

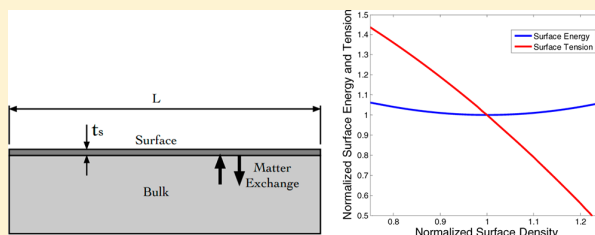
# Surface Tension, Surface Energy, and Chemical Potential Due to Their Difference

C.-Y. Hui<sup>†</sup> and A. Jagota<sup>\*,‡</sup>

<sup>†</sup>Field of Theoretical and Applied Mechanics, Cornell University, Ithaca, New York 14853, United States

<sup>‡</sup>Department of Chemical Engineering and Bioengineering Program, Lehigh University, Bethlehem, Pennsylvania 18015, United States

**ABSTRACT:** It is well-known that surface tension and surface energy are distinct quantities for solids. Each can be regarded as a thermodynamic property related first by Shuttleworth. Mullins and others have suggested that the difference between surface tension and surface energy cannot be sustained and that the two will approach each other over time. In this work we show that in a single-component system where changes in elastic energy can be neglected, the chemical potential difference between the surface and bulk is proportional to the difference between surface tension and surface energy. By further assuming that mass transfer is driven by this chemical potential difference, we establish a model for the kinetics by which mass transfer removes the difference between surface tension and surface energy.



## 1. INTRODUCTION

The presence of an interface between two phases results in a change in free energy compared to the bulk.<sup>1–3</sup> Two resulting equilibrium properties of an interface are its surface energy,  $\gamma$  (J/m<sup>2</sup>), and surface stress,  $\sigma_{ij}$  (N/m), which is a second-order tensor in two dimensions. For amorphous materials, or those with 3-fold or greater rotational symmetry with respect to the surface normal, the surface stress is isotropic; i.e., it can be represented by a single number, the surface tension,  $\sigma$ , formally half of the trace of the surface stress.<sup>4,5</sup> This is the case with which we will be concerned in this work.

For a liquid, it is well-known that surface tension is positive with a numerical value equal to the surface energy.<sup>2</sup> However, it has long been recognized that the surface tension need not equal the surface energy for solids.<sup>4–6</sup> A variety of phenomena in soft solids can be driven by *surface tension* or by *surface energy*. Surface tension, which measures the mechanical work required to stretch the surface (or interface) at fixed composition, must be balanced either by external forces or by volume stresses in the body. The surface energy by contrast is the reversible work necessary to form unit area of surface at a constant equilibrium density of surface atoms.<sup>7</sup> Generally, the constant of proportionality in Laplace's equation for the relation between pressure difference  $\Delta p$  and mean curvature is the surface tension<sup>4,5</sup>

$$\Delta p = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1)$$

where  $R_1$  and  $R_2$  are the principal surface curvatures. The commonly used contact angle measurement relates liquid–vapor surface energy to the difference between solid–vapor and solid–liquid surface energy.<sup>1,8</sup> In Young's equation<sup>1</sup>

$$\gamma_{lv} \cos \theta + \gamma_{sl} = \gamma_{sv} \quad (2)$$

$\gamma_{lv}$ ,  $\gamma_{sl}$ , and  $\gamma_{sv}$  are usually interpreted as surface energies with subscripts lv, sl, and sv, representing the liquid–vapor, solid–liquid, and solid–vapor interfaces, respectively.<sup>4–6</sup>

Elastocapillarity phenomena—solid deformation driven by *liquid surface tension*—have been studied in some detail as reviewed recently<sup>9</sup> but are distinct from phenomena driven by *solid surface tension*. For soft or compliant solids, the deformation caused by surface tension of a contacting liquid can be significant. The characteristic length scale that describes the deformation of a solid due to surface energy is given by the ratio between the surface energy ( $\gamma$ ) and elastic modulus ( $E$ ),  $\gamma/E$ .<sup>10</sup> For stiff solids such as metals and ceramics, this length is smaller than interatomic distances. However, for soft materials such as elastomers and gels with  $E$  ranging from tens of Pa to several MPa,  $\gamma/E$  ranges from tens of nm to hundreds of  $\mu\text{m}$ . Effects of this large value of  $\gamma/E$  can be seen in different contexts. For examples, when a wetting liquid is allowed to fill in an embedded microchannel in a thin layer of PDMS, the thin skin above the channel bulges out by reduction of surface tension.<sup>11</sup> Similarly, a flexible cantilever beam or plate undergoes large deformation driven by contacting liquid drops.

