

12. Methods of surface tension measurements

There are several methods of surface tension measurements:

- 1. Capillary rise method**
- 2. Stallagmometer method – drop weight method**
- 3. Wilhelmy plate or ring method**
- 4. Maximum bulk pressure method.**
- 5. Methods analyzing shape of the hanging liquid drop or gas bubble.**
- 6. Dynamic methods.**

1. Capillary rise method

This is the oldest method used for surface tension determination.

A consequence of the surface tension appearance at the liquid/gas interface is moving up of the liquid into a thin tube, that is capillary, which is usually made of glass.

This phenomenon was applied for determination of the liquid surface tension.

For this purpose, a thin circular capillary is dipped into the tested liquid.

If the interaction forces of the liquid with the capillary walls (adhesion) are stronger than those between the liquid molecules (cohesion), the liquid wets the walls and rises in the capillary to a defined level and the meniscus is hemispherically concave.

In the opposite situation the forces cause decrease of the liquid level in the capillary below that in the chamber and the meniscus is semispherically convex. Both cases are illustrated in Fig. 11.1

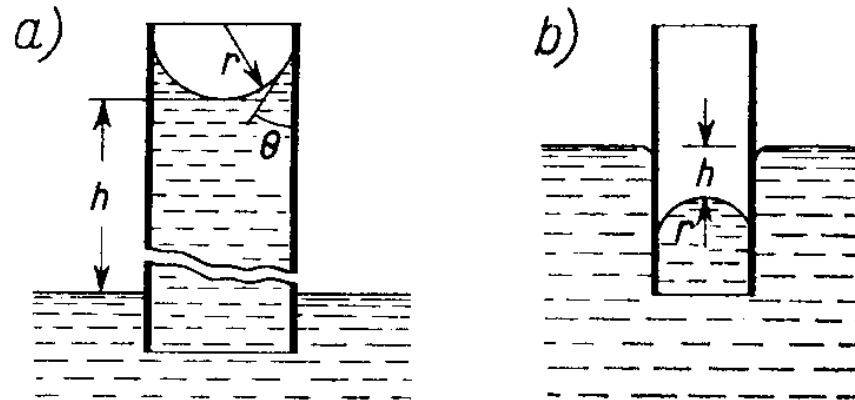


Fig. 12.1. Schematic representation of the capillary rise method.

If the cross-section area of the capillary is circular and its radius is sufficiently small, then the meniscus is semispherical. Along the perimeter of the meniscus there acts a force due to the surface tension presence.

$$f_1 = 2 \pi r \gamma \cos \theta \quad (1)$$

Where: r – the capillary radius, γ – the liquid surface tension, θ – the wetting contact angle.

The force f_1 in Eq.(1) is equilibrated by the mass of the liquid raised in the capillary to the height h , that is the gravity force f_2 . In the case of non-wetting liquid – it is lowered to a distance $-h$.

$$f_2 = \pi r^2 h d g \quad (2)$$

where: d – the liquid density (g/cm³) (actually the difference between the liquid and the gas densities), g – the acceleration of gravity.

In equilibrium (the liquid does not moves in the capillary) $f_1 = f_2$, and hence

$$2\pi r \gamma \cos \theta = \pi r^2 h d g \quad (3)$$

or

$$\gamma = \frac{r h d g}{2 \cos \theta} \quad (4)$$

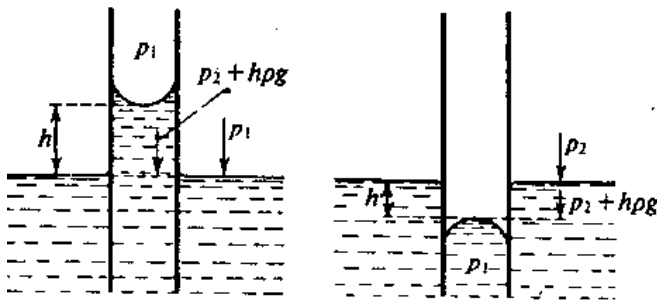
If the liquid completely wets the capillary walls the contact angle $\theta = 0^\circ$, and $\cos \theta = 1$. In such a case the surface tension can be determined from Eq. (5).

$$\gamma = \frac{r h d g}{2} \quad (5)$$

If the liquid does not wet the walls (e.g. mercury in a glass capillary), then it can be assumed that $\theta = 180^\circ$, and $\cos \theta = -1$. As the meniscus is lowered by the distance $-h$, Eq. (5) gives a correct result.

Eq. (5) can be also derived using the Young-Laplace equation, $\Delta P = \frac{2\gamma}{r}$, from which it results that there exists the pressure difference across a curved surface, which is called capillary pressure and this is illustrated in Fig. 12.2.

On the concave side of the meniscus the pressure is p_1 . The mechanical equilibrium is attained when the pressure values are the same in the capillary and over the flat surface. In the case of wetting liquid, the pressure in the capillary is lower than outside it, ($p_2 < p_1$). Therefore the meniscus is shifted to a height h when the pressure difference $\Delta p = p_2 - p_1$ is balanced by the hydrostatic pressure caused by the liquid raised in the capillary.



$$\Delta P = P_1 - P_2 = \Delta d g h \quad (6)$$

Fig. 12.2. The balanced pressures on both sides of the meniscus.

$$\frac{2\gamma}{r} = \Delta \rho g h \quad (7)$$

$$\gamma = \frac{r h \Delta \rho g}{2} \quad (8)$$

Similar considerations can be made for the case of convex meniscus (Fig. 12.2).

2. Drop volume method – stalagmometric method

The **stalagmometric method** is one of the most common methods used for the surface tension determination.

For this purpose the several drops of the liquid leaked out of the glass capillary of the **stalagmometer** are weighed.

If the weight of each drop of the liquid is known, we can also count the number of drops which leaked out to determine the surface tension.

The drops are formed slowly at the tip of the glass capillary placed in a vertical direction.

The pendant drop at the tip starts to detach when its weight (volume) reaches the magnitude balancing the surface tension of the liquid.

The weight (volume) is dependent on the characteristics of the liquid.

