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# Gibbs adsorption equation for planar fluid–fluid interfaces: Invariant formalism

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### ARTICLE INFO

### ABSTRACT

The fundamental underpinnings of the Gibbs adsorption equation (GAE) are enunciated including sundry choices for the location of the zero-volume dividing surface. Comparison is made to the finite-volume thermodynamic analyses of Guggenheim and Hansen. Provided that Gibbs phase rule is properly invoked, only invariant surface properties appear in the GAE. In the framework of invariant surface properties, both the zero-volume (Gibbs) and the finite-volume (Guggenheim) treatments of the surface phase give identical results for the GAE, confirming the thermodynamic generality and rigor of the expression.

Application of the GAE is made to strong and weak electrolytes, to electrified interfaces (Lippmann equation), and to surface complexation. Usefulness of the GAE in molecular simulation of interfaces is outlined. Special attention is paid to the seminal contributions of Fainerman and Miller in applying molecular-thermodynamic interfacial-layer models toward predicting adsorption behavior at fluid/fluid interfaces. Conversion of adsorption isotherms into two-dimensional interfacial-tension equations of state via the GAE is highlighted.

Confusion over interpretation of the Gibbs adsorption equation arises primarily because of imprecise meaning for adsorbed amounts. Once invariant adsorptions are recognized and utilized, the Gibbs adsorption equation yields identical results for Gibbs zero-volume surface thermodynamics and for Guggenheim finite-volume surface thermodynamics.

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## 1. Introduction

The Gibbs adsorption equation (GAE) stands as one of the cornerstones of interfacial science [1]. Its strength and elegance are unparalled. It plays a role in surface-phase equilibria similar to that of the Gibbs–Duhem equations in bulk-phase equilibria. Essentially all textbooks on surface and colloid chemistry derive and discuss the expression [2–8]. In spite of rigorous thermodynamic footing, the GAE has been subject to controversy and to experimental validation [9–17]. The main reason for continuing discussion [14,18–25] is that Gibbs introduced a "surface phase" of zero volume considered by many as aphysical. Gibbs recognized that interfaces are regions of space of molecular dimension between two bulk phases over which densities (energy, entropy, mass, etc.) vary continuously. The idea of a zero-volume dividing surface was introduced precisely because the interface thickness far from critical points is so thin. Nevertheless, objections remain. Both Guggenheim [26] and Hansen [27] introduced surface phases of finite volume leading to different definitions of surface properties compared to that of Gibbs. Most, if not all, of the controversy accompanying the Gibbs adsorption equation, for example, that between Motomura [28] and Good [29] and that between Aratono et al. [30] and Fainerman and Miller [31], can be attributed to differences in defining precisely the meaning of adsorbed amounts.

To clarify and consolidate apparently disparate approaches, we review the GAE adsorption equation from the points of view of Gibbs [1], Guggenheim [26], and Hansen [27]. The main finding is that all three approaches give identical results for the meanings of the coefficients appearing in the GAE, provided that the concept of surface invariants is introduced. A Gibbs invariant quantity is independent of the location of the zero-volume surface phase (i.e., independent of the dividing-surface location) while a Guggenheim invariant quantity is independent of the thickness of the finite-volume surface phase. The approach of Hansen is that of Guggenheim but with a different choice of independent variables compared to Gibbs and Guggenheim. Once surface invariants are evaluated in the GAE, all approaches are equivalent.

After introducing surface thermodynamics in the early part of Section 2, we highlight Guggenheim's approach, followed by that of Gibbs. We then establish their equivalence. Section 3 deals with use of surface species versus thermodynamic components. Several applications of the GAE, including the Lippmann equation for completely polarized interfaces, interfacial-layer models, and surface equations of state, are presented in Section 4. Section 5 concludes the review. The main theme is that only surface invariants are experimentally accessible by macroscopic measurement and, therefore, are thermodynamically meaningful. In the invariant language, the Gibbs adsorption equation and the Guggenheim adsorption equation are rigorous and identical.

## 2. Thermodynamic framework

Consider two equilibrated fluid phases of volumes $V^\alpha$ and $V^\beta$ separated by a planar interface of area $A$. Each phase contains $c$ components that partition between the two phases, and each phase may exchange heat and work with the surroundings. The first law of thermodynamics demands that differential changes in internal energy of the entire system obey the relation $dU = \partial Q + \partial W$ where $U$ is the internal energy, $Q$ is the heat added to the system, $W$ is the work done on the system, and the symbol $\partial$ denotes a path differential. If, in addition, we consider reversible heat and work differential exchanges, classical thermodynamics gives the fundamental relation for the two-phase system

$$dU = dQ_{rev} + dW_{rev} = TdS - PdV + dW_{rev}^\gamma + \sum_{i=1}^{c} \mu_i dn_i \qquad (1)$$

where $T$ is the temperature, $S$ is the total system entropy, $P$ the is pressure, $V$ is the total system volume, $\mu_i$ is the chemical potential of component $i$, and $n_i$ is the total system moles of component $i$. We need not

distinguish the temperature and chemical potentials for phases $\alpha$ and $\beta$ as they are uniform throughout the system including the interfacial region. Pressure in Eq. (1) is that corresponding to equilibrium between phases $\alpha$ and $\beta$. If, for example, phases $\alpha$ and $\beta$ are a single-component gas and liquid, then $P$ is the vapor pressure. Eq. (1) does not specify the reversible work for expansion or contraction of the interface located between the two phases, $dW_{rev}^\gamma$.

### 2.1. Capillary work

Following others [2,3,5,32], Fig. 1 illustrates a simple system to evaluate the reversible capillary work $dW_{rev}^\gamma$. Phases $\alpha$ and $\beta$ are placed in an inert rectangular chamber allowing $PV$ work exchange with the environment. When the right piston translates an increased distance differential $dx$, the two smaller pistons to the left simultaneously compress the system so as to keep the interface level fixed in the right chamber (at $z = 0$). The net result is an expanded interfacial area keeping all else constant. The normal stress exerted on the right piston is denoted as $P_T(z)$ reflecting the tangential stress profile though the fluid/fluid interface. The total reversible work exchange with the environment is therefore

$$dW_{rev}^\gamma = -wdx \int_{-h/2}^{+h/2} P_T(z)dz - P\left(dV^a + dV^b\right) \qquad (2)$$

where $w$ and $h$ are the width and depth of the right chamber, and $V^a$ and $V^b$ are the volumes in the left chambers connected to phases $\alpha$ and $\beta$. Since the net result of the piston movements is a shift in the system center of mass to the right, volumes are conserved: $dV^a + dV^b + whdx = 0$ Accordingly, the reversible work in Fig. 1 is

$$dW_{rev}^\gamma = wdx \int_{-\infty}^{+\infty} [P_N - P_T(z)]dz \qquad (3)$$

where the equal bulk pressures in the two phases are labeled as the normal stress, $P_N$, a constant through the interface, and the limits of the integral are replaced by infinity since only within molecular distances across the interface do the normal and tangential stresses differ. The integral in Eq. (3) is that of Bakker defining interfacial tension [2,3,5,6,8,32,33]

$$\gamma \equiv \int_{-\infty}^{+\infty} [P_N - P_T(z)]dz \qquad (4)$$

and the product $wdx$ is the differential interface area change, $dA$. Thus, Eq. (3) reduces to the desired result

$$dW_{rev}^\gamma = \gamma dA. \qquad (5)$$

Reversible work to expand an interface is positive, and vice versa. By definition, tension is an excess property: namely, the excess stress over that in the bulk (actually a deficiency of stress that gives rise to the contractile-skin nature of the interface). Reversible interfacial work augments $PV$ and mass-exchange work in Eq. (1).

### 2.2. Interfacial thermodynamics

Substitution of Eq. (5) into Eq. (1) gives the fundamental thermodynamic relationship for a system of two fluid phases, $\alpha$ and $\beta$, separated by an intervening interfacial phase labeled below as $\gamma$

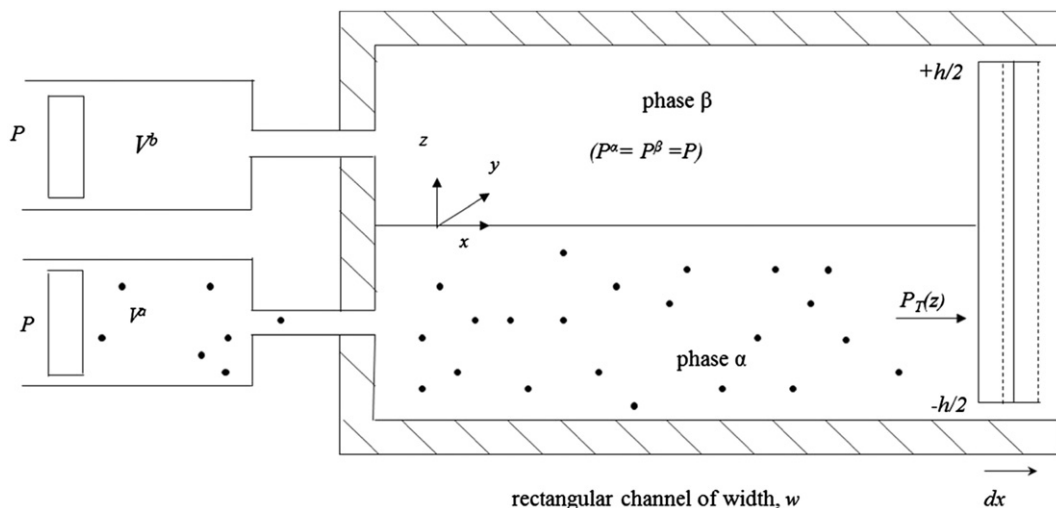$$dU = TdS - PdV + \gamma dA + \sum_{i=1}^{c} \mu_i dn_i. \qquad (6)$$

**Fig. 1.** Schematic of thermodynamic system to calculate interfacial work. The two left and right pistons move so as to maintain a constant level of phase $\alpha$.

Although general, Eq. (6) is not directly helpful since it requires knowledge of all system properties and does not focus on the interface. It is customary to subtract the properties of the two bulk phases encompassing the interface. Because all extensive properties in Eq. (6) are additive (i.e., $U = U^\alpha + U^\beta + U^\gamma$, where superscript $\gamma$ indicates the interfacial phase), we write Eq. (6) for the two bulk phases exhibiting no interface and subtract from the total system internal energy to give

$$dU^\gamma = TdS^\gamma - PdV^\gamma + \gamma dA + \sum_{i=1}^{c} \mu_i dn_i^\gamma. \tag{7}$$

The interfacial phase is of uniform temperature and uniform component chemical potentials, but otherwise is not yet defined. Definition of what constitutes the "surface phase" leads to apparent controversy [34–37].

