



Some remarks to the derivation of the “generalized Lippmann equation”

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Abstract

In the present communication, an attempt is made to demonstrate (once again) some of the problems with the derivation of the “generalized Lippmann equation” considered to be valid by many researchers for solid electrodes and to address the problems in the framework of the Gibbs model of the interface by using only the basic principles of thermodynamics. By surveying the relevant literature, it has been shown that during the derivation of the equation, it was completely ignored that the Gibbs-Duhem equation (i.e., the electrocapillary equation) is a mathematical consequence which follows directly from the homogeneous degree one property of the corresponding thermodynamic potential function; consequently, the resulting expression cannot be correct. Some alternative approaches have also been considered. The adequacy of the open system and the partly closed system approach has been critically discussed, together with the possibility of introducing new thermodynamic potential functions.

Keywords Interfacial thermodynamics · Electrified solid/liquid interface · Gibbs model · Homogeneous and partly homogeneous functions · Legendre transformation · Gibbs-Duhem equation · Lippmann equation

Introduction

The primary goals of all thermodynamic treatments are to describe heterogeneous systems with interfaces in terms of experimentally accessible quantities and to derive functions which enable one to relate and compare the thermodynamic properties of a system described by one set of physicochemical parameters to those corresponding to different thermodynamic states.

The thermodynamic theory describing the properties of the electrified liquid/liquid interface is quite well developed. The Lippmann equation [1]

$$-\left(\frac{\partial \gamma}{\partial E}\right)_{p,T,\mu_i} = q_M \quad (1a)$$

This paper is dedicated to Professor Fritz Scholz on the occasion of his 65th birthday and in recognition of his great contribution to modern electrochemistry.

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for an ideally polarizable electrode is normally derived using thermodynamics principles and the Gibbs or Guggenheim model of the interface [2–4]. In Eq. (1a), γ is the intensive (interfacial) variable conjugate to the surface area as extensive variable, q_M is the charge density on the metal side of the interface, E is the electrode potential, and μ_i is the chemical potential of component i . This equation has been used successfully many times for the analysis of experimental data, especially for determining the charge density at electrified liquid/liquid interfaces from surface (interfacial) tension measurements.

Unfortunately, for electrodes containing electronically conducting solid phase(s), the correct thermodynamic treatment of the interface is not straightforward, and the thermodynamic theory of solid/liquid interfaces cannot be regarded as entirely correct [2–10]. On the other hand, the measurement of surface parameters at the electrified solid/liquid interface is difficult, and the measuring methods are not without their limitations [11–13]. Some of these issues have been discussed recently in excellent articles and reviews [5–8, 14]. The basic concepts of the Gibbs model of interfaces are summarized, e.g., in refs [2, 11, 15].

Since its inception, the *Journal of Solid State Electrochemistry* (under the chief editorship of Fritz Scholz) has provided a forum for critical discussions and studies on

problems connected with surface thermodynamics. Theoretical debates on the derivation and validity of some pertinent equations provide good examples of these activities; see, e.g., [5–7, 16–18]. However, even after many years of disputes, a consensus regarding the different approaches is still being sought.

With the aim to fill up the gaps and deficiencies in the classical theory, several attempts have been made during the past decades to derive thermodynamic equations for the solid/liquid interface. On the basis of theoretical work published in the literature [19–25] (especially on the basis of the review of Linford [24]), a general electrocapillary equation (Eq. (1)) held to be valid generally for solid electrodes was published in a IUPAC recommendation [26].

$$(\partial\gamma_\pi/\partial E)_{T,p,\mu_i} = -\sigma - (\gamma_\pi - \Upsilon)(\partial\varepsilon_e/\partial E)_{T,p,\mu_i} \quad (1)$$

In Eq. (1), γ_π is the superficial work, E is the electrode potential, Υ is the surface stress, σ is the charge density, p is the pressure, T is the temperature, μ_i is the chemical potential of the component i , and ε_e stands for the elastic strain. This equation has been cited in many publications and is sometimes referred to in the literature as the “generalized Lippmann equation” or the “Lippmann equation for a solid electrode”; see, e.g., [27–31].

