

## Methods of solid surface free energy determination

There are no methods for direct determination of solid surface free energy like some of those used for liquids surface tension (surface free energy) determination.

Therefore to determine the energy for a solid surface various indirect methods are used.

Thus the energy can be determined from:

1. wetting contact angles
2. adsorption isotherms of liquid vapours on solid surface
3. heat of wetting
4. heat of adsorption
5. solid solubility parameters
6. rate of liquid penetration into the porous layer of the powdered solid "thin – layer wicking" method.

One of the most often used methods is that based ***on the contact angle measurements.***

A liquid drop placed on a solid (or another immiscible liquid) surface may start to spread to larger or lesser extent.

It depends on the intermolecular forces interacting between the two phases.

⇒ If the interactions between the solid molecules are stronger than those between the liquid molecules themselves, then the liquid spreads over the solid surface, even up to its monomolecular layer if the solid surface is sufficiently large.

This is called '**the wetting process**'.

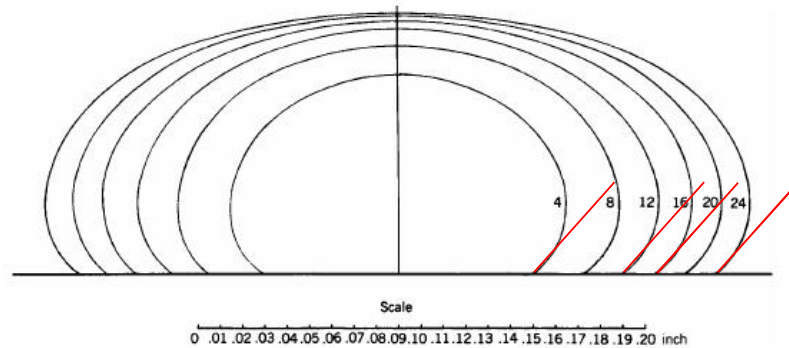


⇒ On the contrary, if the intramolecular interactions between the liquid molecules are stronger than those between the solid and the liquid molecules, the liquid will not spread and will remain as a droplet on the solid (or immiscible liquid) surface.

Generally wetting of a solid surface occurs when one fluid phase repels another one (liquid or gas) being present on the surface.

The angle between the solid surface and the tangent to the drop surface in the line of three-phase contact line, solid/liquid/gas, measured through the liquid phase is called '**wetting contact angle**' or more often '**contact angle**'.

## Contact angles: Liquids on solids



Mercury drops on glass.\*

Drops vary in size from 4 to 24 grains (1 grain = 64.8 mg)

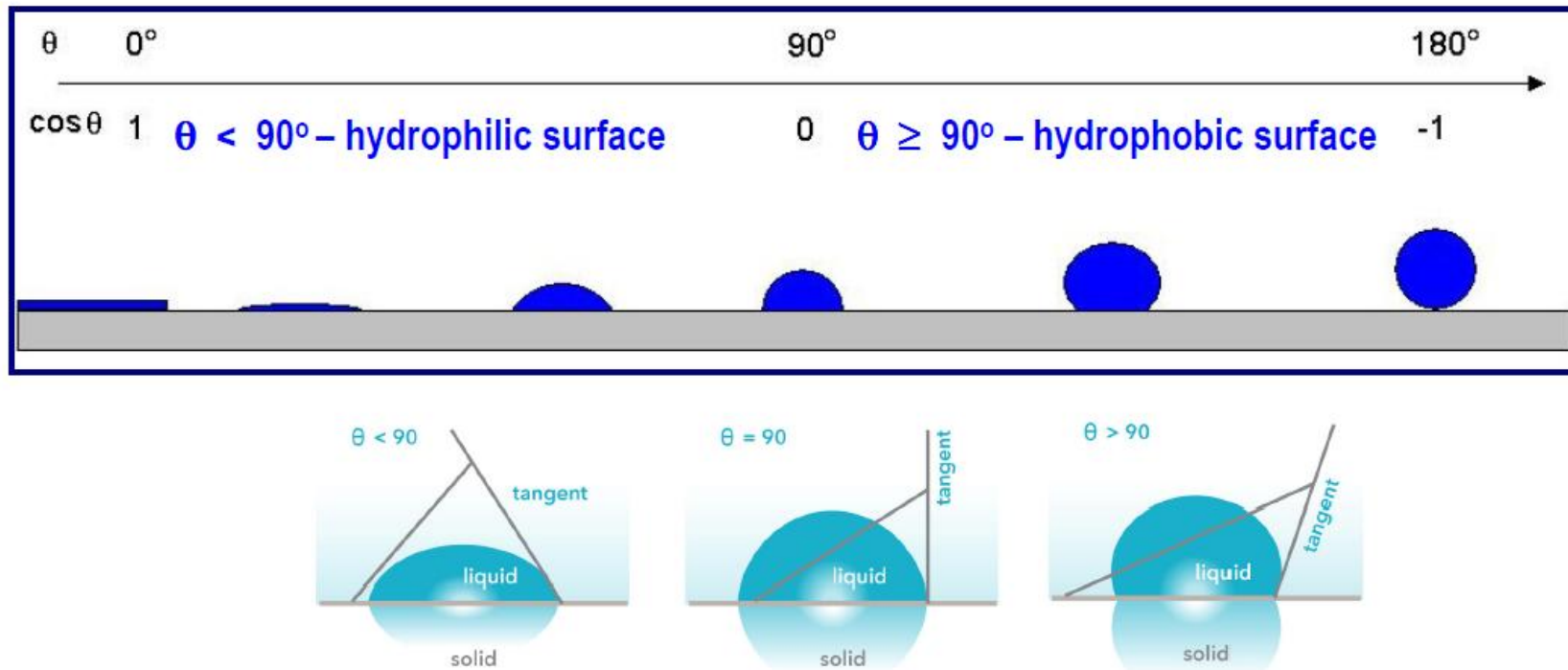
The contact angle of  $140^\circ$  is the same for each drop, independent of drop size.

The observation is that the contact angle depends on the materials but not the particular geometry.



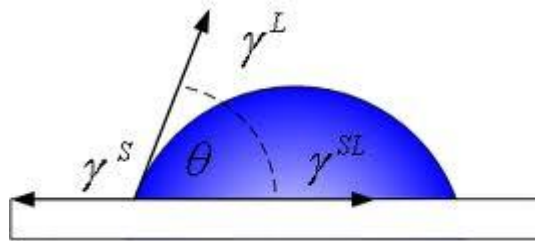
If the liquid is water and it forms a contact angle larger than  $90^\circ$ , such solid surface is customarily called the '**hydrophobic surface**', and if the contact angle is smaller than  $90^\circ$ , such surface is called the '**hydrophilic surface**'. It should be stressed that this is a very rough criterion.