### 2.3. Guggenheim invariants

A conceptually simple definition of the surface "phase" is that of Guggenheim [26] and later, Hansen [27]. These authors introduce a finite surface-phase thickness $\tau$ encompassing the interfacial region. $\tau$ is sufficiently large that densities in the surrounding $\alpha$ and $\beta$ phases are spatially uniform corresponding to bulk densities. All extensive properties of the system are now well defined because $V^\gamma \equiv A\tau$ and because extensive properties are additive: $U = U^\alpha + U^\beta + U^\gamma$; $S = S^\alpha + S^\beta + S^\gamma$; $V = V^\alpha + V^\beta + V^\gamma$; and $n_i = n_i^\alpha + n_i^\beta + n_i^\gamma$. Note, however, that all densities including energy, entropy, mole numbers, etc. are not constant across the interface, but vary strongly in the normal $z$ direction. Surface phases are inhomogeneous. For example, the moles of component $i$ adsorbed in the surface phase is defined by

$$n_{i\tau}^\gamma \equiv \Gamma_{i\tau} A \equiv \int_{-\tau^\alpha}^{+\tau^\beta} \rho_i(z) A dz \tag{8}$$

where $\rho_i$ is the molar density of component $i$, the second subscript $\tau$ on $n_{i\tau}^\gamma$ highlights the Guggenheim finite-volume surface phase, $\tau^\alpha$ is the thickness of the interface into phase $\alpha$, and $\tau^\beta$ is the thickness of the interface into phase $\beta$ based on an arbitrary origin in the interfacial region. Total interfacial thickness is $\tau = \tau^\alpha + \tau^\beta$. Fig. 2 illustrates the meaning of Eq. (8) for the example case of a small alcohol (e.g., ethanol) distributed between immiscible oil and water phases. Alcohol partitions preferentially to the interface. According to Guggenheim's convention in

Eq. (8), the cross-hatched area under the alcohol density profile in Fig. 2 gives the adsorbed surface density, $\Gamma_{i\tau}$. This clearly is not an excess interfacial property but the actual mass in the interface region between planes at $-\tau^\alpha$ and $+\tau^\beta$. All surface properties are defined similarly in terms of density profiles. Let a lower-case letter with an over bar denote a volume density. Then the surface internal energy and entropy are, respectively,

$$U^\gamma \equiv u_\tau^\gamma A = \int_{-\tau^\alpha}^{+\tau^\beta} \overline{u}(z) A dz \quad \text{and} \quad S^\gamma \equiv s_\tau^\gamma A = \int_{-\tau^\alpha}^{+\tau^\beta} \overline{s}(z) A dz. \tag{9}$$

Remaining extensive surface thermodynamic properties follow by analogy. It is not possible to establish, in general, the spatial variation of densities through the inhomogeneous interface using only local homogeneous properties.

All quantities appearing in the fundamental thermodynamic expression, Eq. (7), are now well defined. They do, however, depend on the thicknesses $\tau^\alpha$ and $\tau^\beta$ chosen to define the surface phase. Since Eq. (7) is first-order homogeneous in extensive properties and zero-order homogeneous in intensive properties $T$, $P$, and $\mu_i$, it may be integrated by
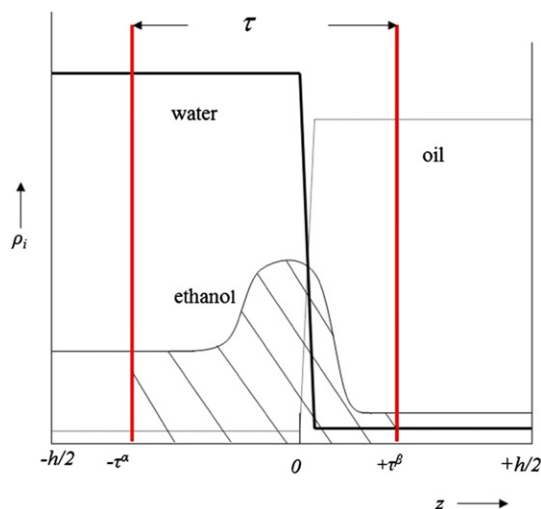


**Fig. 2.** Schematic of density profiles for alcohol adsorbed at the water/oil interface. Cross hatched area gives the adsorption of alcohol in the Guggenheim convention.

Euler's theorem, subsequently differentiated, and compared to Eq. (7). The result after division by interfacial area is

$$-d\gamma = s_\tau^\gamma dT - \tau dP + \sum_{i=1}^{c} \Gamma_{i\tau} d\mu_i. \tag{10}$$

This deceptively simple result is readily mistaken as the Gibbs adsorption equation. However, it is not the GAE because the coefficients multiplying the differentials depend on the thickness of the surface phase and because the system is over specified. Gibbs phase rule after accounting for a planar, transversely isotropic surface phase reduces to the classic form for homogeneous bulk systems [2,38,39]. Thus, for $c$ components and two bulk phases, interfacial tension depends on $c$ independent intensive variables, whereas Eq. (10) indicates that $\gamma$ varies with temperature, pressure, and $c$ chemical potentials or $c + 2$ variables.

To remove these inconsistencies, the Gibbs–Duhem equations are written for phases $\alpha$ and $\beta$ [26]. This leads to three equations in $c + 2$ unknowns. If the variables of pressure and chemical potential of component 1 are eliminated, we recover

$$-d\gamma = s_E^\gamma dT + \sum_{i=2}^{c} \Gamma_{iE} d\mu_i \tag{11}$$

where the summation over chemical potentials no longer includes component 1,

$$s_E^\gamma = \Delta s_\tau^\gamma - \Delta \Gamma_{1\tau} \left( \frac{\bar{s}^\alpha - \bar{s}^\beta}{\rho_1^\alpha - \rho_1^\beta} \right) \tag{12}$$

and

$$\Gamma_{iE} = \Delta \Gamma_{i\tau} - \Delta \Gamma_{1\tau} \left( \frac{\rho_i^\alpha - \rho_i^\beta}{\rho_1^\alpha - \rho_1^\beta} \right) \tag{13}$$

with $\Delta s_\tau^\gamma \equiv s_\tau^\gamma - \tau^\alpha \bar{s}^\alpha - \tau^\beta \bar{s}^\beta$ and $\Delta \Gamma_{i\tau} \equiv \Gamma_{i\tau} - \tau^\alpha \rho_i^\alpha - \tau^\beta \rho_i^\beta$. The Guggenheim surface excess entropy density, $s_E^\gamma$, and component excess adsorption densities, $\Gamma_{iE}$ in Eq. (11) are defined by Eqs. (12) and (13), respectively. They are excess properties in contrast to $s_\tau^\gamma$ and $\Gamma_{i\tau}$, each of which give the total entropy and mass in the surface phase defined by Guggenheim. As discussed later in Section 2.5, the difference excess quantities $\Delta s_\tau^\gamma$ and $\Delta \Gamma_{i\tau}$ in Eqs. (12) and (13) provide the link between Guggenheim and Gibbs formalisms.

Eq. (11) is now properly posed since it satisfies Gibbs phase rule with $c$ degrees of freedom. It may be coined the Gibbs adsorption equation (GAE) or perhaps in this form, the Guggenheim adsorption equation (GAE). It appears more complicated than its inadequate progenitor, Eq. (10). The important distinction is that $s_\tau^\gamma$, $\tau$, and $\Gamma_{i\tau}$ in Eq. (10) depend on the distances $\tau^\alpha$ and $\tau^\beta$, whereas in Eq. (11) the excess surface entropy and excess adsorption densities are readily shown independent of the magnitudes of $\tau^\alpha$ and $\tau^\beta$. Implicit in this conclusion is the restriction that both $\tau^\alpha$ and $\tau^\beta$ are large enough to encompass the entire surface region. With this provision, the excess surface entropy density (Eq. (12)) and excess adsorption densities (Eq. (13)) are invariant with respect to the thickness of the surface phase. This is a requirement of the GAE, since surface tension is measureable and cannot depend on arbitrary choice of the surface-phase width. $s_E^\gamma$ and $\Gamma_{iE}$ are, therefore, Guggenheim invariants [26]. Given theory for and/or measurement of the entropy and molar density profiles across the interface, Eqs. (12) and (13) prescribe how to implement the GAE.

Choices of independent variables other than pressure and the chemical potential of component 1 are possible. For example, Hansen [27] suggested that the chemical potentials of components 1 and 2 be

eliminated from Eq. (10) using the two bulk Gibbs–Duhem equations. After some algebra, the result is

$$-d\gamma = s_H^\gamma dT - \tau_H dP + \sum_{i=3}^{c} \Gamma_{iH} d\mu_i \tag{14}$$

where the summation over chemical potentials no longer involves components 1 and 2,

$$s_H^\gamma \equiv s_\tau^\gamma - \Gamma_{1\tau} \left( \frac{\rho_2^\beta \bar{s}^\alpha - \rho_2^\alpha \bar{s}^\beta}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right) - \Gamma_{2\tau} \left( \frac{\rho_1^\alpha \bar{s}^\beta - \rho_1^\beta \bar{s}^\alpha}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right), \tag{15}$$

$$\tau_H \equiv \Gamma_{1\tau} \left( \frac{\rho_2^\beta - \rho_2^\alpha}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right) + \Gamma_{2\tau} \left( \frac{\rho_1^\alpha - \rho_1^\beta}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right), \tag{16}$$

and

$$\Gamma_{iH} \equiv \Gamma_{i\tau} - \Gamma_{1\tau} \left( \frac{\rho_2^\beta \rho_i^\alpha - \rho_2^\alpha \rho_i^\beta}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right) - \Gamma_{2\tau} \left( \frac{\rho_1^\alpha \rho_i^\beta - \rho_1^\beta \rho_i^\alpha}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right). \tag{17}$$

Each coefficient in Eq. (14) shown in Eqs. (15)–(17) is independent of the location of $\tau^\alpha$ and/or $\tau^\beta$ and, therefore, is a Guggenheim invariant. It does not appear possible to set $\Gamma_{1\tau} = \Gamma_{2\tau} = 0$ in deriving Eq. (14) from Eq. (10), as enunciated by Motomura [28,34]. The pressure dependence of the interfacial tension at constant temperature and chemical potentials of component 3 through $c$ is given by $\tau_H$. This thickness, however, is not the physical thickness of the interface (i.e., $\tau_H \neq \tau$) used in defining the adsorbed amounts in Eq. (8) but rather is defined by Eq. (16). Hansen [27] argues that his choice of independent variables is convenient for an interface between an inert gas and a liquid solution of slightly volatile components. Cahn also adopted the Guggenheim finite-thickness convention with Hansen's choice of independent variables [20]. He points out that this particular choice of thermodynamic variables is useful for equilibrium between condensed phases.

