

# ON THE STATIC CONTACT ANGLE: ITS MACROSCOPIC THERMODYNAMIC INTERPRETATION AND PHYSICAL LOCATION WITHIN A TRANSITION REGION

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**Introduction:** This paper sheds new light on the static contact angle arising from molecular interactions close to a three-phase contact line. A ‘fluid slice’, representing a two-dimensional analogue of a sessile droplet standing on a flat and horizontal surface, is considered. A model is proposed for the vapour-liquid interface that involves a transition from an outer capillary region to an inner molecular region where curvature is dominated by a capillary meniscus and disjoining pressure respectively. Characteristic lengths in the capillary, transition and molecular regions are  $h_c$  (maximum film thickness);  $h_t$  (film thickness at the point of null curvature) and  $h_m$  ( $h_m = \sqrt{(A_{LL}^{[6]} - A_{SL}^{[6]}) / 6\pi\sigma}$ ); that are typically of the order of  $10^{-3}$ m,  $10^{-7}$ m and  $10^{-10}$ m respectively and  $\varepsilon = (h_m / h_t)$  is a small, system parameter.

As a macroscopic concept, the static contact angle is located outside the molecular region where the specific interfacial free energy is equal to the bulk interfacial tension. Integration of the augmented Young-Laplace equation reveals that, although there is no point on the vapour-liquid interface where the angle of inclination is identically equal to the macroscopic static contact angle,  $\theta_o$ , the angle at the point of null curvature is the closest with the difference of  $O(\varepsilon^2)$ . It is also shown that the transition region is essentially a wedge, extending from a few nanometers to a few micrometres, where curvature effects are negligibly small and to  $O(\varepsilon)$ , the angle of inclination is equal to  $\theta_o$ . Hence the transition region can be regarded as the ‘natural’ location for the macroscopic static contact angle and this, in turn, validates an experimental procedure for an accurate and unambiguous measurement of static contact angles. This model of a transition region with slope angle  $\theta_o$  and constant surface tension is entirely compatible with the current interpretation of Young’s equation as a macroscopic relationship between macroscopic, experimentally observable, thermodynamic

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variables and the angle  $\theta_o$ . that is also a boundary condition, at the solid surface, for solutions of the Young-Laplace equation.

**Governing Equations:** In his original publication on the cohesion of fluids, Young (1805) described static contact angle equilibrium as a balance of forces at the three-phase contact line due to interfacial tensions  $\sigma$ ,  $\sigma_{SV}$ ,  $\sigma_{SL}$  at the vapour-liquid, solid-vapour and solid-liquid interfaces respectively

$$\sigma \cos \theta_o = \sigma_{SV} - \sigma_{SL} \quad (1)$$

Using an intermolecular force model, Rayleigh (1890), confirmed Young's equation as a macroscopic relationship that holds away from the contact line and the influence of molecular forces. Benner et al. (1982) referred to Young's equation not being valid in a contact region near the solid where the fluid-fluid meniscus cannot be precisely defined.

Doubts about the validity of Young's equation arose with the derivation of alternative equations for  $\theta_o$  based on various intermolecular force models (Jameson et al. 1976). The issue was subsequently resolved by Merchant and Keller (1991) who used the method of matched asymptotic expansions to validate Young's equation and deal with the alternative equations. They showed that the leading term in the outer expansion for the interface satisfies the YL equation whilst that in the inner (boundary layer) expansion satisfies an integral equation. Matching the solutions of these two equations confirmed that the slope angle, at the solid boundary of the leading term in the outer expansion, is that given by Young's equation. Two further conclusions follow from this key result. It leads to a precise mathematical definition for  $\theta_o$  - as the slope angle of the interface at the point of intersection of a solution of the YL equation with the solid surface, and the model, proposed in this paper, of a transition region with slope angle  $\theta_o$  and constant surface tension is compatible with the current interpretation of Young's equation as a macroscopic relationship between macroscopic, experimentally observable, thermodynamic variables and the angle  $\theta_o$ . The interfacial tensions  $\sigma$ ,  $\sigma_{SV}$ ,  $\sigma_{SL}$  refer to the constant values taken by the specific, interfacial, Gibbs free energies  $g_{VL}$ ,  $g_{SV}$ , and  $g_{SL}$  away from the contact line and the effects of molecular interactions.

The equation for the shape of the vapour-liquid interface, taking full account of disjoining pressure and interfacial free energy is the *fully augmented* Young-Laplace equation (FAYL);

$$g_{VL}(h, \theta) 2H = -\Pi(h, \theta) - (p^L - p^V) \quad (2)$$

where  $p^L$ ,  $p^V$  are pressures in the liquid and vapor phases respectively and,  $g_{VL}(h, \theta)$ , is related to disjoining pressure,  $\Pi(h, \theta)$  as proposed by Derjaguin et al. (1987). Disjoining pressure,  $\Pi(h, \theta)$  and specific interfacial free energy,  $g_{VL}$ , can be expressed in terms of Hamaker constants when only London-van der Waals forces are taken into account

$$g_{VL}(h, \theta) - \sigma = \int_h^{\infty} \Pi(h, \theta) dh = - \int_h^{\infty} \frac{A_{LL}^{[6]} G^{[6]}(\theta) - A_{SL}^{[6]}}{6\pi h^3} dh \quad (3)$$

