

Wetting, Spreading & Adhesion: Lecture 3

Theory of Contact Angles

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Ian Wark Research Institute

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For Particle and Material Interfaces

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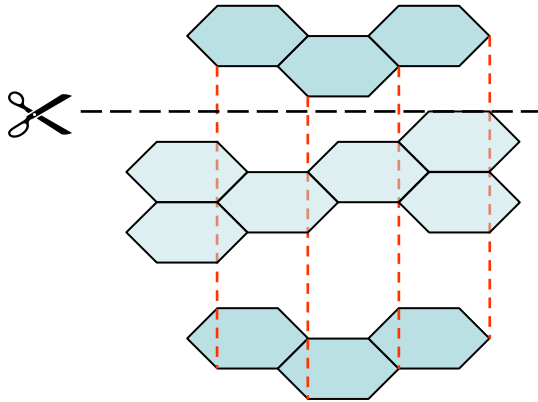
- **Surface Energy of Solids**
- **Empirical Approach**
 - Zisman Plot
- **Analytical Approach**
 - Fowkes Theory
 - van Oss-Good-Chaudhury Theory
- **Wetting Film Approach**
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- **Contact Angle on a Charged Substrate**
 - Young-Lippmann Equation

1. Surface Energetics

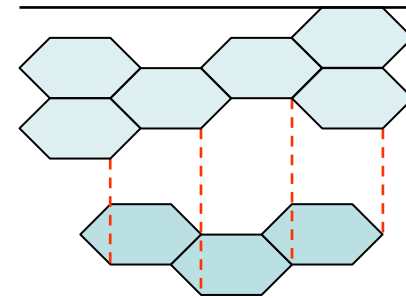
- Surface Energy of Solids
- Contact Angle Interpretation

Surface Energy of Solids

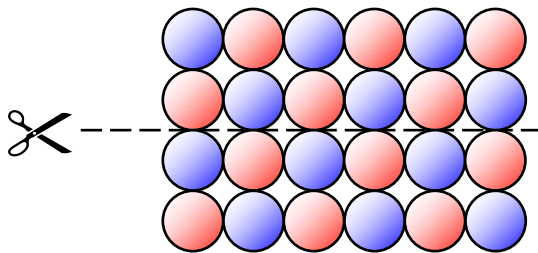
Low-Energy Surfaces (e.g. graphite, polymer surfaces)



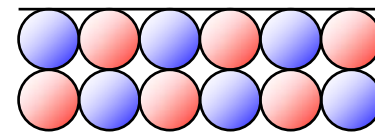
50-100 mJ/m²



High-Energy Surfaces (e.g. metals, metal oxides)



500-1,000 mJ/m²



Young Equation is Not Enough

The equilibrium contact angle on an ideal surface is given by Young equation:

$$\cos \theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L}$$

cannot be measured

can be measured

The Young equation is undefined and therefore a second equation is required to close the system:

$$\begin{cases} \gamma_S = \gamma_{SL} + \gamma_L \cos \theta \\ \gamma_{SL} = f(\gamma_S, \gamma_L) \end{cases}$$

A model for the calculation of W_A is needed. The contact angle equation is:

$$\cos \theta = -1 + \frac{W_A}{\gamma_L}$$

2. Empirical Approach

- Critical Surface Tension
- Zisman Plot

Empirical Approach (Zisman)