Eqs. (15)–(17) are consistent with Hansen's definition of surface excess properties. For example, the excess surface concentration according to Hansen [27] is given by

$$\Gamma_{iH} \equiv \int_{-\tau^\alpha}^{+\tau^\beta} \rho_i(z) dz - l^\alpha \rho_i^\alpha - l^\beta \rho_i^\beta = \Gamma_{i\tau} - l^\alpha \rho_i^\alpha - l^\beta \rho_i^\beta \tag{18}$$

where the lengths $l^\alpha$ and $l^\beta$ are chosen to make $\Gamma_{1H} = \Gamma_{2H} = 0$ or

$$l^\alpha = \left( \frac{\Gamma_{1\tau} \rho_2^\beta - \Gamma_{2\tau} \rho_1^\beta}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right) \quad \text{and} \quad l^\beta = \left( \frac{\Gamma_{2\tau} \rho_1^\alpha - \Gamma_{1\tau} \rho_2^\alpha}{\rho_1^\alpha \rho_2^\beta - \rho_1^\beta \rho_2^\alpha} \right). \tag{19}$$

Substitution of Eq. (19) into Eq. (18) directly gives Eq. (17). $s_H^\gamma$ and $\tau_H$ are obtained similarly confirming Eqs. (15) and (16). There is no fundamental significance to Hansen's definition of surface excess properties and, specifically, to the thicknesses $l^\alpha$ and $l^\beta$. These definitions do, however permit expeditious derivation of Eqs. (14)–(17).

### 2.4. Gibbs invariants

We start, as above, with Eq. (7) and redefine the meaning of the extensive variables appearing there following Gibbs [1] and as summarized by others [2,3,5,6,8]. Apparently motivated by the molecular thickness of the surface region, the volume of the surface phase is set to zero meaning that all surface properties are ascribed to a plane. The location of this plane, defined here as $z_j$, lies within the interfacial region and is known as the Gibbs dividing surface. Because the volumes of phases $\alpha$

and $\beta$ constitute the entire system volume (i.e., $V^\gamma = 0$), the moles of component $i$ in the surface phase are given by

$$n_{ij}^\gamma \equiv \Gamma_{ij}A = \int\limits_{-h/2}^{+h/2} \rho_i(z)A dz - \int\limits_{-h/2}^{z_j} \rho_i^\alpha A dz - \int\limits_{z_j}^{+h/2} \rho_i^\beta A dz. \tag{20}$$

The first term on the far right gives the total mass of component $i$ in the system while the second and third far-right terms reflect the masses of component $i$ in phases $\alpha$ and $\beta$. An additional subscript $j$ appears on the moles of component $i$ at the surface, $n_{ij}^\gamma$, to designate dependence on the choice of the dividing surface, $z_j$, and to distinguish from the Guggenheim convention, $n_{i\tau}^\gamma$ in Eq. (8). These two quantities are quite different. In Eq. (20), no volume is assigned to the adsorbed amounts.

To clarify its meaning, Eq. (20) is re-expressed in the following form

$$n_{ij}^\gamma \equiv \Gamma_{ij}A = \int\limits_{-h/2}^{z_j} [\rho_i(z) - \rho_i^\alpha]A dz + \int\limits_{z_j}^{+h/2} [\rho_i(z) - \rho_i^\beta]A dz. \tag{21}$$

The lower and upper limits in the first and second integrals, respectively, may be replaced by infinity because the corresponding integrands approach zero rather near the interface. Using the alcohol/water/oil system above, Fig. 3 illustrates how the adsorbed surface density, $\Gamma_{ij}$ is calculated according to Gibbs convention. Horizontal lines at the bulk densities in each phase are extrapolated to the Gibbs dividing surface at $z_j$ indicating zero volume for the surface phase The cross-hatched area under the alcohol density profile is determined according to Eq. (21) giving the superficial adsorption density, $\Gamma_{ij}$. The surface mass calculated is assigned to the dividing plane. All other surface properties follow by analogy, such as energy

$$U_j^\gamma \equiv A u_j^\gamma = \int\limits_{-h/2}^{+z_j} [\bar{u}(z) - \bar{u}^\alpha]A dz + \int\limits_{z_j}^{+h/2} [\bar{u}(z) - \bar{u}^\beta]A dz \tag{22}$$

or entropy

$$S_j^\gamma \equiv A s_j^\gamma = \int\limits_{-h/2}^{+z_j} [\bar{s}(z) - \bar{s}^\alpha]A dz + \int\limits_{z_j}^{+h/2} [\bar{s}(z) - \bar{s}^\beta]A dz. \tag{23}$$

All properties in Eq. (7) are now well defined, although defined quite differently than in Guggenheim's convention. We proceed as above by
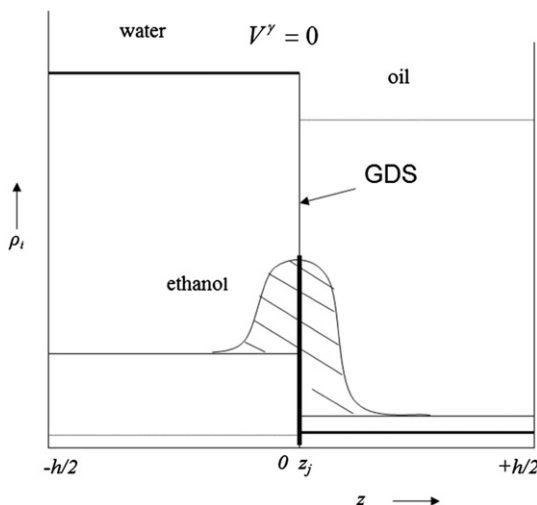


**Fig. 3.** Schematic of density profiles for alcohol adsorbed at the water/oil interface. Cross hatched area gives the adsorption of alcohol in the Gibbs convention.

integrating Eq. (7) in extensive variables, differentiating, and subtracting to yield

$$-d\gamma = s_j^\gamma dT + \sum_{i=1}^c \Gamma_{ij} d\mu_i. \tag{24}$$

This expression is akin to Eq. (10). However, the meanings of the surface entropy and component adsorptions are surface-excess properties rather than total quantities. Also pressure does not appear explicitly (i.e., $V^\gamma = 0$). Rather, pressure is a dependent variable implicit in the chemical potentials. Eq. (24) also is not the GAE. Similar to Eq. (10) in the Guggenheim convention, Eq. (24) is over specified. Further, $s_j^\gamma$ and $\Gamma_{ij}$ depend on the location chosen for the dividing surface and, thus, cannot reflect measureable properties. Let subscript $k$ represent a second dividing-surface location, $z_k$. Eqs. (21) and (23) then demonstrate that

$$s_j^\gamma = s_k^\gamma + (z_k - z_j)(\bar{s}^\alpha - \bar{s}^\beta) \quad \text{and} \quad \Gamma_{ij} = \Gamma_{ik} + (z_k - z_j)(\rho_i^\alpha - \rho_i^\beta). \tag{25}$$

Thus, molecular-size changes in the location of the dividing surface strongly impact values of the surface properties. To overcome these two inconsistencies in Eq. (24), we proceed as above and eliminate the chemical potential of component 1 and pressure from among Eq. (24) and the Gibbs–Duhem expressions for the two bulk phases. The result is

$$-d\gamma = s_E^\gamma dT + \sum_{i=2}^c \Gamma_{iE} d\mu_i \tag{26}$$

where

$$s_E^\gamma = s_j^\gamma - \Gamma_{1j}\left(\frac{\bar{s}^\alpha - \bar{s}^\beta}{\rho_1^\alpha - \rho_1^\beta}\right), \tag{27}$$

and

$$\Gamma_{iE} = \Gamma_{ij} - \Gamma_{1j}\left(\frac{\rho_i^\alpha - \rho_i^\beta}{\rho_1^\alpha - \rho_1^\beta}\right). \tag{28}$$

Eqs. (26)–(28) constitute the Gibbs adsorption equation. Excess properties appear, and each coefficient (defined in Eqs. (27) and (28)) is independent of the location of the dividing surface. Only Gibbs invariants appear in the Gibbs (or Guggenheim) adsorption equation.

In the Gibbs convention, if interfacial tension is considered a function of temperature, pressure, and $c$-3 chemical potentials [27], Eqs. (14)–(17) remain valid but with $s_\tau^\gamma$ replaced by $s_j^\gamma$ and $\Gamma_{i\tau}$ replaced by $\Gamma_{ij}$. Eqs. (14)–(17) provide the basis for neglecting the presence of an inert atmosphere of air in most aqueous-solution surface-tension measurements [2]. The differential coefficients appearing in this alternate Gibbsian version of Eq. (14) are independent of the location of the dividing surface and are, therefore, Gibbs invariants.

### 2.5. Equivalence of Gibbs and Guggenheim

Let $\tau^\alpha$ and $\tau^\beta$ in Fig. 2 be redefined as the respective distances into phases $\alpha$ and $\beta$ from a Gibbs dividing surface at $z_j$ (i.e., presumed located within the surface region). From Eq. (8), we express $\Delta\Gamma_{i\tau}$ as

$$\Delta\Gamma_{i\tau} \equiv \Gamma_{i\tau} - \tau^\alpha \rho_i^\alpha - \tau^\beta \rho_i^\beta = \int\limits_{-(\tau^\alpha - z_j)}^{z_j} [\rho_i(z) - \rho_i^\alpha] dz + \int\limits_{z_j}^{\tau^\beta + z_j} [\rho_i(z) - \rho_i^\beta] dz \equiv \Gamma_{ij}. \tag{29}$$

Since $\tau^\alpha$ and $\tau^\beta$ are large enough to penetrate the bulk of phases $\alpha$ and $\beta$, the lower-most and upper-most integral limits in Eq. (29) are

replaced by infinity. The integrals in Eq. (29) are then identical to those in Eq. (21) and correspond to the Gibbs surface excess adsorption of component $i$ based on a dividing surface at $z_j$ or $\Delta\Gamma_{i\tau} = \Gamma_{ij}$, and, likewise for component 1: $\Delta\Gamma_{1\tau} = \Gamma_{1j}$, i.e., the Gibbs surface excess adsorption of component 1 based on the dividing surface of $z_j$. Thus, Guggenheim invariants (independent of surface width) in Eq. (13) are identical to Gibbs invariants (independent of dividing surface location) in Eq. (28). The same reasoning holds for the excess surface entropies in Eqs. (12) and (27). We conclude that Gibbs and Guggenheim conventions give exactly the same final result for the GAE, as they must. In Gibbs adsorption equation (Eqs. (11) or (26)) one evaluates the coefficients $s_E^\gamma$ and $\Gamma_{iE}$ either by the proscription of Guggenheim with a finite surface-phase volume or by the proscription of Gibbs with a zero-volume surface phase. Equivalency, of course, demands that the coefficients $s_E^\gamma$ and $\Gamma_{iE}$ include all necessary factors in each convention. Hansen's results [27] in Eqs. (14)–(17) also emerge directly from either the Gibbs or Guggenheim invariant conventions after adoption of his choice of independent variables.

