### CONTACT ANGLES: <u>Laplace-Young Equation and</u> Dupre-Young Relationship.

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### OUTLINE OF PRESENTATION

- •Introduction/Motivation: What is wetting? Why is it important?
- •The Fully-Augmented Young-Laplace Equation
- Young's relationship: static contact angles.
- A 2D sessile drop = puddle.
- Capillary rise
- The future behind

#### Wetting applications: boiling and condensation



### Super-hydrophobic surfaces:



Super-hydrophobicity is the result of chemistry and structure.





### Self-cleaning superhydrophobic surfaces



Structure & Chemistry











density kg/m<sup>3</sup>

### Vapor/Liquid Interfaces



Interfaces are:

1.Diffuse (3D)

2. Dynamic

3.Asymmetric





## Static Contact Angles: Young relationship and the Young-Laplace equation.



CAPILLARITY: The curvature of the interface and the specific interfacial free energy of the interface, are related to the pressure jump between the inside and outside of a liquid drop.

#### YOUNG-LAPLACE EQUATION

$$(p_{in}-p_{out})-2H\sigma_{VL}=0$$

WETTING: The contact angle for a three-phase region is the main variable in Young's equation.

#### THOMAS YOUNG, 1805

$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \cos \theta$$



#### Young-Laplace Equation in Differential Form:

$$p_{inside} = p_{outside} - 2H \sigma$$

 $2H = \frac{1}{R_1} + \frac{1}{R_2} \{R_1, R_2: \text{principal radius of curvature}\}$ 



#### The equation of Young and Laplace: Historical introduction.

- Thomas Young [Phil. Trans. Roy. Soc, vol 95, pp. 65-87 (1805)]
  - Born in Milverton, Somerset (1773) youngest of 10 children
  - Studied medicine in London, Edinburgh and physics in Gottingen
  - Entered Emmanuel College in Cambridge and practiced medicine in London
  - Appointed professor of Natural philosophy at Royal Institution (1801)
  - Foreign associate in French Academy of Sciences (1827)
  - Wave theory of light, Young modulus, translated hieroglyphs, etc.
- Pierre Simon de Laplace [Ouvres Completes, pp. 394 (1807)]
  - Born in Normandy, 1749.
  - Univ. of Caen (16 years old)
  - Univ. of Paris (18 years old).
  - Rejected by Acad. of Sciences (22 yr old)
  - Accepted to Berlin Acad. of Sci. (24 yr)
- Young never wrote the equation!
  - "On the attribution of an equation of capillarity to Young and Laplace", Pujado, Huh and Scriven, JCISvol. 38, pp 662-663, (1972).

#### Surfaces in 3D space: Surface geometry

- Surfaces in 3D space:
  - Orientable in space
  - Locally have two sides



- Globally have in general two sides with famous exceptions (Mobius strip)
- If they are closed, separate an inside space from an outside space with famous exceptions (Klein bottle)



- They have shape
  - Globaly shape distinguishes a torus from a sphere
  - Locally it is distinguished by its curvature

#### Surface curvature



$$\underline{r} = \underline{R}(u_1, u_2)$$

$$\kappa_{1} = 1/R_{1} ; \kappa_{2} = 1/R_{2}$$

$$H = \frac{1}{2} \left( \frac{1}{R_{1}} + \frac{1}{R_{2}} \right) = \frac{1}{2} \left( \kappa_{1} + \kappa_{2} \right)$$

$$K = \kappa_{1} \kappa_{2} = \frac{1}{R_{1} R_{2}}$$

- 1. Location: a point on the surface is described by the vector R.
- 2. Orientation: the top and bottom are described by a unit vector n, normal to the surface
- 3. Two tangents unit vectors, a<sub>1</sub> and a<sub>2</sub> are normal to each other and both are normal to the vector n.
- 4. Points on the surface can be described on the basis of a two dimensional system.
- 5. The rate of change of orientation (normal) corresponds to the intuitive notion of shape.
- 6. Curvature is defined as the inverse, 1/R, of the radius of a circle tangent to the surface.
- 7. There are two independent radius of curvature and their directions are normal to each other.

Young-Laplace equation:simplified derivation. Butt et al. pp10. 2003

$$\tilde{F} = \tilde{e}_r F_n + \tilde{e}_t F_t$$



### Minimal surfaces (soap films): Lagrange, Nitsche, others

Lagrange: Lectures on a novel method for the

determination of maxima of integral formulae, 1762

$$z = z(x, y) \implies I(\varepsilon) = \iint_{S} \sqrt{1 + \left(\frac{\partial z}{\partial x}\right)^2 + \left(\frac{\partial z}{\partial y}\right)^2} dxdy$$

Definition: A minimal surface is a surface whose mean curvature is zero at every point of the surface.

