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Simple thermodynamic derivation of the electrocapillary equations

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Abstract

Debate on the equations for surface excess stress and charge density on a solid continues in the literature. The various points of views are supported by complex mathematical argumentations. This hampers forming a unified understanding on the issue. To alleviate the situation, a concise but rigorous thermodynamic analysis is presented here. It shows that the Shuttleworth equation is invalid and the second Gokhshtein equation is incompatible with the thermodynamic formalism. The validity of the Lippman equation and the first Gokhshtein equation depends on the independent variable of the system.

1. Introduction

Understanding on surface excess stress and surface excess charge density is fundamental in surface thermodynamics and electrochemistry. The so called Shuttleworth equation and the Gokhshtein equations are widely used for them. However, the validity of these relations has been frequently questioned and a very lively discussion on them is continuing, e.g. [1-5]. The points of views presented have been supported by extensive verbal and mathematical argumentation, making it difficult to comprehend the key aspects of the issue. The crucial aspects of the problem are, however, quite simple and need not be imbedded into an extensively complex presentation.

The main problem related to derivations of the basic electrocapillary equations has been the wide-spread use of variables that are defined by dividing a total surface excess quantity by the surface area A. These include "excess surface energy density" defined by $\gamma_s = G/A$, where G is the surface excess Gibbs energy, and "surface excess charge density" $q_s = Q/A$, where Q is the surface excess charge. Numerous publications, starting from 1950, include inserting variables defined this way into the fundamental thermodynamic relations or the Maxwell relations.

However, these definitions are incompatible with the mathematical structure of thermodynamics [6,7]. In the thermodynamic theory, an intensive property must be defined as a *derivative of a state function with respect to an extensive property*. Thus the variables used in connection with thermodynamic equations must be of the form $\gamma = \partial G/\partial A$ and $q = dQ/dA$. The erroneous nature of using variables defined as γ_s and q_s in a thermodynamic analysis of surfaces has been thoroughly discussed in the literature [7-12] but, nevertheless, many recent discussions still include this basic error. Simple calculus shows that X/Y equals dX/dY only when $d(X/Y) = 0$. For the thermodynamic variables of a surface this means that (other extensive variables being constant) $d\gamma_s/dA = 0$ and $dq_s/dA = 0$. These are serious

restrictions of the system. In particular, the former restriction, that the excess surface energy density is independent of surface area upon straining, requires that the material in question is a *liquid*.

Here, the issue is clarified by deriving the relevant equations in a rigorous way by using only such definitions that comply with the mathematical theory of thermodynamics.

2. The thermodynamic relations

When straining a liquid, molecules are lifted onto the surface causing an increase in the surface Gibbs energy. When straining of a solid, molecules are not lifted onto the surface in the same manner. Rather, distances between the molecules increase in the lateral direction, which causes an elastic stress, i.e. storing elastic energy. Therefore, in addition to the specific surface energy of creating new surface area, $\gamma^c = (\partial G/\partial A^c)_A{}^e$, we need to define a specific surface elastic energy $\gamma^e = (\partial G/\partial A^e)_{Ns}$ for the process where the surface area changes in such a way that the number of particles at the surface N_s remains constant. Accordingly, here dA^e is the change in the surface area by elastic straining alone.

The starting point of constructing a fundamental thermodynamic equation for a strained surface is the change in the surface Gibbs energy. For simplicity, we assume throughout this analysis that a one-species system and no changes in temperature or pressure, and no phase transitions. In the *general case* of straining, without a surface charge, the fundamental thermodynamic equation for the surface is

$$dG = (\partial G/\partial A^e)_{Ns}\, dA + (\partial G/\partial N_s)_A{}^e\, dN_s \qquad\qquad (1)$$

With the substitution of the definitions of the specific surface energy of creating new surface γ^c and the surface chemical potential μ_s, this is transformed into

$$dG = \gamma^e dA^e + \mu_s dN_s \tag{2}$$

or

$$dG = dG^e + dG^c \tag{3}$$

On the right hand side of eqs. (2) and (3), the first term represents the elastic energy stored in the moving the particles *laterally* further apart from each other, and the second term the excess energy brought by new particles moving *perpendicularly* onto the surface. The change in area due to increasing the number of particles at the surface is $dA^c = (\mu_s/\gamma^c)dN_s$, so that eq. (3) can also be written as

$$dG = \gamma^e dA^e + \gamma^c dA^c \tag{4}$$

One can indeed postulate that there is a way to strain reversibly a soft solid in such a manner that the particles move both laterally and perpendicularly. In such a general case, eq. (4) would apply. However, such a complex situation is outside the scope of the ongoing dispute on the electrocapillary relations, and will not be discussed here. Accordingly, the cases of a liquid and a solid are considered below separately.

Upon straining a *liquid*, $dG^e = 0$ and $dN_s/dA = \gamma^c/\mu_s \neq 0$, Thus, for a liquid system, eq. (4) reads

$$dG = \gamma^c dA \tag{5}$$

Hence, on a liquid, the work spent in creating new surface equals the mechanical work of straining.

