APPLICABILITY OF GIBBS ADSORPTION EQUATION TO DEFORMED SOLID SURFACES

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Abstract
Revisiting derivations of Gibbs adsorption equation show its applicability to solid surfaces without limiting requirement of constant state of strain. The some attempts to use such a restriction to prove the correctness of the Shuttleworth equation have failed.

Introduction

The reason why right now we are discussing this issue is the need to clarify some misconceptions in the interpretation of the theory of Gibbs. In some works it is persistently and repeatedly underlined that the limitation on the validity of the Gibbs adsorption equation (Eq. (1) here, Eq. {675} in [1]) is a *mandatory* requirement: the *solid surface strain should not vary* (e. g., [2, 3, 4], etc.). Simultaneously, to remedy this "shortcoming" of the Gibbs' thermodynamics, they proposed "modernizations" (as so called the "Shuttleworth equation") free of such restriction which, however, remain to be the subject of criticism from 1995 [5] to the present days (e. g., [6, 7], etc.).

Results and discussion

We go on to show the validity of the Gibbs adsorption equation *without the restriction* that solid surface strain should not vary.

For a solid surface Gibbs begins with the fundamental equation ([1], Eq {674}) which he wrote stipulating the condition "any constant state of strain of the surface of the solid"

$$d\varepsilon_{s(1)} = td\eta_{s(1)} + \mu_2 d\Gamma_{2(1)} + \mu_3 d\Gamma_{3(1)} + ... \qquad (1) \ \{674\}$$

"since this relation is implied in the definition of the quantities involved". Here we follow the nomenclature of Gibbs in [1]: ε is the energy, η is the entropy, t is the (absolute) temperature, μ_i is the chemical potential of the component i and the subscript s denotes the surface densities of corresponding quantities of energy and entropy, Γ_i is the superficial density of the component i {"the dividing surface is so placed as to make $\Gamma_1=0$"}, σ is the "gibbsian sigma" introduced by Gibbs as a coefficient in the variation of energy caused by variation of the surface area..

From this relation and the equation ([1], Eq {659})

$$\sigma = \varepsilon_{s(1)} - t\eta_{s(1)} - \mu_2\Gamma_{2(1)} - \mu_3\Gamma_{3(1)} - ... \qquad (2) \ \{659\}$$

one obtains the famous Gibbs adsorption equation ([1], Eq. {675}) written for a solid surface

$$d\sigma = -\eta_{s(1)}dt - \Gamma_{2(1)}d\mu_2 - \Gamma_{3(1)}d\mu_3 - ... \qquad (3) \ \{675\}$$

"which is subject, in strictness, to the same limitation – that the state of strain of the surface of the solid remains the same. But this limitation may in most cases be neglected." ([1], page 328). First let us explore how this constraint arose.

Note that Eq. (2) was written as a postulate for the definition of the quantity σ (p. 315 [1]). Thus, Gibbs has originally adopted in the basic Eq. (1) the condition of unchanged strain of the solid surface and even a surface work term with σ is absent. Therefore the Eq. (3) derived from (2) should have the same limitation.

To understand the reason for absence of the surface term in Eq. (1) (which is written for the densities of quantities) we start out with the basic equation ([1], Eq {501}) which "is of fundamental importance in the theory of capillarity" ([1], page 228)

$$d\varepsilon^s = td\eta^s + \sigma ds + \mu_1 dm_1^s + \mu_2 dm_2^s + ... \qquad (4) \ \{501\}$$

where the superscript s denotes the surface excess of corresponding quantities, m_i is the mass of the component i, s is the surface area of the fluid interface. The Euler integral ([1], Eq {502}) of this equation is obtained "supposing the area s to increase from zero to any finite value s" ([1], page 229)

$$\varepsilon^s = t\eta^s + \sigma s + \mu_1 m_1^s + \mu_2 m_2^s + ... \qquad (5) \ \{502\}$$

Differentiating this equation and comparing the result with Eq. (4) gives ([1], Eq {503})

$$\eta^s dt + sd\sigma + m_1^s d\mu_1 + m_2^s d\mu_2 + ... = 0 \qquad (6) \ \{503\}$$

that is the standard procedure deriving the Gibbs-Duhem (GD) equation.

Developing Eqs. (4)-(6) through the "superficial densities of energy, of entropy and of the several component substances" ([1], Eqs. {11} and {12})

$$\varepsilon_s = \varepsilon^s / s, \qquad \eta_s = \eta^s / s, \qquad (11) \ \{504\}$$

$$\Gamma_1 = m_1^s / s, \qquad \Gamma_2 = m_2^s / s, \text{ etc.}, \qquad (12) \ \{505\}$$

one obtains the basic equation ([1], Eq {506})

$$d\varepsilon_s = td\eta_s + \mu_1 d\Gamma_1 + \mu_2 d\Gamma_2 + ... \qquad (13) \ \{506\}$$

the integral ([1], Eq {507})

$$\varepsilon_s = t\eta_s + \sigma + \mu_1\Gamma_1 + \mu_2\Gamma_2 + ... \qquad (14) \ \{507\}$$

and the adsorption equation ([1], Eq {508})

$$d\sigma = -\eta_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - ... \qquad (15) \ \{508\}$$

It is important to note that here the transition to the densities of the quantities was made in the final GD equation (15) (as dividing Eq. (6) by the area s), but returning to Eqs. (1)-(2) we see that the transition to densities already occurred in the initial Eq. (2). Also, it is worthy to note that Eq. (15) is *free of strain restrictions* in opposite to said for Eq. (3) despite their methods of derivation are similar excluding at what step the transition to densities was made. Note that in

contrast to Eq. (5), the Eq. (14) is not the Euler integral of Eq. (13), but if initially to take the Euler integral (5) and then to divide by *s* then Eq. (14) will be obtained. It is easy to see that Eq. (1) (Eq.{674}[3]) is an "solid" analogue of "fluid" Eq. (13) (Eq.{506}[3]) for $\Gamma_1\neq0$.

