{\boldsymbol{W}} \cdot \widehat{\boldsymbol{N}} \, dL + \int_{\mathfrak{S}_0} \widehat{W}^{\mathrm{p}} \, dA, \quad (17)$$

where $W \coloneqq wJ$ and $\widehat{W}^{\mathrm{p}} \coloneqq \widehat{w}^{\mathrm{p}}\widehat{J}$.

The next step is to localise Eq. (17) for an arbitrary point in the bulk and on the surface, respectively. The procedure, as discussed in Section 2.2, is explained first for the bulk and then for the surface.

3.2.1. Conservation of diffusing species mass in the bulk

Consider a control region completely within the bulk. The surface $\mathfrak{S}_0 = \emptyset$ and, thus, $\mathfrak{S}_0^{\bullet} = \partial\mathfrak{B}_0$. Hence, Eq. (17) becomes

$$\int_{\mathfrak{B}_0} D_t c_0 \, dV = -\int_{\partial\mathfrak{B}_0} \boldsymbol{W} \cdot \boldsymbol{M} \, dA + \int_{\mathfrak{B}_0} W \, dV,$$

and using the divergence theorem for the bulk (7), and localising yields the standard expression for the conservation of diffusing species mass (see e.g. Govindjee and Simo, 1993) given by

$$D_t c_0 = -\mathrm{Div}\, \boldsymbol{W} + W \quad \text{in } \mathcal{B}_0. \tag{18}$$

3.2.2. Conservation of diffusing species mass on the surface

Consider a control region $\mathfrak{B}_0$ that has as part of its boundary the surface $\mathcal{S}_0$. Conceptually the control region is collapsed to an area on the surface such that the areas $\mathfrak{S}_0$ and $\mathfrak{S}_0^{\bullet}$ coincide, and $\boldsymbol{N} = -\boldsymbol{M}$. The volume of the collapsed control region is zero and hence all volume integrals over $\mathfrak{B}_0$ are eliminated from Eq. (17). What remains is given by

$$\int_{\mathfrak{S}_0} D_t \widehat{c}_0 \, dA = \int_{\mathfrak{S}_0} [\boldsymbol{W} \cdot \boldsymbol{N} + \widehat{W}^{\mathrm{p}}] \, dA - \int_{\mathfrak{C}_0} \widehat{\boldsymbol{W}} \cdot \widehat{\boldsymbol{N}} \, dL,$$

and using the divergence theorem for the surface (8) and localising yields

$$D_t \widehat{c}_0 = -\widehat{\mathrm{Div}}\, \widehat{\boldsymbol{W}} + \underbrace{\widehat{W}^{\mathrm{p}} + \boldsymbol{W} \cdot \boldsymbol{N}}_{\widehat{W}} \quad \text{on } \mathcal{S}_0. \tag{19}$$

The quantity $\widehat{W}$ is the net species flux on the surface. It is clear that the prescribed species flux $\widehat{W}^{\mathrm{p}} = \widehat{W} - \boldsymbol{W} \cdot \boldsymbol{N}$ contains contributions from both the surface $\widehat{W}$ and the bulk $\boldsymbol{W} \cdot \boldsymbol{N}$ and arises as a consequence of the balance equations. In the absence of surface effects, i.e. $\widehat{W} = 0$, one recovers the standard definition (see e.g. Hughes, 1987) of the diffusional flux as $\widehat{W}^{\mathrm{p}} = -\boldsymbol{W} \cdot \boldsymbol{N}$. If the boundary under consideration were not the external boundary of the domain but rather an interface within the bulk, as is the more commonly analysed case, then the net species flux on the interface, denoted $\widetilde{W}$, would be

$$\widetilde{W} = \boldsymbol{W}^+ \cdot \boldsymbol{N}^+ + \boldsymbol{W}^- \cdot \boldsymbol{N}^- = [\![\boldsymbol{W}]\!] \cdot \boldsymbol{N}^+, \tag{20}$$

where the notation $\{\bullet\}^{+,-}$ denotes the quantity $\{\bullet\}$ on either side of the interface, arbitrarily denoted $+$ and $-$, and $[\![\bullet]\!]$ denotes the jump in $\{\bullet\}$ over the interface.

3.3. Balance of linear and angular momentum

The Piola–Kirchhoff stress tensors in the bulk and on the surface are denoted $\boldsymbol{P}$ and $\widehat{\boldsymbol{P}}$, respectively. The equilibrium equations for the bulk and the surface, and the symmetry properties of the bulk and surface Cauchy stress tensors, denoted $\boldsymbol{\sigma} \coloneqq j\boldsymbol{P} \cdot \boldsymbol{F}^t$ and $\widehat{\boldsymbol{\sigma}} \coloneqq \widehat{j}\widehat{\boldsymbol{P}} \cdot \widehat{\boldsymbol{F}}^t$, respectively, are detailed in Steinmann (2008), among others. They arise from performing a balance of linear and angular momentum over the spatial control region $\mathfrak{B}_t$. Only the final localised forms are presented here for the sake of brevity:

$$\left. \begin{array}{l} \mathrm{Div}\, \boldsymbol{P} + \boldsymbol{B} = \boldsymbol{0} \\ \boldsymbol{F} \cdot \boldsymbol{P}^t = \boldsymbol{P} \cdot \boldsymbol{F}^t \end{array} \right\} \quad \text{in } \mathcal{B}_0,$$

$$\left. \begin{array}{l} \widehat{\mathrm{Div}}\, \widehat{\boldsymbol{P}} + \widehat{\boldsymbol{B}} = \boldsymbol{0} \quad \text{where } \widehat{\boldsymbol{B}} = \widehat{\boldsymbol{B}}^{\mathrm{p}} - \boldsymbol{P} \cdot \boldsymbol{N} \\ \widehat{\boldsymbol{F}} \cdot \widehat{\boldsymbol{P}}^t = \widehat{\boldsymbol{P}} \cdot \widehat{\boldsymbol{F}}^t \end{array} \right\} \quad \text{on } \mathcal{S}_0,$$

where $\boldsymbol{B}$ denotes the total volume force per unit reference volume and $\widehat{\boldsymbol{B}}^{\mathrm{p}}$ is the prescribed traction vector acting on the exterior of the surface. In the absence of surface effects, one obtains the standard definition (see e.g. Hughes, 1987) of the Neumann boundary condition for the traction as $\widehat{\boldsymbol{B}}^{\mathrm{p}} = \boldsymbol{P} \cdot \boldsymbol{N}$. The surface stress $\widehat{\boldsymbol{P}}$ is, by definition, a superficial second-order tangent tensor, that is, $\widehat{\boldsymbol{P}} \cdot \boldsymbol{N} = \boldsymbol{0}$.

3.4. Balance of internal energy

The enthalpy of the diffusing species per unit volume of the (deformed) solid φ_t (N m/m^3) that contributes to the internal energy is related to the diffusing species concentration in the bulk c_t as

$$\varphi_t = \varphi c_t \quad (\text{N m/m}^3) = (\text{N m/mol}) \cdot (\text{mol/m}^3),$$

where φ (N m/mol) is the enthalpy of diffusing species per unit amount of diffusing species. Similarly, the enthalpy of the diffusing species per unit area of the (deformed) surface $\widehat{\varphi}_t$ (N m/m^2) that contributes to the internal energy is related to the diffusing species concentration on the surface $\widehat{c}_t$ as

$$\widehat{\varphi}_t = \widehat{\varphi}\widehat{c}_t \quad (\text{N m/m}^2) = (\text{N m/mol}) \cdot (\text{mol/m}^2),$$

where $\widehat{\varphi}$ (N m/mol) is the surface enthalpy of diffusing species per unit amount of diffusing species.