**Note that the contact angle is always denoted by symbol  $\theta$ .**



**Fig. 13.1. Scheme of contact angles on the hydrophobic and hydrophilic surfaces**

# Solid-Liquid-Gas Equilibrium

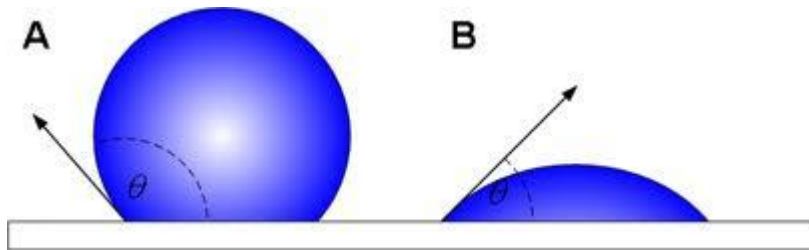


$\theta$ : *Contact Angle*  
Measured in liquid phase

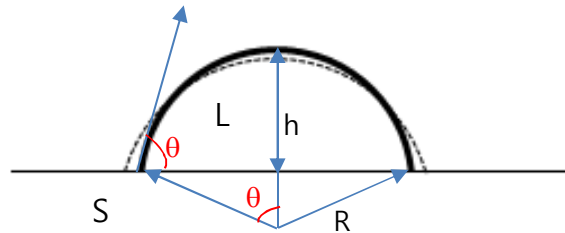
Resolving forces horizontally

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta$$

*Young's Equation*



# Thermodynamic Derivation of Young's Equation



Small drop of liquid on solid:  
(neglect gravity: spherical drop)

Deform drop by infinitesimal amount

$$dG = \gamma_S dA_S + \gamma_{SL} dA_{SL} + \gamma_L dA_L \quad (1)$$

$$\text{But } dA_{SL} = -dA_S$$

$$\therefore \gamma_S = \gamma_{SL} + \gamma_L \frac{dA_L}{dA_{SL}} \quad (2)$$

Drop volume must be constant

$$V = \frac{\pi h^2}{3} (3R - h) \quad h = R(1 - \cos\theta)$$

$$dV = 2\pi R h dh + \pi h^2 dR - \pi h^2 dh = 0$$

$$\frac{dR}{dh} = 1 - \frac{2R}{h} \quad (3)$$

From Geometry

$$A_L = 2\pi R h \quad (4)$$

$$A_{SL} = 2\pi R h - \pi h^2 = A_L - \pi h^2 \quad (5)$$

$$\frac{dA_{SL}}{dA_L} = 1 - 2\pi h \frac{dh}{dA_L} \quad (6)$$

From Eq. (4)

$$\frac{dA_L}{dh} = 2\pi R + 2\pi h \frac{dR}{dh}$$

Then from Eq. (3)

$$\frac{dA_L}{dh} = 2\pi(h - R)$$

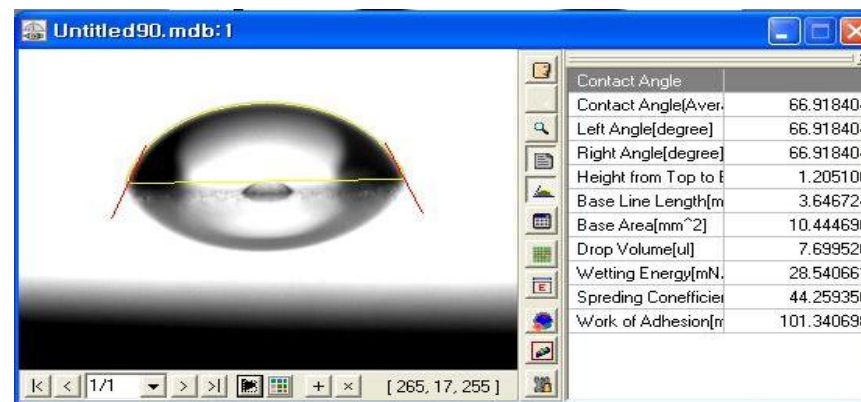
Substitute in Eq. (6)

$$\frac{dA_{SL}}{dA_L} = \frac{R}{R - h} = \frac{1}{\cos\theta}$$

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta$$

# Measurement of $\theta$

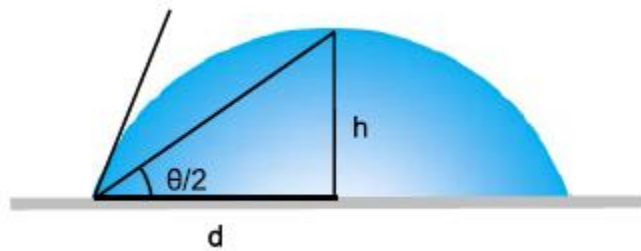
## 1) Direct Method (Sessile Drop)





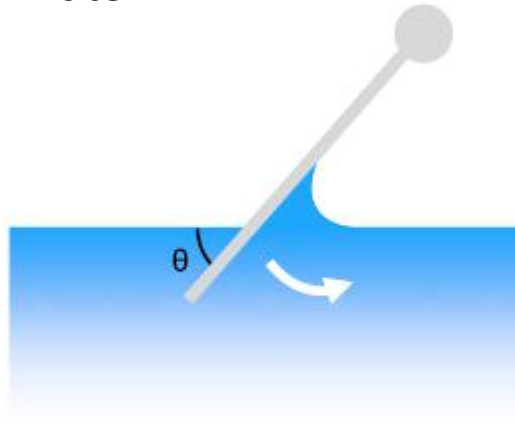
# Measurement of $\theta$

## 2) Drop Dimensions



$$\frac{\theta}{2} = \tan^{-1}\left(\frac{h}{d}\right)$$

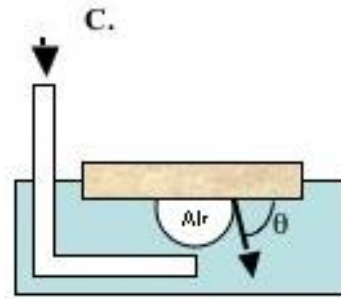
## 3) Tilting Plate



Tilt until meniscus is flat

# Measurement of $\theta$

## 4) Captive Bubble



## 5) Powders

### a. compacted disk

the powders or granules are compressed into a flat cake, to which liquid drops are applied, and contact angles are measured



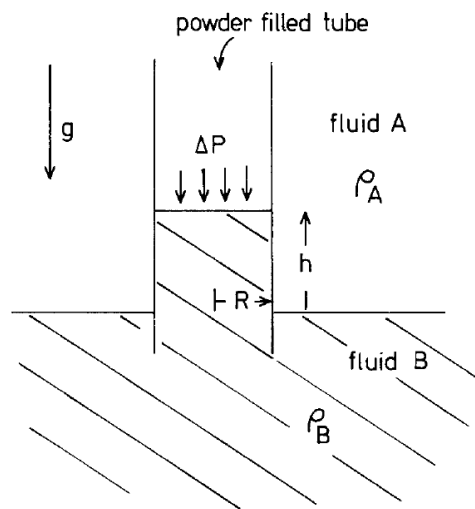
Problem: Spontaneous liquid penetration might occur if the actual contact angle between the liquid and the solid is lower than  $90^\circ$ . But penetration might occur slowly enough that reproducible results can be obtained through direct measurement.

