Surface Energy and Nanoscale Mechanics

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Abstract

The mechanical response of nanostructures, or materials with characteristic features at the nanoscale, differs from their coarser counterparts. An important physical reason for this size-dependent phenomenology is that surface or interface properties are different than those of the bulk material and acquire significant prominence due to an increased surface-to-volume ratio at the nanoscale. In

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this chapter, we provide an introductory tutorial on the continuum approach to incorporate the effect of surface energy, stress, and elasticity and address the size-dependent elastic response at the nanoscale. We present some simple illustrative examples that underscore both the physics underpinning the capillary phenomenon in solids as well as a guide to the use of the continuum theory of surface energy.

1 Introduction

In a manner of speaking, a free surface or an interface is a "defect." We will use the word "surface" to imply both a free surface as well as an interface separating two materials. It represents a drastic interruption in the symmetry of the material – much like the more conventionally known defects such as dislocations. Imagine the atoms on a free surface. They have a different coordination number, charge distribution, possible dangling bonds, and many other attributes that distinguish them from atoms further away in the bulk of the material (Ibach 1997; Cammarata 2009). It is therefore hardly surprising that the surface of a material should have mechanical (or in general other physical) properties that differ from the bulk of the material. In other words, as much as conventional defects (such as dislocations) impact the physical response of materials, so do surfaces. However, for coarse-sized structures, the surface-to-volume ratio is negligible, and so even though surfaces do have different properties, they hardly matter in terms of the overall response of the structure. This situation changes dramatically at the nanoscale. As a rather extreme example, 2 nm cube of Copper has nearly 50% of its atoms on the surface. What length scale is "small enough" for surface effects to become noticeable arguably depends on the strength of the surface properties. For hard crystalline materials, this length scale is certainly below 50 nm and often only of significant importance below 10 nm (Miller and Shenoy 2000). Ultra-soft materials (with elastic modulus in the 1–5 kPa range) are an interesting exception where even at micron scale, surface energy-related size effects may be observable (Style et al. 2013).

In a continuum field setting, the role of surfaces may be captured by assuming that they are zero-thickness entities and possess a nontrivial *excess* energy that is distinct from the bulk. The surface energy concept for solids encompasses the fact that surfaces appear to possess a residual "surface tension"-like effect known as surface stress and also an elastic response, termed "surface or superficial elasticity." In the context of fluids, "capillarity" has long been studied, and the concept of surface tension is well-known (see Fig. 1). The situation for solid surfaces is somewhat more subtle than fluids in many ways since deformation is a rather important contributor to surface energy – which is not the case for simple liquids. For a simple liquid, surface energy, the so-called surface stress and surface tension are the same concept. This is not the case for solid surfaces. For further details, see a recent review article by Style et al. (2017). Given the existence of an extensive body of work on this subject, we avoid a detailed literature review and simply point to the following overview articles that the reader may consult (and the references

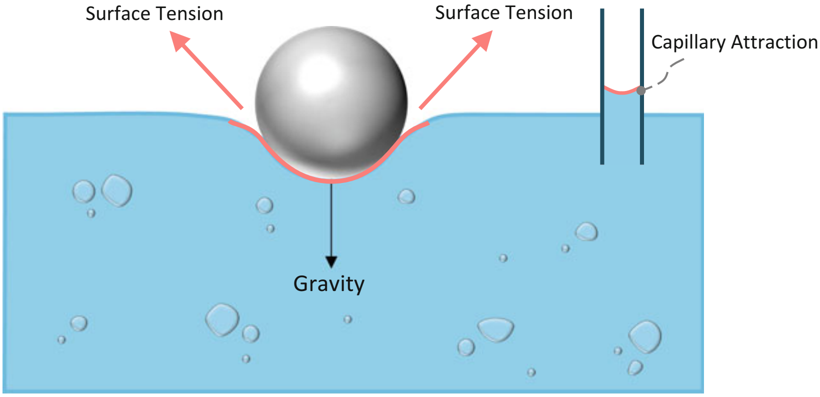

Fig. 1 The ramifications of surface energy – in the form of surface tension – are well-known from our daily lives and are illustrated in this schematic. Surface tension forces, for instance, assist in overcoming gravity and enable the floatation of a ball. The ability of a water spider to walk on the water surface is another example. Also shown is a schematic of a capillary tube, frequently used by biologists and chemists, to highlight how surface tension causes water to be drawn up the tube

therein): (Javili et al. 2013; Duan et al. 2009; Wang et al. 2010, 2011; Li and Wang 2008; Cammarata 2009; Ibach 1997; Müller and Saúl 2004). We will primarily follow the approach pioneered by Gurtin, Murdoch, Fried, and Huang (Gurtin and Murdoch 1975b; Biria et al. 2013; Huang and Sun 2007) and attempt to present a simplified tutorial on the continuum theory for surface energy. For the sake of brevity and with the stipulation that this chapter is merely meant to be a first step to understand surface elasticity, we avoid several complexities and subtleties that exist on this topic such as choice of reference state in the development of the continuum theory (Huang and Wang 2013; Javili et al. 2017), consistent linearization from a nonlinear framework and differences in the various linearized theories (Javili et al. 2017; Liu et al. 2017), curvature dependence of surface energy (Steigmann and Ogden 1997, 1999; Chhapadia et al. 2011; Fried and Todres 2005), and generalized interface models that may allow greater degree of freedom than just a “no slip” surface c.f. (Gurtin et al. 1998; Chatzigeorgiou et al. 2017). We also present three simple case studies or illustrative examples that both highlight the use of the theory and the physical consequence of surface energy effects. While the focus of the chapter is primarily on mechanics and, specifically, elasticity, the framework used in this chapter can be used as a starting point for applications outside mechanics. Indeed, surface energy effects are of significant interest to a variety of disciplines and permeate topics as diverse as fluid mechanics (de Gennes et al. 2004), sensors and resonators (Park 2008), catalysis (Müller and Saúl 2004; Haiss 2001; Pala and Liu 2004), self-assembly (Suo and Lu 2000), phase transformations (Fischer et al. 2008), biology (Liu et al. 2017), and composites (Duan et al. 2005), among others.

2 Preliminary Concepts

2.1 The Need for Surface Tensors

In the study of mechanics of surfaces, we have to contend with tensor fields that "live" on a surface. For example, we will need to define the strain field experienced by a surface. The general machinery of curvilinear tensor calculus then becomes necessary to describe surface mechanics which (at least for our taste) becomes somewhat cumbersome. A direct notation was developed by Gurtin and Murdoch (1975b) which we (prefer and) briefly motivate in this section.

To establish the basic idea, for now, consider just a flat surface shown in Fig. 2 with outward unit normal $\boldsymbol{n} = \boldsymbol{e}_3$. On physical grounds, assuming that there is no "slip" between the surface and the underlying bulk material, the surface strain is simply the strain field of the bulk material *at the spatial position of the surface*. In addition, intuitively, the normal components of the strain tensor ought not to exist for the zero-thickness surface, i.e., $\boldsymbol{E}_s(\boldsymbol{x}) = \boldsymbol{E}^{bulk}(\boldsymbol{x})$ projected on the tangent plane of the surface where $\boldsymbol{x}$ is on the surface. To make this idea more concrete, assume a body occupies a domain Ω_0 experiencing a strain $\boldsymbol{E} : \Omega_0 \to \mathbb{R}^{3\times3}_{sym}$. We then expect the surface strain to be simply

$$\boldsymbol{E}_s := \begin{bmatrix} E_{11} & E_{12} & 0 \\ E_{21} & E_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{1}$$

Our intuition works well for flat surfaces, but we must generalize the mathematical framework to contend with general curved surfaces. This brings to fore the question of how we define surface tensors on arbitrarily curved surfaces. To understand this, we define next the surface projection tensor. More details on the mathematical preliminaries can be found in the work of Gurtin, Murdoch, and co-workers (Gurtin and Murdoch 1975b, 1978; Gurtin et al. 1998).

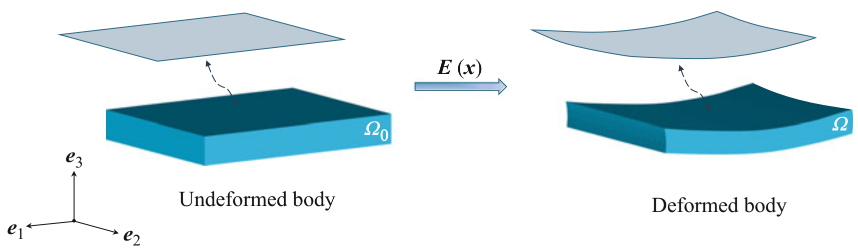

Fig. 2 Schematic of the deformation of a body that occupies the domain Ω_0. The upper surface is artificially separated from the underlying bulk to highlight the surface deformation $\boldsymbol{E}(\boldsymbol{x})$. Cartesian coordinates with a positively oriented orthonormal basis $\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}$ are shown here and the outward unit normal to the upper surface is $\boldsymbol{n}(\boldsymbol{x}) = \boldsymbol{e}_3$

2.1.1 Surface Projection Tensor

As discussed in the preceding section, we will often need to project second-order tensors on to a curved surface. To that end, the surface projection tensor for the tangent surface with outward unit normal $\boldsymbol{n}(\boldsymbol{x})$ is defined as

$$\mathbb{P}(\boldsymbol{x}) = \mathbf{I} - \boldsymbol{n}(\boldsymbol{x}) \otimes \boldsymbol{n}(\boldsymbol{x}). \tag{2}$$

Here $\mathbf{I}$ is the second-order identity tensor, and "$\otimes$" denotes the tensor product (or the dyadic product).

If we choose the flat upper surface shown in Fig. 2 as an example, the normal to the upper surface is $\boldsymbol{n} = \boldsymbol{e}_3$ in Cartesian coordinates with a positively oriented orthonormal basis $\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}$. With the definition in (2), the projection tensor on the flat upper surface admits the form

$$\mathbb{P}(\boldsymbol{x}) = \mathbf{I} - \boldsymbol{e}_3 \otimes \boldsymbol{e}_3 = \boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2 := \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}_{\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}}. \tag{3a}$$

Another example is the projection tensor on a spherical surface with radius R that can be represented by $S = \{\boldsymbol{x} \in \mathbb{R}^3 : \boldsymbol{x} \cdot \boldsymbol{x} - R^2 = 0\}$. The outward unit normal to this surface is $\boldsymbol{n} = \boldsymbol{e}_r$ in spherical coordinates $\{r, \theta, \phi\}$ with basis $\{\boldsymbol{e}_r, \boldsymbol{e}_\theta, \boldsymbol{e}_\phi\}$. From the definition of the projection tensor in (2), we have

$$\mathbb{P}(\boldsymbol{x}) = \mathbf{I} - \boldsymbol{e}_r \otimes \boldsymbol{e}_r = \boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi := \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}_{\{\boldsymbol{e}_r, \boldsymbol{e}_\theta, \boldsymbol{e}_\phi\}}. \tag{3b}$$

The projection tensor in (3b) can also be easily expressed in the Cartesian coordinates by using the identities $\boldsymbol{e}_\theta = \cos\theta\cos\phi\boldsymbol{e}_1 + \cos\theta\sin\phi\boldsymbol{e}_2 - \sin\theta\boldsymbol{e}_3$ and $\boldsymbol{e}_\phi = -\sin\phi\boldsymbol{e}_1 + \cos\phi\boldsymbol{e}_2$ as well as the tensor product between two vectors.