Consider now a material control region $\mathfrak{B}_0 \subset \overline{\mathcal{B}}_0$. The rate of change of enthalpy associated with the diffusing species is due to the (net) diffusing species flux over the boundary of $\mathfrak{B}_0$, source terms in $\mathfrak{B}_0$, and the prescribed flux on the surface $\mathfrak{S}_0$. Therefore, the contribution of the diffusing species to the rate of change of the internal energy follows directly from the balance of diffusing species mass given in Eq. (17) as

$$\int_{\mathfrak{B}_0} \mathrm{D}_t \varphi_0 \, \mathrm{d}V + \int_{\mathfrak{S}_0} \mathrm{D}_t \widehat{\varphi}_0 \, \mathrm{d}A = -\int_{\mathfrak{S}_0^\bullet} \varphi \boldsymbol{W} \cdot \boldsymbol{M} \, \mathrm{d}A + \int_{\mathfrak{B}_0} \varphi W \, \mathrm{d}V - \int_{\mathfrak{C}_0} \widehat{\varphi}\widehat{\boldsymbol{W}} \cdot \widehat{\boldsymbol{N}} \, \mathrm{d}L + \int_{\mathfrak{S}_0} \widehat{\varphi}\widehat{W}^{\mathrm{p}} \, \mathrm{d}A, \tag{21}$$

where

$$\varphi_0 = J\varphi_t \quad \text{and} \quad \widehat{\varphi}_0 = \widehat{J}\widehat{\varphi}_t. \tag{22}$$

The heat flux vector per unit current area in the bulk and the tangential heat flux vector per unit current length on the surface, denoted $\boldsymbol{q}$ (N m/m^2 s) and $\widehat{\boldsymbol{q}}$ (N m/m s), respectively, are related to the heat flux vector per unit reference area in the bulk $\boldsymbol{Q}$ and the heat flux vector per unit reference length on the surface $\widehat{\boldsymbol{Q}}$, respectively, via the Piola transforms (pullbacks) as

$$\boldsymbol{Q} = \boldsymbol{q} \cdot \mathrm{cof}\,\boldsymbol{F} \quad \text{and} \quad \widehat{\boldsymbol{Q}} = \widehat{\boldsymbol{q}} \cdot \widehat{\mathrm{cof}\,\widehat{\boldsymbol{F}}}.$$

The material quantities Q (N m/m^3 s) and $\widehat{Q}^{\mathrm{p}}$ (N m/m^2 s) represent the heat sources and the prescribed heat flux, respectively. The global rate of change of total internal energy u_0 due to deformation, species diffusion and sources (see Eq. (21)), heat conduction and heat sources is therefore

$$\int_{\mathfrak{B}_0} \mathrm{D}_t u_0 \, \mathrm{d}V + \int_{\mathfrak{S}_0} \mathrm{D}_t \widehat{u}_0 \, \mathrm{d}A = \int_{\mathfrak{B}_0} [\boldsymbol{P} : \mathrm{D}_t \boldsymbol{F} + \underbrace{[Q + \varphi W]}_{Q_{\mathrm{eff}}}] \, \mathrm{d}V + \int_{\mathfrak{S}_0} [\widehat{\boldsymbol{P}} : \mathrm{D}_t \widehat{\boldsymbol{F}} + \underbrace{[\widehat{Q}^{\mathrm{p}} + \widehat{\varphi}\widehat{W}^{\mathrm{p}}]}_{\widehat{Q}_{\mathrm{eff}}^{\mathrm{p}}}] \, \mathrm{d}A$$
$$- \int_{\mathfrak{S}_0^\bullet} \underbrace{[\boldsymbol{Q} + \varphi \boldsymbol{W}]}_{\boldsymbol{Q}_{\mathrm{eff}}} \cdot \boldsymbol{M} \, \mathrm{d}A - \int_{\mathfrak{C}_0} \underbrace{[\widehat{\boldsymbol{Q}} + \widehat{\varphi}\widehat{\boldsymbol{W}}]}_{\widehat{\boldsymbol{Q}}_{\mathrm{eff}}} \cdot \widehat{\boldsymbol{N}} \, \mathrm{d}L, \tag{23}$$

where Q_{eff} denotes the effective heat source due to heat and species sources in the bulk, $\widehat{Q}_{\mathrm{eff}}^{\mathrm{p}}$ denotes the effective heat flux due to the prescribed heat and diffusion flux on the surface, and $\boldsymbol{Q}_{\mathrm{eff}}$ and $\widehat{\boldsymbol{Q}}_{\mathrm{eff}}$ denote the effective heat flux vectors in the bulk and on the surface, respectively.

Localising Eq. (23) at a point in the bulk $\mathcal{B}_0$ and on the surface $\mathcal{S}_0$ gives the local balance equations for internal energy, expressed in material quantities, as

$$\mathrm{D}_t u_0 = \boldsymbol{P} : \mathrm{D}_t \boldsymbol{F} + Q_{\mathrm{eff}} - \mathrm{Div}\,\boldsymbol{Q}_{\mathrm{eff}} \quad \text{in } \mathcal{B}_0, \tag{24}$$

$$\mathrm{D}_t \widehat{u}_0 = \widehat{\boldsymbol{P}} : \mathrm{D}_t \widehat{\boldsymbol{F}} + \widehat{Q}_{\mathrm{eff}} - \widehat{\mathrm{Div}}\,\widehat{\boldsymbol{Q}}_{\mathrm{eff}} \quad \text{where } \widehat{Q}_{\mathrm{eff}} = \widehat{Q}_{\mathrm{eff}}^{\mathrm{p}} + \boldsymbol{Q}_{\mathrm{eff}} \cdot \boldsymbol{N} \quad \text{on } \mathcal{S}_0. \tag{25}$$

The quantity $\widehat{Q}_{\mathrm{eff}}$ represents the net effective heat flux on the surface.

In the balance of internal energy on the surface (25), the effective surface heat flux $\widehat{Q}_{\mathrm{eff}}$ contains a contribution from the bulk $\boldsymbol{Q}_{\mathrm{eff}} \cdot \boldsymbol{N}$ and a prescribed quantity on the surface $\widehat{Q}_{\mathrm{eff}}^{\mathrm{p}}$ and arises due to the coupling between the surface and bulk, and heat conduction and species diffusion.

3.5. Balance of entropy

The entropy densities of the diffusing species in the volume and on the surface are denoted σ_t (N m/K m^3) and $\widehat{\sigma}_t$ (N m/K m^2), respectively. They are related to the diffusing species concentration in the bulk c_t and on the surface $\widehat{c}_t$ via the entropy of the diffusing species per amount of diffusing species in the bulk σ (N m/K mol) and on the surface $\widehat{\sigma}$ (N m/K mol) as

$$\sigma_t = \sigma c_t \quad (\text{N m/K m}^3) = (\text{N m/K mol}) \cdot (\text{mol/m}^3), \tag{26}$$

$$\widehat{\sigma}_t = \widehat{\sigma}\widehat{c}_t \quad (\text{N m/K m}^2) = (\text{N m/K mol}) \cdot (\text{mol/m}^2), \tag{27}$$

respectively.