In the present work, an attempt is made to demonstrate (once again) some of the problems with the derivation of Eq. (1). In addition, it is also aimed to contribute to the better understanding of the key issues in the field of the thermodynamics of electrified interfaces which are relevant to electrochemistry. Therefore, for simplicity, the discussions are restricted to isotropic plane interfaces in equilibrium systems (similarly as, e.g., in refs. [22–24]) in the absence of (complex) external force fields.

The derivation of the “general electrocapillary equation”

The derivation of Eq. (1) is briefly summarized below (keeping the notation in [24], i.e., using the symbol σ instead of γ_π and q^π instead of σ in ref. [26], respectively). (One should pay attention to the fact that symbol σ has completely different meanings in refs. [20, 22].)

First, the differential of the excess internal energy function $U^\pi(S^\pi, Q^\pi, n_1^\pi, \dots, n_m^\pi, \Omega)$ was defined according to the Gibbs model and written as:

$$dU^\pi = TdS^\pi + \sum_i \mu_i dn_i^\pi + EdQ^\pi + \gamma^s d\Omega \quad (2)$$

The “surface intensive parameter” γ^s has been formally defined in terms of the superficial work, γ^π , and surface stress, Υ , by the equation:

$$\gamma^s = \frac{d\varepsilon_p}{d\varepsilon_{\text{tot}}}\sigma + \frac{d\varepsilon_e}{d\varepsilon_{\text{tot}}}\gamma \quad (3)$$

where

$$d\varepsilon_{\text{tot}} = \frac{d\Omega}{\Omega} \quad (4)$$

is the total strain, $d\varepsilon_p$ is the plastic, and $d\varepsilon_e$ is the elastic strain. In Eqs. (2) and (3), in analogy with Eq. (1), the superscript π designates surface excess quantities. T is the temperature, S is the entropy, σ is the superficial work, Ω is the surface area, E is the potential, Q is the charge, and μ_i and n_i are the chemical potential and excess amount of substance of the species i , respectively.

On the other hand, the excess internal energy has been written in the integral form:

$$U^\pi = TS^\pi + \sum_i \mu_i n_i^\pi + EQ^\pi + \sigma\Omega \quad (5)$$

A “Gibbs-Duhem relation” for the surface has been obtained by differentiation of Eq. (4) and subtraction of Eq. (2) in the form:

$$0 = S^\pi dT + \sum_i n_i^\pi d\mu_i + Q^\pi dE + \sigma d\Omega + \Omega d\sigma - \gamma^s d\Omega \quad (6)$$

Dividing Eq. (6) by Ω yields:

$$0 = s^\pi dT + \sum_i \Gamma_i^\pi d\mu_i + q^\pi dE + \sigma d\varepsilon_{\text{tot}} + d\sigma - \gamma^s d\varepsilon_{\text{tot}} \quad (7)$$

where the superficial quantities are defined by $s^\pi = S^\pi/\Omega$, $\Gamma_i^\pi = n_i^\pi/\Omega$, and $q^\pi = Q^\pi/\Omega$, respectively. Taking into account that:

$$d\varepsilon_{\text{tot}} = d\varepsilon_p + d\varepsilon_e \quad (8)$$

and substituting Eqs. (3) and (8) into Eq. (6) gives

$$0 = s^\pi dT + \sum_i \Gamma_i^\pi d\mu_i + q^\pi dE + d\sigma + (\sigma - \Upsilon) d\varepsilon_e \quad (9)$$

Equation (1) follows directly from Eq. (9).

Doubts about the derivation of Eq. (9)

Problems with the mathematical derivation of Eq. (9) were first pointed out in [32]. It was shown in [32] and later in much more detail in [33] that the conjectures used to derive Eq. (9) fail to hold if the excess internal energy function (U^π) is a homogeneous functions of degree 1. In the review article [24], the author apparently did not question that U^π is a homogeneous function of degree one (it should be noted here that according to the converse of Euler’s theorem on homogeneous functions if Eq. (5) holds, then U^π is necessarily a homogeneous function of degree one [4, 11, 34, 35]), but

simply adopted the rather confusing suggestion in [22, 23] that it is a homogeneous function only, if the relationship is written in the integral form.