2.1.2 Surface Vector and Tensor Fields

Let $\boldsymbol{v}(\boldsymbol{x})$ be a smooth vector field and $\boldsymbol{T}(\boldsymbol{x})$ be a smooth second-order tensor. Their projections $\boldsymbol{v}_s(\boldsymbol{x})$ and $\boldsymbol{T}_s(\boldsymbol{x})$ on a smooth surface with outward unit normal $\boldsymbol{n}(\boldsymbol{x})$, respectively, are

$$\boldsymbol{v}_s = \mathbb{P}\boldsymbol{v} \quad \text{and} \quad \boldsymbol{T}_s = \mathbb{P}\boldsymbol{T}\mathbb{P}, \tag{4}$$

where the projection tensor $\mathbb{P}$ is defined in (2).

For example, consider a vector field $\boldsymbol{v} = v_i \boldsymbol{e}_i$ and a second-order tensor field $\boldsymbol{T} = T_{ij}\boldsymbol{e}_i \otimes \boldsymbol{e}_j$ in Cartesian coordinates with a positively oriented orthonormal basis $\{\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3\}$. Take the upper surface with outward unit normal $\boldsymbol{n}(\boldsymbol{x}) = \boldsymbol{e}_3$. The projection tensor in (2) becomes $\mathbb{P}(\boldsymbol{x}) = \mathbf{I} - \boldsymbol{e}_3 \otimes \boldsymbol{e}_3 = \boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2$. Thus, with (4), the projected vector and tensor on the upper surface, respectively, are

$$\boldsymbol{v}_s = \mathbb{P}\boldsymbol{v} = (\boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2)v_i\boldsymbol{e}_i = v_1\boldsymbol{e}_1 + v_2\boldsymbol{e}_2 \tag{5a}$$

and

$$\begin{aligned}\boldsymbol{T}_s = \mathbb{P}\boldsymbol{T}\mathbb{P} &= (\boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2) \cdot T_{ij}\boldsymbol{e}_i \otimes \boldsymbol{e}_j \cdot (\boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2) \\ &= T_{11}\boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + T_{12}\boldsymbol{e}_1 \otimes \boldsymbol{e}_2 + T_{21}\boldsymbol{e}_2 \otimes \boldsymbol{e}_1 + T_{22}\boldsymbol{e}_2 \otimes \boldsymbol{e}_2 \\ &:= \begin{bmatrix} T_{11} & T_{12} & 0 \\ T_{21} & T_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix}.\end{aligned} \tag{5b}$$

Equation (5b) makes it evident how the surface strain in (1), written earlier by intuition, may be formally derived from the bulk strain field.

By $(4)_2$, the projection of the identity tensor $\mathbf{I}$ on the surface with outward unit normal $\boldsymbol{n}(\boldsymbol{x})$ can be obtained as

$$\mathbb{I} = \mathbb{P}\mathbf{I}\mathbb{P}, \tag{6}$$

which is called the *surface identity tensor* on the surface and is often used in the context of second-order tensors.

2.2 Differentiation and Integration on a Surface

2.2.1 Surface Gradient, Normal Derivative, and Curvature Tensor

Consider a smooth scalar field $\phi(\boldsymbol{x}) : \Omega_0 \to \mathbb{R}$ and a smooth vector field $\boldsymbol{v}(\boldsymbol{x}) : \Omega_0 \to \mathbb{R}^3$ over the domain Ω_0. By using the gradient operator ∇, their (three-dimensional) gradients are represented by $\nabla\phi(\boldsymbol{x})$ and $\nabla\boldsymbol{v}(\boldsymbol{x})$, respectively. In contrast, the surface gradient operator on a surface with unit normal $\boldsymbol{n}$ is denoted by ∇_s, and together with the projection tensor $\mathbb{P}$ in (2), the *surface gradients* of the two fields can be represented by (Gurtin et al. 1998)

$$\nabla_s\phi = \mathbb{P}\nabla\phi \quad \text{and} \quad \nabla_s\boldsymbol{v} = (\nabla\boldsymbol{v})\mathbb{P}. \tag{7}$$

We now define the *normal derivative* of fields on a surface with outward unit normal $\boldsymbol{n}$. Following the scalar field ϕ and the vector field $\boldsymbol{v}$ in (7), we define their normal derivatives as

$$\frac{\partial\phi}{\partial n} = \boldsymbol{n} \cdot \nabla\phi \quad \text{and} \quad \frac{\partial\boldsymbol{v}}{\partial n} = (\nabla\boldsymbol{v})\boldsymbol{n}. \tag{8}$$

The normal derivative $\frac{\partial\phi}{\partial n}$ can be regarded as the rate of change of ϕ in the direction $\boldsymbol{n}$. By (2) and (8), the surface derivatives (7) can be recast as

$$\nabla_s\phi = \nabla\phi - \left(\frac{\partial\phi}{\partial n}\right)\boldsymbol{n} \quad \text{and} \quad \nabla_s\boldsymbol{v} = \nabla\boldsymbol{v} - \left(\frac{\partial\boldsymbol{v}}{\partial n}\right) \otimes \boldsymbol{n}. \tag{9}$$

Equation (9) represents the relation between the surface gradient, the gradient, and the normal derivative. We note that Eqs. (7) and (9) are two (alternative but equivalent) ways to represent the surface gradient.

The *curvature tensor* of a surface with outward unit normal $\boldsymbol{n}$ is then defined as (Gurtin et al. 1998)

$$\mathbb{L} = -\nabla_s \boldsymbol{n}, \tag{10}$$

which is symmetric and hence tangential, that is, $\mathbb{L} = \mathbb{L}^T$ and $\mathbb{L}^T \boldsymbol{n} = \boldsymbol{0}$.

In order to enhance the understanding of these definitions, we now consider some simple examples by referring to Fig. 2. In Cartesian coordinates, the gradients of the scalar and vector fields, respectively, are $\nabla\phi = \frac{\partial\phi}{\partial x_i}\boldsymbol{e}_i$ and $\nabla\boldsymbol{v} = \frac{\partial\boldsymbol{v}}{\partial x_j} \otimes \boldsymbol{e}_j = \frac{\partial v_i}{\partial x_j}\boldsymbol{e}_i \otimes \boldsymbol{e}_j$. The outward unit normal to the flat upper surface is $\boldsymbol{n} = \boldsymbol{e}_3$, and then its projection tensor is $\mathbb{P} = \boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2$ which was mentioned in (3a).

By (7) and the Kronecker delta, the surface gradients on the flat surface in Fig. 2 are

$$\nabla_s\phi = (\boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2)\frac{\partial\phi}{\partial x_i}\boldsymbol{e}_i = \frac{\partial\phi}{\partial x_1}\boldsymbol{e}_1 + \frac{\partial\phi}{\partial x_2}\boldsymbol{e}_2 \tag{11a}$$

and

$$\nabla_s\boldsymbol{v} = \left(\frac{\partial\boldsymbol{v}}{\partial x_j} \otimes \boldsymbol{e}_j\right)(\boldsymbol{e}_1 \otimes \boldsymbol{e}_1 + \boldsymbol{e}_2 \otimes \boldsymbol{e}_2) = \frac{\partial\boldsymbol{v}}{\partial x_1} \otimes \boldsymbol{e}_1 + \frac{\partial\boldsymbol{v}}{\partial x_2} \otimes \boldsymbol{e}_2. \tag{11b}$$

By (8), the normal derivatives on the surface in the example are

$$\frac{\partial\phi}{\partial n} = \boldsymbol{e}_3 \cdot \frac{\partial\phi}{\partial x_i}\boldsymbol{e}_i = \frac{\partial\phi}{\partial x_3} \quad \text{and} \quad \frac{\partial\boldsymbol{v}}{\partial n} = \left(\frac{\partial\boldsymbol{v}}{\partial x_j} \otimes \boldsymbol{e}_j\right)\boldsymbol{e}_3 = \frac{\partial\boldsymbol{v}}{\partial x_3}. \tag{12}$$

Using (9), together with (12), we can obtain the same surface gradients as (11). Similarly, using (10), together with (11b), we find the obvious answer that the curvature tensor $\mathbb{L}$ of the flat upper surface in Fig. 2 is

$$\mathbb{L} = -\nabla_s\boldsymbol{e}_3 = -\frac{\partial\boldsymbol{e}_3}{\partial x_1} \otimes \boldsymbol{e}_1 - \frac{\partial\boldsymbol{e}_3}{\partial x_2} \otimes \boldsymbol{e}_2 = \boldsymbol{0}. \tag{13}$$

As another illustration, we may consider the curvature tensor for a spherical surface of radius R. In spherical coordinates $\{r, \theta, \phi\}$ with orthonormal basis $\{\boldsymbol{e}_r, \boldsymbol{e}_\theta, \boldsymbol{e}_\phi\}$, the outward unit normal to the spherical surface is $\boldsymbol{n} = \boldsymbol{e}_r$, whose gradient is $\nabla\boldsymbol{e}_r = r^{-1}(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi)$. By (7) and (10), the curvature tensor in this example is

$$\mathbb{L} = -\nabla_s\boldsymbol{e}_r = -(\nabla\boldsymbol{e}_r)\mathbb{P} = -\frac{1}{R}(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi), \tag{14}$$

which is symmetric $\mathbb{L} = \mathbb{L}^T$ and tangential $\mathbb{L}^T\boldsymbol{e}_r = \boldsymbol{0}$.

2.2.2 Surface Divergence, Trace, and Mean Curvature

The *surface divergences* of a vector field $\boldsymbol{v}(\boldsymbol{x})$ and a tensor field $\boldsymbol{T}(\boldsymbol{x})$ are defined as follows:

$$\text{div}_s \boldsymbol{v} = \text{tr}(\nabla_s \boldsymbol{v}) \quad \text{and} \quad \boldsymbol{a} \cdot \text{div}_s \boldsymbol{T} = \text{div}_s(\boldsymbol{T}^T \boldsymbol{a}), \tag{15}$$

where "tr", here and henceforth, denotes the *trace* and $\boldsymbol{a} \in \mathbb{R}^3$ is an arbitrary constant vector. An important identity related to the surface divergence operator is

$$\text{div}_s(\boldsymbol{T}^T \boldsymbol{n}) = \boldsymbol{n} \cdot \text{div}_s \boldsymbol{T} + \boldsymbol{T} \cdot \nabla_s \boldsymbol{n}. \tag{16}$$

For further useful surface identities, the reader is referred to the work (Gurtin and Murdoch 1975b).