Consider now a control region $\mathfrak{B}_0 \subset \overline{\mathcal{B}}_0$. Using the same arguments employed to derive the internal energy contribution due to diffusion and sources in Eq. (21), the rate of change of entropy associated with the diffusing species is given by

$$\int_{\mathfrak{B}_0} D_t \sigma_0 \, dV + \int_{\mathfrak{S}_0} D_t \widehat{\sigma}_0 \, dA = -\int_{\mathfrak{S}_0^\bullet} \sigma \boldsymbol{W} \cdot \boldsymbol{M} \, dA + \int_{\mathfrak{B}_0} \sigma W \, dV - \int_{\mathfrak{C}_0} \widehat{\sigma}\widehat{\boldsymbol{W}} \cdot \widehat{\boldsymbol{N}} \, dL + \int_{\mathfrak{S}_0} \widehat{\sigma}\widehat{W}^{\mathrm{p}} \, dA, \tag{28}$$

where

$$\sigma_0 = J\sigma_t \quad \text{and} \quad \widehat{\sigma}_0 = \widehat{J}\widehat{\sigma}_t. \tag{29}$$

We denote by the material quantities s_0 and $\widehat{s}_0$ the total bulk entropy density and the total surface entropy density, respectively. The second law of thermodynamics imposes the physical restriction that the rate of increase of entropy in a body is not less than the total entropy supplied to the body. We adopt the commonly made Clausius–Duhem assumption that the heat flux vector $\boldsymbol{Q}$ and the heat source Q are proportional to the entropy flux vector $\boldsymbol{H}$ and the entropy source H, respectively. Furthermore, we assume that the form of this relation holds on the surface. Thus,

$$\boldsymbol{H} = \theta^{-1}\boldsymbol{Q}, \quad H = \theta^{-1}Q, \quad \widehat{\boldsymbol{H}} = \widehat{\theta}^{-1}\widehat{\boldsymbol{Q}} \quad \text{and} \quad \widehat{H}^{\mathrm{p}} = \widehat{\theta}^{-1}\widehat{Q}^{\mathrm{p}}, \tag{30}$$

where $\theta > 0$ and $\widehat{\theta} > 0$ (K) are the absolute temperatures in the bulk and on the surface, respectively.

Note that in contrast to Fischer et al. (2008), for example, who, for an interface within the bulk, assumed $[\![\theta]\!] = 0$, the assumption that the bulk and surface temperatures are equal (that is, thermal slavery) is not made at this point in the presentation. It will be shown in Section 3.6 that the thermal slavery condition need not be assumed a priori, rather it is one of the possible relations required for thermodynamic consistency.

We denote via the non-negative material quantities π_0 and $\widehat{\pi}_0$ the entropy production density in the bulk and on the surface, respectively, and, furthermore, define by

$$\delta_0 \coloneqq \pi_0\theta \geq 0 \quad \text{and} \quad \widehat{\delta}_0 \coloneqq \widehat{\pi}_0\widehat{\theta} \geq 0 \tag{31}$$

the dissipation densities in the bulk and on the surface, respectively. The global balance of entropy over a material control region $\mathfrak{B}_0$ thus reads

$$\int_{\mathfrak{B}_0} D_t s_0 \, dV + \int_{\mathfrak{S}_0} D_t \widehat{s}_0 \, dA = \int_{\mathfrak{B}_0} \pi_0 \, dV + \int_{\mathfrak{S}_0} \widehat{\pi}_0 \, dA + \int_{\mathfrak{B}_0} \underbrace{[H + \sigma W]}_{H_{\mathrm{eff}}} \, dV + \int_{\mathfrak{S}_0} \underbrace{[\widehat{H}^{\mathrm{p}} + \widehat{\sigma}\widehat{W}^{\mathrm{p}}]}_{\widehat{H}^{\mathrm{p}}_{\mathrm{eff}}} \, dA$$

$$- \int_{\mathfrak{S}_0^\bullet} \underbrace{[\boldsymbol{H} + \sigma \boldsymbol{W}]}_{\boldsymbol{H}_{\mathrm{eff}}} \cdot \boldsymbol{M} \, dA - \int_{\mathfrak{C}_0} \underbrace{[\widehat{\boldsymbol{H}} + \widehat{\sigma}\widehat{\boldsymbol{W}}]}_{\widehat{\boldsymbol{H}}_{\mathrm{eff}}} \cdot \widehat{\boldsymbol{N}} \, dL, \tag{32}$$

where H_{eff} denotes the effective entropy source due to heat and species sources in the bulk, $\widehat{H}^{\mathrm{p}}_{\mathrm{eff}}$ denotes the effective entropy flux due to the prescribed heat and diffusion fluxes on the surface, and $\boldsymbol{H}_{\mathrm{eff}}$ and $\widehat{\boldsymbol{H}}_{\mathrm{eff}}$ denote the effective entropy flux vectors in the bulk and on the surface, respectively. We note that $\widehat{\boldsymbol{H}}_{\mathrm{eff}}$ is a tangent vector.

The local form of the conservation of entropy in the bulk (i.e. the Clausius–Duhem form) follows from Eq. (32) as

$$D_t s_0 = \pi_0 + H_{\mathrm{eff}} - \mathrm{Div}\,\boldsymbol{H}_{\mathrm{eff}}, \tag{33}$$

and using the localised expression for the conservation of species mass in the bulk given in Eq. (18) as

$$= \pi_0 + H - \mathrm{Div}\,\boldsymbol{H} + \sigma D_t c_0 - \boldsymbol{W} \cdot \mathrm{Grad}\,\sigma. \tag{34}$$

Multiplying both sides of the above equation by the bulk temperature θ, using the relations given in Eq. (30) and (31) and exploiting the relationship $\theta\,\mathrm{Div}\,\boldsymbol{H} = [\mathrm{Div}\,\boldsymbol{Q} - \boldsymbol{H} \cdot \mathrm{Grad}\,\theta]$ one obtains

$$\theta D_t s_0 = \delta_0 + Q + \theta\sigma D_t c_0 - \mathrm{Div}\,\boldsymbol{Q} + \boldsymbol{H} \cdot \mathrm{Grad}\,\theta - \theta\boldsymbol{W} \cdot \mathrm{Grad}\,\sigma. \tag{35}$$

The localised form of the balance of entropy given in Eq. (32) on the surface takes the form

$$D_t \widehat{s}_0 = \widehat{\pi}_0 + \underbrace{[\widehat{H}^{\mathrm{p}}_{\mathrm{eff}} + \boldsymbol{H}_{\mathrm{eff}} \cdot \boldsymbol{N}]}_{\widehat{H}_{\mathrm{eff}}} - \widehat{\mathrm{Div}}\,\widehat{\boldsymbol{H}}_{\mathrm{eff}}, \tag{36}$$

where $\widehat{H}_{\mathrm{eff}}$ is the net effective entropy flux on the surface.

