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The equivalency of surface tension, surface energy and surface free energy

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In much of the available literature, there is confusion regarding the correct use of the terms surface tension, surface energy and surface free energy. As a result, these three terms have been used interchangeably to describe the same quantity. This problem is particularly serious in the area of solid surface science. Linford has examined and discussed such inconsistencies but failed to differentiate the three quantities clearly. In the present paper, the definitions and the relationships between surface tension, surface energy and surface free energy are examined and their proper usage clarified.

1. Introduction

Capillarity, the terminology referring to the rise of a liquid in a tube of small diameter, has been studied from as far back as the time of Leonardo da Vinci (1452–1519). In the 1700s, Newton realized that the rise in liquid level can be attributed to intermolecular forces acting on the liquid within the tube. He called the driving forces the force of adhesion and cohesion. Later in the middle of the 18th century, Von Segner proposed the first theory on capillarity. Von Segner was also the first to use the term "surface tension" and the notion of a "contractile skin" on liquid surfaces, which are now an integral part of surface science [1]. In 1805, the fundamental theory on capillarity, which relates the cohesive forces in the liquid to the shape of the liquid surface, was independently published by both Young [2] and Laplace [3]. Their theory is now the basis for the majority of techniques used in surface tension studies. Since the work of Young and Laplace, some confusion has arisen regarding the proper use of the terms, surface tension, surface energy and surface free energy. In the area of solid surface science, these three quantities have been used synonymously in numerous articles. Although Linford [4] has examined and discussed the inconsistencies in the terminology, he failed to differentiate the three quantities clearly.

2. Surface curvature and surface tension

The fundamental relationship developed by Young and Laplace, better known as the Laplace equation, relates the surface curvature of a liquid to the surface tension. Their derivation is given below in a simplified format [5].

As shown in Fig. 1, consider a point P on a curved liquid surface. Using P as the centre, draw a circle on the surface whose radius is ρ. As a result, a liquid cap bounded by the circle is isolated. To derive the Laplace equation, the mechanical equilibrium on this isolated element is considered as ρ tends towards zero. Construct any set of orthogonal lines AB and CD through point P. The radii of curvature of these two lines are r_1 and r_2. The length of the path along the liquid surface from P to any of A, B, C or D can be approximated by ρ, because ρ is very small. At point A on the circular boundary of the cap, a small element, δl, experiences a surface tension force of $\gamma\delta l$. Because ϕ is a small angle as ρ approaches zero, the component of this force along the line PN is

$$\begin{aligned}\gamma\delta l \sin\phi &= \gamma\phi\delta l \\ &= \gamma\frac{\rho}{r_1}\delta l \end{aligned} \qquad (1)$$

If all four elements A, B, C, and D are considered, the combined force along PN is

$$\gamma\delta l\left(\frac{2\rho}{r_1}+\frac{2\rho}{r_2}\right) = 2\rho\gamma\delta l\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \qquad (2)$$

by Euler's theorem [5]

$$\frac{1}{r_1}+\frac{1}{r_2} = \frac{1}{R_1}+\frac{1}{R_2} \qquad (3)$$

where R_1 and R_2 refer to the principal radii of curvature. As a result of Equation 3, the validity of Equation 2 is independent of the choice of AB and CD. To calculate the surface tension force contribution for the entire cap, Equation 2 is integrated with respect to δl along the circumference of the cap. Because four elements are considered in Equation 2, the integration required should be one-quarter of a resolution around the circumference. The result yields

$$\int_0^{\pi\rho/2} 2\rho\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\delta l = \pi\rho^2\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \qquad (4)$$

To keep this isolated surface element in mechanical equilibrium, the surface tension force as shown in Equation 4 must be balanced by the hydrostatic force (pressure times area) exerted on the surface. Therefore

$$(p_2 - p_1)\pi\rho^2 = \pi\rho^2\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \qquad (5)$$

