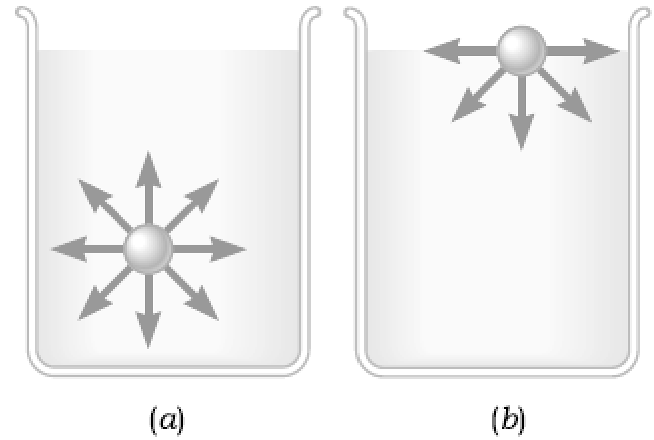
Surface Tension



- The molecular basis for surface tension:
- Part *a shows a molecule* within the bulk liquid, so that it is surrounded on all sides by other molecules.
- The surrounding molecules attract the central molecule equally in all directions, leading to a zero net force.
- In contrast part *b shows a molecule in the surface. Since there are no* molecules of the liquid above the surface, this molecule experiences a net attractive force pointing toward the liquid interior.
- This net attractive force causes the liquid surface to contract toward the interior until repulsive collisional forces from the other molecules halt the contraction at the point when the surface area is a minimum.
- If the liquid is not acted upon by external forces, a liquid sample forms a sphere, which has the minimum surface area for a given volume.
- Nearly spherical drops of water are a familiar sight, for example, when the external forces are negligible.

Surface Tension

- The short-range intermolecular forces which are responsible for surface/interfacial tensions include
- van der Waals forces (in particular, London dispersion forces, universal)
- Other types of bonding
  - Hydrogen bonding (as, for example, in water)
  - Metal bonding (as, for example, in mercury).
  - The relatively high values of the surface tensions of water and mercury reflect the contributions of hydrogen bonding and metal bonding, respectively.
- These forces are not appreciably influenced by one another, and so may be assumed to be additive.
- The surface tension of water may, therefore, be considered as the sum of a dispersion force contribution, and a hydrogen bonding contribution,

$$\gamma_w = \gamma_w^d + \gamma_w^h$$

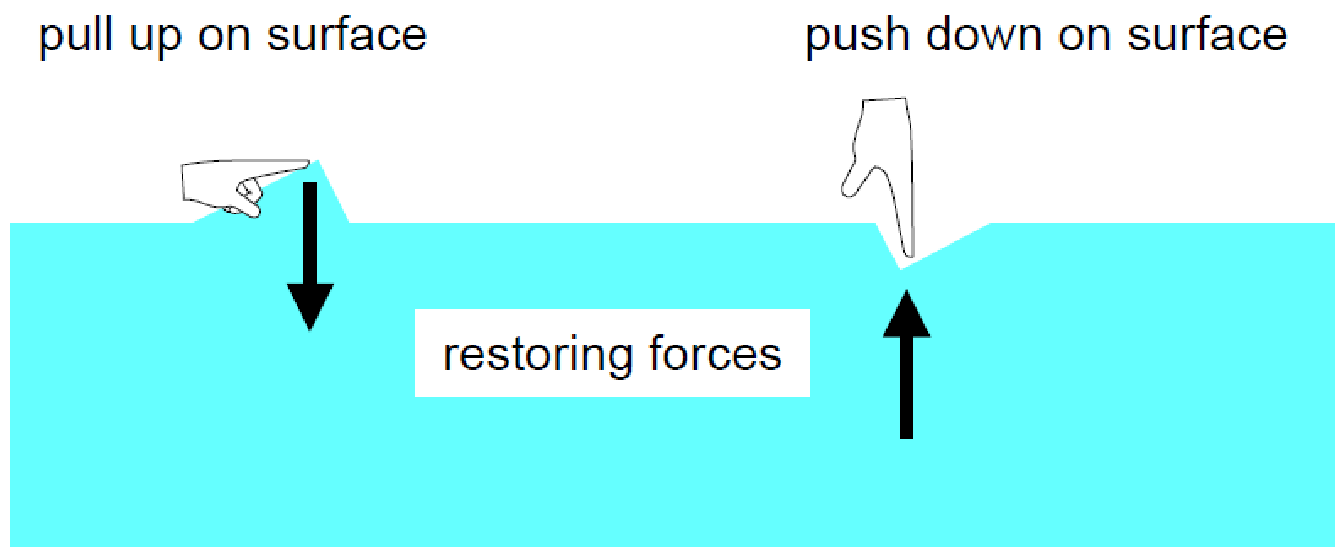
- In the case of hydrocarbons the surface tension is entirely the result of the dispersion force contribution.