- The contact angle obtained  $>$  on a smooth surface.
- influenced by surface roughness, particle swelling and tablet porosity
- Furthermore, during sample preparation, the topmost powder particles are likely to undergo plastic deformation by the compression, which might give different results than the uncompressed powders

# Measurement of $\theta$

## 5) Powders

### a. porous plug



1. Compact into porous plug
2. Measure pressure needed to prevent liquid from entering pores

$$\Delta P = \frac{2\gamma \cos \theta}{r} \quad r: \text{pore radius}$$

3. Repeat with wetting liquid ( $\theta=0$ )

$$\Delta P_0 = \frac{2\gamma_0}{r}$$

$$\cos \theta = \frac{\Delta P}{\Delta P_0} \frac{\gamma}{\gamma_0}$$

# Measurement of $\theta$

## 5) Powders: c. Infiltration Method

It is known that the penetration rate of liquid into the powder is represented by the Washburn equation.

$$\frac{l^2}{t} = \frac{r \cdot \gamma \cos \theta}{2\eta}$$

$l$  ...Liquid Penetration Height

$t$  ...Time

$r$  ...Capillary radius of the filling powder

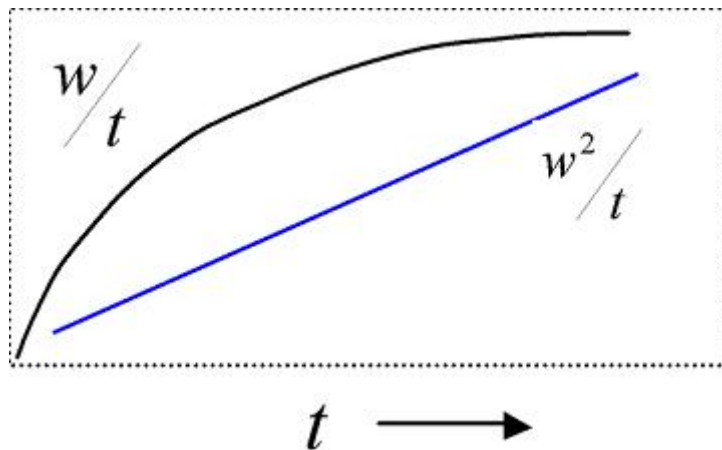
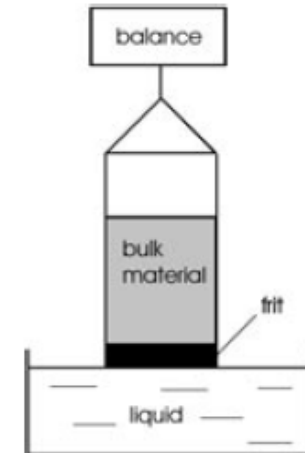
$\gamma$ ...Surface tension of the liquid

$\eta$ ...The viscosity of the liquid

$\theta$ ...Contact angle



Appearance and penetration of powder packed column



In actual measurement, a liquid sample is infiltrated into a column filled with powder, and the change in the weight  $W$  is tracked for the elapsed time  $t$ . Ideally, the linear relationship is obtained by plotting  $t$  for  $W^2$ . The contact angle and infiltration rate is calculated from the slope of this line. In addition, in order to calculate the contact angle, for the powder-filled capillary radius value is required besides the values of liquid surface tension and viscosity.

$$r_{eff} = \frac{2(1 - \phi)}{\phi \rho A}$$

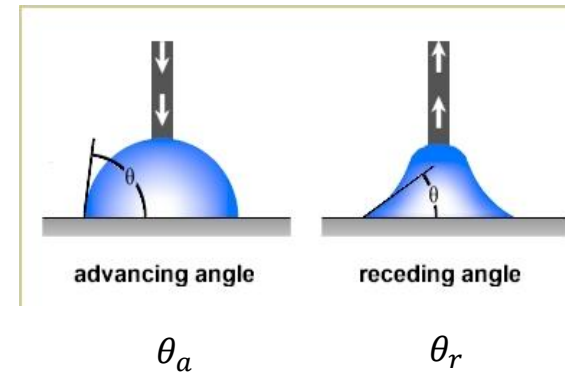
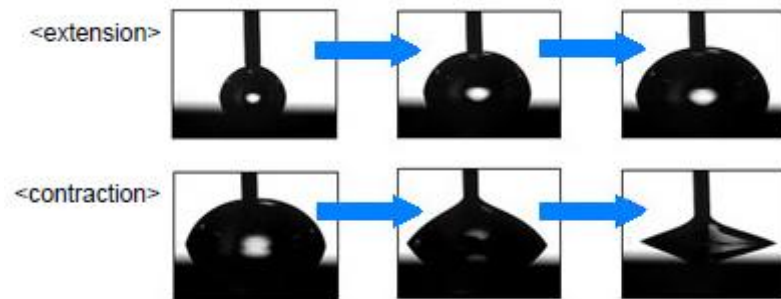
$\phi$ : vol. fraction of solid in the packed bed

$\rho$ : density of the solid

$A$ : specific surface area per gram of solid

# Dynamic contact angle

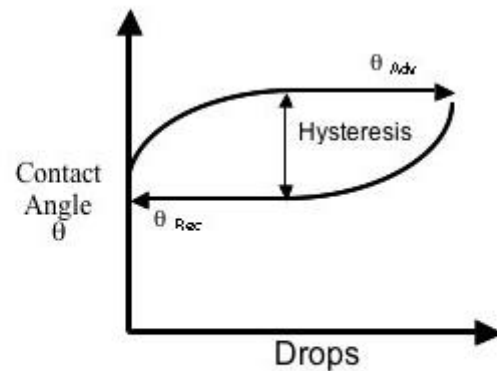
The dynamic contact angle is the contact angle which occurs in the course of wetting (advancing angle) or de-wetting (receding angle) of a solid.