The *mean curvature* is then simply

$$\kappa = \frac{1}{2}\text{tr}(\mathbb{L}) = -\frac{1}{2}\text{tr}(\nabla_s \boldsymbol{n}) = -\frac{1}{2}\text{div}_s \boldsymbol{n}. \tag{17}$$

For the same example in Eq. (11b), the corresponding surface divergence is

$$\text{div}_s \boldsymbol{v} = \text{tr}(\nabla_s \boldsymbol{v}) = \text{tr}\left(\frac{(\partial v_i \boldsymbol{e}_i)}{\partial x_1} \otimes \boldsymbol{e}_1 + \frac{\partial (v_i \boldsymbol{e}_i)}{\partial x_2} \otimes \boldsymbol{e}_2\right) = \frac{\partial v_1}{\partial x_1} + \frac{\partial v_2}{\partial x_2}. \tag{18}$$

Similarly, for a second-order tensor $\boldsymbol{T} = T_{ij} \boldsymbol{e}_i \otimes \boldsymbol{e}_j$, its surface gradient is a vector, and its k-th component, by $(15)_2$, can be represented by

$$(\text{div}_s \boldsymbol{T})_k = \boldsymbol{e}_k \cdot \text{div}_s \boldsymbol{T} = \text{div}_s(\boldsymbol{T}^T \boldsymbol{e}_k) = \frac{\partial T_{k1}}{\partial x_1} + \frac{\partial T_{k2}}{\partial x_2}, \tag{19}$$

where the identity $\boldsymbol{T}^T \boldsymbol{e}_k = T_{ki} \boldsymbol{e}_i$ and the example result in (18) are used. Regarding the examples of the curvature tensors (13) and (14), their mean curvatures are 0 and $-R^{-1}$, respectively.

2.2.3 Divergence Theorem for Surfaces

Consider a surface $\mathsf{S}_0 \subset \partial \Omega_0$ with a smooth boundary curve $\partial \mathsf{S}_0$. For a smooth vector $\boldsymbol{u}$ that is tangential on the surface S_0 and a smooth tensor field $\boldsymbol{T}$, the divergence theorem is defined by Gurtin and Murdoch (1975b) and Gurtin et al. (1998)

$$\int_{\mathsf{S}_0} \text{div}_s \boldsymbol{u} = \int_{\partial \mathsf{S}_0} \boldsymbol{u} \cdot \boldsymbol{\nu}, \qquad \int_{\mathsf{S}_0} \text{div}_s \boldsymbol{T} = \int_{\partial \mathsf{S}_0} \boldsymbol{T} \boldsymbol{\nu}, \tag{20}$$

where $\boldsymbol{\nu}$ is the outward unit normal to the boundary curve $\partial \mathsf{S}_0$.

3 Theoretical Framework for Surface Mechanics

With the mathematical preliminaries necessary for surface mechanics described earlier, we can now proceed in a rather standard manner to derive the pertinent governing equations. The original theory by Gurtin and Murdoch (1975b) was derived by employing stress as the primitive concept. We (following Huang and co-workers Huang and Wang 2006; Huang and Sun 2007) favor a variational approach where we take the surface energy as the primitive concept.

3.1 Kinematics

Assume a deformable solid that occupies the domain Ω_0 in the reference configuration shown in Fig. 3. The boundary of the domain is denoted by $\partial\Omega_0$, which can be divided into two parts: the displacement boundary $\partial\Omega_0^u$ and the traction boundary $\partial\Omega_0^t$. Mathematically, $\partial\Omega_0^u \cup \partial\Omega_0^t = \partial\Omega_0$ and $\partial\Omega_0^u \cap \partial\Omega_0^t = \varnothing$.

A material point is denoted by $\boldsymbol{x} \in \Omega_0$. Consider a smooth mapping $\boldsymbol{y} : \Omega_0 \to \mathbb{R}^3$, that is, $\boldsymbol{y}(\boldsymbol{x}) = \boldsymbol{x} + \boldsymbol{u}(\boldsymbol{x})$. Here $\boldsymbol{u}$ is the displacement vector. The deformation gradient is defined as $\boldsymbol{F} = \nabla \boldsymbol{x}$. The displacement and traction boundary conditions are

$$\boldsymbol{u} = \boldsymbol{u}_0 \quad \text{on } \partial\Omega_0^u \quad \text{and} \quad \boldsymbol{t} = \boldsymbol{t}_0 \quad \text{on } \partial\Omega_0^t. \tag{21}$$

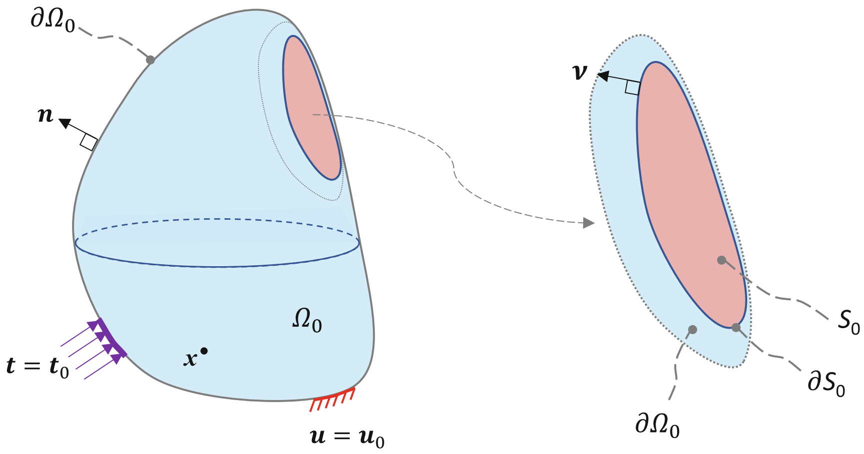

Fig. 3 Schematic of a deformable body that occupies the domain Ω_0 with the boundary $\partial\Omega_0$. The material point is denoted by $\boldsymbol{x} \in \Omega_0$, and the outward unit normal to $\partial\Omega_0$ is represented by $\boldsymbol{n}$. The displacement boundary is $\boldsymbol{u} = \boldsymbol{u}_0$ while the traction boundary is $\boldsymbol{t} = \boldsymbol{t}_0$. In particular, the surface effect is shown on the surface $\mathsf{S}_0 \subset \partial\Omega_0$. On the boundary curve $\partial\mathsf{S}_0$ of the surface S_0, the outward unit normal to $\partial\mathsf{S}_0$ is denoted by $\boldsymbol{v}$

3.2 Energy Variation and Equations of Equilibrium

We explicitly assume that the surface or the interface does not “slip” from the rest of the material. Gurtin et al. (1998) have dealt with the special case where interfaces may not be coherent and admit jumps in displacements. We do not consider that complexity here. The energy functional of the general system shown in Fig. 3 is then:

$$\mathscr{F}[\boldsymbol{u};\boldsymbol{x}] = \int_{\Omega_0} \Psi(\nabla \boldsymbol{u}) + \int_{\mathsf{S}_0} \Gamma_s(\nabla \boldsymbol{u}) - \int_{\partial\Omega_0^t} \boldsymbol{t}_0 \cdot \boldsymbol{u}, \tag{22}$$

where Ψ is the strain energy function per unit volume of the bulk, Γ_s is the surface energy function per unit area of the surface $\mathsf{S}_0 \subset \partial\Omega_0$, and $\boldsymbol{t}_0$ is the dead load applied on the traction boundary $\partial\Omega_0^t$ in the reference configuration. The reference configuration taken here is actually the initial configuration, which is neither subjected to any body force nor tractions. We note that in the reference configuration, there exists the surface stress, which is regarded as “residual.” The residual stress field can be described according to the surface energy function Γ_s. To further clarify the surface effects on the energy functional, Huang and Wang (2006, 2013) proposed an extra configuration, a “fictitious stress-free configuration.” For further details on such subtleties, the reader is referred to their work.

We now invoke the principle of minimum energy to seek the equilibrium state of the deformed body:

$$\min\{\mathscr{F}[\boldsymbol{u}] : \boldsymbol{u} \in \mathscr{S}\}. \tag{23}$$

Here the set $\mathscr{S}$ denotes the smooth function space over the domain Ω_0, and the displacement field must satisfy $\boldsymbol{u} = \boldsymbol{u}_0$ on $\partial\Omega_0^u$ in $(21)_1$.

If we assume the state $\boldsymbol{u}$ to be the minimizer of the energy functional in (22), then by the principle of energy minimization (23), we have

$$\mathscr{F}[\boldsymbol{u}] \leq \mathscr{F}[\boldsymbol{u} + \epsilon \boldsymbol{u}_1], \tag{24}$$

where $\epsilon \in \mathbb{R}$ and $\boldsymbol{u} + \epsilon\boldsymbol{u}_1$ belongs to the set of all kinematically admissible deformations in the neighborhood of the deformation $\boldsymbol{u}$. We only consider small perturbations, so the norm $\|\epsilon\boldsymbol{u}_1\| \ll 1$. By the displacement boundary $(21)_1$, the variation $\boldsymbol{u}_1$ satisfies

$$\boldsymbol{u}_1 = \boldsymbol{0} \quad \text{on } \partial\Omega_0^u. \tag{25}$$

The inequality (24) leads to the following first and second variation conditions

$$\delta\mathscr{F}[\boldsymbol{u}] = 0 \quad \text{and} \quad \delta^2\mathscr{F}[\boldsymbol{u}] \geq 0. \tag{26}$$

In this book chapter, we only limit our attention to the first variation that leads to the equilibrium equations and the natural boundary conditions. The first variation is written as

$$\delta\mathscr{F}[\boldsymbol{u}] := \left.\frac{\mathrm{d}\mathscr{F}[\boldsymbol{u}+\epsilon\boldsymbol{u}_1]}{\mathrm{d}\epsilon}\right|_{\epsilon=0}. \tag{27}$$

Using (27) and the chain rule, the first variation of (22) reads

$$\delta\mathscr{F}[\boldsymbol{u}] = \int_{\Omega_0} \boldsymbol{S}\cdot\nabla\boldsymbol{u}_1 + \int_{\mathsf{S}_0} \mathbb{S}\cdot\nabla\boldsymbol{u}_1 - \int_{\partial\Omega_0^t} \boldsymbol{t}_0\cdot\boldsymbol{u}_1, \tag{28}$$

where

$$\boldsymbol{S} = \frac{\partial\Psi}{\partial\nabla\boldsymbol{u}} \quad \text{and} \quad \mathbb{S} = \frac{\partial\Gamma_s}{\partial\nabla\boldsymbol{u}}. \tag{29}$$

Here $\mathbb{S}$ in (29) is the first Piola-Kirchhoff surface stress tensor (Gurtin et al. 1998), and $\boldsymbol{S}$ is the first Piola-Kirchhoff bulk stress tensor.

Employing the surface gradient of a vector in $(9)_2$ as well as the property of the surface tensor $\mathbb{S}$, that is, $\mathbb{S}\boldsymbol{n} = \boldsymbol{0}$, the integrand $\mathbb{S}\cdot\nabla\boldsymbol{u}_1$ in (28) can be recast as

$$\mathbb{S}\cdot\nabla\boldsymbol{u}_1 = \mathbb{S}\cdot\nabla_s\boldsymbol{u}_1 + \frac{\partial\boldsymbol{u}_1}{\partial n}\cdot\mathbb{S}\boldsymbol{n} = \mathbb{S}\cdot\nabla_s\boldsymbol{u}_1. \tag{30}$$

In the work by Gurtin et al. (1998), they derived the identity $\mathbb{S}\boldsymbol{n} = \boldsymbol{0}$ on the surface S_0 (see their Eq.(37)) by assuming an arbitrary function $\frac{\partial\boldsymbol{u}_1}{\partial n}$ on the surface S_0. Here we obtain this identity through the definition of a surface tensor $(4)_2$, that is, for an arbitrary surface tensor $\boldsymbol{T}_s = \mathbb{P}\boldsymbol{T}\mathbb{P}$, we have $\boldsymbol{T}_s\boldsymbol{n} = \mathbb{P}\boldsymbol{T}\mathbb{P}\boldsymbol{n} = \mathbb{P}\boldsymbol{T}\boldsymbol{0} = \boldsymbol{0}$ since $\mathbb{P}\boldsymbol{n} = (\mathbf{I} - \boldsymbol{n}\otimes\boldsymbol{n})\boldsymbol{n} = \boldsymbol{0}$.