The stalagmometric method

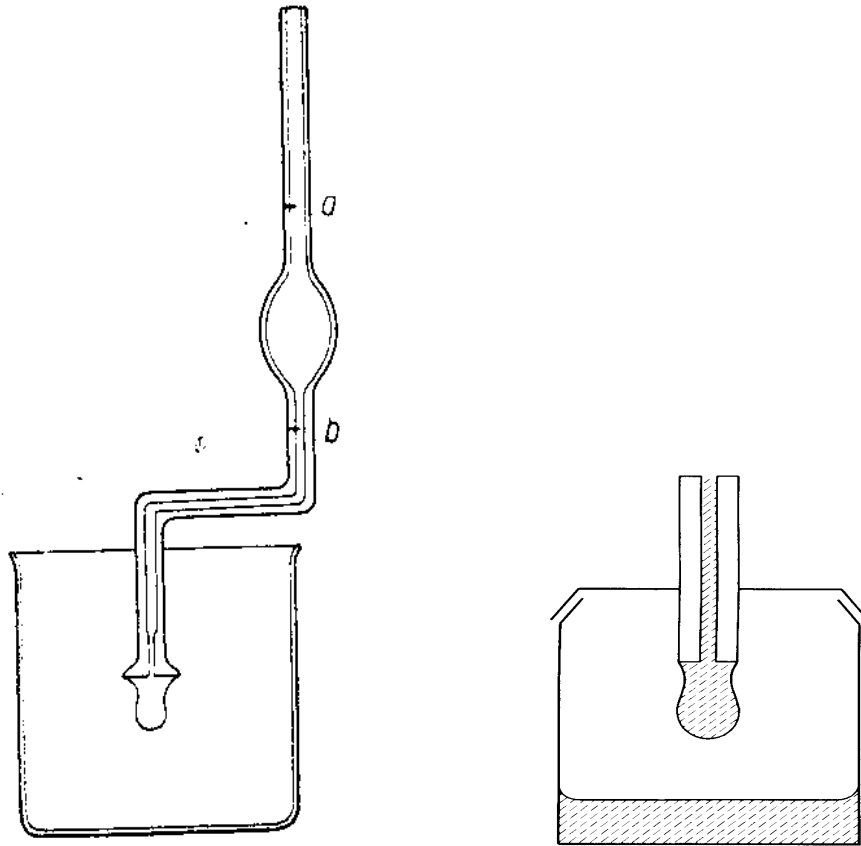


Fig. 12.2. Stalagmometer and the stalagmometer tip.

This method was first time described by Tate in 1864 who formed an equation, which is now called the Tate's law.

$$W = 2\pi r\gamma \quad (9)$$

Where: W is the drop weight, r is the capillary radius, and γ is the surface tension of the liquid.

The drop starts to fall down when its weight g is equal to the circumference ($2\pi r$) multiplied by the surface tension γ .

In the case of a liquid which wets the stalagmometer's tip the r value is that of the outer radius of the capillary and if the liquid does not wet – the r value is that of the inner radius of the capillary (Fig. 12.3).



Fig. 12.3. The drops wetting area corresponding to the outer and inner radii of the stalagmometer's tip.

In fact, the weight of the falling drop W' is lower than W expressed in Eq.(9). This is a result of drop formation, as shown in Fig.12.4.

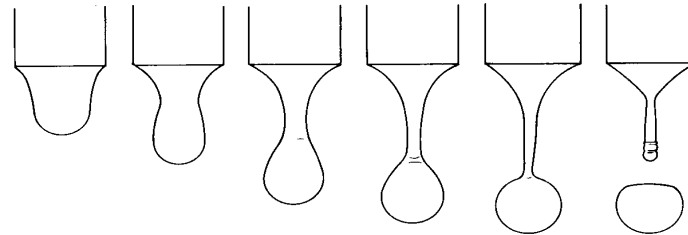


Fig. 12.4. Subsequent steps of the detaching drop

Up to 40% of the drop volume may be left on the stalagmometer tip. Therefore a correction f has to be introduced to the original Tate's equation.

$$W' = 2\pi r \gamma f \quad (10)$$

Where: f expresses the ratio of W'/W .

Harkins and Brown found that the factor f is a function of the stalagmometer tip radius, volume of the drop v , and a constant, which is characteristic of a given stalagmometer, $f = f(r, a, v)$

$$f = f\left(\frac{r}{a}\right) = f\left(\frac{r}{v^{1/3}}\right) \quad (11)$$

The f values for different tip radii were determined experimentally using water and benzene, whose surface tensions were determined by the capillary rise method. They are shown in Table 1.

Tabeli 1. Values of the factor f

$r/v^{1/3}$	f	$r/v^{1/3}$	f	$r/v^{1/3}$	f
0.00	(1.000)	0.70	0.6093	1.15	0.6407
0.30	0.7256	0.75	0.6032	1.20	0.6535
0.35	0.7011	0.80	0.6000	1.25	0.6520
0.40	0.6828	0.85	0.5992	1.30	0.6400
0.45	0.6669	0.90	0.5998	1.35	0.6230
0.50	0.6515	0.95	0.6034	1.40	0.6030
0.55	0.6362	1.00	0.6098	1.45	0.5830
0.60	0.6250	1.05	0.6179	1.50	0.5670
0.65	0.6171	1.10	0.6280	1.55	0.5510

It appeared that the factor f changes the least if:

$$0.6 < r / v^{1/3} < 1.2$$

In practice, after having determined the mean weight m of the liquid drop calculated from several drops weighed, one can calculate its volume at the measurement temperature if the liquid density is known, and then the value of $r/v^{1/3}$. Next the f value can be found in the table. Finally, the surface tension can be calculated from Eq. (10) where $W' = m g$.

$$\gamma = \frac{m g}{2\pi r f} \quad (12)$$

The f value depends also on the kind of liquid tested.

Therefore the relative measurements (in comparison to another liquid of known surface tension) can not be applied here, that is, γ can not be calculated from the ratio of the weights of two drops of two liquids and known surface tension of one of them.

However, such measurement can be done with 0.1 % accuracy if the shape of the stalagmometer tip is like that shown in figure 12.5.

$$\text{Then: } \frac{\gamma_1}{\gamma_2} = \left(\frac{m_1}{m_2} \right)^{2/3} \left(\frac{d_1}{d_2} \right)^{1/3} \quad (13)$$

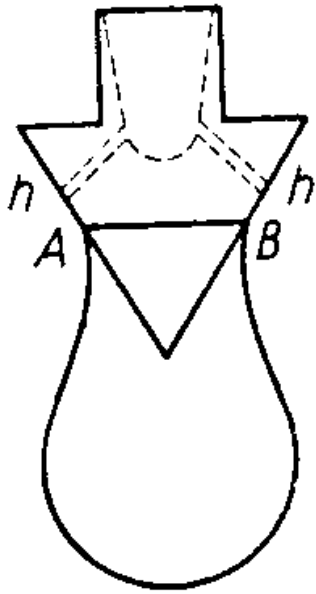


Fig. 12.5. Shape of the stalagmometer tip for relative surface tension measurements.

$$\text{Then: } \frac{\gamma_1}{\gamma_2} = \left(\frac{m_1}{m_2} \right)^{2/3} \left(\frac{d_1}{d_2} \right)^{1/3} \quad (13)$$

Having known the drop volume the surface tension can be calculated from Eq. (14).

$$\gamma = \frac{m g}{2 \pi r f} = \frac{m g}{k} = \frac{v d g}{k} \quad (14)$$

$$\gamma = \frac{V d g}{n k} \quad (15)$$

3. Wilhelmy plate or ring method

Wilhelmy plate method

This method was elaborated by Ludwig Wilhelmy. In this method a thin plate (often made of platinum or glass) is used to measure equilibrium surface or interfacial tension at air-liquid or liquid-liquid interfaces.