Gibbs<sup>12</sup> and de Gennes et al.<sup>1</sup> have noted that the effect of surface tension of solids is usually small because for any deformation the elastic energy of the bulk overwhelms contributions from the surface. For this reason, in stiff, crystalline materials, the phenomena driven by their surface tension are generally important only for very small objects and

**Received:** March 12, 2013

**Revised:** July 28, 2013

**Published:** August 8, 2013



are not easy to measure.<sup>5,13</sup> For example, in early work Nicolson<sup>14</sup> showed that surface stress can be deduced by measuring the change in lattice spacing but that this requires very small crystals; the strain is approximately  $\sigma/Ed$ , where  $d$  is a characteristic size of the material, say the diameter of a nanoparticle. The length scale  $\sigma/E$  can be amplified, for example, by deflection of a beam or wafer caused by difference in surface stress on two sides.<sup>13,15,16</sup> Atomic force microscopy has shown that surface tension can cause an apparent increase in elastic modulus of nanowires and nanotubes. In addition, it is possible to determine these surface tensions experimentally from atomic force microscopy measurements.<sup>17</sup>

Deformation of soft solids due to the solid surface tension, which has been less studied, can be quite significant. (See refs 18 and 19 for a discussion of what constitutes a solid.) Compliant solid cylinders undergo an instability analogous to the Rayleigh–Plateau instability of a liquid;<sup>20</sup> solid surface tension influences the elastic substrate deformation due to a contact line;<sup>21,22</sup> bubble growth<sup>23</sup> and debonding instabilities<sup>24,25</sup> in compliant solids are influenced by surface tension; sharp edges in a soft elastic solid are rounded to a radius of curvature on the order of  $\sigma/E$ <sup>10</sup> and rippled surfaces flatten due to surface tension.<sup>26</sup>

Surface energy and tension were related by Shuttleworth,<sup>4</sup> who provided the relation

$$\sigma = \gamma + A \left( \frac{\partial \gamma}{\partial A} \right) \quad (3)$$

The understanding of Shuttleworth's equation (3) is a subject of considerable controversy. Many authors, see for example refs 27–31, have argued against its validity. A discussion and summary of this point of view can be found in reviews by Marichev.<sup>32,33</sup> Others have reaffirmed its status as a fundamental relation.<sup>34,35</sup> We will return to a discussion of Shuttleworth's equation later in this paper.

The main focus of this work is to consider a closely related but relatively unexplored problem stated by Mullins: that surface tension and surface energy can evolve with the stretching process.<sup>36</sup> The physics behind this evolution can be readily understood by noting that in the fluid-like limit the surface energy does not change with change in area, and in that case surface tension equals surface energy. However, if we consider a solid-like system in which there is no transport of species to the surface as it is stretched, the surface energy will likely change with change of surface area, and then surface tension and surface energy will be different. Indeed, surface energy is very likely to change as we show later, for it is a function of surface particle density and temperature and, in the absence of matter transport to the surface, the density changes with stretch. For any material, it is reasonable to suppose that for fast-enough stretching there will be insufficient time for mass transport or surface rearrangement; surface energy and tension will be different. However, over time, as Mullins<sup>36</sup> pointed out, “the key point that determines whether surface stress reduces to surface energy is whether the state of the surface is sensibly changed by the stretching process. In practice, this question in turn hinges on the duration of the stretch compared with the temperature-dependent relaxation time,  $\tau$ , required for the particular surface, instantaneously stretched, to regain its original state by atomic migration.”

In this work we develop a mathematical model to explore further this question of whether and how, given an initial difference between them, surface tension and surface energy

approach each other. We begin by establishing that the driving force for mass transport to, or rearrangement of, the surface when contributions due to elastic energy are negligible is proportional to the difference between surface tension and surface energy. We then assume that this driving force results in mass transport that follows first-order kinetics and provides some simple examples illustrating our idea. We close with a discussion of the Shuttleworth equation written explicitly in terms of independent intensive variables, which we believe removes some of the confusion associated with it.

## 2. CHEMICAL POTENTIAL FOR MASS TRANSPORT TO THE INTERFACE

We restrict ourselves to the case of a single mobile species and an isotropic surface. Our system consists of the surface of the solid, its bulk, and adjoining fluid. We assume that we can treat these three as distinct subsystems and that the temperature,  $T$ , is uniform throughout our system. This approach is due to Guggenheim,<sup>37</sup> who treated the surface as a layer of small but finite thickness; it is consistent with Gibbs's treatment that uses bulk properties on two sides of a zero thickness dividing surface where surface quantities are defined as the excess compared to those so obtained.<sup>2,7</sup>

It has been pointed out<sup>7,19</sup> that chemical potential in a solid under nonhydrostatic stress may only be definable for a secondary, mobile (e.g., fluid) component that is an “actual” component both of the solid and of an adjoining liquid phase. This Gibbs solid<sup>7,19</sup> is one in which the primary component is immobile (for which one does not define a chemical potential), but there exists a secondary mobile component, for which the chemical potential is well-defined everywhere and, in equilibrium, is uniform. For this reason, we have in mind here also a Gibbs solid, a specific example of which might be a hydrogel with an immobile, cross-linked solid network as the primary component and water as the mobile component that is a component of the bulk solid phase, the surface phase, and an adjoining fluid phase. This adjoining fluid phase could be a liquid or vapor. Strains are defined with respect to deformation of the primary component, and we consider slow enough rates and small enough deformation such that the stress is related linearly to the (small) strains. Moreover, for simplicity, we will allow exchange of the secondary component only between the surface and bulk of the solid phase. Indeed, it is the experimentally observed surface-driven deformation of such a solid that has motivated this work.<sup>26</sup>

The starting point is that, for constant temperature  $T$ , the change in Helmholtz free energy of the surface  $F_s$  is

$$dF_s = \sigma dA + \mu_s dN_s \quad (4)$$

where  $A$  is the surface area,  $N_s$  is the number of mobile particles,  $\sigma$  is the surface tension, and  $\mu_s$  the surface chemical potential. As mentioned above, we have assumed that there is only one type of mobile particle even though the surface can have many components. Also, for simplicity, we have neglected the work contribution due to change in volume of the surface. (Adding this term does not change our argument.) Finally, it is important to note that the surface tension, not the surface energy, is the work conjugate of surface area.