However, it can be shown that the derivation followed in [22–24] is mathematically incorrect because of the following major reasons:

According to Euler’s theorem, U^π can be given as:

$$\begin{aligned}
 U^\pi &= \left(\frac{\partial U^\pi}{\partial S^\pi}\right)_{n_1^\pi, \dots, m, Q^\pi, \Omega} S^\pi \\
 &+ \sum_i^m \left(\frac{\partial U^\pi}{\partial n_i^\pi}\right)_{S^\pi, n_1^\pi, \dots, \#j, \dots, m, Q^\pi, \Omega} n_i^\pi \\
 &+ \left(\frac{\partial U^\pi}{\partial Q^\pi}\right)_{S^\pi, n_1^\pi, \dots, m, \Omega} Q^\pi + \left(\frac{\partial U^\pi}{\partial \Omega}\right)_{S^\pi, n_1^\pi, \dots, m, Q^\pi} \Omega \quad (10)
 \end{aligned}$$

or by replacing the partial derivatives with the corresponding symbols

$$U^\pi = TS^\pi + \sum_i^m \mu_i n_i^\pi + EQ^\pi + \gamma \Omega \quad (10a)$$

(γ is the intensive variable conjugate to the extensive variable Ω).

On the other hand, the total differential of U^π ($S^\pi, Q^\pi, n_1^\pi, \dots, n_m^\pi, \Omega$) is

$$\begin{aligned}
 dU^\pi &= \left(\frac{\partial U^\pi}{\partial S^\pi}\right)_{n_1^\pi, \dots, m, Q^\pi, \Omega} dS^\pi \\
 &+ \sum_i^m \left(\frac{\partial U^\pi}{\partial n_i^\pi}\right)_{S^\pi, n_1^\pi, \dots, \#j, \dots, m, Q^\pi, \Omega} dn_i^\pi \\
 &+ \left(\frac{\partial U^\pi}{\partial Q^\pi}\right)_{S^\pi, n_1^\pi, \dots, m, \Omega} dQ^\pi + \left(\frac{\partial U^\pi}{\partial \Omega}\right)_{S^\pi, n_1^\pi, \dots, m, Q^\pi} d\Omega \quad (11)
 \end{aligned}$$

or after replacing the partial derivatives with the corresponding symbols

$$dU^\pi = TdS^\pi + \sum_i^m \mu_i dn_i^\pi + EdQ^\pi + \gamma d\Omega \quad (11a)$$

In Eqs. (10) and (11), the partial derivatives are the same being homogeneous functions of degree 0 of the extensive variables. It follows that the intensive (interfacial) parameter conjugate to the extensive variable Ω is $\gamma = \left(\frac{\partial U^\pi}{\partial \Omega}\right)_{S^\pi, n_1^\pi, \dots, m, Q^\pi}$ and the introduction of two different parameters into Eqs. (2) and (5) is mathematically incorrect, and therefore, Eq. (1) is the result of the misunderstanding or misuse of the mathematical formalism.

Since in refs. [32, 33], the attention was focused only on the mathematical consequences of the homogeneous property of

the fundamental equation, and the problems with the meaning of some of the parameters in Eq. (2) (e.g., why is the introduction of Q^π as an independent variable highly questionable [2]) were not discussed.

On the other hand, as was pointed out first by Gutman [36], Eq. (6) which is often called “the Gibbs-Duhem equation” (see, e.g., ref. [24]) cannot, in fact, bear this name, since it contains differentials of the extensive parameter Ω . This means that equations like Eq. (6) are inconsistent with classical thermodynamics stating that the Gibbs-Duhem equation presents the relationship between the intensive variables in the differential form.

Approaching the problem with the derivation of Eq. (1) from a different point of view

Although the argumentation presented in the previous section is sufficient to demonstrate the incorrectness of the derivation of Eq. (1), it is nonetheless interesting to look at the problem from a different viewpoint.