Theorem: If there is a portion of a surface of minimum area among all portions of surfaces bounded by the same closed curve, then the surface is a minimal surface.

Minimal surfaces are sometimes defined as surfaces with the property that any portion of them bounded by a closed curve has the minimum area.

$$2H = \frac{z_{xx}}{\left[1 + (z_x)^2 + (z_y)^2\right]^{1/2}} - \frac{2z_x z_y z_{xy}}{\left[1 + (z_x)^2 + (z_y)^2\right]^{3/2}} + \frac{z_{yy}}{\left[1 + (z_x)^2 + (z_y)^2\right]^{1/2}}$$



### Static Contact Angles Young's relationship (1805):

 $\sigma_{SV} - \sigma_{SL} = \sigma_{VL} \cos \theta_o$ 

An Essay on the Cohesion of Fluids Phil. Trans. Roy. Soc. v. 95, 65-87 "We may therefore inquire into the conditions of equilibrium of the three forces acting on the angular particles, one on the direction of the surface of the fluid only, a second in that of the common surface of the solid and fluid, and the third in that of the exposed surface of the solid. Now supposing the angle of the fluid to be obtuse, the whole superficial cohesion of the fluid being represented by the radius, the part of which acts in the direction of the surface of the solid will be proportional to the cosine of the inclination; and its force added to the force of the solid, will be equal to the force of the common surface of the solid and fluid, or to the difference of their forces; consequently, the cosine added to twice the force of the fluid; will be equal to ....

### Interfaces are not 2D surfaces!





1.Diffuse (3D)

2. Dynamic

3.Asymmetric





#### Macroscopic definition of contact angles



$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \cos \theta$$

- •Young (1805) derived relation as a balance of forces.
- Equation can be derived using macroscopic arguments.
- •Specific interfacial free energies are macroscopic/thermodynamic parameters.
- Contact angles are macroscopic parameters and thermodynamic functions.

#### Surface forces of the second kind: Derjaguin et al. Surface Forces, (1987) Plenum

Derjaguin and Obuchov (1936)





At the contact line, there is an interaction of molecular force fields due to the presence of a third phase.

"unhappy"

'happy''

- Forces of the second kind are the same forces determining surface tension:
- (1) Dipole-dipole, nonpolar or chargedipole interactions.(van der Waals)
- (2) Electrical double layers
- (3) Structural forces induced by molecular order.

#### Augmented and Fully-augmented Young-Laplace equation:

Static Jump-Momentum balance: Normal component:

$$2H g_{VL}(r,\theta) + (p^B - p^A + \Pi(r,\theta)) = 0$$

Derjaguin et al. Surface **Forces** (1987) Teletzke, Davis and Scriven (1988)

$$2H g_{VL}(r,\theta) + (p^B - p^A + \Pi(r,\theta)) = 0$$



Miller and Ruckenstein (1974) Jameson and del Cerro (1976).

Tangential component:

$$g_{VL}(r,\theta) =$$
  
=  $\sigma_{VL} + \int_{\theta-\delta_L}^{\theta+\delta_L} (\Pi(r,\theta)) r d\theta$ 

The Young-Laplace equation is valid away from the solid surface where disjoining pressure is negligible and surface tension is constant!

### **MOTIVATION:** molecular interactions



- Derjaguin and Obuchov (1936)
- disjoining pressure,  $\Pi$

$$\Pi = \frac{A_{SL}^{[6]} - A_{LL}^{[6]}}{6 \pi h^3}$$

• variable surface tension,  $g_{VL}$ 

$$\frac{d g_{VL}}{d h} = -\Pi$$

- Is Young's equation really valid?
  - What is the proper definition for  $\theta_o$ ?
  - How is  $\theta_o$  to be measured?
  - Where is  $\theta_o$  located on the vapor/liquid interface?

### Contact Angles (Merchant and Keller, 1992)

Used the method of matched asymptotic expansions to validate Young's equation!

- Leading term in the outer expansion for the interface shape satisfies the Young-Laplace equation.
- Leading term in the inner expansion satisfies an integral equation.

 Matched the two solutions and confirmed that the *slope angle* – of the leading term in the outer expansion is θ<sub>o</sub> -as given by Young's equation.