Gibbs outlined a particularly convenient methodology to set the location of the dividing surface [1]. Many surface-active components are dilute in a solvent. In Figs. 2 and 3, water is typically chosen as the solvent, but the hydrocarbon component serves as well. Gibbs set the location of the dividing surface at $z_1$ defined such that the surface excess adsorption of solvent, usually numbered as component 1, is zero relative to $z_1$. Thus in Eq. (21), $\Gamma_{11} = 0$ where the first subscript denotes component 1 and the second subscript indicates a dividing surface at $z_1$. With Gibbs formalism, the surface excess entropy and surface excess mass densities in Eqs. (26) and (27) become $s_E^\gamma = s_1^\gamma$ and $\Gamma_{iE} = \Gamma_{i1}$, and their calculation is simplified. The Gibbs adsorption equation in its classic form emerges as

$$-d\gamma = s_1^\gamma dT + \sum_{i=2}^{c} \Gamma_{i1} d\mu_i \tag{30}$$

$s_1^\gamma$ and $\Gamma_{i1}$ remain Gibbs invariants as elucidated by Eqs. (27) and (28)

$$s_1^\gamma = s_j^\gamma - \Gamma_{1j}\left(\frac{\bar{s}^\alpha - \bar{s}^\beta}{\rho_1{}^\alpha - \rho_1{}^\beta}\right) \quad \text{and} \quad \Gamma_{i1} = \Gamma_{ij} - \Gamma_{1j}\left(\frac{\rho_i{}^\alpha - \rho_i{}^\beta}{\rho_1{}^\alpha - \rho_1{}^\beta}\right). \tag{31}$$

Thus, the coefficients in the GAE of Eq. (30) have two interpretations. First, they are Gibbsian surface excesses with respect to a dividing surface chosen to give zero solvent excess adsorption. Second, from Eq. (31), $s_1^\gamma$ and $\Gamma_{i1}$ are Gibbsian surface excesses with respect to a dividing surface located at any $z_j$. The first implementation is economic.

Gibbs (or Guggenheim) adsorption equation for inhomogeneous surface phases is rigorous and is of the same authority as is the Gibbs–Duhem equation for bulk homogeneous phases. There is no question of thermodynamic validity. Provided invariants are correctly evaluated, whatever convention is used to define the surface phase gives the same final result. There is no distinction in the GAE between the Guggenheim finite-volume surface phase and the zero-volume Gibbs surface phase.

## 2.6. Other Gibbs invariants

Guggenheim and Adams [35] noted that Gibbs dividing surfaces are possible other than the convention of zero adsorption of component 1. These authors suggested a family of dividing surfaces set at the location $z_\alpha$ by the definition

$$\sum_{i=1}^{c} \alpha_i \Gamma_{i\alpha} = 0 \tag{32}$$

where the coefficients $\alpha_i$ are constants characterizing the particular choice of the dividing surface. The choice of zero adsorption of component 1 corresponds to $\alpha_i = 0$ for $i \geq 2$. If, for example, $\alpha_i$ is fixed as the partial molar volume of component $i$ in phase $\alpha$ or $\bar{v}_i^\alpha$, then the Gibbs dividing surface at $z_v$ is determined by the relation

$$\sum_{i=1}^{c} \bar{v}_i^\alpha \Gamma_{iv} = 0. \tag{33}$$

Hansen utilized this particular convention under the assumption that partial molar volumes of all components are equal in both $\alpha$ and $\beta$ phases [27]. Substitution of Eq. (33) into the expression for the Gibbs invariant adsorption of component $i$ in Eq. (28) gives

$$\Gamma_{iE} = \Gamma_{iv} + \left[\sum_{i=2}^{c} \frac{\bar{v}_i^\alpha}{\bar{v}_1^\alpha} \Gamma_{iv}\right] \frac{\left(\rho_i^\alpha - \rho_i^\beta\right)}{\left(\rho_1^\alpha - \rho_1^\beta\right)}. \tag{34}$$

Guggenheim and Adams [35] present several other choices for $\alpha_i$ that expose subcases of Eq. (34). The meaning of Eq. (34) is that the location of the Gibbs dividing surface, $z_v$, is set from the (presumed known) component density profiles through the interface according to Eq. (33). Gibbs excess adsorption, $\Gamma_{iv}$, relative to this dividing surface is calculated following Eq. (21) and substituted into Eq. (28) (which is valid for any choice of Gibbs dividing surface). The resulting Gibbs invariant adsorption $\Gamma_{iE}$ is then identical to that based on the dividing surface, $z_1$, of zero adsorption of component 1 (see Eq. (31)). The same conclusion can be made for the remaining choices of $\alpha_i$ suggested by Guggenheim and Adams and indeed for any other choice of dividing-surface location. Only invariants appear in the GAE. If density profiles are available either from theory or experiment, there seems little advantage in choosing a dividing surface other than that suggested by Gibbs.

If the adsorbed amounts appearing in Eq. (32) are evaluated according to Guggenheim (i.e., from Eq. (8)), then an interface thickness of $\tau_v$ emerges. Using this thickness and knowledge of the component density profiles, adsorptions $\Gamma_{i\tau_v}$ are established and substituted into the Guggenheim invariant adsorption in Eq. (13). The result is Eq. (33) with $\Gamma_{iv}$ replaced by $\Gamma_{i\tau_v}$. Thus, Eq. (32) may be viewed not only as defining various Gibbs dividing surfaces, but equivalently as establishing various interface thicknesses in the Guggenheim finite-surface-volume convention. This exercise again proves the equivalence of the Gibbs and Guggenheim approaches.

Some 30 years following Guggenheim and Adams, Lucassen-Reynders and van den Temple [36] and Joos [37] proposed a Gibbs dividing surface based on interfacial partial molar areas $\bar{\omega}_i$ [2]

$$\sum_{i=1}^{c} \bar{\omega}_i \Gamma_{i\omega} = 1 \tag{35}$$

where $\Gamma_{i\omega}$ is Gibbs excess adsorption of component $i$ based on a dividing surface defined by Eq. (35). Lucassen-Reynders [36,40–44] and Joos [37,45,46] differ slightly in application of Eq. (35) depending on how surface partial-molar areas vary with interface composition. The stated advantage for this particular dividing-surface location is that excess adsorptions of all components, including solvent-component 1, are nonzero and positive. Accordingly, interfacial mole or area fractions may be defined. Such definitions are not possible with Gibbs' choice of the dividing surface $\Gamma_{11} = 0$. Although appealing for modeling efforts, interfacial mole or area fractions are strictly not thermodynamic because they vary with choice of dividing-surface location. As with Guggenheim and Adams collection of dividing surfaces, those based on Eq. (35) obey the GAE when invariant excess adsorptions are calculated

$$\Gamma_{iE} = \Gamma_{i\omega} - \left[\frac{1}{\bar{\omega}_1} - \sum_{j=2}^{c} \frac{\bar{\omega}_i}{\bar{\omega}_1} \Gamma_{i\omega}\right] \frac{\left(\rho_i^\alpha - \rho_i^\beta\right)}{\left(\rho_1^\alpha - \rho_1^\beta\right)}. \tag{36}$$

Similar to Guggenheim and Adams dividing surfaces [35], the Gibbs adsorptions, $\Gamma_{i\omega}$ in Eq. (36), can be replaced by ones calculated according to Guggenheim finite-volume interphase, $\Gamma_{i\tau_\omega}$. Eq. (35) then defines yet another the thickness of the interphase: $\tau_\omega$. The invariant-component adsorption value in Eq. (36) is unchanged by using this convention to evaluate $\Gamma_{i\omega}$.

Buff [47] and Melrose [48] point out yet other choices for the location of the Gibbs dividing surface including: $u_j^\gamma = 0$ and $s_j^\gamma = 0$. These choices have not found application to planar fluid/fluid interfaces since interest is primarily in understanding the relation between interfacial tension and adsorbed amounts at constant temperature. However, application of the Gibbs adsorption equation to non-isothermal systems speaks against referring to it as the Gibbs adsorption isotherm.

If theory is available for component density profiles through a fluid/fluid interface, the benefit of dividing surfaces different from that suggested by Gibbs (i.e., $\Gamma_{11} = 0$) is minimal. However, if simplified molecular-thermodynamic models are sought, the Lucassen-Reynders–Joos framework in Eq. (35) may be useful.

## 3. Components versus species

Analogous to bulk thermodynamic analyses, the GAE does not recognize molecular species. In many applications, however, consideration of molecular speciation is paramount. Fortunately, this topic is well covered in the literature [23,49–51]. We give three examples. The basic procedure is to write Eq. (24) for all molecular species and then to impose chemical-reaction equilibria, electroneutrality, if pertinent, and bulk-phase Gibbs–Duhem relations.

### 3.1. Aqueous strong electrolyte

Fig. 4 graphs surface tension against air for three strong aqueous electrolytes at ambient temperature. Measured surface tension rises as the concentration of salt increases, a feature opposite to that of most aqueous solutes, such as alcohol at the air/water or oil/water interface in Fig. 2. To understand this behavior, recognition must be given to salt dissociation in the aqueous solution. Consider a strong electrolyte solution consisting of dissociated $K^+$ ions $Cl^-$ ions, and water in equilibrium with air (taken as inert). For illustration, water consists of $H_2O$

molecules, and $H^+$ and $OH^-$ ions at pH $= 7$. From Eq. (24) at constant temperature, we have that

$$-d\gamma = \Gamma_{K^+}d\tilde{\mu}_{K^+} + \Gamma_{Cl^-}d\tilde{\mu}_{Cl^-} + \Gamma_{H^+}d\tilde{\mu}_{H^+} + \Gamma_{OH^-}d\tilde{\mu}_{OH^-} + \Gamma_{H_2O}d\mu_{H_2O} \quad \text{constant } T \tag{37}$$

where an over tilde is written above the chemical potential of each charged species to emphasize the electrochemical potential that depends on the charged state of the system [53]. For convenience, we drop the subscript designating the particular choice of dividing surface, although each species adsorption is understood as defined by the Gibbs convention. Reaction equilibria demand that

$$\mu_{KCl} = \tilde{\mu}_{K^+} + \tilde{\mu}_{Cl^-} \quad \text{and} \quad \mu_{H_2O} = \tilde{\mu}_{H^+} + \tilde{\mu}_{OH^-}. \tag{38}$$

Since salt and water are the constituent thermodynamic components and since the overall system is electrically neutral, $\Gamma_{K^+} = \Gamma_{Cl^-} \equiv \Gamma_{KCl}$ and $\Gamma_{H^+} = \Gamma_{OH^-}$. Substitution of these results and Eq. (38) into Eq. (37) gives

$$-d\gamma = \Gamma_{KCl}d\mu_{KCl} + \left(\Gamma_{H^+} + \Gamma_{H_2O}\right)d\mu_{H_2O} \equiv \Gamma_{KCl}d\mu_{KCl}$$
$$+ \Gamma_1 d\mu_1 \quad \text{constant } T. \tag{39}$$

Adsorption of component 1 is defined by $\Gamma_1 \equiv \Gamma_{H^+} + \Gamma_{H_2O}$. Here again, Eq. (39) is over specified. We relieve the inconsistency by invoking Gibbs–Duhem in the aqueous phase

$$x_{KCl}d\mu_{KCl} + \left(x_{H^+} + x_{H_2O}\right)d\mu_{H_2O} = x_{KCl}d\mu_{KCl} + x_1 d\mu_1 \quad \text{constant } T, P \tag{40}$$

and by eliminating the chemical potential of water (component 1) to yield

$$-d\gamma = \left[\Gamma_{KCl} - \Gamma_1 \frac{x_{KCl}}{x_1}\right]d\mu_{KCl} \equiv \Gamma_{KCl1}d\mu_{KCl} \quad \text{constant } T, P. \tag{41}$$

Thus, the classic form of the GAE emerges with the surface excess adsorption of salt defined relative to a zero-solvent surface-excess dividing surface. At neutral pH, the concentrations of hydronium and hydroxide ions are low making their surface concentrations minimal compared to that of the salt. Likewise, distinction between adsorption of molecular water species and component water is immaterial.