By the identity (16), we further have

$$\mathbb{S}\cdot\nabla_s\boldsymbol{u}_1 = \mathrm{div}_{\mathrm{s}}(\mathbb{S}^T\boldsymbol{u}_1) - \boldsymbol{u}_1\cdot\mathrm{div}_{\mathrm{s}}\mathbb{S}. \tag{31}$$

Thus, by (31) and the divergence theorem (20), the second integral in (28) becomes

$$\int_{\mathsf{S}_0} \mathbb{S}\cdot\nabla\boldsymbol{u}_1 = \int_{\mathsf{S}_0} \left[\mathrm{div}_{\mathrm{s}}(\mathbb{S}^T\boldsymbol{u}_1) - \boldsymbol{u}_1\cdot\mathrm{div}_{\mathrm{s}}\mathbb{S}\right] = \int_{\partial\mathsf{S}_0} \boldsymbol{u}_1\cdot\mathbb{S}\boldsymbol{v} - \int_{\mathsf{S}_0} \boldsymbol{u}_1\cdot\mathrm{div}_{\mathrm{s}}\mathbb{S}. \tag{32}$$

Similarly, by using the divergence theorem in volume, we obtain

$$\int_{\Omega_0} \boldsymbol{S}\cdot\nabla\boldsymbol{u}_1 = \int_{\Omega_0} \left[\mathrm{div}(\boldsymbol{S}^T\boldsymbol{u}_1) - \boldsymbol{u}_1\cdot\mathrm{div}\boldsymbol{S}\right] = \int_{\partial\Omega_0} \boldsymbol{u}_1\cdot\boldsymbol{S}\boldsymbol{n} - \int_{\Omega_0} \boldsymbol{u}_1\cdot\mathrm{div}\boldsymbol{S}. \tag{33}$$

Substituting (32) and (33) into (28), we have

$$\delta\mathscr{F}[\boldsymbol{u}] = -\int_{\Omega_0} \boldsymbol{u}_1 \cdot \mathrm{div}\boldsymbol{S} + \int_{\partial\Omega_0\backslash\mathsf{S}_0} \boldsymbol{u}_1 \cdot \boldsymbol{S}\boldsymbol{n} + \int_{\mathsf{S}_0} \boldsymbol{u}_1 \cdot (\boldsymbol{S}\boldsymbol{n} - \mathrm{div}_{\mathrm{s}}\mathbb{S})$$
$$+ \int_{\partial\mathsf{S}_0} \boldsymbol{u}_1 \cdot \mathbb{S}\boldsymbol{v} - \int_{\partial\Omega_0^t} \boldsymbol{t}_0 \cdot \boldsymbol{u}_1. \tag{34}$$

It is known that $\partial\Omega_0^u \cup \partial\Omega_0^t = \partial\Omega_0$ and $\partial\Omega_0^u \cap \partial\Omega_0^t = \varnothing$ as well as $\mathsf{S}_0 \subset \partial\Omega_0$. However, the relation between S_0 and $\partial\Omega_0^t$ (or $\partial\Omega_0^u$) is not given before. To simplify the discussion, we regard S_0 as a subset of $\partial\Omega_0^t$, that is, $\mathsf{S}_0 \subset \partial\Omega_0^t$. Thus, the last integral in (34) can be reformulated as

$$-\int_{\partial\Omega_0^t} \boldsymbol{t}_0 \cdot \boldsymbol{u}_1 = -\int_{\partial\Omega_0^t\backslash\mathsf{S}_0} \boldsymbol{t}_0 \cdot \boldsymbol{u}_1 - \int_{\mathsf{S}_0} \boldsymbol{t}_0 \cdot \boldsymbol{u}_1. \tag{35}$$

Also, with $\boldsymbol{u}_1 = \mathbf{0}$ on $\partial\Omega_0^u$ in (25), the second integral in (34) reduces to

$$\int_{\partial\Omega_0\backslash\mathsf{S}_0} \boldsymbol{u}_1 \cdot \boldsymbol{S}\boldsymbol{n} = \int_{\partial\Omega_0^t\backslash\mathsf{S}_0} \boldsymbol{u}_1 \cdot \boldsymbol{S}\boldsymbol{n}. \tag{36}$$

Using (35) and (36), the first variation finally becomes

$$\delta\mathscr{F}[\boldsymbol{u}] = -\int_{\Omega_0} \boldsymbol{u}_1 \cdot \mathrm{div}\boldsymbol{S} + \int_{\partial\Omega_0^t\backslash\mathsf{S}_0} \boldsymbol{u}_1 \cdot (\boldsymbol{S}\boldsymbol{n} - \boldsymbol{t}_0) + \int_{\mathsf{S}_0} \boldsymbol{u}_1 \cdot (\boldsymbol{S}\boldsymbol{n} - \mathrm{div}_{\mathrm{s}}\mathbb{S} - \boldsymbol{t}_0)$$
$$+ \int_{\partial\mathsf{S}_0} \boldsymbol{u}_1 \cdot \mathbb{S}\boldsymbol{v}. \tag{37}$$

Since the variation $\boldsymbol{u}_1$ in (37) is arbitrary, the vanishing of the first variation $\delta\mathscr{F}[\boldsymbol{u}] = 0$ and the fundamental lemma of calculus of variations (Courant and Hilbert 1953) leads us to the following set of governing equations

$$\left.\begin{aligned} \mathrm{div}\boldsymbol{S} &= \mathbf{0} && \text{in } \Omega_0, \\ \boldsymbol{S}\boldsymbol{n} &= \boldsymbol{t}_0 && \text{on } \partial\Omega_0^t \setminus \mathsf{S}_0, \\ \boldsymbol{S}\boldsymbol{n} - \mathrm{div}_{\mathrm{s}}\mathbb{S} = \boldsymbol{t}_0, \quad \mathbb{S}\boldsymbol{n} &= \mathbf{0} && \text{on } \mathsf{S}_0, \\ \mathbb{S}\boldsymbol{v} &= \mathbf{0} && \text{on } \partial\mathsf{S}_0. \end{aligned}\right\} \tag{38}$$

Here we rewrite the equation $\mathbb{S}\boldsymbol{n} = \mathbf{0}$ on S_0 (see the statement above (30)) in (38). Equation (38), together with $(21)_1$ and (29), forms a well-defined boundary value problem. For the readers convenience, we reiterate the notations here: $\boldsymbol{S}$ denotes the first Piola-Kirchhoff stress, $\mathbb{S}$ the first surface Piola-Kirchhoff stress, $\boldsymbol{n}$ the outward unit normal to the surface, $\boldsymbol{v}$ the outward unit normal to the boundary curve, and $\boldsymbol{t}_0$ the applied dead load.

3.3 Constitutive Equations and Elastic Stress Tensors

In (29), we have defined the first Piola-Kirchhoff bulk stress tensor $\boldsymbol{S}$ and the first Piola-Kirchhoff surface stress tensor $\mathbb{S}$ through the partial derivative with respect to the displacement gradient $\nabla \boldsymbol{u}$. By the chain rule, these two first Piola-Kirchhoff stresses can also be defined as

$$\boldsymbol{S} = \frac{\partial \bar{\Psi}(\boldsymbol{F})}{\partial \boldsymbol{F}} \quad \text{and} \quad \mathbb{S} = \frac{\partial \bar{\Gamma}_s(\boldsymbol{F})}{\partial \boldsymbol{F}}, \tag{39}$$

where $\boldsymbol{F} = \nabla(\boldsymbol{x} + \boldsymbol{u}) = \mathbf{I} + \nabla \boldsymbol{u}$ and

$$\bar{\Psi}(\boldsymbol{F}) = \Psi(\nabla \boldsymbol{u})\big|_{\nabla \boldsymbol{u} = \boldsymbol{F} - \mathbf{I}} \quad \text{and} \quad \bar{\Gamma}_s(\boldsymbol{F}) = \Gamma_s(\nabla \boldsymbol{u})\big|_{\nabla \boldsymbol{u} = \boldsymbol{F} - \mathbf{I}}. \tag{40}$$

By the *frame indifference* in the strain energy functions (Gurtin et al. 2010) and the polar decomposition $\boldsymbol{F} = \boldsymbol{R}\boldsymbol{U}$, $\boldsymbol{R} \in \text{Orth}^+ = \{\text{all rotations}\}$, and $\boldsymbol{U}$ is the right stretch tensor, we have

$$\begin{aligned} \bar{\Psi}(\boldsymbol{F}) &= \bar{\Psi}(\boldsymbol{R}^T\boldsymbol{F}) = \bar{\Psi}(\boldsymbol{R}^T\boldsymbol{R}\boldsymbol{U}) = \bar{\Psi}(\boldsymbol{U}), \\ \bar{\Gamma}_s(\boldsymbol{F}) &= \bar{\Gamma}_s(\boldsymbol{R}^T\boldsymbol{F}) = \bar{\Gamma}_s(\boldsymbol{R}^T\boldsymbol{R}\boldsymbol{U}) = \bar{\Gamma}_s(\boldsymbol{U}). \end{aligned} \tag{41}$$

Using the relation $\boldsymbol{U} = \sqrt{\boldsymbol{U}^T\boldsymbol{U}} = \sqrt{\boldsymbol{U}^T\boldsymbol{R}^T\boldsymbol{R}\boldsymbol{U}} = \sqrt{\boldsymbol{F}^T\boldsymbol{F}} = \sqrt{\boldsymbol{C}}$, we can introduce strain energy functions $\hat{\Psi}(\boldsymbol{C})$ and $\hat{\Gamma}_s(\boldsymbol{C})$, such that

$$\begin{aligned} \hat{\Psi}(\boldsymbol{C}) &= \bar{\Psi}(\sqrt{\boldsymbol{C}}) = \bar{\Psi}(\boldsymbol{U}) = \bar{\Psi}(\boldsymbol{F}), \\ \hat{\Gamma}_s(\boldsymbol{C}) &= \bar{\Gamma}_s(\sqrt{\boldsymbol{C}}) = \bar{\Gamma}_s(\boldsymbol{U}) = \bar{\Gamma}_s(\boldsymbol{F}). \end{aligned} \tag{42}$$

Similarly, by the definition of the Green strain tensor $\boldsymbol{E} = \frac{1}{2}(\boldsymbol{C} - \mathbf{I})$, we can express strain energy functions $\Psi^*(\boldsymbol{E})$ and $\Gamma_s{}^*(\boldsymbol{E})$, such that

$$\begin{aligned} \Psi^*(\boldsymbol{E}) &= \hat{\Psi}(\boldsymbol{C}) = \bar{\Psi}(\boldsymbol{U}) = \bar{\Psi}(\boldsymbol{F}), \\ \Gamma_s{}^*(\boldsymbol{E}) &= \hat{\Gamma}_s(\boldsymbol{C}) = \bar{\Gamma}_s(\boldsymbol{U}) = \bar{\Gamma}_s(\boldsymbol{F}). \end{aligned} \tag{43}$$