Surface Tension

- One of most important phenomena in nature
  - Especially in nature & biology –
    - Water climbing up trees
    - Shape of raindrops
- Surface tension is a property that allows the surface of a liquid to behave somewhat as a trampoline does.
- When a person stands on a trampoline, the trampoline stretches downward a bit and, in so doing, exerts an upward elastic force on the person. This upward force balances the person’s weight. The surface of the water behaves in a similar way.
- For instance, you can see the indentations in the water surface made by the feet of an insect known as a water strider, because it can stride or walk on the surface just as a person can walk on a trampoline.

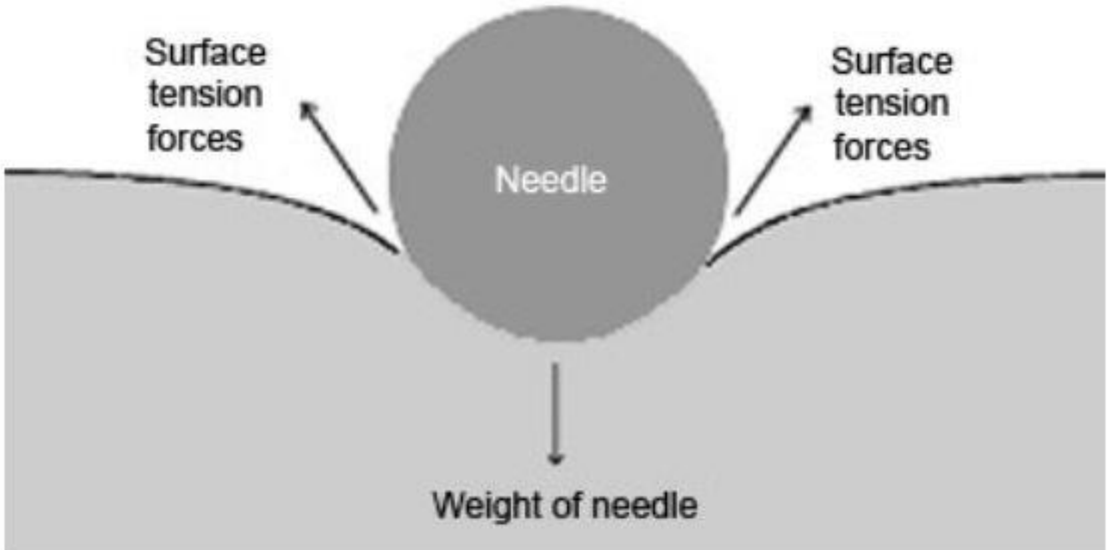
Surface Tension

- The surface of a liquid behaves as an elastic rubber membrane (spring).
- If you try to pull a molecule from the surface an attractive restoring force due to cohesive forces acts on the molecule.
- If a surface molecule is depressed slightly into a liquid, then molecule experience a repulsive restoring force. .



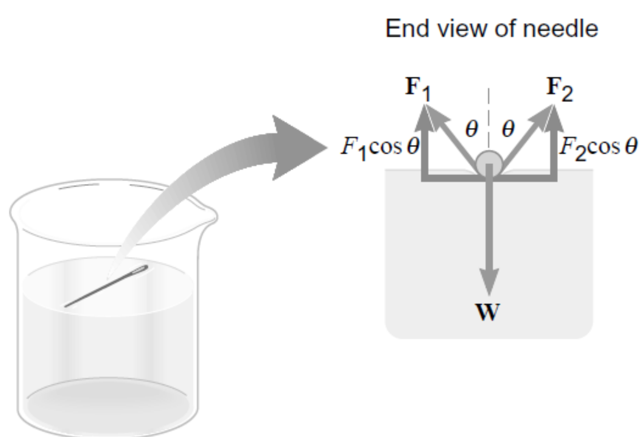
Surface Tension

- When an object falls onto the surface, it has to push the water molecules apart.
- If the effect of the weight of the object is insufficient to match the attractive forces between molecules in the surface layer, the object will not enter the surface.
- Careful observation of the floating needle will show that the water surface is bent down under the weight of the needle, the surface tension causing it to behave as if the needle was supported by a flexible skin.



Surface Tension

- A needle has a length of 3.2 cm. When placed gently on the surface of the water (γ =0.073 N/m) in a glass, this needle will float if it is not too heavy. What is the weight of the heaviest needle that can be used in this demonstration?