where p_1 and p_2 refer to the pressures within and

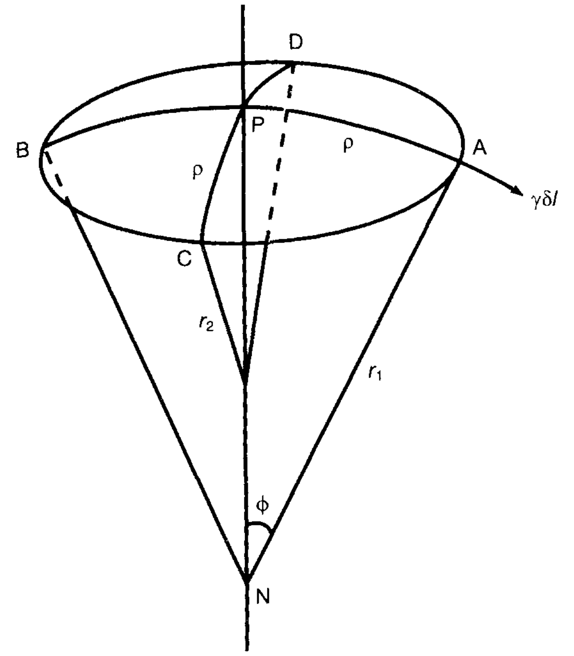

Figure 1 Isolated liquid surface for equilibrium analysis.

without the liquid surface. With $\Delta p = p_2 - p_1$, Equation 5 immediately reduces to Equation 6 which is the well-known Laplace equation

$$\Delta p = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{6}$$

From mechanical consideration, Equation 6 provides the first correct definition of *surface tension.* As will be discussed in the following sections, surface free energy is defined thermodynamically.

3. Thermodynamics of surfaces and interfaces

In a physical system when two fluids, for example a solution and a gas, come into contact, there exist three separate regions whose properties are distinctively different from each other. Namely, they are the homogeneous gas and solution phases and the interface which separates them. The composition of the interface is generally different from that of the two bulk phases. Another characteristic of the interface is the variation of concentration of any particular species across the thickness of the interface. In 1805, Young [2] concluded that it is mechanically correct to represent the interface of finite thickness as a membrane-like surface and attributed all the forces exerted on the interface to this *surface of tension.* In a similar manner, Gibbs [6] also replaced the three-dimensional interface with a two-dimensional surface in his thermodynamic treatment of the interface. Thus in Gibbs' model, all the thermodynamic properties associated with the three-dimensional interface become properties of the two-dimensional surface.

To understand the implication of Gibbs' model, assume that the real system contains n_i mole of component i. In order to make the real and the model system equivalent, a mass must be assigned to the model surface so that

$$n_i = n_i^g + n_i^l + n_i^s \tag{7}$$

where the superscripts g, l, and s refer to the gas, liquid and surface phase, respectively. By rearranging Equation 7, the number of moles of i adsorbed at the surface or the molar surface excess is defined as

$$n_i^s = n_i - n_i^g - n_i^l \tag{8}$$

In Gibbs' model, all the thermodynamic quantities associated with the surface or interface are considered to be excess quantities with respect to the two bulk phases.

Analogous to Equation 8, thermodynamic quantities such as the internal energy of the surface, U^s, may be expressed as

$$U^s = U - U^g - U^l \tag{9}$$

with U representing the total internal energy of the system.

Because the Helmholtz free energy of the system, F, is defined as

$$\begin{aligned} F &= U - TS \\ &= F^g + F^l + F^s \end{aligned} \tag{10}$$

the Helmholtz free energy of the surface, F^s, is expressed by

$$F^s = U^s - TS^s \tag{11}$$

where T, S, S^S refer to temperature, entropy and surface entropy of the system, respectively.

4. Surface tension and surface free energy

To relate surface tension to thermodynamic properties of the system, the dividing surface selected for thermodynamic consideration must coincide with the surface of tension which is defined in the mechanical treatment of the system. Thus, the validity of the relationships to be developed in this section relies on the satisfaction of this criterion.

In a capillary system, mechanical work, dW, done on the system can either be in the form of a volume change, dV, in the two bulk phases or a change in the area, dA, of the interface, that is

$$dW = -p\,dV + \gamma\,dA \tag{12}$$

If dQ is the reversible heat received by the system, the first law of thermodynamics states that

$$dU = dQ + dW \tag{13}$$

which gives

$$dQ = dU + p\,dV - \gamma\,dA \tag{14}$$

In a system where heat is also generated through chemical means, Equation 13 becomes

$$dU = dQ + dQ' + dW \tag{15}$$

where

$$dQ' = \sum_i \mu_i\,dn_i \tag{16}$$

μ_i and n_i refer to the chemical potential and number of mole of the ith species, respectively. Differentiating

Equation 10 gives

$$\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \quad (17)$$

The definition of the entropy change, $\mathrm{d}S$, for heat received from the surroundings through a reversible process is