Since  $F_s$  is a state function, the surface tension is

$$\sigma = \left. \frac{\partial F_s}{\partial A} \right|_{N,T} \quad (5)$$

We emphasize that the Helmholtz surface free energy is a function of the surface area, number of mobile particles, and temperature, that is

$$F_s = F_s(A, N_s, T) \quad (6)$$

A question is: how does the surface energy appear in this formulation? Imagine an isothermal process where the particle density (number of particles per unit area),  $\rho_s = N_s/A$ , is kept constant. For this case,  $F_s$  must be directly proportional to  $A$ . This is because  $F_s$  is an extensive property, and increasing the surface area and the number of mobile particles by a factor  $\chi$  will increase  $F_s$  by the same factor. This means that  $F_s$  must be proportional to  $A$  in a constant density process, i.e.

$$F_s = \gamma(\rho_s, T)A \quad (7)$$

The proportionality “constant”  $\gamma = \gamma(\rho_s, T)$  is, by definition, the surface energy. It is an intensive property of the surface and is completely determined by two independent properties  $\rho_s, T$ . Thus, if one changes the surface area by rapidly stretching it so that  $N_s$  remains fixed, the density  $\rho_s$  will decrease which is likely to result in a change of surface energy.

Still proceeding with the constant surface density and temperature process where

$$dN_s = \rho_s dA \quad (8)$$

Substituting eq 8 into eq 4 gives

$$dF_s = \sigma dA + \mu_s dN_s \quad (9)$$

Since  $\rho_s$  is fixed, we also have, by eq 7,

$$dF_s = \gamma(\rho_s, T) dA \quad (10)$$

Equating (9) and (10) leads to an expression for the chemical potential:

$$\mu_s = \frac{\gamma(\rho_s, T) - \sigma(\rho_s, T)}{\rho_s} \quad (11)$$

Note that the surface tension and chemical potential are intensive properties that are completely determined by the surface density of mobile particles and temperature. As long as the bulk is so large so that addition of particles does not affect  $\rho_b$  (the density of mobile particles in the bulk), the chemical potential in (11) should be interpreted as the chemical potential difference between the surface and bulk.

Thus, the primary driving force for mobility is the difference between the surface tension and surface energy. The role of elastic energy will be discussed in one of the examples below and in the discussion.

Using the definition of surface tension and surface energy, eqs 5 and 7, respectively, we can obtain a relation between surface tension and surface energy:

$$\sigma = \left. \frac{\partial F_s}{\partial A} \right|_{T, N_s} = \left. \frac{\partial [\gamma(\rho_s, T)A]}{\partial A} \right|_{T, N_s} = \gamma(\rho_s, T) - \rho_s \frac{\partial \gamma(\rho_s, T)}{\partial \rho_s} \quad (12)$$

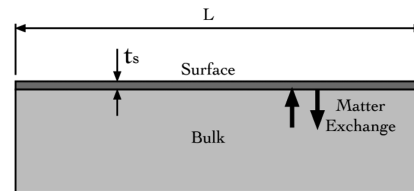
Equation 12 is a restatement of Shuttleworth's eq 3 in a form that makes explicit the independent state variables on which surface tension and energy depend. We return to a discussion of eq 12 in section 3.4. Here, we note that it provides the condition under which surface tension equals surface energy

$\partial \gamma(\rho_s, T) / \partial \rho_s = 0$ . Indeed, let the “natural” equilibrium state at which the chemical potential difference between the surface and bulk vanishes correspond to a surface density,  $\rho_o$ . Then, eq 12 requires  $(\partial \gamma(\rho_s, T) / \partial \rho_s)|_{\rho_s = \rho_o} = 0$ . This condition places a constraint on the relationship between surface energy and surface density.

### 3. EXAMPLES

In this section we first consider two simple cases: a one-dimensional sheet held at a fixed length and a sphere. For the case of the one-dimensional sheet, we show how the difference in chemical potential between the surface and bulk can drive transport of matter, specifically for the case of first order kinetics. For the case of sphere we verify the more abstract derivation of eq 11 by computing the chemical potential difference directly and illustrate the effect of bulk elasticity on chemical potential difference. In section 3.3, we consider the case of a rippled surface that changes its amplitude because of the action of surface tension. We show how evolution of surface tension would cause a time-dependent change in measured amplitude. In section 3.4, we discuss our alternative presentation of Shuttleworth's equation relating surface tension and surface energy, and we end with section 3.5, which discusses the effect of elastic strain energy, which we have generally neglected.

**3.1. One-Dimensional Sheet under Tension. Kinetics To Eliminate the Difference between Surface Tension and Energy.** Imagine our surface as a thin layer of material with thickness  $t_s$  (Figure 1). Specifically, consider a sheet of uniform cross-section with area,  $A$ , and length,  $L$ . The sheet can exchange matter with the surrounding, the bulk.



**Figure 1.** Surface region of a bulk solid is represented as a one-dimensional sheet under tension.

Suppose that the surface represented by the sheet in Figure 1 is created at time  $t = 0$ , with an initial difference between surface tension and energy. The resulting difference in chemical potential between the surface and bulk is given by eq 11. We now assume this difference drives transport of particles by a first-order process; that is, the time rate of change of the density of particles on the surface is given by

$$\frac{d\rho_s}{dt} = -k(\mu_s - \mu_b) = k \frac{\sigma - \gamma}{\rho_s} \quad (13)$$

To solve eq 13, we need to specify how the surface energy and stress depend on the surface density at constant temperature.