Upon straining a *solid*, $dG^e = \gamma^e dA^e \neq 0$ and $dN_s/dA = 0$. Thus, on a solid system, the mechanical work of straining arises solely from the elastic deformation and eq. (4) becomes

$$dG = \gamma^e dA \qquad\qquad (6)$$

The considerations above demonstrate that the independent variable upon straining a liquid is γ^c, while upon straining a solid it is N_s. This difference must be taken into account when considering the fundamental thermodynamic relations, as outlined above. The two cases represented by eqs. (5) and (6), are fundamentally different physical processes, where the operating force vectors are of different magnitude as well as direction.

3. The electrocapillary relations

Next, we consider a solid surface with an electric charge. Due to the similar form of equations (5) and (6) we use, for simplicity, a common notation γ so that for an electrocapillary system involving a liquid $\gamma = \gamma^c$, and for a solid electrode $\gamma = \gamma^e$.

As was demonstrated above, we need to know, prior to writing up the fundamental thermodynamic equation, which is the independent variable in the process. Thus, the process or experiment that is supposed to be described by the theory must determine the terms involved. The fundamental thermodynamic equation for a surface of a solid with a total excess surface charge Q and electric potential E includes an additional term related to the electric surface potential energy.

In analogy with eq. (1), we may now consider what follows from taking either E or Q as the independent variable, i.e. the extensive variable of the thermodynamic equation.

If one follows [1,13] and takes the total excess surface charge Q as the independent variable, then the fundamental thermodynamic relation reads

$$dG = \gamma dA + EdQ \qquad\qquad (7)$$

In writing up the thermodynamic relation (8), one assumes that $q = (\partial Q/\partial A)_\gamma = 0$. The corresponding Maxwell relation is

$$(\partial \gamma/\partial Q)_A = (\partial E/\partial A)_Q \qquad\qquad (8)$$

which is the first Gokhshtein equation. Considering that Q is the independent variable here, equation (8) may be valid e.g. for an experiment where an electrode is charged from an external circuit and disconnected, resulting in elastic elongation [1].

If one instead follows [3,14,15] and considers a system where E is the independent variable, then the corresponding fundamental thermodynamic relation must be written as

$$dG = \gamma dA - QdE \qquad\qquad (9)$$

Note that eq. (9) is not a transform of eq. (7), but a fundamental thermodynamic relation for another system. In this system, E is the independent variable instead of Q. The Maxwell relation for eq. (9) is

$$(\partial \gamma/\partial E)_A = - (\partial Q/\partial A)_E \qquad\qquad (10)$$

that equals

$$(\partial \gamma/\partial E)_A = - q \qquad\qquad (11)$$

which is the Lippman equation. Considering that E is independent variable here, equation (11) is valid e.g. for an experiment where elastic deformation is achieved by applying a

voltage to an ideally polarizable electrode, in which case only the cell voltage can be varied [3,16].

It should be stressed again that in case of a solid electrode, the variable γ in eqs. (8) and (11) equals γ^e. In other words, regardless of the independent variable, the change in the surface energy of a solid electrode is due to an elastic deformation.

4. Discussion and conclusions

The analysis above relies only on the definitions that are compatible with the mathematical structure of thermodynamics and specific to the system in question. No other useful fundamental surface electrocapillary equations can be deduced by a correct thermodynamic treatment. This outlines that the very extensive and complex attempts over more than six decades to derive such equations have unnecessarily complicated the issue. The problems in many of these developments have been confusing the modes of deformation on a liquid and on a solid, as well as including in the analysis variables that are incompatible with the thermodynamic theory.

An example of such problems is that for a system (an unstrained solid) for which dA^e and dN_s in eq. (1) are zero, a relation has been obtained by inserting $G = G^c = \gamma_s A$ into a definition of surface stress $\sigma = dG/dA$. This procedure formally results in the Shuttleworth equation $\sigma = \gamma_s + A(d\gamma_s/dA)$, but includes three errors: 1) A definition of $\gamma_s = G/A$ that is incompatible with the thermodynamic theory, is used in a thermodynamic equation, 2) γ_s is interpreted as γ^c instead of γ^e, i.e. liquid and solid systems are confused, and 3) A misleading illusion of a physical surface stress due to capillarity is created by separating the zero-term

$\sigma = dG^c/dA = 0$ into two non-zero terms. Detailed analysis of such terms [2] is irrelevant as long as their sum equals zero, i.e. the physical variable being analysed does not exist.

The following conclusion can be made based on the analysis in this paper.

- The thermodynamic theory, eq. (6), shows no connection, on a solid, between the surface excess stress σ and specific surface energy of creating new surface γ^c. Thus, the interpretation that the Shuttleworth equation provides such a relationship is invalid.

- Since the fundamental thermodynamic relation, eq. (7) requires that there is no dependence of the specific surface energy γ of a solid on the electric potential E, the second Gokhstein equation cannot be deduced from it. On the other hand, eq. (10) can be transformed into the second Gokhsthein equation only by introducing the variable q_s which is incompatible with the mathematical theory of thermodynamics.

- The derivations leading to eqs. (8) and (11) show that the when the electric potential is an independent variable, the Lippman equation is valid. It follows that the first Gokhstein equation is valid only when the system is such that the total charge is an independent variable. Whether such systems exist is an issue of present dispute [1,3,16].

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