$$\theta_a > \theta_r$$

Contact Angle Hysteresis

$$H = \theta_a - \theta_r$$

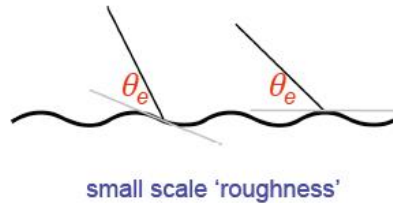


**Figure 3.** A generalized contact angle plot showing the advancing (qAdv) and receding (qRec) contact angles.



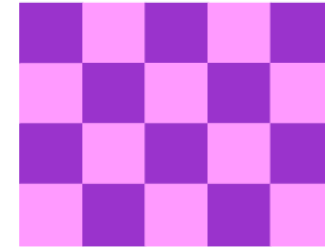
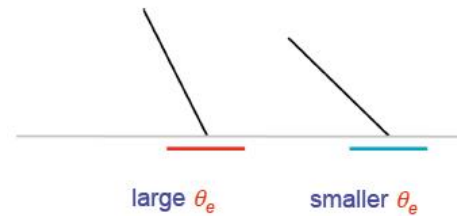
# Microscopic Origin

geometric heterogeneity



- With increasing roughness  $H$  increases
- With increasing roughness  $\theta_a$  increases and  $\theta_r$  decreases

chemical heterogeneity:



High energy spots: low contact angle  
Low energy spots: high contact angle

Advancing contact angles (in air) sense the hydrophobic portion of surface properties  
Water drop on surface at equilibrium



Add water to the drop (advancing)

Drop probes hydrophobic regions and  $\theta_{adv}$  is high.

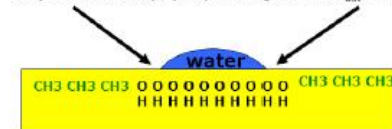


Receding contact angles (in air) sense the hydrophilic portion of surface properties  
Water drop on surface at equilibrium



Remove water to the drop (receding)

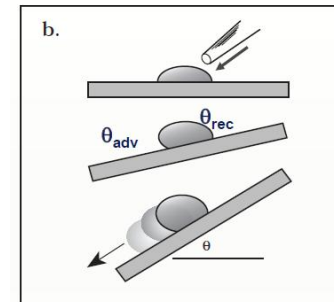
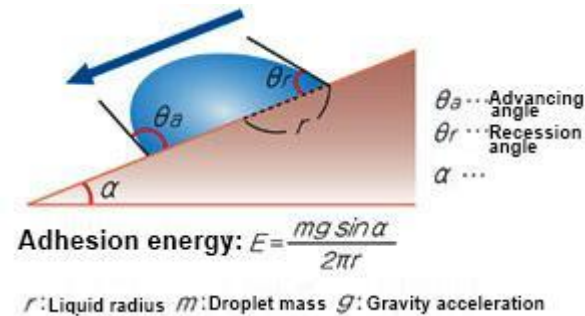
Drop is held back by hydrophilic regions and  $\theta_{adv}$  is high.



Advancing liquids are held up by low energy sports and show high contact angles.  
Receding liquids are help up by high energy sports and show low contact angles.

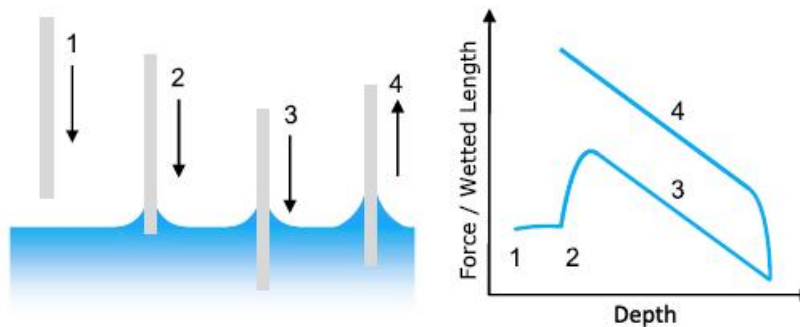
# Calculation of $\theta_a$ and $\theta_r$

## Tilted Plane

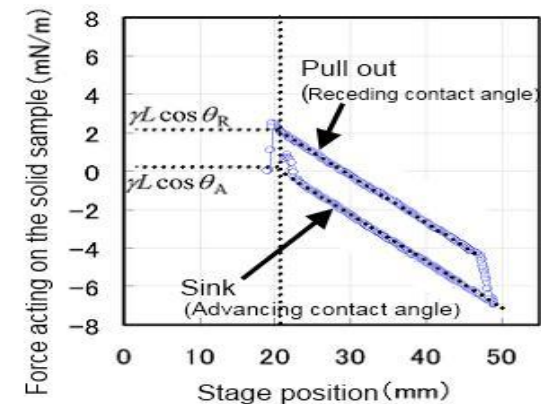


Tilting plane gives both advancing and receding contact angles in same drop.

## Wilhelmy Plate



**Fig. 1.8** A submersion cycle for the Wilhelmy balance measurement: (1) The sample approaches the liquid, and the force/length is zero. (2) The sample is in contact with the liquid surface, forming a contact angle  $\theta < 90^\circ$ ; the liquid rises up, causing a positive wetting force. (3) The sample is immersed further, and the increase of buoyancy causes a decrease in the force detected on the balance; the force is measured for the advancing angle. (4) The sample is pulled out of the liquid after having reached the desired depth; the force is measured for the receding angle



It has been suggested that both advancing and retreating contact angles should be measured wherever possible. Because, there is likely to be chemical information residing in retreating contact angle data that is different from the information in advancing contact angles for the same solid surface [11, 13, 18].

As a result of the analysis of Good and Neumann, it has been established that for smooth, heterogeneous solids the advancing contact angle corresponds approximately to Young's equilibrium contact angle associated with low energy patches of the surface, whereas the receding contact angle corresponds to that of high energy patches [12]. Whilst advancing contact angles ( $\theta_a$ ) have been held to be a measure of the apolar aspect of a surface, and receding contact angles ( $\theta_r$ ) a measure of the polar aspects of the solid [16], it would be hazardous to take that statement so literally as to attempt to derive the polar surface tension component of the solid by measuring  $\theta_r$ .

One criterion for deciding between dynamic and static contact angle is the technical wetting process observed. Dynamic processes, such as coating, are better modelled by means of dynamic measurements. Static contact angles are often more meaningful for assessing quasi-static processes, e.g. bonding in semiconductor technology.

