# Surface Tension and its measurements

# Physical origin of surface tension/surface energy

Molecules at the surface: they are missing half their attractive interactions. Unbalanced forces for the molecules at the surface lead to additional energy. The additional free energy at the surface is known as surface energy. This is the fundamental reason behind liquids adjusting their shapes to expose the smallest possible area. Liquid-air interfaces, surface tension results from the greater attraction of liquid molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). The net effect is an inward force at its surface that causes the liquid to behave as if its surface were covered with a stretched elastic membrane.





Thus, the surface comes under tension from the imbalanced forces, which is probably where the term "surface tension" came from. *Because of the relatively high attraction of water molecules to each other through a web of hydrogen bonds, water has a higher surface tension (72.8 millinewtons per meter at 20 °C) than most other liquids. Surface tension is an important factor in the phenomenon of capillarity.* 

#### Estimation of surface tension based on intermolecular forces



U is the cohesion energy per molecule inside the liquid

Energy shortfall for a molecule sitting at the surface  $\sim U/2$ 

a is the size of a molecule;  $a^2$  is the exposed area of a molecule

Surface tension is then of order  $\gamma \cong \frac{U}{2a^2}$ 

For van der Waals type interactions,  $U \cong kT$ 

#### Mechanical definition: In terms of force



This diagram illustrates the force 🛛 🗗

This diagram illustrates the force necessary to increase the surface area. This force is proportional to the surface tension

Surface tension  $\gamma$  of a liquid is the force per unit length. In the illustration on the above, the rectangular frame composed of three unmovable sides (black) that form a "U" shape, and a fourth movable side (blue) that can slide to the right. Surface tension will pull the blue bar to the left; the force *F* required to hold the immobile side is proportional to the length *L* of the movable side. Thus the ratio *F/L* depends only on the intrinsic properties of the liquid (composition, temperature, etc.), not on its geometry. For example, if the frame had a more complicated shape, the ratio *F/L*, with *L* the length of the movable side and *F* the force required to stop it from sliding, is found to be the same for all shapes. We therefore define the surface tension as:

$$\gamma = \frac{1}{2} \frac{F}{L}.$$

The reason for the 1/2 is that the film has two sides (two surfaces), each of which contributes equally to the force; so the force contributed by a single side is  $\gamma L = F/2$ .

## In terms of energy

Surface tension  $\gamma$  of a liquid is the ratio of the change in the energy of the liquid, and the change in the surface area of the liquid (that led to the change in energy). This can be easily related to the previous definition in terms of force: if *F* is the force required to stop the side from *starting* to slide, then this is also the force that would keep the side in the state of *sliding at a constant speed* (by Newton's Second Law). However, if the side is moving to the right (in the direction the force is applied), then the surface area of the stretched liquid is increasing while the applied force is doing work on the liquid. This means that increasing the surface area increases the energy of the film. The work done by the force *F* in moving the side by distance  $\Delta x$  is  $W = F\Delta x$ ; at the same time the total area of the film increases by  $\Delta A = 2L\Delta x$  (the factor of 2 is here because the liquid has two sides, two surfaces). Thus, multiplying both the numerator and the denominator of  $\gamma = 1/2F/L$  by  $\Delta x$ , we get



### Mechanical definition: as a capillary force

Surface tension ( $\gamma$ ) can also be viewed as a force per unit length (mN/m or N/m). Capillary action (sometimes capillarity, capillary motion, capillary effect, or wicking) is the ability of a liquid to flow in narrow spaces without the assistance of, or even in opposition to, external forces like gravity. The effect can be seen in the drawing up of liquids between the hairs of a paint brush, in a thin tube, in

porous materials such as paper and plaster, in some non-porous materials such as sand and liquefied carbon fiber, or in a biological cell. It occurs because of intermolecular forces between the liquid and surrounding solid surfaces. If the diameter of the tube is sufficiently small, then the combination of surface tension (which is caused by cohesion within the liquid) and adhesive forces between the liquid and container wall act to propel the liquid



#### Height of a meniscus

Water height in a capillary plotted against capillary diameter the height h of a liquid column is given by Jurin's law.

$$h = rac{2\gamma\cos heta}{
ho gr},$$

where  $\gamma$  is the liquid-air surface tension (force/unit length) and  $\theta$  is the contact angle(the contact angle is the angle, conventionally measured through the liquid, where a liquid–vapor interface meets a solid surface),  $\rho$  is the density of liquid (mass/volume), g is the local acceleration due to gravity (length/square of time), and r is the radius of tube. Thus the thinner the space in which the water can travel, the further up it goes.