At the outset, it is worth highlighting two important concepts of theoretical thermodynamics: (i) State principle. According to thermodynamic theory, the thermodynamic state of equilibrium of any system can be completely and uniquely determined by the independent thermodynamic variables. Thermodynamic fundamental relations (state functions, point functions) describe the state (condition) of a system at a given time rather than how the system arrived at that state. The advantage of the use of state functions is that one can tabulate them once for all as functions of the state of the substance and one does not have to be concerned about how the state has been achieved. (ii) Reversible processes. In ref. [7], the author summarizes the key points of the second statement (relevant to the thermodynamics of interfaces) impeccably, so I quote him verbatim here: “surface scientists prescribe a special way of changing A {in ref. [7] A is the surface area denoted by Ω in the present work} so that friction forces, trapped configurations, and multiple pathways are avoided. What they do is focus on (thought) experiments in which the work of forming A is absolutely minimal at every stage so that the value of γ depends only on the value of A and not at all on the path by which A is reached. In the jargon of thermodynamics, this is called the ‘reversible’ path.”

On the other hand, it may be instructive to quote here some paragraphs from one of the papers in which the “dual definition” of the intensive parameter conjugate to the surface area was first introduced. According to the authors of [22], the “thermodynamic formalism” introduced in [21] for one component systems was extended “to multicomponent systems with, in general, nonzero surface excess of matter”.

In ref. [22], the following statements were made: “There are three relevant surface parameters that have been

introduced for the one-component system and have the same meanings in the multicomponent system. If dW_p^s , denotes the reversible work increment to effect an entirely plastic area increment, dA_p , at constant temperature, elastic strain, and surface composition, i.e., at constant chemical potential, then formally

$$dW_p^s \equiv \sigma dA_p \quad (1a)$$

The scalar σ , which symbol for historical and other reasons we now prefer for the property previously denoted by γ (...), is conceptually identifiable with Gibbs' σ or, "the work spent in forming a unit of the surface of discontinuity" (...). This parameter, the surface parameter that appears in homogeneous first-order energy relations (...) in general cannot be properly regarded as the tension to be ascribed to the surface of tension (...) which here will be denoted by f . A measure of this latter parameter may be simply defined if we consider the reversible isothermal surface work increment dW_e^s to effect an entirely elastic surface area increment dA_e , at constant composition for an isotropic surface, whence formally (...):

$$dW_e^s \equiv f dA_e, \quad (1b)$$

This definition then illustrates that f is the surface intensive parameter conjugate to the (surface) elastic stretching process and is the mechanical tension to be ascribed to the surface of tension. In addition to the above-mentioned parameters, it is possible and conceptually useful to define a more general surface-intensive parameter. If dW^s denotes the reversible isothermal work increment to effect a general (part elastic and part plastic) surface area change dA at constant composition then formally (...):

$$dW^s \equiv \gamma^s dA \quad (1c)$$

The parameter γ^s , is thus the surface-intensive parameter conjugate to the general surface area change and, consequently, is in general path-dependent; only for particular systems can this parameter be identified with either of the two above-mentioned surface parameters, σ and f (...).

The definition of f in ref. [21] is given as "... if the surface of tension is isothermally stretched while maintaining the number N^s of atoms associated with the surface constant, then $\gamma^s = f$, where f , called the surface stress, is the mechanical resistance of the surface of tension to the elastic stretching process (...) and has the units of force per unit length. The surface work increment, dW_e^s , required to elastically change the area of the surface of tension by an amount dA_e , is formally written as $dW_e^s \equiv f dA_e$."

A "generalization" of the relevant equations introduced in [16] for one component systems was done in ref. [22] but, unfortunately, without any further explanation from the authors. According to [22]: "it then follows from a comparison of the two possible differential forms of the internal energy

that the Gibbs-Duhem relation for a surface in this system becomes

$$S^\sigma dT + A d\sigma + \sum_i N_i^\sigma d\mu_i + (\sigma - \gamma^s) dA = 0 \quad (2)$$

The parameters of Eq.[2] not discussed here have their usual meanings; the superscript σ denotes quantities referred to the Gibbs surface".

A similar reasoning can also be found in [37].