The plate is oriented perpendicularly to the interface and the force exerted on it is measured. The principle of method is illustrated in Fig. 12.6.

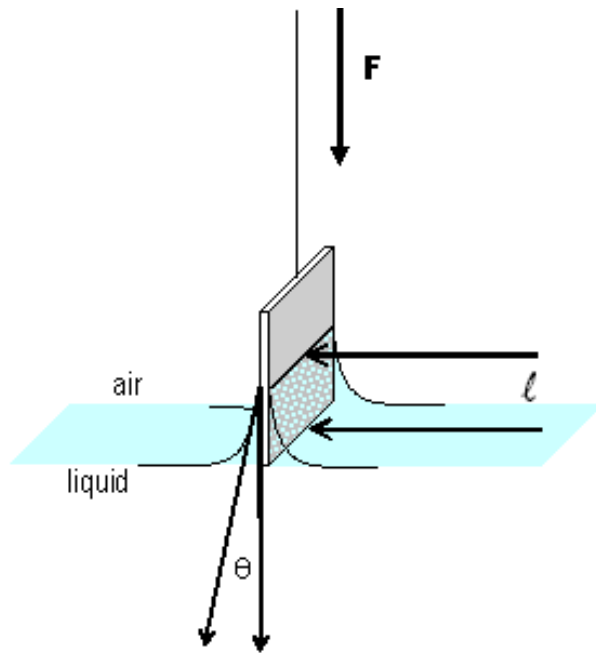


Fig. 12.6. Illustration of Wilhelmy plate method.

(http://en.wikipedia.org/wiki/Wilhelmy_plate)

The plate should be cleaned thoroughly (in the case of platinum – in a burner flame) and it is attached to a scale or balance by means of a thin metal wire.

The plate is moved towards the surface until the meniscus connects with it.

The force acting on the plate due to its wetting is measured by a **tensiometer** or **microbalance**.

To determine the surface tension γ the Wilhelmy equation is applied.

If the plate has a width l and its weight is W_{plate} , then the force F needed to detach it from the liquid surface equals:

$$F = W_{\text{total}} = W_{\text{plate}} + 2 l \gamma \cos\theta \quad (16)$$

Multiplying by 2 is needed because the surface tension acts on both sides of the plate, whose thickness is neglected. If the liquid wets completely the plate, then $\cos\theta = 1$ and the surface tension is expressed by Eq. (17).

$$\gamma = \frac{W_{\text{tot.}} - W_{\text{plate}}}{2 \cdot l} \quad (17)$$

The accuracy of this method reaches 0.1%, for the liquids wetting the plate completely.

The ring method – the tensiometric method (Du Noüy Ring Tensiometer)

Instead of a plate a platinum ring can be used, which is submerged in the liquid. As the ring is pulled out of the liquid, the force required to detach it from the liquid surface is precisely measured. This force is related to the liquid surface tension. The platinum ring should be very clean without blemishes or scratches because they can greatly alter the accuracy of the results. Usually the correction for buoyancy must be introduced.

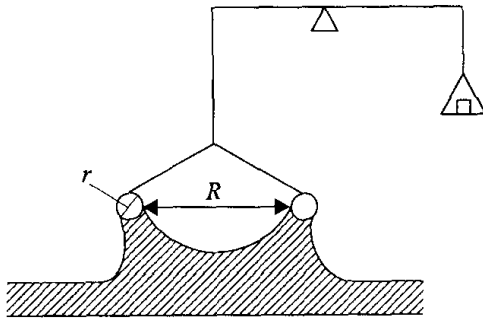


Fig.12.7. Scheme of the tensiometric method for liquid surface tension determination.

The total force needed to detach the ring W_{tot} equals the ring weight W_r and the surface tension multiplied by 2 because it acts on the two circumferences of the ring (inside and outside ones).

$$W_{\text{tot}} = W_r + 4\pi R \gamma = W_r + 2l \gamma \quad (18)$$

Where: R – the ring radius. It is assumed here that the inner and outer radii of the ring are equal because the wire the ring is made of is very thin.

The γ value determined from Eq.(3) can be charged with an error up to 25%, therefore correction has to be introduced. Harkins and Jordan determined experimentally the correction connected with the ring radius R , the ring wire radius r , volume of the liquid V raised by the ring during its detachment, and the ring height above the liquid surface.

Therefore the correction factor f is a function of these parameters:

$$f\left(\frac{R^3}{V}, \frac{R}{r}\right)$$

There are tables where the f values are listed for given values of these parameters. This allows exact determination of the liquid surface tension and the interfacial liquid/liquid tension as well.

Fig. 12.8 shows a modern tensiometers, type K6 and K9 Krüss, and Fig. 12. 9 the tehsiometer of KSV, type 700.



Fig. 12.8. type K6



Krüss. type K9



Fig. 12. 9. KSV. type 700

Tabele 2. Surface tension of water at different temperatures.

Temperature. °C	γ_w , mN m⁻¹	Temperature. °C	γ_w ,mN m⁻¹
10	74.22	21	72.59
11	74.07	22	72.44
12	73.93	23	72.28
13	73.78	24	72.13
14	73.64	25	71.97
15	73.49	26	71.82
16	73.34	27	71.66
17	73.19	28	71.50
18	73.05	29	71.35
19	72.90	30	71.18
20	72.75	40	69.56