Sufficiently far from the contact line, the integral term in (3) vanishes,  $g_{VL}$  attains a constant value,  $\sigma$ , and equation (2) reduces to the AYL equation. Hamaker constants are shown as  $A_{ij}^{[6]}$  indicating that they are used in a Lennard-Jones potential and the exponent of the binary interaction distance is -6. The sub-index  $ij$  corresponds to interaction between phases  $i$  and  $j$ . The function  $G^{[6]}$  depends on the angle of inclination of the interface and results from the integration of a truncated Lennard-Jones potential over the volume of the adjacent phases. Integration of molecular forces was first done by Miller and Ruckenstein (1974) and later by Jameson and del Cerro (1976), but details of this integration for a range of exponents are given by Fuentes (2003). Here, only London-van der Waals forces are taken into account and the angular function is assumed to be approximately constant,  $G^{[6]}(\theta) \approx 1$ . As a consequence both disjoining pressure and interfacial free energy are functions of film thickness only. For the fluid slice, the hydrostatic pressure term is given by

$$p^L - p^V = \rho g (h_c - h) \quad (4)$$

where  $h(z)$ , the thickness of the liquid film becomes a constant,  $h_c$ , for large values of  $z$ . With an  $(r; \varphi)$  coordinate system centered at the contact line, Cartesian variables  $z$  and  $h(z)$ , as well as the curvature of the curve  $h(z)$  are given by (Scriven, 1982):

$$\begin{aligned} z(r) &= r \cos \varphi ; h(r) = r \sin \varphi \\ \frac{dh}{dz} &= \tan \theta ; 2H = - \frac{d \cos \theta}{dh} \end{aligned} \quad (5)$$

**Four Region Model:** A four region model is proposed for a liquid film on a solid surface with a static, three-phase contact line. Based on film thickness, the liquid domain is divided into four distinct regions (see

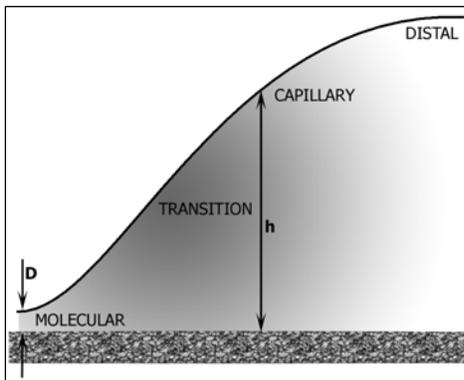


Figure 1) from the vicinity of the contact line to the bulk film thickness; these are the molecular, transition, capillary and distal regions. The *molecular* region,  $D < h \leq h_L$ , is the inner region where molecular interactions due to the presence of a solid phase give rise to disjoining pressure and interfacial free energies that determine the shape of the interface. The *transition* region takes the shape of a wedge in which variations, in the angle of inclination of the interface, can be made as small as one wishes by a judicious choice of its limits,  $h_L$  and  $h_U$ . Within this region,

disjoining pressure competes with capillary and hydrostatic pressures whilst interfacial free energies have attained constant values. The *capillary* region<sup>23</sup>,  $h_U \leq h \leq h_C$ , is where capillary and gravity forces dominate over all other external forces and the characteristic length is the capillary length,  $L_C = \sqrt{\sigma / (\rho g)}$ . Finally, there is a distal region, for  $h > h_C$ , where the characteristic length may be a macroscopic length such as the size of the container. All four regions are defined outside a molecular cutoff distance,  $h > D$ , where  $D \sim 10^{10}$  m since there can be no liquid film for  $h < D$ . For a full Leonard-Jones potential between two molecules<sup>7</sup>, the molecular cutoff distance  $D$  is the minimum approach between two molecules before repulsion forces pulls them apart.

**Identifying and Measuring the Macroscopic Contact Angle.** The four region model allows the definition of  $\theta_0$  as the limit of analytical or numerical solutions of the YL equation. Although it does not identify where the macroscopic contact angle is located, it is, nevertheless, particularly helpful for anyone wishing to measure contact angles directly from an image of the interface. The procedure involves matching a digitized image of the vapour-liquid interface to a solution of the YL equation<sup>13</sup> and extending this solution until it intersects the tangent to the solid surface. Clearly this method removes the uncertainty of how much we should amplify a digitized image and how close to the solid surface we should measure the contact angle.

The question now arises as to where, on the vapor-liquid interface, the angle is to be found? In fact, our analysis produces three key results (i)  $\theta_0$  is greater than all angles of inclination on the interface and there is, therefore, no location on the interface where the slope angle is identical to  $\theta_0$ . (ii) the angle of inclination at the position of null curvature is the closest to  $\theta_0$  with the difference of  $O(\varepsilon^2)$ , (iii) in the transition region where curvature effects are negligibly small, then to  $O(\varepsilon)$ , the slope angle is equal to  $\theta_0$ . Hence, to this order of approximation, the macroscopic static contact angle  $\theta_0$  can be identified as the slope of the transition region or 'wedge angle'.

And so to conclude; the definition of the static contact angle as a boundary condition at the solid-liquid surface for solutions of the YL equation enables us to identify  $\theta_0$ , to  $O(\varepsilon)$ , as the angle of inclination of the wedge-shaped transition region and, to  $O(\varepsilon^2)$ , as the inclination angle at the position of null curvature.

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