"The differential surface excess internal energy is

$$dU^\pi = T dS^\pi + \gamma^\pi d\Omega + \sum_r \mu_r n_r^\pi + E dQ^\pi \quad (21)$$

since customarily no work of expansion term is associated with the surface ... The surface Gibbs-Duhem equation is obtained in the usual way by integration and subsequent differentiation of this equation, followed by comparison of the result with eqn. [21]. We need only note that in the integrated relationship $\sigma\Omega$ rather than $\gamma^\pi\Omega$ is the legitimate term ... This gives:

$$0 = S^\pi dT + \sum_r n_r^\pi d\mu_r + Q^\pi dE + (\sigma - \gamma^\pi) d\Omega + \Omega d\sigma \quad (22)$$

... "This line of argumentation completely ignores (again) the fact that the Gibbs-Duhem equation is a mathematical consequence which follows directly from the homogeneous degree one property of the corresponding thermodynamic potential function.

In case of a one-component solid phase, e.g., a metal far from its melting point, the plastic and elastic surface deformations (strains) may have a relatively clear meaning settled by convention (see, e.g., [24]), and the "total strain" can perhaps be imagined to be formally divided into "plastic" and "elastic" contributions in the above sense. However, when dealing with electrified solid-liquid interfaces, the situation is much more complicated. In such cases, it is rather impossible to set up a consistent model to account for all the above features, and the separation of the deformation into purely "plastic" and purely "elastic" contributions is highly questionable, even if the solid phase contains only one pure component. If an interface in a multicomponent system containing a liquid and a pure solid phase is strained, the surface density of the "atoms of the solid substance" n_s/A may not remain constant; however, this is not necessarily true for the ions and molecules originating from the liquid phase, i.e., the amounts of the different components can be exchanged between the interfacial region and interior of the liquid (solution), and the surface densities of one or more of these components may remain unchanged. As a consequence, the concept of "elastic strain" can only make sense for the solid (immobile?) substance. Although the latter conclusion clearly contradicts the definition of "surface stress" formulated, e.g., in refs. [21] and [22, 24], many authors still prefer this terminology. There are two additional facts worth noting here. One is that in electrochemical/mechanical experiments carried out using solid/liquid interfaces ("solid

electrodes”), the change in the area of the interface is typically small, and the surface strain of the solid remains within the elastic limit. The other is that it was already concluded in [5] that “The main problem in electrocapillarity of solid electrodes is the lack of clarity in determining the surface stress and basic equations”.

In the following, an attempt will be made to address the above problems in the framework of the Gibbs model of the interface and by using only the basic principles of thermodynamics, i.e., thermodynamic relations for independent variables not including stress. It is emphasized again that in the Gibbs model, the interface is treated as a *mathematical* dividing plane between the two macroscopic phases, and its properties are given in terms of the surface excess values relative to a hypothetical reference system containing homogeneous phases in which the values of all intensive variables and associated properties are uniform and equal with those in the interface.

Some concepts and methodology of classical thermodynamics

In thermodynamics functions of state, variables are multivariable functions. The internal energy function (U) is completely specified by the entropy (S), the volume (V), the amounts of the system’s chemical constituents n_i , and eventually some other extensive variables, e.g., Ω . This set of independent variables is not by any means the most convenient. Nevertheless, there are many other possible representations that enable us to write fundamental equations as functions of parameters that are often conveniently controllable, such as intensive variables like temperature or pressure. These new functions are often called thermodynamic potential functions (or thermodynamic potentials). From a mathematical point of view, the different thermodynamic potential functions are just Legendre transforms as used in other disciplines, e.g., in mechanics, the Lagrangian is a function of coordinates and velocities, but it is often more convenient to define the Hamiltonian function applying a Legendre transform because the Hamiltonian is a function of coordinates and momenta. The important point about Legendre transforms is that the thermodynamic potential functions defined in this way all contain exactly the same thermodynamic information as the internal energy function. The introduction of such functions is not necessary for the logical completeness of thermodynamics, but they can greatly simplify the calculations. For example, the “free energy function”, “Helmholtz free energy function,” or “Helmholtz potential,” $F(T,V,\dots)$, is the (negative) Legendre transform of $U(S,V,\dots)$ with respect to S , defined (formally) as $F = U - TS$, and the “Gibbs free energy function,” “free enthalpy function,” or “Gibbs potential,” $G(T,p,\dots)$, is defined as the (negative) Legendre transform of the internal energy $U(S,V,\dots)$ with respect to the entropy S

and the volume V , i.e., $G = U - TS + pV$ [4, 35], etc. The introduction of the Gibbs free energy function can be particularly useful if the multicomponent, multiphase system under consideration is closed.