Surface Tension

Table 2.1: Surface tensions γ of some liquids at different temperatures T.

Substance	T	γ ($\mathrm{mNm^{-1}}$)	Substance	T	γ ($\mathrm{mNm^{-1}}$)
Water	10°C	74.23	Mercury	25°C	485.48
	25°C	71.99	Phenol	50°C	38.20
	50°C	67.94	Benzene	25°C	28.22
	75°C	63.57	Toluene	25°C	27.93
	100°C	58.91	Dichloromethane	25°C	27.20
Argon	90 K	11.90	n-pentane	25°C	15.49
Methanol	25°C	22.07	n-hexane	25°C	17.89
Ethanol	10°C	23.22	n-heptane	25°C	19.65
	25°C	21.97	n-octane	10°C	22.57
	50°C	19.89		25°C	21.14
1-propanol	25°C	23.32		50°C	18.77
1-butanol	25°C	24.93		75°C	16.39
2-butanol	25°C	22.54		100°C	14.01
Acetone	25°C	23.46	Formamide	25°C	57.03

Surface Tension

The surface tension of most liquids decreases with increasing temperature in a nearly linear fashion (some metal melts being exceptional in this respect) and becomes very small in the region of the critical temperature, when the intermolecular cohesive forces approach zero. A number of empirical equations have been suggested which relate surface tension and temperature, one of the most satisfactory being that of Ramsay and Shields:

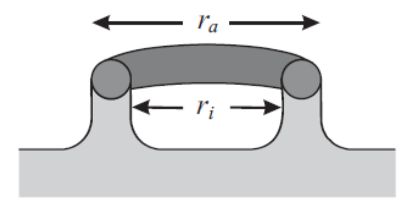
$$\gamma\left(\frac{Mx}{\rho}\right)^{2/3} = k(T_c - T - 6) \tag{4.5}$$

where M is the molar mass of the liquid, ρ is the density of the liquid, x is the degree of association of the liquid, T_c is the critical temperature and k is a constant.

Surface tension measurement techniques

DU NOÜY RING

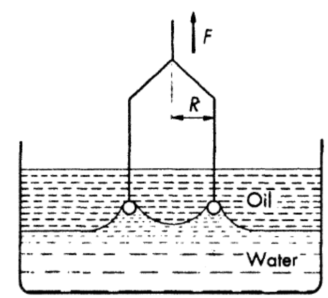
- The Du Noüy ring method utilizes the interaction of a platinum ring with the test surface.
- The ring is submerged and then raised to form a meniscus of liquid.
- Eventually this meniscus tears from the ring and returns to its original position.



Du-Noüy ring tensiometer

- A common device is the **ring tensiometer**, called also the **Du-Noüy**[3] tensiometer.
- In a ring tensiometer the force necessary to detach a ring from the surface of a liquid is measured
- The force required for the detachment is

