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

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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^α and V^β 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 $dU = \dj Q + \dj W$ 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 $\dj$ 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

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

where T is the temperature, S is the total system entropy, P the is pressure, V is the total system volume, μ_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 α and β as they are uniform throughout the system including the interfacial region. Pressure in Eq. (1) is that corresponding to equilibrium between phases α and β. If, for example, phases α and β 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^γ_{rev}.

2.1. Capillary work

Following others [2,3,5,32], Fig. 1 illustrates a simple system to evaluate the reversible capillary work dW^γ_{rev}. Phases α and β 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

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

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 α and β. 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

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

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

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

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, α and β, separated by an intervening interfacial phase labeled below as γ

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