# STATIC CONTACT ANGLES: THE FULLY AUGMENTED YOUNG-LAPLACE EQUATION

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## 1. Introduction.

In his original publication on the cohesion of fluids, Young [1] describes static contact angle equilibrium as a balance of forces at the three-phase contact line. The current interpretation of Young's equation, however, regards Young's equation as a relationship between specific interface free energies [2].

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

where $\sigma$ is the specific free energy of the vapor/liquid interface and $\sigma_{SV}$ and $\sigma_{SL}$ are the specific free energies of the solid/vapor and solid/liquid interfaces, respectively. Under this definition, Young's equation is a macroscopic thermodynamic relationship and the angle $\theta_o$ determined by experimental observation, is the *macroscopic* static contact angle [3-4]. In a typical experimental procedure, one matches visual experimental data on interface shapes with a solution of the Young-Laplace equation and the contact angle is defined by extension of the numerical solution to the interface until it intersects the tangent to the solid surface. This procedure for measuring static contact angles removes the uncertainty about the degree of optical magnification needed for accurate contact angle measurements.

In the close vicinity of a phase boundary, such as a gas/liquid interface, fields of molecular and electrical double-layer forces give raise to behavior different from the bulk material but these effects decrease rapidly with distance into each contiguous phase. Interfacial regions are three-dimensional volumes involving mass that can be affected by molecular forces induced by the surrounding bulk phases. Molecular forces considered here are of three types: (1) molecular forces resulting of dipole-dipole, nonpolar or charge-dipole interactions and (2) electrical double layer forces originated by microscopic electrostatic fields, and (3) structural forces induced by molecular order within the liquid phase [4]. When molecular forces are introduced into the jump momentum balance, two distinct contributions arise: (1) The normal component of molecular forces affect the isotropic pressure field and appear in the jump bulk stress tensor bracket as an isotropic component, the *disjoining pressure*. (2) The tangential component of molecular forces affect interfacial tension and become the gradient of a surface integral along the interface. The complete expression, in cylindrical coordinates, for the jump momentum balance at a fluid interface in the close vicinity of a third phase is

$$\nabla_{\sigma} \left\{ \sigma + \int_{\theta-\delta}^{\theta+\delta} \Phi^{[corr]} \, rd\theta \right\} + 2H \left\{ \sigma + \int_{\theta-\delta}^{\theta+\delta} \Phi^{[corr]} \, rd\theta \right\} \underset{\sim}{n} + \nabla_{\sigma} \cdot \underset{\approx}{\tau}^{\sigma} + \left[ \left( \underset{\approx}{T} - \Phi \underset{\approx}{I} \right) \cdot \underset{\sim}{n} \right] = 0 \qquad (2)$$

At rest, the jump momentum balance in the close presence of a third phase, reduces to the *fully-augmented-Young-Laplace* equation. The normal component of the jump momentum balance includes disjoining pressure [4] and a variable surface tension

$$2H\sigma(r,\theta) + \left( p^{B} - p^{A} + \Phi \right) = 0 \qquad (3)$$

and the tangential component of the jump momentum balance reflects the effect on interfacial tension of molecular forces of the second kind.

$$\nabla_{\sigma} \left\{ \sigma + \int_{\theta-\delta}^{\theta+\delta} \Phi^{[corr]}(r,\theta) \, r \, d\theta \right\} = 0 \qquad (4)$$

Away from the third phase, $\sigma$, the vapor/liquid interface tension is a constant in the absence of temperature and concentration gradients, thus the sum of local interfacial tension and the correction due to molecular forces, $\sigma_{\infty} = \sigma(r) + \sigma^{[corr]}(r)$, add to a constant equal to the interfacial tension on the vapor/liquid interface away from a third phase. An explicit function relating van der Waals forces to a variable surface tension was developed by Jameson and del Cerro [5].