As with the net effective energy flux, $\widehat{Q}_{\mathrm{eff}}$, defined in the expression for the balance of energy on the surface given in Eq. (25), the net effective entropy flux on the surface $\widehat{H}_{\mathrm{eff}}$ contains prescribed contributions from the external surface and contributions from the bulk.

3.6. Constitutive relations for the bulk and the surface

As is customary in solid mechanics we choose to work with the bulk material Helmholtz energy $\psi_0 \coloneqq u_0 - \theta s_0$ and the bulk chemical potential $\mu \coloneqq \varphi - \theta\sigma$, as defined via Legendre transforms (see e.g. Malvern, 1969). In the same spirit, we

define the corresponding surface Helmholtz energy $\widehat{\psi}_0 := \widehat{u}_0 - \widehat{\theta}\widehat{s}_0$ and the surface chemical potential $\widehat{\mu} := \widehat{\varphi} - \widehat{\theta}\widehat{\sigma}$. (Examples providing additional details of the form of the Helmholtz energies will be given in Section 4.) Notice that as for the temperature in Section 3.5, and in contrast to Dolbow et al. (2004), for example, who for an interface in the bulk assumed $[\![\mu]\!] = 0$, we do not impose the constraint that the chemical potential in the bulk and on the surface coincide, that is we do not assume chemical slavery $\widehat{\mu} = \mu|_{\mathcal{S}_0}$. It will be shown in Section 3.6 that the chemical slavery condition need not be assumed a priori, rather it is one of the possible relations required for thermodynamic consistency.

The functional form of the Helmholtz energy densities are chosen, generally, as

$$\psi_0 = \psi_0(\boldsymbol{C},\theta,c_0,\boldsymbol{\Xi};\boldsymbol{X}) \quad \text{and} \quad \widehat{\psi}_0 = \widehat{\psi}_0(\widehat{\boldsymbol{C}},\widehat{\theta},\widehat{c}_0,\widehat{\boldsymbol{\Xi}};\boldsymbol{X}|_{\mathcal{S}_0},\boldsymbol{N}), \tag{37}$$

where $\boldsymbol{\Xi}$ and $\widehat{\boldsymbol{\Xi}}$ denote the set of material internal variables that describe the viscoelastic response of the solid. Here the arguments of the Helmholtz energy densities in the second slot denote the parameterisation of the energy in terms of position and, in the case of the surface, the outward normal $\boldsymbol{N}$. This parameterisation is required to account for anisotropy on the surface. Henceforth, for the sake of simplicity, we shall assume an isotropic response and furthermore, for the sake of brevity, omit the parameterisation of the energy in terms of position from the notation. The reader is referred to Steinmann (2008) and references therein for additional details on capturing surface anisotropy. Note that in order to satisfy the principle of material objectivity (Truesdell and Noll, 2004) the dependence of the Helmholtz energies ψ_0 and $\widehat{\psi}_0$ on the deformation gradients $\boldsymbol{F}$ and $\widehat{\boldsymbol{F}}$ is via the right Cauchy–Green tensors $\boldsymbol{C}$ and $\widehat{\boldsymbol{C}}$, respectively.

Using the local expressions for the conservation of species mass (Eq. (18)) and the conservation of energy (Eq. (24)) and entropy (Eq. (35)), one obtains, after some straightforward manipulations, the following relation for the bulk:

$$\begin{aligned}
D_t u_0 - \theta D_t s_0 &= D_t \psi_0 + s_0 D_t \theta \\
&= \boldsymbol{P} : D_t \boldsymbol{F} + \mu D_t c_0 - \boldsymbol{W} \cdot \text{Grad } \mu - \delta_0 - \boldsymbol{H}_{\text{eff}} \cdot \text{Grad } \theta \\
&= \left[2\boldsymbol{F} \cdot \frac{\partial \psi_0}{\partial \boldsymbol{C}} \cdot D_t \boldsymbol{F} + \frac{\partial \psi_0}{\partial \theta} D_t \theta + \frac{\partial \psi_0}{\partial c_0} D_t c_0 + \frac{\partial \psi_0}{\partial \boldsymbol{\Xi}} : D_t \boldsymbol{\Xi} \right] + s_0 D_t \theta.
\end{aligned} \tag{38}$$

Following a similar procedure for the surface we obtain the relation

$$\begin{aligned}
D_t \widehat{u}_0 - \widehat{\theta} D_t \widehat{s}_0 &= D_t \widehat{\psi}_0 + \widehat{s}_0 D_t \widehat{\theta} \\
&= \widehat{\boldsymbol{P}} : D_t \widehat{\boldsymbol{F}} + \widehat{\mu} D_t \widehat{c}_0 - \widehat{\boldsymbol{W}} \cdot \widehat{\text{Grad }} \widehat{\mu} - \widehat{\delta}_0 - \widehat{\boldsymbol{H}}_{\text{eff}} \cdot \widehat{\text{Grad }} \widehat{\theta} + [\![\theta]\!]_{\mathcal{S}} \boldsymbol{H}_{\text{eff}} \cdot \boldsymbol{N} + [\![\mu]\!]_{\mathcal{S}} \boldsymbol{W} \cdot \boldsymbol{N} \\
&= \left[2\widehat{\boldsymbol{F}} \cdot \frac{\partial \widehat{\psi}_0}{\partial \widehat{\boldsymbol{C}}} \cdot D_t \widehat{\boldsymbol{F}} + \frac{\partial \widehat{\psi}_0}{\partial \widehat{\theta}} D_t \widehat{\theta} + \frac{\partial \widehat{\psi}_0}{\partial \widehat{c}_0} D_t \widehat{c}_0 + \frac{\partial \widehat{\psi}_0}{\partial \widehat{\boldsymbol{\Xi}}} : D_t \widehat{\boldsymbol{\Xi}} \right] + \widehat{s}_0 D_t \widehat{\theta}.
\end{aligned} \tag{39}$$

The notation $[\![\bullet]\!]_{\mathcal{S}} := [\{\bullet\} - \{\widehat{\bullet}\}]$ denotes the jump in a field between the surface and the bulk and is the surface–bulk counterpart of the definition of the jump over an internal interface introduced in Eq. (20).

We now proceed to determine the form of the constitutive relations for the bulk and the surface required to ensure thermodynamic consistency.