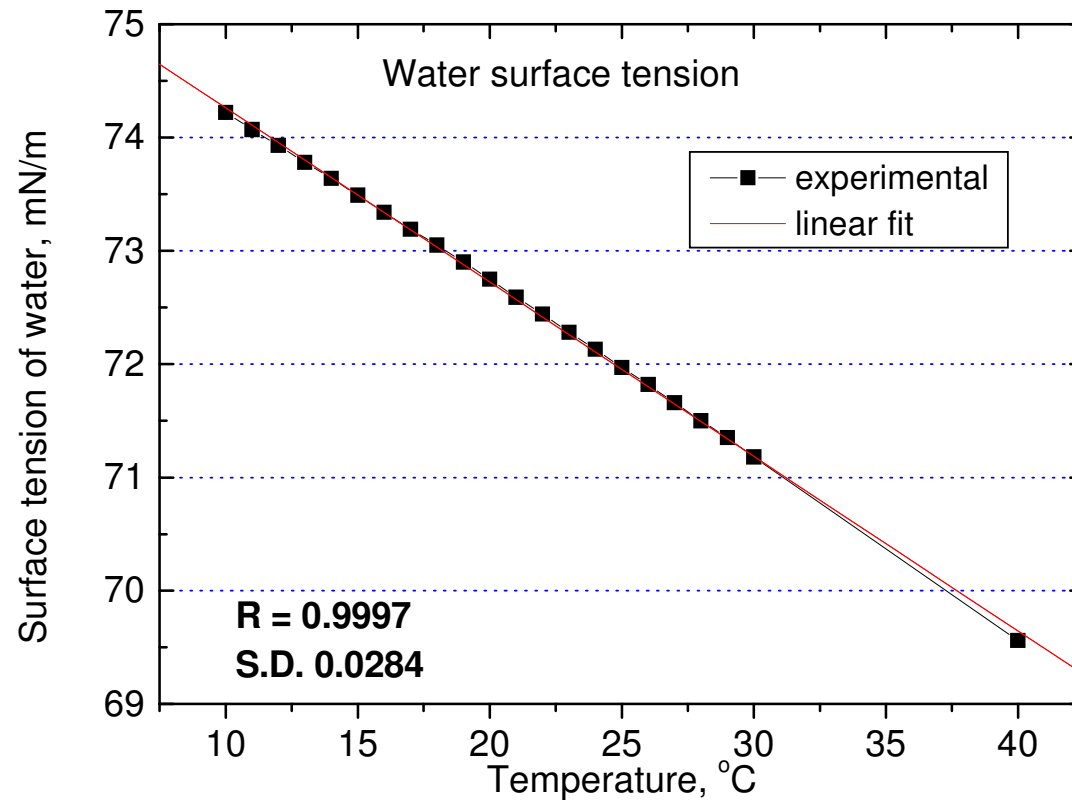


Fig. 12.10. Changes of water surface tension as a function of temperature.

4. Maximum bubble pressure method

This method is also called **the bubble pressure method**. In this method air gas bubble is blown at constant rate through a capillary which is submerged in the tested liquid.

The scheme of the apparatus proposed by Rebinder is shown in Fig. 12.11.

The pressure inside the gas bubble is increasing. Its shape from the very beginning is spherical but its radius is decreasing. This causes the pressure increase inside it and the pressure is maximal when the bubble has a hemispherical size. At this moment the bubble radius equals to the radius of the capillary, inner if the liquid wets the tip of the capillary and outer if it does not wet it.

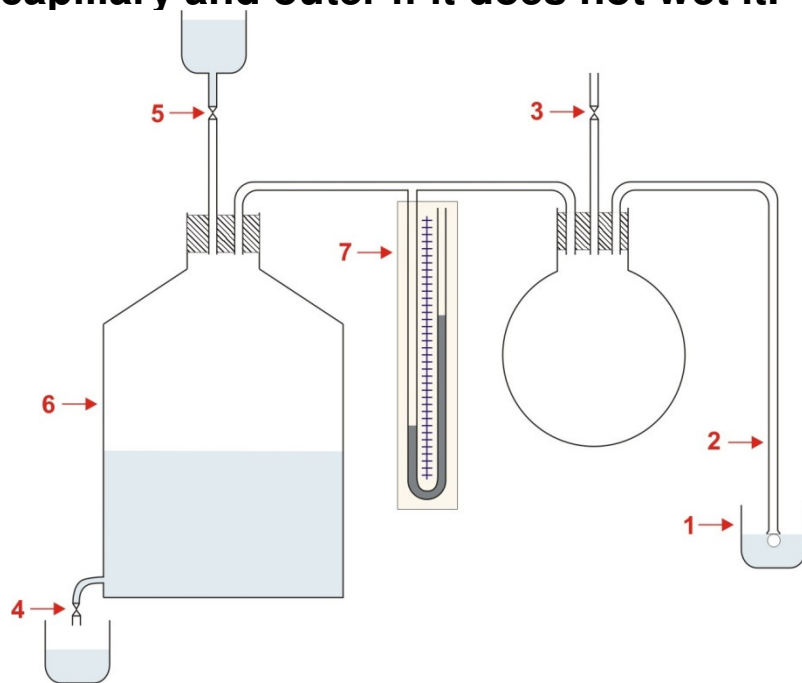


Fig. 12.11. Scheme of the apparatus for surface tension measurements by the bubble pressure method.

Fig. 12.12 shows the changes in the bubble radius with each step of the bubble formation.

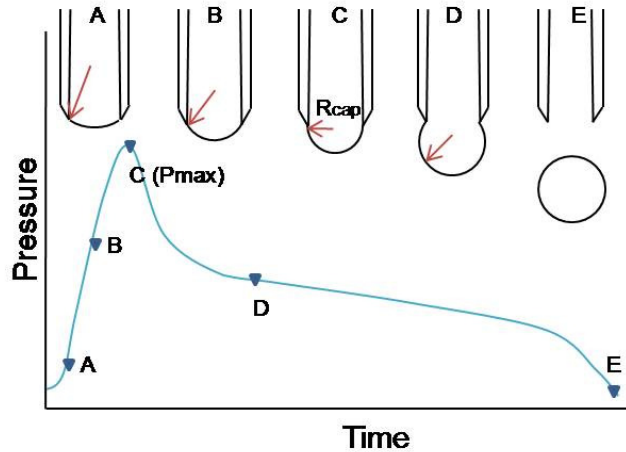


Fig. 12.12. The subsequent steps of the bubble formation and changes in the pressure inside the bubble.

http://en.wikipedia.org/wiki/Bubble_pressure_method.

Then the maximum pressure difference ΔP_{\max} is described by the Laplace equation.

$$\Delta P_{\max} = P_1 - P_2 = \frac{2\gamma}{r_{\text{capill}}} \quad (19)$$

If the capillary tip is dipped into the liquid to a depth h from the liquid surface, then the correction reducing ΔP_{\max} should be introduced. The correction is due to the additional hydrostatic pressure caused by the liquid layer of thickness h , the pressure that the detaching bubble has to overcome, $P_{\max} - P_h$.

For very accurate determination of the surface tension, other corrections are needed. They can be found in special tables. The accuracy of this method is about several tenth of percent and it is applied both for surface and interface tensions measurement.

5. Methods analyzing shape of the pendant or sessile liquid drop or gas bubble.

While small gas bubbles or liquid droplets are spherical, suitably large droplets are deformed, owing to the gravitation force action. The surface area of a sphere is proportional to its squared radius and the gravitational deformation depends on its volume which is proportional to the radius raised to the third power. If the effects of surface and gravitational forces are comparable, then the surface tension of the liquid (or interfacial liquid/liquid) can be calculated from the droplet or bubble shape.