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \quad (18)$$

where T is the temperature. If Equations 14–16 and 18 are combined together with the elimination of $\mathrm{d}Q$ and $\mathrm{d}Q'$, Equation 19 is obtained

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \gamma\mathrm{d}A + \sum_i \mu_i \mathrm{d}n_i \quad (19)$$

Substituting Equation 19 into Equation 17, the expression for the Helmholtz free energy becomes

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \gamma\mathrm{d}A + \sum_i \mu_i \mathrm{d}n_i \quad (20)$$

The relationship between surface tension and the Helmholtz free energy is obtained by keeping the temperature, T, volume, V, and molecular number, n_i, constant. This is shown in Equation 21

$$\left(\frac{\partial F}{\partial A}\right)_{T,V,n} = \gamma \quad (21)$$

Furthermore, because only the internal energy of the system, U, and surface, U^S, and entropy of the system, S, and surface, S^S, in the system are functions of the interfacial area, then

$$\left(\frac{\partial F^s}{\partial A}\right)_{T,n} = \left(\frac{\partial F}{\partial A}\right)_{T,V,n} = \gamma \quad (22)$$

By definition, F^s is an excess quantity with respect to the bulk phases, therefore, from Equation 22 surface tension is also an excess quantity. Equation 22 is considered to be the thermodynamic definition of surface tension.

To express surface tension in terms of Gibbs free energy, the total differential (Equation 23) is taken

$$\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p \quad (23)$$

Substituting Equation 19 into Equation 23 gives

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \gamma\mathrm{d}A + \sum_i \mu_i \mathrm{d}n_i \quad (24)$$

From Equation 24, the definition of surface tension in terms of Gibbs free energy at constant temperature, pressure and molecular number is

$$\left(\frac{\partial G}{\partial A}\right)_{T,p,n} = \gamma \quad (25)$$

In a manner similar to the derivation of Equation 22, Equation 25 becomes

$$\left(\frac{\partial G^s}{\partial A}\right)_{T,n} = \left(\frac{\partial G}{\partial A}\right)_{T,p,n} = \gamma \quad (26)$$

In the past, there had been much misunderstanding and misuse of the terms surface tension, surface energy and surface free energy in the literature. The misconception arises partly from the lack of standardization of nomenclature which results in the interchanging use of these three terms to identify the same quantity. Also, Equations 22 and 26 have been misinterpreted to mean that the surface tension, γ, is equal to the surface free energy per unit area or surface free energy. Such misinterpretation, as given in the books by Swalin [7] (corrected in the second edition (1972)) and Hiemenz [8], is rather unfortunate, because when Gibbs first developed his thermodynamic theory on surfaces, he showed that the surface tension cannot be equal to the surface free energy unless the adsorption at the surface is zero [6]. This is shown mathematically in Equation 28. The term f^s is referred to as the *surface free energy* or the Helmholtz surface free energy per unit area and the definition of Γ_i, the surface excess of species i, is given in Equation 29. Equation 28 is derived from Equation 27 which is an analogous form of Equation 20. According to Gibbs' model, the surface phase does not have an associated volume, therefore, the term involving volume in Equation 20 is not applicable and thus is not shown in Equation 27. The superscript s associated with the quantities shown in Equation 27 signifies that they are surface quantities. To obtain Equation 28 from Equation 27, the surface free energy involved in a surface area change (from an initial state of zero to a final state of A) is calculated by keeping the intensive properties T and μ_i^s of the surface constant. This is equivalent to integrating Equation 27 at constant T and μ_i^s. Thus the $S^s\mathrm{d}T$ term drops out from the equation.

$$\mathrm{d}F^s = -S^s\mathrm{d}T + \gamma\mathrm{d}A + \sum_i \mu_i^s \mathrm{d}n_i^s \quad (27)$$