3.6.1. Constitutive relations in the bulk

Following the standard Colemann–Noll procedure one obtains the constitutive relations for the Piola–Kirchhoff stress $\boldsymbol{P}$, the chemical potential μ and the entropy s_0, in the bulk from Eq. (38) as

$$\boldsymbol{P} = 2\boldsymbol{F} \cdot \frac{\partial \psi_0}{\partial \boldsymbol{C}}, \quad \mu = \frac{\partial \psi_0}{\partial c_0} \quad \text{and} \quad s_0 = -\frac{\partial \psi_0}{\partial \theta}. \tag{40}$$

The reduced dissipation inequality for the bulk then follows from Eq. (38) as

$$\delta_0 = -\boldsymbol{W} \cdot \text{Grad } \mu - \boldsymbol{H}_{\text{eff}} \cdot \text{Grad } \theta - \frac{\partial \psi_0}{\partial \boldsymbol{\Xi}} : D_t \boldsymbol{\Xi} \geq 0. \tag{41}$$

In order to automatically satisfy the reduced dissipation inequality for the bulk given in Eq. (41) (and thereby ensure thermodynamic consistency) we postulate constitutive relations of the form[4]

$$\boldsymbol{W} \propto -\text{Grad } \mu \quad \text{and} \quad \boldsymbol{H}_{\text{eff}} = [\boldsymbol{H} + \sigma \boldsymbol{W}] \propto -\text{Grad } \theta. \tag{42}$$

The proposed structure for the effective entropy flux vector $\boldsymbol{H}_{\text{eff}}$ illustrates the coupling between heat conduction and species diffusion. The enthalpy associated with the diffusing species gives rise to the additional term $\sigma \boldsymbol{W}$ that would be absent in a purely thermomechanical model. The proposed structure for the diffusion flux vector $\boldsymbol{W}$ emphasises that the natural quantity conjugate to the diffusion flux vector is the gradient of the chemical potential.

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[4] Further remarks on the form of the constitutive relations in the bulk are given in Appendix A.

3.6.2. Constitutive relations on the surface

Application of the Colemann–Noll procedure to Eq. (39) renders the constitutive relations for the Piola–Kirchhoff stress $\widehat{\boldsymbol{P}}$, the chemical potential $\widehat{\mu}$ and the entropy $\widehat{s}_0$, on the surface, as

$$\widehat{\boldsymbol{P}} = 2\widehat{\boldsymbol{F}} \cdot \frac{\partial \widehat{\psi}_0}{\partial \widehat{\boldsymbol{C}}}, \quad \widehat{\mu} = \frac{\partial \widehat{\psi}_0}{\partial \widehat{c}_0} \quad \text{and} \quad \widehat{s}_0 = -\frac{\partial \widehat{\psi}_0}{\partial \widehat{\theta}}, \tag{43}$$

and the reduced dissipation inequality on the surface follows as

$$\widehat{\delta}_0 = [\![\,\theta\,]\!]_{\mathcal{S}} \boldsymbol{H}_{\text{eff}} \cdot \boldsymbol{N} + [\![\,\mu\,]\!]_{\mathcal{S}} \boldsymbol{W} \cdot \boldsymbol{N} - \widehat{\boldsymbol{W}} \cdot \widehat{\text{Grad}}\, \widehat{\mu} - \widehat{\boldsymbol{H}}_{\text{eff}} \cdot \widehat{\text{Grad}}\, \widehat{\theta} - \frac{\partial \widehat{\psi}_0}{\partial \widehat{\boldsymbol{\Xi}}} : \text{D}_t \widehat{\boldsymbol{\Xi}} \geq 0. \tag{44}$$

In an analogous manner to the derivation of the constitutive relations for the bulk, the forms of the constitutive relations required to satisfy thermodynamic consistency on the surface are

$$\widehat{\boldsymbol{W}} \propto -\widehat{\text{Grad}}\, \widehat{\mu}, \quad \widehat{\boldsymbol{H}}_{\text{eff}} \propto -\widehat{\text{Grad}}\, \widehat{\theta}, \tag{45}$$

$$\text{D}_t \widehat{\boldsymbol{\Xi}} = \widehat{\mathbb{F}}(\widehat{\boldsymbol{C}}, \widehat{\boldsymbol{\Xi}}, \widehat{c}_0, \widehat{\theta}) : \widehat{\boldsymbol{\chi}}, \tag{46}$$

where $\widehat{\mathbb{F}}$ is the fourth-order, positive-definite surface fluidity tensor and $\widehat{\boldsymbol{\chi}}$ is the non-equilibrium surface stress conjugate to the history variable $\widehat{\boldsymbol{\Xi}}$.

Choosing the form of the constitutive relations as proposed in Eqs. (45) and (46), further reduces the dissipation inequality (44) on the surface to

$$0 \leq [\![\,\theta\,]\!]_{\mathcal{S}} \boldsymbol{H}_{\text{eff}} \cdot \boldsymbol{N} + [\![\,\mu\,]\!]_{\mathcal{S}} \boldsymbol{W} \cdot \boldsymbol{N}. \tag{47}$$

The most obvious way in which to guarantee that the above further reduced dissipation inequality on the surface is satisfied is to impose the conditions $[\![\,\theta\,]\!]_{\mathcal{S}} = [\theta|_{\mathcal{S}_0} - \widehat{\theta}] = 0$ and $[\![\,\mu\,]\!]_{\mathcal{S}} = [\mu|_{\mathcal{S}_0} - \widehat{\mu}] = 0$, that is, to impose thermal and chemical slavery. We emphasise that the thermal and chemical slavery conditions are not a priori assumptions but arise, rather, as natural consequences of the thermodynamics. In the work of Fischer et al. (2008), for example, the thermal slavery condition over an interface is an a priori assumption. Similarly, Dolbow et al. (2004), for example, assume chemical slavery from the onset.

A second novel option to ensure that Eq. (47) is satisfied is to impose a constraint between the temperature on the surface $\widehat{\theta}$ and in the bulk θ and the effective entropy flux $\boldsymbol{H}_{\text{eff}} \cdot \boldsymbol{N}$ that resembles the Robin boundary condition used to impose Newton cooling when approximating surface convection. In the case of classical surface convection the constraint is in the form of a mixed boundary condition that relates an external temperature and the surface temperature to the heat flux. Such a non-standard Robin type constraint between the surface and the bulk mimics the thermodynamic constraint on the effective entropy flux vector in the bulk and the bulk temperature gradient given in Eq. $(42)_2$.

As for the temperature, a similar Robin-like constraint between the diffusion flux $\boldsymbol{W} \cdot \boldsymbol{N}$ and the jump in the chemical potential between the surface and the bulk could be imposed in order to ensure satisfaction of Eq. (47). Such a non-standard Robin type constraint between the surface and the bulk mimics the thermodynamic constraint on the diffusion flux vector and the gradient of the chemical potential, in the bulk, given in Eq. $(42)_1$.

To the best of the authors' knowledge, such constraints have not been exploited in the literature.

Remark. The form of the constitutive relations governing the response of the bulk can be postulated from basic principles and experimental observation, see for example Holzapfel (2001) for an overview. They represent a continuum description of the, generally complex, material's response to physical processes. In the same spirit it is generally postulated that such continuum descriptions for the behaviour of a surface can be obtained. For example, El Afif and Grmela (2002) in an Eulerian model of case II diffusion[5] assume that the same equations governing the bulk are valid on the surface.   □

3.7. Temperature evolution equations

The final step in the development of the governing equations is to determine the evolution equations for the bulk and surface temperatures.