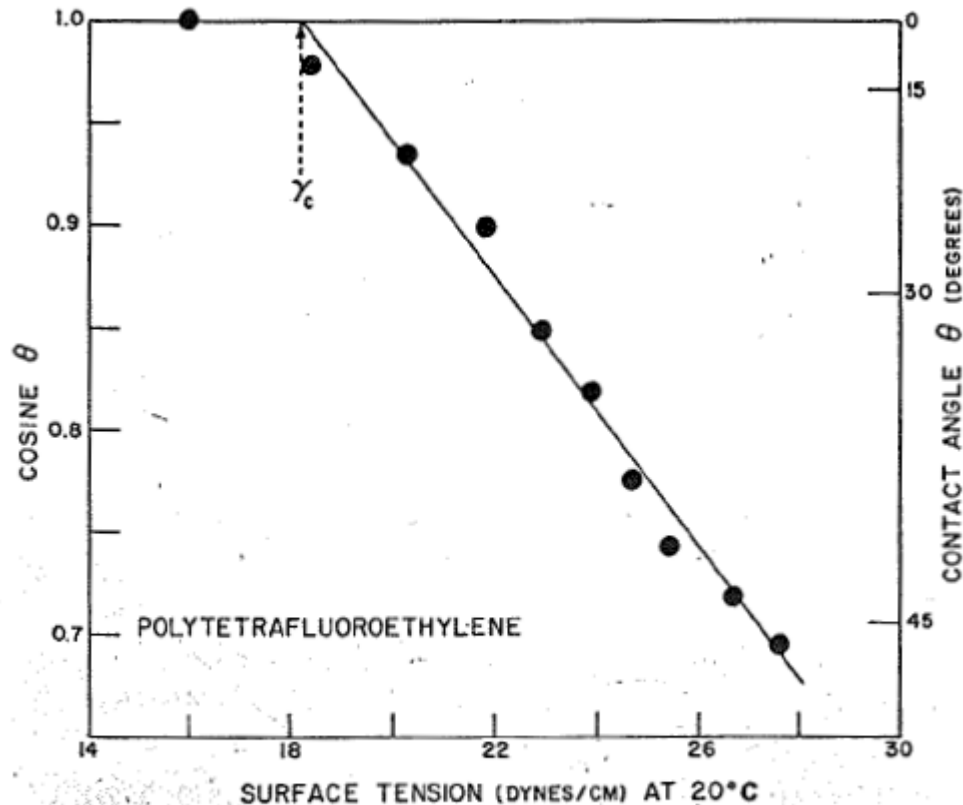


Figure 4—Wettability of polytetrafluoroethylene by the n-alkanes

- Use pure liquids;
- Use homologues (e.g. alkanes);
- Use advancing contact angles;
- Extrapolate linearly to $\theta = 0$.

$$\gamma_C = \lim_{\cos \theta \rightarrow 1} \gamma_L$$

*From Zisman (1972)

Critical Surface Tension of Wetting

The critical surface tension of wetting, γ_C , is obtained from a $\cos \theta$ vs. γ_L plot. The Zisman equation can be written as:

$$\cos \theta = 1 - a(\gamma_L - \gamma_C)$$

The critical surface tension of wetting behaves similarly to the specific surface free energy of the solid:

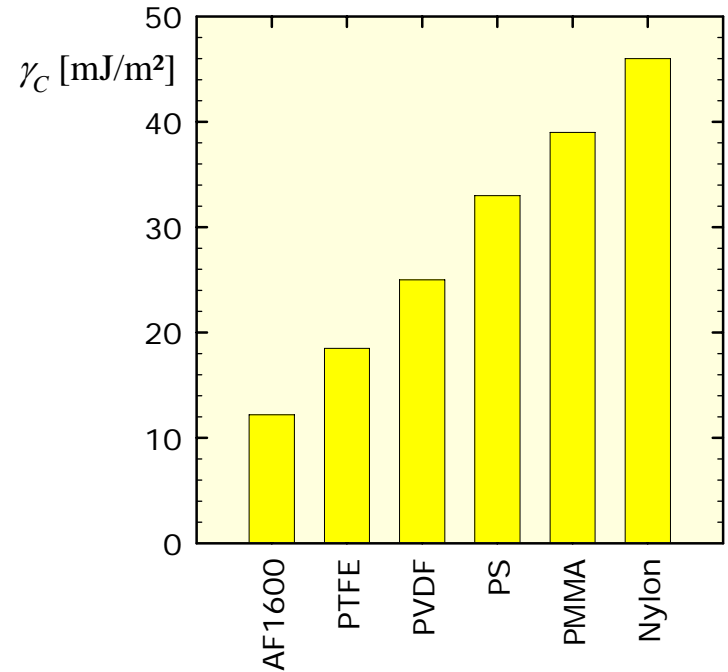
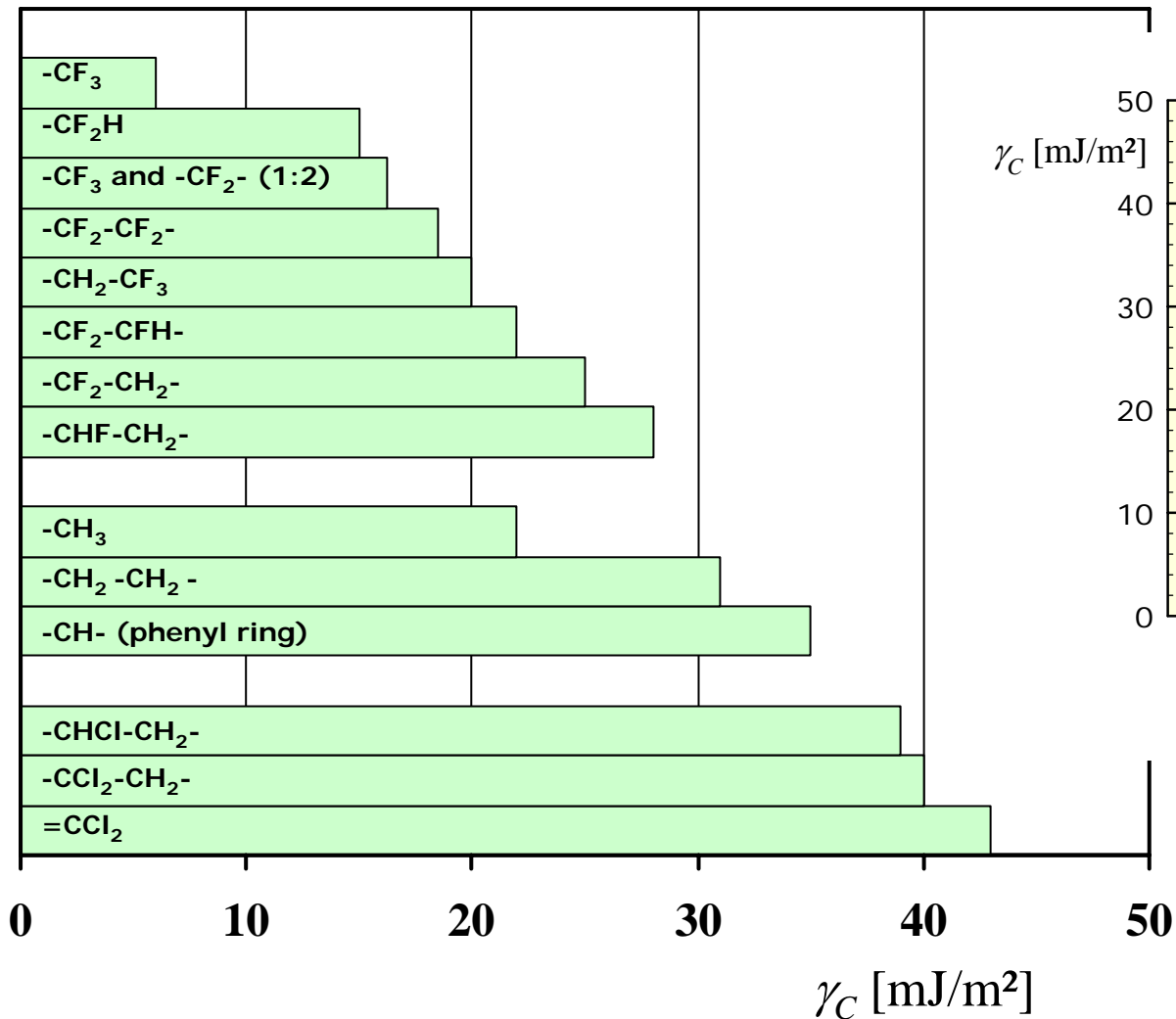
- liquids with $\gamma_L < \gamma_C$ will spread completely;
- liquids with $\gamma_L > \gamma_C$ will form finite contact angles.