Thus for a 2 m (6.6 ft) radius glass tube in lab conditions given above, the water would rise an unnoticeable 0.007 mm (0.00028 in). However, for a 2 cm (0.79 in) radius tube, the water would rise 0.7 mm (0.028 in), and for a 0.2 mm (0.0079 in) radius tube, the water would rise 70 mm (2.8 in).

# Surface energy of liquids and melts

# Existing experimental methods for determining the surface tension of liquids

# Capillary rise method

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.



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.

$$f_1 = 2\pi r \gamma \cos\theta \tag{1}$$

Where: r – the capillary radius,  $\gamma$  – the liquid surface tension,  $\theta$  – 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.

$$f_2 = \pi r^2 h dg$$
<sup>(2)</sup>

where: d – the liquid density (g/cm<sup>3</sup>) (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

$$2\pi r \gamma \cos \theta = \pi r^{2} h dg$$

$$\gamma = \frac{r h dg}{2 \cos \theta}$$
(3)
(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).

$$\gamma = \frac{r h d g}{2}$$
(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.

#### Wilhelmy plate or ring method

or

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.



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 $\gamma$ the Wilhelmy equation is applied.

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

$$F = W_{total} = W_{plate} + 2 I \gamma \cos \theta$$
(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).

$$\gamma = \frac{W_{\text{tot.}} - W_{\text{plate}}}{2 \cdot 1} \tag{17}$$

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

## Estimation of surface tension from related properties

#### **Parachor method**

Sugden proposed the following equation to calculate surface tension from the physical properties of the compound:

$$\gamma = \left[\frac{\phi(\rho_1 - \rho_{\nabla})}{M}\right]^4 \qquad -----3$$

Where  $\rho_l$  and  $\rho_v$  are the densities of the liquid and vapor, respectively, and M is the molecular weight.  $\varphi$  is known as parachor, which means comparative volume.

If we neglect the density of vapor in comparison with the density of the liquid, we have  $\varphi = v_1 * \gamma^{1/4}$  where  $v_1$  is the molar volume of the liquid.

A comparison of the parachors of different liquids is equivalent to the comparison of their molar volumes under the condition of equal surface tension.

 $\varphi$  is a weak function of temperature for a variety of liquids over wide ranges of temperature, and generally assumed to be a constant. Additive procedures exist for calculating  $\varphi$ .

Equation (3) suggests that surface tension is very sensitive to the value of parachor and the liquid density. The structural contributions for calculating  $\varphi$  are given in Table 1. The total value of  $\varphi$  for a compound is the summation of the values of the structural units.

# Example:

Calculate the surface energy of PS using Parachor method. Use table below



Density(g/cm <sup>3</sup> )	Parachor No			Atomic Mass		
0.91	С	H	Double bond	6-membered ring	С	Η
	4.8	17.1	23.2	6.1	12.01	1.007

# Solution:

The surface tension is given by:

$$\gamma = \left[\frac{\varphi(\rho_l)}{M}\right]^4$$

 $M=8\times1.007+8\times12.01=104.136 \text{ g/mol}$ 

$$\rho = 0.91 \text{ g/cm}^3$$
  
 $v_1 = \frac{M}{\rho} = 104.136 / 0.91 = 114.435$   
 $\varphi = (8 \times 17.1) + (8 \times 4.8) + (3 \times 23.2) + 6.1 = 250.9$ 

$$\gamma = \left[\frac{\phi}{v_l}\right]^4 = \left[\frac{250.9}{114.435}\right]^4 = 23.1 \text{ J/mol}$$

#### Effect of temperature on surface tension

The surface tension of most liquids decreases with increasing temperature. Since the forces of attraction between the molecules of a liquid decrease with increasing temperature, the surface tension decreases with increasing temperature.

One of the classical equations correlating the surface tension and temperature is the Eotvos-Ramsay-Shields equation:

$$\gamma(v_1)^{2/3} = K_e(T_C - T - 6)$$
 ------4

Where  $v_1$  is the molar volume of the liquid which can be represented by  $(\frac{M}{\rho_l})$ ,  $T_c$  is the critical temperature and  $K_e$  is a constant. For non-associated liquids, the value of  $K_e$  is 2.12, and for associated liquids, its value is less than this value.

