Advances in Colloid and Interface Science 165 (2011) 60–69

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Wetting and surface forces

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ARTICLE INFO

Available online 13 March 2011

Keywords:
Contact angles
Disjoining pressure
Surface forces
Wetting films
Adsorption films
Liquid films
Hysteresis

ABSTRACT

In this review we discuss the fundamental role of surface forces, with a particular emphasis on the effect of the disjoining pressure, in establishing the wetting regime in the three phase systems with both plane and curved geometry. The special attention is given to the conditions of the formation of wetting/adsorption liquid films on the surface of poorly wetted substrate and the possibility of their thermodynamic equilibrium with bulk liquid. The calculations of contact angles on the basis of the isotherms of disjoining pressure and the difference in wettability of flat and highly curved surfaces are discussed. Mechanisms of wetting hysteresis, related to the action of surface forces, are considered.

Contents

1. Introduction

The analysis of wetting of a solid or a liquid surface touches many fields, from the physical chemistry of surfaces and interfaces to thermodynamics, materials science, and physics of fluids. The wetting phenomenon plays a key role in many modern technologies such as brazing and soldering, three-dimensional printing, tissue engineering, surface coating and cleaning, microelectronics, optical and optoelectronic technology, and many others.

The conditions of the equilibrium in heterogeneous systems, which can be derived with accounting for the peculiarities of transition zones in two- and three-phase systems, are connected with the manifestation of surface forces of the first and the second kind. The distinguishing between the two kinds of surface forces was considered in Chapter 2.1 of the monograph by Derjaguin, Churaev and Muller [1]. Briefly, the surface forces of the first kind, acting on the molecules at the vicinity of a single interface between two bulk phases, are responsible for the appearance and for the equilibrium value of the interfacial tension. Forces due to the effects of the overlap of two interfacial regions, confining a thin layer, in the course of surfaces approaching, refer to the surface forces of the second kind. Thus, the surface forces of the second kind are acting between the two interfaces, separated by a fluid interlayer, no part of which retains the intensive properties of the bulk phase. Derjaguin showed that analysis of the surface forces of the second kind can be performed by consideration of the dependence of the disjoining pressure $\Pi(h)$ on the film thickness h [1]:

$$\Pi(h) = P_N(h) - P_b \tag{1}$$

In Eq. (1), $P_N(h)$ is the normal component of the pressure tensor in the thin interlayer of thickness h and P_b is the pressure in a bulk isotropic liquid which is in the equilibrium with the interlayer

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doi:10.1016/j.cis.2011.03.002

considered. On the other hand, the overlap of the transition regions results in the appearance of excess Gibbs free energy of the interlayer induced by above overlapping. Thus, the disjoining pressure or the surface forces per unit of film area may be defined as [1]:

$$\Pi(h) = -(\partial G/\partial h)_{T,P,\mu_i} \tag{2}$$

where G is the Gibbs free energy per unit of the interlayer area, T and P are the temperature and the pressure in the system, containing thin film, μ_i is the chemical potential of i-th component of the system.

Surface forces of both kinds are responsible for the particular features of three-phase equilibrium, for the nature of wetting, established in one or another system, and, finally, for the coexistence of bulk and confined liquids. Certainly, surface forces of both kinds originate from the intermolecular forces. Therefore the feeling may appear that the description of different aspects of manifestation of these forces on the basis of various kinds of surfaces forces, as well as the introduction of various concepts, like surface (interfacial) tension, line tension, and disjoining pressure is mainly a question of terminology. In particular, there exists a point of view that both the line tension and the disjoining pressure describe one and the same peculiarities of the three phase contact. However, all the above mentioned concepts are related to different aspects of manifestation of the intermolecular forces, and each of them is responsible for different phenomena. For example, neither the line tension, nor the disjoining pressure affects the shape of the pendant drop; this shape is completely determined by the surface tension and the gravitational forces. Contrary, the equilibrium thickness of the wetting film on a flat substrate is determined by the disjoining pressure; neither the surface tension nor the line tension affects this thickness. Another example is the drop on a fiber in equilibrium with the wetting film, covering the fiber. In this case the line tension acts in direction perpendicular to the substrate (fiber) surface and hence does not affect the contact angle value. At the same time both the surface tension and the disjoining pressure do affect the contact angle.

Thus, the effect of the line tension and that of the disjoining pressure is not one and the same. These two phenomena supplement, but not substitute each other. However, many of line tension effects can be described through the variation of the disjoining pressure in the transition zone. At the same time the disjoining pressure effects in plane-parallel films have nothing to do with the line tension. In this sense the disjoining pressure concept is much more general than the line tension concept.

