



THE ENERGY OF A GROWING ELASTIC SURFACE

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Abstract—The potential energy of the elastic surface of an elastic body which is growing by the coherent addition of material is derived. Several equivalent expressions are presented for the energy required to add a single atom, also known as the chemical potential. The simplest involves the Eshelby stress tensors for the bulk medium and for the surface. Dual Lagrangian/Eulerian expressions are obtained which are formally similar to each other. The analysis employs two distinct types of variations to derive the governing bulk and surface equations for an accreting elastic solid. The total energy of the system is assumed to comprise bulk and surface energies, while the presence of an external medium can be taken into account through an applied surface forcing. A detailed account is given of the various formulations possible in material and current coordinates, using four types of bulk and surface stresses: the Piola–Kirchhoff stress, the Cauchy stress, the Eshelby stress and a fourth, called the nominal energy-momentum stress. It is shown that inhomogeneity surface forces arise naturally if the surface energy density is allowed to be position dependent. © 1998 Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

Accretion is a process by which the material surface of a body changes, either by mass rearrangement via bulk and surface diffusion, or by mass transfer from the surrounding environment. The former has received considerable attention because of its potential for stress-driven surface instability (Mullins, 1956; Asaro and Tiller, 1972; Grinfeld, 1986; Freund, 1995), while the latter subject is at the heart of equilibrium and non-equilibrium mechanics of multi-phase systems (Larché and Cahn, 1973, 1985; Alexander and Johnson, 1985; Leo and Sekerka, 1989; Gurtin, 1993). A crucial feature in thermomechanical formulations of these problems is the notion of the solid chemical potential, defined as the energy associated with the addition of a single atom to the surface. This is the subject of the present paper.

It is possible to generate an expression for the chemical potential using variational arguments, the main ingredients being bulk and surface elastic energy functions. The groundwork for this was laid by Alexander and Johnson (1985) and Johnson and Alexander (1986), who considered multi-phase systems with curved interfaces, although they did not include an elastic surface energy in their formulation. Subsequently, Leo and Sekerka (1989) considered the effect of surface energy, and gave a thorough analysis of the variational derivation of the equilibrium conditions associated with multi-phase interfaces. Based upon their results one can readily derive expressions for the chemical potential phrased in both Lagrangian (or material) and Eulerian (or current) coordinates. The Lagrangian/Eulerian results of Leo and Sekerka (1989) although they are formally identical to one another, do not appear symmetric. That is, their expression in one coordinate system looks quite different in the dual formulation. This distinction, which might not appear serious, can lead to complications. For instance, as pointed out by Wu (1995a, b) the expressions for the chemical potential adopted by Asaro and Tiller (1972) and by Rice and Chuang (1981) appear to be the same. However, they are in Lagrangian and Eulerian descriptions, respectively, and are not equivalent. This important distinction has long been appreciated (Herring, 1953) but only recently has it been examined in detail by Grinfeld (1994), who distinguishes two types of surface energy associated with the two descriptions:

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Table 1. Stresses and their divergence based upon the Euler–Lagrange equations for the “standard” variation δx . The relations among the bulk and surface stresses follow from the definitions of the Piola–Kirchhoff stresses, for instance. The bulk and surface equilibrium equations are all consequences of the first ones : VP.4 and SP.4

Stress	Symbol	Definition	Relation	Balance equation	
Piola–Kirchhoff	$\mathbf{P}$	$(\partial W/\partial \mathbf{F})^T$	$J\boldsymbol{\sigma}$	$\text{Div } \mathbf{P} = -\mathbf{G}$	VP
Cauchy	$\boldsymbol{\sigma}$	$\mathbf{w}\mathbf{I} - \mathbf{p}\mathbf{f}$	$j\mathbf{F}\mathbf{P}$	$\text{div } \boldsymbol{\sigma} = -\mathbf{g}$	VC
Energy-mom.	$\mathbf{E}$	$\mathbf{W}\mathbf{I} - \mathbf{P}\mathbf{F}$	$J\mathbf{f}\mathbf{p}$	$\text{Div } \mathbf{E} = \mathbf{G}\mathbf{F} - \mathbf{G}^{\text{inh}}$	VE
Nominal E-M	$\mathbf{p}$	$(\partial w/\partial \mathbf{f})^T$	$j\mathbf{F}\mathbf{E}$	$\text{div } \mathbf{p} = \mathbf{g}\mathbf{F} - \mathbf{g}^{\text{inh}}$	VN
Piola–Kirchhoff	$\hat{\mathbf{P}}$	$(\partial \hat{W}/\partial \hat{\mathbf{F}})^T$	$\hat{J}\hat{\boldsymbol{\sigma}}$	$\widehat{\text{Div}} \hat{\mathbf{P}} = \mathbf{N}\mathbf{P} - \mathbf{G}^{\text{sur}}$	SP
Cauchy	$\hat{\boldsymbol{\sigma}}$	$\hat{w}\hat{\mathbf{I}} - \hat{\mathbf{p}}\hat{\mathbf{f}}$	$\hat{j}\hat{\mathbf{F}}\hat{\mathbf{P}}$	$\widehat{\text{div}} \hat{\boldsymbol{\sigma}} = \mathbf{n}\boldsymbol{\sigma} - \mathbf{g}^{\text{sur}}$	SC
Energy-mom.	$\hat{\mathbf{E}}$	$\hat{W}\hat{\mathbf{I}} - \hat{\mathbf{P}}\hat{\mathbf{F}}$	$\hat{J}\hat{\mathbf{f}}\hat{\mathbf{p}}$	$\widehat{\text{Div}} \hat{\mathbf{E}} = \mathbf{G}^{\text{sur}}\hat{\mathbf{F}} - \hat{\mathbf{G}}^{\text{inh}} + \hat{\mathbf{Q}}\mathbf{K} - \mathbf{N}\mathbf{P}\hat{\mathbf{F}} + (\hat{\mathbf{E}} \cdot \mathbf{K})\mathbf{N}$	SE
Nominal E-M	$\hat{\mathbf{p}}$	$(\partial \hat{w}/\partial \hat{\mathbf{f}})^T$	$\hat{j}\hat{\mathbf{F}}\hat{\mathbf{E}}$	$\widehat{\text{div}} \hat{\mathbf{p}} = \mathbf{g}^{\text{sur}}\hat{\mathbf{F}} - \hat{\mathbf{g}}^{\text{inh}} + \hat{j}\hat{\mathbf{Q}}\mathbf{K} - \mathbf{n}\boldsymbol{\sigma}\hat{\mathbf{F}} + \hat{j}(\hat{\mathbf{E}} \cdot \mathbf{K})\mathbf{N}$	SN
(Column)	1	2	3	4	

Herring and Laplace, respectively. The former is based on the work of Herring (1953) who assumes a surface energy based on Lagrangian surface area, whereas the more traditional concept of surface energy, as a surface tension on a liquid for instance (and hence the descriptor Laplace), is most readily discussed using Eulerian coordinates. Recently, Wu (1996b) deduced symmetric expressions for the chemical potential, but his results are for two-dimensional systems only, and are of limited use. The equilibrium conditions of Leo and Sekerka (1989) were extended to non-equilibrium situations by Gurtin and Struthers (1990). They did not avail of variational methods but used more direct concepts such as force, introducing the notion of accretive forces, later generalized to configurational forces by Gurtin (1995). These are closely linked to concepts of force developed extensively by Eshelby, e.g. (Eshelby, 1951, 1975), and others, and are known generally as material forces. Maugin (1995) provides a good review of the literature of material forces.

In this paper we re-examine the variational derivation of the entire system of equations for a solid with a changing material surface. We consider the basic question of the static equilibrium of an elastic body and its surface. No dynamic or quasi-static effects are assumed or discussed. Our objective is a complete overview of the various formulations possible in material and current coordinates, and the many types of stresses with which to express the results: Piola–Kirchhoff stress, Cauchy stress, Eshelby stress (also called the energy-momentum tensor) and a fourth one, called the nominal energy-momentum stress. The Eshelby stress is a central feature of material forces, whatever their origin, and its role in the surface chemical potential has been recognized by Bartholomeusz (1995). The analysis of Bartholomeusz, similar in many ways to that followed here, is limited to small strains. We do not assume any such restriction here, hoping that the generality of the formalism will permit us to see the wood from the trees.

