



Discussion

Comments on the article entitled “Incompatibility of the Shuttleworth equation with Herman’s mathematical structure of thermodynamics” by D.J. Bottomley, Lasse Makkonen and Kari Kolari [Surface Science 603 (2009) 97]

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1. Introduction

In a recent paper Bottomley et al. [1] have questioned the validity of the so-called Shuttleworth equation relating surface stress, surface tension and the strain derivative of the surface tension as they found it to be “inconsistent with Hermann’s mathematical structure of thermodynamics”. The paper has drawn several comments [2] (see also [3]); two of them have been submitted as formal comments to this journal [4,5]. These two comments grossly contradict each other, one supporting the view of Bottomley et al. the other one denouncing it as plain nonsense. In my comment I will show that the argument of Bottomley et al. is incorrect, firstly because the theory of Hermann concerns independent variables that span a Euclidian space (and not variables where one is the product of two others) and, secondly, by a different derivation of the Shuttleworth equation.

I furthermore comment on the definition of interface thermodynamic potentials and excess quantities since the adaption of Gibbs’ thermodynamics to modern requirements has often led to rather confused treatments (even in textbooks). In Section 4 finally, I point out the qualitative and quantitative differences of the “surface tensions” used in various disciplines.

To have a common basis for the discussion to follow, let me (in agreement with most authors) define the surface (interface) tension as the isothermal work per area to create a new surface (interface) under particular experimental side conditions. To avoid confusion I would tend to abstain from using terms such as

“mechanical surface tension” [4]. For a surface in ultrahigh vacuum with a constant coverage of adsorbates the surface tension γ is the Helmholtz free energy $F^{(s)}$ per area A which has independent variables the temperature T , the elastic strain components ε_{kl} , and the “surface excess” particle numbers $n_i^{(s)}$ (for adsorbates e.g. see also Section 3).

2. Derivation of the Shuttleworth equation

The Helmholtz free energy $F^{(s)}(T, \varepsilon_{kl}, n_i^{(s)})$ of the surface has the form

$$F^{(s)}(T, \varepsilon_{kl}, n_i^{(s)}) = U^{(s)} - S^{(s)}T + \sum_i \mu_i n_i^{(s)} \equiv A\gamma(T, \varepsilon_{kl}, n_i^{(s)}) \quad (1)$$

in which $U^{(s)}$ is the surface energy including the energy of elastic deformation, $S^{(s)}$ the surface entropy, and μ_i are the chemical potentials for the excess particles. Because of the assumed homogeneity of the system, $F^{(s)}$ is proportional of the surface area and therefore an “extensive quantity”. This means if one considers an enlargement of the area by adding the amount ΔA to the system the free energy would increase by $\Delta F^{(s)} = \gamma \Delta A$. By invoking the first thermodynamic principle that the total differential dU is the sum of the applied (here mechanical) work δW and the supplied isothermal heat $\delta Q = TdS$ the total differential of $F^{(s)}$ becomes

$$\begin{aligned} dF^{(s)}(T, \varepsilon_{kl}, n_i^{(s)}) &\equiv d(A\gamma(T, \varepsilon_{kl}, n_i^{(s)})) \\ &= -S^{(s)}dT + A \sum_{kl} \tau_{kl}^{(s)} d\varepsilon_{kl} + \sum_i \mu_i dn_i^{(s)} \end{aligned} \quad (2)$$

in which A is the area and $\tau_{kl}^{(s)}$ are the components of the surface stress tensor. The indices k, l denote the orientations in the surface

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plane. The second term thus describes the differential form of the mechanical work on the surface. For isotropic systems the surface stress is therefore

$$\tau^{(s)} = \left. \frac{\partial F^{(s)}}{\partial A} \right|_{T, n_i^{(s)}} \quad (2a)$$

if ∂A is the elastic expansion of the surface area. It may look a bit too meticulous to keep the variables in the notation. It is however very necessary to bear in mind the independent variables (that are controlled externally by the experiment), since the work required to create a surface and therefore the surface tension, depends on the experimental conditions (see Section 4). From Eq. (2) we see that the total differential of $F^{(s)}(T, \varepsilon_{kl}, n_i^{(s)})$ involves strain of the surface area A . In the product $A\gamma$ of Eq. (2) strain therefore affects the area directly and also the surface tension γ . Hence we need to write

$$d(A\gamma(T, \varepsilon_{kl}, n_i^{(s)})) = \gamma dA + Ad\gamma = \gamma A \sum_{kl} \delta_{kl} d\varepsilon_{kl} + Ad\gamma \quad (3)$$

Note that dA here explicitly means the variation of the area by strain, not a variation of the considered area by an amount ΔA ! As noted above, in the latter case we have simply $\Delta F^{(s)} = \gamma \Delta A$. It seems to me that most of the confusion about the Shuttleworth equation arises from the insufficient distinction between the two cases. Inserting (3) into (2) leads to the differential form of γ

$$d\gamma = -s^{(s)} dT + \sum_{kl} (\tau_{kl}^{(s)} - \gamma \delta_{kl}) d\varepsilon_{kl} + \sum_i \mu_i d\Gamma_i^{(s)} \quad (4)$$

Here $d\Gamma_i^{(s)} = dn_i^{(s)}/A$, so that $\Gamma_i^{(s)}$ are the excess numbers of particles i per area, in other words the coverage of the surface with adsorbate i . The Shuttleworth equation (or rather one particular form of it) follows immediately from (4), namely

$$\left. \frac{\partial \gamma}{\partial \varepsilon_{kl}} \right|_{T, \Gamma_i} = \tau_{kl}^{(s)} - \gamma \delta_{kl} \quad (5)$$

