Advances in Colloid and Interface Science 206 (2014) 382–398

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

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

Simultaneous spreading and evaporation: Recent developments

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ARTICLE INFO

Available online 4 September 2013

Keywords:
Wetting
Evaporation
Hysteresis of contact angle
Universal behaviour
Nanofluids
Surfactant solutions

ABSTRACT

The recent progress in theoretical and experimental studies of simultaneous spreading and evaporation of liquid droplets on solid substrates is discussed for pure liquids including nanodroplets, nanosuspensions of inorganic particles (nanofluids) and surfactant solutions. Evaporation of both complete wetting and partial wetting liquids into a nonsaturated vapour atmosphere are considered. However, the main attention is paid to the case of partial wetting when the hysteresis of static contact angle takes place. In the case of complete wetting the spreading/evaporation process proceeds in two stages. A theory was suggested for this case and a good agreement with available experimental data was achieved. In the case of partial wetting the spreading/evaporation of a sessile droplet of pure liquid goes through four subsequent stages: (i) the initial stage, spreading, is relatively short (1–2 min) and therefore evaporation can be neglected during this stage; during the initial stage the contact angle reaches the value of advancing contact angle and the radius of the droplet base reaches its maximum value, (ii) the first stage of evaporation is characterised by the constant value of the radius of the droplet base; the value of the contact angle during the first stage decreases from static advancing to static receding contact angle; (iii) during the second stage of evaporation the contact angle remains constant and equal to its receding value, while the radius of the droplet base decreases; and (iv) at the third stage of evaporation both the contact angle and the radius of the droplet base decrease until the drop completely disappears. It has been shown theoretically and confirmed experimentally that during the first and second stages of evaporation the volume of droplet to power 2/3 decreases linearly with time. The universal dependence of the contact angle during the first stage and of the radius of the droplet base during the second stage on the reduced time has been derived theoretically and confirmed experimentally. The theory developed for pure liquids is applicable also to nanofluids, where a good agreement with the available experimental data has been found. However, in the case of evaporation of surfactant solutions the process deviates from the theoretical predictions for pure liquids at concentration below critical wetting concentration and is in agreement with the theoretical predictions at concentrations above it.

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http://dx.doi.org/10.1016/j.cis.2013.08.006

1. Introduction. Kinetics of wetting of pure liquids and contact angle hysteresis

It is well established that kinetics of wetting and spreading of pure liquids in the absence of body forces is completely determined by the surface forces action in a vicinity of the three phase contact line [1]. There are numerous publications on the measurements of surface forces and their applications (see for example [1–6]). A manifestation of surface forces action is the presence of disjoining/conjoining pressure, which was suggested to refer as “Derjaguin's pressure” to recognise B. Derjaguin's contribution to the area [7].

A theory of kinetics of spreading of droplets in the case of complete wetting has been suggested some time ago and experimentally verified [1,8,9]. Comparison with available experimental data of the theoretical predictions showed both a qualitative and a quantitative agreement [1]. It is important to notice for the discussion below that in the case of complete wetting there is no contact angle hysteresis: a liquid droplet being deposited on a solid substrate spreads out completely, a dynamic contact angle, $\theta(t)$, decreases over time to zero value. Isotherm of Derjaguin's pressure in the case of complete wetting is schematically shown by curve 1 in Fig. 1.

Isotherms of type 1 are observed in cases of complete wetting, for example, oil on quartz, glass, and metal surfaces [2]. Isotherms for the partial wetting (curve 2 in Fig. 1) are observed for water and aqueous electrolyte solutions on a wide range of solid surfaces, for example on quartz, glass, and metal surfaces [2]. Liquid films with a thickness $h < h_{min}$ are referred to as α — films, which are thermodynamically stable. Much thicker films with $h > h_{max}$ are referred to as meta-stable β-films. Flat liquid films in between $h_{min} < h < h_{max}$ are unstable.