### Example

Calculate critical temperature (T<sub>c</sub>) of Co<sub>2</sub> using Ramsay-Shield Equation if you know:

Temperature C <sup>o</sup>	Density (g/cm <sup>3</sup> )	SurfaceTension (Dyne/cm)
0	0.926	5.4
20	0.772	1.16

Solution:

$$\gamma(v_l)^{2/3} = K_e(T_C - T - 6)$$

### At 0 C°

 $M_{Co2} = 12 + (2 \times 16) = 44 \text{ g/mol}$   $0 \text{ C}^{\circ} = 273 \text{ K}$   $5.4(\frac{44}{0.927})^{2/3} = \text{K}_{e}(\text{T}_{c} - 273 - 6)$  $71.712 = \text{K}_{e}(\text{T}_{c} - 279) \qquad -----1$  At 20 C°

$$1.1(\frac{44}{0.772})^{2/3} = K_e(T_c - 293 - 6)$$
  
16.29 = K<sub>e</sub>(T<sub>c</sub> - 299) ------2

From (Eq. 1) and (Eq. 2) :

$$\frac{71.712}{16.28} = \frac{K_e(T_c - 279)}{K_e(T_c - 299)}$$
$$T_c =$$

According to the equation  $[\gamma(v_l)^{2/3} = K_e(T_c - T - 6)]$ , the surface tension will become zero at a temperature six degrees below the critical temperature, which has been observed experimentally.

Theoretically, the value of surface tension should become zero at the critical temperature, since at this temperature; the surface of separation between a liquid and its vapor disappears. However, it has been observed that the meniscus disappears a few degrees below the critical temperature for some liquids.

The Brock-Bird correlation relates surface tension to the critical properties of the liquid by the relationship,

$$\gamma = P_c^{2/3} T_c^{1/3} Q (1 - T_r)^{11/9}$$
------(5)

Where Q is given by:

$$Q = 5.55134 \times 10^{-8} \left[ 1 + \frac{(T_b/T_c)\ln(P_c/101325)}{1 - T_b/T_c} \right] - 1.295 \times 10^{-7}$$
 -----(6)

Where  $T_b$  is the normal boiling point of the liquid,  $P_c$  is the critical pressure and  $T_r$  is the reduced temperature.

The quantity  $\gamma P_c^{-1/3} T_c^{-1/3} k^{-1/3}$  (where k is Boltzmann's constant) is dimensionless. It was suggested by van der Waals that this group may be correlated with the quantity (1-T<sub>r</sub>). This method of estimation of surface tension is also known as corresponding states method.

The Brock-Bird method is not suitable for liquids which exhibit strong hydrogen bonding (such as alcohols and acids). Sastri and Rao (1995) have presented the following correlations for surface tension of such liquids.

For alcohols, they proposed:

$$\gamma = 1.282 \times 10^{-4} P_c^{0.25} T_b^{0.175} \left( \frac{1 - T/T_c}{1 - T_b/T_c} \right)^{0.8}$$
(7)

For acids, the Sastri–Rao correlation is,

$$\gamma = 3.9529 \times 10^{-7} P_c^{0.5} T_b^{-1.5} T_c^{1.85} \left( \frac{1 - T/T_c}{1 - T_b/T_c} \right)^{11/9}$$
(8)

For any other type of liquid, the following correlation was suggested by them.

$$\gamma = 4.9964 \times 10^{-7} P_c^{0.5} T_b^{-1.5} T_c^{1.85} \left( \frac{1 - T/T_c}{1 - T_b/T_c} \right)^{11/9}$$
(9)

**Example** Estimate the surface tension of acetic acid at 293 K using Brock–Bird and Sastri–Rao correlations. Given:  $T_c = 591.95$  K,  $P_c = 5.74 \times 10^6$  Pa and  $T_b = 391.1$  K. The experimental value of surface tension of acetic acid is 0.0274 N/m.

Solution: From Brock-Bird correlation:

$$Q = 5.55134 \times 10^{-8} \left[ 1 + \frac{(391.1/591.95)\ln(5.74 \times 10^{6}/101325)}{1 - 391.1/591.95} \right] - 1.295 \times 10^{-7} = 3.6239 \times 10^{-7}$$

$$\gamma = (5.74 \times 10^6)^{2/3} (591.95)^{1/3} Q(1 - 293/591.95)^{11/9} = 0.0423 \text{ N/m}$$

From Sastri-Rao correlation:

$$\gamma = 3.9529 \times 10^{-7} \left( 5.74 \times 10^{6} \right)^{0.5} (391.1)^{-1.5} (591.95)^{1.85} \left( \frac{1 - 293/591.95}{1 - 391.1/591.95} \right)^{11/9} \text{N/m}$$
  
= 0.0268 N/m

Estimation of surface tension using the parachor data usually gives good results. Its simplicity makes it a popular method for calculating surface tension. Escobedo and Mansoori (1996) have suggested that  $\varphi$  is a function of temperature. They proposed the following temperature-dependence for  $\varphi$ .

$$\varphi = \varphi \circ f(T_r), \quad T_r = \frac{T}{T_c}$$
 (10)

Where  $\varphi_{\circ}$  is independent of temperature, but depends on the physical properties of the compound, such as its critical temperature, pressure, normal boiling point and molar refraction.