Bottomley et al. now argue that (5) is not valid because the term $\gamma dA + Ad\gamma$ “is inconsistent with the Hermann’s formal structure thermodynamic theory” in which terms of the form $x_i dy_i + y_i dx_i$ must not occur in differentials of extensive thermodynamic potentials. While this statement is correct, it has no bearing on the issue as Hermann’s formal theory concerns the properties of functions defined on the Euclidian space of (independent) Cartesian coordinates. For the five-dimensional space of the ideal gas these coordinates would be U, T, S, P and V (see [6] p. 260ff). $F^{(s)}, A$ and γ do not span a Euclidian space as $F^{(s)} = \gamma A$ by definition. The surface free energy $F^{(s)}$ is proportional to the area since thermodynamic potentials are extensive quantities, that is, for homogenous phases as assumed here they are proportional to the amount of material involved. The corresponding equation for the free energy of bulk systems F would be $F = fV$ in which V is the volume and f is the volume specific free energy. This does not make f and V conjugate variables as P and V are.

Furthermore, if I understood Hermann’s treatise correctly, the terms “thermodynamic potential” and “conjugate variables” to which Bottomley et al. frequently refer are not part of the mathematical theory. Hermann merely refers to these terms to make contact between mathematics and conventional thermodynamics. Neither Hermann nor most conventional treatments of thermodynamics deal with volume specific quantities such as $f = F/V$ for which again one can derive an equation that is equivalent to the Shuttleworth equation.

Aside from this formal argument one can easily convince oneself that the Shuttleworth equation is correct by calculating $\partial\gamma/\partial\varepsilon_{kl}$ directly from the definition of the surface tension as

$$\gamma \equiv F^{(s)}(T, \varepsilon_{kl}, n_i^{(s)})/A(\varepsilon_{kl}) \quad (6)$$

The dependence of the area on the strain for infinitesimally small strains is

$$A(\varepsilon_{kl}) = A|_{\varepsilon_{kl}=0} (1 + \varepsilon_{11})(1 + \varepsilon_{22}) \quad (7)$$

with ε_{11} and ε_{22} the components of strain in the surface plane.

Derivation of (6) with respect to ε_{kl} leads to

$$\left. \frac{\partial \gamma}{\partial \varepsilon_{kl}} \right|_{\varepsilon_{kl}=0} = \left. \frac{\partial F^{(s)}}{\partial \varepsilon_{kl}} \frac{1}{A} \right|_{\varepsilon_{kl}=0} - \frac{F^{(s)}}{A} \delta_{kl} \Big|_{\varepsilon_{kl}=0} \quad (8)$$

The first term on the right hand side is the surface stress $\tau_{kl}^{(s)}$ (see Eq. (2))

$$\tau_{kl}^{(s)} = \frac{1}{A} \left. \frac{\partial F^{(s)}}{\partial \varepsilon_{kl}} \right|_{\varepsilon_{kl}=0} \quad (9)$$

and the second term is the surface tension γ . We have therefore recovered the Shuttleworth equation (5) without making use of the incriminated (but nevertheless correct) Eq. (3). The Shuttleworth equation is also easily verified for any concrete model of a solid.

3. How to define surface thermodynamic potentials and excess quantities

For all the credit which Gibbs deserves it must be said that his treatment of surface thermodynamics was designed in days when even the atomic structure of solids was not established and therefore does not meet present-day requirements where we have not only the atom structure of surfaces in mind but wish to consider also the thermodynamics of entities on a surface such as atomic steps and islands. For example Gibbs has defined the thermodynamic position of the interface (“dividing plane”) such that

$$\sum_i \mu_i n_i^{(s)} = 0 \quad (10)$$

For the standard surface science case of a single adsorbate on a solid surface this condition leads to the awkward concept of an interface position moving back and forth with coverage inside one atom layer. The concept of Gibbs also does not allow for partial equilibria between certain objects on the surface. An island for example may well possess the equilibrium shape but nevertheless be engaged in an Ostwald ripening process, i.e. in a non-equilibrium situation with respect to its size. Partial equilibria are also considered in adsorption phenomena where one rarely takes dissolution into the bulk into account because of the slowness of the process.

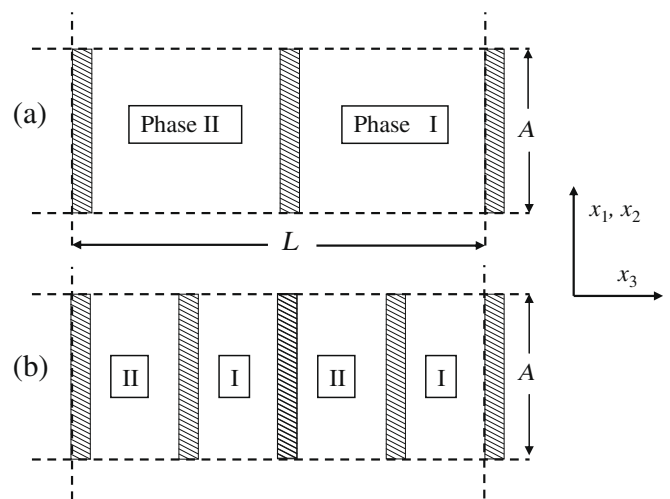


Fig. 1. A supercell of two phases and interface regions between them.

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