The value γ_C of is intimately related to the constitution of the surface layer of the solid.

The approach is empirical:

- the linear behaviour is not universal (depends on the type of liquids used);
- no attention is paid to the slope a .

Wettability & Surface Composition



Zisman (1964)

Empirical vs. Analytical Approach

"holistic"



Knowledge comes from:

- Direct observation
- Experimentation

It is very useful (+)

It is case specific (-)

"detailed"



Knowledge is based on:

- Components
- Mechanisms

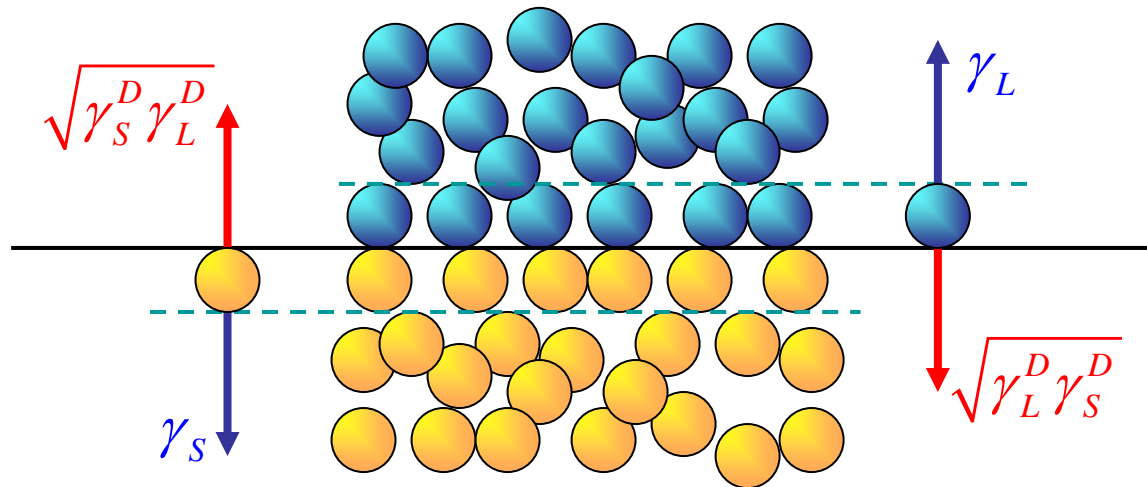
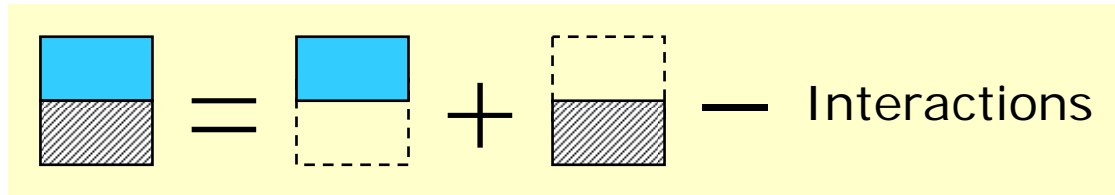
Based on understanding (+)