3.7.1. Temperature evolution equation for the bulk

Using the localised expression for the entropy balance in Eq. (33) and the reduced dissipation inequality in Eq. (41), the equation for the evolution of the entropy in the bulk becomes

$$\theta \text{D}_t s_0 = -\boldsymbol{W} \cdot \text{Grad}\, \mu + \theta H_{\text{eff}} - \text{Div}(\theta \boldsymbol{H}_{\text{eff}}) + \boldsymbol{\chi} : \text{D}_t \boldsymbol{\Xi},$$

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[5] Further details are provided in Section 4.

and using the constitutive relation for the entropy in Eq. (40)$_3$,

$$= \underbrace{-\theta\frac{\partial^2\psi_0}{\partial\theta\partial\theta}}_{c_v}D_t\theta - \theta\frac{\partial}{\partial\theta}(\boldsymbol{P}:D_t\boldsymbol{F} + \mu D_t c_0 - \boldsymbol{\chi}:D_t\boldsymbol{\Xi}),$$

$$\Rightarrow c_v D_t\theta = -\boldsymbol{W}\cdot\mathrm{Grad}\,\mu + \theta H_{\mathrm{eff}} - \mathrm{Div}(\theta\boldsymbol{H}_{\mathrm{eff}}) + \boldsymbol{\chi}:D_t\boldsymbol{\Xi} + \theta\frac{\partial}{\partial\theta}(\boldsymbol{P}:D_t\boldsymbol{F} + \mu D_t c_0 - \boldsymbol{\chi}:D_t\boldsymbol{\Xi}), \tag{48}$$

where c_v denotes the specific heat capacity at constant deformation in the bulk. Even ignoring inelastic effects, the form of Eq. (48) is non-standard due to the coupling of heat conduction and diffusion. The first term on the right-hand side of the equation arises purely from species diffusion. The second and third terms on the right-hand side represent the influence of effective entropy sources (thermal and diffusive) and the effective entropy flux vector on the evolution of the temperature. The term involving the thermal gradient of the stress power $\boldsymbol{P}:D_t\boldsymbol{F}$ gives rise to the well known Gough–Joule effect (that is, structural thermoelastic heating) which couples the temperature evolution and the deformation (see e.g. Holzapfel and Simo, 1996a).

3.7.2. Temperature evolution equation for the surface

In a similar fashion to the bulk, the temperature evolution equation on the surface follows from the localised expression for the entropy balance in Eq. (36) and the reduced dissipation inequality in Eq. (44) as

$$\widehat{\theta}D_t\widehat{s}_0 = -\widehat{\boldsymbol{W}}\cdot\widehat{\mathrm{Grad}}\,\widehat{\mu} + \widehat{\theta}\widehat{H}_{\mathrm{eff}} - \widehat{\mathrm{Div}}(\widehat{\theta}\widehat{\boldsymbol{H}}_{\mathrm{eff}}) + \widehat{\boldsymbol{\chi}}:D_t\widehat{\boldsymbol{\Xi}} + [\![\,\theta\,]\!]_{\mathcal{S}}\boldsymbol{H}_{\mathrm{eff}}\cdot\boldsymbol{N} + [\![\,\mu\,]\!]_{\mathcal{S}}\boldsymbol{W}\cdot\boldsymbol{N},$$

and using the constitutive relation for the surface entropy in Eq. (43)$_3$,

$$= \underbrace{-\widehat{\theta}\frac{\partial^2\widehat{\psi}_0}{\partial\widehat{\theta}\partial\widehat{\theta}}}_{\widehat{c}_v}D_t\widehat{\theta} - \widehat{\theta}\frac{\partial}{\partial\widehat{\theta}}(\widehat{\boldsymbol{P}}:D_t\widehat{\boldsymbol{F}} + \widehat{\mu}D_t\widehat{c}_0 - \widehat{\boldsymbol{\chi}}:D_t\widehat{\boldsymbol{\Xi}}),$$

$$\Rightarrow \widehat{c}_v D_t\widehat{\theta} = -\widehat{\boldsymbol{W}}\cdot\widehat{\mathrm{Grad}}\,\widehat{\mu} + \widehat{\theta}\widehat{H}_{\mathrm{eff}} - \widehat{\mathrm{Div}}\,(\widehat{\theta}\widehat{\boldsymbol{H}}_{\mathrm{eff}}) + \widehat{\boldsymbol{\chi}}:D_t\widehat{\boldsymbol{\Xi}} + [\![\,\theta\,]\!]_{\mathcal{S}}\boldsymbol{H}_{\mathrm{eff}}\cdot\boldsymbol{N} + [\![\,\mu\,]\!]_{\mathcal{S}}\boldsymbol{W}\cdot\boldsymbol{N}$$

$$+ \widehat{\theta}\frac{\partial}{\partial\widehat{\theta}}(\widehat{\boldsymbol{P}}:D_t\widehat{\boldsymbol{F}} + \widehat{\mu}D_t\widehat{c}_0 - \widehat{\boldsymbol{\chi}}:D_t\widehat{\boldsymbol{\Xi}}), \tag{49}$$

where $\widehat{c}_v$ denotes the specific heat capacity at constant deformation on the surface.

The structure of the temperature evolution equation for the surface given in Eq. (49) is more complex than that for the bulk given in Eq. (48) but, clearly, has a similar structure. If one assumes thermal and chemical slavery, then the similarities are more apparent. Additional terms arise on the surface due to the contributions from the prescribed effective entropy flux on the exterior surface and the effective entropy flux from the bulk; compare the terms θH_{eff} and $\widehat{\theta}\widehat{H}_{\mathrm{eff}} = \widehat{\theta}[\widehat{H}_{\mathrm{eff}}^{\mathrm{p}} + \boldsymbol{H}_{\mathrm{eff}}\cdot\boldsymbol{N}]$, and $\mathrm{Div}(\theta\boldsymbol{H}_{\mathrm{eff}})$ and $\widehat{\mathrm{Div}}(\widehat{\theta}\widehat{\boldsymbol{H}}_{\mathrm{eff}})$ on the right-hand sides of Eqs. (48) and (49), respectively.

4. Examples of the Helmholtz energy functions

The objectives of this section are twofold. The first is to elucidate the constitutive relations developed in Section 3 by providing examples of the Helmholtz energy functions proposed most generally in Eq. (37). The second objective is to provide additional insight into the coupling between heat conduction, species diffusion and inelastic deformations at finite strains; a subject which appears to have received relatively little attention when compared to the work on finite thermoelasticity and thermoplasticity, see, for example, Armero and Simo (1992), Holzapfel (2001), Simo (1998), and Simo and Miehe (1992). Details of the Helmholtz energy are given for the bulk only. The form of the energy is assumed to hold on the surface and thus, to avoid unnecessary repetition, only the general structure of the relations on the surface is given.

Two models in the literature are summarised here to illustrate the key features of thermomechanical coupling and inelasticity, and diffusion–deformation coupling. The first is the model by Holzapfel and Simo (1996b) that accounts for viscous effects in a geometrically nonlinear thermomechanical continuum (see Reese and Govindjee, 1997 for an alternative model). The second is the isothermal model by Govindjee and Simo (1993), developed to describe a phenomenon known as case II diffusion. Case II type diffusion can occur when a low molecular weight solvent is exposed to the surface of a polymeric solid. The diffusion of the solvent within the polymer causes the polymer to swell significantly. Furthermore, the polymer undergoes a glass-to-rubber type transition. The rate at which the solvent diffuses within the polymer is dependent upon the relaxation state of the polymer. In the model of Govindjee and Simo, the polymer is approximated as a viscoelastic solid with a relaxation time dependent upon the solvent concentration. A major contribution in Govindjee and Simo (1993) was the development of an energy of mixing which extended the Flory–Huggins model (Flory, 1941; Huggins, 1941) to the transient case. The model of Govindjee and Simo is complex due to the extensive micromechanical considerations and, hence, only the key concepts required to illustrate the coupling of diffusion and inelastic deformation are presented. Related works coupling diffusion, deformation and additional physical processes include those by Hong et al. (2008) on the diffusion of solvent in polymeric gels, and the extension to polyelectrolyte gels in Hong et al. (2010).

