INTRINSIC CONTACT ANGLE HYSTERESIS

Elena Diaz Martin(1), Michael Savage(2) and Ramon L. Cerro (3)

(1) Departamento de Ing. Quimica y Textil, Universidad de Salamanca, Salamanca, Spain.
(2) Physics and Astronomy Department, University of Leeds, Leeds, UK.
(3) Chemical and Materials Engineering, University of Alabama in Huntsville, Huntsville, AL, 35899

1. **Introduction: Measuring static contact angles**.

Static contact angles are properly measured by placing a sessile drop on top of a flat solid surface and, after a *reasonable* relaxation time, the digital image of the contour of the air/liquid interface of the drop is matched with a solution of the Young-Laplace equation. The static contact angle is computed as the angle defined by the normal to the solid surface and the normal to the digital match of the interface. This method of measurement is unambiguous and precise. The macroscopic contact angle is not defined at the point where the liquid contacts the solid surface since the sessile drop, at the line of contact with the solid, is surrounded by an adsorbed film of molecular-size thickness (Diaz et al. 2010B).

The projection of the solution to the Young-Laplace equation matching the air/liquid interface until it meets the tangent to the solid surface, avoids the erroneous quest for closer (10X) views of the contact line. In addition, it is consistent with the definition of the macroscopic contact angle as the boundary condition of the Young-Laplace equation. The *reasonable* time needed after a drop is placed in contact with the solid is designed to allow evaporation of the liqid and adsorption of molecules of the liquid on the solid surface in the immediate vecinity of the drop. It has been argued that a sessile drop is never in equilibrium with its surrounding (Shanahan, 2002). However, for the purpose of measuring contact angles the quasi-equilibrium of the adsorbed film should not extend more than a few nanometers from the air/liquid interface.

If the solid surface has not been previously in contact with a vapor phase saturated with the molecules of the liquid phase, the solid surface is free of adsorbed liquid molecules. There is ample experimental evidence that when a sessile drop is first placed on a solid surface, the apparent contact angle is larger than the equilibrium contact angle, sometimes by several degrees (Chen et al. 1991). After some time, due to an evaporation/adsorption process, the interface of

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the drop coexists with an adsorbed film of liquid molecules as part of the equilibrium configuration, known as the static contact angle. This equilibrium configuration is quasi-stable because the droplet has a larger vapor pressure than the surrounding flat film. As the drop evaporates, the vapor/liquid interface contracts and the apparent contact line moves towards the center of the drop. During this process, the film left behind is thicker than the adsorbed film and molecular attraction results in a receding contact angle smaller than the equilibrium contact angle. In a similar way, if liquid is removed from the droplet, the apparent contact angle is smaller than the equilibrium contact angle (Chibowski, 2007). Thus, one can measure multiple values of contact angles, even on surfaces that are smooth and homogeneous down to the atomic level (Torregiani, 2005).

This process is known as *intrinsic* hysteresis of the static contact angle, that is hysteresis not associated to heterogeneity or roughness of the solid surface (A. Schwartz, 1980) and can be explained on the basis of the effect of the thickness of the adsorbed film on disjoining pressure and force fields determining the angle of inclination of the air/liquid interface near the solid surface. In addition, intrinsic hysteresis provides a model for contact line movement and dynamic contact angles during dewetting of a solid surface.

2. **Intrinsic Contact Angle Hysteresis**.

When the drop is placed on a clean surface, Figure 1, there is no adsorbed film and the angle of inclination of the air/liquid interface can be assumed to be nearly constant down to the
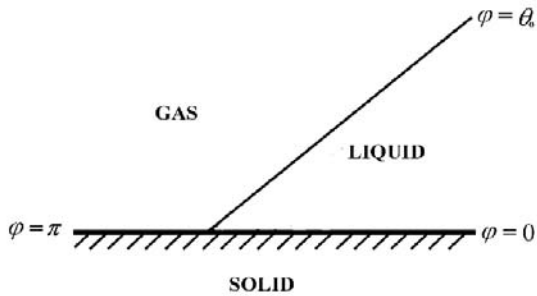

Figure 1: Schematic of a fluid wedge over a solid surface

solid surface. Under these conditions, the balance of molecular forces is described by a relationship developed by Miller and Ruckenstein (1974) and later by Jameson and del Cerro (1976). Jameson and del Cerro (1976) incorrectly assumed their result was the expression for the equilibrium contact angle. Indeed it would represent a contact angle for a system that cannot develop an adsorbed film in contact with the bulk meniscus. Eq. (1) below is identical to Eq. (26) of Jameson and del Cerro (1976) paper:

$$\frac{1}{2} + \frac{3}{4}\cos\theta_o - \frac{1}{4}\cos^3\theta_o = \frac{A_{SL}}{A_{LL}} \qquad (1)$$