Our main result is that the chemical potential is

$$\mu = [\mathbf{N} \cdot \mathbf{E}\mathbf{N} - \hat{\mathbf{E}} \cdot \mathbf{K} + \hat{J}\mathbf{g}^{\text{sur}} \cdot \mathbf{F}\mathbf{N} - \widehat{\text{Div}} \hat{\mathbf{Q}}]\Omega, \tag{1}$$

where Ω is the volume of a single atom in the reference coordinates,¹ and $\mathbf{E}$ and $\hat{\mathbf{E}}$ are bulk and surface energy-momentum tensors. These are defined (see Table 1) as $\mathbf{E} = \mathbf{W}\mathbf{I} - \mathbf{P}\mathbf{F}$ and $\hat{\mathbf{E}} = \hat{W}\hat{\mathbf{I}} - \hat{\mathbf{P}}\hat{\mathbf{F}}$, where W , $\mathbf{P}$ and $\mathbf{F}$ are bulk energy density, Piola–Kirchhoff stress, and deformation gradient, and $\hat{W}$, $\hat{\mathbf{P}}$ and $\hat{\mathbf{F}}$ are surface counterparts. The surface curvature in reference coordinates is $\mathbf{K}$. The final two terms in eqn (1) involve the force $\mathbf{g}^{\text{sur}}$ acting on the surface, with normal $\mathbf{N}$ in the reference configuration and surface Jacobian $\hat{J}$, and the

¹ The volume of an atom is immutable but we use the reference volume Ω in eqn (1) because all other quantities are defined in terms of reference coordinates. The real, or current, atomic volume is ω and $\Omega = \omega/J$. The definition of chemical potential per atom, as opposed to a molar unit, is common.

Table 2. Summary of notation. Note that the gradients indicate the explicit or partial derivatives of W and $\hat{W}$ with respect to $\mathbf{X}$, i.e., $G_i^{\text{inh}} = -\partial W(\mathbf{F}, \mathbf{X})/\partial X_i$ with $\mathbf{F}$ fixed

Quantity	Eulerian/ volume	Lagrangian/ volume	Eulerian/ surface	Lagrangian/ surface
Energy density	w	$W = Jw$	$\hat{w}$	$\hat{W} = j\hat{w}$
Force (applied)	$\mathbf{g}$	$\mathbf{G} = J\mathbf{g}$	$\mathbf{g}^{\text{sur}}$	$\mathbf{G}^{\text{sur}} = J\mathbf{g}^{\text{sur}}$
Force (inhom)	$\mathbf{g}^{\text{inh}} = j\mathbf{G}^{\text{inh}}$	$\mathbf{G}^{\text{inh}} = -\nabla_{\mathbf{R}} W$	$\hat{\mathbf{g}}^{\text{inh}} = j\hat{\mathbf{G}}^{\text{inh}}$	$\hat{\mathbf{G}}^{\text{inh}} = -\nabla_{\mathbf{R}} \hat{W}$
Force (rotate)	—	—	$\hat{\mathbf{q}} = j\hat{\mathbf{F}}\hat{\mathbf{Q}}$	$\hat{\mathbf{Q}} = -(\partial \hat{W}/\partial \mathbf{N})$
Jacobian	$j = (dV/dv)$	$J = (1/j)$	$\hat{j} = (dS/ds)$	$\hat{j} = (1/\hat{j})$

surface divergence of a surface force $\hat{\mathbf{Q}}$ associated with orientational dependence of the surface energy density (see Table 2).

The initial kinematics and notation are summarized in Section 2, followed by the variational analysis in Section 3. Care must be taken in defining the proper type of variation associated with a changing material surface, and a good deal of space is devoted to this topic. The results are discussed and interpreted in Section 4.

2. NOTATION AND KINEMATICS

The calculations involve both vectors, tensors, and their differential properties inside an elastic body and on its surface. Variational techniques will be used for functionals defined on these domains, so it is therefore imperative to have a clear understanding of the quantities and their functional dependence. Regarding notation, components will be used on occasion, with the summation of repeated subscripts understood. Products such as $\mathbf{A} = \mathbf{B}\mathbf{C}$ are² $A_{ij} = B_{iK}C_{Kj}$, or $A_j = B_K C_{Kj}$, or $A_i = B_{iK} C_K$, depending upon whether $\mathbf{B}$ and $\mathbf{C}$ are first or second order quantities. Inner or dot products are denoted by $\cdot$ and signify contraction over all indices; thus, $\mathbf{A} \cdot \mathbf{B} = A_i B_i$ or $\mathbf{A} \cdot \mathbf{B} = A_{ij} B_{ji} = \text{tr } \mathbf{A}\mathbf{B}$. We will not use special subscripts to distinguish surface quantities (except in the Appendix), nor use the fact that true surface quantities exist in a lower dimensional space. Some quantities that exist only on the surface and have bulk analogs will be denoted by the same symbol as the bulk quantity with a hat, e.g. $\mathbf{P}$ and $\hat{\mathbf{P}}$. Generally, we prefer to recognize the surface quantities as projections of three-dimensional objects whenever possible. We now introduce some kinematic identities and associated quantities.

Consider a volume of material and its surface, denoted by V and S in material coordinates ($\mathbf{X}$), or v and s in current coordinates ($\mathbf{x}$). The deformation $\mathbf{X} \rightarrow \mathbf{x}$ is assumed to be continuous with a well defined deformation gradient $\mathbf{F}$ and inverse $\mathbf{f}$,

$$\mathbf{F} = \nabla_{\mathbf{R}} \mathbf{x}, \quad \mathbf{f} = \nabla \mathbf{X}, \quad \text{for } \mathbf{X} \in V \cup S \quad \text{and} \quad \mathbf{x} \in v \cup s. \quad (2)$$

In components, $F_{ij} = \partial x_i / \partial X_j$, $f_{ji} = \partial X_j / \partial x_i$. Thus, $\mathbf{F}\mathbf{f} = \mathbf{f}\mathbf{F} = \mathbf{I}$, where $\mathbf{I}$ denotes the identity. Alternatively, $\mathbf{F}$ and $\mathbf{f}$ may be defined in terms of the gradient of the displacement vector $\mathbf{u} = \mathbf{x} - \mathbf{X}$, i.e. $\mathbf{F} = \mathbf{I} + \nabla_{\mathbf{R}} \mathbf{u}$ and $\mathbf{f} = \mathbf{I} - \nabla \mathbf{u}$, where $\mathbf{I} = \mathbf{I}$ denotes the identity in the Eulerian description. The Jacobian of the deformation and its inverse are defined as $J = dv/dV > 0$ and $j = dV/dv$, or

$$J = \det \mathbf{F}, \quad j = \det \mathbf{f}, \quad jJ = 1, \quad (3)$$

and we note the identities

$$\text{div } \mathbf{a} = j \text{Div}(J\mathbf{f}\mathbf{a}), \quad \text{Div } \mathbf{A} = J \text{div}(j\mathbf{F}\mathbf{A}). \quad (4)$$

² The simultaneous use of lower and upper case indices is intended to aid the readers interpretation.

These are simple consequences of the Euler–Piola–Jacobi identities (Truesdell and Toupin, 1960, p. 246).