## 2. Molecular forces

To compute the effect of molecular forces in multiphase systems, we use binary energy interaction functions. The energy interaction functions are generically represented by means of decaying potential functions of the type

$$\phi_{ij}(r) = \frac{\beta_{ij}^{[12]}}{r^{12}} - \sum_{n=4}^{n=6} \frac{\beta_{ij}^{[n]}}{r^{n}} \qquad (5)$$

where r is the distance between molecules, dipoles or charges and $\beta_{ij}^{[n]}$ are binary interaction parameters for a given value of n, where n is the exponent of the decaying functional. When n = 6 and retaining the repulsive force term, we recover the standard Lennard-Jones interaction potential where for small values of r, repulsive forces predominate. The exponent n varies from n = 4 for dipole-dipole, through charge-dipole and charge-nonpolar interactions, up to n = 6 for nonpolar-nonpolar (London) interactions [6]. Following standard assumptions, to simplify the model we will substitute the repulsive potential due to steric interactions among atoms by a hard-sphere repulsive material located at a distance r = D. After integration, the disjoining pressure at a point in the liquid phase has the following expression

$$\Phi(h,\theta) = \frac{D^{6} \sin^{6}\theta}{6\pi \, h^{9}} \left( A_{LL}^{[6]} G_{6}(\theta) - A_{SL}^{[6]} \right) - \sum_{n=4}^{6} \frac{C_{n}}{h^{n-3}} \left( A_{LL}^{[n]} G_{n}(\theta) - A_{SL}^{[n]} \right) \qquad (6)$$

where the constants and angular functions $G_{n}(\theta)$ for all values of n can be easily found by integration. We have chosen the coefficient of repulsive forces to make the potential function equal to zero at h = D sin$\theta$.

Integration of molecular force components in the tangential direction results in expressions for the interfacial energies at an interface in the vicinity of the contact line. Equation (7) is similar to Jameson and del Cerro [5], except that we include here also electrostatic and structural molecular forces.

$$\sigma\left(h,\theta\right)=\sigma_{\infty}-\sigma^{[corr]}\left(h\right)=\sigma_{\infty}-\left\{\frac{C_{\sigma}^{[6]}G_{\sigma}^{[6]}\left(\theta\right)A_{LL}}{h^{2}}\left(\frac{D^{6}\sin^{6}\theta}{h^{6}}-1\right)-\left[\sum_{n=4}^{5}C_{\sigma}^{[n]}\frac{A_{LL}^{[n]}G_{\sigma}^{[n]}\left(\theta\right)}{h^{n-4}}\right]\right\} \qquad (7)$$

### 3. Static Equilibrium and the Transition Film on the Vicinity of a Contact Line

At equilibrium, normal and tangential components of the jump momentum balance vanish. In a preliminary analysis, we assume that there is only one component of molecular forces corresponding to values of n = 6 and that repulsive forces can be substituted by a square-well potential at r = D. The choice of van der Waals forces is consistent with the accepted understanding that they are the predominant molecular forces in the close vicinity of the static contact line.

$$2H\sigma\left(h,\theta\right)-\frac{A_{LL}^{[6]}G^{[6]}\left(\theta\right)-A_{SL}^{[6]}}{6\pi h^{3}}=\rho g\left(h_{\infty}-h\right) \qquad (8)$$

while the tangential component becomes

$$\sigma\left(h,\theta\right)=\sigma_{\infty}-\sigma^{[corr]}\left(h,\theta\right)=\sigma_{\infty}+\frac{C_{\sigma}^{[6]}A_{LL}^{[6]}G_{\sigma}^{[6]}\left(\theta\right)}{h^{2}} \qquad (9)$$

where h is the local thickness of the liquid film and θ angle of inclination of the interface with respect to the solid surface. The constant, $\sigma_{\infty}$, is standard interfacial tension at a point away from the contact line where molecular forces of the second kind are negligible.

Equations (8-9) can be easily integrated for simple two-dimensional geometries and approximating the angular functions using constant values. A simple two dimensional geometry of interest, a fluid wedge is a two dimensional analog of a sessile drop. The fully augmented Young Laplace equation for the 2D fluid wedge is

$$-\frac{d\cos\theta}{dh}\left\{\sigma_{\infty}+\frac{C_{\sigma}^{[6]}A_{LL}^{[6]}G_{\sigma}^{[6]}\left(\theta\right)}{h^{2}}\right\}-\frac{A_{LL}^{[6]}G^{[6]}\left(\theta\right)-A_{SL}^{[6]}}{6\pi h^{3}}=\rho g\left(h_{\infty}-h\left(z\right)\right) \qquad (10)$$

The solution of Eqs. (9 and 10) can be formulated as a regular domain perturbation problem [7], and focus on the solution of an inner problem within the proximal region and an outer problem within the central and distal regions. Matching inner and outer solutions provides an accurate definition of the macroscopic static contact angle.