If "the dividing surface is so placed as to make $\Gamma_1=0$" ([1], page 234) then Eq. (15) reduces to ([1], Eq {514})

$$d\sigma = -\eta_{s(1)}dt - \Gamma_{2(1)}d\mu_2 - \Gamma_{3(1)}d\mu_3 - \textbf{etc}., \quad (16) \ \{514\}$$

and it being written for the *liquid* surface nevertheless exactly coincides with Eq. (1) written for the *solid* surface although is free of any strain restrictions. By the way, concerning analogies Gibbs notes (p. 231): "The reader will not fail to notice the analogy between these fundamental equations, which relate to surfaces of discontinuity, and those relating to homogeneous masses...". It will not be a mistake to say that the same relates to the analogy between fundamental equations for fluid and solid surfaces.

The combination of Eqs. (5)-(6) with (11)-(12) to obtain Eqs (14)-(15) as the transition to superficial densities does not cause problems. However, when doing it for Eq. (4) to obtain Eq. (13) then some complications arise and Eq. (13) can not be obtained from Eq. (4) by similar combining without additional condition.

If it is so, let us to try to derive the Eq. (1) without any limiting conditions as is shown below completely remaining within the framework of Gibbs' theory. Indeed, the fundamental equation of kind Eq. (4) for the case $\Gamma_1=0$ reduces to

$$d\varepsilon^s_{(1)} = td\eta^s_{(1)} + \sigma ds + \mu_2 dm^s_{2(1)} + \mu_3 dm^s_{3(1)} + ... \quad (27)$$

and then the Euler integral of it is

$$\varepsilon^s_{(1)} = t\eta^s_{(1)} + \sigma s + \mu_2 m^s_{2(1)} + \mu_3 m^s_{3(1)} + ... \quad (28)$$

Differentiating this equation and combining the fundamental equation (27) we obtain

$$sd\sigma = -\eta^s_{(1)}dt - m^s_{2(1)}d\mu_2 - ... \quad (29)$$

Turning to the densities in this equation (dividing by *s*) we just obtain Eq. (1) ([1], Eq. {675} *without any limitations on the state of strain of the surface of a solid*.

Returning to the criticism of attempts at modernization Gibbs' theory mentioned beginning the paper, we note that "modernization" was resulted in the appearance of an extensive variable (the differential of volume or area weighted strain) in the equation of "Gibbs-Duhem relation type" (e. g., [2, 3, 4, 8], etc.) which made it wrong [5, 6]. These examples should suffice to demonstrate the confusion in the literature with regard to the proper form of the Gibbs-Duhem equation. Thus, we were strongly motivated to investigate this question in more detail. Shuttleworth

Conclusions

1. Gibbs adsorption equation is applicable to solid surfaces without limiting requirement of constant state of strain and therefore the classical theory does not need to upgrade.
2. The derivation of so called "Gibbs-Dugem relation" contained volume or area weighted strain (an extensive variable) and given in many papers is not correct.
3. The Shuttleworth equation directly following the distorted "Gibbs-Dugem relation" (Table 1) is wrong and should be removed from use.

References

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Table 1   Comparative derivation of Gibbs-Duhem and Shuttleworth equations

Step of procedure	Gibbs	Shuttleworth et all
1	3	3
(1) Fundamental equation	$dU= \sigma da+TdS+\mu dm$	$dU= \gamma da+TdS+\mu dm$
(2) Euler integral of (1)	$U= \sigma a+TS+m\mu$	$U= \gamma a+TS+m\mu$
(3) Differential of integral (2)	$dU= \sigma da+ad\sigma+TdS+SdT+$ $+md\mu+\mu dm$	$dU= \gamma da+ad\gamma+TdS+SdT+$ $+md\mu+\mu dm$
(4) Fundamental equation to be equating to (3)	$dU= \sigma da+TdS+\mu dm$	$dU^*= \sigma^* da+TdS+\mu dm$
Result	**Gibbs-Duhem equation (correct)** $0= ad\sigma+SdT+md\mu$ $0= d\sigma+S_a dT+m_a d\mu$	**Shuttleworth equation (incorrect)** $0= (\gamma-\sigma^*)da +ad\gamma+ SdT+md\mu$ $0= (\gamma-\sigma^*)d\varepsilon+d\gamma+ S_a dT+m_a d\mu$ $0= (\gamma-\sigma^*)d\varepsilon +d\gamma \quad (T, \mu = const)$
Note: the artificial substituting "gibbsian sigma" σ for two quantities (the surface energy density γ and the surface stress $\sigma*$) makes the step (4) in the column 3 to be illegal because $dU\neq dU^*$, if $\gamma\neq \sigma*$ **(solid).**		