The surface unit normal in the material and current coordinates is denoted by $\mathbf{N}$ and $\mathbf{n}$, respectively. Define the surface projection operators

$$\hat{\mathbf{I}} = \mathbf{I} - \mathbf{N} \otimes \mathbf{N}, \quad \hat{\mathbf{i}} = \mathbf{i} - \mathbf{n} \otimes \mathbf{n}, \tag{5}$$

then the surface deformation gradients are the on-surface projections of $\mathbf{F}$ and $\mathbf{f}$:

$$\hat{\mathbf{F}} = \mathbf{F}\hat{\mathbf{I}} \quad \text{for } \mathbf{X} \in S, \quad \hat{\mathbf{f}} = \mathbf{f}\hat{\mathbf{i}} \quad \text{for } \mathbf{x} \in s. \tag{6}$$

Therefore, according to these mathematical definitions,

$$\hat{\mathbf{F}}\hat{\mathbf{I}} = \hat{\mathbf{F}} \quad \text{and} \quad \hat{\mathbf{f}}\hat{\mathbf{i}} = \hat{\mathbf{f}}. \tag{7}$$

In addition, the explicit fact that S is a material surface and s its image, implies the following kinematic identities,

$$\hat{\mathbf{i}}\hat{\mathbf{F}} = \hat{\mathbf{F}} \quad \text{and} \quad \hat{\mathbf{I}}\hat{\mathbf{f}} = \hat{\mathbf{f}}. \tag{8}$$

As defined, $\hat{\mathbf{F}}$ and $\hat{\mathbf{f}}$ are rank deficient and are therefore not the inverse of one another, in the sense of three-dimensional tensors. They do, however, satisfy

$$\hat{\mathbf{f}}\hat{\mathbf{F}} = \hat{\mathbf{I}} \quad \text{and} \quad \hat{\mathbf{F}}\hat{\mathbf{f}} = \hat{\mathbf{i}}. \tag{9}$$

These are consequences of the two sets of identities (7) and (8), and

$$\hat{\mathbf{f}}\hat{\mathbf{F}} = \hat{\mathbf{f}}\hat{\mathbf{F}} = \mathbf{f}\hat{\mathbf{F}} = \mathbf{f}\mathbf{F}\hat{\mathbf{I}} = \hat{\mathbf{I}}, \tag{10}$$

$$\hat{\mathbf{F}}\hat{\mathbf{f}} = \mathbf{F}\hat{\mathbf{f}} = \mathbf{F}\hat{\mathbf{f}} = \mathbf{F}\mathbf{f}\hat{\mathbf{i}} = \hat{\mathbf{i}}, \tag{11}$$

completing the proofs of eqn (9).

The surface deformation maps material lengths on the undeformed surface S to current lengths on the deformed surface s . Thus, a tangent vector $d\mathbf{L} \in S$ is mapped to $d\mathbf{l} = \hat{\mathbf{F}} d\mathbf{L} \in s$ with length $d\ell$ given by $(d\ell)^2 = (\hat{\mathbf{F}} d\mathbf{L}) \cdot (\hat{\mathbf{F}} d\mathbf{L})$. In general, surface quantities that are analogous to bulk parameters, such as $\mathbf{F}$, will be denoted by the same letters with a hat, i.e. $\hat{\mathbf{F}}$. Further results concerning the surface deformation tensors are presented in the Appendix.

The surface Jacobian and its inverse are

$$\hat{J} = ds/dS, \quad \hat{j} = dS/ds, \quad \hat{j}\hat{J} = 1. \tag{12}$$

They may be determined from eigenvalues of $\hat{\mathbf{F}}$, although, because of the rank deficiency of the latter we do not use this procedure. An explicit formula for $\hat{J}$ is given in the Appendix. It may also be found from the well-known relations

$$\mathbf{n} = \hat{j}\hat{J}\mathbf{N}\mathbf{f} \Leftrightarrow \mathbf{N} = j\hat{J}\mathbf{n}\mathbf{F}, \tag{13}$$

which imply $\hat{J} = \hat{J}\mathbf{N}\mathbf{f} \cdot \mathbf{n} = J/(\mathbf{n}\mathbf{F} \cdot \mathbf{N})$. The surface divergence operators $\widehat{\text{Div}}$ and $\widehat{\text{div}}$ are defined in the usual manner (using the divergence theorem, for example, to express the

surface divergence of a quantity as a line integral). The surface analogs of the volumetric identities 4 are

$$\widehat{\text{div}} \mathbf{a} = \hat{j} \widehat{\text{Div}}(\hat{\mathbf{J}} \mathbf{a}), \quad \widehat{\text{Div}} \mathbf{A} = \hat{j} \widehat{\text{div}}(\hat{\mathbf{F}} \mathbf{A}), \quad (14)$$

where $\mathbf{a}$ and $\mathbf{A}$ are vectors or tensors which may be defined for all positions, on or off the surface, although the divergence only uses surface values.

The surface curvature tensor is denoted as $\mathbf{K}$ in the material description and by $\mathbf{k}$ in the current description,³

$$\mathbf{K} = -\hat{\mathbf{V}}_R \mathbf{N}, \quad \mathbf{k} = -\hat{\mathbf{V}} \mathbf{n}, \quad (15)$$

where $\hat{\mathbf{V}}_R$ and $\hat{\mathbf{V}}$ denote the on-surface gradient operators. Note that $\mathbf{k}$ is the actual curvature of the surface, while $\mathbf{K}$ may be thought of as the curvature of the undeformed state. The double mean curvatures are defined as $K = \text{tr} \mathbf{K}$, $k = \text{tr} \mathbf{k}$, or

$$K = \mathbf{K} \cdot \hat{\mathbf{I}}, \quad k = \mathbf{k} \cdot \hat{\mathbf{i}}. \quad (16)$$

Thus, a solid sphere of radius r has $k = -2/r$. We note the well-known identities

$$\widehat{\text{div}} \hat{\mathbf{i}} = k \mathbf{n}, \quad \widehat{\text{Div}} \hat{\mathbf{I}} = K \mathbf{N}. \quad (17)$$

The following identities are a direct consequence of eqns (14) and (17),

$$\hat{j} \widehat{\text{Div}}(\hat{\mathbf{J}}) = k \mathbf{n}, \quad \hat{j} \widehat{\text{div}}(\hat{\mathbf{F}}) = K \mathbf{N}. \quad (18)$$

These are perhaps not as well known as eqn (17), for instance, but they offer a useful means to determine the mean curvatures from the deformation. In particular, the mean curvature in the reference (current) state can be found in terms of the surface divergence on the current (reference) surface, thus,

$$K = \hat{j} \widehat{\text{div}}(\hat{\mathbf{F}}) \cdot \mathbf{N} = \hat{j} \widehat{\text{div}}(\hat{\mathbf{F}}) \cdot \mathbf{f} \mathbf{n}, \quad (19)$$

$$k = \hat{j} \widehat{\text{Div}}(\hat{\mathbf{J}}) \cdot \mathbf{n} = \hat{j} \widehat{\text{Div}}(\hat{\mathbf{J}}) \cdot \mathbf{F} \mathbf{N}. \quad (20)$$

Finally, we note for later use the following results

$$(\widehat{\text{Div}} \mathbf{A}) \cdot \mathbf{N} = \mathbf{A} \cdot \mathbf{K} + \widehat{\text{Div}}(\mathbf{A} \mathbf{N}), \quad (\widehat{\text{div}} \mathbf{a}) \cdot \mathbf{n} = \mathbf{a} \cdot \mathbf{k} + \widehat{\text{div}}(\mathbf{a} \mathbf{n}). \quad (21)$$

Their derivation may be considered an exercise in differential geometry.

3. VARIATIONAL EQUATIONS

3.1. *Equilibrium equations*

The bulk and surface energy densities per unit reference volume and surface area are assumed to depend upon their respective deformation gradients through the isothermal thermodynamic potentials W and $\hat{W}$:

³ Although $\mathbf{K}$ and $\mathbf{k}$ are surface quantities we do not use hats because there are no bulk equivalents.

$$W = W(\mathbf{F}, \mathbf{X}), \quad \hat{W} = \hat{W}(\hat{\mathbf{F}}, \mathbf{N}, \hat{\mathbf{X}}). \quad (22)$$

Note that we allow for inhomogeneity through the explicit dependence of the energies on the material position. The surface energy is also assumed to vary with the surface orientation, $\mathbf{N}$. The dependence upon $\mathbf{N}$ is assumed to be continuous, which is contrary to observations, e.g. Herring (1953). However, this assumption permits us to generate pointwise equilibrium equations, and it could be subsequently relaxed by allowing the material forces to have distribution-type functional behavior. The corresponding energy densities in current coordinates are w and $\hat{w}$, which are related to the Lagrangian quantities by

$$w = jW \quad \text{and} \quad \hat{w} = \hat{j}\hat{W}. \quad (23)$$

The Piola–Kirchhoff bulk stress and the analogous surface stress, $\mathbf{P}$ and $\hat{\mathbf{P}}$, respectively, are defined in the usual manner as

$$\mathbf{P} = (\partial W / \partial \mathbf{F})^T, \quad \hat{\mathbf{P}} = (\partial \hat{W} / \partial \hat{\mathbf{F}})^T. \quad (24)$$

These relations are repeated in Table 1 in items VP.2 and SP.2, respectively.