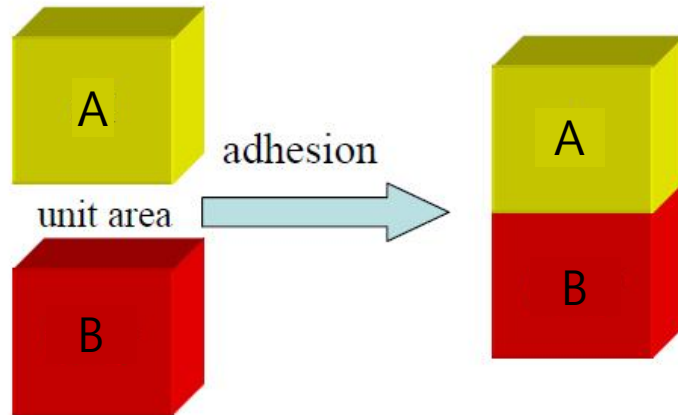
# Calculation of Surface Free Energy of Solids

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta$$

*Young's Equation*

- Although contact angle itself also gives indications on the wetting properties of the surface, contact angle always depends also on the liquid used for the measurements.
- In Young's eq,  $\gamma_L$ , *and*  $\cos\theta$  are easily measured but the problem is the unknown  $\gamma_{SL}$  which cannot be measured directly.
- To be able to solve the equation, more assumptions of the relationship between  $\gamma_S$ ,  $\gamma_{SL}$  *and*  $\gamma_L$  has to be made.
- To be able to understand the different methods, term "work of adhesion" has to be explained.

# Work of Adhesion and Cohesion



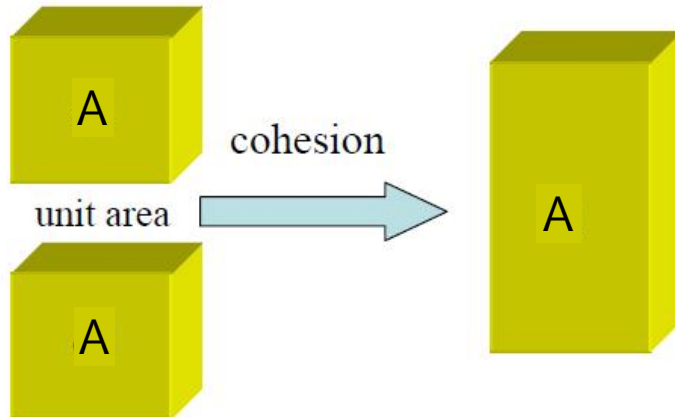
Work of Adhesion =  
work involved in separating A and B

$$W_a = \gamma_A + \gamma_B - \gamma_{AB}$$

creation of  
**A** surface

creation of  
**B** surface

destruction  
of **AB**  
interface



Work of Cohesion

$$W_c = 2\gamma_A$$



# Spreading



Spreading will be spontaneous if it lowers the energy of system.  
Gibbs Free Energy Change

$$\Delta G = \gamma_B + \gamma_{AB} - \gamma_A$$

Spreading is spontaneous if  $\Delta G < 0$

Define Work of Spreading or Spreading Coefficient  $(-\Delta G)$

$$W_S = S_{B/A} = \gamma_A - \gamma_B - \gamma_{AB}$$

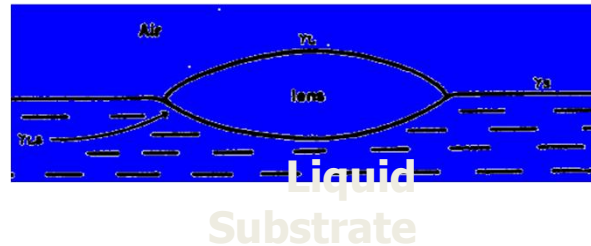
*If  $S_{B/A} > 0$  Spontaneous Spreading*

*$S_{B/A} < 0$  not Spontaneous*

# Spreading

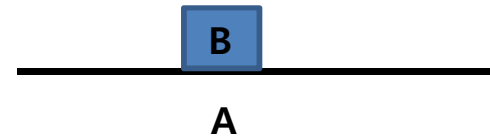
*If  $S_{B/A} = \gamma_A - \gamma_B - \gamma_{AB} > 0$  Spontaneous Spreading*

Spreading occurs ( $S$  is positive) when the surface tension of the sub-layer liquid is greater than the sum of the surface tension of the spreading liquid and the interfacial tension between the sub-layer and the spreading liquid. If not, the substance forms globules or a *floating lens* and fails to spread over the surface.



$$W_a = \gamma_A + \gamma_B - \gamma_{AB}$$

$$W_c = 2\gamma_B$$

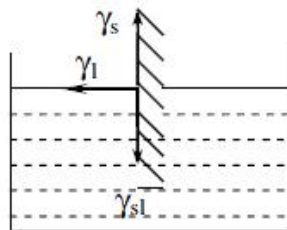


$$S_{B/A} = W_{a(AB)} - W_{c(B)}$$

Spreading occurs if  $W_{a(AB)} > W_{c(B)}$

# Immersional Wetting

The immersional wetting process occurs, for example, when a plate of a solid is in a reversible process dipped into a liquid perpendicularly to the liquid surface (Fig. 13.6). Then, because the liquid surface tension vector is normal to the solid surface, it does not contribute to the work of immersion  $W_I$ .



The work of immersion equals:

$$W_I = \gamma_s - \gamma_{sl}$$

Fig.13.6. Scheme of the immersional wetting process.

# Liquid/Solid (A:Solid, B:Liquid)

Comparison of the work of wetting in particular processes:

$$W_S = (\gamma_s - \gamma_{sl}) - \gamma_l$$

$$W_I = (\gamma_s - \gamma_{sl})$$

$$W_A = (\gamma_s - \gamma_{sl}) + \gamma_l$$

From this comparison it can be seen that:

$$W_s < W_I < W_A$$

Moreover, the relationship between the works of wetting can be derived:

$$W_S = (\gamma_s - \gamma_{sl}) - \gamma_l = W_A \{= (\gamma_s - \gamma_{sl}) + \gamma_l\} - 2\gamma_l$$

$$W_S = W_A - W_C$$

# Contact Angle and Work of Adhesion

In the Young equation:

contact angle  $\theta$

liquid surface tension  $\gamma_l$

solid surface free energy  $\gamma_s$

interfacial solid/liquid free energy  $\gamma_{sl}$

$$\gamma_s = \gamma_l \cos\theta + \gamma_{sl}$$

- measurable

- unknown

However, the work of adhesion can be determined experimentally.

$$\gamma_s = \gamma_l \cos\theta + \gamma_{sl} \quad \Rightarrow \quad \gamma_{sl} = \gamma_s - \gamma_l \cos\theta$$

$$W_A = \gamma_s + \gamma_l - \gamma_{sl} = \gamma_s + \gamma_l - \gamma_s + \gamma_l \cos\theta$$



$$W_A = \gamma_l (1 + \cos\theta)$$

Young-Dupre Eq.