As an example, take the dependence of surface energy on density simply to be

$$\gamma = \gamma_o + \alpha(\rho_s - \rho_o)^2 \quad (14)$$

Here  $\alpha$  is a positive material constant that measures how strongly surface energy increases when density differs from its natural value,  $\rho_o$ , which is the density for which surface tension

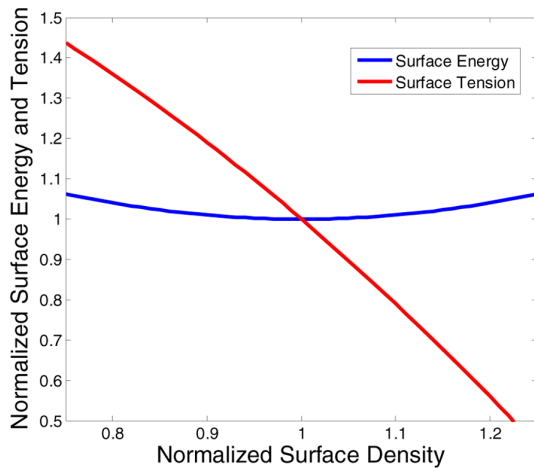
equals surface energy, and  $\gamma_o$  is the surface energy of that state. (We assume that the surface density departs only modestly from its natural value.) Using eq 12, we find surface tension to be

$$\sigma = \gamma_o - \alpha(\rho_s^2 - \rho_o^2) \quad (15)$$

Convenient dimensionless forms of eqs 14 and 15 are

$$\begin{aligned} \bar{\gamma} &\equiv \frac{\gamma}{\gamma_o} = 1 + \bar{\alpha}(\bar{\rho}_s - 1)^2 \\ \bar{\sigma} &\equiv \frac{\sigma}{\gamma_o} = 1 - \bar{\alpha}(\bar{\rho}_s^2 - 1) \\ \bar{\rho}_s &= \rho_s/\rho_o; \bar{\alpha} = \alpha\rho_o^2/\gamma_o \end{aligned} \quad (16)$$

That is, surface energy and surface tension are both normalized by the surface energy of the natural state, surface density is normalized by its value in the natural state, and  $\bar{\alpha}$  is a dimensionless parameter that represents how strongly departure from the natural state affects surface energy and tension. Note that surface energy equals the surface tension, and both assume their “natural” value when the density is at its natural surface state,  $\rho_o$ . Figure 2 plots normalized surface



**Figure 2.** Normalized surface energy  $\gamma/\gamma_o$  and surface tension  $\sigma/\gamma_o$  as a function of normalized surface density  $\rho_s/\rho_o$  for  $\bar{\alpha} = 1$ .

energy and tension as a function of surface density for  $\bar{\alpha} = 1$ . If the initial surface density is larger than its natural value, the surface tension is smaller than surface energy and the chemical potential of the surface is higher than that of the bulk. Thus, there is a driving force for particles to move from the surface to the bulk. Conversely, if the surface density is smaller than its natural value, there is a driving force for particles to move from the bulk to the surface.

Substituting eq 16 into eq 13, we obtain the differential equation governing evolution of surface density, i.e.

$$\begin{aligned} \frac{d\bar{\rho}_s}{d\tau} &= 1 - \bar{\rho}_s \\ \tau &= 2\alpha kt \end{aligned} \quad (17)$$

where  $\tau$  is a normalized time. Suppose that the initial condition is  $\rho_s = \rho_o(1 + \varepsilon)$  at  $t = 0$ , where  $\varepsilon$  is a number, small compared to unity. That is,  $\varepsilon$  is the difference of initial and equilibrium

surface density as a fraction of the equilibrium surface density. Then, eq 17 is readily integrated to yield the solution

$$\bar{\rho}_s = 1 + \varepsilon e^{-\tau} \quad (18)$$

Substituting eq 18 into eq 16, we obtain expressions for the evolution of surface energy and tension

$$\begin{aligned} \bar{\gamma} &= 1 + \bar{\alpha}(1 + \varepsilon e^{-\tau} - 1)^2 \approx 1 + \bar{\alpha}\varepsilon^2 e^{-2\tau} \\ \bar{\sigma} &= 1 - \bar{\alpha}(1 + \varepsilon^2 e^{-2\tau} + 2\varepsilon e^{-\tau} - 1) \approx 1 - 2\bar{\alpha}\varepsilon e^{-\tau} \end{aligned} \quad (19)$$

That is, whatever the initial state, the system exchanges particles between the surface and bulk to return to its natural equilibrium state in which the surface energy has its natural value and surface tension equals surface energy.

**3.2. A Sphere.** Consider a compressible sphere in vacuum with initial radius  $r_o$  and surface density  $\rho_s$ . The initial Helmholtz free energy of the system  $F_o$  consists of the surface energy and the stored elastic energy in the bulk<sup>38</sup>

$$F_o = \gamma(\rho_s, T)A_o + \frac{p_o^2}{2K}V_o \quad (20)$$

where  $K$  is the bulk modulus of the sphere and  $p_o < 0$  is the pressure acting on the sphere due to the surface tension  $\sigma$

$$p_o = -2\sigma(\rho_s, T)/r_o \quad (21)$$

(Notice that we are using a sign convention in which tensile pressure is positive, i.e., positive or tensile surface tension results in negative values of pressure.) For convenience, we have assumed that the initial chemical potential of the bulk is zero.