#### Interesting relationships for 2D systems: L. E. Scriven, class notes UofM, circa 1980



$$\frac{d\sin\theta}{dx} = \frac{\frac{d^2y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{1/2}} - \frac{\frac{d^2y}{dx^2}\left(\frac{dy}{dx}\right)^2}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}} = \frac{\frac{d^2y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}} = 2\mathbf{H}$$

$$h = y(x), \quad \tan \theta = \frac{dy}{dx}$$
$$\sin \theta = \frac{\frac{dy}{dx}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{1/2}}$$
$$\cos \theta = \frac{1}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{1/2}}$$

Macroscopic approach:  
Two-dimensional fluid wedge.de Gennes, Brochard,  
Quere (2004) the  
housewife problem.Young-Laplace Equation:
$$\sigma 2H = -(p^L - p^V)$$
,  $p^L - p^V = \rho g (h_C - h)$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} / \left[ 1 + \left( \frac{\partial h}{\partial z} \right)^2 \right]^{3/2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} = \frac{\partial^2 h}{\partial z^2} \right]$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} = \frac{\partial^2 h}{\partial z^2} = \frac{\partial^2 h}{\partial z^2}$  $\mathcal{I} = \frac{\partial^2 h}{\partial z^2} = \frac{\partial^2 h}{\partial z^$ 

# Integrate and introduce one boundary condition at a time:

$$\cos\theta = \frac{h_C h}{L_C^2} - \frac{h^2}{2L_C^2} + C \quad \left\{ B.C. \quad \cos\theta = 1 \quad at \quad h = h_C \right\}$$

$$C = 1 - \frac{h_C^2}{2L_C^2}$$

$$\cos\theta = 1 - \frac{h_C^2}{2L_C^2} + \frac{h_C h}{L_C^2} - \frac{h^2}{2L_C^2} \implies h = 0 \quad \Rightarrow \cos\theta_o = 1 - \frac{h_C^2}{2L_C^2}$$

$$\int Defines \text{ contact angle as the parales of intersection between$$

Solution to Young –Laplace equation describes the gas-liquid interface of a liquid puddle resting on a smooth, horizontal surface. Defines contact angle as the angle of intersection between solution of YL equation and the solid surface.

### Second method:

$$\cos\theta = \frac{h_C h}{L_C^2} - \frac{h^2}{2L_C^2} + C \quad \{B.C. \ \cos\theta = \cos\theta_o \ at \ h \to 0$$
$$C = \cos\theta_o$$
$$C = \cos\theta_o$$
$$\log\theta_o = \cos\theta - \frac{h_C h}{L_C^2} + \frac{h^2}{2L_C^2} \Rightarrow h = h_C \quad \Rightarrow \cos\theta = 1$$

Solution to Young –Laplace equation describes the gas-liquid interface of a liquid puddle resting on a smooth, horizontal surface. Defines contact angle as the angle of intersection between gas-liquid interface and the solid surface.







#### **3-Region Model: Characteristic Film Thicknesses**



#### Molecular region: Derjaguin

#### $g_{VL}$ = specific interfacial free energy



### **Transition Region: Null Curvature Point**



#### **Transition region:** Location of $\theta_o$



At  $h = h_t$  and  $\theta = \theta_t$ 

θ

h<sub>t</sub>

$$-\frac{d\cos\theta}{dh} = \frac{h_m^2}{h^3} - \frac{h_c - h}{L_c^2} \qquad \cos\theta_o = 1 - \frac{h_c^2}{2L_c^2}$$
$$BC \quad h = h_c \implies \theta = 0$$
$$\cos\theta - \cos\theta_o = \frac{h_m^2}{2h^2} - \frac{h_m^2}{2h_c^2} + \left(\frac{h}{h_c} - \frac{h^2}{2h_c^2}\right) 2(1 - \cos\theta_o)$$
$$\Box$$
$$\Box$$
$$Cos\theta_i - \cos\theta_o = \frac{h_m^2}{2h_t^2} + \left(\frac{h_i}{h_c}\right) 2(1 - \cos\theta_o) + \left(\frac{\text{smaller}}{\text{terms}}\right)$$
$$\cong \frac{3}{2} \left(\frac{h_m}{h_t}\right)^2 = \frac{3}{2}\varepsilon^2$$

### **Transition region:** Location of $\theta_0$

Where, on the vapor/liquid interface, is  $\theta_o$  to be found?



$$\cos\theta_t - \cos\theta_o \cong \frac{3}{2} \varepsilon^2$$

$$\theta_o \cong \theta_t + \frac{3}{2\sin\theta_o}\varepsilon^2$$

Nowhere!

$$\begin{cases} \text{since} \quad \theta_o > \theta_t > \theta \\ \text{for all } \theta \text{ on interface} \end{cases}$$

But: 
$$\theta_o \cong \theta_t$$
 to  $O(\varepsilon^2)$ 

#### **Numerical Integration of FAYL equation**

#### HEPTANE ON PTFE



\*Continuous line: YL solution; Dotted line: FAYL solution

### CAPILLARY RISE: MACROSCOPIC APPROACH θ $\mathbf{x} = \mathbf{h}(\mathbf{y})$ у $\frac{dy}{dx} = \frac{dy}{dh} = \tan\left(\frac{\pi}{2} - \theta\right)$ y =0