Always simplified (-)

3. Analytical Approach

- Components of Surface Tension
- Fowkes Theory
- van Oss Theory

Dispersion Interactions



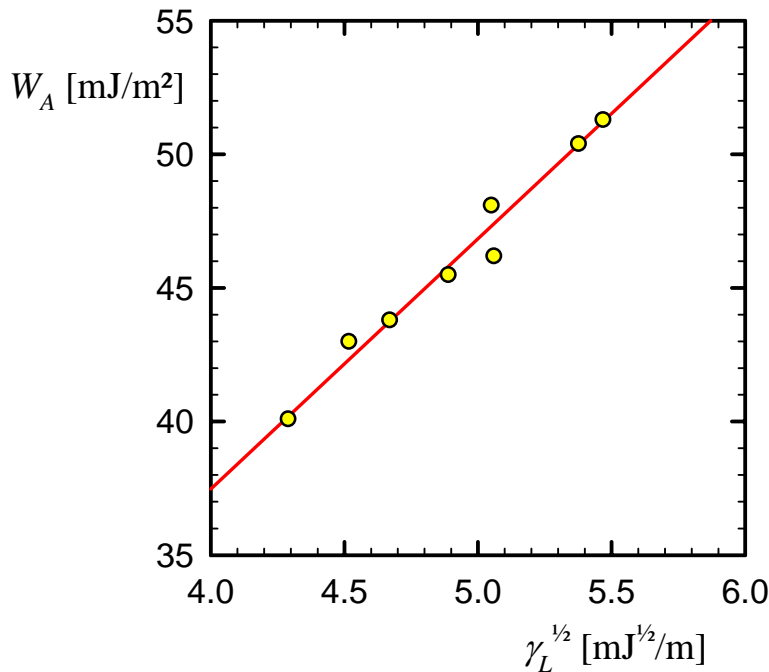
$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D} \quad \text{Fowkes (1964)}$$

Surface Tension of Water

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^D \gamma_2^D}$$

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} = 2\sqrt{\gamma_1^D \gamma_2^D} \xrightarrow{\gamma_2^D \equiv \gamma_2} 2\sqrt{\gamma_1^D} \sqrt{\gamma_2}$$

↑ water ↑ alkane



$$\gamma_W = \underbrace{21.8}_{\text{dispersion interactions}} + \underbrace{51.0}_{\text{polar interactions}} = 72.8 \text{ mJ/m}^2$$

Fowkes (1963)

Fowkes Theory

$$\cos \theta = -1 + \frac{W_A}{\gamma_L} = -1 + \frac{2}{\gamma_L} \sqrt{\gamma_S^D \gamma_L^D}$$

Alkanes are useful liquids as their surface tension is entirely dispersive, i.e. $\gamma_L^D = \gamma_L$
With purely dispersive liquids:

$$\cos \theta = -1 + 2 \sqrt{\frac{\gamma_S^D}{\gamma_L}}$$

Girifalco-Good equation

The correct scale for
extrapolating to γ_C :

$$\cos \theta \sim \frac{1}{\sqrt{\gamma_L}}$$

The γ_C obtained is only
the dispersive part of γ_S :

$$\gamma_S^D = \gamma_L \frac{(1 + \cos \theta)^2}{4}$$

Small Contact Angles

$$\cos \theta = -1 + 2 \sqrt{\frac{\gamma_S^D}{\gamma_L}}$$

Taylor series expansion for small θ , i.e. when $\gamma_L \rightarrow \gamma_S^D$:

$$\cos \theta = 1 - \frac{1}{\gamma_S^D} (\gamma_L - \gamma_S^D) + \frac{3}{4\gamma_S^{D2}} (\gamma_L - \gamma_S^D)^2 + O\left((\gamma_L - \gamma_S^D)^3\right)$$

$$\cos \theta = 1 - \alpha (\gamma_L - \gamma_C) \quad \text{Zisman equation}$$

$$\alpha = \frac{1}{\gamma_S^D}$$
$$\gamma_C = \gamma_S^D$$

van Oss-Good-Chaudhury Theory

Only two components (LW & AB) are considered:

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB}$$

The Lifshitz-van der Waals (LW) component encompasses:

- Keesom interactions (orientation forces between permanent dipoles);
- Debye interactions (induction forces between a permanent and induced dipoles);
- London interactions (dispersion forces between fluctuating dipoles).