We evaluate the chemical potential of the system by considering a process where we increase the surface area by  $dA$  while holding the surface density fixed.

$$dN_s = \rho_s dA \quad (22)$$

During this process, the free energy of the system changes to, according to 20,

$$F_o + dF = \gamma(\rho_s, T)(A_o + dA) + \frac{(p_o + dp)^2}{2K}(V_o + dV) \quad (23)$$

It is important to note that for a sphere the surface area and volume are *not independent quantities*. Indeed,  $dA = 8\pi r_o dr$  and  $dV = 4\pi r_o^2 dr$  so that

$$dV = r_o dA/2 \quad (24)$$

The new pressure due to this increment of surface area is

$$p_o + dp = -2\sigma(\rho_s, T)/(r_o + dr) \quad (25)$$

The increase in pressure causes an incremental increase in volumetric strain which is related to  $dV$  by

$$dV/V_o = \frac{dp}{K} = \frac{2\sigma(\rho_s, T)}{Kr_o^2} dr \quad (26)$$

Substituting eq 26 into eq 23, we have

$$F_o + dF = \gamma(\rho_s, T)(A_o + dA) + \frac{2\sigma^2(\rho_s, T)/(r_o + dr)^2}{K}(V_o + dV)$$



$$= \gamma(\rho_s, T)(A_0 + dA) + \frac{2\sigma^2(\rho_s, T)}{Kr_0^2} \left[ 1 - 2\frac{dr}{r_0} \right] (V_0 + dV) + \text{higher order terms} \quad (27)$$

Neglecting higher order terms of the form  $dr dV$ , and using eq 20, the change in total Helmholtz free energy  $dF$  during this process is

$$dF = \gamma(\rho_s, T)(A_0 + dA) + \frac{2\sigma^2(\rho_s, T)}{Kr_0^2} \left[ 1 - 2\frac{dr}{r_0} \right] (V_0 + dV) - \gamma(\rho_s, T)A_0 - \frac{p_0^2}{2K}V_0 \\ = \gamma(\rho_s, T) dA + \frac{2\sigma^2(\rho_s, T)}{Kr_0^2} dV - \frac{2\sigma(\rho_s, T)}{r_0} dV \quad (28)$$

According to eq 4, the right-hand side of (27) is

$$dF = dF_s + dF_b = \sigma(\rho_s, T) dA + \mu_s(\rho_s, T)\rho_s dA + p_s dV - \mu_b(\rho_b, T)\rho_b dA \quad (29)$$

where we have used  $dN_b = -dN_s = -\rho_s dA$  as well as the fact that the surface density is kept constant during this process. Equating eqs 29 and 28, the  $p_0 dV$  term cancels out, resulting in

$$\sigma(\rho_s, T) dA + \mu_s(\rho_s, T)\rho_s dA - \mu_b(\rho_b, T)\rho_b dA \\ = \gamma(\rho_s, T) dA + \frac{2\sigma^2(\rho_s, T)}{Kr_0^2} dV \quad (30)$$

Thus, the change in chemical potential of the system is given by

$$\mu_s(\rho_s, T) - \mu_b(\rho_b, T) = \frac{\gamma(\rho_s, T) - \sigma(\rho_s, T)}{\rho_s} + \frac{1}{\rho_s} \left[ \frac{\sigma^2(\rho_s, T)}{Kr_0} \right] \quad (31)$$

The square bracket term in eq 31 corresponds to the elastic strain density stored in the bulk. In the limit of an incompressible material, this term vanishes and we retrieve eq 11. (We have assumed implicitly that the chemical potential of the bulk does not change by addition or removal of particles.)

**3.3. Rippled Surface.** In this section we consider a problem of the flattening of a rippled surface due to surface tension including its subsequent time evolution. It has recently been shown experimentally that a gel replica of a rippled surface has significantly attenuated amplitude.<sup>26</sup> The reduction in amplitude has been modeled as being due to elastic deformation driven by surface tension.

In ref 26 the surface profile of the poly(dimethylsiloxane) (PDMS) master against which the relatively compliant gel is molded is given by

$$z = b_0 \cos \frac{2\pi x}{\lambda} \quad (32)$$

where  $b_0$  and  $\lambda$  are the amplitude and wavelength of the surface profile, respectively.

At time  $t = 0$ , the gel and PDMS surfaces are separated, creating a gel–air surface with its associated surface tension and energy. The gel deforms in response to the surface tension, and its deformed surface profile depends only on the surface

tension  $\sigma$ . For a constant surface tension, the resulting displacement of the surface is given by approximately by<sup>26</sup>

$$u = -4\pi \left( \frac{b}{\lambda} \right) \left( \frac{\sigma}{E^*} \right) \cos \frac{2\pi x}{\lambda}; \quad E^* = E/(1 - \nu^2) \quad (33)$$

where  $b$  is the amplitude of the deformed rippled surface,  $E$  is the Young's modulus of the bulk material, and  $\nu$  is its Poisson's ratio. Using eq 32, the deformed rippled surface has an amplitude of

$$b = \frac{b_0}{1 + 4\pi \left( \frac{\sigma}{E^* \lambda} \right)} \approx b_0 \left( 1 - 4\pi \left( \frac{\sigma}{E^* \lambda} \right) \right) \quad (34)$$