In contrast to the two first Piola-Kirchhoff stresses (39), by (43) and $\boldsymbol{E} = \frac{1}{2}(\boldsymbol{C} - \mathbf{I})$, the two second Piola-Kirchhoff stresses are defined as

$$\boldsymbol{T} = 2\frac{\partial \hat{\Psi}(\boldsymbol{C})}{\partial \boldsymbol{C}} = \frac{\partial \Psi^*(\boldsymbol{E})}{\partial \boldsymbol{E}} \quad \text{and} \quad \mathbb{T} = 2\frac{\partial \hat{\Gamma}_s(\boldsymbol{C})}{\partial \boldsymbol{C}} = \frac{\partial \Gamma_s{}^*(\boldsymbol{E})}{\partial \boldsymbol{E}}. \tag{44}$$

By (39), (43), (44), and the chain rule, the relations between the first P-K stresses $(\boldsymbol{S}, \mathbb{S})$ and the second P-K stresses $(\boldsymbol{T}, \mathbb{T})$ are (P-K is the abbreviation for the Piola-Kirchhoff stress.)

$$\boldsymbol{S} = \boldsymbol{F}\boldsymbol{T} \quad \text{and} \quad \mathbb{S} = \boldsymbol{F}\mathbb{T}. \tag{45}$$

The relations between the first P-K stresses $(\boldsymbol{S}, \mathbb{S})$ and the Cauchy stresses $(\boldsymbol{\sigma}, \sigma^s)$ are

$$\boldsymbol{S} = (\det \boldsymbol{F})\boldsymbol{\sigma} \boldsymbol{F}^{-T} \quad \text{and} \quad \mathbb{S} = (\det \boldsymbol{F})\sigma^s \boldsymbol{F}^{-T}. \tag{46}$$

3.4 Linearized Bulk and Surface Stresses and Constitutive Choice

A peculiarity of considering surface effects is the perceived presence of residual stresses – the surface tension-like quantity in solids is precisely a residual stress state. This becomes evident if we linearize the energy functions around a reference configuration which is not stress-free.

For small deformation, the Cauchy-Green tensor $\boldsymbol{C} = \boldsymbol{F}^T\boldsymbol{F} = (\mathbf{I} + \nabla \boldsymbol{u})^T(\mathbf{I} + \nabla \boldsymbol{u})$ can be reduced to $\boldsymbol{C} = \mathbf{I} + \nabla \boldsymbol{u} + \nabla \boldsymbol{u}^T$, $|\nabla \boldsymbol{u}| \ll 1$, by dropping the higher-order terms $o(|\nabla \boldsymbol{u}|)$. Thus, the strain tensor $\boldsymbol{E} = \frac{1}{2}(\boldsymbol{C} - \mathbf{I})$ in (44) may be approximated by the infinitesimal strain:

$$\boldsymbol{E} = \frac{1}{2}(\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^T), \tag{47}$$

Using Taylor series, $(44)_1$ gives

$$\boldsymbol{T} = \left.\frac{\partial \Psi^*(\boldsymbol{E})}{\partial \boldsymbol{E}}\right|_{\boldsymbol{E}=\mathbf{0}} + \left.\frac{\partial^2 \Psi^*(\boldsymbol{E})}{\partial \boldsymbol{E}^2}\right|_{\boldsymbol{E}=\mathbf{0}} \cdot \boldsymbol{E} + o(|\boldsymbol{E}|), \tag{48}$$

where $o(|\boldsymbol{E}|)$ denotes the higher-order terms.

Since the reference configuration is assumed to be stress-free for the bulk portion of the material, it follows that $\frac{\partial \Psi^*(\boldsymbol{E})}{\partial \boldsymbol{E}}\big|_{\boldsymbol{E}=\mathbf{0}} = \mathbf{0}$ and the elasticity tensor is

$$\mathbb{C} := \left.\frac{\partial^2 \Psi^*(\boldsymbol{E})}{\partial \boldsymbol{E}^2}\right|_{\boldsymbol{E}=\mathbf{0}}. \tag{49}$$

Thus, as usual, the linearized small-deformation stress-strain relation of bulk portion of the material is

$$\boldsymbol{T} = \mathbb{C}\boldsymbol{E}. \tag{50}$$

Consider the first P-K stresses $\boldsymbol{S} = \boldsymbol{F}\boldsymbol{T}$ in $(45)_1$ and the Cauchy stresses $\boldsymbol{\sigma} = (\det \boldsymbol{F})^{-1}\boldsymbol{S}\boldsymbol{F}^T$ in $(46)_1$ of bulk materials at small deformations. By the relation (50) and the infinitesimal strain (47), it is easy to show that to a first order

$$\boldsymbol{S} = \boldsymbol{T} = \boldsymbol{\sigma}. \tag{51}$$

The equivalence of the first P-K, the second P-K, and the Cauchy stresses in (51), however, does not hold for surface stresses due to the existence of the residual stress. This is rather important to note. In linearized elasticity (without residual stresses), it is usual to ignore the distinction between the various stress measures. For surface elasticity, even in the linearized case, we must take cognizance of the different interpretations of the various stress measures. The first P-K stress measure is the most useful since it represents the force per unit *referential* area and is likely to be the quantity controlled in traction-controlled experiments (as opposed to Cauchy traction).

From previous works (see Eq. (40) in the work of Gurtin et al. 1998 and Eq. (7.9) in the work of Gurtin and Murdoch 1975b), we can show that the second P-K surface stress $\mathbb{T}$ in $(44)_2$ and the first P-K surface stress $\mathbb{S}$ in $(45)_2$ can be recast as

$$\mathbb{T} = \frac{\partial \Gamma_s{}^*(\boldsymbol{E}_s)}{\partial \boldsymbol{E}_s}, \quad \mathbb{S} = (\mathbb{I} + \mathbb{P}\nabla_s \boldsymbol{u})\mathbb{T}, \tag{52}$$

where $\boldsymbol{E}_s$, in contrast to the infinitesimal strain (47), is the infinitesimal surface strain

$$\boldsymbol{E}_s = \mathbb{P}\boldsymbol{E}\mathbb{P} = \frac{1}{2}[\mathbb{P}\nabla_s \boldsymbol{u} + (\mathbb{P}\nabla_s \boldsymbol{u})^T]. \tag{53}$$

Using the Taylor series for $(52)_1$, for small deformation, we have

$$\mathbb{T}(\boldsymbol{E}_s) = \left.\frac{\partial \Gamma_s{}^*(\boldsymbol{E}_s)}{\partial \boldsymbol{E}_s}\right|_{\boldsymbol{E}_s=\boldsymbol{0}} + \left.\frac{\partial^2 \Gamma_s{}^*(\boldsymbol{E}_s)}{\partial \boldsymbol{E}_s^2}\right|_{\boldsymbol{E}_s=\boldsymbol{0}} \cdot \boldsymbol{E}_s + o(|\boldsymbol{E}_s|). \tag{54}$$

With an appropriate choice of an elastic constitutive law (i.e., specification of $\Gamma_s{}^*$ and Ψ^*), we now have all the governing equations and can solve the pertinent boundary value problems of physical interest. Analytical solutions are rather hard to come by for the anisotropic case, and by far, most problems solved in the literature have been restricted to isotropic continua.

For isotropic linear elastic materials incorporating the residual surface stress, we have (Gurtin and Murdoch 1975a,b)

$$\tau_0\mathbb{I} := \left.\frac{\partial \Gamma_s{}^*(\boldsymbol{E}_s)}{\partial \boldsymbol{E}_s}\right|_{\boldsymbol{E}_s=\boldsymbol{0}}, \quad \mathbb{C}_s := \left.\frac{\partial^2 \Gamma_s{}^*(\boldsymbol{E}_s)}{\partial \boldsymbol{E}_s^2}\right|_{\boldsymbol{E}_s=\boldsymbol{0}}, \tag{55}$$

where $\tau_0\mathbb{I}$ is the residual stress and the surface elasticity tensor $\mathbb{C}_s$ gives

$$\mathbb{C}_s[\boldsymbol{E}_s] = \lambda_0 \mathrm{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0 \boldsymbol{E}_s \tag{56}$$

with surface elastic moduli λ_0 and μ_0.

By (55) and (56), a general linearized constitutive law for isotropic linear materials in terms of the second P-K surface stress $\mathbb{T}$ in (54) can be written as

$$\mathbb{T}(\boldsymbol{E}_s) = \tau_0\mathbb{I} + \lambda_0\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0\boldsymbol{E}_s. \tag{57}$$

For solving actual boundary value problems (including the ones we present later in this chapter), we will need the first P-K stress tensor. To do so, we take cognizance of the relation between the two P-K stresses. By $(52)_2$ and (57), the first P-K surface stress $\mathbb{S}$ becomes

$$\mathbb{S}(\nabla_s\boldsymbol{u}) = \tau_0\mathbb{I} + \lambda_0\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0\boldsymbol{E}_s + \tau_0\nabla_s\boldsymbol{u}, \tag{58}$$

where the higher-order terms $|(\nabla_s\boldsymbol{u})\text{tr}(\boldsymbol{E}_s)|$ and $|(\nabla_s\boldsymbol{u})\boldsymbol{E}_s|$ are omitted. Here and henceforth, the difference between $\nabla_s\boldsymbol{u}$ and $\mathbb{P}\nabla_s\boldsymbol{u}$ is not specified for simplicity.

By $(46)_2$ and a similar argument as (52), the Cauchy surface stress σ^s and the first P-K stress $\mathbb{S}$ in (58) have the relation

$$\sigma^s = [\det(\mathbb{I} + \nabla_s\boldsymbol{u})]^{-1}\mathbb{S}(\mathbb{I} + \nabla_s\boldsymbol{u})^T. \tag{59}$$

For small deformation, $[\det(\mathbb{I} + \nabla_s\boldsymbol{u})]^{-1} = 1 - \text{tr}(\nabla_s\boldsymbol{u}) = 1 - \text{tr}(\boldsymbol{E}_s)$; thus, σ^s in (59) can be recast as

$$\begin{aligned}
\sigma^s &= [1 - \text{tr}(\boldsymbol{E}_s)][\tau_0\mathbb{I} + \lambda_0\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0\boldsymbol{E}_s + \tau_0\nabla_s\boldsymbol{u}](\mathbb{I} + \nabla_s\boldsymbol{u}^T) \\
&= [\tau_0\mathbb{I} + \lambda_0\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0\boldsymbol{E}_s + \tau_0\nabla_s\boldsymbol{u} - \tau_0\text{tr}(\boldsymbol{E}_s)\mathbb{I}](\mathbb{I} + \nabla_s\boldsymbol{u}^T) \\
&= \tau_0\mathbb{I} + \lambda_0\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0\boldsymbol{E}_s + \tau_0\nabla_s\boldsymbol{u} - \tau_0\text{tr}(\boldsymbol{E}_s)\mathbb{I} + \tau_0\nabla_s\boldsymbol{u}^T \\
&= \tau_0\mathbb{I} + (\lambda_0 - \tau_0)\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0\boldsymbol{E}_s + \tau_0(\nabla_s\boldsymbol{u} + \nabla_s\boldsymbol{u}^T)
\end{aligned} \tag{60}$$

by dropping the higher-order terms related to the product between these terms $\text{tr}(\boldsymbol{E}_s)$, $\boldsymbol{E}_s$, $\nabla_s\boldsymbol{u}$, and $\nabla_s\boldsymbol{u}^T$.