# The Wetting of Surfaces by Liquids

The energetics of solid surfaces and their effect on the interaction with liquids play an important role in a variety of applications such as adhesive bonding, polymer coatings, printing, etc., where a high degree of wetting is desired. In other applications such as water and ice repellency and anti-sticking, easycleaning or self-cleaning surfaces, wetting is undesirable.

# The contact angle

When a small amount of liquid is placed on the surface of a solid, it forms a drop which covers a limited area of the surface. This is illustrated in (Figure 3), in which the contact angle,  $\theta$ , is the angle between the tangent to the liquid surface at the contact line and the solid surface [1]. The limiting condition is that  $0^{\circ} < \theta < 180^{\circ}$ .

1. If we take the condition where the contact angle approaches zero, we have a surface that is completely wetted by the liquid. Water on clean glass is an example of this.

The glass is hydrophilic due to the silica surface, which is made up of a large number of oxygen atoms and surface silanol groups that can hydrogen bond with the water surface.



Figure 3

- 1. Mercury on a polytetrafluoroethylene (PTFE) surface forms drops with a contact angle of about 150° and this can be considered to be complete non-wetting of the surface.
- 2. If the value of contact angle is  $\theta \ge 90^\circ$ , the droplet does not spread readily.

Generally, when the water contact angle is less than  $90^{\circ}$  the surface is considered hydrophilic. When the water contact angle is greater than  $90^{\circ}$  the surface is considered hydrophobic.



Figure 1 Illustration of contact angles formed by sessile liquid drops on a smooth homogeneous solid surface

If liquid is withdrawn, the angle is reduced from the value that we see when liquid is added. These experiments have to be carried out slowly and carefully so that we are as close to an equilibrium value as possible. The angle obtained as we have just finished expanding the drop is known as the advancing contact angle,  $\theta_A$ , and the angle that is observed when the liquid has just been withdrawn is the receding contact angle,  $\theta_R$ . These angles change if they are measured while the wetting line is in motion. They are then the dynamic contact angles and merit a discussion in some detail due to their importance in many coating and printing processes.

#### **The Young Equation**

In the illustration of the liquid drop shown in Figure above, the contact line will move until equilibrium is established. We may describe this situation in terms of the force balance in the plane of the surface shown in Figure 2a and expressed as the vector addition

$$\gamma_{\rm vs} = \gamma_{\rm ls} + \gamma_{\rm vl} \cos\theta \tag{6.2}$$

where  $\gamma_{12}$  is the interfacial tension between phases 1 and 2 [e.g. vapour (v) and solid (s)] (it is only referred to as the surface tension if it refers to the liquid–saturated vapour interface). It should be noted that



Figure 2 The balance of interfacial tensions at the vapour-liquid-solid contact line shown for (a) a flat surface and (b) a 'non-flat' surface



Figure 3 Schematic of the line tension, TL, acting along the contact line of a liquid drop

Equation 6.2 refers to a drop on a flat surface. If the surface is not flat, then the balance shown in Figure 3 gives [2, 3]

$$\alpha + \beta \neq 180: \quad \gamma_{vs} \geq \gamma_{ls} + \gamma_{lv} \cos \beta; \quad \gamma_{ls} \geq \gamma_{vs} + \gamma_{lv} \cos \alpha \qquad (6.3)^{\text{Ser}}$$

However, the contact line is not straight – it is curved and the radius of curvature is important, as this results in what is known as the line tension,  $T_L$ , which acts in opposition to the expansion of the drop (as illustrated in Figure 3). Equation 6.2 should be written for a drop of radius r as follows:

$$\gamma_{\rm vs} = \gamma_{\rm ls} + \gamma_{\rm vl} \cos \theta + \frac{T_{\rm L}}{r} \tag{6.4}$$

The line tension is not very large, being typically of the order of  $TL \approx 10^{-11}$  N, with the value  $T_L/r > 1 \text{mNm}^{-1}$  being required if it is to make a significant contribution. Therefore, we need only use Equation 6.4 for very small systems such as capillary condensation in porous solids.

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