The acid-base (AB) component includes:

- Interactions between hydrogen ion donor & hydrogen ion acceptor (Brønsted-Lowry acids & bases);
- Interactions between electron pair acceptor & electron pair donor (Lewis acids & bases);
- Hydrogen bonding.

Apolar (LW) & Polar (AB) Interactions

The LW component is calculated according to Fowkes:

$$\gamma_{ij}^{LW} = \gamma_i^{LW} + \gamma_j^{LW} - 2\sqrt{\gamma_i^{LW} \gamma_j^{LW}}$$

The AB component is further decomposed into acidic (γ^+) & basic (γ^-) parameters:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}$$

The AB component is calculated as:

$$\gamma_{ij}^{AB} = \gamma_i^{AB} + \gamma_j^{AB} - 2\left(\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_j^+ \gamma_i^-}\right)$$

The Contact Angle Equation

$$W_A = \gamma_L + \gamma_S - \gamma_{SL} \quad \text{definition}$$

$$W_A = W_A^{LW} + W_A^{AB} \quad \text{LW \& AB components}$$

$$W_A^{LW} = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}} \quad \text{Fowkes}$$

$$W_A^{AB} = 2\sqrt{\gamma_S^+ \gamma_L^-} + 2\sqrt{\gamma_L^+ \gamma_S^-} \quad \text{van Oss et al.}$$

$$W_A = \gamma_L (1 + \cos \theta) = 2 \left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_L^+ \gamma_S^-} \right)$$

LW & AB Components – Some Values

| Surface Tension | Total | LW | AB | + | - |
|----------------------------|-------------|-------------|-------------|--------------|--------------|
| Dodecane | 25.4 | 25.4 | 0.0 | 0.0 | 0.0 |
| Ethanol | 21.4 | 18.8 | 2.6 | 0.019 | 68 |
| Benzene | 28.8 | 28.8 | 0.0 | 0.0 | 2.7 |
| Nitrobenzene | 43.9 | 41.3 | 2.6 | 0.26 | 6.6 |
| α -Bromonaphthalene | 44.4 | 44.4 | 0.0 | 0.0 | 0.0 |
| Diiodomethane | 50.8 | 50.8 | 0.0 | 0.0 | 0.0 |
| Formamide | 58.0 | 39.0 | 19.0 | 2.28 | 39.6 |
| Water | 72.8 | 21.8 | 51.0 | 25.5* | 25.5* |
| Teflon FEP | 17.9 | 17.9 | 0.0 | 0.0 | 0.0 |
| Nylon 6,6 | 37.7 | 36.4 | 1.3 | 0.02 | 21.6 |

*postulated.

* van Oss (1994)



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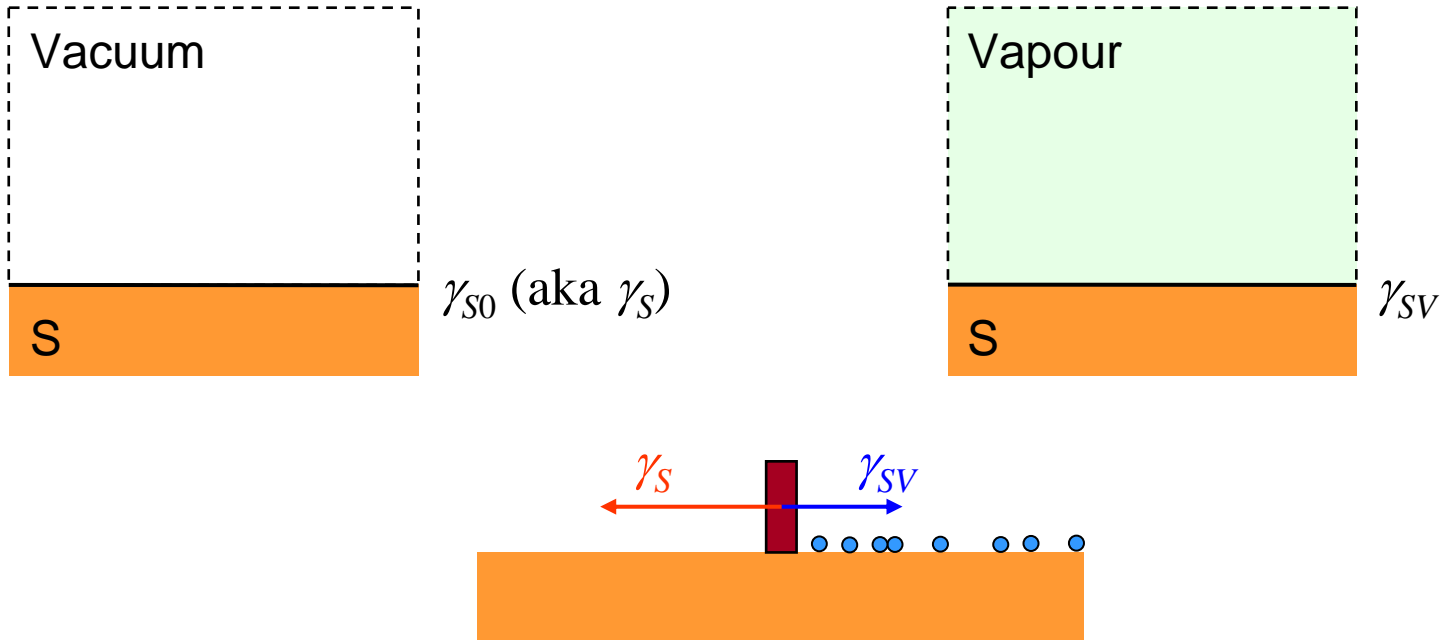
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4. Thin Film Approach