Using the definition of surface strain in (53) and (60) finally becomes

$$\sigma^s = \tau_0\mathbb{I} + (\lambda_0 - \tau_0)\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2(\mu_0 + \tau_0)\boldsymbol{E}_s = \tau_0\mathbb{I} + \lambda_s\text{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_s\boldsymbol{E}_s. \tag{61}$$

Here

$$\lambda_s = \lambda_0 - \tau_0 \quad \text{and} \quad \mu_s = \mu_0 + \tau_0 \tag{62}$$

are the Lamé constants of the surface.

In contrast to the equivalence (51), $\mathbb{S}$ in (58), $\mathbb{T}$ in (57), and σ^s in (61) are not equivalent if the residual stress is nonzero $\tau_0 \neq 0$, namely:

$$\mathbb{S} \neq \mathbb{T} \neq \sigma^s \qquad \text{for} \quad \tau_0 \neq 0. \tag{63}$$

In the literature, sometimes (including the work by the corresponding author), the distinction between the various forms of the surface stress has often been blurred.

For the most part, this does not lead to qualitative differences, but care must be exercised when solving surface elasticity problem to ascertain which precise stress measure and constitutive parameters are being deployed. As self-evident, there is a distinction between (λ_s, μ_s) and (λ_0, μ_0).

If we set the surface Lamé constants (λ_s, μ_s) to zero in (62), we obtain $\lambda_0 = \tau_0$ and $\mu_0 = -\tau_0$, and then the result in (58) is what is often called the *surface tension* (in the reference configuration) (Gurtin and Murdoch 1975a)

$$\mathbb{S} = \tau_0[1 + \mathrm{tr}(\boldsymbol{E}_s)]\mathbb{I} - 2\tau_0 \boldsymbol{E}_s + \tau_0 \nabla_s \boldsymbol{u}. \tag{64}$$

This is to be contrasted with the expression in the current configuration where the Cauchy surface tension from (61) by setting (λ_s, μ_s) to zero will be in the form of isotropic "pressure"

$$\sigma^s = \tau_0 \mathbb{I}. \tag{65}$$

4 Illustrative Examples

In this section we choose three illustrative examples that highlight both the use of the surface elasticity theory as well as provide insights into the physical consequences of surface energy at the nanoscale. These examples are inspired from Altenbach et al. (2013), Murdoch (2005), and Sharma et al. (2003) although, to be consistent with our own style (presented in the preceding sections), we have modified them slightly. Germane to the study of analytical study of nanostructures, we also note parallel developments in the literature on the so-called surface Cauchy-Born rule and numerical methods (Park et al. 2006).

4.1 Young's Modulus of a Nano-rod Considering Surface Effects

This example addresses how the elastic modulus of an isotropic nano-rod alters due to the influence of surface energy. This particular problem is inspired from the work by Altenbach et al. (2013) although there are some minor differences in our solution. Consider a circular cylinder (rod) with radius R_0 whose axis coincides with the $\boldsymbol{e}_z$ direction. To interrogate the elastic response, we assume that the rod is under uniaxial tension and the coordinate system used for this problem is cylindrical coordinate with basis $(\boldsymbol{e}_r, \boldsymbol{e}_\theta, \boldsymbol{e}_z)$ as shown in Fig. 4.

For isotropic elastic materials without surface effects, the uniaxial tension along the axial direction admits a homogeneous deformation. To simplify the discussion, we assume the deformation here incorporating the surface effect is also homogeneous, namely:

$$\boldsymbol{u} = Ar\boldsymbol{e}_r + Bz\boldsymbol{e}_z, \tag{66}$$

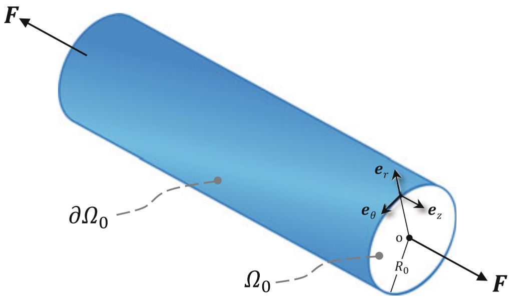

Fig. 4 A schematic of a nano-rod under a uniaxial tension. Surface effects are only considered on the radial surface $\partial\Omega_0$, and edge effects are ignored. Force $\boldsymbol{F}$ is exerted in the $\boldsymbol{e}_z$ direction

where A and B are constants. The assumed displacement (66) can be used for either small or finite deformation.

For the radial surface with outward unit normal $\boldsymbol{n} = \boldsymbol{e}_r$, the projection tensor is $\mathbb{P} = \boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_z \otimes \boldsymbol{e}_z$. By (66), the displacement gradient $\nabla \boldsymbol{u}$, the strain tensor $\boldsymbol{E} = \frac{1}{2}(\nabla\boldsymbol{u}+\nabla\boldsymbol{u}^T)$ for small deformation, the surface displacement gradient $\nabla_s \boldsymbol{u} = (\nabla\boldsymbol{u})\mathbb{P}$, and the surface strain tensor $\boldsymbol{E}_s = \mathbb{P}\boldsymbol{E}\mathbb{P}$ for small deformation become

$$\begin{aligned} \nabla \boldsymbol{u} &= \boldsymbol{E} = A(\boldsymbol{e}_r \otimes \boldsymbol{e}_r + \boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta) + B\boldsymbol{e}_z \otimes \boldsymbol{e}_z, \\ \nabla_s \boldsymbol{u} &= \boldsymbol{E}_s = A\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + B\boldsymbol{e}_z \otimes \boldsymbol{e}_z. \end{aligned} \tag{67}$$

By the constitutive law of isotropic linear materials and $(67)_1$, we have

$$\boldsymbol{S} = \lambda \mathrm{tr}(\boldsymbol{E})\mathbf{I} + 2\mu\boldsymbol{E} := \begin{bmatrix} S_{rr} & 0 & 0 \\ 0 & S_{\theta\theta} & 0 \\ 0 & 0 & S_{zz} \end{bmatrix}, \tag{68a}$$

where λ and μ are Lamé constants of bulk materials and

$$S_{rr} = S_{\theta\theta} = \lambda(2A + B) + 2\mu A, \quad S_{zz} = \lambda(2A + B) + 2\mu B. \tag{68b}$$

In addition, by the constitutive law (58) and by setting $\tau_0 = 0$, together with $(67)_2$, we have

$$\mathbb{S} = \lambda_0 \mathrm{tr}(\boldsymbol{E}_s)\mathbb{I} + 2\mu_0 \boldsymbol{E}_s := \begin{bmatrix} \mathbb{S}_{\theta\theta} & 0 \\ 0 & \mathbb{S}_{zz} \end{bmatrix}, \tag{69a}$$

where

$$\mathbb{S}_{\theta\theta} = \lambda_0(A + B) + 2\mu_0 A, \quad \mathbb{S}_{zz} = \lambda_0(A + B) + 2\mu_0 B. \tag{69b}$$

Using the Young-Laplace equation $(38)_3$, without external load $\boldsymbol{t}_0 = \boldsymbol{0}$ on the radial surface ($r = R_0$) with unit normal $\boldsymbol{e}_r$, we have the equality $\boldsymbol{S}\boldsymbol{e}_r = \mathrm{div}_s\mathbb{S}$. By (68a), the identity (16), and $\mathbb{S}^T\boldsymbol{e}_r = \boldsymbol{0}$ in $(38)_3$, we can obtain

$$S_{rr} = \boldsymbol{e}_r \cdot \boldsymbol{S}\boldsymbol{e}_r = \boldsymbol{e}_r \cdot \mathrm{div}_s \mathbb{S} = -\mathbb{S} \cdot \nabla_s \boldsymbol{e}_r. \tag{70}$$

Since $\nabla_s \boldsymbol{e}_r = (\nabla \boldsymbol{e}_r)\mathbb{P} = \left(\frac{1}{r}\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta\right)(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_z \otimes \boldsymbol{e}_z) = \frac{1}{r}\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta$, (70) implies

$$S_{rr} = -\frac{\mathbb{S}_{\theta\theta}}{R_0}. \tag{71}$$

By (68b), (69b), and (71) be written as

$$\lambda(2A + B) + 2\mu A = -\frac{\lambda_0(A + B) + 2\mu_0 A}{R_0}, \tag{72}$$

which gives the ratio

$$\frac{A}{B} = -\frac{\lambda + \lambda_0/R_0}{2\lambda + 2\mu + (\lambda_0 + 2\mu_0)/R_0}. \tag{73}$$

By (67) and (68b), the Young modulus for uniaxial tension is

$$E^{\mathrm{rod}} = \frac{S_{zz}}{E_{zz}} = \frac{\lambda(2A + B) + 2\mu B}{B} = \lambda\left(1 + 2\frac{A}{B}\right) + 2\mu, \tag{74}$$

where the ratio A/B is given by (73). By the equilibrium of the rod in the axial direction (Altenbach et al. 2013), the effective Young's modulus can be defined as $E^{\mathrm{eff}} = (S_{zz} + \frac{2}{R_0}\mathbb{S}_{zz})/E_{zz} = \lambda\left(1 + 2\frac{A}{B}\right) + 2\mu + \frac{2}{R_0}[\lambda_0(1 + \frac{A}{B}) + 2\mu_0]$.

This simple example makes clear that the effective or apparent elastic response of nanostructures becomes size-dependent as a result of surface energy effects and that with smaller R_0, the effective elastic modulus may become significantly different than its bulk value. We remark that if surface effects are ignored, that is, $\lambda_0 = \mu_0 = 0$ and the ratio $A/B = -\lambda/(2\lambda + 2\mu)$ in (73), then the Young modulus in (74) becomes $E^{\mathrm{rod}} = \mu(3\lambda + 2\mu)/(\lambda + \mu)$–which is essentially the relation between bulk Young's modulus and the Lamé constants.

4.2 Influence of Surface Effects on the Thermoelastic State of a Ball

We consider the equilibrium state of a spherical ball (radius R_0) in vacuum undergoing thermal expansion – following Murdoch (2005). Only traction boundary conditions need to be considered here; hence, $(21)_1$ can be omitted. Moreover, $(38)_2$ and $(38)_4$ are also omitted since the entire surface of the sphere is considered, that is, $\mathsf{S}_0 = \partial\Omega_0 = \partial\Omega_0^t$.

We now proceed to solve the reduced boundary value problem that consists of $(38)_1$, $(38)_3$, and (29). As before, we assume the ball material to be isotropic and that the ball is in its natural, stress-free state in the reference configuration. Hence, we assume constitutive equations for the bulk and surface as follows:

$$\boldsymbol{S} = \lambda_b \mathrm{tr}(\boldsymbol{E})\mathbf{I} + 2\mu_b \boldsymbol{E} - \alpha \Delta T \mathbf{I}, \tag{75}$$

$$\mathbb{S} = \tau_0 \mathbb{I} + (\lambda_s + \tau_0)\mathrm{tr}(\boldsymbol{E}_s)\mathbb{I} + 2(\mu_s - \tau_0)\boldsymbol{E}_s + \tau_0(\nabla_s \boldsymbol{u}) - \alpha_0 \Delta T \mathbb{I}, \tag{76}$$

where $\boldsymbol{S}$ is the first P-K stress field in the reference configuration, λ_b and μ_b are Lamé constants for the ball material, ΔT is the temperature difference, α is the coefficient of thermal expansion, and α_0 is the thermal expansion coefficient of the surface.