Eq. (41) and Fig. 4 reveal that surface excess adsorption of salt anions and cations is equal and negative at the air/water interface. Although the concentration profiles of each may differ, both give a net negative and equal surface-excess adsorption. Onsager and Samaras [54] first quantified this phenomenon. The aqueous electrolyte solution was treated as point ions dissolved in a dielectric continuum. Ions are repelled from the gas (inert)/water interface by image charges located in the lower permittivity gas phase. For symmetric electrolytes, calculated concentration profiles are identical for each ion; they are lower near the interface than in the bulk solution and increase toward the bulk solution. The model of Onsager and Samaras confirms the underlying tenets of the GAE, as all theories must. However, the treatment of Onsager and Samaras applies only to dilute electrolyte solutions (i.e., within the Debye–Hückel approximation), distinguishes salts by valence only (in opposition to Fig. 4), and ignores possible nascent charge at the air/water interface [55].

### 3.2. Completely polarized interface

Much of our understanding of the diffuse electrical double layer comes from measurements of interfacial tension at the mercury/aqueous electrolyte interface versus applied voltage [53,56,57]. This interface is unique in that fluidity of the liquid metal allows direct measurement of interfacial tension under ambient conditions and in that
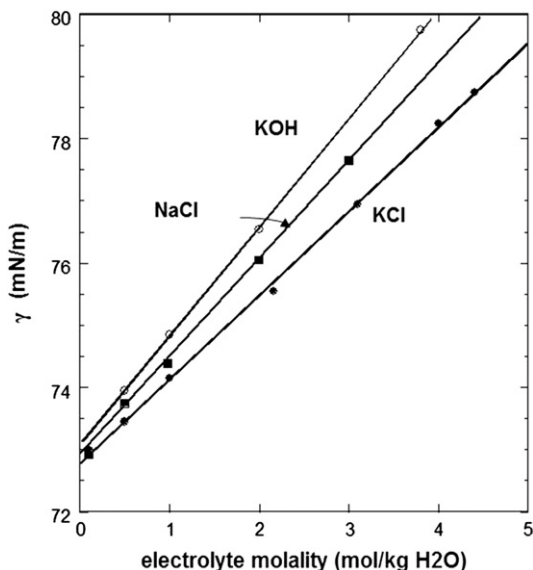


**Fig. 4.** Air/water surface-tension isotherms for several strong 1:1 aqueous salts at ambient temperature. Lines guide the eye.
Data are from the Handbook of Chemistry and Physics [52].

application of a voltage difference does not pass current. This second feature allows the interface to maintain a uniform surface charge provided that a range of applied voltages is chosen where no electrode reactions occur (e.g., no hydrogen or oxygen evolution). Fig. 5 illustrates the electrochemical cell of a so-called Lippmann capillary electrometer [53,56,57]. Liquid Hg is in contact with an aqueous KCl solution of known concentration. An applied voltage difference, $E$, charges the mercury/aqueous electrolyte interface and is detected relative to a reversible silver/silver chloride electrode by a high-impedance electrometer. The ability to set the interfacial charge adds an additional thermodynamic degree of freedom to the system. Interface charging alters the interfacial tension measured in Fig. 5 by axisymmetric-drop-shape analysis. Not shown in Fig. 5 are the counter electrode that applies the desired voltage and the salt bridge that protects the mercury/water interface from unwanted electrode-reaction products (e.g., $Ag^+$ ions) [53].

Assume that the aqueous electrolyte consists of the species: $K^+$ and $Cl^-$ ions, $H^+$ and $OH^-$ ions at pH = 7, and $H_2O$ molecules. Electrons exist only at the liquid metal/water interface. Upon dropping the subscript $j$ denoting the location of the dividing surface, Eq. (24) reads at constant temperature [53,58]

$$-d\gamma = \Gamma_{Hg}d\mu_{Hg} + \Gamma_{e^-}d\tilde{\mu}_{e^-} + \Gamma_{K^+}d\tilde{\mu}_{K^+} + \Gamma_{Cl^-}d\tilde{\mu}_{Cl^-}$$
$$+ \Gamma_{H^+}d\tilde{\mu}_{H^+} + \Gamma_{OH^-}d\tilde{\mu}_{OH^-} + \Gamma_{H_2O}d\mu_{H_2O}. \qquad \text{constant } T \qquad (42)$$

Species originating from each phase may adsorb at the interface. In addition, Eqs. (38) and (40) hold, $\Gamma_{H^+} = \Gamma_{OH^-}$, and the Gibbs–Duhem equation for the pure mercury phase applies (i.e., $d\mu_{Hg} = 0$ at constant $T$ and $P$) giving

$$-d\gamma = \left(\Gamma_{K^+} - \frac{x_{KCl}}{x_1}\Gamma_1\right)d\mu_{KCl} + \Gamma_{e^-}d\tilde{\mu}_{e^-} + (\Gamma_{Cl^-} - \Gamma_{K^+})d\tilde{\mu}_{Cl^-} \quad \text{constant } T, P. \tag{43}$$

Electroneutrality of the interface (i.e., $\sum z_i\Gamma_i = 0$) demands that $\Gamma_{K^+} - \Gamma_{Cl^-} - \Gamma_{e^-} = 0$. We recognize that the interface charge on the metal is given by $q_m \equiv -F\Gamma_{e^-}$ where $F$ is Faraday's constant. Substitution of these expressions into Eq. (43) reveals that

$$-d\gamma = \Gamma_{K^+1}d\mu_{KCl} + \frac{q_m}{F}(d\tilde{\mu}_{Cl^-} - d\tilde{\mu}_{e^-}) \quad \text{constant } T, P \tag{44}$$

where $\Gamma_{K^+1}(= \Gamma_{Cl^-1} - q_m/F)$ is the surface-excess adsorption of cation relative to the adsorption of water as defined in Eq. (43). To simplify the term $(d\tilde{\mu}_{Cl^-} - d\tilde{\mu}_{e^-})$, we represent the cell electrical circuit as

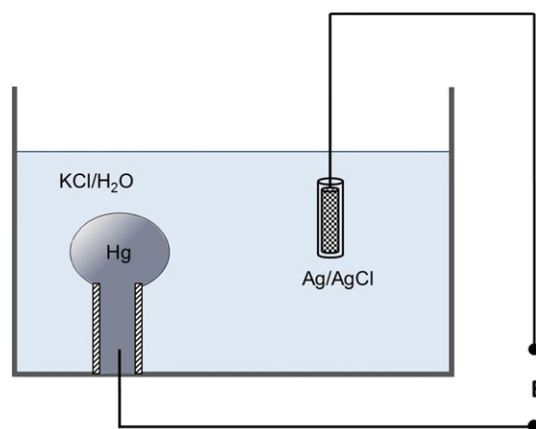$$Pt|Ag|AgCl|KCl/H_2O|Hg|Pt. \tag{45}$$



**Fig. 5.** Schematic of a Lippmann capillary electrometer. Interfacial tension and applied voltage are measured.

Following Newman and Thomas-Alyea [53], the cell voltage difference is

$$FE = \mu_{Ag} - \mu_{AgCl} + \tilde{\mu}_{Cl^-} - \tilde{\mu}_{e^-}. \tag{46}$$

Since the silver and silver-chloride phases are pure, differentiation of Eq. (46) at constant temperature and pressure specifies that $FdE = d\tilde{\mu}_{Cl^-} - d\tilde{\mu}_{e^-}$. Accordingly, Eq. (44) reduces to the desired result

$$-d\gamma = \Gamma_{K^+1}d\mu_{KCl} + q_m dE \quad \text{constant } T, P. \tag{47}$$

This is the celebrated Lippmann equation [53,56–59]. Each coefficient of the differentials in the Lippmann equation is a Gibbs invariant as is the surface charge. From Eq. (25), $\Gamma_{e^-}$ is a Gibbs invariant because free electrons do not exist in the bulk mercury and aqueous phases [53]. Thus, the Lippmann equation is the GAE for a completely polarizable fluid/fluid interface. Eq. (47) permits evaluation of the surface-excess adsorption of cations

$$\Gamma_{K^+1} = -\left(\frac{\partial\gamma}{\partial\mu_{KCl}}\right)_E \qquad \text{constant } T, P \tag{48}$$

and the interface charge

$$q_m = -\left(\frac{\partial\gamma}{\partial E}\right)_{\mu_{KCl}} \qquad \text{constant } T, P. \tag{49}$$

Since $\Gamma_{Cl^-1} = \Gamma_{K^+1} + q_m/F$, surface charge, adsorption of cations, and adsorption of anions are all known from the capillary electrometer as functions of applied potential difference and aqueous salt composition. Considerable effort has been expended along these lines [53,56–59]. Essentially all experimental knowledge about the structure of the electrical double layer (or triple layer) originates from the Lippmann capillary electrometer.