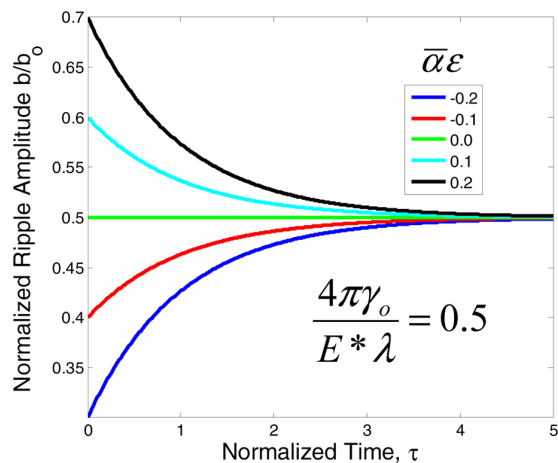
where the approximation holds when  $4\pi\sigma/(E^*\lambda) \ll 1$ , i.e., the relative change of shape due to surface tension is small. Assume that when the gel–air surface is created at time  $t = 0$ , its surface tension does not equal its surface energy. Since the state of the surface at fixed temperature depends only on the surface density  $\rho_s$ , the surface tension and surface energy can change only if particles are transported to or from the surface.

Using eq 19 for the evolution of the surface tension in eq 34 gives the ripple amplitude as a function of time:

$$\frac{b(t)}{b_0} = 1 - \frac{4\pi\gamma_0}{E^*\lambda} (1 - 2\bar{\alpha}\epsilon e^{-t}) \quad (35)$$

Suppose that surface tension is initially smaller in value than the surface energy ( $\epsilon$  is positive). Then, at time  $t = 0$  the ripple amplitude is determined by this initial value of surface tension. If we wait sufficiently long, the surface tension equals surface energy and ripple amplitude is accordingly smaller. Figure 3 shows ripple amplitude versus time curves for different values of  $\epsilon$ . Such a decay has been reported in experiments,<sup>26</sup> although it is by no means clear if it was due to change of surface tension or some other time-dependent process.

**3.4. Shuttleworth's Equation.** We have taken as given that surface tension and surface energy can be different



**Figure 3.** Example to demonstrate how evolution of surface tension to match surface energy can result in time-dependent change in amplitude of a rippled solid. If the surface tension is initially smaller than the surface energy ( $\epsilon$  is positive), then the ripple amplitude reduces with time as surface tension increases. Conversely, if the surface tension is initially larger than the surface energy ( $\epsilon$  is negative), then the ripple amplitude increases with time as the surface tension decreases.

quantities, at least initially. We then showed that the difference between them generates a chemical potential difference between the bulk and surface that will presumably drive transport of matter so that over time they will approach each other. Since Shuttleworth provided an equation linking surface tension and surface energy (eq 3), it is natural to ask how our model relates to Shuttleworth's equation. Note that Shuttleworth's formula contains no reference to time or kinetic processes.

As mentioned in the Introduction, the Shuttleworth equation has been a subject of some controversy. For example, Bottomley and Ogino<sup>28</sup> argued that the Shuttleworth equation is incompatible with the mathematical structure of thermodynamics. More recently, Makkonen has argued out that Shuttleworth's equation provides no additional relation to the physics of surfaces,<sup>31</sup> although it is consistent with the definition of surface tension derived from mechanics. Eriksson and Rusanov<sup>34,35</sup> have argued to the contrary, supporting the validity of the Shuttleworth equation as a fundamental relation.

Instead of adding to this discussion, our purpose here is to point out a source of confusion in Shuttleworth's derivation, which is that he did not explicitly state the independent variables in his free energy function (Helmholtz free energy as stated in the abstract of his paper). It appears that he assumed that the number of surface particles  $N_s$  is always fixed, and hence it can be neglected as a variable in the free energy function. As a result, his free energy is a function of the surface area  $A$  only (implied by the equation in the abstract of his paper). Specifically, Shuttleworth assumed the surface Helmholtz free energy is given by

$$F_s = \gamma(A, T)A \quad (36)$$

Such a form causes confusion since the surface Helmholtz free energy is an extensive property, so  $\gamma$  must be a constant independent of surface area. If, instead, we use eqs 4, 6, or 7 for the surface free Helmholtz energy, then it clarifies the idea that the variables  $A$  and  $T$  are not enough to determine the surface energy, whereas the independent variables  $\rho_s$  and  $T$  are sufficient. That is, the surface energy does not depend on only the surface area and temperature; rather it depends solely on the surface density of particles (at constant temperature). With this understanding, it is straightforward to rewrite the Shuttleworth equation in a form we believe is clearer, as presented in eq 12.

**3.5. Effect of Elastic Energy.** Although it is considered in the simple example in section 3.2, we have generally neglected the elastic energy of the bulk phase in our formulation of the surface chemical potential. As demonstrated in section 3.2, even without particle diffusion from the surface to the bulk, surface tension in general causes internal stresses in an elastic body, and these stress and strain fields are typically spatially inhomogeneous. Diffusion of particles from the surface to the bulk or vice versa will generate additional stresses since these particles have to be accommodated by deformation of the bulk. As pointed out by Gibbs<sup>12</sup> (page 193) and Larche and Cahn,<sup>19</sup> the chemical potential of the primary component of the solid is not well-defined in this case unless the solid is in a state of pure hydrostatic stress. In applications, a pure hydrostatic state of stress is highly unlikely due to the geometry of the elastic body. In this class of problems, additional terms which account for the elasticity of the bulk must be appended to the Helmholtz free energy, and as a result, the difference in chemical potential between the surface and the bulk will have additional elasticity

terms. Furthermore, these potentials are spatially inhomogeneous. It must be noted that, except for infinite bodies, the surface area and the bulk volume are not independent quantities. In general, the relation between the surface area and the bulk volume of an object must be determined by solving an elasticity boundary value problem. When the contribution of bulk elasticity to the chemical potential dominates (e.g., when  $r_0$  in eq 31) is sufficiently small), it is necessary to use continuum field theory such as those employed by Wu<sup>39</sup> to carry out the analysis, which is beyond the scope of this present work. It is interesting to note that, for isotropic surfaces, continuum field theory assumes that the surface energy density is a function of surface area (not surface density), and it is not clear how this approximation affects the solution.