In this example we use spherical coordinates with basis $(\boldsymbol{e}_r, \boldsymbol{e}_\theta, \boldsymbol{e}_\phi)$ with the origin at the center of the ball. For the surface with outward unit normal $\boldsymbol{n} = \boldsymbol{e}_r$, the projection tensor is $\mathbb{P} = \boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi$. Given that the problem is spherically symmetric, the form of the displacement field can be assumed to be

$$\boldsymbol{u} = u_r(r)\boldsymbol{e}_r. \tag{77}$$

Then the displacement gradient, the strain tensor, the surface gradient of the displacement, and the surface strain in (75) and (76) can be written, similar to (67), as

$$\begin{aligned} \nabla \boldsymbol{u} = \boldsymbol{E} &= \frac{\partial u_r}{\partial r}\boldsymbol{e}_r \otimes \boldsymbol{e}_r + \frac{u_r}{r}(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi), \\ \nabla_s \boldsymbol{u} = \boldsymbol{E}_s &= \frac{u_r}{r}(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi). \end{aligned} \tag{78}$$

From (78), (75), and (76), we have

$$\begin{aligned} \boldsymbol{S} &= \lambda_b \left(\frac{\partial u_r}{\partial r} + \frac{2u_r}{r}\right)\mathbf{I} + 2\mu_b\left(\frac{\partial u_r}{\partial r}\boldsymbol{e}_r \otimes \boldsymbol{e}_r + \frac{u_r}{r}(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi)\right) - \alpha \Delta T \mathbf{I}, \\ \mathbb{S} &= \tau_0 \mathbb{I} + \lambda_s \left(\frac{2u_r}{r}\right)\mathbb{I} + (2\mu_s + \tau_0)\left(\frac{u_r}{r}\right)(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi) - \alpha_0 \Delta T \mathbb{I}. \end{aligned} \tag{79}$$

Substituting $(79)_1$ into the equilibrium equation $(38)_1$, together with the divergence of a tensor in spherical coordinates, we obtain

$$r^2 \frac{\partial^2 u_r}{\partial r^2} + 2r\frac{\partial u_r}{\partial r} - 2u_r = 0. \tag{80}$$

The general solution of (80) is $u_r(r) = Ar + Br^{-2}$, where A and B are constants to be determined by the boundary conditions. The displacement at the origin must vanish for the field to be bounded, i.e., and consequently $B = 0$ and then

$$u_r(r) = Ar. \tag{81}$$

Thus, the stresses (79) are reduced to

$$\boldsymbol{S} = [A(3\lambda_b + 2\mu_b) - \alpha \Delta T]\mathbf{I}, \quad \mathbb{S} = [\tau_0 + A(2\lambda_s + 2\mu_s + \tau_0) - \alpha_0 \Delta T]\mathbb{I}. \tag{82}$$

We must now deploy the boundary condition in $(38)_3$. Since the ball surface is traction-free, that is, $\boldsymbol{t}_0 = \mathbf{0}$, $(38)_3$ can be reduced to $\boldsymbol{S}\boldsymbol{e}_r = \mathrm{div_s}\mathbb{S}$. By (82), we can further simplify this to

$$S_{rr} = \boldsymbol{e}_r \cdot \boldsymbol{S}\boldsymbol{e}_r = \boldsymbol{e}_r \cdot \mathrm{div_s}\mathbb{S} \quad \text{at } r = R_0. \tag{83}$$

By using the identity (16), $(82)_2$, $(38)_3$, and (14), we finally obtain

$$S_{rr} = \boldsymbol{e}_r \cdot \mathrm{div_s}\mathbb{S} = -\mathbb{S} \cdot \nabla_s \boldsymbol{e}_r = -\mathbb{S} \cdot \left\{ \frac{1}{r}(\boldsymbol{e}_\theta \otimes \boldsymbol{e}_\theta + \boldsymbol{e}_\phi \otimes \boldsymbol{e}_\phi) \right\} = -\frac{2\mathbb{S}_{\theta\theta}}{R_0}. \tag{84}$$

By (82) and (84), we have

$$3\lambda_b A + 2\mu_b A - \alpha \Delta T = -\frac{2}{R_0}\{\tau_0(1 + A) + 2A(\lambda_s + \mu_s) - \alpha_0 \Delta T\}. \tag{85}$$

By defining the *surface modulus* K_s as

$$K_s = 2(\lambda_s + \mu_s), \tag{86}$$

(85) yields the solution of A in the displacement (81), namely:

$$A = \frac{-2\tau_0/R_0}{(3\lambda_b + 2\mu_b + 2K_s/R_0 + 2\tau_0/R_0)} + \frac{(\alpha + 2\alpha_0/R_0)\Delta T}{(3\lambda_b + 2\mu_b + 2K_s/R_0 + 2\tau_0/R_0)}. \tag{87}$$

This example, as can be noted from (87), nicely shows how a positive surface residual stress τ_0 may hinder the thermal expansion in a size-dependent manner.

4.3 Effect of Residual Stress of Surfaces on Elastic State of Spherical Inclusion

The solution of an embedded inclusion in another material is a canonical problem in classical solid mechanics (known as Eshelby's inclusion problem) and has been applied to situations as diverse as phase transformation to effective properties of composites. Accordingly, in this section, we consider the problem of spherical inclusion with radius R_0 but incorporating surface effects. The solution here is a slight modification of the work by Sharma et al. (2003). We use spherical coordinates with basis $(\boldsymbol{e}_r, \boldsymbol{e}_\theta, \boldsymbol{e}_\phi)$ with the origin at the center of the sphere in this problem. We assume that a far field stress is exerted on the matrix as follows:

$$S_{rr}\Big|_{r\to\infty} = S^{\infty}. \tag{88}$$

To make analytical progress, we further stipulate that the inclusion, the matrix, and the interface are isotropic and that the inclusion is in its natural state in the reference configuration. The constitutive equations for the bulk are as follows:

$$\boldsymbol{S} = \lambda_\nu \mathrm{tr}(\boldsymbol{E})\mathbf{I} + 2\mu_\nu \boldsymbol{E}, \tag{89}$$

where $\boldsymbol{S}$ is the first Piola-Kirchhoff stress and λ_ν and μ_ν are Lamé constants of the material corresponding to either the inclusion(I) or the matrix(M). For the surface we use the constitutive equation defined in (58), i.e.:

$$\mathbb{S} = \tau_0\mathbb{I} + (\lambda_s + \tau_0)\mathrm{tr}(\boldsymbol{E}_s)\mathbb{I} + 2(\mu_s - \tau_0)\boldsymbol{E}_s + \tau_0(\nabla_s \boldsymbol{u}). \tag{90}$$

Like the previous example, this problem also has spherical symmetry and accordingly the displacement vector is of the form

$$\boldsymbol{u} = u_r(r)\boldsymbol{e}_r. \tag{91}$$

Therefore, the displacement gradient and the strain are similar to (78). Hence, the stress in the bulk and on the surface stress can be expressed as

$$\begin{aligned}
\boldsymbol{S} &= \lambda_b\left(\frac{\partial u_r}{\partial r} + \frac{2u_r}{r}\right)\mathbf{I} + 2\mu_b\left(\frac{\partial u_r}{\partial r}\boldsymbol{e}_r\otimes\boldsymbol{e}_r + \frac{u_r}{r}(\boldsymbol{e}_\theta\otimes\boldsymbol{e}_\theta + \boldsymbol{e}_\phi\otimes\boldsymbol{e}_\phi)\right),\\
\mathbb{S} &= \tau_0\mathbb{I} + \lambda_s\left(\frac{2u_r}{r}\right)\mathbb{I} + (2\mu_s + \tau_0)\left(\frac{u_r}{r}\right)(\boldsymbol{e}_\theta\otimes\boldsymbol{e}_\theta + \boldsymbol{e}_\phi\otimes\boldsymbol{e}_\phi).
\end{aligned} \tag{92}$$

We have used (38) in spherical coordinates. The boundary value problem that consists of $(38)_1$–$(38)_3$ becomes

$$\left.\begin{aligned}
& r^2\frac{\partial^2 u_r}{\partial r^2} + 2r\frac{\partial u_r}{\partial r} - 2u_r = 0 && r \leqslant R_0,\\
& r^2\frac{\partial^2 u_r}{\partial r^2} + 2r\frac{\partial u_r}{\partial r} - 2u_r = 0 && r > R_0,\\
& [\![S_{rr}]\!] = \frac{2\mathbb{S}_{\theta\theta}}{r} && r = R_0,\\
& S_{rr}\Big|_{r\to\infty} = S^{\infty} && r \to \infty.
\end{aligned}\right\} \tag{93}$$

The "$[\![\cdot]\!]$" denotes the jump across the interface. Similar to (80), the general solutions of $(93)_1$ and $(93)_2$ are

$$u_r(r) = \begin{cases} A\,r + B\,r^{-2} & r \leqslant R_0,\\ C\,r + D\,r^{-2} & r > R_0,\end{cases} \tag{94}$$

where A, B, C, and D are constant. Since $u_r(0) = 0$, $B = 0$. Substituting (94)$_2$ into (92)$_1$, the far field (93)$_4$ gives $C = S^\infty/(3K_M)$, where $K_M = \lambda_M + 2\mu_M/3$. Using the continuity of the displacement at the interface, that is, $[\![u_r]\!] = 0$ at $r = R_0$, and the Young-Laplace equation (93)$_3$, we obtain two algebraic equations of A and D. The routine calculation is not shown here and we just list the final results. Thus, the displacement (94) is obtained as

$$u(r) = \begin{cases} \alpha r & r \leqslant R_0, \\ E^\infty r + (\alpha - E^\infty)\dfrac{R_0^3}{r^2} & r > R_0, \end{cases} \tag{95}$$

where $E^\infty = S^\infty/(3K_M)$, $\alpha := \dfrac{(3K_M + 4\mu_M)E^\infty - 2\tau_0/R_0}{4\mu_M + 3K_I + 2K_s/R_0 + 2\tau_0/R_0}$, $K_I = \lambda_I + 2\mu_I/3$ is the inclusion bulk modulus, and $K_s = 2(\lambda_s + \mu_s)$ is defined as the surface modulus.