It is common to formulate dual sets of equations in Lagrangian and Eulerian descriptions using the action integral as the starting point (Herrmann, 1981). However, we are interested in the possibility of non-conservative forces in the bulk and on the surface, and are restricting attention to static phenomena. We therefore adopt as the starting point the potential energy functional

$$\Pi = \mathcal{E} - \mathcal{V}, \quad (25)$$

where $\mathcal{V}$ is the work done by all external and applied forces acting on the body and its surface, and $\mathcal{E}$ represents elastic stored energy, bulk and surface combined. It may be defined by integrals in the current or reference domains:

$$\begin{aligned} \mathcal{E} &= \int_v dv w + \int_s ds \hat{w} \\ &= \int_V dV W + \int_S dS \hat{W}, \end{aligned} \quad (26)$$

respectively.

All our results are based upon two types of variations of the potential energy functional. The first type of variation is a standard virtual displacement, for which Hamilton's principle implies that the variation of Π vanishes. That is, $\delta\Pi = \delta\mathcal{E} - \delta\mathcal{V} = 0$, with

$$\begin{aligned} \delta\mathcal{V} &= \int_v dv \mathbf{g} \cdot \delta\mathbf{u} + \int_s ds \mathbf{g}^{\text{sur}} \cdot \delta\mathbf{u} \\ &= \int_V dV \mathbf{G} \cdot \delta\mathbf{u} + \int_S dS \mathbf{G}^{\text{sur}} \cdot \delta\mathbf{u}, \end{aligned} \quad (27)$$

where the vector $\mathbf{g}$ represents an arbitrary body force acting in the solid, while $\mathbf{g}^{\text{sur}}$ is a force applied on the surface. The analogous material quantities $\mathbf{G}$, $\mathbf{G}^{\text{sur}}$ are defined in Table 2. In order to evaluate the variation $\delta\mathcal{E}$ we consider the integrands of the two integrals in eqn (26) as functions of the displacement $\mathbf{u} = \mathbf{x} - \mathbf{X}$ and its gradient, subject to the restriction that $\mathbf{X}$ does not change with the virtual displacement. That is, $\delta\mathbf{u} = \delta\mathbf{x}$, and consequently $\delta\mathbf{F} = \partial\delta\mathbf{u}/\partial\mathbf{X}$. The restriction $\delta\mathbf{X} = 0$ suggests that we use the Lagrangian forms for $\delta\mathcal{E}$ because the variation will obviously commute with the integrals, that is

$$\begin{aligned}
 \delta \mathcal{E} &= \delta \int_V dV W + \delta \int_S dS \hat{W} \\
 &= \int_V dV \left(\frac{\partial W}{\partial \mathbf{F}} \right)^T \cdot \delta \mathbf{F} + \int_S dS \left(\frac{\partial \hat{W}}{\partial \hat{\mathbf{F}}} \right)^T \cdot \delta \hat{\mathbf{F}}.
 \end{aligned} \quad (28)$$

Combining this with the Lagrangian form for $\delta \mathcal{V}$ in eqn (27) and integrating by parts, yields

$$\delta \Pi = - \int_V dV (\text{Div } \mathbf{P} + \mathbf{G}) \cdot \delta \mathbf{u} + \int_S dS (\widehat{\text{Div}} \hat{\mathbf{P}} - \mathbf{N} \mathbf{P} + \mathbf{G}^{\text{sur}}) \cdot \delta \mathbf{u}. \quad (29)$$

This may be converted into Eulerian form using eqns (4), (13) and (14),

$$\delta \Pi = - \int_v dv (\text{div } \boldsymbol{\sigma} + \mathbf{g}) \cdot \delta \mathbf{u} + \int_s ds (\widehat{\text{div}} \hat{\boldsymbol{\sigma}} - \mathbf{n} \boldsymbol{\sigma} + \mathbf{g}^{\text{sur}}) \cdot \delta \mathbf{u}. \quad (30)$$

Equations (29) and (30) imply the bulk and surface equilibrium equations which are listed in Table 1 as VP.4, VC.4, SP.4 and SC.4.

The quantities $\mathbf{E}$ and $\mathbf{p}$ defined in Table 1 have dimensions of stress, and they are clearly duals to the more familiar stresses $\boldsymbol{\sigma}$ and $\mathbf{P}$, respectively. Based upon their definitions, it is clear that the divergence of each of the four quantities $\mathbf{P}$, $\boldsymbol{\sigma}$, $\mathbf{E}$ and $\mathbf{p}$ are linearly related. Thus, from the definitions in VE.2 and VN.3, and using eqn 4, we have

$$\text{Div } \mathbf{E} = -(\text{Div } \mathbf{P})\mathbf{F} - \mathbf{G}^{\text{inh}}, \quad \text{div } \mathbf{p} = j \text{Div } \mathbf{E}, \quad (31)$$

where the material inhomogeneity force $\mathbf{G}^{\text{inh}}$ is defined in Table 2. The two identities in eqn (31) imply the results VE.4 and VN.4, respectively. The remaining surface equilibrium conditions in Table 1, viz SE.4 and SN.4, are also consequences of the basic equilibrium equations for the Piola–Kirchhoff and Cauchy surface stresses, SP.4 and SC.4, respectively. The value of $\widehat{\text{Div}} \hat{\mathbf{E}}$ follows from its definition in SE.2 and by use of eqn (21) with $\hat{\mathbf{E}}\mathbf{N} = 0$. The surface inhomogeneity force $\hat{\mathbf{G}}^{\text{inh}}$ arises from the explicit dependence of the surface energy on material position. In addition, the orientational dependence of $\hat{W}$ introduces the rotational “force” $\hat{\mathbf{Q}}$, defined as

$$\hat{\mathbf{Q}} = - \frac{\partial \hat{W}}{\partial \mathbf{N}}. \quad (32)$$

The specific form of the term $\hat{\mathbf{Q}}\mathbf{K}$ in SE.4 follows from the identity (15)₁. Note that $\hat{\mathbf{Q}}$ is a tangential vector on S , i.e., $\hat{\mathbf{Q}} \cdot \mathbf{N} = 0$. The final result in column 4 of Table 1, for $\widehat{\text{div}} \hat{\mathbf{p}}$, follows using the relation SN.3 between $\hat{\mathbf{p}}$ and $\hat{\mathbf{E}}$, the equilibrium equation for the latter, and eqns (13) and (14).

Regarding notation, we use the term nominal energy-momentum stress because the stresses $\mathbf{P}$ and $\hat{\mathbf{P}}$ with this descriptor are the energy-momentum tensors dual to the Piola–Kirchhoff stress, which is itself related to (by transpose), or sometimes called, the nominal stress (Ogden, 1984).

The relations among the volumetric quantities in Table 1 are well known, but we have repeated them briefly here for completeness. We refer to Chadwick (1975) for a detailed discussion. The surface equations have not, to our knowledge, been presented in this form. The results in column 4 of the Table are called balance equations for want of a different name. They could equally well be called equilibrium equations; however, it has been pointed out that one person’s equilibrium equation can be another’s conservation law (Herrmann, 1981).

3.2. *Material variation*

We emphasize that the equations in column 4 of Table 1 all follow from VP.4 and SP.4, which are consequences of the Principle of Virtual Work as we have defined it above. No other type of variation is required to establish these equations, although one could use other variational devices. Our purpose here is to establish a new equation, one which does not follow from those derived above. In order to arrive at this we need a different type of variation based upon a virtual “reverse” displacement in which $\delta \mathcal{E}$ is considered a function of the material coordinates. The virtual displacement is associated with a fixed material particle. This did not present a problem with the previous variation because we chose the “standard” variation with $\delta \mathbf{X} = 0$. In this case we need to be a bit more specific about the definition of the variation.

Both types of variation considered here are but special cases of the most general type permissible, for which $\delta \mathbf{x}$ and $\delta \mathbf{X}$ are considered independent. Surface equations obtained using this general $(\delta \mathbf{x}, \delta \mathbf{X})$ variation, the so-called transversality condition (Edelen, 1981), provide a relation between $\delta \mathbf{x}$ and $\delta \mathbf{X}$, the interpretation of which depends upon the problem at hand. It is usually associated with a moving boundary condition, as occurs in fracture mechanics, for instance. In the present case we will prescribe a relation between $\delta \mathbf{x}$ and $\delta \mathbf{X}$, which defines the type of moving boundary. As such, the constraint we impose on $(\delta \mathbf{x}, \delta \mathbf{X})$ can be viewed as a definition of accretion.

