Available online at www.sciencedirect.com
ScienceDirect
Journal of Colloid and Interface Science 317 (2008) 241–246
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

As-placed contact angles for sessile drops

Rafael Tadmor *, Preeti S. Yadav

Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, USA

Received 25 May 2007; accepted 13 September 2007
Available online 18 September 2007

Abstract

As-placed contact angle is the contact angle a drop adapts as a result of its placement on a surface. As expected, the as-placed contact angle, θ_{AP}, of a sessile drop on a horizontal surface decreases with the drop size due to the increase in hydrostatic pressure. We present a theoretical prediction for θ_{AP} which shows that it is a unique function of the advancing contact angle, θ_A, drop size, and material properties (surface tensions and densities). We test our prediction with published and new data. The theory agrees with the experiments. From the relation of the as-placed contact angle to drop size the thermodynamic equilibrium contact angle is also calculated.

Keywords: Advancing contact angle; Receding contact angle; Line tension; Line energy; Three phase contact line; Young contact angle; Young equation; Surface tension; Interfacial tension; Hydrostatic pressure

1. Introduction

Drop–surface contact angle, θ [1,2], is a generic term that describes a wide variety of angles that a drop can make with a surface spanning over a wide variety of purposes which includes relating wettability to pH using as-placed contact angle [3]; characterizing super-hydrophobic surfaces using advancing contact angle and contact angle hysteresis [4], building a phase diagram based on as-placed contact angle measurements [5] or following spontaneous changes during brine oil displacement process [6] using the time variation of drop size and contact angle using drops which are not "as-placed" nor advancing or receding. Thus we see that there are many useful forms of contact angles used in a variety of fields. Absent from the above list is the Young equilibrium contact angle, θ_Y. Though θ_Y is theoretically better established than other contact angles, it is less commonly used experimentally [7–9], especially for $\theta > 10°$ [10] due to the difficulty in determining its value within the spectrum between the advancing and receding angles. Instead, maximal advancing, θ_A, and minimal receding, θ_R, contact angles [11–22] and the as-placed contact angle [3,5,23–25], θ_{AP}, which is considered in this study, are more commonly reported.

Indeed the Young contact angle is not easily obtained as it corresponds to a perfectly smooth surface. In a rough surface the equilibrium contact angle differs from the Young contact angle and there are two important relations in this context [26]. The Wenzel equation [27] relates the Wenzel (apparent) angle θ_W to θ_Y as $\cos\theta_W = \frac{A_T}{A_N}\cos\theta_Y$, where A_T is the true area of the solid surface at the homogeneous solid–liquid contact and A_N is its nominal area. The Cassie–Baxter equation [28] considers a heterogeneous solid–liquid contact in which only a fraction, f, of the projected area of the solid is wetted by the liquid. Then the apparent Cassie–Baxter contact angle, θ_{C-B}, is related to θ_Y as $\cos\theta_{C-B} = f\frac{A_{Tw}}{A_{Nw}}\cos\theta_Y + f - 1$, where the index w signifies that A_{Tw} and A_{Nw} relate only to the wetted fraction of the surface. For the purpose of this paper we consider an equilibrium contact angle θ_0 which corresponds to a global minimum [26] of the system's free energy. Thus θ_0 can be θ_W or θ_{C-B} or even (in extreme smooth surface) θ_Y, but at any case it corresponds to the global minimum [26].

Though there are ways to experimentally obtain the global minimum [29–32], most researchers use θ_A and θ_R to investigate the drop contact angle phenomena per se while θ_{AP} is common as an auxiliary measurement. This is in part due to ease of measurement and in part because being extreme values

* Corresponding author. Fax: +1 (409) 880 2197.
E-mail address: rafael.tadmor@lamar.edu (R. Tadmor).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2007.09.029

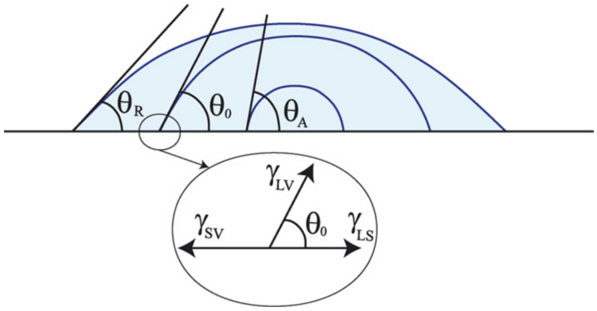

Fig. 1. The as-placed contact angle, θ_{AP}, is somewhere within the spectrum of advancing and receding contact angles (θ_A and θ_R). We show that drops for which $\theta_{AP} = \theta_0$ are smaller than drops for which $\theta_{AP} \to \theta_R$ and bigger than drops for which $\theta_{AP} \to \theta_A$.