Situation differs in the case of partial wetting: a liquid droplet after a deposition spreads out until some critical contact angle is reached, which is referred to as a static advancing contact angle, θ_a. After that a macroscopic motion does not proceed any longer, though a slow microscopic spreading in front of the meniscus in the region of thin liquid films still goes on [1,10]. In the case of decreasing of volume, for example due to evaporation, droplet will start receding only after a static receding contact angle, θ_r, is reached. The latter phenomenon is referred to as a contact angle hysteresis and it is present in the case of partial or non-wetting. Derjaguin's pressure in the case of partial wetting is schematically shown by curve 2 in Fig. 1. Note that the equilibrium contact angle, θ_e, in the case of partial wetting on smooth homogeneous solid substrate can be expressed approximately as $\cos\theta_e \approx 1 - \frac{S_- - S_+}{\infty\gamma}$ (see Fig. 1), where γ is a liquid–air interfacial tension, $S_+ - S_- = \int_{h0} \Pi(h)dh$, and Π is the disjoining pressure. See [1] for more details.

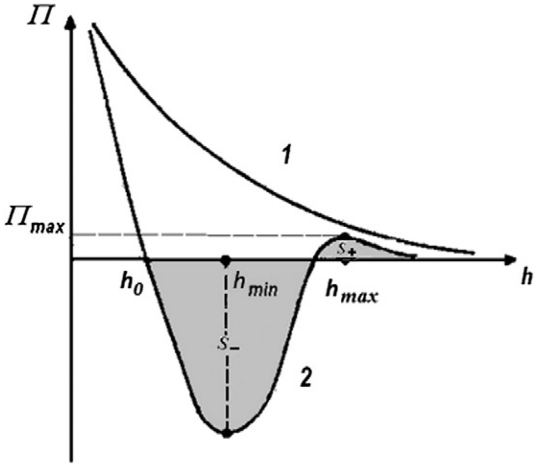

Fig. 1. Two types of isotherms of disjoining pressure: 1 — complete wetting case, 2 — partial wetting case.

Explanation of a hysteresis of contact angle on smooth homogeneous solid substrates is related to the s-shape isotherm of Derjaguin's pressure [1,7] (curve 2 in Fig. 1). This explanation is qualitatively described below.

Let us consider the static hysteresis of contact angle in the case of partial wetting in a flat capillary (Fig. 2). Consideration of the advancing contact angle in the case of droplet is given in [7]. The capillary is in contact with a reservoir, where the pressure, $P_a - P_e$, is kept, that is the pressure in the reservoir is lower than the atmospheric pressure, P_a, by the value of the excess pressure, P_e.

If we increase the pressure under the meniscus then the meniscus does not move but changes its curvature to compensate the excess pressure and, as a consequence, the contact angle increases accordingly. The meniscus does not move until some critical pressure and critical contact angle, θ_a, are reached. After further increase in pressure the meniscus starts to advance. A similar phenomenon takes place if we decrease the pressure under the meniscus: it does not recede until a critical pressure and corresponding critical contact angle, θ_r, are reached. The latter means that in the whole range of contact angles, $\theta_r < \theta < \theta_a$, the meniscus does not move macroscopically. The presence of the contact angle hysteresis shows that the actual equilibrium contact angle is very difficult to determine experimentally. It is the reason why only θ_a or θ_r is usually reported.

It is obvious that on the smooth homogeneous solid substrate only one contact angle corresponds to the equilibrium position and all the other positions are not equilibrium ones. Explanation of the hysteresis of contact angle on smooth homogeneous solid substrates is based on the s-shaped isotherm of Derjaguin's pressure in the case of partial wetting (curve 2, Fig. 1). Note, there are two branches on the isotherm corresponding to stable films (curve 2, Fig. 1). The thin α-films are thermodynamically stable ones, whereas thick β-films are metastable. This particular shape of isotherm determines a very special shape of the transition zone in the case of equilibrium meniscus [1,7]. In the case of increasing of the pressure behind the meniscus (Fig. 2a) a detailed consideration [1,7] of the transition zone shows: close to the “dangerous” point marked in Fig. 2a, the slope of the profile becomes steeper with increasing pressure. In region 3 in Fig. 2a there is a zone of flow. Viscous resistance in this region is very high because of very small thickness of the film, that is why the advancing of the meniscus proceeds very slowly. After some critical pressure behind the meniscus is reached, the slope at the “dangerous” point reaches π/2 and the fast “caterpillar” motion starts as shown in Fig. 2a. (See [11] for more details).

In the case of decreasing the pressure behind the meniscus the event proceeds according to Fig. 2b. In this case again up to some critical