There are other means of defining an accretive variation. For instance, Larché and Cahn (1973) introduced the notion of a network, which imbues a solid with a characteristic not found in a fluid. The network can be thought of as a lattice extending beyond the confines of the solid, but associated with a lattice if there is one. Newly added atoms are assigned positions on this network, thus providing a rule for accretion. The method adopted here is clearly different than the network model, but the final results should be independent of such details. It should be noted that the accretion process considered here involves only substitutional atoms, in the terminology of Cahn (1980). The necessity for such finesse in defining variations for solids is one of the features which makes solids different from fluids. The difficult question of what exactly distinguishes a solid from a fluid is addressed in some detail by Larché and Cahn (1985).

The rule used for applying the variation under accretion is based on ideas of Maugin (1979) for constrained variations. Thus, we introduce a one-parameter pair of vector functions: $\bar{\mathbf{X}}(\mathbf{x}, \varepsilon)$ and $\bar{\mathbf{x}}(\mathbf{X}, \varepsilon)$, such that

$$\mathbf{X} = \bar{\mathbf{X}}(\mathbf{x}, 0) \quad \text{and} \quad \mathbf{x} = \bar{\mathbf{x}}(\mathbf{X}, 0). \tag{33}$$

Let $f = f(\mathbf{X}, \varepsilon)$ and $g = g(\mathbf{x}, \varepsilon)$ be arbitrary functions, and define

$$\delta_{\mathbf{x}} f = \left. \frac{\partial f(\mathbf{X}, \varepsilon)}{\partial \varepsilon} \right|_{\substack{\varepsilon=0 \\ \mathbf{X} \text{ fixed}}}, \quad \delta_{\mathbf{x}} g = \left. \frac{\partial g(\mathbf{x}, \varepsilon)}{\partial \varepsilon} \right|_{\substack{\varepsilon=0 \\ \mathbf{x} \text{ fixed}}}. \tag{34}$$

As defined, these variations are completely independent. The crucial step is to link them to one another via the deformation. Specifically, the mappings are assumed to satisfy the constraints

$$\mathbf{x} = \bar{\mathbf{x}}(\bar{\mathbf{X}}(\mathbf{x}, \varepsilon), \varepsilon) \quad \text{and} \quad \mathbf{X} = \bar{\mathbf{X}}(\bar{\mathbf{x}}(\mathbf{X}, \varepsilon), \varepsilon), \tag{35}$$

for all⁴ ε . These are natural conditions and are mutually dual, in the sense that one implies the other. For instance, the first one implies that the same material point (particle) is referred to by the mapping. Expanding the first condition to first order in ε gives the relation

$$\delta_{\mathbf{x}} \bar{\mathbf{x}} + \mathbf{F} \delta_{\mathbf{x}} \bar{\mathbf{X}} = 0. \tag{36}$$

⁴This condition is perhaps overly stringent, as we only require that it hold in a neighborhood of $\varepsilon = 0$.

This is the basic relation sought—but what does it mean? The fact that we employed the deformation constraints (35) provides a clue, suggesting that the material variation δ_x represents the addition (or accretion) of new material that conforms to the underlying deformation. That is, new material is added with the same deformation as the neighboring surface and of the underlying bulk material. In this sense the procedure replaces the concept of a prevailing network (Larché and Cahn, 1973) with a calculus basis for the same result. The present procedure is more akin to that employed by, for example, Maugin and Trimarco (1992) in similar variational analyses.

Equation (36) allows us to compute the displacement variation $\delta \mathbf{u}$ for a material variation, that is, one using δ_x rather than δ_χ which was the basis of the previous variation results. Recalling that $\delta \mathbf{u}$ must be evaluated with reference to a fixed particle, i.e., $\delta \mathbf{u} = \delta_x \mathbf{u}$, we have,

$$\begin{aligned}\delta_x \mathbf{u} &= \delta_x \mathbf{x} \\ &= -\mathbf{F} \delta_x \mathbf{X}.\end{aligned}\tag{37}$$

It is now clear that the previous variational results, specifically eqns (29) and (30), are actually based upon the vanishing of $\delta_x \Pi$. We will now compute $\delta_x \Pi$, starting with the Eulerian form of $\mathcal{E}$ in eqn (26) as integrals over the current volume and surface because these integrals commute with δ_x . We also use the first form for $\delta \mathcal{V}$ given in eqn (27), combined with the identity (37) for $\delta \mathbf{u}$. The one remaining quantity required is the variation of the surface normal, which satisfies the kinematic identity

$$\begin{aligned}\delta_x \mathbf{N} &= \delta \mathbf{X} \cdot \hat{\mathbf{V}}_R \mathbf{N} - \hat{\mathbf{V}}_R (\mathbf{N} \cdot \delta \mathbf{X}) \\ &= -\mathbf{N} (\hat{\mathbf{V}}_R \delta \mathbf{X}) \\ &= -\mathbf{N} (\hat{\mathbf{V}} \delta \mathbf{X}) \hat{\mathbf{F}}.\end{aligned}\tag{38}$$

Proceeding as before, and using the definitions of the nominal stresses in Table 1 (VN.2 and SN.2), and of $\hat{\mathbf{g}}^{\text{inh}}$, $\hat{\mathbf{q}}$ and $\mathbf{g}^{\text{sur}}$ in Table 2, we find

$$\delta_x \Pi = \int_V dv (\mathbf{gF} - \mathbf{g}^{\text{inh}} - \text{div } \mathbf{p}) \cdot \delta \mathbf{X} + \int_S ds (\mathbf{g}^{\text{sur}} \mathbf{F} + \mathbf{n} \mathbf{p} + j \hat{\mathbf{Q}} \mathbf{K} - (\hat{\text{div}} \hat{\mathbf{q}}) \mathbf{N} - \hat{\mathbf{g}}^{\text{inh}} - \hat{\text{div}} \hat{\mathbf{p}}) \cdot \delta \mathbf{X}.\tag{39}$$

This may be converted to integrals over the reference domains by using eqns (4) and (14) and the relations between the various stresses given in Table 1,

$$\begin{aligned}\delta_x \Pi &= \int_V dV (\mathbf{G} \mathbf{F} - \mathbf{G}^{\text{inh}} - \widehat{\text{Div}} \hat{\mathbf{E}}) \cdot \delta \mathbf{X} \\ &\quad + \int_S dS (\mathbf{G}^{\text{sur}} \mathbf{F} + \mathbf{N} \mathbf{E} + \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{Div}} \hat{\mathbf{Q}}) \mathbf{N} - \hat{\mathbf{G}}^{\text{inh}} - \widehat{\text{Div}} \hat{\mathbf{E}}) \cdot \delta \mathbf{X}.\end{aligned}\tag{40}$$

Setting the variation $\delta_x \Pi$ to zero for arbitrary $\delta \mathbf{X}$, both within the body and on the surface, implies that the quantities in parentheses in the integrals of eqns (39) and (40) all vanish. The associated equations generated by the volumetric integrals are precisely the balance

equations VE.4 and VN.4, derived previously. The surface terms, however, give new equations :

$$\widehat{\text{Div}} \hat{\mathbf{E}} = \mathbf{G}^{\text{sur}} \mathbf{F} + \mathbf{N} \mathbf{E} - \hat{\mathbf{G}}^{\text{inh}} + \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{Div}} \hat{\mathbf{Q}}) \mathbf{N}, \quad (41)$$

$$\widehat{\text{div}} \hat{\mathbf{p}} = \mathbf{g}^{\text{sur}} \mathbf{F} + \mathbf{n} \mathbf{p} - \hat{\mathbf{g}}^{\text{inh}} + \hat{j} \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{div}} \hat{\mathbf{q}}) \mathbf{N}. \quad (42)$$

Although these look similar to SE.4 and SN.4, they do indeed differ from those relations which were consequences of the fundamental surface equilibrium equation, SP.4 or SC.4.

In summary, the material variation $\delta_x \Pi$ gives exactly the same set of bulk equations that were obtained from the standard variation, but the surface equations are different. In the next section we will demonstrate that the surface terms in eqns (39) and (40) provide some new information, in addition to the previously obtained equilibrium conditions listed in Table 1.

