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Alternative reference system in the thermodynamics of solid elastic electrodes

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Abstract Basic quantities in the thermodynamics of the solid elastic electrode are the surface tension tensor g_{mn} and the work needed for the formation of the surface (interface) γ. It is scarcely mentioned explicitly anywhere that these intensive (specific) quantities are related to the surface of the elastically deformed electrode. On the other hand, in the thermodynamics of the volume elasticity, the free energy density of the deformed solid is related to the volume of the undeformed solid. In this paper, we introduce equivalently the undeformed surface of the solid elastic electrode as reference for both the surface tension tensor and the work of formation of the surface. Generalizing the analysis of two model systems, we deduce the corresponding alternative form of the Shuttleworth equation, where the two quantities appear as generalized force and generalized potential, and discuss consequences for the formulation of the differential of the surface excess of the internal energy.

Keywords Solid electrode · Surface thermodynamics · Shuttelworth equation

Introduction

In spite of a long history [1–6], the surface tension of solid electrodes has attracted much research in the past few years [7–16], partly with controversial statements and conclusions. A clear evidence of the complexity of the problem gives us the fact that in his thermodynamic work, Gibbs [1] did not give a detailed treatment of the surface tension at the solid–liquid interface. There is only the statement that the surface tension g and the work needed for the formation of the surface (interface), γ, are different from each other, in contrast to the interface between liquids, where the two quantities are identically the same. The connection between the two quantities has been formulated first by Shuttleworth [3]. Though questioned by several authors [12, 15], the now usually accepted formulation [7, 13] is given (in its tensor form) by

$$(g_{mn})_{\varepsilon=0} = \gamma_{\varepsilon=0}\delta_{mn} + \left(\frac{\partial\gamma}{\partial\varepsilon_{mn}}\right)_{\varepsilon=0}, \tag{1}$$

where ε_{mn} is the 2D-tensor of elastic deformation. Actually, Eq. (1) is valid at ε_{mn}=0 (denoted by the subscript ε=0), a restriction, which is usually not mentioned explicitly. Additional contributions do occur for small but finite deformation, as pointed out recently [11, 14, 16].

There is another peculiarity, which has been either overlooked or it has been regarded at least as unimportant: γ and g_{mn} are specific quantities, which are both related to the deformed surface. In the present article, we establish an alternative reference system in the theory of the surface tension of the solid elastic electrode, which is connected with the undeformed surface. As successfully done in [16], the derivation makes use of model systems. As we show below, the resulting alternative for the Shuttleworth Eq. (1) takes the following differential form

$$dw = f_{mn}d\varepsilon_{mn}, \tag{2}$$

where w and f_{mn} are the work of formation of the deformed electrode related to the surface of the undeformed electrode and the tensor of the surface tension of the deformed electrode related to the line on the surface of the undeformed electrode, respectively. Consequences for the thermodynamic formulation of the internal surface energy

Dedicated to the memory of K. Schwabe

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are discussed. For the sake of simplicity, we suppose throughout the present derivations that the electrode material is homogeneous and isotropic.

Undeformed electrode as reference system

As already mentioned, in the common theory of the surface tension of the solid elastic electrode, the relevant intensive quantities γ and g_{mn} are related to the deformed surface. This is in striking contrast to the thermodynamics of the (volume) elasticity [17–19], where volume and surface of the undeformed solid play an important role. Indeed, in the linear theory of elasticity, the free-energy density of the deformed solid is related to the volume of the undeformed solid, and the elastic forces are related to the surface of the undeformed solid. Applying this approach to electrochemistry, the work for the formation of the deformed surface has to be related to the surface of the initial undeformed electrode and the force (tensor) of the surface tension to the line on the surface of the initial undeformed electrode. To elucidate the consequences of choosing the undeformed electrode as the reference system, two model systems are considered, the spherical electrode and the cylindrical electrode.

Spherical electrode

For the spherical electrode with the initial undeformed surface $A_0=4\pi a^2$ with radius a, one can relate the differential elastic change of the undeformed surface $\mathrm{d}\varepsilon=\mathrm{d}A/A_0$ to the deformation in the volume by

$$d\varepsilon = 2dr/a, \tag{3}$$

where dr is the differential change of the radius due to the deformation. It should be mentioned that Eq. (3) is valid only for the case of a spherical deformation of the spherical electrode. Let us now denote the work of formation of the deformed surface relative to the undeformed surface area as w. For the differential dw, one obtains from the energy conservation law

$$4\pi a^2 dw = \Delta p 4\pi r^2 dr, \tag{4}$$

where Δp is the difference between the inner and outer pressures. The latter can be expressed via the Laplace formula [3, 20] by the surface tension g of the deformed electrode surface, related to the line on the surface of the deformed spherical electrode as

$$\Delta p = \frac{2g}{r} = \frac{2f}{a}\left(\frac{a}{r}\right)^2. \tag{5}$$

Here in the second step, f is the surface tension of the deformed electrode surface, related to the line on the surface of the undeformed spherical electrode where we took into account $fa=gr$. Combining Eqs. (3), (4), and (5), one obtains up to first order in the deformation

$$dw = f\,d\varepsilon \tag{6}$$

as the alternative formulation of the Shuttleworth equation. Considering that other variables are kept constant, it can be written for ε=0 in a form more similar to the well known expression (Eq. 1) as

$$(f)_{\varepsilon=0} = \left(\frac{\partial w}{\partial \varepsilon}\right)_{\varepsilon=0}. \tag{7}$$