х

x=0

$$2H\sigma = \rho g y$$

McNutt and Andes, J. of Chemical Physics (1969) Legendre transformation

$$2\mathbf{H} = -\frac{d\sin\theta}{dy} = \frac{y}{L_c^2}$$
  

$$y \to 0 \quad ; \sin\theta = 1$$

$$1 - \sin\theta = \frac{y^2}{2L_c^2} = \frac{Y^2}{2} \quad \Leftarrow \quad Y = \frac{y}{L_c}$$
  

$$\sin\theta_0 = 1 - \frac{\rho g y_o^2}{2\sigma} = 1 - \frac{Y_o^2}{2} \quad \Rightarrow \quad \cos\theta_o = \sqrt{Y_o^2 - (Y_o^2/2)^2}$$

#### Capillary Rise: Molecular Approach

h<sub>s</sub>

y<sub>s</sub>

y<sub>o</sub>



$$\cos\theta_o = \frac{h_m^2}{2h_s^2} - \int_{\infty}^{h_s} \frac{y}{L_c^2} dh$$

$$dh = (dh / dy) dy = -\cot(\pi / 2 - \theta) dy = -\tan\theta dy$$

$$\int_{0}^{y} \frac{y \tan \theta \, dy}{L_{c}^{2}} = \int_{0}^{y} \frac{Y - Y^{3} / 2}{\left(Y^{2} - \left(Y^{2} / 2\right)^{2}\right)^{1/2}} \, dY = \left(Y^{2} - \left(Y^{2} / 2\right)^{2}\right)^{1/2}$$
$$\cos \theta_{o} \approx \sqrt{Y_{s}^{2} - \left(Y_{s}^{2} / 2\right)^{2}} + \frac{h_{m}^{2}}{2h_{s}^{2}} = \sqrt{Y_{o}^{2} - \left(Y_{o}^{2} / 2\right)^{2}}$$



#### **Molecular region:**

$$h < 10^{-9} m$$

$$\cos\theta = \cos\theta_0 - \ln\left[1 - \frac{1}{2}\left(\frac{h_m}{h}\right)^2\right] + O\left(\frac{h_m}{h_L}\right)^4$$

\* Gives  $\theta = \theta(h, h_m, \theta_o)$  in molecular region.



 $h_m^2 = \frac{A_{LL}^{[6]} - A_{SL}^{[6]}}{6 \,\pi \,\sigma}$ 

\* Proceed down to  $\theta = 0!$ 

$$h = h_D$$
;  $\theta = 0$ 

$$\cos \theta_o = 1 + \ln \left[ 1 - \frac{1}{2} \left( \frac{h_m}{h_D} \right)^2 \right]$$

## **Comparison with experiments:**

| Alkanes   | σ                    | A <sub>SL</sub>     | A <sub>LL</sub>            | D                   | θ exper. | θ comp. |
|-----------|----------------------|---------------------|----------------------------|---------------------|----------|---------|
|           | 10 <sup>-3</sup> N/m | 10 <sup>-20</sup> J | <b>10</b> <sup>-20</sup> J | 10 <sup>-10</sup> m | (deg)    | (deg)   |
| Heptane   | 20.3                 | 4.03                | 4.31                       | 2.979               | 21       | 20.8    |
| Octane    | 21.8                 | 4.11                | 4.49                       | 2.811               | 26       | 25.8    |
| Nonane    | 22.9                 | 4.18                | 4.66                       | 2.656               | 32       | 31.7    |
| Decane    | 23.9                 | 4.25                | 4.81                       | 2.617               | 35       | 34.5    |
| Undecane  | 24.7                 | 4.28                | 4.87                       | 2.501               | 39       | 38.7    |
| Dodecane  | 25.4                 | 4.35                | 5.03                       | 2.489               | 42       | 41.8    |
| Tetradec. | 26.7                 | 4.38                | 5.09                       | 2.421               | 44       | 43.7    |
| Hexadec.  | 27.6                 | 4.43                | 5.22                       | 2.402               | 46       | 46.2    |

### **Conclusions:**

Molecular Interactions (close to the contact line) give rise to variations in  $\begin{cases} g_{VL} - \text{surface tension} \\ \theta - \text{slope of interface} \end{cases}$ s.t  $\theta \rightarrow \theta_o$  $g_{VL} \rightarrow \sigma$  as  $h \rightarrow h_L$ 

Macroscopic contact angle,  $\theta_o$ , is

- the B.C. for solutions of YL equation at surface h = 0
- obtained by matching data points to solutions
   of the YL equation, extending the solution to h = 0
   and measuring the angle.
- may or may not be found anywhere in the interface.