4. INTERPRETATION

4.1. The chemical potential

The surface inhomogeneity forces $\hat{\mathbf{G}}^{\text{inh}}$ and $\hat{\mathbf{g}}^{\text{inh}}$ are, from their definition in Table 2, both tangential to the reference surface S . It therefore follows from the equilibrium equations outlined in column 4 of Table 1 that the vectors appearing in the surface integral of eqns (39) and (40), $(\mathbf{g}^{\text{sur}} \mathbf{F} + \mathbf{n} \mathbf{p} - \hat{\mathbf{g}}^{\text{inh}} + \hat{j} \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{div}} \hat{\mathbf{q}}) \mathbf{N} - \widehat{\text{div}} \hat{\mathbf{p}})$ and $(\mathbf{G}^{\text{sur}} \mathbf{F} + \mathbf{N} \mathbf{E} - \hat{\mathbf{G}}^{\text{inh}} + \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{Div}} \hat{\mathbf{Q}}) \mathbf{N} - \widehat{\text{Div}} \hat{\mathbf{E}})$, respectively, are both parallel to $\mathbf{N}$. Hence, the surface components of eqns (41) and (42) are identical to the surface components of SE.4 and SN.4, respectively. Also, the component of SE.4 in the $\mathbf{N}$ -direction is just the kinematic identity $\widehat{\text{Div}} \hat{\mathbf{E}} \cdot \mathbf{N} = \hat{\mathbf{E}} \cdot \mathbf{K}$, which follows from eqn (21)₁ and the fact that $\hat{\mathbf{E}} \cdot \mathbf{N} = 0$, by definition, and the $\mathbf{N}$ -component of SN.4 is a consequence of the definition of $\hat{\mathbf{p}}$ in SN.3. In other words, the $\mathbf{N}$ -components of SE.4 and SN.4 are differential identities for tensors and surfaces, and as such they do not contain any mechanics. In contrast, the $\mathbf{N}$ -components of eqns (41) and (42) contain new information of a mechanical nature. We will first examine this and return later to the question of which set of Euler–Lagrange equations is “correct”.

The additional scalar information in eqns (41) and (42) is associated with the freedom to vary $\delta \mathbf{X}$ on the surface in the direction of $\mathbf{N}$. We therefore first consider the two vectors mentioned above which arise in the variational eqns (39) and (40). These vectors are parallel to one another and to $\mathbf{N}$, and based on the discussion above, may be written as

$$\mathbf{G}^{\text{sur}} \mathbf{F} + \mathbf{N} \mathbf{E} - \hat{\mathbf{G}}^{\text{inh}} + \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{Div}} \hat{\mathbf{Q}}) \mathbf{N} - \widehat{\text{Div}} \hat{\mathbf{E}} = \lambda \mathbf{N}, \quad (43)$$

$$\mathbf{g}^{\text{sur}} \mathbf{F} + \mathbf{n} \mathbf{p} - \hat{\mathbf{g}}^{\text{inh}} + \hat{j} \hat{\mathbf{Q}} \mathbf{K} - (\widehat{\text{div}} \hat{\mathbf{q}}) \mathbf{N} - \widehat{\text{div}} \hat{\mathbf{p}} = \hat{j} \lambda \mathbf{N}, \quad (44)$$

where λ vanishes if we impose the condition $\delta_x \Pi = 0$ for variations $\delta \mathbf{X} \parallel \mathbf{N}$. The scalar λ is directly related with the chemical potential of the surface, defined as the energy required to add one atom to the surface. Thus if ω is the volume of one atom, then $\Omega = j\omega$ is the reference volume, and the chemical potential is

$$\begin{aligned} \mu &= \lambda \Omega \\ &= j \lambda \omega. \end{aligned} \quad (45)$$

The new information in the “equilibrium” eqn (41), or (42) which is the same, is therefore that the chemical potential at the surface must be zero for material equilibrium.

We will now derive several alternative expressions for the fundamental parameter λ which is defined by eqn (43) as

$$\lambda = (\mathbf{G}^{\text{sur}} \mathbf{F} + \mathbf{N} \mathbf{E} - \hat{\mathbf{G}}^{\text{inh}} - \widehat{\text{Div}} \hat{\mathbf{E}}) \cdot \mathbf{N} - \widehat{\text{Div}} \hat{\mathbf{Q}}. \quad (46)$$

It is assumed that the body and surface are in static or quasi-static equilibrium, so that Table 1 may be employed. Thus, using SE.4, we have

$$\lambda = \mathbf{G}^{\text{sur}} \cdot \mathbf{F} \mathbf{N} + \mathbf{N} \mathbf{E} \cdot \mathbf{N} - \hat{\mathbf{E}} \cdot \mathbf{K} - \widehat{\text{Div}} \hat{\mathbf{Q}}. \quad (47)$$

This is perhaps the simplest and most concise form for λ , as it illustrates the influence of the applied surface force, the bulk elasticity, and the surface elasticity separately. The final terms in eqn (47), $\widehat{\text{Div}} \hat{\mathbf{Q}}$, has been interpreted by Gurtin (1995) as arising from a surface shear force, and the explicit use of the surface Eshelby tensor $\hat{\mathbf{E}}$ in this context was first noted by Gurtin (1993). There are many alternative forms for λ , as we now illustrate. Thus,

$$\begin{aligned} \lambda &= W - \hat{W} K + \mathbf{G}^{\text{sur}} \cdot \mathbf{F} \mathbf{N} - \mathbf{N} \mathbf{P} \cdot \mathbf{F} \mathbf{N} + \hat{\mathbf{P}} \hat{\mathbf{F}} \cdot \mathbf{K} - \widehat{\text{Div}} \hat{\mathbf{Q}} \\ &= W - \hat{W} K - (\widehat{\text{Div}} \hat{\mathbf{P}}) \cdot \mathbf{F} \mathbf{N} - (\hat{\mathbf{P}} \hat{\mathbf{F}}) \cdot \hat{\mathbf{V}}_{\text{R}} \mathbf{N} - \widehat{\text{Div}} \hat{\mathbf{Q}}, \end{aligned} \quad (48)$$

where we have used VE.2, SE.2, SP.4, and eqn (15), in that order. Alternatively, $\hat{\mathbf{F}}$ may be replaced by $\mathbf{F}$ in the final term in eqn (48), and using the identity

$$(\hat{\mathbf{V}}_{\text{R}} \mathbf{F}) \mathbf{N} = \frac{\partial \mathbf{F}}{\partial N} \hat{\mathbf{I}}, \quad (49)$$

where $\partial/\partial N = \mathbf{N} \cdot \nabla_{\text{R}}$, the surface derivatives can be simplified to yield

$$\lambda = W - \hat{W} K - \widehat{\text{Div}}(\hat{\mathbf{P}} \mathbf{F} \mathbf{N}) + \hat{\mathbf{P}} \cdot \frac{\partial \mathbf{F}}{\partial N} - \widehat{\text{Div}} \hat{\mathbf{Q}}. \quad (50)$$

The previous expressions for λ are all in terms of Lagrangian quantities. We now focus on Eulerian representations. Our main objective is to deduce an expression using Eulerian quantities which is formally similar to one of the above expressions. One's first guess might be that the expression in eqn (47) can be translated in this manner. However, as an example, the following expression is obtained from $(\mathbf{N} \mathbf{E} \cdot \mathbf{N} - \hat{\mathbf{E}} \cdot \mathbf{K})$ by the interchange of dual quantities, according to Table 1 and 2,

$$\mathbf{N} \mathbf{E} \cdot \mathbf{N} - \hat{\mathbf{E}} \cdot \mathbf{K} \rightarrow \mathbf{n} \boldsymbol{\sigma} \cdot \mathbf{n} - \hat{\boldsymbol{\sigma}} \cdot \mathbf{k}. \quad (51)$$

But this is simply zero because, using SC.4 and eqn (21), $\hat{\boldsymbol{\sigma}} \cdot \mathbf{k} = \mathbf{n} \boldsymbol{\sigma} \cdot \mathbf{n}$. Therefore, the simple “translation” suggested by eqn (51) cannot yield the correct Eulerian expression for λ . It is, however, possible to obtain an Eulerian form similar to eqn (50). We start by taking the inner product of eqn (44) with $\mathbf{f} \mathbf{n}$, implying

$$j\lambda = (\mathbf{g}^{\text{sur}} \mathbf{F} + \mathbf{n} \mathbf{p} - \hat{\mathbf{g}}^{\text{inh}} - \widehat{\text{div}} \hat{\mathbf{p}}) \cdot \mathbf{f} \mathbf{n} - j\hat{f} \widehat{\text{div}} \hat{\mathbf{q}}. \quad (52)$$