The difference of Eq. (1) (in its isotropic form) is evident and is a result of using the undeformed electrode as a reference system. The transition between both forms is rather simple considering $A_0w=A\gamma$ and, hence, $A_0dw = \gamma dA+Ad\gamma$. Then one obtains from (Eq. 7)

$$\begin{aligned}(f)_{\varepsilon=0} &= \frac{dA}{A_0 d\varepsilon}(\gamma)_{\varepsilon=0} + \left(\frac{A}{A_0}\frac{\partial\gamma}{\partial\varepsilon}\right)_{\varepsilon=0} \\ &= (\gamma)_{\varepsilon=0} + \left(\frac{\partial\gamma}{\partial\varepsilon}\right)_{\varepsilon=0},\end{aligned} \tag{8}$$

where the definition of $d\varepsilon = dA/A_0$ has been taken into account. With $f(\varepsilon=0)=g(\varepsilon=0)$, Eq. (8) gives directly the common Shuttleworth Eq. (1) in the case of the spherical electrode.

A further remark seems to be important. The common equation connects the surface tension with the work of formation and its derivative with respect to the deformation, with volume and area of the deformed electrode as reference. By contrast, the alternative formulation (Eq. 7) gives the surface tension directly as the derivative of the work of formation, but now, with the initial undeformed electrode as reference. Thus, this form allows one immediately to identify the energy (of formation of new deformed surface related to the initial undeformed surface) w as the generalized potential of the generalized force (related to the line on the undeformed surface) f.

Cylindrical electrode

Let us consider the cylindrical electrode with the initial undeformed surface area per unit length l of $A_0/l = 2\pi a$ with cylinder radius a. The radius of the deformed cylinder is a+dr. We denote locally the direction of increasing azimuthal angle by a lower index 1. Under the cylindrical deformation, the strain in the azimuthal direction is the same as in radial direction (due to the linear relations

between radius, circumference, and surface area of the cylinder), $d\varepsilon = d\varepsilon_1 = dA/A_0$, and is related to the change of the surface. Hence, one has

$$d\varepsilon_1 = \frac{dr}{a}. \tag{9}$$

It should be mentioned that Eq. (9) is valid only for the case of a cylindrical deformation of the cylindrical electrode. With the analog meaning for w, as in the spherical case, the conservation law of energy is now

$$2\pi a dw = \Delta p 2\pi dr. \tag{10}$$

The force of the surface tension in the direction 1, f_1 or g_1, is related to the line length in axial direction, which remains unchanged and, therefore, f_1=g_1. Consequently, the Laplace formula for the cylindrical case is

$$\Delta p = \frac{g_1}{r} = \frac{f_1}{a}\frac{a}{r}. \tag{11}$$

Combining Eqs. (9), (10), and (11), one arrives at the alternative Shuttleworth equation for this case,

$$dw = f_1 d\varepsilon_1. \tag{12}$$

As before, the reference for w and f_1 is the initial undeformed cylindrical electrode. Again, the generalized energy quantity w acts as the generalized potential for the generalized force quantity f_1.

General form of the alternative Shuttleworth equation

Equations (6) and (12), for the spherical and the cylindrical electrode, are special cases of the Shuttleworth equation in the alternative reference system. The general form is easily deduced from these two special cases as

$$dw = f_1 d\varepsilon_1 + f_2 d\varepsilon_2, \tag{13}$$

where the lower indices 1 and 2 indicate the principal axes system for the surface stress tensor f_{mn} and for the tensor of the surface deformation ε_{mn}:

$$f_{mn} = \begin{pmatrix} f_1 & 0 \\ 0 & f_2 \end{pmatrix} \quad , \quad \varepsilon_{mn} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \tag{14}$$

For an arbitrary orientation of the coordinate system on the electrode surface, one has to replace Eq. (13) by

$$dw = f_{mn} d\varepsilon_{mn}, \quad f_{mn} = \frac{\partial w}{\partial \varepsilon_{mn}}. \tag{15}$$

This equation represents the alternative to the conventional Shuttleworth Eq. (1) in the tensor form under the condition that the intensive quantities for formation energy and force are related to the initially undeformed electrode. The roles of w and f_{mn} as generalized potential and generalized force are self-evident.