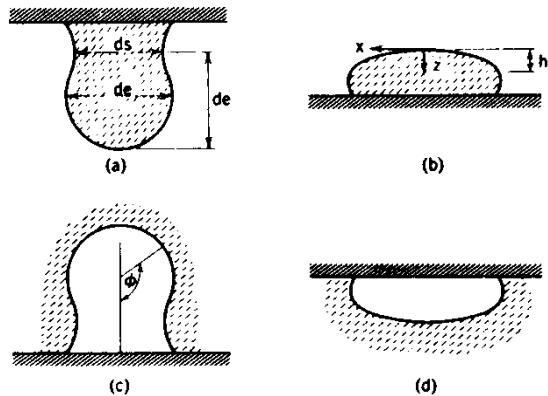


Fig. 12.13. Shapes of droplet: pendant (a) and sessile (b), and gas bubbles: sessile (c) and trapped (d).

In the case of pendant drop, the S value should be determined, which is expressed as (see Fig. 12.13):

Where d_e is the drop (or the bubble) diameter at its maximum width, d_s is the width at the distance d_e from the drop (bubble) bottom.

$$S = \frac{d_s}{d_e} \quad (20)$$

The surface tension can be calculated from equation (21):

$$\gamma = \frac{\Delta \rho g d_e^2}{H} \quad (21)$$

Where: H is a value dependent on S . The $1/H$ values are listed in special tables.

In the case of sessile drop or sessile bubble, the liquid surface tension can be calculated from Eq.(22) and to calculate it h and r_{max} have to be measured (see Fig. 12.13).

$$\gamma = \frac{\Delta \rho g h^2}{2} \quad (22)$$

In modern apparatus a computer program analyses the droplet or bubble shapes and calculates the surface tension of the liquid.

6. Dynamic methods

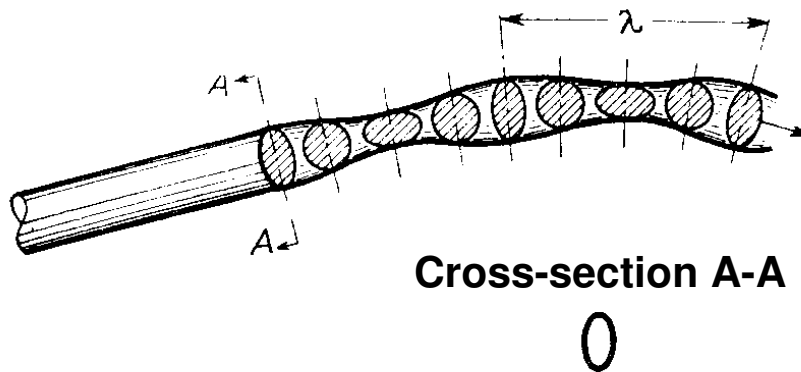
One of these methods is based on the analysis of the shape of an oscillating liquid jet. The jet flows out from an elliptic orifice and therefore it oscillates as shown in Fig.12.14. Mathematical analysis of such a jet was given for the first time by Lord Rayleigh in 1879, who derived Eq. (23).

$$t = k \left(\frac{d r^3}{\gamma} \right)^{1/2} \quad (23)$$

or

$$\gamma = \frac{k^2 d}{\pi^2 r} \left(\frac{v}{\lambda} \right)^2 \quad (24)$$

Where: t – the oscillation period time, λ – the wave length, r – the radius of the jet at its spherical place, v – the jet flow rate.



This method is rather rarely used nowadays.

Fig. 12.14. Oscillations of the jet flowing out from an elliptic orifice.

Table 3. Surface tension of water determined using different methods.

Temperature, °C	γ, mN/m	Method
20	72.78	capillary rise
20	72.91	max.bubble pressure
20	72.73	capillary rise
20	72.70	capillary rise
25	71.76	stalagmometric (drop weight)
25	71.89	Wilhelmy plate
25	72.00	pendant drop

Table 4. Surface tension of different liquids at 20 °C

Liquid/air	γ, mN m⁻¹
benzene	28.1–29.03 (28.88)
ether	16.96
ethanol	22.52
n-heptane	20.40
mercury	476.0
n-pentane	16.0

13. 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**'.

If the liquid is water and it forms a contact angle larger than 90° , such solid surface is customarily called the '**hydrophobic surface**', and if the contact angle is smaller than 90° , 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 θ .

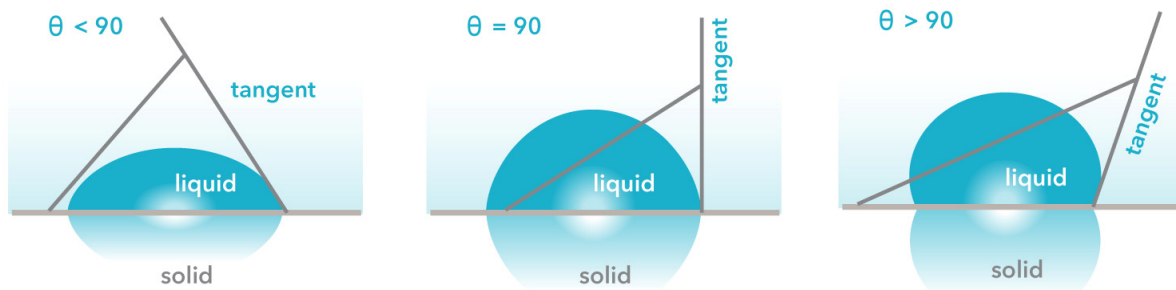
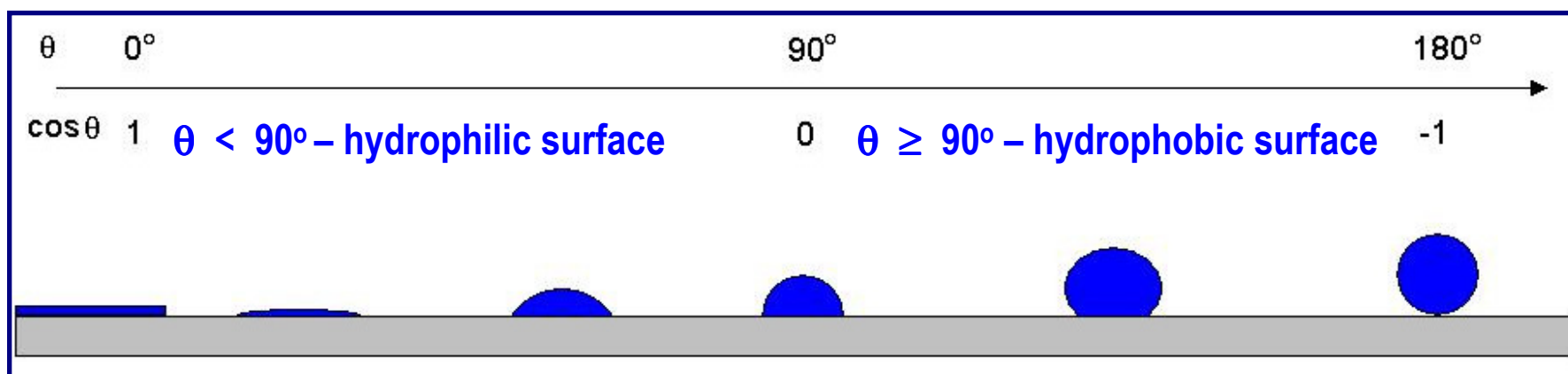