Table 3. The listed expressions are equivalent and are based upon the equations in the right hand column

Row	The chemical potential of a surface μ	Equation
1	$[G^{sur} \cdot FN + NE \cdot N - \hat{E} \cdot K - Div \hat{Q}] \Omega$	47
2	$[W - \hat{E} \cdot K - Div(\hat{P}) \cdot FN - Div \hat{Q}] \Omega$	47, 48
3	$\{W - \hat{W}K + [Div(\hat{P}F) - (Div \hat{P})F] \cdot N - Div \hat{Q}\} \Omega$	Row 2
4	$[W - \hat{W}K - Div(\hat{P}FN) + \hat{P} \cdot (\partial F / \partial N) - Div \hat{Q}] \Omega$	50
5	$[w - \hat{\sigma} \cdot k - div(\hat{p}) \cdot fn - \hat{g}^{inh} \cdot fn - j\hat{J} div \hat{q}] \omega$	52, 53
6	$\{w - j\hat{J}\hat{W}K + \hat{J}^2[div(\hat{\sigma} \hat{F}) - (div \hat{\sigma})F] \cdot (nF) - j\hat{J} div \hat{q}\} \omega$	Row 3
7	$[w - \hat{W}k - div(\hat{p}fn) + \hat{p} \cdot (\partial f / \partial n) - \hat{g}^{inh} \cdot fn - j\hat{J} div \hat{q}] \omega$	56

Using $p = wF - \sigma F$, we have

$$\begin{aligned} np \cdot fn &= w - n\sigma \cdot n \\ &= w - (div \hat{\sigma}) \cdot n - g^{sur} \cdot n \\ &= w - \hat{\sigma} \cdot k - g^{sur} \cdot n. \end{aligned} \tag{53}$$

At the same time,

$$div(\hat{p}fn) = (div \hat{p}) \cdot fn + \hat{p} \cdot \frac{\partial f}{\partial n} - \hat{p}\hat{f} \cdot k, \tag{54}$$

and using Table 1 to eliminate $(\hat{p}\hat{f})$,

$$-(div \hat{p}) \cdot fn = -div(\hat{p}fn) + \hat{p} \cdot \frac{\partial f}{\partial n} - \hat{W}k + \hat{\sigma} \cdot k. \tag{55}$$

Combining eqns (52), (53) and (55) we obtain the Eulerian counterpart of eqn (50),

$$j\lambda = w - \hat{W}k - div(\hat{p}fn) + \hat{p} \cdot \frac{\partial f}{\partial n} - \hat{g}^{inh} \cdot fn - j\hat{J} div \hat{q}. \tag{56}$$

Note the presence of the additional penultimate term in eqn (56), associated with the inhomogeneity “force”.

In summary, we now have quite a few alternative formulae for the chemical potential μ , based upon eqn (45) and the derived formulae for λ . Several different looking but equivalent expressions are listed in Table 3. The expressions in rows 3 and 6 are most similar in form to those of Leo and Sekerka (1989) [see their eqn (104)] who derived equilibrium equations for accreting single and two phase systems. The fourth and seventh expressions in Table 3 are related to the expressions for the chemical potential derived by Wu (1996b), although Wu’s results were restricted to two-dimensions and did not take into account the dependence of the surface energy on N .

4.2. Example

As a simple illustration of the above formulae we consider the case for which the surface energy depends only upon the surface Jacobian,

$$\hat{W} = \Gamma(\hat{J}) \Leftrightarrow \hat{w} = \gamma(\hat{j}), \quad (57)$$

where the two functions Γ and γ are related by $\gamma(\xi) = \xi^{-1}\Gamma(\xi^{-1})$. Using Table 1 and the identity,

$$\Gamma - \hat{J}\Gamma' = \gamma', \quad (58)$$

where the prime denotes the derivative with respect to the argument, it follows that the four surface stresses are

$$\begin{aligned} \hat{\mathbf{P}} &= \Gamma' \hat{\mathbf{J}}\hat{\mathbf{f}}, \\ \hat{\boldsymbol{\sigma}} &= \Gamma' \hat{\mathbf{i}}, \\ \hat{\mathbf{E}} &= \gamma' \hat{\mathbf{f}}, \\ \hat{\mathbf{p}} &= \gamma' \hat{j} \hat{\mathbf{F}}. \end{aligned} \quad (59)$$

We may now substitute these surface stresses into the various formulae in Table 3 to get several equivalent expressions for the chemical potential :

$$\begin{aligned} \mu &= [\mathbf{G}^{\text{sur}} \cdot \mathbf{F}\mathbf{N} + \mathbf{N}\mathbf{E} \cdot \mathbf{N} - \gamma' K] \Omega \\ &= [W - \gamma' K - \Gamma' Jk - \Gamma'' \hat{J}(\hat{\mathbf{V}}_{\mathbf{R}} \hat{\mathbf{J}} \hat{\mathbf{f}} \cdot \mathbf{F}\mathbf{N})] \Omega \\ &= [w - \Gamma' k - \gamma' jK - \gamma'' \hat{j}(\hat{\mathbf{V}} \hat{j}) \hat{\mathbf{F}} \cdot \mathbf{f}\mathbf{n}] \omega. \end{aligned} \quad (60)$$

These correspond to rows 1, 2 and 5 in Table 3, respectively, and have been simplified using the identities (17) and (19).

A special case of the above is the Laplace–Herring model of Grinfeld (1994), which corresponds to linear functions

$$\Gamma = \Gamma_0 + \gamma_0 \hat{J} \Leftrightarrow \gamma = \gamma_0 + \Gamma_0 \hat{j}. \quad (61)$$

In this case the latter pair of expressions in eqn (60) become

$$\begin{aligned} \mu &= [W - \Gamma_0 K - \gamma_0 Jk] \Omega \\ &= [w - \gamma_0 k - \Gamma_0 jK] \omega. \end{aligned} \quad (62)$$

Hence, the coefficients Γ_0 and γ_0 determine the dependence upon the reference and current mean surface curvatures, respectively. Note that for an initially flat surface deformed into a flat surface ($\mathbf{k} = \mathbf{K} = 0$) the chemical potential in eqn (62) depends only on the bulk elastic energy.

More generally, the quantities Γ'' and γ'' in the second and third expressions in eqn (60) do not vanish if Γ is a nonlinear function, or equivalently, if γ is a nonlinear function of its argument. These terms persist even for the case of a flat surface deformed into another flat surface. Referring to the Appendix, we may rewrite the second and third expressions for μ in eqn (60) as

$$\begin{aligned} \mu &= [W - \gamma' K - \Gamma' Jk - \Gamma'' \hat{\mathbf{R}} \cdot \hat{\mathbf{V}}_{\mathbf{R}} \hat{J}] \Omega \\ &= [w - \Gamma' k - \gamma' jK + \gamma'' \hat{j} \hat{\mathbf{f}} \cdot \hat{\mathbf{V}} \hat{j}] \omega. \end{aligned} \quad (63)$$

The tangent vector $\hat{\mathbf{R}} \in S$ and its image $\hat{\mathbf{f}} \in s$ represent the shear in a plane orthogonal to the surface. This may be seen by noting, from the Appendix, that

$$\mathbf{FN} = \hat{\mathbf{j}}(\hat{\mathbf{f}} + \mathbf{J}\mathbf{n}), \quad (64)$$

which combined with eqn (74)₁ implies that the plane spanned by $\hat{\mathbf{R}}$ and $\mathbf{N}$ is locally deformed into the plane spanned by $\hat{\mathbf{f}}$ and $\mathbf{n}$. However, eqn (64) implies that the right angle between $\hat{\mathbf{R}}$ and $\mathbf{N}$ is skewed by an amount $\pm |\hat{\mathbf{f}}|/\sqrt{|\hat{\mathbf{f}}|^2 + \mathbf{J}^2}$. Hence, the terms involving Γ'' and γ'' in the two expressions for μ in eqn (63) both vanish if there is no shear orthogonal to the surface, or equivalently, if the image of $\mathbf{N}$ is parallel to $\mathbf{n}$.