- The Solid – Dry or Wet?
- Disjoining Pressure
- Frumkin-Deryagin Theory

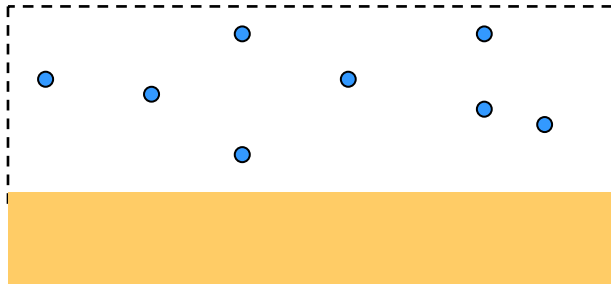
Surface Pressure

$$\pi_0 = \gamma_S - \gamma_{SV}$$

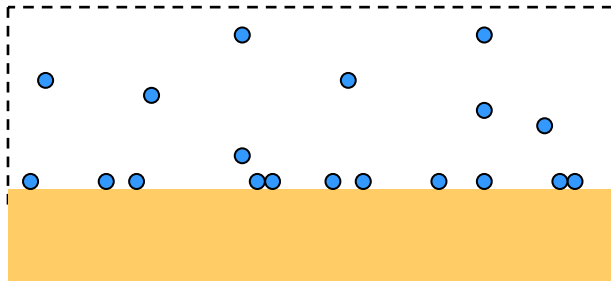


Good (1977): “provided a low-energy solid surface is molecularly smooth and homogeneous, π_0 should be negligible in the case of almost all liquids for which $\theta > 0$.”

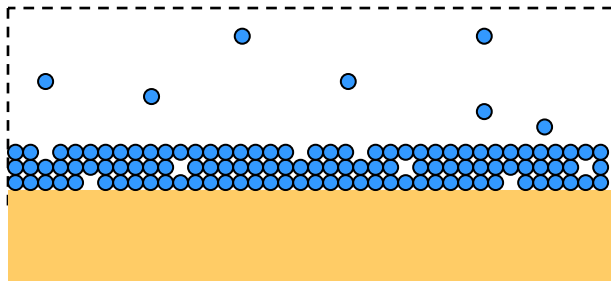
The Solid Surface – Dry or Wet?



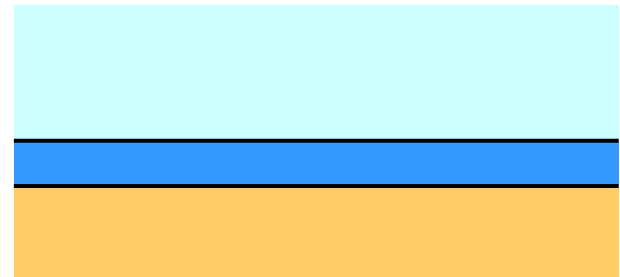
The solid surface is completely dry, i.e. $\pi_0 = 0$.



The solid surface is modified by the vapours, i.e. $\pi_0 > 0$ but small.



wetting film

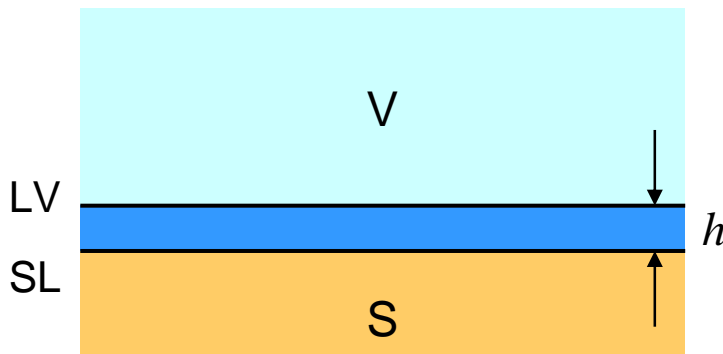


Disjoining Pressure

The wetting film is so thin that the two surfaces (SL & LV) interact with each other. As a result of this interaction the pressure inside the film, $P(h)$, is different from the pressure in the bulk liquid, $P(\infty)$ (under the same conditions). The difference is termed disjoining pressure, Π :

$$\Pi(h) = P(h) - P(\infty)$$

The interaction between the two interfaces can be discussed in terms of disjoining pressure or, alternatively, free energy (per unit area):



