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Comment on "Misinterpretation of the Shuttleworth equation"

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Abstract

In a published paper (Scripta Materialia, **2012**, 66, 627–629), it is concluded that the so-called Shuttleworth equation holds no implications for the relationship between surface tension and surface energy. In this correspondence, we provide clarifications to demonstrate that this conclusion is not valid.

In Ref. 1, Makkonen asserts that the so-called Shuttleworth equation 'reduces to the definition of surface tension derived from mechanics' and that 'it does not provide an additional law of surface physics.' We respectfully disagree with Makkonen's interpretation.

Shuttleworth (1949) demonstrated[2] that 'the surface tension of a crystal face is related to the surface free energy by the relation

$$\gamma = F + A(dF/dA) \tag{1}$$

where A is the area of the surface', γ is the surface tension, and F is the specific surface free energy, with $F = H/A$, H being the total Helmholtz free energy.

Since then, numerous claims both in support[3–7] and criticism[8–13] of this equation's derivation and its consistency with Hermann's mathematical structure of thermodynamics have been raised. We do not intend to stir these discussions further; rather, our aim is to challenge Makkonen's viewpoint as presented in Ref. 1.

Let us first clarify the terms *surface tension* and *surface stress*. In the literature, there are cases where surface tension is defined as the reversible work required to create a surface per unit area, similar to Gibbs' introduction.[5] Nevertheless, when Shuttleworth states 'the surface tension is the tangential stress,' he is specifically referring to surface stress within the surface layer in his equation and discussions.

Let us now explore Makkonen's perspectives. Makkonen defines surface stress as the strain derivative of the total free energy, i.e.

$$\gamma = \frac{\partial H}{\partial A} \tag{2}$$

This definition is certainly accurate but not aligned with Makkonen's intended use. Expanding the differential dH as $AdF + FdA$ indeed yields Eq. (1). However, there are a few considerations to note here. Makkonen claims that Eq. (2) is the definition of stress 'in mechanics', but this is not accurate. Rather, it is the definition of stress in the thermodynamics of deformation.[14] The definition of stress in mechanics is typically based on Cauchy's stress principles, representing the surface force per unit area (or line) that tends to return the deformed mass to its mechanical equilibrium state. This understanding of stress predates the introduction of free energy. When discussing surface stress, it is essential to consider the *excess* stress (either positive or negative) in surface atoms compared to bulk atoms, necessary to keep surface atoms in their positions as if they were in the bulk. While the interpretation of excess properties dates back to the era of Gibbs, it extends beyond free energy and can relate to any extensive thermodynamic property. Therefore, the definition of surface stress is not contingent upon the interpretation of free energy. Shuttleworth effectively discusses excess stress without directly referring to Gibbs' formulation.

Shuttleworth interprets an infinitesimal elastic change in the surface of a solid in terms of both mechanics and thermodynamics, which lead, respectively, to the left and right sides of his equation. Makkonen, on the other hand, solely relies on thermodynamic evaluations and asserts that the Shuttleworth equation is trivial. This approach oversimplifies the matter. To draw a parallel in fluid dynamics, it is akin to defining the components of the velocity field for an incompressible flow as derivatives of the stream function ($u = \partial\psi/\partial y$, $v = -\partial\psi/\partial x$) and concluding that the law of continuity holds no additional implication and essentially reduces to the definition of velocity (since it inherently satisfies itself when defined through the stream function). It is also analogous to stating that the Young-Laplace equation, which estimates the pressure difference over a curved interface, is essentially a result of static equilibrium and basic geometry. We agree with Makkonen in acknowledging that the Shuttleworth equation is not a 'law of surface physics' but rather an equation, as initially asserted by Shuttleworth himself.

Additionally, Makkonen states, 'the evaluation of surface stress should be based on its mechanical definition, as outlined by Gurtin and Murdoch[15] and Wolfer.[16]' Gurtin and Murdoch's work does not directly reference free energy, and Wolfer defines surface stress as $\partial F/\partial\epsilon$ (ϵ being the strain, similar to the Gibbs formulation). Deriving Eq. (2) from $\partial F/\partial\epsilon$ requires keeping A constant, or essentially neglecting FdA in contrast to AdF. This essentially brings Makkonen's arguments back to Gutman's objections to Shuttleworth,[8] which have been thoroughly discussed by Kramer and Weissmüller.[5] While thermodynamic properties need to be interpreted in their unstrained state, this does not imply that, in an Eulerian derivation where measurements are taken in a deformed state (similar to Shuttleworth's approach), one could neglect dA meanwhile the derivation.

To sum up, is Eq. (2), as used by Makkonen, incorrect? No, but referencing $\partial F/\partial\epsilon$ introduces unnecessary confusion regarding the proper definition of specific free energy.[5] A simpler and more appropriate formulation could be to simply relate the work required for infinitesimal deformation to the differential of the extensive total free energy, similar to Shuttleworth's approach. It is still appropriate for Makkonen to use $F = H/A$ (similar to Shuttleworth), in contrast to several other works that use $F = \partial H/\partial A$,[10,12,17] as with the latter definition it is impossible to derive Eq. (1) from Eq. (2).

Now, what are the implications of the Shuttleworth equation? The Shuttleworth equation is designed specifically for properly defined elastic strains and should not be interpreted beyond its intended scope. For instance, Gutman's arguments[8] concerning the movement of atoms from the bulk to the surface, as in the case of liquids, are not appropriate, because Shuttleworth explicitly hedged 'provided the deformation is reversible'.

Regarding liquids, although dF/dA is zero, which simplifies the Shuttleworth equation to $\gamma = F$ (making it trivial for liquids), it should not be applied in this context. This is due to the pressure gradient at the surface relative to the bulk, which introduces a source of irreversibility. Even though the Shuttleworth equation coincidentally describes the end state of this process correctly, its derivation is not suitable for liquids. It would have been better if Shuttleworth had stated this explicitly.

Kramer and Weissmüller simply illustrate how the surface energy of solids may change without causing surface stress.[5] A broader discussion is available in Ref. 18, where it is elaborated how solids may have more than one stress-free configuration. Therefore, one excellent application of the Shuttleworth equation could be in wetting problems. In these scenarios, the surrounding thermodynamic conditions, such as interfacial free energy, can alter the stress distribution within the solid without changing its mechanical response.

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