# Spreading Coefficient

Having determined  $W_A$ , work of spreading  $W_S$  can be calculated for the system in which the liquid droplet does not spread completely and forms given contact angle.

$$\begin{aligned} S_{L/S} &= W_{a(SL)} - W_{c(L)} = W_{a(SL)} - 2\gamma_L = \gamma_L(1 + \cos\theta) - 2\gamma_L \\ &= \gamma_L(\cos\theta - 1) \end{aligned}$$

Spreading occurs if  $S_{L/S} > 0$



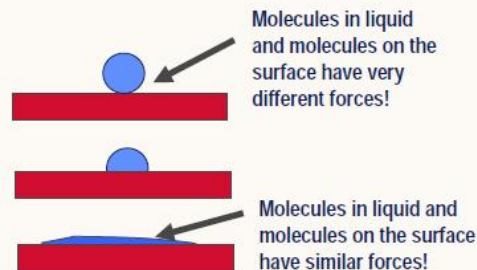
But,  $-1 < \cos\theta < 1 \longrightarrow \theta = 0$  is a limiting case.

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad \text{if } > 1 \rightarrow \text{no three phase contact}$$

$$\theta = 180^\circ \quad \cos\theta = -1$$

$$\theta = 90^\circ \quad \cos\theta = 0$$

$$\theta = 0^\circ \quad \cos\theta = 1$$



When  $\theta = 0$ ,  $W_{a(SL)} \geq 2\gamma_L$

## Practical application of the Young-Dupre equation

At equilibrium:

$$\cos \theta = \frac{\gamma_{SV^0} - \gamma_{L/S}}{\gamma_{LV^0}} \quad (\text{Young-Dupre})$$

For water wetting to improve:

$\theta \downarrow$  or  $\cos \theta \uparrow$

$\gamma_{SV^0} \uparrow$

Increase surface polarity  
(e.g., oxidize in corona discharge)

$\gamma_{L/S} \downarrow$

Add surfactant

$\gamma_{LV^0} \downarrow$

Add surfactant

**Wetting agents: Lower surface tension of liquid**

**For water wetting to get worse:**

$$\theta \uparrow \text{ or } \cos \theta \downarrow$$

$$\gamma_{sv} \downarrow$$

**Increase surface hydrophobicity  
(coat with HC or Silicone oils,  
HC waxes, or HC, Silicone or FC  
polymers)**

$$\gamma_{L/S} \uparrow$$

**Increase surface hydrophobicity  
(coat with HC or Silicone oils,  
HC waxes, or HC, Silicone or FC  
polymers)**

$$\gamma_{LV} \uparrow$$

**Not practical**

## Young-Dupre Equation

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}}$$

Note that for solving this equation, we know

$\theta$  and  $\gamma_{lv}$ , but we are missing two values!

We want  $\gamma_{sv}$

We do not know  $\gamma_{ls}$

However, still the surface free energy of solids cannot be determined in this way. This is possible if the work of adhesion is formulated in such a way that it involves the solid surface free energy. This problem has not been fully solved yet.

# Critical Surface Tension-Zisman Plot

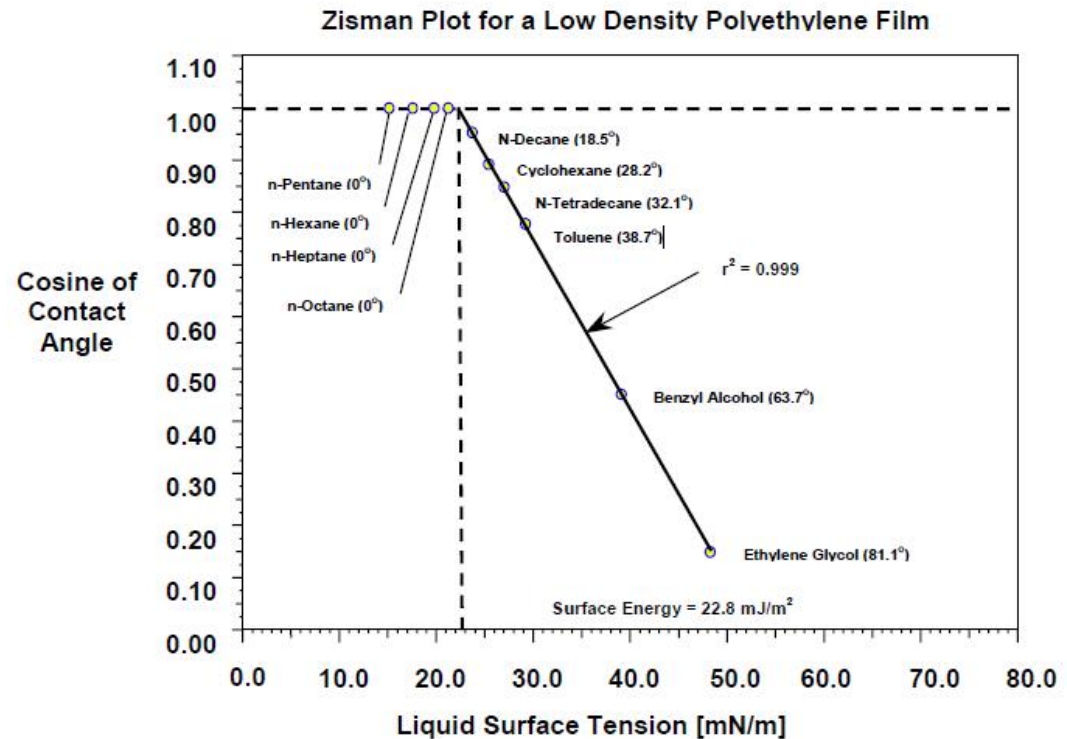
Zisman et al. (1950)<sup>1</sup> found an empirical connection between  $\cos\theta$  and  $\gamma_1$ :

If we measure the contact angle of many liquids on the same surface, and plot  $\cos\theta$  against  $\gamma_1$ , we get a curve that can be extrapolated to  $\cos\theta = 1$ .