pressure

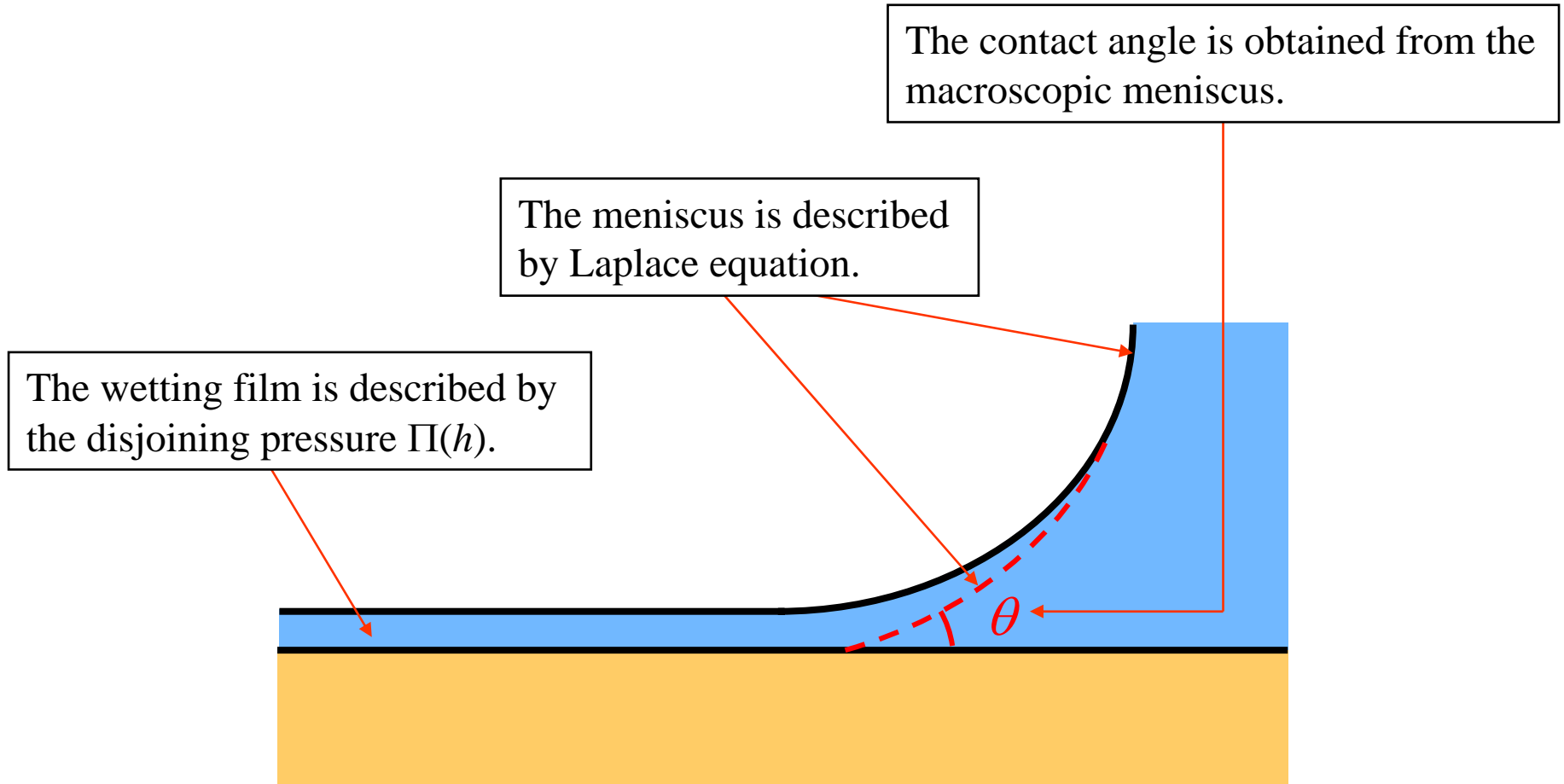
$$\Pi(h) = - \left[\frac{\partial f(h)}{\partial h} \right]_{T, V, \mu_i}$$

energy

$$f(h) = - \int_{\infty}^h \Pi(h) dh$$

Wetting Film Approach

- The meniscus is connected to a thin liquid film;
- The contact angle is finite.