Fig. 13.1. Scheme of contact angles on the hydrophobic and hydrophilic surfaces
<http://www.attension.com/?id=1092&cid=>

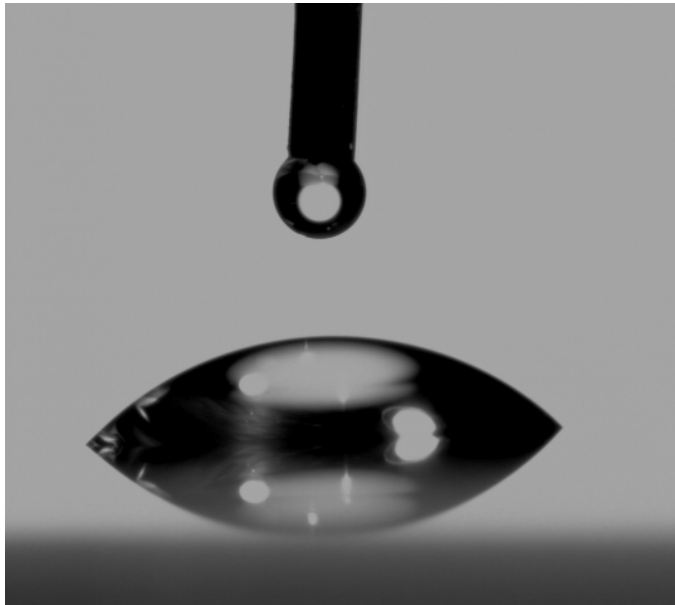


Fig. 13.2. Photographs of a water droplet on the hydrophilic and hydrophobic surfaces

[http://en.wikipedia.org/wiki/
Contact_angle#Typical_contact_angles](http://en.wikipedia.org/wiki/Contact_angle#Typical_contact_angles)

[http://www.google.pl/imgres?imgurl=http://
dailyheadlines.uark.edu/ images/water
contact_angle.jpg&imgrefurl= http://
dailyheadlines.uark.edu/](http://www.google.pl/imgres?imgurl=http://dailyheadlines.uark.edu/images/water_contact_angle.jpg&imgrefurl=http://dailyheadlines.uark.edu/)

The forces acting in the line of three phase contact were for the first time described in words by Thomas Young in 1850. The mathematical expression of this description is now known as the '**Young equation**'. It relates surface free energy of solid being in equilibrium with the liquid vapor γ_{sv} , liquid (surface tension) γ_{lv} , interfacial solid/liquid free energy γ_{sl} , and the contact angle θ .

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (1)$$

This is illustrated in Fig. 13.3.

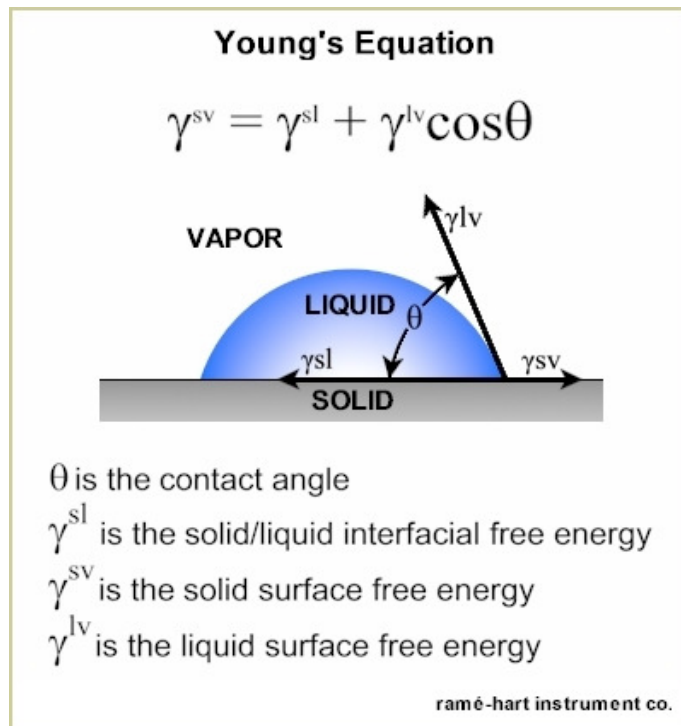


Fig. 13.3.

<http://www.google.pl/imgres?imgurl=http://www.ramehart.com/images>

An apparatus for contact angle measurements is presented in Fig. 13.4.

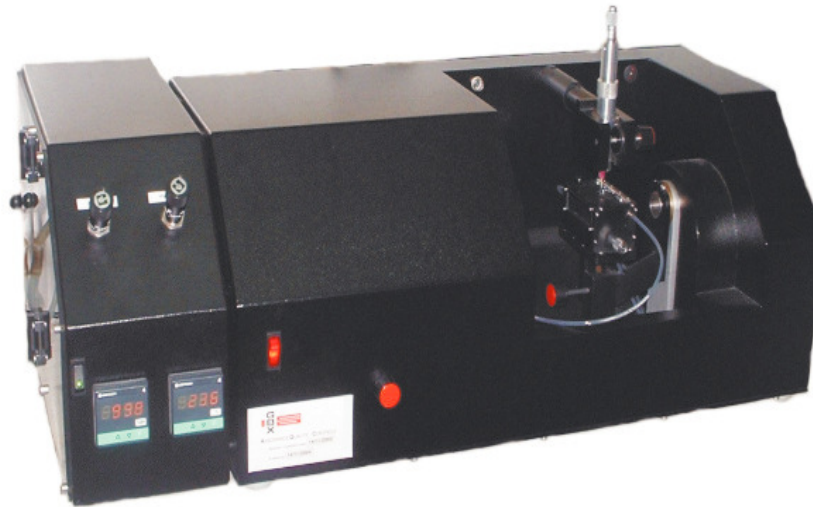


Fig. 13.4. Contact Angle Meter, Digidrop, GBX, France

Spreading wetting

Quantitative measure of the spreading wetting is the **work of spreading W_s** , also called the '**spreading coefficient S_s** '.

$$W_s = S_s = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \quad (2)$$

Wetting spreading is illustrated in Fig. 13.5.

Scheme of wetting spreading shows Fig. 13.5.

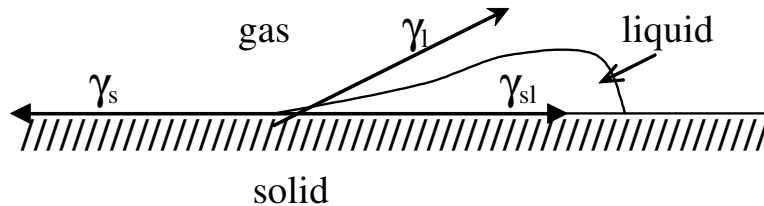


Fig.13.5. Illustration of the wetting spreading process.