Inner problem solution:

Within the proximal region, at very short distances from the contact line, where molecular forces are important, Eq. (10) must be solved subject to the following conditions

$$-\frac{d\cos\theta}{df}\left\{1+\frac{C_{1}G_{\sigma}^{[6]}\left(\theta\right)}{4f^{2}}\right\}-\frac{C_{1}G^{[6]}\left(\theta\right)-C_{2}}{f^{3}}=0$$

B. C. 1 $\quad \xi \to 0$ ; $\quad f\left(0\right)=1$ ; $\quad f'\left(0\right)=\tan\theta_{i}=0$

B. C. 2 $\quad \xi_{o} \gg 1$ ; $\quad f=f\left(\xi_{o}\right)$ ; $\quad f'\left(\xi_{o}\right)\to\tan\theta_{o}$

$\qquad (11)$

Where $C_1 = A_{LL}^{[6]} / 6\pi\sigma D^2$, $\quad C_2 = A_{SL}^{[6]} / 6\pi\sigma D^2$. Hamaker constants are of order $10^{-20}$ J while the molecular

parameter D is of order $10^{-10}$ m. As a consequence both $C_1$ and $C_2$ are of order unity. The third constant, $\varepsilon$, is the

ratio of molecular to capillary lengths and is a very small parameter. The outer angle $\theta_o$ of the inner solution matches

the inner angle from the outer solution. The outer solution is the solution of the Young-Laplace equation, and the

inner angle of the outer solution is the macroscopic contact angle satisfying Young's equation (Eq. (1)). Under these

conditions Eq. (11) is easily integrated, and after neglecting smaller terms we get

$$\cos\theta_0 = 1 + \frac{C_1 - C_2}{C_1} \ln\left(1 - \frac{C_1}{2}\right) \qquad (12)$$

Outer problem solution:

　　　Within the central region, the characteristic length is the capillary length and Eq. (10) reduces to the

standard Young-Laplace equation

$$-\frac{d\cos\theta}{d\,g(\eta)} = (g_\infty - g(\eta)) \qquad \begin{cases} \eta_o \ll 1 \;\; ; \;\; g(\eta_o) \to 0 \;\; ; \;\; g'(\eta_o) = \tan\theta_o \\ \eta \to \infty \;\; ; \;\; g \to g_\infty \;\; ; \;\; g' \to 0 \end{cases} \qquad (13)$$

The inner boundary condition to the outer problem is applied at $r = r_o$ where $g(\eta_o) \sim 0$. The outer boundary

condition is the position at the top of the fluid wedge where the film thickness becomes constant. Equation (13) is

easily integrated to get:

$$1 - \frac{1}{\left[1 + [g'(\eta_o)]^2\right]^{1/2}} = 1 - \cos\theta_o = \frac{g_\infty^2}{2} \qquad (14)$$

Matching inner and outer solutions

　　　The cosine of the angle formed by intersecting the tangent to the interface with the tangent to the solid

surface, $\theta_o$, becomes the matching condition for the inner and outer solutions and Eqs. (12) and (14), in

dimensional variables reduce to

$$\cos\theta_o = 1 + \left(1 - \frac{A_{SL}^{[6]}}{A_{LL}^{[6]}}\right)\ln\left(1 - \frac{A_{LL}^{[6]}}{12\pi\sigma_\infty D^2}\right) = 1 - \frac{\rho g h_\infty^2}{2\sigma_\infty} \qquad (15)$$

　　　Since only London-van der Waals forces are included in Eq. (15) it is an excellent model for computing

static contact angles for non-polar molecules such as hydrocarbons on polymer surfaces. In order to develop a

relationship similar to Eq. (15) for polar fluids and fluids that undergo structural ordering near interfaces, one should

include all molecular forces of the second kind as it was done in Eqs. (6) and (7).

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