4.3. Spatial and material equilibrium equations

The balance equations in column 4 of Table 1 were derived using the first variation, δ_x . We will denote these as the spatial equilibrium equations, to distinguish them from the material equations obtained with the δ_s variation. The two sets are identical for the bulk, but have different surface equations. Thus, setting $\lambda = 0$ gives eqns (41) and (42) instead of SE.4 and SN.4, respectively. A further pair of surface equations based upon the material variation can be obtained from eqns (41) and (42), using SC.2 and SP.2. After some calculation, we obtain

$$\widehat{\text{Div}} \hat{\mathbf{P}} = \mathbf{N}\hat{\mathbf{P}}\hat{\mathbf{i}} - \mathbf{G}^{\text{sur}}\hat{\mathbf{i}} + \hat{\mathbf{j}}(\hat{\boldsymbol{\sigma}} \cdot \mathbf{k})\mathbf{n}, \quad (65)$$

$$\widehat{\text{div}} \hat{\boldsymbol{\sigma}} = \mathbf{n}\hat{\boldsymbol{\sigma}}\hat{\mathbf{i}} - \mathbf{g}^{\text{su}}\hat{\mathbf{i}} + (\hat{\boldsymbol{\sigma}} \cdot \mathbf{k})\mathbf{n}. \quad (66)$$

These clearly differ from the Euler–Lagrange equations SP.4 and SC.4 obtained from the δ_x variation. We note that the same pair of equations, i.e. (65) and (66), are obtained if we use SE.4 and SN.4 as the starting point, rather than eqns (41) and (42).

A close examination of eqns (65) and (66) indicates that their on-surface components are the same as those of SP.4 and SC.4, respectively, but they have different $\mathbf{n}$ -components. In this regard they bear the same relation to the spatial equations SP.4 and SC.4 as SE.4 and SN.4 did to the material eqns (41) and (42). One way of interpreting this situation is by viewing SP.4 and SC.4 as the fundamental spatial surface equations, and eqns (41) and (42) are the fundamental material surface equations. The remaining equations, SE.4, SN.4 in the spatial case, eqns (65) and (66) in the material case, are derived from the fundamental equations but contain less information than these. The loss of information can be ascribed to the fact that $\hat{\mathbf{E}}$ in the spatial case, and $\hat{\boldsymbol{\sigma}}$ in the material case, are projections onto S and s , respectively. Thus, the normal components of the fundamental equations, viz.

$$\widehat{\text{div}} \hat{\boldsymbol{\sigma}} \cdot \mathbf{n} = \mathbf{n}\hat{\boldsymbol{\sigma}} \cdot \mathbf{n} - \mathbf{g}^{\text{sur}} \cdot \mathbf{n} \quad \text{and} \quad \widehat{\text{Div}} \hat{\mathbf{E}} \cdot \mathbf{N} = \mathbf{N}\hat{\mathbf{E}} \cdot \mathbf{N} + \mathbf{G}^{\text{sur}}\mathbf{F} \cdot \mathbf{N} - \widehat{\text{Div}} \hat{\mathbf{Q}}, \quad (67)$$

are lost in the process, to be replaced by the purely kinematic relations

$$\widehat{\text{div}} \hat{\boldsymbol{\sigma}} \cdot \mathbf{n} = \hat{\boldsymbol{\sigma}} \cdot \mathbf{k} \quad \text{and} \quad \widehat{\text{Div}} \hat{\mathbf{E}} \cdot \mathbf{N} = \hat{\mathbf{E}} \cdot \mathbf{K}, \quad (68)$$

respectively.

5. CONCLUSION

We have derived two sets of balance equations for the bulk and surface of an elastic body using spatial and material variational methods. The former variation is quite standard, and leads to the eight equations listed in column 4 of Table 1. The material variation, on the other hand, produces exactly the same bulk equations, but slightly different surface equations, i.e. eqns (41), (42), (65) and (66) instead of SP.4, SC.4, SE.4 and SN.4, respectively. The differences lie with the normal components, and are associated with the possibility of accretion which changes the underlying material. The energy required to perform

this is the chemical potential μ , which may be represented in various ways, including dual Lagrangian/Eulerian expressions, see Table 3. Perhaps the simplest expression of the chemical potential is by means of the Eshelby (or energy-momentum) bulk and surface stresses.

It should be noted that the additional equilibrium equation, which can be cast as $\mu = 0$, only makes sense if the material is permitted this additional degree of freedom. Solids do not normally exhibit the ability to spontaneously accrete, and the material equilibrium equation is not relevant to most problems in solid mechanics. However, there are circumstances under which it comes into play, by, for instance, surface diffusion effects. Another important example is multi-phase equilibrium with an inviscid melt. In the present study we have restricted attention to a single phase where all external influences on the surface are mechanical and are defined by the distributed force $\mathbf{g}^{\text{sur}}$. This offers a means to consider interactions with the outside environment. In future papers we will discuss the separate issues of surface kinetics and phase equilibrium.

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APPENDIX: THE SURFACE DEFORMATION TENSOR

Let $\mathbf{S}^1$ and $\mathbf{S}^2$ represent unit tangent vectors to the surface S in the reference configuration, such that $\{\mathbf{S}^1, \mathbf{S}^2, \mathbf{N}\}$ form an orthonormal triad with $\mathbf{N} = \mathbf{S}^1 \wedge \mathbf{S}^2$. Similarly, let $\mathbf{s}^1$ and $\mathbf{s}^2$ be tangent vectors to s in the current state, so that $\{\mathbf{s}^1, \mathbf{s}^2, \mathbf{n}\}$, $\mathbf{n} = \mathbf{s}^1 \wedge \mathbf{s}^2$, is another orthonormal triad. Note that $\mathbf{s}^\alpha$, $\alpha = 1$ or 2 , is not the unit vector of the image of the tangent vector $\mathbf{S}^\alpha$ under the deformation. However, the span of $\mathbf{S}^1$ and $\mathbf{S}^2$ is mapped into the span of $\mathbf{s}^1$ and $\mathbf{s}^2$, with $\hat{\mathbf{I}} = \mathbf{S}^\alpha \otimes \mathbf{S}^\alpha$ and $\hat{\mathbf{i}} = \mathbf{s}^\alpha \otimes \mathbf{s}^\alpha$ where repeated Greek subscripts indicate summation over 1 and 2 only. The surface deformation tensors can be expressed explicitly as

$$\hat{\mathbf{F}} = D_{\alpha\beta} \mathbf{s}^\alpha \otimes \mathbf{S}^\beta, \quad \hat{\mathbf{f}} = d_{\alpha\beta} \mathbf{S}^\alpha \otimes \mathbf{s}^\beta, \quad (69)$$

where

$$D_{\alpha\gamma} d_{\gamma\beta} = \delta_{\alpha\beta}, \quad \hat{\mathbf{f}} = \det[D_{\alpha\beta}], \quad \hat{\mathbf{F}} = \det[d_{\alpha\beta}]. \quad (70)$$

The surface values of the bulk deformation tensors may then be written as

$$\mathbf{F} = \hat{\mathbf{F}} + \hat{\mathbf{f}} \otimes \mathbf{N} + \hat{\mathbf{f}} \mathbf{N} \otimes \mathbf{N} \quad \text{for } \mathbf{X} \in S, \quad (71)$$

$$\mathbf{f} = \hat{\mathbf{f}} - \hat{\mathbf{f}} \otimes \mathbf{n} + \hat{\mathbf{f}} \mathbf{n} \otimes \mathbf{n} \quad \text{for } \mathbf{x} \in s, \quad (72)$$

where $\hat{\mathbf{f}}$ and $\hat{\mathbf{R}}$ are tangent vectors in the current and reference configurations:

$$\hat{\mathbf{f}} = r_\alpha \mathbf{s}^\alpha, \quad \hat{\mathbf{R}} = R_\alpha \mathbf{S}^\alpha. \quad (73)$$

The following identities are a consequence of the fact that $\mathbf{f}$ and $\mathbf{F}$ are mutual inverses,

$$\hat{\mathbf{F}} \hat{\mathbf{R}} = \hat{\mathbf{f}} \Leftrightarrow \hat{\mathbf{f}} \hat{\mathbf{R}} = \hat{\mathbf{R}}. \quad (74)$$

In fact,

$$\mathbf{F} \hat{\mathbf{R}} = \hat{\mathbf{f}} \Leftrightarrow \hat{\mathbf{f}} \hat{\mathbf{R}} = \hat{\mathbf{R}}, \quad (75)$$

implying that $\hat{\mathbf{f}}$ and $\hat{\mathbf{R}}$ are images of one another under the deformation.