Analogously, we may consider the Legendre transforms of U^π with respect to some extensive variables. For instance, the surface excess (Helmholtz) free energy function can be obtained from the internal energy function via Legendre transformation as:

$$F^\pi = U^\pi - TS^\pi \tag{12}$$

If $U^\pi = U^\pi(S^\pi, Q^\pi, n_1^\pi, \dots, n_m^\pi, \Omega)$ (or more correctly, if charge is not considered an independent variable $U^\pi = U^\pi(S^\pi, n_1^\pi, \dots, n_c^\pi, \Omega)$), then F^π is given as $F^\pi = F^\pi(T, Q^\pi, n_1^\pi, \dots, n_m^\pi, \Omega)$ (or $F^\pi(T, n_1^\pi, \dots, n_c^\pi, \Omega)$), and the intensive parameter conjugate to Ω is $\gamma = \left(\frac{\partial F^\pi}{\partial \Omega}\right)_{T, n_1^\pi, \dots, n_m^\pi, Q^\pi}$ (or $\gamma = \left(\frac{\partial F^\pi}{\partial \Omega}\right)_{T, n_1^\pi, \dots, n_c^\pi}$). (We should remember that according to the preceding sections, the intensive (interfacial) variable conjugate to the extensive variable Ω can be defined as the partial derivative of U^π with respect to Ω .)

The “grand thermodynamic potential,” “Kramers energy function,” or “mechanical work function”, Ψ , is usually defined as the (negative) Legendre transform of the internal energy U function with respect to the entropy S and the chemical amounts n_i [35, 38].

Especially, in ref. [24], the superficial Kramers energy is given as:

$$\begin{aligned} \Psi^\pi(T, E, \mu_1^\pi \dots \mu_m^\pi, \Omega) &= U^\pi - TS^\pi - EQ^\pi - \sum_{i=1}^m \mu_i n_i^\pi \\ &= \sigma \Omega \end{aligned} \tag{13}$$

and the superficial work, i.e., “the work required to form unit area of new surface,” is expressed as:

$$\sigma = \frac{\Psi^\pi}{\Omega} \tag{14}$$

On the other hand,

$$\sigma = \left(\frac{\partial \Psi^\pi}{\partial \Omega}\right)_{T, E, \mu_1^\pi, \dots, \mu_m^\pi} \tag{15}$$

It should be noted here that Ψ^π is a (partly) homogeneous function of degree one with respect to Ω [2, 35]. If the charge is not considered an independent variable, the $\Psi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_m^\pi, \Omega)$ function can be given as:

$$\Psi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_m^\pi, \Omega) = U^\pi - TS^\pi - \sum_{i=1}^c \tilde{\mu}_i^\pi n_i^\pi = \sigma \Omega \tag{16}$$

where $\tilde{\mu}_i^\pi$ is the electrochemical potential of component i [2, 11, 32, 39] and

$$\sigma = \left(\frac{\partial \Psi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_c^\pi, \Omega)}{\partial \Omega} \right)_{T, \tilde{\mu}_1^\pi, \dots, \tilde{\mu}_c^\pi} \quad (17)$$

Equations (15) and (17) can be interpreted as corresponding to a situation in which the surface area is changed while keeping constant the remaining variables, including the (electro)chemical potentials of all chemical constituents. This may be considered equivalent to the assumption that the system is connected to reservoirs (“bulk phases”) of constant temperature, pressure, and constant chemical potentials and the interface can exchange energy and particles with the reservoirs without altering the composition of the “bulk phases,” i.e., the system is an “open” system. The above approach can be legitimately applied for fluid–fluid interfaces.

On the adequacy of a partly closed system approach

In case of a solid, e.g., a metal, the change of the surface area is not necessarily accompanied by the change of the number of metal atoms in the surface region. In heterogeneous systems containing solid–liquid interfaces, there may be at least a single “immobile” component. The mechanisms for equalizing chemical potentials may not operate with respect to the immobile components; however, the system may contain any number of “mobile” components with uniform chemical potentials [11]. It should also be noted that, as a consequence of the special selection criteria of the reference system (homogeneous reference phases), the Gibbs model allows, in principle, also the change of the amount of an immobile constituent in the two-dimensional phase if the composition of the liquid phase changes, but the amount of the immobile constituent in the whole system remains constant.

