Title	Misinterpretation of the Shuttleworth equation
Author(s)	Makkonen, Lasse
Citation	Scripta Materialia. Elsevier. Vol. 66 (2012) No: 9, Pages 627 - 629
Date	2012
URL	http://dx.doi.org/10.1016/j.scriptamat.2012.01.055
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Misinterpretation of the Shuttleworth equation

Lasse Makkonen

VTT Technical Research Centre of Finland, Box 1000, 02044 VTT, Espoo, Finland

Abstract

It has been argued for sixty years that there exists a relation between surface tension and surface energy on an unstrained solid as given by the Shuttleworth equation. It is shown here that the Shuttleworth equation reduces to the definition of surface tension derived from mechanics. Therefore, it provides no additional relation to the physics of surfaces. This derivation also reveals precisely how the misinterpretation of the Shuttleworth equation has arisen, and should thus close the discussion on its applicability.

Corresponding author: Tel.: +358 20 7224914; fax +358 20 722 7007

E-mail address: lasse.makkonen@vtt.fi

Understanding of the state of a solid surface is becoming more important in the rapidly developing fields of nanotechnology, microsensors and electrochemical wetting. Accordingly, the stress state of a solid surface has been widely discussed in the scientific literature. In this connection, the Shuttleworth equation is frequently referred to. Using the original notations by Shuttleworth [1], this equation reads

$$\gamma = F + A\frac{\partial F}{\partial A} \qquad (1)$$

Here A is surface area, γ is surface tension and F is surface free energy per unit area. Shuttleworth [1] defined γ as the tangential stress (force per unit length) in the surface layer and F as the total Helmholtz free energy H per unit area of a surface, i.e. $F = H/A$.

Equation (1) has subsequently been re-derived in various ways, for example in some recent review papers [2-5]. Equation (1) has sometimes been considered as the second most important equation in surface physics, e.g. [6]. Commonly, the Shuttleworth equation is considered to be a thermodynamic equation that provides the excess surface stress at a solid surface. In particular, F has been widely interpreted as the thermodynamic energy required in forming unit area of new unstrained surface by cleaving and the second right hand side term in Eq. (1) as a term which separates the surface tension on liquid from that on a solid.

Claims have been made that the derivations of the Shuttleworth equation are flawed [e.g. 7-14]. The issue is conceptually difficult and prone to controversy [15-20]. In several recent reviews, the criticism of applying the Shuttleworth equation has been dismissed as incorrect, e.g. [3,15,21] and the statements, supporting its use [2-5,15,22-33] have been firm.

In this paper, it is shown that the interpretation of the Shuttleworth equation as a relation between surface tension and surface energy on an unstrained crystal is inappropriate. It is also revealed, by precise mathematical derivation, how the misunderstanding has arisen.

In order to avoid confusion between mathematics and the physical interpretation we first outline the mathematical background of the problem without any reference to physics.

Any function $y(x)$ can be presented as a sum of a constant term and a variable term as

$$y(x) = y_0 + h(x) \tag{2}$$

for which $y(x_0) = y_0$ is a constant that is not a function of x.

Dividing Eq. (2) by x yields

$$z = z_0 + z_h \tag{3}$$

where $z = y/x$; $z_0 = y_0/x$; $z_h = h/x$. The derivative θ of y with respect to x is

$$\theta = \frac{\partial y}{\partial x} \tag{4}$$

which, because $\partial y_0/\partial x = 0$, reduces to

$$\theta = \frac{\partial h}{\partial x} \tag{5}$$

Inserting $y = xz$ into Eq. (4) yields

$$\theta = \frac{\partial (xz)}{\partial x} = z + x\frac{\partial z}{\partial x} \tag{6}$$

Equations (5) and (6) are alternative and equally valid equations for the derivative θ.

For clarity, the original definitions and notations of Shuttleworth [1] are used in the following. Shuttleworth based his derivation on that the work done in straining a crystal equals the increase in the total surface Helmholtz free energy, so that

$$\gamma = \frac{\partial H}{\partial A} \tag{7}$$

Shuttleworth's [1] explanation for his derivation reads as follows.

