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Wetting of Solid Surfaces: Fundamentals and Charge effects[☆]

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ABSTRACT

Wetting is important when solids are brought in contact with a liquid and for movement of micro-drops on solids. The Young equation that describes the wetting of a solid and the relations between adhesion and wetting and vapor adsorption and wetting are discussed first. The characterization of low-energy surfaces is discussed as these surfaces are important for electrowetting on a dielectric (EWOD) and the characterization methods reveal that both dispersion and acid–base interactions are important for wetting. Surfactant solutions are very suitable for modifying the wetting behavior; the distinct differences between low- and high-energy surfaces in relation to surfactant adsorption are discussed. The effects of surface charges on the wetting behavior are considered for both adsorbed charges and charges due to an applied electric potential (electrowetting). The physical interpretation of Young-Lippmann equation, which describes EWOD, is critically examined and contact angle saturation is briefly discussed.

Contents

1. Introduction

Wetting is an important subject in interface science with many practical applications. The work of Ralston [1–8] and his former coworkers [9–13] can be used as an example to illustrate the various practical aspects of wetting. Ralston's interest in mineral flotation has led to his early wetting studies: wetting of model heterogeneous surfaces [1], contact angle measurements on powders [2], and adsorbed surface charge effects on wetting [3]. In later work the kinetic aspects of wetting have been given attention [e.g., 4,5]. Applying an external voltage across an interface also affects the contact angle, this is called electrowetting. Recently, electrowetting of low-energy surfaces is booming and also here Ralston [e.g., 6–8] and his former coworkers [9–13] have made significant contributions. Most applications of electrowetting are based on

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[☆] Dedicated to the occasion of John Ralston's 65th anniversary.

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the fact that it is possible, with no mechanical parts, to control liquid movement and/or a quick change of states of the system. Applications include, for instance, electronic paper [10], cooling of electronic circuits by transport of cold drops across them, transport of micro-drops [14], suction of liquids in microtubes [15] and lab-on-a-chip applications for analysis of the chemical composition of liquids [16–18].

In this paper some fundamental aspects of wetting will be briefly reviewed. For a good understanding the relations between wetting and adhesion and vapor adsorption and wetting are important. The characterization of low-energy surfaces will be given attention because (1) these studies have led to good insight between surface chemistry and wetting and ultimately to the new applications of electrowetting and (2) the methods show that for a given solid the adhesion depends on the type of liquid that is used and that in general both dispersion and acid–base interactions are important for wetting. In many cases it is necessary to modify the wetting of a solid. Surfactant solutions are very suitable for this purpose and they can modify the wetting of both low- and high-energy surfaces; therefore, the distinct differences between the two types of surfaces in relation to surfactant adsorption will be discussed. The effect of charging a surface on the wetting behavior will be discussed for both adsorbed charges and electronic charges due to an applied electric potential. Special attention will be given to the Young-Lippmann equation, which plays an important role in the explanation of electrowetting. The phenomenon of contact angle saturation will be briefly discussed.

2. Fundamentals

2.1. Young's law

De Gennes [19] has reviewed the principles of wetting; the contact angle of a liquid droplet placed on a solid surface is the most direct measure of wetting. The magnitude of the contact angle is directly related to the interfacial tensions working in the line of contact between the solid, the liquid and the gas phase. In order to illustrate this, a droplet with an acute contact angle on a surface that is ideal, smooth, homogeneous, and that cannot be deformed is depicted in Fig. 1. The interfacial tensions acting on the line of contact are indicated. The vertical component of γ_{LG} is compensated by the cohesion of the solid, the horizontal components of the interfacial tensions (Gibbs energies) balance each other and this leads to *Young's* law:

$$\cos\alpha = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \tag{1}$$

Before applying Young's law, it is useful to discuss the meaning of γ_{LG}, γ_{SG} and γ_{SL}. When the droplet is made up of a *pure liquid* $L(1)$ then $\gamma_{LG} = \gamma_{L(1)}$ and $\gamma_{SL} = \gamma_{SL(1)}$. At equilibrium the gas phase G is made up of saturated vapor L and vapor adsorption will take place on the S interface. This adsorption makes γ_{SG} smaller than $\gamma_S (= \gamma_S{}^*)$ the surface tension of S in vacuum. It is convenient to express the difference via the surface pressure defined as $\pi_{SG} \equiv \gamma_S - \gamma_{SG}$. Therefore, in practice wetting of S with a pure liquid $L(1)$ can also be written as

$$\cos\alpha = \frac{\gamma_S - \pi_{SG} - \gamma_{SL(1)}}{\gamma_{L(1)}} \tag{2}$$