$$\gamma = f^s - \sum_i \Gamma_i \mu_i^s \quad (28)$$

where

$$\Gamma_i = \frac{n_i^s}{A} \quad (29)$$

and

$$f^s = \frac{F^s}{A} \quad (30)$$

At first glance, it may seem improper to keep μ_i^s constant during the integration of Equation 27 because μ_i^s is a function of n_i^s. As a consequence, the generality of Equation 28 appears restricted. However, if the constant μ_i^s constraint is examined closely, it becomes clear that even though the number of n_i^s increases as the area of the surface increases, the molecular fraction of i remains constant because the moles of the other species present at the surface must also increase proportionally. Because μ_i^s is actually a function of the molecular fraction of i, keeping μ_i^s constant during the integration does not limit the generality of Equation 28. Also, at equilibrium, the chemical potentials of the different components in the various phases within the system are equal to each other. As a result, μ_i^s remains constant regardless of any change to the area of the surface. This further illustrates that the integration of Equation 27 at constant μ_i^s is valid physically. In some of the literature encountered, the derivation of Equation 28 was not shown in sufficient clarity and as a result it obscured the true meaning of the equation. For example, in Adamson's [9] derivation, he failed to clarify the validity of maintaining μ_i^s constant for the integration. In the works of Defay and Prigogine [5] and Guggenheim [10], the derivation procedure was not clearly illustrated, which makes Equation 28 difficult to comprehend.

Osipow [11] showed incorrectly that surface tension is equivalent to surface free energy ($f^s = \gamma$) by integrating Equation 27 at constant temperature and composition (for which he really meant n_i^s). The major flaw in his derivation is that physically speaking, n_i^s cannot be constant. The integration of Equation 27 corresponds to the evaluation of the surface free energy due to a change in the surface area with all the intensive quantities in the equation being constant. The variable n_i^s cannot remain constant during the integration because atoms or molecules must be supplied or removed from the surface in order to change the surface area. Fixing the number of molecules or atoms at the surface during an area change is analogous to the physically impossible task of increasing the volume of a liquid in a beaker without the addition of extra material to the beaker. Therefore, the proposition of integrating Equation 27 at constant n_i^s is totally erroneous.

From Equation 28, the surface tension of a liquid is clearly not equal to the surface free energy unless the term $\sum\Gamma_i\mu_i^s$ is equal to zero. This can be realized when either the adsorption or the chemical potentials (relative to the standard state) of all the species at the surface are zero. However, as will be shown below, these conditions can only be achieved in hypothetical situations. In order for the chemical potential to be zero, the system must only consist of a *pure* liquid in contact with its own vapour. In such a *one-component* system, the activity, a_i, is unity. Thus, the chemical potential, μ_i^s becomes zero. Nevertheless, even with the best vacuum equipment available, it is physically impossible to remove all the air molecules within a sealed volume. With the air molecules always present, a one-component system can never be realized. Theoretically, it is possible to attain a state where the adsorption, Γ_i, at the dividing surface is zero. This is achieved by properly selecting the location of the dividing surface so that the concentrations of the adsorbed species are zero. However, to define the dividing surface in such a manner bears little significance to the real system. Therefore, it can be concluded that the surface tension and surface free energy of any system cannot be equal to each other in real systems.

Another possible source of misconception between surface tension and surface free energy arises from Equation 28. As discussed in the preceding paragraph, in a one-component system, the surface tension and surface free energy are numerically equal. Researchers such as Adamson [9], Padday [1], Goodrich [12] and Ono and Kondo [13] have expanded on this fact and discussed the relationships between surface tension, surface internal energy and entropy. Consequently, for a *one-component* system, the following equations result.

$$f^s = \gamma \tag{31}$$

$$f^s = \gamma = u^s - Ts^s \tag{32}$$

where u^s and s^s refer to the *surface energy* and *surface entropy* respectively [13]. Because

$$\frac{d\gamma}{dT} = -s^s \tag{33}$$

thus

$$u^s = \gamma - T\frac{d\gamma}{dT} \tag{34}$$

The misunderstanding of such discussion arises when the above four equations are applied to multicomponent systems. Therefore, it is very important to emphasize again that Equations 31–34 are valid for *one-component* systems only.

5. Conclusions

1. The mechanical definition of surface tension is given by the Laplace equation

$$\Delta p = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

2. Thermodynamically, surface tension is an excess quantity which can be defined by

$$\left(\frac{\partial F^s}{\partial A}\right)_{T,n} = \left(\frac{\partial F}{\partial A}\right)_{T,V,n} = \gamma$$

3. Surface energy and surface free energy are defined, respectively, as

$$u^s = \frac{U^s}{A}$$

$$f^s = \frac{F^s}{A}$$

4. In general, surface free energy is not numerically equivalent to the surface tension, as illustrated by Gibbs in the following equation

$$\gamma = f^s - \sum_i \Gamma_i\mu_i^s$$

5. Only in a one-component system (e.g. a pure liquid in contact with its own vapour), is the surface tension numerically equivalent to the surface free energy.

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