Thus, according to the formalism of thermodynamics, it may be expedient to introduce an appropriate new thermodynamic potential function for the description of such systems. For example, a thermodynamic potential function can be introduced via Legendre transforms of U^π (if charge is not considered an independent variable):

$$\Phi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_{c-1}^\pi, n_c^\pi, \Omega) = U^\pi - TS^\pi - \sum_{i=1}^{c-1} \tilde{\mu}_i^\pi n_i^\pi \quad (18)$$

where \tilde{n}_c^π is the excess amount of the “immobile” constituent. This function is formally analogous to the “hybrid thermodynamic potential” introduced first in [40].

The intensive variable conjugate to Ω can be given as:

$$\gamma = \left(\frac{\partial \Phi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_{c-1}^\pi, n_c^\pi, \Omega)}{\partial \Omega} \right)_{T, \tilde{\mu}_1^\pi, \dots, \tilde{\mu}_{c-1}^\pi, n_c^\pi} \quad (19)$$

and is clear that in this case

$$\gamma \neq \frac{\Phi^\pi}{\Omega} \quad (20)$$

By comparing Eqs. (16) and (18), it is easy to see that $\Psi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_c^\pi, \Omega)$ is the (negative) Legendre transform of $\Phi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_{c-1}^\pi, n_c^\pi, \Omega)$ with respect to \tilde{n}_c^π .

The expressions of σ (Eq. (17)) and γ (Eq. (19)) are written in terms of different variable sets and have different functional forms, but they both represent the same underlying physical quantity. This can be shown, e.g., if we consider an arbitrary analytic function $f(x, y)$ and its negative Legendre transform with respect to x , defined as

$$g(f_x, y) = f(x, y) - x \frac{\partial f(x, y)}{\partial x} \quad (21)$$

where $f_x = \frac{\partial f(x, y)}{\partial x}$. A necessary condition is the existence of a one-to-one relation between f_x and x , i.e., the function $f_x(x, y)$ can be inverted to give x . This means that $\frac{\partial^2 f(x, y)}{\partial x^2} \neq 0$; consequently, f_x is bijective, and x can be expressed as a function of f_x and y :

$$x = z(f_x, y). \quad (22)$$

Substituting z and f_x into Eq. (21) yields:

$$g(f_x, y) = f(z(f_x, y), y) - z(f_x, y) f_x. \quad (23)$$

The partial derivative of g with respect to y is:

$$\begin{aligned} \frac{\partial g(f_x, y)}{\partial y} &= \frac{\partial f(z(f_x, y), y)}{\partial z} \frac{\partial z}{\partial y} \\ &+ \frac{\partial f(z(f_x, y), y)}{\partial y} - \frac{\partial z(f_x, y)}{\partial y} f_x \end{aligned} \quad (24)$$

and since $\frac{\partial f(z, y)}{\partial z} = f_x$,

$$\frac{\partial g(f_x, y)}{\partial y} = \frac{\partial f(z(f_x, y), y)}{\partial y} = \frac{\partial f(x, y)}{\partial y} \quad (25)$$

This means that for the function values in a given state of the system:

$$\begin{aligned} \gamma &= \left(\frac{\partial \Phi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_{c-1}^\pi, n_c^\pi, \Omega)}{\partial \Omega} \right)_{T, \tilde{\mu}_1^\pi, \dots, c-1, n_c^\pi} \\ &= \left(\frac{\partial \Psi^\pi(T, \tilde{\mu}_1^\pi \dots \tilde{\mu}_c^\pi, \Omega)}{\partial \Omega} \right)_{T, \tilde{\mu}_1^\pi, \dots, c} = \sigma \end{aligned} \tag{26}$$

Two things should be noticed at this point. First, it is sometimes claimed that for a solid-fluid interface, the “mathematical homogeneity property cannot in general be associated with the process of stretching the surface phase” (see, e.g., [19]). However, the internal energy of a thermodynamic system is determined by its state and not by processes (see, the state principle formulated above). This brings us to our second point, namely, although the (excess) thermodynamic potential *functions* introduced in the Gibbs or Guggenheim models to describe the thermodynamic properties of the interface are homogeneous functions of degree one with respect to its extensive variables, changes in the system (“processes”) in which the change of an extensive variable (e.g., an increase in the surface area Ω) is not accompanied by a proportional increase in the number of moles of the surface atoms are also allowed. It is completely analogous with the situation in a homogeneous bulk phase. In these cases, some of the extensive variables can remain constant or can change in different ratios. The *function values* will then change according to the state of the system.