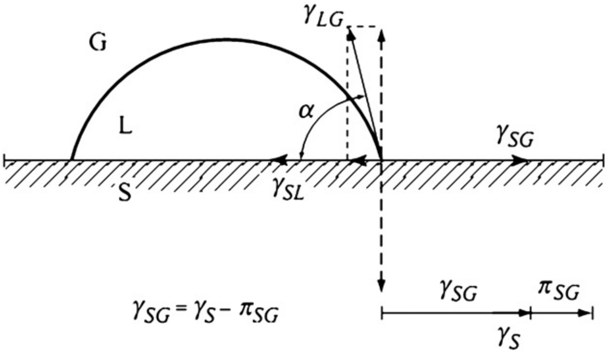

Fig. 1. Balance between the interfacial tensions and the contact angle on a smooth, homogeneous, solid surface.

It should further be noted that a contact angle of $L(1)$ on S can only exist if the vapor adsorption of $L(1)$ on S is very small; below this will be explained in detail. With complete wetting a macroscopically thick adsorbed layer will occur when the surface is in contact with the saturated vapor pressure of $L(1)$. Mostly π_{SG} will be negligibly small if α is larger than 10°. However, for α close to 0° the value of γ_{SG} will be significantly smaller than that of γ_S and π_{SG} will be large. Provided that α is large enough, it is not so important whether or not the gas phase is fully saturated with the vapor, because the difference with the equilibrium situation is very small. However, a small value of α can lead to time dependent values of α when the gas phase is not fully saturated.

When the droplet is a *solution* $L(1,2)$ with components 1 (the solvent) and 2 (the solute), the situation is more complex than with a pure liquid 1. If the solute adsorbs on the *LG*, the *LS* and the *SG* interface, then the following applies:

$$\gamma_{LG} = \gamma_{L(1)} - \pi_{LG(1,2)};\ \gamma_{SL} = \gamma_{SL(1)} - \pi_{SL(1,2)} \text{ and } \gamma_{SG} = \gamma_S - \pi_{SG(1,2)}$$

In this case the Young equation should be used in the form (1) and each γ is determined by the composition of the solution!

For polar surfaces finite values of π_{SG} may occur not only because of vapor adsorption of the solvent, but also because of adsorption of solute molecules at the *SG* interface (even if the dissolved molecules are not volatile). This is, for example, the case with surfactants; these molecules will be present the *SG* surface after retraction of the droplet and adsorb at the *SG* surface. In this case π_{SG} may become much larger than at contact with pure $L(1)$ and surfactant adsorption can lead to time and history dependent contact angles and π_{SG} values. In the section of surfactant adsorption and wetting this situation will be discussed further.

2.2. Wetting and adhesion

Intuitively one expects a relation between wetting and adhesion. The work of adhesion W_{SL} of a liquid L on a solid S in equilibrium with a liquid L is defined as

$$W_{SL} = \gamma_{LG} + \gamma_{SG} - \gamma_{SL} \tag{3}$$

Substitution of $\gamma_{SG} - \gamma_{SL}$ according to Young's law shows that the adhesion is directly related to $\gamma_{LG}\cos\alpha$:

$$W_{SL} = \gamma_{LG}(1 + \cos\alpha) \tag{4}$$

Eq. (4) applies to both pure liquids and solutions. Moreover, it indicates that with complete wetting W_{SL} equals $2\gamma_{LG}$ and that for complete non-wetting ($\alpha = 180°$) the work of adhesion is zero. For wetting of S with pure $L(1)$ it applies that

$$\gamma_{LG} = \gamma_{L(1)} \text{ and } W_{SL} = W_{SL}^{vac} - \pi_{SG(1)}.$$

In the case of solutions γ_{LG} as well as W_{SL} will be influenced by adsorption, which may occur on all three interfaces (*LG*, *SL*, *SG*).