In this paper we review recent theoretical and experimental advances in the analysis of wetting on the basis of surface forces, with a particular emphasis on the role of the disjoining pressure. In Sections 2–3 the role of surface forces in establishing the wetting regime in the three phase systems is discussed. Section 4 considers the formation of wetting/adsorption liquid films on the surface of poorly wetted substrate. The application of the concept of the disjoining pressure for control of the wettability and the prediction of contact angles is illustrated in Section 5, jointly with the description of the peculiarities of three phase equilibrium for the systems with both plane and curved substrates. Finally, in Section 6 the analysis of the mechanisms of wetting hysteresis, general for all systems and based on the action of surface forces, is given.

2. The Young equation and the main problems in its application

Among numerous approaches relating the equilibrium wettability of solid by liquid with the properties of interfaces through their thermodynamic parameters one of the most popular is based on the application of the Young equation:

$$cos\theta_0 = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}, \tag{3}$$

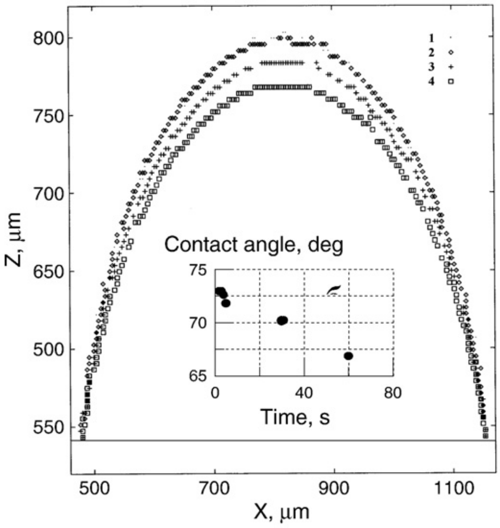

Fig. 1. Digitized profiles of sessile drop of benzyl alcohol on stainless steel [11] at different time after drop deposition: 2 s (1); 3 s (2); 30 s (3) and 60 s (4). Inset shows the time evolution of measured contact angles. The measurements were conducted in an open cell at 20 °C (saturated vapor pressure of benzyl alcohol at that temperature is $1.3 \cdot 10^{-4}$ bar).

where θ_0 is the contact angle, σ_{sv} and σ_{sl} are the surface energies at the solid/vapor and solid/liquid interfaces, respectively, and σ_{lv} is the surface tension of liquid. The application of this equation typically implies the assumption that solid is smooth, homogeneous, non-deformable, and insoluble in the probe non-reactive liquid. The Young's contact angle defined by Eq. (3) is affected by physico-chemical and geometrical peculiarities[1] of contacting phases through the surface energies. It has been noted [1] that Young's equation gives a macroscopic contact angle, defined as the angle of intersection of capillary surface of liquid (liquid meniscus or drop) and solid substrate, which are not perturbed by the field of surface forces of the second kind. However, these surface forces (acting between the solid/liquid and the liquid/fluid interfaces within the transition zone) modify the shape of liquid and solid surfaces on the nanoscopic scale [1,3–8].

As a result, the macroscopic contact angle differs from the local nanoscopic angles in the vicinity of three phase contact line. Thus, Young's angle does not concern itself with the slope of liquid surface in the close vicinity of the substrate and has to be considered as the macroscopic parameter of three phase coexistence.

The Young equation is applicable for the description of three phase equilibrium in systems with various geometries, like liquid meniscus near the wall and inside the capillaries, sessile drops, captive bubbles etc. However, below for definiteness we will mainly refer to the geometry of sessile drop (if not specified another) as to the system most frequently used for contact angle measurement.

The exploiting of the Young equation for the interpretation of experimental data on contact angle measurement meets some problems. Thus, the contact angle associated with the conventional Young equation is the equilibrium contact angle while on practice in the process of contact angle measurement we deal with nonequilibrium conditions. Among the reasons for the above nonequilibrium are the drop evaporation [9], initiated by undersaturation of vapor in the surrounding atmosphere relative to convex liquid/vapor interface and the drop cooling due to its evaporation [10]. Although the evaporation is partly suppressed by the drop cooling, the drop shape changes in time even for low volatile liquids and at short observation times (Fig. 1) [11].

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[1] The influence of substrate curvature on the substrate-vapor surface energy was discussed in Ref. [2].