Where A_{SL} and A_{LL} are the Hamaker cosntants for solid/liquid and liquid/liquid interaction respectively. To include the effect of 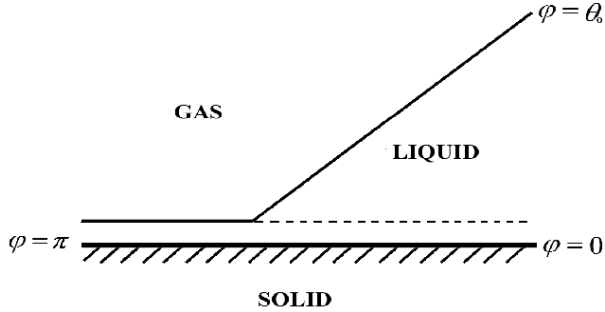an adsorbed film, we must modify the domain of integration of the molecular forces adding a film of constant thickness to the already existing wedge of constant inclination, as shown schematically in Figure 2. Assuming that the contributions of the film and liquid wedge are simply additive, for an adsorbed film of thickness Dads, disjoining pressure at any point on the wedge region of the vapor/liquid interface is given by Eq. (2) (Diaz et al., 2010A).

Figure 2: Schematic of a fluid wedge with an adsorbed film

$$\Pi\left(h,\theta_o\right)=-\frac{A_{LL}^{[6]}-A_{SL}^{[6]}}{6\pi\left(h+D_{ads}\right)^3}-\frac{A_{LL}^{[6]}}{12\pi h^3}\left[-1+\frac{3}{2}\cos\theta_o-\frac{1}{2}\cos^3\theta_o\right] \qquad (2)$$

Integration of the augmented Young-Laplace equation using Eq. (2) as an expression for disjoining pressure renders an equation relating the equilibrium contact angle with molecular forces and the thickness of the adsorbed film:

$$\cos\theta_o=1+\ln\left[1-\frac{A_{LL}^{[6]}-A_{SL}^{[6]}}{12\pi\sigma\left(D_{ads}+D_m\right)^2}-\frac{A_{LL}^{[6]}}{12\pi\sigma D_m^2}\left[-\frac{1}{2}+\frac{3}{4}\cos\theta_o-\frac{1}{4}\cos^3\theta_o\right]\right] \qquad (3)$$

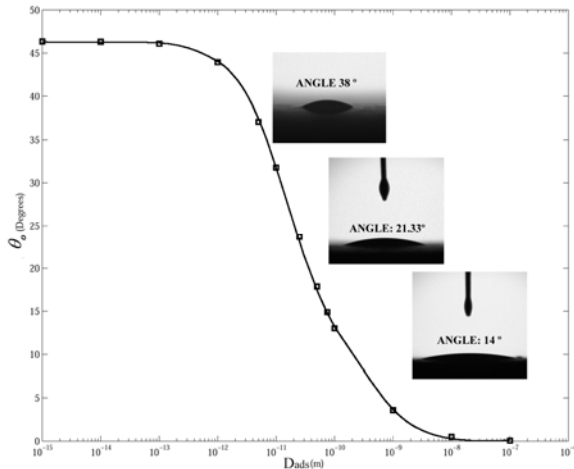Contact angles computed using Eq. (3) require values of the molecular cutoff distance, D_m. and of the adsobed film thickness, D_{ads}. For lack of actual data, the molecular cutoff distance is taken to be constant and of the order of a molecular diameter, $D_m = 1.2 \ 10^{-10}$ m. When $D_{ads} = 0$, contact angles computed using Eq. (3) are identical to angles computed using Eq. (1).

Figure 3: Variation of the static contact angle with the thickness of the adsorbed film.

For any value of $D_{ads} > 0$, we get a sequence of contact angles that includes the static contact angle when D_{ads} is equal to the

average thickness of the equilibrium adsorbed film. The sequence of contact angles as a function of th thickness of the adsorbed film is shown in Figure 3 for a drop of heptane on teflon.

3. **A model for a receding contact line.**

When a flat solid slab, perfectly smooth and homogeneous, moves up at a velocity, U, small and steady a regime described as dynamic dewetting is reached (Sedev and Petrov 1991). Observations show a macroscopic contact angle formed at the apparent three-phase line of contact. The dynamic dewetting regime is characterized by a dynamic receding contact angle, [Burley (1976), Gutoff and Kendric, (1982)]. The dynamic contact angle is a function of the solid speed and it becomes increasingly smaller as the solid speed increases. Experimental observations (Shim et al, 2008) during the dynamic dewetting regime ignore the presence of a liquid film on the solid surface above the apparent dynamic contact line. However, by assuming the presence of a remaining liquid film of molecular thickness, one can explain the variation of dynamic contact angles during the dewetting regime.

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