Its value can be positive or negative, depending on the surface free energy of the solid and the liquid used for the wetting.

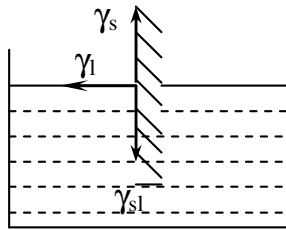
If the work of spreading is negative, the liquid drop will not spread but will remain on the surface and form a definite wetting contact angle.

$$W_s > 0 \quad \text{if} \quad \gamma_s > (\gamma_{sl} + \gamma_l)$$

$$W_s < 0 \quad \text{if} \quad \gamma_s < (\gamma_{sl} + \gamma_l)$$

Immersional wetting

Another way of wetting a solid surface is 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_l .



The work of immersion equals:

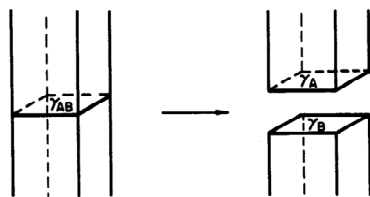
$$W_I = \gamma_s - \gamma_{sl} \quad (3)$$

Fig.13.6. Scheme of the immersional wetting process.

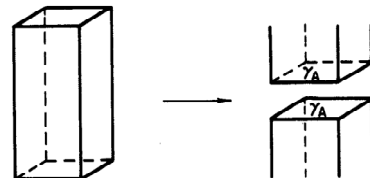
Adhesional wetting

In this a wetting process two unit areas are contacted in a reversible way thus forming the interface of solid/liquid or liquid/liquid.

The value of work of adhesion in the solid/ liquid system equals:



(a)



(b)

$$W_A = \gamma_s + \gamma_l - \gamma_{sl} \quad (4)$$

Fig. 13.7. Illustration of the adhesion wetting process between phases A and B

(after A.W. Adamson and A.P. Gast, *Physical Chemistry of Surfaces*).

If the process deals with the same phase (e.g. a column of liquid) this work is equal to the work of cohesion W_C , and Eq.(4) reduces to Eq. (5).

$$W_C = 2\gamma_l \quad (5)$$

Comparison of the work of wetting in particular processes:

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

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

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

From this comparison it can be seen that:

$$W_S < W_l < W_A$$

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

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

$$W_S = W_A - W_C \quad (6)$$

However, if the solid surface behind the liquid droplet is bare, the contact angle is termed as the '**advancing contact angle**' θ_a , which is larger than the equilibrium one. Moreover, practically in all systems when the three-phase line has retreated, for example by sucking a volume of the liquid drop, the contact angle at this new equilibrium is smaller, and it is termed the '**receding contact angle**' θ_r

$$\theta_a > \theta_e > \theta_r$$

In case the liquid vapour has adsorbed on the solid surface behind the droplet (the solid remains in equilibrium with the liquid vapour), Young equation (Eq. (1)) can be written as follows:

$$\gamma_{sv} = (\gamma_s + \pi) = \gamma_l \cos \theta_e + \gamma_{sl} \quad (7)$$

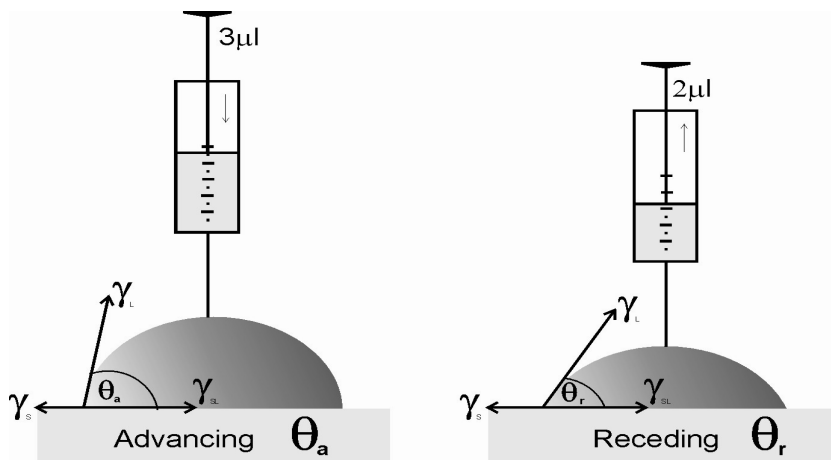


Fig.13.8. Illustration of advancing and receding contact angle measurements.

Wetting of a solid surface by the adsorption process

During the adsorption process the solid surface free energy is changed. The change depends on the nature of adsorbing molecules. This change is termed the **surface pressure** (or **film pressure**), π .

In general, it may be negative or positive. The resulting **work of the adsorption** process may correspond to the work of spreading, immersionsal or even **adhesional** wetting. The shape of adsorption isotherm depends on whether the liquid wets the surface completely or only partially, i.e. whether the liquid forms a definite contact angle or not.

The film pressure, π equals to the difference between the surface free energy of bare solid γ_s , and the solid surface free energy with the adsorbed film γ_{sv} . The adsorbed amount is determined by the surface excess Γ .

From Eq.(1) one would expect that on a flat solid surface, insoluble in the liquid, being in equilibrium with the liquid vapour, only one contact angle value will describe the solid/liquid drop/gas (vapour) system. Such contact angle is termed the '**equilibrium contact angle**' θ_e , or the '**Young's contact angle**'.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

(1)

The difference between the advancing and receding contact angles is named the 'contact angle hysteresis', H .

$$H = \theta_a - \theta_r \quad (8)$$

Contact angle and the work of adhesion

In the Young equation:

contact angle θ

liquid surface tension γ_l

solid surface free energy γ_s

interfacial solid/liquid free energy γ_{sl}

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

- measurable

- unknown

However, the work of adhesion can be determined experimentally.