#### 4. DISCUSSION AND SUMMARY

We have shown that there is a contribution to the chemical potential difference between the surface and bulk due to the difference between surface tension and surface energy given by  $(\mu_s - \mu_b) = -(\sigma - \gamma)/\rho_s$ . This difference can drive mass transfer between the surface and the bulk and will remain until the difference between surface tension and energy is removed. It should be noted that the expression for surface chemical potential can be used to model diffusion of particles constrained to move on a surface, for example, in situations where bulk diffusion is comparatively slow and diffusion is driven by gradient of surface chemical potential. Likewise, it can be used to model diffusion of particles between the liquid phase and the surface. Shemesh et al.<sup>40</sup> have obtained a similar result in the context of exchange of particles between a cell membrane and the cytosol using the surface Gibbs–Duhem equation.

Our approach follows that of Guggenheim,<sup>37</sup> who treated the surface as a layer of small but finite thickness  $t_s$ . A disadvantage of Guggenheim's approach is that the number of particles varies with the distance normal to the interface. As a result, the surface density  $\rho_s$  must be defined as the number of particles averaged through the layer thickness divided by the surface area. Thus, the surface density is well-defined only if the boundary between the layer and the bulk is sharp, and  $t_s$  is chosen to be the distance between the interface and this boundary.

We proposed a rewritten form of the Shuttleworth equation which links surface tension to surface energy. This form shows that the Shuttleworth's equation is a direct consequence of the fact that the surface tension is the derivative of the Helmholtz free energy with respect to surface area at fixed number of particles and temperature. For our simple system with one mobile species, two independent variables, namely surface density and temperature, are sufficient to completely determine the surface energy, surface tension, and chemical potential.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*E-mail anj6@lehigh.edu (A.J.).

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award DE-FG02-07ER46463. A. Jagota

acknowledges support from Cornell University through the Mary Upson visiting professorship in the spring of 2012 and the hospitality of the Sibley School of Mechanical and Aerospace Engineering at Cornell University. The authors also appreciate several constructive comments by anonymous reviewers. In particular, one of the reviewers pointed out the difficulty associated with our definition of surface density.