### 3.3. Surface complexation

Some surface-active species complex at the interface to form surface aggregates [31,60–64]. Consider a solute–solvent mixture where the solute forms equilibrium complexes at the fluid/fluid interface according to

$$gA_1 \rightleftarrows A_g \quad \text{for} \quad g = 2, ..., g_{max} \tag{50}$$

where species of subscript 1 represents the solute monomer that forms surface aggregates of size $g$. The aggregates exist only at the interface and do not exchange with the surrounding bulk phases. In this section, it is convenient to represent the solvent as component 0. Following Eq. (24), all species at the interface are accounted for

$$-d\gamma = \Gamma_{0j}d\mu_0 + \Gamma_{1j}d\mu_1 + \sum_{g=2}^{g_{max}}\Gamma_{gj}d\mu_g^\gamma \qquad \text{constant } T \tag{51}$$

where again the subscript $j$ indicates a Gibbs excess adsorption with respect to a dividing surface at $z_j$, and the chemical potentials of the surface aggregates are labeled with a superscript to emphasize that these species are confined to the interface. The Gibbs–Duhem equations involving only species zero and one are written for phases $\alpha$ and $\beta$, combined to eliminate pressure, and substituted into Eq. (51)

$$-d\gamma = \left[\Gamma_{1j} - \Gamma_{0j}\left(\frac{\rho_1^\alpha - \rho_1^\beta}{\rho_0^\alpha - \rho_0^\beta}\right)\right]d\mu_1 + \sum_{g=2}^{g_{max}}\Gamma_{gj}d\mu_g^\gamma \quad \text{constant } T \tag{52}$$

where the Gibbs invariant adsorption, $\Gamma_{1E}$, for monomer species now appears in the first term on the right. Reaction equilibrium among the

surface complexes demands that $g\mu_1 - \mu_g^\gamma = 0$. Accordingly, Eq. (52) simplifies to the final expression

$$-d\gamma = \left[\Gamma_{1E} + \sum_{g=2}^{g_{max}} \Gamma_{gj}\right] d\mu_1 \quad \text{constant } T. \tag{53}$$

Eq. (53) appears incomplete because adsorption of the surface complexes, $\Gamma_{gj}$, apparently depends on the location of the dividing surface. Since the surface complexes exist only at the interface (i.e., $\rho_g^\alpha = \rho_g^\beta = 0$), however, Eq. (25) or (28) reveals that $\Gamma_{gj}$ is a Gibbs invariant similar to that for an insoluble-surfactant monolayer (see also Section 3.2 for electrons at the mercury/water interface). Thus, Eq. (53) is the rigorous GAE for surface-aggregate formation. Because excess adsorptions in Eq. (53) are Gibbs invariants, Eqs. (13) and (28) confirm that they are also Guggenheim invariants. Thus, Gibbs excess adsorptions may be replaced in Eq. (53) by corresponding Guggenheim adsorbed amounts with no change in results.

## 4. Applications of GAE

The Gibbs (Guggenheim) adsorption equation is indispensable for understanding adsorption behavior at fluid/fluid interfaces. We cite three applications: theory concordance, interconversion of interfacial tension and adsorption, and thermodynamic consistency. Proposed theories for adsorption and/or tension must obey the GAE. This exercise provides a physical test of the theory and, in the case of molecular simulation, validation of the simulation. Next, given experiment or theory for the interfacial-tension isotherm, the corresponding adsorption isotherm can be established, and vice versa. For example, a proposed adsorption isotherm can be transformed into a surface equation of state using the GAE. Finally, mixture-adsorption data and theory must be thermodynamically consistent with the GAE. In all cases, it is the invariant adsorptions in Eqs. (13) or (28) that must be utilized in the GAE. Each of these applications is illustrated below.

### 4.1. Theory concordance

#### 4.1.1. Molecular thermodynamics

A number of simple molecular-based models are available that treat the fluid/fluid interface as a separate phase of given composition [2,65–68], especially for aqueous surfactants [69–75]. We illustrate from the extensive studies of Fainerman and Miller [31,60–64,76–96]. These authors adopt the Butler or monolayer equation for the interfacial region [2,97]

$$\mu_i = \mu_i^{\gamma o} + RT \ln f_i^\gamma \theta_i + \gamma \overline{\omega}_i \tag{54}$$

where $\mu_i^{\gamma o}$ is component $i$ standard state at the interface, $\theta_i$ is the area-fraction composition of component $i$ in the interfacial layer, and $f_i^\gamma$ is the interfacial activity coefficient of component $i$. The interfacial-layer approximation described in Eq. (54) is a pleasing analogy to that of bulk phases. However, it does not account for or recognize density profiles through the interface. Indeed, composition profiles vary strongly through the interface (see Fig. 2). Thus, the exact meanings of the surface-layer composition and activity coefficient are extra thermodynamic. Adoption of the Butler interfacial-layer model also bypasses the GAE in calculating interfacial tension from expressions for adsorption isotherms.

Fainerman and Miller adopt the Lucassen-Reynders–Joos convention in Eq. (35) for the Gibbs dividing surface so that $\theta_i = \overline{\omega}_i \Gamma_{i\omega}$. With the Lucassen-Reynders–Joos dividing surface, all components are present at the interface including, for example, solvents water and oil for liquid/liquid interfaces. Equality of the chemical potentials in Eq. (54) with those in the corresponding bulk phases specifies both the interphase composition and the interfacial tension. Many embodiments

of this approach have been put forward including aqueous surfactant mixtures, both ideal and nonideal with respect to surface interaction and size dissimilarity, surfactants that aggregate at the surface and/or change orientation and conformation, proteins, mixtures of proteins and surfactants, ionic surfactants, and the effect of oil at oil/water interfaces, all with considerable predictive power [31,60–64,76–96].

By way of example, consider a nonvolatile solvent/inert-gas interface with a single dissolved nonvolatile surface-active component. Solvent (water) is component 1 and the surface-active solute is component 2. Let the partial molar areas of both components be identical and equal to $\omega$. The bulk solution is dilute and ideal; the surface phase is ideal in the dilute Henry limit. Equating chemical potentials of components 1 and 2 from Eq. (54) to their bulk counterparts gives [78]

$$\theta_2 = \frac{K_2 x_2}{1 + (K_2 - 1)x_2} \tag{55}$$

where $x_2$ is the mole fraction of solute in the bulk solution and

$$K_2 \equiv \exp\left[-\left(\mu_2^{\gamma o} - \mu_2^{\alpha o} - \mu_1^{\gamma o} + \mu_1^{\alpha o}\right)\right]/RT]. \tag{56}$$

Superscripts $o$ on the chemical potentials indicate standard state. $K_2$ is the equilibrium constant for solute adsorption characterized by the difference in standard Gibbs free energies of adsorption of the solvent and solute in an exchange process at the interface. In the limit of strong solute adsorption (i.e., $K_2 > 1$), Eq. (55) is that of Langmuir. Interfacial tension also follows from the two chemical-potential equalities

$$(\gamma_o - \gamma)\omega/RT \equiv \pi\omega/RT = \ln[1 + (K_2 - 1)x_2] \quad \text{constant } T, P \tag{57}$$

where the symbol $\pi$ denotes the spreading pressure. Eq. (57) corresponds to the classic Langmuir–Szyszkowski relation [2].

Nowhere in the Lucassen-Reynders/Joos/Fainerman/Miller framework is the Gibbs adsorption equation utilized. Nevertheless, it must be obeyed by physically correct models. To assess agreement with the GAE, the solute invariant adsorption in Eq. (28) is first established from Eq. (55)

$$\Gamma_{2E} \equiv \Gamma_{21} = \Gamma_{2\omega} - \Gamma_{1\omega}x_2 = \frac{(K_2-1)x_2 + x_2^2}{\omega[1 + (K_2-1)x_2]} \sim \frac{(K_2-1)x_2}{\omega[1 + (K_2-1)x_2]} \tag{58}$$

where the term $0(x_2^2)$ is neglected in the far-right expression. When the free energies of the adsorption-exchange process sum to zero in Eq. (56), the solute Gibbs invariant adsorption in Eq. (58) is also zero, a pleasing result since only invariant adsorptions have thermodynamic significance.

To verify obedience with the GAE, surface tension in Eq. (57) is differentiated with respect to $d\mu_2 = RTd \ln x_2$. The far-right form of Eq. (58) is confirmed. This result means that for this case, the GAE is satisfied in dilute solution and for strong solute adsorption. The small error in disobedience to the GAE likely arises because Eq. (54) is apparently not rigorous. All molecular-thermodynamic models must be validated against the GAE.

Probably the least-involved theory explicitly accounting for molar density profiles and, hence, for local mole-fraction profiles is that of Cahn and Hilliard [98], also coined gradient or square-gradient theory [5]. Because species concentrations vary through the interface, there are positive penalty terms in the free-energy density that are proportional to the square of the local density gradients with scaling coefficients, $C_{ij}$, known as influence parameters. At equilibrium, the local chemical potential is everywhere constant and equal to

$$\mu_i = \mu_i^H\left(\rho_i(z)\right) - \sum_{j=1}^c C_{ij} \frac{d^2\rho_j(z)}{dz^2} \quad \text{constant } T \tag{59}$$

where the chemical potential of component $i$ consists of a local homogeneous term $\mu_i^H$ and inhomogeneous terms involving how strongly density variation of each component influences the uniform chemical potential. Although not necessary, influence parameters in the formulation of Eq. (59) are taken as constants. $\rho_i(z)$ denotes an array consisting of all density profiles. Eq. (59) requires information on the local homogeneous chemical potential, typically obtained from a bulk-phase equation of state (EOS). For example, for van der Waals EOS, the local homogeneous chemical potential is given by [5,99]

$$\mu_i^H(z) = \mu_i^o(T) + RT \ln \frac{\rho_i RT}{(1 - \rho b)} + \frac{RT\rho b_i}{(1 - \rho b)} - 2RT \sum_{j=1}^{c} \rho_j \sqrt{a_i a_j} \quad \text{constant } T \tag{60}$$

where $a_i$ and $b_i$ are the van der Waals EOS interaction and finite-size parameters, respectively, $\rho = \sum_{i=1}^{c} \rho_i$, $b\rho = \sum_{i=1}^{c} \rho_i b_i$, and $\mu_i^o$ is the standard chemical potential for an ideal gas at 1 bar and temperature $T$. Units of $\rho_i RT$ in Eq. (60) are in bar, and a geometric mixing rule specifies $a_{ij}$. As in the Butler model of Eq. (54), chemical potentials in Eq. (59) are equated to their bulk-phase counterparts. Resulting coupled, nonlinear ordinary differential equations are evaluated numerically with boundary conditions of compositions equal to those in the bulk $\alpha$ and $\beta$ phases at $\tau^\alpha$ and $\tau^\beta$, respectively. Bulk-phase equilibrium compositions are predetermined by equating pressures and chemical potentials in Eq. (60) for each component to those in the homogeneous $\alpha$ and $\beta$ phases (i.e., Eq. (59) but with $d\rho_i/dz = 0$). Once density profiles are established, interfacial tension follows from the expression [5]

$$\gamma = \int_{-\tau^\alpha}^{+\tau^\beta} \sum_{i,j}^{c} C_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} dz. \tag{61}$$