On the other hand, regardless of the above, the derivation of Eq. (25) is also valid for functions that are not homogeneous of degree one with respect to its variables.

Concluding notes

It is well-known that in a system containing a solid/liquid interface, many physical properties (e.g., the concentration of the components, density) can vary as a function of the distance perpendicular to the interface. In the model of Gibbs, the real interfacial region is replaced by a mathematical dividing surface, and the surface excess quantities are the respective differences between the real system and the chosen reference system (homogeneous reference phases). According to the Gibbs model, the reference phases are thought to be making up the volume of the actual real system ($V_{\text{ref},1} + V_{\text{ref},2} = V_{\text{system}}$). The “surface of discontinuity” or “dividing surface” in the idealized system is a homogeneous two-dimensional region (phase) without thickness [2, 35]. Although it is widely accepted that Gibbs’ mathematical plane model is “extrathermodynamic” [41], it is logically coherent and mathematically sound [15]. As a consequence of the model assumptions, the excess internal energy function becomes a homogeneous function of degree one in the extensive variables, including the surface area, and its Legendre transforms

are partly homogeneous functions of degree one with respect to the extensive variables. This gives a considerable advantage in the mathematical treatment of the thermodynamic functions, and most probably, this was the main reason for setting up such a mathematical model. The same may be true for the Guggenheim model [3, 11, 35] as well. Namely, if the excess internal energy function is a homogeneous function of degree one in its variables, then the mathematical formalism of classical (equilibrium) thermodynamics (which is based on the theory of homogeneous functions and Legendre transformations [35, 42]) can be used for the study of the two-dimensional “phase”. The Gibbs-Duhem equation is a mathematical consequence which follows directly from the homogeneous degree one property of the corresponding thermodynamic potential function. Since the Gibbs-Duhem equation (the “electrocapillary equation” in the present case) is the unique constraint on all intensive variables, it seems highly questionable to introduce two different parameters for the intensive variable conjugated to the surface area, and one is forced to conclude that the “modified Lippmann equation” given in the IUPAC recommendation [26] cannot be obtained without violating mathematical principles.

Of course, one could argue that in certain systems, more than one extensive surface variable may be needed to describe the thermodynamic state in practical situations; therefore, the number of intensive variables conjugate to these extensive variables is also greater than one. For instance, a possible way to describe the simultaneous mechanical and chemical equilibrium at the interface between an electrolyte solution and a solid conductor in terms of a continuum theory has been presented in ref. [43]. Nevertheless, it is well-known that a common approach in thermodynamics is to introduce additional generalized work terms into the fundamental equation. An interesting attempt for introducing a new thermodynamic potential function for solid or mixed systems subjected to a complex external mechanical force field can be found in ref. [44]. This function (which could be called “Rusanov potential” after its proposer) is defined as:

$$\mathfrak{R} = \Psi - \oint_{\Omega} (\mathbf{P} \cdot \mathbf{u}) \, d\Omega \tag{27}$$

or

$$\tilde{\mathfrak{R}} = \Phi - \oint_{\Omega} (\mathbf{P} \cdot \mathbf{u}) \, d\Omega \tag{28}$$

where \mathbf{P} is an external force (stress) per unit area of the system surface as a function of location on the surface (Ω), \mathbf{u} is the local vector of the surface displacement. In principle, an analogous potential function could also be used to describe the behavior of electrified solid/liquid interfaces. However, it is not completely clear (at least for the present author) how to

bring the definitions of the variables of Eqs. (27) and (28) into line with the definition of surface excesses. Moreover, as it was correctly pointed out by one of the anonymous reviewers of the original manuscript, the calculations using the J -potential in [44] may lead to the same problem as in Eq. (9), namely, to the appearance of the questionable binomial term.

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