"*Consider a crystal in which the surface tension is balanced entirely by external forces. If these are the only external forces that are applied to the crystal there will be neither stress nor strain in the volume of the crystal and any infinitesimal distortion will cause no change in the volume energy of the crystal; the work done by the external forces will be equal to the increase in surface energy. Suppose the crystal is deformed so that a square, of area A, in the crystal face is deformed into a rectangle whose sides are parallel to the square. An amount of work* $\gamma_1 dA_1 + \gamma_2 dA_2$ *must be done against the surface stress, where* γ_1 *and* γ_2 *are the components of the surface stress perpendicular to the sides of the square, and* dA_1 *and* dA_2 *are the increases in area in these two directions (for this kind of deformation no work is done against any shear component of the surface stress). Provided the deformation is reversible and occurs at constant temperature, the additional work is equal to the increase in surface free energy of the square,* $\gamma_1 dA_1 + \gamma_2 dA_2 = d(AF)$*; eq. (S2). For an isotropic substance, or for a crystal face with a three- (or greater) fold axis of symmetry, all normal components of the surface stress equal the surface tension and equation (S2) reduces to*

$$\gamma = \frac{\partial (AF)}{\partial A} = F + A\frac{\partial F}{\partial A} \tag{8}$$

where dA is the total increase in area."

As noted in Section 1, Eq. (8) has been derived, not only as originally done by Shuttleworth, but by many alternative approaches. For example, a derivation by the fundamental equations of thermodynamics has been used by many [2-4,21,23-25]. Our aim here is not to reveal problems in each of these derivations separately. Instead, we submit a general and compelling argument by showing that the interpretation of Eq. (8) as a relation between surface tension and the surface energy on an unstrained solid is meaningless regardless of how it is derived.

As outlined in Section 2, the Helmholtz free energy $H = AF$ can be presented as

$$H(A) = H_0 + H_h(A) \qquad (9)$$

Note that no assumptions are made in Eq. (9) of the physical origins or interdependence of H_0 and H_h. The term H_0 is simply the total Helmholtz free energy *in the unstrained state* and the term H_h is the total Helmholtz free energy *stored in straining*, regardless of the physical processes involved.

Here, analogously with the derivation of Eq. (5), $\partial H_0/\partial A = 0$. Differentiating Eq. (9) with respect to A thus yields

$$\gamma = \frac{\partial H_h}{\partial A} \qquad (10)$$

In mechanics, stress is defined as the strain derivative of the free energy stored in straining. Thus, Eq. (10) is the definition of the tangential surface stress, i.e. surface tension, as it was called by Shuttleworth [1].

We have thus shown that Eqs. (8) and (10) are the same. In other words, by applying mathematics, Eq. (8) reduces to Eq. (10). With this in mind it is now easy to see how the

Shuttleworth equation should be interpreted. Shuttleworth equation *equals the mechanical definition of surface tension*.

By the derivation above it also becomes clear how the Shuttleworth equation should *not* be interpreted. Because it reduces to a basic definition, it does not provide an additional law of surface physics. By a mere definition, one cannot prove that a non-zero excess surface tension exists or tell anything of the origins of it. In particular, the common interpretation of F in Eq. (8) as the energy per unit surface area spent in forming new unstrained surface is false, since the mechanical definition of surface tension relates to straining a surface at constant number of atoms and not to forming new surface by cleaving or accretion of atoms at constant strain.

Consequently, evaluation of the surface stress should be based on its mechanical definition as outlined by Gurtin and Murdoch [34] and Wolfer [35].

Acknowledgements

This work was funded by the Academy of Finland and Tekes. Thanks are due to M. Pajari, M. Tikanmäki and K. Kolari for many fruitful discussions and J. Molarius, P. Koukkari and C.T. Campbell for comments on the manuscript.

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