Fig. 6 displays calculated density profiles across the water (component 1)/heptane (component 2) interface at 298 K and 1 atm with a
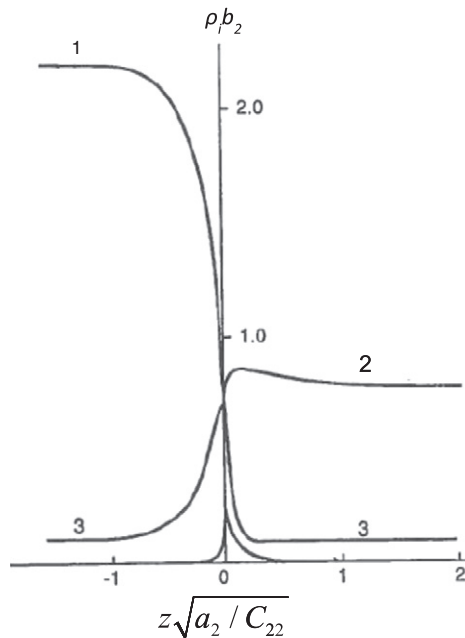


**Fig. 6.** Molar density profiles for water (1), heptane (2), and a prototypical alcohol (3) at 298 K and 1 atm with 10 mol% aqueous alcohol predicted from gradient theory and van der Waals EOS. $ij$ interaction parameters follow a geometric mixing rule: $a_{ij} = \sqrt{a_i a_j}$ and $C_{ij} = \sqrt{C_i C_j}$.
After [5] with permission.

prototypical alcohol, such as pentanol (component 3), present in the aqueous phase at 10 mol% [5,100]. van der Waals constants are obtained from critical-point data for the pure components; influence parameters for the pure components are obtained from surface-tension data, and $C_{ij} = C_{ji} = \sqrt{C_{ii}C_{jj}}$. The abscissa origin in Fig. 6 is chosen conveniently. As expected, water and oil densities vary steeply through the interface, whereas pentanol displays surface activity due to molecular amphiphilicity. Interestingly, the oil density profile exhibits a shallow maximum because of increased oil solubility in the presence of the surface-active alcohol, an observation not anticipated in Fig. 2. Agreement with experimental interfacial tension for the system in Fig. 6 is qualitative depending strongly on the particular choice of influence parameters [100]. Gradient theory is oversimplified in that the molecular orientation is not accounted for.

As with the Butler-based interfacial-layer models, gradient theory does not make use of the GAE when predicting interfacial tension. Nonetheless, as with all molecular-thermodynamic interfacial models, it is incumbent upon practitioners to establish concordance with rigorous thermodynamics [16,17,101]. Accordingly, several authors have confirmed obedience of gradient theories to the GAE [102–104]. In particular, Widom [102] established that provided the gradient-correction term in Eq. (59) depends at most on $\rho_i(z)$, consistency is guaranteed. If, however, other dependencies arise, then gradient theory must be corrected to provide agreement.

### 4.1.2. Molecular simulation

Molecular simulation gives information not only on density profiles but also on surface molecular architecture. Because of attention paid to the GAE, we illustrate the results of Howes and Radke [105] on Lennard–Jones (LJ) surfactants [106–112] at the liquid/vapor interface. In the Monte-Carlo simulations of Howes and Radke, nonionic block-copolymer amphiphilic surfactants consisting of a solvophilic head and a solvophobic tail with $m$ head monomers and $n$ tail monomers, $H_m T_n$, adsorb to the liquid/vapor interface of a monomeric LJ solvent. Fig. 7 shows simulated density profiles, $\rho_2(z)$, at a reduced temperature of 0.9 for the surfactant $H_4 T_4$ including the center-of-mass profile compared to the center-of-mass profiles for the heads and tails. An insert gives the simulated density profile for the LJ solvent, $\rho_1(z)$. Clearly, adsorbed surfactant tails penetrate into the vapor phase due to strong dislike for the solvent while surfactant heads prefer the liquid phase.

Howes and Radke [105] establish the Gibbs plane of zero-solvent adsorption, $z_1$, as shown by the vertical dashed line in the insert. Surfactant adsorption with respect to this dividing surface, $\Gamma_{21}(=\Gamma_{2E})$, is then calculated from the surfactant center-of-mass profile according to Eq. (21). Results are shown as points in Fig. 8 for three surfactants: $H_4 T_4$, $H_4 T_5$, and $H_4 T_6$. All units are expressed in terms of the LJ solvent intermolecular-energy well depth, $\varepsilon$, and collision diameter, $\sigma$. Typical Langmuir adsorption-isotherm shapes emerge. As the tail length of the surfactant increases, both the initial isotherm slope and the maximum adsorption increase. The reason why maximum coverage increases with increasing tail length is that surfactant orientation trends toward perpendicular, surfactant penetrates toward the vapor phase, and tail moiety stretches, all permitting increased adsorption. Lines in Fig. 8 are best fit to the Langmuir isotherm in Eq. (58) with good agreement.

Fig. 9 displays as points independent-simulated interfacial tensions for increasing bulk concentrations of the three block-copolymer surfactants [105]. At higher concentrations, the tensions level off for all three surfactants. Simulations at these higher concentrations reveal surfactant aggregates in the bulk solution [105]. Therefore, following common practice [6], a critical aggregation concentration, CAC, is defined by the intersection of the horizontal constant-tension line and the tension isotherm at lower surfactant bulk concentrations. Lines in Fig. 9 below the CAC are not fit, but are calculated from the GAE using the Langmuir isotherm and the fit parameters from the adsorption simulations in Fig. 8. Agreement between predicted lines, obeying the Langmuir–
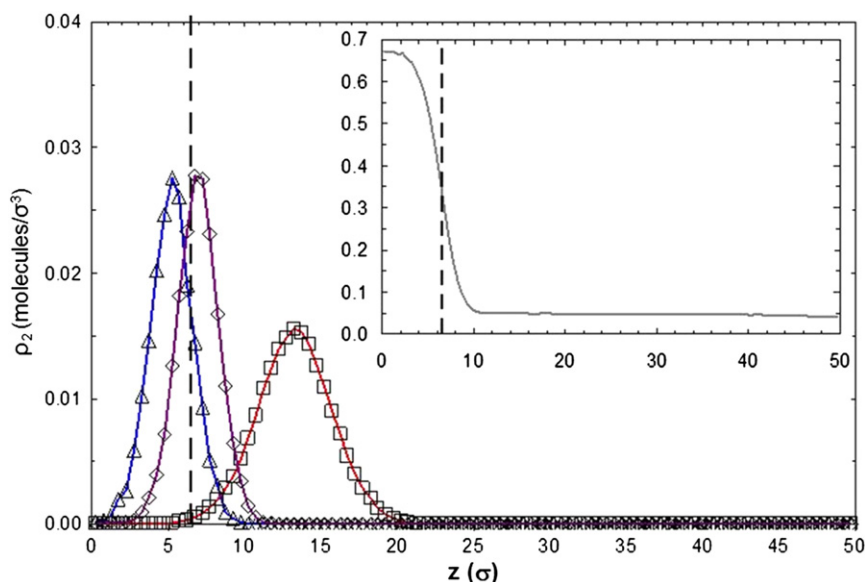
**Fig. 7.** Center-of-mass density profiles for $H_4T_6$ surfactant at a bulk concentration of 0.41 CAC ($1.2 \pm 0.2 \times 10^{-4}$ molecules/$\sigma^3$). Triangles outline the head-group center-of-mass density profile, diamonds outline the surfactant center-of-mass density profile, and squares outline the tail-group center-of-mass density profile. Vertical dashed lines represent the zero-adsorbed-solvent Gibbs dividing surface, $z_1$. An inset shows the solvent density profile, $\rho_1$. Zero on the z-axis corresponds to the center of the simulation film. From [105] with permission.

Szyszkowski equation [Eq. (57)], and the simulated tensions indicates consistency with the GAE. This exercise does not provide a test of the GAE since it is thermodynamic and rigorous. Rather, the comparison in Fig. 9 indicates that the simulations are consistent with sufficient system size and run time to establish equilibrium. In this situation, the GAE provides a test of the simulations.

Not all interfacial molecular simulations are evaluated carefully for conformance to the GAE. Starting in 2000, Jungwirth and Tobias reported important simulations of aqueous sodium-halide salts adsorbing at the water liquid/vapor interface [113–117]. The important feature of these simulations is implementation of polarizable intermolecular force fields in which interaction between ions and atoms in water depends on local environment. Fig. 10 shows density profiles for the oxygen atom in water, sodium cation, and iodide anion. As in Fig. 7, a

vertical dashed line locates the Gibbs dividing surface of zero surface-excess water adsorption. The surprising feature of Fig. 10 is the positive adsorption of both sodium ions and iodide ions at the water/gas interface. Jungwirth et al. explain this observation as asymmetric polarization of larger anions by water near the interface, although the exact mechanisms remain in debate [118]. Smaller halide anions do not demonstrate positive accumulation near the interface. Likewise, simple fixed intermolecular potentials also do not capture this effect [119]. Using surface harmonic generation, Sakally and colleagues provide experimental verification of polarizable anion accumulation near the water/air interface [120–123].