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

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

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

(9)

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 formd given contact angle.

$$W_S = W_A - W_C = W_A - 2\gamma_l = \gamma_l (1 + \cos\theta) - 2\gamma_l$$

$$W_S = \gamma_l (\cos\theta - 1)$$

(10)

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. **There have to be considered the intermolecular forces, which are: dispersion, dipole-dipole, π -electrons, hydrogen bonding, or generally Lewis acid-base, i.e. electron-donor and electron-acceptor.**

In 1960 F.M. Fowkes taking into account that between paraffin hydrocarbon molecules only dispersion forces interact, assumed that the same is true for n-alkane/water molecules interactions. Applying the Berthelot's rule $(u_{11}u_{22})^{1/2} = u_{12}$ for the interfacial dispersion interactions between two phases, Fowkes expressed the work of adhesion for hydrocarbon/water as:

$$W_A = 2(\gamma_H^d \gamma_W^d)^{1/2} \quad (11)$$

Because:

$$W_A = \gamma_H + \gamma_W - \gamma_{HW}$$

$$\gamma_{HW} = \gamma_H + \gamma_W - 2(\gamma_H^d \gamma_W^d)^{1/2} \quad (12)$$

Where: H - hydrocarbon (n-alkane); W – water

- ◆ For n-alkanes: $\gamma_H = \gamma_H^d$
- ◆ The interfacial tension of n-alkane/water γ_{HW} can be measured.
- ◆ 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

$$\gamma_W^n = 51 \text{ mN/m}$$

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

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

Fowkes (and later others) considered that surface tension (surface free energy) of a liquid or solid can be expressed as a sum of several components, of which not necessarily all are present at a surface.

$$\gamma = \gamma^d + \gamma^p + \gamma^i + \gamma^h + \gamma^\pi + \gamma^{da} + \gamma^e \quad (13)$$

Where the superscripts denote the interactions: *d* – the dispersion interaction, *p* – the dipole-dipole, *i* – the dipole-induce dipole, *h* – the hydrogen bond, *π* – the electron π, *da* – donor-acceptor, *e* – electrostatic.

As there is no means to determine all kinds of the interactions Eq. (13) was reduced to Eq.(14).

$$\gamma = \gamma^d + \gamma^p \quad (14)$$

Where superscript *p* denotes one or more polar interactions if present, e.g. *h*, *i*, *ad*, *π*.

$$\gamma^d = - \frac{nN_i^2 \alpha_i^2 I_i}{8r_{11}^2} \quad (15)$$

Where: N_i – the volume unit (it may be a molecule), e.g. in the case of saturated hydrocarbons $-\text{CH}_2$ group is the volume unit, and for aromatic ones, it is $-\text{CH}$ group, α – the unit's (molecule's) polarizability, I – the ionization energy.

Fowkes derived the relationship describing the interfacial energy γ_{12} in the system where only the dispersion interactions are present:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1\gamma_2)^{1/2} \quad (16)$$

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

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

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

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

γ_i^- – the electron-donor
 γ_i^+ – the electron-acceptor
 }
 – mostly hydrogen bonding

Note that the polar interactions are expressed by the geometric mean.

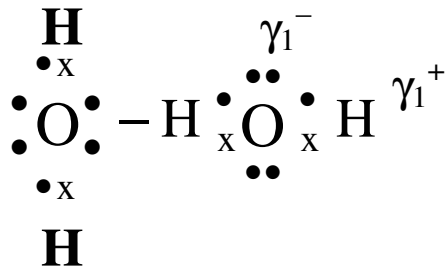


Fig. 13.9. A scheme of hydrogen bonding between two water molecules. The ‘free’ the electron-donor γ_1^- and electron-acceptor γ_1^+ interactions are also shown.

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

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

And the work of adhesion reads:

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

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.

Van Oss et al. assumed for **water** at room temperature **equal electron-donor and electron-acceptor interactions**.

Because: $\gamma_w^{AB} = 2(\gamma_w^- \gamma_w^+)^{1/2} = 51 \text{ mN/m}$,

Hence: $\gamma_1^- = \gamma_1^+ = 25.5 \text{ mN/m}$.

Basing on this value the relative values for other liquids have been determined.

Table 1. Surface tension and its components, in mN/m, of some liquids, usually used as the probe liquids for solid surface free energy determination.

Liquid	γ_l^{TOT}	γ_l^{LW}	γ_l^+	γ_l^-
Diiodomethane	50.8	50.8	0 (0.4-0.7)	0
α -Bromonaphthalene	44.4	43.6	0.4	0.4
Decane	23.8	23.8	0	0
Water	72.8	21.8	25.5	25.5
Formamide	58.0	39.0	2.28	39.0
Ethylene glycol	48.0	29.0	1.92	47.0
Glycerol	64.0	34.0	3.92	57.4
Dimethylsulfoxide	44	44	0	30

$\gamma_i^{LW} \neq 0; \quad \gamma_i^- = 0; \quad \gamma_i^+ = 0$ - nonpolar (apolar) surface

$\gamma_i^{LW} \neq 0; \quad \gamma_i^- \neq 0; \quad \text{or} \quad \gamma_i^+ \neq 0$ - monopolar surface

$\gamma_i^{LW} \neq 0; \quad \gamma_i^- \neq 0; \quad \gamma_i^+ \neq 0$ - bipolar surface

The electron donor γ_i^- and electron acceptor γ_i^+ interactions are complementary.

It means that electron acceptor γ_i^+ cannot interact with electron acceptor γ_i^+ interactions, as well as electron donor γ_i^- cannot interact with electron donor γ_i^- interactions.

Superhydrophobic surfaces

If one takes water contact angle as a measure of surface hydrophobicity, then 'superhydrophobic' means that the hydrophobic surface becomes abnormally more hydrophobic.

For example, on a hydrophobic surface contact angle of water is, say, $100\text{-}120^\circ$, so on the superhydrophobic surface the contact angle increases up to 150° and more.

This is possible if micro- or nano- size protrusions (roughness) are produced on the surface.

Therefore a water droplet rests on it like on a brash, and in fact, the droplet contact with the surface is much smaller than on the same flat surface.

The air trapped between the wax roughness on the leaf surface minimizes the contact area of the water droplet. There are several naturally superhydrophobic surfaces, and the most known is that of lotus leaf on which θ equals up to 170° .

A)



B)

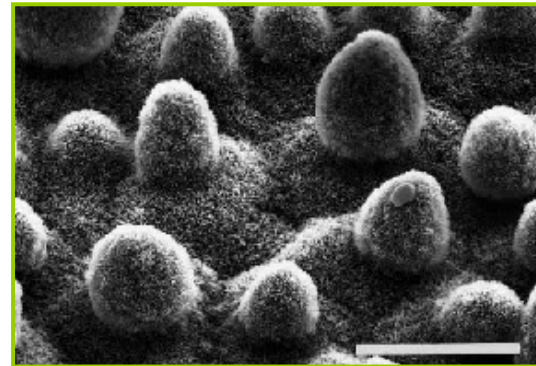


Fig. 13.10.

A) A water droplet on a lotus leaf.

(From: <http://www.botanik.unibonn.de/system/lotus/en/prinzip.html.html>).

B) SEM-image of lotus leaf. The micro structural epidermal cells are covered with nanoscopic wax crystals.

Bar: 20 μm .

(from W. Barthlott and C. Neinhuis, *Planta* 202, 1(1997).

A few examples of solid surface free energy are shown in Table 5.

Table 5. Surface free energy of some solids.

Solid	γ_s mJ/m²	Solid	γ_s mJ/m²
Teflon (PTFE)	18-25	halite (NaCl)	230
parafin wax	25	fluorite (CaF₂)	450
graphit	110	Gold	1800
sulphur	124	diamond	5600