A further motivation to consider case II diffusion and the structure of the Helmholtz energy proposed by Govindjee and Simo (1993) is that the behaviour of the system at the surface exposed to the solvent is distinct from that in the bulk. El Afif and Grmela (2002) have developed and numerically implemented an Eulerian model of case II diffusion where the surface and the bulk evolve in a coupled manner. In the absence of experimental information, they assume that the structure of the governing equations in the bulk holds on the surface. Care should be taken, however, that the definition of the constitutive parameters in the bulk are not simply assumed to hold on the surface (see Javili and Steinmann, 2010b for further details).

4.1. Helmholtz energy for the bulk

The general form of the Helmholtz energy for the bulk ψ_0 is chosen as

$$\psi_0(\boldsymbol{C},\theta,c_0,\boldsymbol{\Xi}) = \psi_0^{eq}(\boldsymbol{C},\theta) + \psi_0^{neq}(\boldsymbol{C},\theta,c_0,\boldsymbol{\Xi}) + \psi_0^{mix}(J,\theta,c_0), \tag{50}$$

where ψ_0^{eq} and ψ_0^{neq} are the parts of the Helmholtz energy that account for the equilibrium and non-equilibrium (inelastic) response, respectively, and ψ_0^{mix} is the energy associated with the mixing of the solvent and the polymer. The models by Holzapfel and Simo (1996b) and Govindjee and Simo (1993) are both encompassed within the general structure of Eq. (50).

4.1.1. Model of Holzapfel and Simo (1996b)

The Helmholtz energy proposed by Holzapfel and Simo is of the form

$$\psi_0^{HS}(\boldsymbol{C},\theta,\boldsymbol{\Xi}) = \psi_0^{eq}(\boldsymbol{C},\theta) + \psi_0^{neq}(\boldsymbol{C},\theta,\boldsymbol{\Xi}), \tag{51}$$

where

$$\psi_0^{eq}(\boldsymbol{C},\theta) = \psi_0^{eq:tm}(\boldsymbol{C},\theta) + \psi_0^{eq:t}(\theta). \tag{52}$$

The term $\psi_0^{eq:tm}$ accounts for the thermomechanical coupling and $\psi_0^{eq:t}$ accounts for purely thermal effects. Javili and Steinmann (2010b) give extensive details of a model with an energy ψ_0^{eq} of the form given in Eq. (52) for both the bulk and the surface, and should be consulted, along with Holzapfel and Simo (1996b), for further information.

The non-equilibrium part of the Helmholtz energy proposed by Holzapfel and Simo was developed for elastomers, here assumed to be composed of identical polymer chains, and is given by

$$\psi_0^{neq}(\boldsymbol{C},\theta,\boldsymbol{\Xi}) = \zeta|\boldsymbol{\Xi}|^2 - 2\frac{\partial(\beta_\infty \psi_0^{eq}(\boldsymbol{C},\theta))}{\partial \boldsymbol{C}} : \boldsymbol{\Xi} + \beta_\infty \psi_0^{eq}(\boldsymbol{C},\theta), \tag{53}$$

where $\zeta \in \mathbb{R}_+$ is a temperature-dependent parameter and $\beta_\infty \in \mathbb{R}_+$ is a non-dimensional constitutive parameter associated with the temperature-dependent relaxation time τ. The form of the energy in Eq. (53) is non-standard due to the presence of the derivative with respect to a measure of the deformation $\boldsymbol{C}$ in the second term on the right-hand side. The inelastic process is assumed here to be describable via a single internal variable $\boldsymbol{\Xi}$. Here and henceforth, $\boldsymbol{\Xi}$ shall thus denote a single internal variable as opposed to a set of internal variables. The choice of the energy in Eq. (53) renders the fourth-order fluidity tensor $\mathbb{F}$ introduced in Eq. (A.4) as $\mathbb{F} := [2\zeta\tau]^{-1}\mathbb{I}$, where $\mathbb{I}$ is the fourth-order identity tensor. The choice of the non-equilibrium energy in Eq. (53) coincides with an evolution equation for the internal variable $\boldsymbol{\chi}$ of the form

$$\left.\begin{aligned} D_t\boldsymbol{\chi} + \frac{\boldsymbol{\chi}}{\tau} &= D_t\left(2\frac{\partial(\beta_\infty \psi_0^{eq}(\boldsymbol{C},\theta))}{\partial \boldsymbol{C}}\right) - \boldsymbol{\chi}^{cpl} \\ \boldsymbol{\chi}|_{t=0} &= \boldsymbol{\chi}_0 \end{aligned}\right\} \quad \text{in } \mathcal{B}_0 \times \mathbb{T},$$

where the thermal coupling term $\boldsymbol{\chi}^{cpl} := [2D_t\zeta]\boldsymbol{\Xi}$. The inelastic evolution is thus coupled to the temperature via the temperature-dependent relaxation time τ and the tensorial thermal coupling term $\boldsymbol{\chi}^{cpl}$.

4.1.2. Model of Govindjee and Simo (1993)

The model of Govindjee and Simo accounts for the influence of the concentration of the diffusing species c_0 on the viscoelastic response of the polymer via a concentration-dependent relaxation time τ chosen to reflect the glass-to-rubber transition that occurs in case II diffusion.

The energy due to mixing ψ_0^{mix} proposed by Govindjee and Simo is simplified here to

$$\psi_0^{mix}(J,c_0) = r_1\theta_0 h(J)\left[\frac{A}{r_2[r_2+A]}\ln A - \frac{1}{r_2}\ln(r_2+A)\right], \tag{54}$$

where $h(J) := r_3^{-1}J - 1$, and the activity $A := \exp(\theta_0^{-1}r_4\mu)$, where $r_1,\ldots,r_4$ are constitutive parameters and θ_0 is the reference temperature. In the Govindjee and Simo model, the activity A (expressed as a function of the chemical potential μ), as opposed to the species concentration c_0, is viewed as a primary variable. This is possible as the actual expression for the energy of mixing allows the chemical potential–concentration relationship, given most generally in Eq. (40)$_2$, to be inverted. The introduction of the activity A negates complications surrounding the higher-order continuity required for subsequent computations using, for example, the finite element method, and, additionally, a singularity that arises when the initial concentration tends to zero (a physically meaningful situation).

For additional information on the numerical implementation and the model itself, the reader is referred to Vijalapura and Govindjee (2003, 2005).

4.1.3. A general Helmholtz energy for the bulk

A Helmholtz energy corresponding to a geometrically nonlinear thermomechanical solid exhibiting a viscoelastic response and coupled to diffusion is proposed here by combining the two aforementioned models. Furthermore, the isothermal energy of mixing proposed by Govindjee and Simo (1993) is trivially extended to account for thermal effects.

