The Enigmas of Surfaces

Abraham Marmur*

Chemical Engineering Department, Technion – Israel Institute of Technology, Haifa, Israel

Email: marmur@technion.ac.il (A. M.)

Abstract The properties of surfaces are crucial for many processes in a variety of areas in biology, industry, and daily life. Surprisingly, even though surface phenomena have been studied for more than 200 years by some of the greatest physicists, mathematicians, and engineers, there are still quite a few enigmas to be solved. This paper presents some fundamental enigmas related to the surface tensions of liquids and solids that were either partially solved or yet mostly unsolved.

Keywords surface, surface tension

The importance of surfaces goes much beyond what we are inclined to think. Without surfaces, we would all be a continuous soup of molecules. In other words, our ability to distinguish between objects depends on the discontinuity associated with their surfaces. A common example is the optical discontinuity between liquid and vapor that enables the distinction between the two phases. In fact, surfaces define the objects they cover. In addition, surface properties are of utmost importance in biology, industry, and daily life. Examples include keeping the eyes properly wet, reducing the work needed for breathing, penetration of water into soil, foams, coatings, and cleaning. The study of surfaces is old^[1] and its implications are ubiquitous. Therefore, it is surprising to realize how much there is to be studied yet, in addition to work already done. The main purpose of this perspective is to highlight some of these open enigmas.

Surface Tension of a Liquid

The basic property that characterizes the surface of liquids in a gaseous environment (usually their vapors or air) is the surface tension. Gibbs^[2] developed an ingenious, intuitive definition of surface tension. The idea was to consider a model of a liquid-gas surface as it is seen macroscopically, namely the density of the liquid is constant over the whole bulk of the liquid, but at the surface it goes down discontinuously, as a step function (Figure 1a). The plane at which the discontinuity occurs is called “the dividing surface.” Obviously, this is not a realistic picture since the surface and the relevant associated thermodynamic functions change gradually from their values at the liquid to those of the gas (Figure 1). The surface is defined as a thin layer, within which most of these gradual changes occur. The difference between the energies per unit area of the two models, was defined as the surface tension. This is shown graphically in Figure 1. However, the concept of the dividing surface, as attractive as it is, suffers from a fundamental problem.^[3] The value of the surface tension may depend on the exact location that we assign to this dividing surface.^[3] Thus, one enigma was replaced by another, as explained below.

Bakker^[4] developed a different approach to the definition of surface tension. He realized that the stress components within the surface must be different than those in the bulk. The latter is isotropic, thus all three stress components (acting in the three space directions) are equal and constant. Consequently, the pressure, which is defined as the average of the three stress

Figure 1 The definition of the location of the dividing surface and the resulting surface tension. The two figures clearly demonstrate that a different location of the dividing surface leads to a different value for the surface tension.

components, equals each of them. Within the surface, the component perpendicular to the surface must be constant and equal to the pressure in the bulk, otherwise there will be flow. The two stress components that are parallel to the surface are equal, but their value must depend on their location within the surface since the molecular interactions near the surface must depend on the distance within the surface. This surface model leads to the following definition of surface tension for a planar surface:^[4]

$$\sigma \equiv \int_{-\infty}^{\infty} [P^{\infty} - \tau(z)] dz \quad (1)$$

In this equation, $\tau(z)$ is the stress tensor component that is parallel to the surface, z is the coordinate perpendicular to the surface, and P^{∞} is the pressure in the bulk phases. This equation is extensively used to calculate surface tension by molecular dynamics.

Recently, I developed a simple, classical thermodynamic model that avoids the problem caused by the dividing surface.^[5] The surface of the liquid is assumed to be a narrow film of liquid that is of constant thickness. The thickness must be slightly bigger than the actual thickness of the surface layer, but there is no need to assign it a specific value. The energy of the surface is proportional to its area. This is so since the thickness is constant, therefore, the volume is also proportional to the area. Interestingly, this new, constant-thickness model also leads to Eq. (1) for the surface tension.

Eq. (1) is accepted as a reliable equation for calculating surface tension, but it leads to another enigma. To present this enigma, Eq. (1) can be written in the following form:

$$\sigma \equiv \int_{-\infty}^{\infty} [P^{\infty} - \tau(z)] dz = \Delta \tau Z \quad (2)$$

In this equation, $Z = (b - a)$ is defined as the thickness of the interface, where a and b are the practical limits of the surface, and $\Delta \tau$ is the average stress difference. It should be noted that the quantity in square brackets in this equation, $[P^{\infty} - \tau(z)]$ becomes zero outside the surface region, where all components of the stress tensor are equal and their value is the pressure, P^{∞} . Therefore, this integral does not contribute to the value of surface tension outside the surface region. Order of magnitude analysis of Eq. (1)^[5] leads to surprising conclusions. If we assume that the stresses in the surface cannot be negative, the highest $\Delta \tau$ is of order of magnitude of atmospheric pressure. For a liquid with surface tension of 50 mN/m, the thickness Z comes out to be 500 nanometers. This is certainly too big as shown by some measurements.^[6] If, however, we limit the thickness of the surface to a few nanometers, the average stress difference turns out to be order of magnitude of -100 bar. This is a huge stress difference that needs yet to be explained.^[6]