Internal surface energy

By using the initial undeformed surface as the reference, the surface excess of the internal energy U^s is directly given as the product of the work of formation of the surface w, and the electrode surface A_0 in the undeformed state:

$$U^s = wA_0. \tag{16}$$

Therefore, one becomes for the differential

$$dU^s = wdA_0 + A_0 dw, \tag{17}$$

or with Eq. (15)

$$dU^s = wdA_0 + A_0 f_{mn} d\varepsilon_{mn}. \tag{18}$$

From its form, this equation is essentially the same as Eq. (1) in [7] (herein referred to as LSKP), which reads as

$$dU^s = \gamma dA_p + A g_{mn} d\varepsilon_{mn}. \tag{19}$$

Comparing Eqs. (18) and (19), one sees that in both cases the tensor of the surface deformation is connected only with elastic deformations. A closer look is needed to elucidate the non-trivial differences between the two equations. Concerning the first term, it is merely stated in LSKP that dA_p is a change in area due to plastic deformation, such as cleavage, in which the number of surface atoms is changed. In our Eq. (18), it becomes clear that dA_0 is a change in the initial and undeformed surface. In a solid, such a change can be achieved *solely* by cleavage. Except for this special case of cleavage, any plastic deformation with an infinitesimal change in area changes the energy as $\delta W^S = \overline{\gamma}(A, history)\delta A_p$, which

cannot be included in the total differential of a state variable.

Thus, also in the LSKP equation, the only process allowed for the changed A_p is again the cleavage process. Though it has not been mentioned explicitly in LSKP and in other former publications, the work of formation γ is related to this deformed surface, and the stress g_{mn} represents the force components per unit line on the elastically deformed surface. The proof is given in the above derivation by comparing the two formulations of the Shuttleworth equation in the case of the spherical electrode. Concerning the area A in the LSKP Eq. (19), we mentioned at first the following: As in the thermodynamics of volume elasticity [19], in Eq. (18), the densities w and f_{mn} are related to the undeformed surface and its unit line, respectively. In contrast to the LSKP equation, in the differential for the inner surface energy (Eq. 18), the deformation does occur only up to first order as in the linear theory of elasticity. However, both equations become identical for infinitesimal deformation according to

$$\begin{aligned} w(\varepsilon_{mn}=0) &= \gamma(\varepsilon_{mn}=0), \\ f_{mn}(\varepsilon_{mn}=0) &= g_{mn}(\varepsilon_{mn}=0), \\ A_0(\varepsilon_{mn}=0) &= A(\varepsilon_{mn}=0). \end{aligned} \tag{20}$$

Now we show that the LSKP equation is valid only at zero deformation. Using the principal axes system again, one has the relations

$$\begin{aligned} &f_1 = (1+\varepsilon_2)g_1\ ,\ f_2 = (1+\varepsilon_1)g_2\ , \\ &A = A_0(1+\varepsilon_1)(1+\varepsilon_2) \end{aligned}\ . \tag{21}$$

Consequently, the second term of the exact Eq. (18) can be rewritten as.

$$\begin{aligned} A_0(f_1 d\varepsilon_1 + f_2 d\varepsilon_2) &= A_0[(1+\varepsilon_2)g_1 d\varepsilon_1 + (1+\varepsilon_1)g_2 d\varepsilon_2] \\ &= A\left[\tfrac{g_1 d\varepsilon_1}{(1+\varepsilon_1)} + \tfrac{g_2 d\varepsilon_2}{(1+\varepsilon_2)}\right]. \end{aligned} \tag{22}$$

Therefore, the second term in the LSKP Eq. (19) is indeed valid only for zero deformation. It is not applicable to an electrode, which is already elastically deformed.

Conclusions

It has been explicated that the reference system in the usual formulation of the thermodynamics of the solid elastic electrode is the deformed surface of the electrode, whereas, in the thermodynamics of volume elasticity, specific quantities as the free-energy density are related to the volume of the undeformed solid. It has been shown that in the frame of Hooke's law, an equivalent formulation is possible also for the thermodynamics of the solid elastic electrode. Then the work for the formation of the deformed surface related to the surface of the initial undeformed electrode, w, and the force tensor of the surface tension related to the line on the initial undeformed surface, f_{mn}, appear as the basic quantities. The differential connection between both is the alternative Shuttleworth equation. It has the general form of a connection between a generalized potential, in this case w, and a generalized force, in this case f_{mn} (Eq. 15).

The alternative expression (Eq. 18) for the differential of the internal surface energy is formally similar to the usually accepted LSKP Eq. (19). However, differences in the detail show that the formulation with the undeformed surface, as reference gives more insight into the underlying processes. Moreover, this equation is not applicable for a pre-existing elastic deformation of the electrode. A detailed formulation of this case will be published elsewhere. In this paper, we would like to stress that the alternative expression (Eq. 18) for the differential of the internal surface energy is valid for both infinitesimal and small but finite deformations. Finally, in any case, the only non-elastic change in area that can be included in the differential of the internal surface energy is the cleavage process.

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