Frumkin-Deryagin Theory

Force balance: $\gamma_F - \gamma_{SL} = \gamma_{LV} \cos \theta$

Additive interactions: $\gamma_F = \gamma_{SL} + \gamma_{LV} + f(h)$

Interaction energy from $\Pi(h)$: $f(h) = \int_h^{\infty} \Pi(h) dh$

The contact angle, θ , is linked to the disjoining pressure isotherm, $\Pi(h)$:

$$\cos \theta = 1 + \frac{1}{\gamma} \int_h^{\infty} \Pi(h) dh \quad \text{Frumkin-Deryagin Equation}$$

Using the Disjoining Pressure Isotherm

$$\cos \theta = 1 + \frac{1}{\gamma} \int_h^{\infty} \Pi(h) dh$$

For a thick film $\Pi(h) = 0$ and therefore:

$$\cos \theta = 1 + \frac{1}{\gamma} \int_h^{\infty} 0 dh = 1 \Rightarrow \theta = 0$$

$\Pi(h)$ can be modelled:

$$\Pi(h) = \underbrace{\Pi_{VW}(h) + \Pi_{EL}(h)}_{\text{DLVO}} + \Pi_{ST}(h) + \dots$$

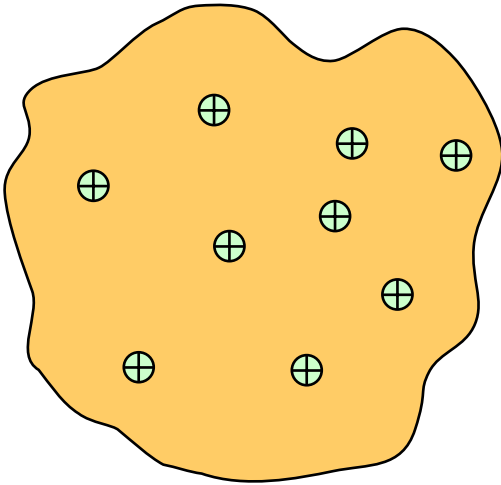
$\Pi(h)$ can be measured but:

- for flat films and liquid inclination (i.e. contact angle) must be small;
- there must be a film, i.e. cannot be too thin.

5. Charged Surfaces

- Lippmann Equation
- Young-Lippmann Equation
- Spontaneous & Forced Charging

Charged Interfaces



The surface charge density, σ , affects the interfacial tension, γ , as follows:

$$\sigma \equiv \frac{q}{A} = - \left(\frac{\partial \gamma_{ij}}{\partial \phi} \right)_{T,P,\mu}$$

Lippmann Equation

The differential capacitance, C , can be expressed through Lippmann's equation. The integration is very simple when the capacitance is constant:

$$C = \frac{\partial \sigma}{\partial \phi} = - \frac{\partial^2 \gamma_{ij}}{\partial \phi^2} \xrightarrow{C=\text{const}} \gamma = \gamma_0 - \frac{1}{2} C \phi^2$$

Contact Angle on a Charged Substrate

Force balance (neutral or charged):

$$\cos \theta(\sigma) = \frac{\gamma_{SV} - \gamma_{SL}(\sigma)}{\gamma} \quad \text{Young Equation}$$

Split into chemical & electrical components:

$$\gamma_{SL} = \gamma_{SL}^0 + \gamma_{SL}^\sigma$$

Electrical work for charging:

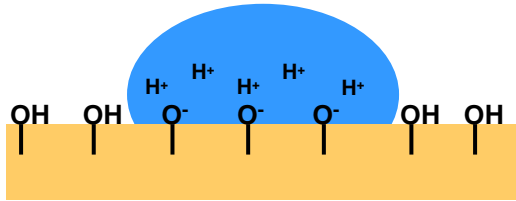
$$\gamma_{SL}^\sigma = - \int_0^{\varphi_0} \sigma d\varphi \quad \text{Lippmann Equation}$$

Contact angle equation:

$$\cos \theta = \cos \theta_0 + \frac{1}{\gamma} \int_0^{\varphi_0} \sigma d\varphi \quad \text{Young-Lippmann Equation}$$

Young-Lippmann Equation

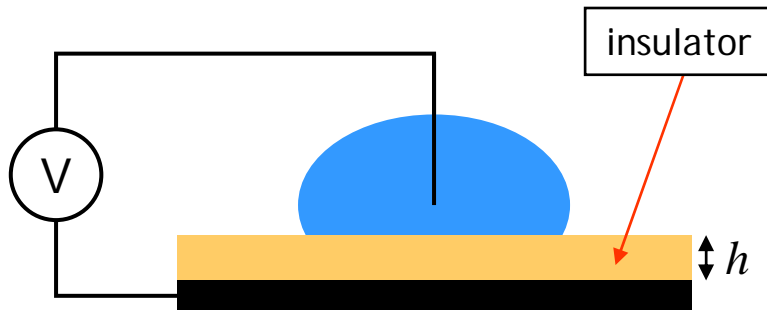
Spontaneous charging (e.g. oxide surfaces):



The energy is spent on creating the electrical double layer:

$$\cos \theta = \cos \theta_0 + \frac{8RTc_0}{\kappa\gamma} \left(\cosh \frac{ze\phi_0}{2k_B T} - 1 \right)$$

Forced charging (i.e. electrowetting):



The energy is spent on polarizing the insulator (i.e. charging the capacitor):

$$\cos \theta = \cos \theta_0 + \frac{1}{2\gamma} CV^2$$

$$C = \frac{\epsilon\epsilon_0}{h}$$