The extrapolated value is called the **critical surface tension** of the solid surface.

Note: This is not necessarily the same as the surface tension of the solid,  $\gamma_2$ .

But empirical approximation of it.





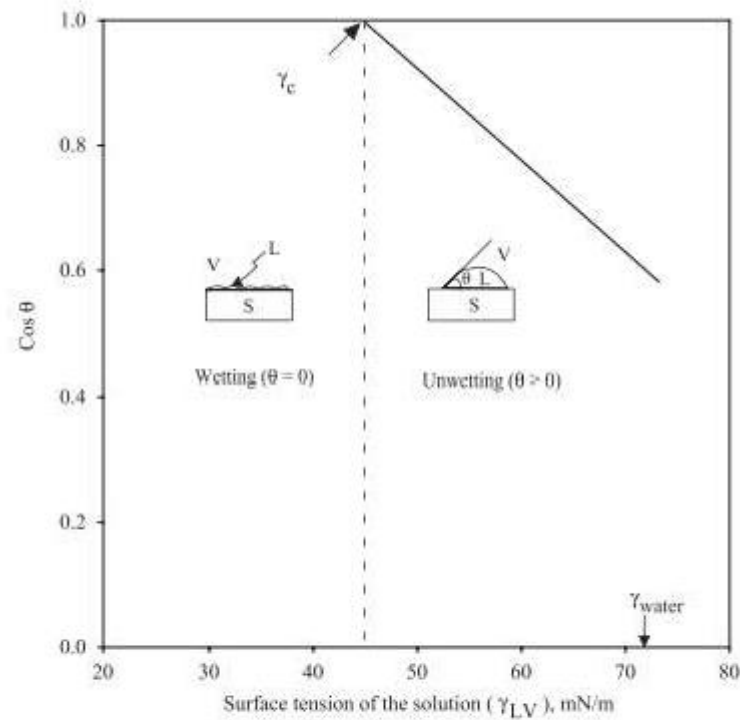
## Liquids used in critical surface tension measurements

	<u>Surface tension, dynes/cm (22°C)</u>
Water	72.9
Glycerol	63.7
Formamide	58.4
Thiodiglycol	53.5
Methylene iodide	51.7
Tetrabromoethane	49.8
1-bromonaphthalene	45.0
Dibromobenzene	42.9
1-methyl naphthalene	38.9
Dicyclohexyl	32.7
Hexadecane	27.6
Decane	24.1

### Why these liquids?

**They're stable, and can be purified. They have relatively low viscosity and low volatility. Only pure liquids will have a well-known surface tension.**

Any liquid with  $\gamma_L < \gamma_C$  will wet solid spontaneously



The determination of the critical surface tension of a solid by Zisman's contact angle measurement approach (U.Ulusoy, M. Yekeler, 2004)

### Values of $\gamma_C$

Teflon:	18.5
Polyethylene:	31
Polystyrene:	33
PVA:	37
PMMA:	39
PVC:	39
Coal:	46

# Theory for Interfacial Tensions

## Good and Girifalco (1960) Theory

The work of adhesion has been expressed by the geometric mean of the surface tensions.

$$W_a = 2\Phi\sqrt{\gamma_1\gamma_2} \quad \Phi : \text{Interaction parameter, } 0.5 < \Phi < 1.15$$

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12}$$

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

Combined with Young's Eq.

$$\cos\theta = 2\Phi\sqrt{\frac{\gamma_s}{\gamma_L}} - 1$$

Combined with Young-Dupre Eq.

$$W_a = \gamma_1(1 + \cos\theta)$$

$$\gamma_2 = \gamma_1 \frac{(1 + \cos\theta)^2}{4\Phi^2}$$

# Fowkes' Theory

1. Surface forces (energies) are additive:  $\gamma = \gamma^d + \gamma^p + \gamma^h + \gamma^i + \gamma^{ab} + \dots$

where d = dispersion force  
 p = polar force  
 h = hydrogen bonding force  
 i = induction force (Debye)  
 ab = acid/base force  
 ... etc.

*In a similar fashion, the surface tension of any liquid can be equated to the sum of each individual energy contribution to the total surface tension:*

2. Geometric mean is used for the work of adhesion for each type of force (energy):

$$W_{12}^d = 2\left(\gamma_1^d \gamma_2^d\right)^{1/2}, W_{12}^p = 2\left(\gamma_1^p \gamma_2^p\right)^{1/2}, W_{12}^h = 2\left(\gamma_1^h \gamma_2^h\right)^{1/2}, \text{ etc.}$$

The general expression for  $W_{12}$  is:  $W_{12} = \gamma_1(1 + \cos \theta) = W_{12}^d + W_{12}^p + \dots$

And for  $\gamma_{12}$  thus:  $\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^d \gamma_2^d\right)^{1/2} - 2\left(\gamma_1^p \gamma_2^p\right)^{1/2} - \dots$

# Interfacial Interaction

- 1) All solid or liquid surfaces or interfaces have dispersion interactions.
- 2) Only polar surfaces also have significant polar or acid-base interactions.
- 3) Only metal surfaces also have metallic interactions.

## Owens and Wendt

- assume that the sum of all the components, except  $\gamma_s^d$  can be considered as associated with the polar interaction ( $\gamma_s^p$ ). Consequently

$$\begin{aligned}\gamma_{12} &= \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} \\ &= \gamma_2 - \gamma_1 \cos \theta\end{aligned}$$

The objective now is to:

- 1) Obtain  $\gamma_1^p + \gamma_1^d$  for a series of liquids
- 2) Measure contact angle of these same liquids on different solids, and then
- 3) Use the  $\theta$ 's and  $\gamma_1^p + \gamma_1^d$  to estimate  $\gamma_s^p$  and  $\gamma_s^d$  for the different solids

# Fowkes' Theory

By using a liquid that only interacts with the surface by dispersion forces, we can write:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2}$$

$$W_{12} = \gamma_1(1 + \cos \theta) = 2(\gamma_1^d \gamma_2^d)^{1/2}$$

$$\gamma_2^d = \frac{\gamma_1^2 (1 + \cos \theta)^2}{4\gamma_1^d}$$

If one phase is nonpolar solid

$$\gamma_s = \gamma_s^d = \frac{\gamma_1^2 (1 + \cos \theta)^2}{4\gamma_1^d}$$

*PTFE*(polytetrafluoroethylene:  $\gamma_s = \gamma_s^d = 18 \text{ mJ} / \text{m}^2$ )

$$\gamma_1^d = \frac{\gamma_1^2 (1 + \cos \theta)^2}{72}$$

- Dispersion component of any liquid can be calculated.
- Also, polar component since  $\gamma_1^p = \gamma_1 - \gamma_1^d$

# $\gamma_d + \gamma_p$ of Water

- ◆ Fowkes determined in this way contribution of the dispersion interactions to water surface tension, i.e. the **dispersion component** of water surface tension

$$\gamma_w^d = 21.8 \pm 0.7 \text{ mN/m.}$$

- ◆ The total surface tension of water equals 72.8 mN/m at 20°C.
- ◆ The difference between the two

$$\gamma_w^p = 51 \text{ mN/m}$$

results from the presence of **nondispersion forces** originating from water molecules.