The equilibrium part of the Helmholtz energy ψ_0^{eq} remains as given in Eq. (52). The non-equilibrium part of the Helmholtz energy ψ_0^{neq} in Eq. (53) is modified, in the spirit of the model of Govindjee and Simo (1993), to account for the influence of the diffusing species by specifying the scalar relaxation time to be a function of both the temperature θ and the diffusing species concentration c_0. Finally, the energy of mixing ψ_0^{mix} proposed in Eq. (54) is extended to account for thermal effects by replacing the reference temperature θ_0 with the temperature θ.

4.2. Helmholtz energy for the surface

We assume that the form of the Helmholtz energy for the surface is the same as that for the bulk. Clearly such an assumption should be verified via experimental investigation and numerical simulation. In the absence of such studies, it seems reasonable to postulate a surface Helmholtz energy of the form

$$\widehat{\psi}_0(\widehat{\boldsymbol{C}},\widehat{\theta},\widehat{c}_0,\widehat{\boldsymbol{\Xi}}) = \widehat{\psi}_0^{\mathrm{eq}}(\widehat{\boldsymbol{C}},\widehat{\theta}) + \widehat{\psi}_0^{\mathrm{neq}}(\widehat{\boldsymbol{C}},\widehat{\theta},\widehat{c}_0,\widehat{\boldsymbol{\Xi}}) + \widehat{\psi}_0^{\mathrm{mix}}(\widehat{J},\widehat{\theta},\widehat{c}_0),$$

where the meaning of the various terms is clear from the derivation in Section 4.1 for the bulk.

5. Discussion and conclusions

The equations governing the response of a continuum body with a surface possessing its own Helmholtz energy have been presented. The use of a canonical control region for deriving both the surface and bulk equations is natural and simplifies the presentation. The derivation was based on sound thermodynamical arguments and elucidates the nature of the coupling between diffusion, heat conduction and finite inelastic deformation both in the bulk and on the surface. The presence of a surface energy results in balance equations for the various surface fluxes (heat, concentration and traction). The classical Neumann boundary conditions are recovered by omitting the surface contribution. The formulation presented here is thus consistent with the standard (bulk) formulation. Furthermore, by viewing the external surface as an internal interface one recovers the form of the more widely adopted theory for interfaces. Clearly, the theory presented here needs to be extended to fully account for propagating interfaces, but such an extension would be relatively straightforward.

Thermodynamically consistent forms for the constitutive relations in the bulk have been presented and the structure of those on the surface suggested. The coupling between heat conduction and species diffusion gives rise to a non-standard Fourier–Duhamel type law between the effective entropy flux vector and the gradient of the temperature. The effective entropy flux vector is the cumulative entropy flux vector due to heat conduction and the enthalpy associated with the diffusing species.

It has been shown that, in order to satisfy the reduced dissipation inequality on the surface, two types of constraints between the temperature, and the chemical potential, on the surface and in the bulk, respectively, exist. The most obvious constraint is to stipulate that discontinuities in the temperature and the chemical potential fields between the bulk and the surface cannot occur. Such assumptions are standard for interfacial problems, but prohibit thermal or chemical shock. It is enlightening not to assume thermal and chemical slavery a priori but rather to observe that they arise as logical thermodynamic constraints. Robin-like boundary conditions on the jumps in the temperature and the chemical potential are also thermodynamically feasible and mimic the constitutive relations in the bulk.

Motivated by the phenomenon of case II diffusion, the framework for a Helmholtz energy that accounts for finite thermo-inelasticity coupled to diffusion and mixing was described.

The current presentation has been based on classical deformational mechanics and has not exploited the powerful framework of configurational mechanics (see e.g. Maugin, 2010). A transferal of the work presented here to the configurational setting would certainly further understanding of the role of surface energies in coupled problems.

Numerical computations based on the finite element method that extend those presented by the authors in Javili and Steinmann (2009, 2010a, 2011) will be presented in a future work.

Acknowledgements

Appendix A. Remarks on the constitutive relations in the bulk

Remark. A relationship for the diffusion flux vector W that satisfies Eq. (42)$_1$ is obtained from a classical Stokes–Einstein type argument (Govindjee and Simo, 1993) wherein the molecular velocity is assumed proportional to the driving force (i.e. the gradient of the chemical potential μ) via the potentially concentration, temperature and deformation dependent, second-order, positive-definite mobility tensor $\mathbb{B}$. Thus,

$$\boldsymbol{v}^{\star} - \boldsymbol{v} = -\mathbb{B}(c_t, \theta, \boldsymbol{F}) \cdot \operatorname{grad} \mu,$$

and using the definition of the spatial diffusion flux vector $\boldsymbol{w}$ given on the right-hand side of Eq. (13) yields

$$\boldsymbol{w} = c_t[\boldsymbol{v}^{\star} - \boldsymbol{v}] = -c_t \mathbb{B}(c_t, \theta, \boldsymbol{F}) \cdot [\boldsymbol{f}^t \cdot \operatorname{Grad} \mu]. \tag{A.1}$$

The relation for the diffusing species flux vector in the reference configuration is thus

$$\boldsymbol{W} = -c_0 \mathbb{B}(c_0, \theta, \boldsymbol{F}) \cdot \boldsymbol{C}^{-1} \cdot \operatorname{Grad} \mu. \tag{A.2}$$

Note that even for a constant mobility tensor $\mathbb{B}$ there is coupling between deformation and diffusion due to the presence of the Finger tensor $\boldsymbol{C}^{-1}$ which is a measure of the stretch.   □

Remark. A relationship of the form suggested by Eq. (42)$_2$ for the effective entropy flux vector $\boldsymbol{H}_{\text{eff}}$ is given by a non-standard Fourier–Duhamel type law of the form

$$\boldsymbol{H}_{\text{eff}} = -\mathbb{K}(c_0, \theta, \boldsymbol{F}) \cdot \boldsymbol{C}^{-1} \cdot \operatorname{Grad} \theta, \tag{A.3}$$

where $\mathbb{K}$ is the positive-definite, second-order conductivity-like tensor for the bulk. Note that, as in the constitutive relation for the diffusing species flux vector in Eq. (A.2), even for a constant conductivity-like tensor $\mathbb{K}$ there is geometric coupling due to the presence of the term $\boldsymbol{C}^{-1}$. Additional coupling arises as the non-standard effective entropy flux vector $\boldsymbol{H}_{\text{eff}}$ contains contributions due to thermal conduction and species diffusion.   □

Remark. An evolution equation for the inelastic internal variables $\boldsymbol{\Xi}$ that satisfies the reduced dissipation inequality is required. By defining $\boldsymbol{\chi} \coloneqq -\partial \psi_0 / \partial \boldsymbol{\Xi}$ as the non-equilibrium stress conjugates to the history variable $\boldsymbol{\Xi}$, a suitable form for the evolution of the history variable is (Simo and Hughes, 1998)

$$D_t \boldsymbol{\Xi} = \mathbb{F}(\boldsymbol{C}, \boldsymbol{\Xi}, c_0, \theta) : \boldsymbol{\chi}, \tag{A.4}$$

where $\mathbb{F}$ is the positive-definite, fourth-order fluidity tensor for the bulk. For further details on the development of constitutive relations for viscoelastic solids the reader is referred to Simo and Hughes (1998).   □

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