In particular, by setting $\lambda_I = 0$ and $\mu_I = 0$, we obtain the much-studied case of a void in a solid. The displacement (95)$_2$ for this special case is

$$u(r) = E^\infty r + \beta \frac{R_0^3}{r^2} \qquad r > R_0, \tag{96}$$

where $\beta := \dfrac{(3K_M + 4\mu_M)E^\infty - 2\tau_0/R_0}{4\mu_M + 2K_s/R_0 + 2\tau_0/R_0} - E^\infty$ and $E^\infty = S^\infty/(3K_M)$. Thus, the bulk stress (92)$_1$ in the matrix ($r > R_0$) is

$$\boldsymbol{S} = S^\infty \mathbf{I} + 2\mu_M \beta \frac{R_0^3}{r^3}\left(\mathbf{I} - 3\boldsymbol{e}_r \otimes \boldsymbol{e}_r\right). \tag{97}$$

If there is no far stress field, $S^\infty = E^\infty = 0$, the bulk stress $\boldsymbol{S}$ becomes

$$\boldsymbol{S}^0 = 2\mu_M \left(\frac{-2\tau_0/R_0}{4\mu_M + 2K_s/R_0 + 2\tau_0/R_0}\right)\frac{R_0^3}{r^3}\left(\mathbf{I} - 3\boldsymbol{e}_r \otimes \boldsymbol{e}_r\right). \tag{98}$$

Assume a nonzero far stress field, $S^\infty \neq 0$. By (97) and (98), we may then define the stress concentration factor at $r \to R_0$ as

$$S.C. = \left.\frac{S_{\theta\theta} - S^0_{\theta\theta}}{S^\infty}\right|_{r \to R_0} = 1 + \frac{1}{2}\left(\frac{1 - 2\left(K_s + \tau_0\right)/(3K_M R_0)}{1 + K_s/(2\mu_M R_0) + \tau_0/(2\mu_M R_0)}\right). \tag{99}$$

In the absence of surface energy effects, i.e., $\tau_0 = K_s = 0$ in (99), we obtain a stress concentration factor of 1.5 which is the well-known classical elasticity result for a spherical void under hydrostatic stress. We have graphically plotted the results in Fig. 5 that illustrates the qualitative behavior of how stress concentration on a void alters due to size and the surface elasticity modulus (Interestingly, the surface

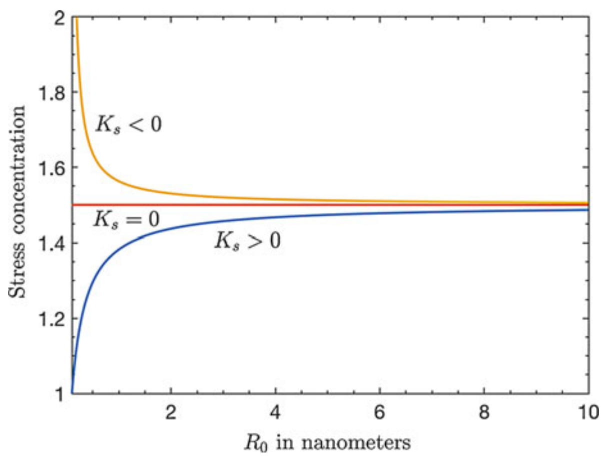

Fig. 5 Stress concentration on a spherical void under hydrostatic stress is plotted with respect to the size of the void for three different surface modulus K_s. For coarser void size, the stress concentration asymptotically approaches the bulk value of 3/2. For the plot, we have chosen properties of Aluminum as bulk, with ($\lambda_M = 62.29$ GPa, $\mu_M = 36.71$ GPa). The surface properties are the following: *Case* (a) considering positive surface modulus $K_s = 2(\lambda_s + \mu_s)$ by using $\lambda_s = 6.842\,N/m$, $\mu_s = -0.3755\,N/m$, and $\tau_0 = 0$; *Case* (b) without considering surface effects; and $K_s = 0$; *Case* (c) considering negative surface modulus $K_s = 2(\lambda_s + \mu_s)$ by using $\lambda_s = 3.48912\,N/m$, $\mu_s = -6.2178\,N/m$, and $\tau_0 = 0$. (The surface and material properties are taken from Miller and Shenoy 2000; Cammarata et al. 2000)

elasticity modulus can have negative values as shown via atomistic simulations by Miller and Shenoy 2000.).

5 Perspectives on Future Research

Despite extensive work on surface elasticity, some aspects of this field are still somewhat understudied and represent avenues for future exploration. We briefly articulate them below:

- As well-motivated by Steigmann and Ogden (1999, 1997), under certain circumstances, the dependence of surface energy on curvature must be accounted for. This was recently explored by Fried and Todres (2005), who examined the effect of the curvature-dependent surface energy on the wrinkling of thin films, and Chhapadia et al. (2011) who (using both atomistics and a continuum approach) explained certain anomalies in the bending behavior of nanostructures. However, due to the complexity of the Steigmann-Ogden curvature-dependent surface elasticity, relatively few works exist on this topic.
- Intriguing recent experiments by Style and co-workers (Style et al. 2013, 2017) on capillarity and liquid inclusions in soft solids have revealed that the pertinent size effects due to surface effects may be observed at *micron* length scales (in

contrast to the nanoscale for hard materials). This represents an important future direction and requires the use of *nonlinear* surface elasticity due to the need to account for the inevitable large deformations in soft matter. Arguably, the study of capillarity in soft matter will also require the development and use of numerical methods cf. Henann and Bertoldi (2014).

- Finally, the literature on coupling of capillarity with electrical and magnetic fields is quite sparse.

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References

Altenbach H, Eremeyev VA, Morozov NF (2013) Mechanical properties of materials considering surface effects. In: IUTAM symposium on surface effects in the mechanics of nanomaterials and heterostructures. Springer, pp 105–115

Biria A, Maleki M, Fried E (2013) Continuum theory for the edge of an open lipid bilayer. Adv Appl Mech 21:1–78

Cammarata RC (2009) Generalized thermodynamics of surfaces with applications to small solid systems. Solid State Phys 61:1–75

Cammarata R, Sieradzki K, Spaepen F (2000) Simple model for interface stresses with application to misfit dislocation generation in epitaxial thin films. J Appl Phys 87(3):1227–1234

Chatzigeorgiou G, Meraghni F, Javili A (2017) Generalized interfacial energy and size effects in composites. J Mech Phys Solids 106:257–282

Chhapadia P, Mohammadi P, Sharma P (2011) Curvature-dependent surface energy and implications for nanostructures. J Mech Phys Solids 59(10):2103–2115

Courant R, Hilbert D (1953) Methods of mathematical physics, vol I (First English ed.). Interscience Publishers, Inc., New York

Duan H, Wang Jx, Huang Z, Karihaloo BL (2005) Size-dependent effective elastic constants of solids containing nano-inhomogeneities with interface stress. J Mech Phys Solids 53(7): 1574–1596

Duan H, Wang J, Karihaloo BL (2009) Theory of elasticity at the nanoscale. In: Advances in applied mechanics, vol 42. Elsevier, Amsterdam, pp 1–68

Fischer F, Waitz T, Vollath D, Simha N (2008) On the role of surface energy and surface stress in phase-transforming nanoparticles. Prog Mater Sci 53(3):481–527

Fried E, Todres RE (2005) Mind the gap: the shape of the free surface of a rubber-like material in proximity to a rigid contactor. J Elast 80(1–3):97–151

de Gennes PG, Brochard-Wyart F, Quere D (2004) Capillarity and wetting phenomenon. Springer, New York

Gurtin ME, Murdoch AI (1975a) Addenda to our paper a continuum theory of elastic material surfaces. Arch Ration Mech Anal 59(4):389–390

Gurtin ME, Murdoch AI (1975b) A continuum theory of elastic material surfaces. Arch Ration Mech Anal 57(4):291–323

Gurtin ME, Murdoch AI (1978) Surface stress in solids. Int J Solids Struct 14(6):431–440

Gurtin M, Weissmüller J, Larche F (1998) A general theory of curved deformable interfaces in solids at equilibrium. Philos Mag A 78(5):1093–1109

Gurtin ME, Fried E, Anand L (2010) The mechanics and thermodynamics of continua. Cambridge University Press, Cambridge

Haiss W (2001) Surface stress of clean and adsorbate-covered solids. Rep Prog Phys 64(5):591

Henann DL, Bertoldi K (2014) Modeling of elasto-capillary phenomena. Soft Matter 10(5): 709–717

Huang Z, Sun L (2007) Size-dependent effective properties of a heterogeneous material with interface energy effect: from finite deformation theory to infinitesimal strain analysis. Acta Mech 190(1–4):151–163

Huang Z, Wang Jx (2006) A theory of hyperelasticity of multi-phase media with surface/interface energy effect. Acta Mech 182(3–4):195–210

Huang Z, Wang J (2013) Micromechanics of nanocomposites with interface energy effect. Handbook of micromechanics and nanomechanics. Pan Stanford Publishing, Singapore

Ibach H (1997) The role of surface stress in reconstruction, epitaxial growth and stabilization of mesoscopic structures. Surf Sci Rep 29(5–6):195–263

Javili A, McBride A, Steinmann P (2013) Thermomechanics of solids with lower-dimensional energetics: on the importance of surface, interface, and curve structures at the nanoscale. A unifying review. Appl Mech Rev 65(1):010802

Javili A, Ottosen NS, Ristinmaa M, Mosler J (2017) Aspects of interface elasticity theory. Math Mech Solids 23:1081286517699041

Li S, Wang G (2008) Introduction to micromechanics and nanomechanics. World Scientific Publishing Company, Singapore

Liu L, Yu M, Lin H, Foty R (2017) Deformation and relaxation of an incompressible viscoelastic body with surface viscoelasticity. J Mech Phys Solids 98:309–329

Miller RE, Shenoy VB (2000) Size-dependent elastic properties of nanosized structural elements. Nanotechnology 11(3):139

Müller P, Saúl A (2004) Elastic effects on surface physics. Surf Sci Rep 54(5–8):157–258

Murdoch AI (2005) Some fundamental aspects of surface modelling. J Elas 80(1–3):33

Pala RGS, Liu F (2004) Determining the adsorptive and catalytic properties of strained metal surfaces using adsorption-induced stress. J Chem Phys 120(16):7720–7724

Park HS (2008) Strain sensing through the resonant properties of deformed metal nanowires. J Appl Phys 104(1):013516

Park HS, Klein PA, Wagner GJ (2006) A surface cauchy–born model for nanoscale materials. Int J Numer Methods Eng 68(10):1072–1095

Sharma P, Ganti S, Bhate N (2003) Effect of surfaces on the size-dependent elastic state of nano-inhomogeneities. Appl Phys Lett 82(4):535–537

Steigmann D, Ogden R (1997) Plane deformations of elastic solids with intrinsic boundary elasticity. In: Proceedings of the royal society of London A: mathematical, physical and engineering sciences, the royal society, vol 453, pp 853–877

Steigmann D, Ogden R (1999) Elastic surface substrate interactions. In: Proceedings of the royal society of London A: mathematical, physical and engineering sciences, the royal society, vol 455, pp 437–474

Style RW, Hyland C, Boltyanskiy R, Wettlaufer JS, Dufresne ER (2013) Surface tension and contact with soft elastic solids. Nat Commun 4:2728

Style RW, Jagota A, Hui CY, Dufresne ER (2017) Elastocapillarity: surface tension and the mechanics of soft solids. Ann Rev Conden Matter Phys 8:99–118

Suo Z, Lu W (2000) Forces that drive nanoscale self-assembly on solid surfaces. J Nanopart Res 2(4):333–344

Wang J, Huang Z, Duan H, Yu S, Feng X, Wang G, Zhang W, Wang T (2011) Surface stress effect in mechanics of nanostructured materials. Acta Mechanica Solida Sinica 24(1):52–82

Wang ZQ, Zhao YP, Huang ZP (2010) The effects of surface tension on the elastic properties of nano structures. Int J Eng Sci 48(2):140–150