- ◆ These nondispersion forces are **dipole-dipole and hydrogen bonds**.



# Calculation $\gamma_s$ of any Solid (Fowkes)

By using a liquid that only interacts with the surface by dispersion forces, we can write:

$$\gamma_s^d = \frac{\gamma_1^2 (1 + \cos \theta)^2}{4 \gamma_1^d}$$

If the liquid is also nonpolar

$$\gamma_1^d = \gamma_1 \quad \gamma_s^d = \frac{\gamma_1 (1 + \cos \theta)^2}{4}$$

Therefore,  $\gamma_s^d$  is calculated.

Next, the contact angle ( $\theta$ ) is measured using a liquid for which  $\gamma_1 = \gamma_1^d + \gamma_1^p$

Using  $\gamma_s^d$  and  $\theta$ ,  $\gamma_s^p$  can be calculated from the following formula.

$$\gamma_1 (1 + \cos \theta) = 2(\gamma_s^d \gamma_1^d)^{1/2} + 2(\gamma_s^p \gamma_1^p)^{1/2} \rightarrow \gamma_s^p = \left[ 0.5 \gamma_1 (1 + \cos \theta) - (\gamma_s^d \gamma_1^d)^{0.5} \right]^2 / \gamma_1^p$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

# Calculation $\gamma_s$ of any Solid (Owens and Wendt)

$$(\gamma_s^d \gamma_1^d)^{1/2} + (\gamma_s^p \gamma_1^p)^{1/2} = 0.5 \gamma_1 (1 + \cos \theta)$$

Because two unknowns  $\gamma_s^d$  and  $\gamma_s^p$ , two measurements of  $\theta$  using two liquids with known  $\gamma_1^d, \gamma_1^p$  and thus  $\gamma$ .

And then the resulting two linear equations are solved for  $\gamma_s^d$  and  $\gamma_s^p$ .

To reduce the error, the liquid with a dominant polar component should be chosen as one of the liquids and the dispersion liquid as the other one (e.g., water/diiodomethane).

Let's assume that, for the material the surface energy of which we want to determine, the contact angles with water and diiodomethane were found to be  $49.6^\circ$  and  $75.2^\circ$ , respectively. In this case, the following algebraic system of equations needs to be solved,

$$\begin{cases} 72.8 \times (1 + \cos 49.6^\circ) = 2[\sqrt{21.8 \times \gamma_s^d} + \sqrt{51.0 \times \gamma_s^p}] \\ 50.8 \times (1 + \cos 75.2^\circ) = 2\sqrt{50.8 \times \gamma_s^d} \end{cases} \quad (13)$$

whence we get  $\gamma_s^d = 20$  and  $\gamma_s^p = 30$  mJ/m<sup>2</sup>.

Some Polar and Dispersive Contributions to Liquid  
and Solid Surface Energies @ 20° C

LIQUIDS

$$\gamma = \gamma_d + \gamma_p$$

water 72.8 = 21.8 + 51.0 (dynes/cm)

fomamide 58.2 = 39.5 + 18.7

CH<sub>2</sub>l<sub>2</sub> 50.8 = 48.5 + 2.3

C<sub>16</sub>H<sub>34</sub> 27.6 = 27.6 + 0.0

SOLIDS

$$\gamma = \gamma_d + \gamma_p \quad \gamma_c$$

Nylon 66 41.4 = 33.6 + 7.8 46

Dacron 39.5 = 38.4 + 2.2 43

P.E. 32.4 = 31.3 + 1.1 31

PDMS 22.1 = 20.5 + 1.6 22

PTFE 15.6 = 14.6 + 1.0 18.5

Values of  $\gamma^d$

Hg	200
Graphite	100
Cu	60
Ag	74
Fe	100
Fe <sub>2</sub> O <sub>3</sub>	107
SiO <sub>2</sub>	78
TiO <sub>2</sub>	100

In the late 80th of the 20th century van Oss, Good and Chaudhury introduced a new formulation of the surface and interfacial free energy.

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} = \gamma_i^{LW} + 2(\gamma_i^- \gamma_i^+)^{1/2} \quad (17)$$

$\gamma_i^{LW}$  – the apolar Lifshitz-van der Waals component a phase ‘i’

$\gamma_i^{AB}$  – the polar Lewis acid-base interactions (hydrogen bonding).

$\gamma_i^-$  – the electron-donor  
 $\gamma_i^+$  – the electron-acceptor

} – mostly hydrogen bonding

Based on Eq. (4), the interfacial solid/liquid free energy can be derived.

$$\gamma_{SL} = \gamma_S + \gamma_L - W_A = \gamma_S + \gamma_L - 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} - 2(\gamma_S^+ \gamma_L^-)^{1/2} - 2(\gamma_S^- \gamma_L^+)^{1/2} \quad (15)$$

And the work of adhesion reads:

$$W_A = \gamma_l(1 + \cos \theta) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_S^- \gamma_L^+)^{1/2} \quad (16)$$

If one has measured contact angles of three probe liquids, whose surface tension components are known, then three equations of type (16) can be solved simultaneously and the surface free energy components of the solid can be determined.

# Prediction of Contact Angle

$$\gamma_2^d = \frac{\gamma_1^2 (1 + \cos \theta)^2}{4\gamma_1^d} \quad \rightarrow \quad \cos \theta = -1 + 2\sqrt{\gamma_2^d} \frac{\sqrt{\gamma_1^d}}{\gamma_1}$$

Example) Hg on SiO<sub>2</sub>

$$\gamma_{\text{Hg}} = \gamma_{\text{Hg}}^d + \gamma_{\text{Hg}}^m + \dots$$

$$\gamma_{\text{SiO}_2} = \gamma_{\text{SiO}_2}^d + \gamma_{\text{SiO}_2}^c + \gamma_{\text{SiO}_2}^i$$

No interaction

$$\cos \theta = -1 + 2\sqrt{78} \frac{\sqrt{200}}{484} = -0.48$$

$$\theta \cong 119^\circ$$