θ_A and θ_R are perceived means of obtaining thermodynamic properties. Indeed, there are studies that show how to obtain the θ_0 from θ_A and θ_R [29,33]. Yet there is a question as to the true value of θ_A and θ_R. Krasovitski and Marmur [34] showed that θ_A and θ_R obtained by tilting the surface are in fact functions of the tilt angle and differ from those of planar surfaces. On the other hand, there are many studies (e.g., [18,20–22]) that show that the θ_A and θ_R for drops on horizontal surfaces are functions of drop size. Thus we see that θ_A and θ_R depend on the measurement conditions: drop size and surface tilt angle and there is a difficulty in determining one value of θ_A (or θ_R) for a given drop–surface–medium system. This study offers a partial solution by obtaining a unique value of θ_A which is independent of drop size. We obtain this unique θ_A value by building a model for a drop that is placed gently on a surface ("as-placed" drop). The model describes the deviation of θ_{AP} from θ_A due to the hydrostatic pressure that the finite size drop exerts on the three phase contact line. We show that this model predicts the same θ_A for different drop sizes. The model is restricted to non-volatile drops with no vapor available for condensation.

By "as-placed" we refer to the contact angle, θ_{AP}, that a drop makes upon being placed gently on a horizontal surface, and after allowing some time for the drop to equilibrate and pin to the surface in some metastable position somewhere between θ_A and θ_R. As we shall see, for very small drops θ_{AP} approaches θ_A and for big drops it approaches θ_R and at some size it matches the equilibrium contact angle, θ_0 (see Fig. 1).

2. Theoretical background

The combination of the Young equation and the Wenzel equation gives the relation between the surface tensions and the global energy minimum equilibrium contact angle θ_0 for the liquid drop:

$$\gamma_{SL} + \gamma_{LV}\frac{A_N}{A_T}\cos\theta_0 = \gamma_{SV}, \tag{1}$$

where γ_{ij} are the interfacial tensions (or interfacial energies [35–37]) between phases i and j, and the indexes S, L and V stand for solid, liquid and vapor, respectively (though vapor may sometimes refer to another liquid medium surrounding the drop). The reason a drop can have a contact angle that is different from θ_0 is related to the pinning of the three phase contact line to its position which induces a force resisting drop motion. One can describe the force per length associated with this pinning, k/r, by Eq. (2) (see [8,33,38–41]) (where r is the radius of the circle the drop makes with the surface). In this description k has opposite values, k_A and k_R corresponding to advancing and receding contact angles:

$$k_A/r_A = \gamma(\cos\theta_A - \cos\theta_0), \tag{2a}$$

$$k_R/r_R = \gamma(\cos\theta_R - \cos\theta_0), \tag{2b}$$

where r_A and r_R are drop radii that correspond to the advancing and receding curvatures and $\gamma \equiv \gamma_{LV}$.

From this, the relation between the θ_A, θ_R and θ_0 is given by [33]

$$\theta_0 = \cos^{-1}\left(\frac{\Gamma_A\cos(\theta_A) + \Gamma_R\cos(\theta_R)}{\Gamma_A + \Gamma_R}\right), \tag{3}$$

where

$$\Gamma_A \equiv \left(\frac{\sin^3\theta_A}{2 - 3\cos\theta_A + \cos^3\theta_A}\right)^{1/3} \quad \text{and}$$

$$\Gamma_R \equiv \left(\frac{\sin^3\theta_R}{2 - 3\cos\theta_R + \cos^3\theta_R}\right)^{1/3}.$$

2.1. Modeling the effect of hydrostatic force

In the following model we often use the term "force" as short for force per length. The reader is asked to realize the dimensions from the context.

Without the hydrostatic force (e.g., if gravitational acceleration $g = 0$), the line pinning force equals the capillary force. Regardless of the nature of the line pinning force, we can write (cf. Eq. (2)):

$$\text{Line pinning force} = \gamma(\cos\theta - \cos\theta_0), \tag{4}$$

i.e. the line pinning force that resists the capillary force is calculated with respect to θ_0 and the actual angle, θ, regardless of how it was obtained (be it as-placed or induced in any other way).

In the case of zero hydrostatic force, a drop that is placed gently (!) on a surface will have an as-placed contact angle of $\theta_{AP} = \theta_A$. Thus the maximal resistance of the line pinning force (per unit length) can be written based on Eq. (4) as:

$$\text{Maximal advancing line pinning force} = \gamma(\cos\theta_A - \cos\theta_0). \tag{5}$$

Consider a drop that is placed on a surface and slowly advances without gravity (only due to capillarity) toward its equilibrium contact angle. Due to pinning of the contact line the drop will never reach its equilibrium position and toward the end of the motion, when the motion speed indeed approaches zero, Eq. (5) is valid.

If we now introduce gravity, then at the moment the drop stops, the hydrostatic pressure is $\rho g h$ (ρ, drop's density; h, drop's height) and the capillary force is given by

$$\text{Capillary related force} = \gamma(\cos\theta_0 - \cos\theta_{AP}). \tag{6}$$