In addition to Eq. (1), several attempts have been made to approximately predict surface tension based on simplified models. A prominent example is the one based on intermolecular forces.^[7] Using this approach, one may calculate from the intermolecular forces the work needed to separate two plates from each other. This work per unit area is considered as twice the surface tension (the work needed to create a new unit of surface area). One of the weak points of this approach is that the local density is assumed uniform (the same in the bulk and the interface) and constant (density distribution does not change with distance between the plates). Therefore, the result of the integration does not reflect the true changes in density profile during separation of the plates. Another seminal example is the study of various density profiles made by Widom and Rowlinson.^[8]

In many cases, the system consists of multiple, partially immiscible liquids. In these cases, we refer to “interfacial tension” rather than “surface tension.” As in the case of single-material systems and their surface tensions, there are quite a few enigmas related to solutions and their interfacial tensions, and there is much to learn yet about such systems. For example, the question of partial solubility and the correlation between interfacial tension and the individual surface tensions

Surface Tension of a Solid

A difficult enigma that has not been solved yet is that of the so called “surface tension” of a rigid solid.^[9] First, all methods of experimentally measuring surface tension depend on the deformability of the surface. Thus, if a solid is completely rigid, there is no experimental method for directly measuring its “surface tension.” On the theoretical side, this surface tension is calculated using the Young equation:

$$\cos \theta_Y = \frac{\sigma^S - \sigma^{sl}}{\sigma^l} \quad (3)$$

In this equation, θ_Y is the Young contact angle, σ^S is the (so called) surface tension of the solid surface, σ^{sl} is the interfacial tension of the solid-liquid interface, and σ^l is the surface tension of the liquid. This equation is used to calculate σ^S , however, it contains two unknowns, σ^S and σ^{sl} . So, we need an additional equation that correlates the “surface tension” of the solid with

the surface tension of the liquid and the “interfacial tension” of the solid-liquid interface. Quite a few such equations have been developed,^[10] but there is no way to substantiate their validity because of the impossibility to measure them experimentally. Thus, this inability is an open enigma.

An even more fundamental enigma is the following. For a surface tension to be a physico-chemical, characteristic property of a solid, it must be independent of the other properties of the solid surface, such as its shape, rigidity/elasticity, solubility, and chemical inertness. However, if the solid is so inert to its environment, bringing it in touch with different liquids may affect the solid only to a very small effect slightly. On the other hand, the properties of the liquid at the solid-liquid interface may be significantly affected by the strong molecular forces of the solid. Then, the Young equation may be written as:^[9]

$$\cos \theta_Y \equiv \frac{\sigma^*}{\sigma^l} \equiv -1 + 2\varepsilon \quad (4)$$

where σ^* is the effect of the solid surface on the wetting liquid. The parameter ε can be called the “wettability index” because $\varepsilon = 0$ indicates complete nonwettability; $\varepsilon = 1$ indicates complete wettability, and $\varepsilon = 1/2$ corresponds to a CA of 90° . Instead of calculating σ^S from the Young equation, it is suggested to get values of ε directly from properly measured contact angles and use a suitable average to get an empirical measure of wettability of the solid surface.^[9]

Conclusions

(1) Surface are more important and influential than we usually consider. They define the object they cover. In addition, their properties are essential for the proper conduction of processes in all areas.

(2) It is possible and advantageous to define surface tension without the dividing surface concept.

(3) Very low negative pressures, order of magnitude of -100 bar, determine the thickness of the surface layer.

(4) The concept of surface tension of a solid is questionable, and a new, empirical wettability index should be looked for.

Conflict of Interest

The authors declare no conflict of interest.

Copyright © 2021 Abraham Marmur. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). The use, distribution or reproduction in other forums is permitted, provided the original author(s) or licensor are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

References

- [1] Ed.: Niven, W. D. *The Scientific Papers of James Clerk Maxwell*, Dover Publications, Inc., New York, **1890**.
- [2] Gibbs, J. W. *The Collected Wworks of J. Willard Gibbs*, V. 1, Yale University Press, New Haven, **1948**.
- [3] Tolman, R. C. Consideration of the Gibbs Theory of Surface Tension. *J. Chem. Phys.* **1948**, 16, 758–774.
- [4] Guggenheim, E. A. *Thermodynamics an Advanced Treatment for Chemists and Physicists*, 4th ed., Amsterdam, North-Holland, **1959**.
- [5] Marmur, A. Surface tension and adsorption without a dividing surface. *Langmuir* **2015**, 31, 12653–12657.
- [6] Srebnik, S.; Marmur, A. Negative Pressure within a Liquid–Fluid Interface Determines Its Thickness. *Langmuir* **2020**, 36, 7943–7947.

- [7] Israelachvili, J. N. *Intermolecular and Surface Forces*, Academic Press, **1985**.
- [8] Widom, B.; Rowlinson, J. S. *J. Chem. Phys.* **1970**, *52*, 1670–1684.
- [9] Marmur, A. Surface tension of an ideal solid: What does it mean? *Curr. Opin. Colloid In.* **2021**, *51*, 101388.
- [10] Marmur, A.; Valal, D. Correlating Interfacial Tensions with Surface

Tensions: A Gibbsian Approach. *Langmuir* **2010**, *26*, 5568–5575.

Received November 19, 2020

Accepted December 27, 2020