Jungwirth and Tobias report simulated surface tensions of the aqueous sodium-halide electrolytes larger than that of pure water [114]. Based on the arguments presented in Section 3.1, strong-electrolyte
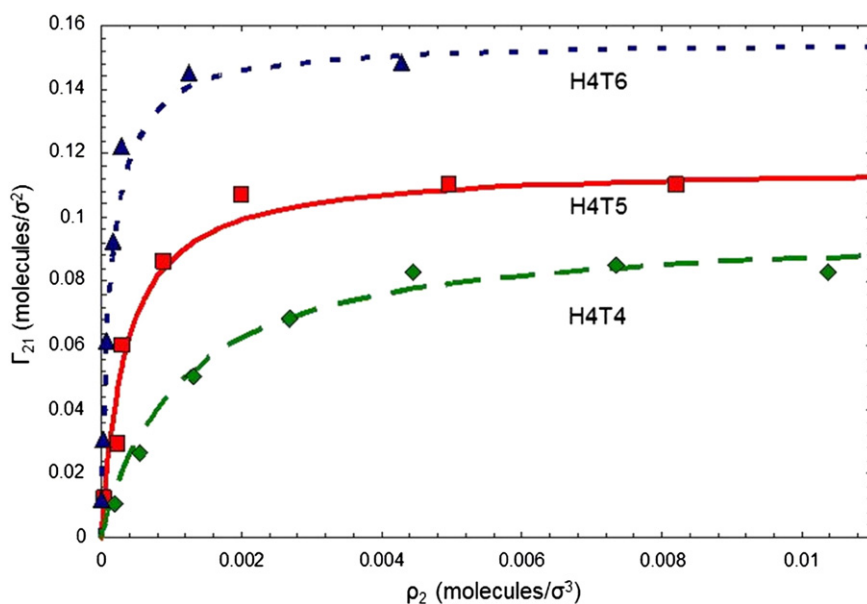


**Fig. 8.** Gibbs excess adsorption isotherms for three surfactants. Points represent simulation data: triangles for the $H_4T_6$, squares for the $H_4T_5$, and diamonds for the $H_4T_4$. Lines represent Langmuir-isotherm fit to Eq. (58): a dotted line for the $H_4T_6$ simulation, a solid line for the $H_4T_5$ simulation, and a dashed line for the $H_4T_4$ simulation. From [105] with permission.
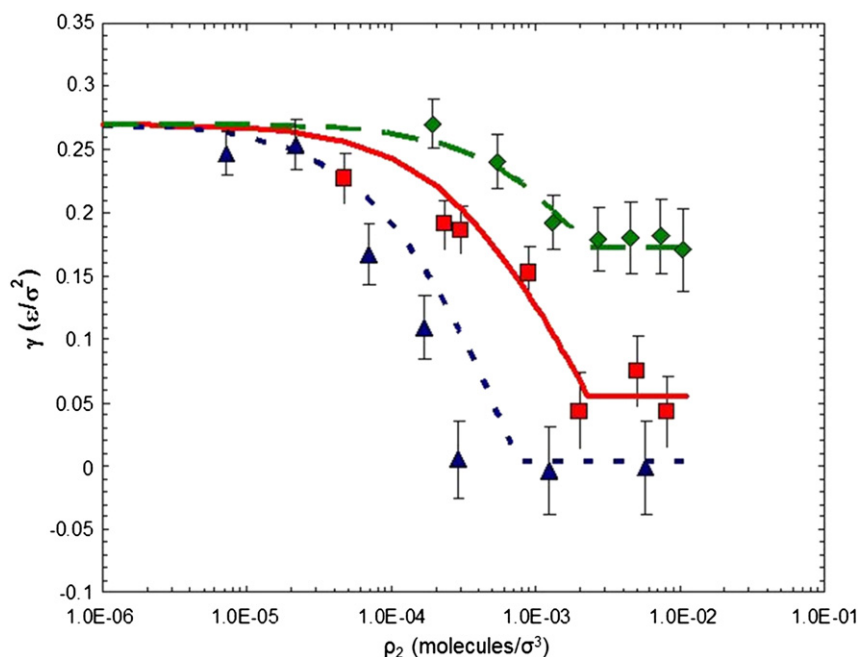
**Fig. 9.** Surface-tension isotherms for three surfactants. Points represent simulation data: triangles for the $H_4T_6$, squares for the $H_4T_5$, and diamonds for the $H_4T_4$. Lines represent the Langmuir–Szyszkowski isotherm in Eq. (57): a dotted line for the $H_4T_6$ simulation, a solid line for the $H_4T_5$ simulation, and a dashed line for the $H_4T_4$ simulation. Horizontal lines begin at the critical aggregation concentration (CAC).
From [105] with permission.

surface tensions larger than that of the solvent arise because of equal and negative surface-excess adsorption for both salt ions: $\Gamma_{Na^+1} = \Gamma_{I^-1} < 0$. The simulations of Jungwirth and Tobias in Fig. 10 do not satisfy these criteria leading them and others [124] to question the classic ion-repulsion interpretation of the GAE for large halide anions as "too simplistic". However, the GAE does not recognize molecules. This feature is both a strength and a weakness. The GAE is valid independent of molecular structure, but conversely it gives no information on molecular density profiles or surface molecular architecture.

A likely resolution of the results in Fig. 10 [117,120,124,125] is that the particular simulations of Jungwirth and Tobias [115] were not carried out in large enough systems to capture the entire density profiles. Close examination of Fig. 10 shows that the two salt ions do not attain bulk concentration away from the interface and that electroneutrality of the interfacial region is not precisely achieved. The GAE provides a tool to assess molecular simulations, not vice versa.
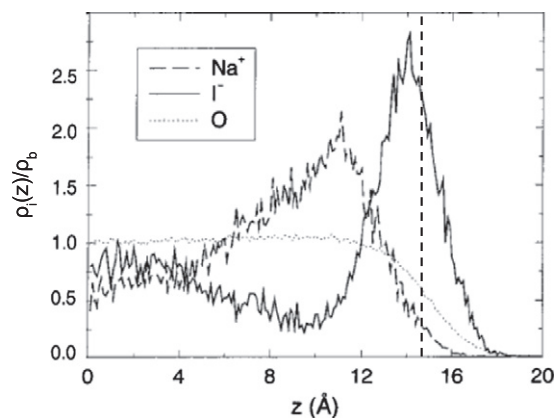


**Fig. 10.** Simulated density profiles at ambient temperature relative to bulk liquid density for aqueous sodium iodide and oxygen atoms in water at the liquid/vapor interface. Bulk salt concentration is 1.2 M. A vertical dashed line approximates the Gibbs dividing surface for zero solvent adsorption.
After [115] with permission.

## 4.2. Interchanging tension and adsorption

The Gibbs adsorption equation is a tool to convert adsorption isotherms to tension isotherms and vice versa. For example, substitution of the invariant adsorption isotherm in Eq. (58) for a single, ideal dilute, nonvolatile solute at a solvent/inert-gas interface into the GAE followed by integration gives the Langmuir–Szyszkowski tension isotherm in Eq. (57). Likewise, substitution of Eq. (57) into the GAE followed by differentiation gives the Langmuir solute invariant adsorption isotherm in Eq. (58).

It is instructive to rewrite the Langmuir–Szyszkowski expression in the following form

$$\frac{\pi a_{21}}{RT} = \frac{a_{21}}{\omega} \ln\left[1 - (\omega/a_{21})\right]^{-1} \tag{62}$$

where $a_{21} \equiv \Gamma_{21}^{-1}$ is the molar area occupied by component 2 at the interface. In the limit of small coverage of solute 2, Eq. (62) reduces to the expression for an ideal two-dimensional equation of state: $\pi a_{21}/RT = 1$. Thus, the Langmuir–Szyszkowski relation for surface tension may be viewed as a two-dimensional, noninteracting solute of finite size residing at the interface. Many analogies to other two-dimensional equations of state can be drawn [126]. For example, a two-dimensional van der Waals tension isotherm is given by

$$\left(\pi + \alpha/a_{21}^2\right)(a_{21} - \omega) = RT \tag{63}$$

where $\alpha$ is a two-dimensional interaction parameter. The corresponding adsorption isotherm is given by

$$(K_2 - 1)x_2 = \frac{\omega\Gamma_{21}}{(1 + \omega\Gamma_{21})} \exp\left[\frac{\omega\Gamma_{21}}{(1 + \omega\Gamma_{21})} - \frac{2\alpha\Gamma_{21}}{RT}\right] \tag{64}$$

which is an extended Langmuir equation accounting for both finite size and surface lateral interaction. Note that the Gibbs invariant adsorption $\Gamma_{21}$ appears in the van der Waals tension isotherm. Accordingly, adsorbed amounts can also be defined in the Guggenheim framework, provided

that the Guggenheim invariant adsorption for solute 2 (i.e., Eq. (13)) is utilized in Eq. (64). Extension of two-dimensional equations of state to mixed-solute adsorption is straightforward by analogy to bulk equations of state with mixing rules for the EOS parameters [94]. Because the interfacial region is inhomogeneous on a molecular scale, two-dimensional equations of state are not literal. Caution must be taken in attributing physical meaning to the parameters appearing in the particular 2-D EOS chosen.

### 4.3. Thermodynamic consistency

Because Gibbs adsorption equation is an exact differential, cross differentials must be equal. Thus, Eq. (30) demands that

$$\left(\frac{\partial \Gamma_{i1}}{\partial \mu_j}\right)_{T,\mu_{i\neq 1,j}} = \left(\frac{\partial \Gamma_{j1}}{\partial \mu_i}\right)_{T,\mu_{j\neq 1,i}} \quad \text{constant } T. \qquad (65)$$

Only Gibbs (or Guggenheim) invariant adsorptions appear in Eq. (65). Mixture adsorption data or theory must satisfy Eq. (65). Otherwise, those data or theories are thermodynamically inconsistent. For example, extension of the Fainerman–Miller Langmuir model in Eq. (58) to an equal-size multicomponent solute mixture adsorbing at a liquid/gas interface reads

$$\Gamma_{iE} \equiv \Gamma_{i1} = \frac{(K_i-1)x_i}{\omega\left[1+\sum_{j=2}^{c}\left(K_j-1\right)x_j\right]}. \qquad (66)$$

This model satisfies thermodynamic consistency. Likewise, the so-called ideal adsorbed solution (IAS) mixture model is thermodynamically consistent because it utilizes the GAE in the calculation framework [127–130]. Many simple models do not obey thermodynamic consistency including that of Langmuir with unequal-sized adsorbates [131]. Because only simple models can be evaluated analytically according to Eq. (65) [132], most mixture theories are not evaluated for thermodynamic consistency.

## 5. Conclusions

The Gibbs adsorption equation is indispensable for understanding equilibrium adsorption behavior at fluid/fluid interfaces. It provides a benchmark for molecular-thermodynamic models and molecular simulation. It provides a tool to convert between adsorption theories and tension isotherms and vice versa. It provides a means for assessing thermodynamic consistency of mixture adsorption data and theory. In spite of the fundamental thermodynamic origin and rigor of the GAE, implementation is fraught with confusion primarily over the physical meaning of a zero-volume surface phase. This led others, primarily Guggenheim and Hansen, to reformulate Gibbs thermodynamic analysis for a finite-thickness surface phase. By paying careful attention to the phase rule, however, we show that both Gibbs and Guggenheim approaches give identical results. It makes no difference in the GAE whether adsorption is gauged by a zero-volume surface excess in the Gibbsian sense with various choices of dividing surface or the actual amount of material in a finite-volume surface phase as in the Guggenheim framework. However, equivalence is achieved if and only if excess invariant quantities appear in the GAE that are independent of the location of the Gibbs dividing surface or are independent of the interfacial thickness in Guggenheim's treatment.

Application of the GAE to electrified fluid/fluid interfaces, interfaces with surface aggregation, interfaces of strong and weak electrolytes, etc. is straightforward provided that all equilibrium restrictions are accounted for including the Gibbs–Duhem relations in the bounding bulk phases. Both molecular simulation and molecular-thermodynamic

models must conform to the GAE. Conformance is an important screen that should always be applied.

Most of the confusion of the GAE originates with differences in the exact meaning of the surface excess properties under debate. Provided that invariant surface properties are correctly employed, the GAE is general and rigorous.

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