## REFERENCES

- (1) deGennes, P.-G.; Brochard-Wyart, F.; Quere, D. *Capillarity and Wetting Phenomena. Drops, Bubbles, Pearls, Waves*; Springer Science +Business Media, Inc.: New York, 2002.
- (2) Rowlinson, J. S.; Widom, B. *Molecular Theory Of Capillarity*; Oxford University Press: New York, 1989.
- (3) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*; John Wiley & Sons: New York, 1997.
- (4) Shuttleworth, R. The Surface Tension of Solids. *Proc. Phys. Soc. A* **1950**, 63 (5), 444.
- (5) Cammarata, R. C.; Sieradzki, K. Surface and Interface Stresses. *Annu. Rev. Mater. Sci.* **1994**, 24, 214–234.
- (6) Orowan, E. Surface Energy and Surface Tension in Solids and Liquids. *Proc. R. Soc. London, A* **1970**, 316 (1527), 473–491.
- (7) Cammarata, R. C. Generalized Surface Thermodynamics with Application to Nucleation. *Philos. Mag.* **2008**, 88 (6), 927–948.
- (8) Chaudhury, M. K. Interfacial Interaction between Low-Energy Surfaces. *Mater. Sci. Eng. Rep.* **1996**, 16, 97–159.
- (9) Roman, B.; Bico, J. Elasto-capillarity: Deforming an Elastic Structure with a Liquid Droplet. *J. Phys.: Condens. Matter* **2010**, 22 (49), 493101.
- (10) Hui, C.-Y.; Jagota, A.; Lin, Y. Y.; Kramer, E. J. Constraints on Micro-Contact Printing Imposed by Stamp Deformation. *Langmuir* **2002**, 18, 1394–1404.
- (11) Majumder, A.; Ghatak, A.; Sharma, A. Microfluidic Adhesion Induced by Subsurface Microstructures. *Science* **2007**, 318 (5848), 258–261.
- (12) Gibbs, J. W. *Collected Works*; Longman and Green: London, 1876; p 315.
- (13) Sander, D. Surface Stress: Implications and Measurements. *Curr. Opin. Solid State Mater. Sci.* **2003**, 7, 51–57.
- (14) Nicolson, M. M. Surface Tension in Ionic Crystals. *Proc. R. Soc. London, Ser. A* **1955**, 228 (1175), 490–510.
- (15) Berger, R.; Delamarche, E.; Lang, H. P.; Gerber, C.; Gimzewski, J. K.; Meyer, E.; Guentherodt, H.-J. Surface Stress in the Self-Assembly of Alkanethiols on Gold. *Science* **1997**, 276, 2021–2024.
- (16) Stoney, G. G. The Tension of Metallic Films Deposited by Electrolysis. *Proc. R. Soc. London, Ser. A* **1909**, 82 (553), 172–175.
- (17) Cuenot, S.; Frétygn, C.; Demoustier-Champagne, S.; Nysten, B. Surface Tension Effect on the Mechanical Properties of Nanomaterials Measured by Atomic Force Microscopy. *Phys. Rev. B* **2004**, 69 (16), 165410.
- (18) Cahn, J. W.; Larche, F. Surface Stress and the Chemical Equilibrium of Small Crystals. II. Solid Particles Embedded in a Solid Matrix. *Acta Metall.* **1982**, 30 (1), 51–56.
- (19) Larche, F. C.; Cahn, J. W. The Interactions of Composition and Stress in Crystalline Solids. *Acta Metall.* **1985**, 33 (3), 332–357.
- (20) Mora, S.; Phou, T.; Fromental, J.-M.; Pismen, L. M.; Pomeau, Y. Capillarity Driven Instability of a Soft Solid. *Phys. Rev. Lett.* **2010**, 105, 214301.
- (21) Jerison, E. R.; Xu, Y.; Wilen, L. A.; Dufresne, E. R. Deformation of an Elastic Substrate by a Three-Phase Contact Line. *Phys. Rev. Lett.* **2011**, 106 (18), 186103.
- (22) Style, R. W.; Boltyskiy, R.; Che, Y.; Wettlaufer, J. S.; Wilen, L. A.; Dufresne, E. R. Universal Deformation of Soft Substrates Near a Contact Line and the Direct Measurement of Solid Surface Stresses. *Phys. Rev. Lett.* **2013**, 110, 066103.
- (23) Zimmerlin, J. A.; Sanabria-DeLong, N.; Tew, G. N.; Crosby, A. J. Cavitation Rheology for Soft Materials. *Soft Matter* **2007**, 3, 763–767.
- (24) Chung, J. Y.; Chaudhury, M. K. Roles of Discontinuities in Bio-Inspired Adhesive Pads. *J. R. Soc. Interface* **2005**, 2 (2), 55–61.
- (25) Gonuguntla, M.; Sharma, A.; Sarkar, J.; Subramanian, S. A.; Ghosh, M.; Shenoy, V. Contact Instability in Adhesion and Debonding of Thin Elastic Films. *Phys. Rev. Lett.* **2006**, 97, 018303.
- (26) Jagota, A.; Paretkar, D.; Ghatak, A. Surface-Tension-Induced Flattening of a Nearly Plane Elastic Solid. *Phys. Rev. E* **2012**, 85, 051602.
- (27) Gutman, E. On the Thermodynamic Definition of Surface Stress. *J. Phys.: Condens. Matter* **1999**, 7 (48), L663.
- (28) Bottomley, D.; Ogino, T. Alternative to the Shuttleworth Formulation of Solid Surface Stress. *Phys. Rev. B* **2001**, 63 (16), 165412.
- (29) Bottomley, D. J.; Makkonen, L.; Kolary, K. Incompatibility of the Shuttleworth Equation with Hermann's Mathematical Structure of Thermodynamics. *Surf. Sci.* **2009**, 603, 97–101.
- (30) Makkonen, L. The Gibbs-Thomson Equation and the Solid-Liquid Interface. *Langmuir* **2002**, 18 (4), 1445–1448.
- (31) Makkonen, L. Misinterpretation of the Shuttleworth Equation. *Scr. Mater.* **2012**.
- (32) Marichev, V. Hierarchy of Equations for the Surface Tension of Solids. *Philos. Mag.* **2009**, 89 (33), 3037–3047.
- (33) Marichev, V. A. Update on Current State and Problems in the Surface Tension of Condensed Matter. *Adv. Colloid Interface Sci.* **2010**, 157, 34–60.
- (34) Eriksson, J. C.; Rusanov, A. I. Comments on the article entitled “Incompatibility of the Shuttleworth Equation with Hermann's Mathematical Structure of Thermodynamics”. *Surf. Sci.* **2009**, 603 (15), 2348–2349.
- (35) Eriksson, J. C.; Rusanov, A. I. Additional remarks related to the discussion inaugurated by the article “Incompatibility of the Shuttleworth Equation with Hermann's Mathematical Structure of Thermodynamics”. [*Surf. Sci.* **2009**, 603, 97]. *Surf. Sci.* **2010**, 604, 1062–1063.
- (36) Mullins, W. W. Solid Surface Morphologies Governed by Capillarity. In *Metal Surfaces: Structure, Energetics, and Kinetics*; papers presented at a Joint Seminar of the American Society of Metals and the Metallurgical Society of AIME; Roberts, W. D., Gjostein, N. A., Eds., 1962.
- (37) Guggenheim, E. A. The Thermodynamics of Interfaces in Systems of Several Components. *Trans. Faraday Soc.* **1940**, 35, 397.
- (38) Timoshenko, S.; Goodier, J. *Theory of Elasticity*; McGraw-Hill Book Co.: New York, 1951; p 412.
- (39) Wu, C. H. The Chemical Potential for Stress-Driven Surface Diffusion. *J. Mech. Phys. Solids* **1996**, 44, 2059–2077.
- (40) Shemesh, T.; Geiger, B.; Bershadsky, A. D.; Kozlov, M. M.; Kirschner, M. W. Focal Adhesions as Mechanosensors: A Physical Mechanism. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, 102 (35), 12383–12388.