$$2\pi \cdot (r_i + r_a) \cdot \gamma$$



$$= \frac{\beta F}{4\pi R}$$

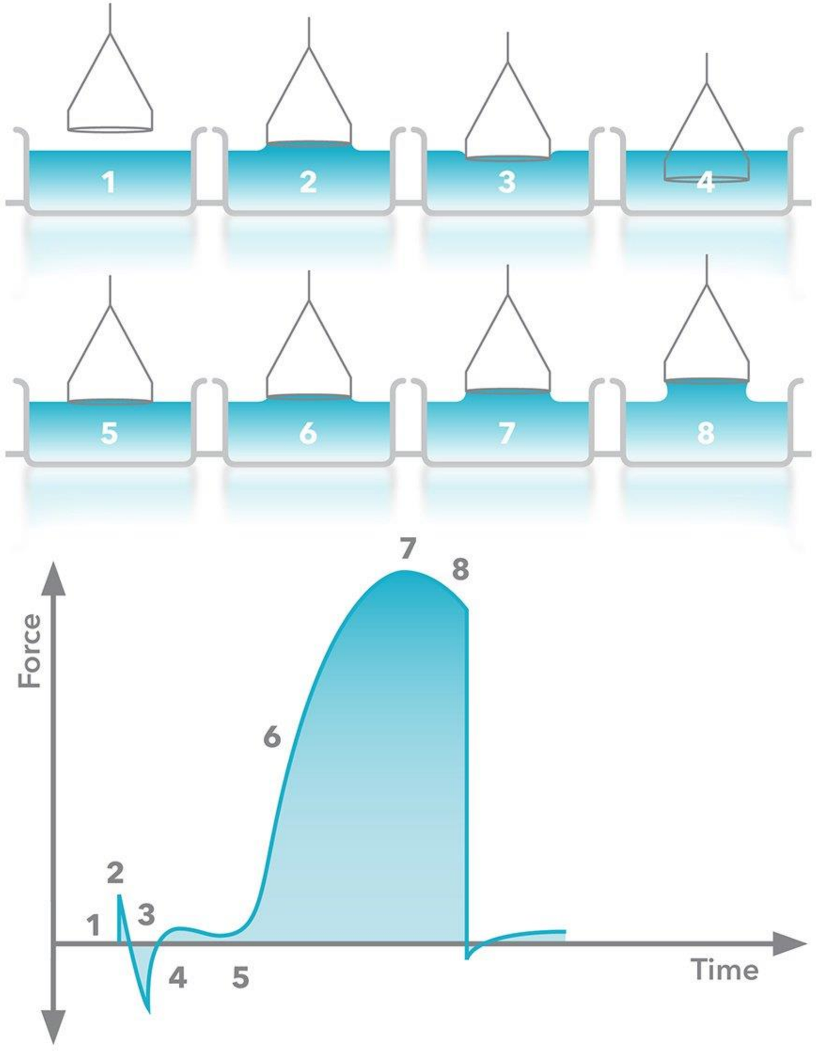
- R: mean Radius
- β: correction factor

- A necessary condition is that the ring surface must be completely wetting (Contact angle of 0º)
- A platinum wire is often used which can be annealed for cleaning before the measurement.
- An empirical correction factor is often used

Surface tension measurement techniques

DU NOÜY RING

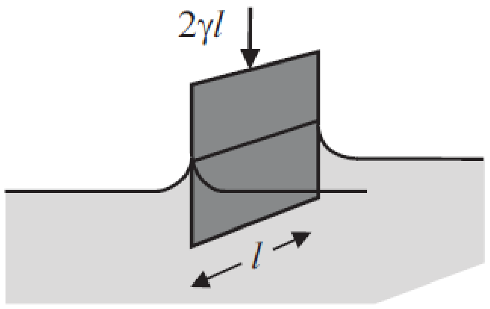
- The ring is above the surface and the force is zeroed.
- The ring hits the surface and there is a slight positive force due to the adhesive force between ring and surface.
- The ring must be pushed through the surface (due to the surface tension), which causes a small negative force.
- The ring breaks through the surface and a small positive force is measured due to the supporting wires of the ring.
- When lifted through the surface the measured force starts to increase.
- The force keeps increasing until the maximum force is reached.
- After the maximum there is a small decrease of in the force until the lamella breaks.



Surface tension measurement techniques

WILHELMY PLATE

- A thin plate of glass, platinum, or filter paper is vertically placed halfway into the liquid.
- In fact, the specific material is not important, as long as it is wetted by the liquid.
- Close to the three-phase contact line the liquid surface is oriented almost vertically (provided the contact angle is 0◦).
- Thus the surface tension can exert a downward force.
- One measures the force required to prevent the plate from being drawn into the liquid.
- plate.
- The Wilhelmy-plate method is simple and no correction factors are required.
- Care has to be taken to keep the plates clean and prevent contamination in air.



Wilhelmy plate

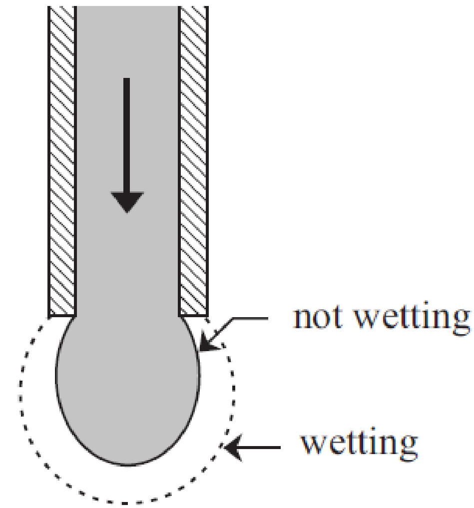
$$F = W_{total} = W_{plate} + 2\, l\, \gamma \cos\theta$$

If the liquid wets completely the plate, then $\cos\theta = 1$

Surface tension measurement techniques

DROP-WEIGHT METHOD

- The liquid is allowed to flow out from the bottom of a capillary tube.
- Drops are formed which detach when they reach a critical dimension.
- The weight of a drop falling out of a capillary is measured.
- To get a precise measure, this is done for a number of drops and the total weight is divided by this number.
- As long as the drop is still hanging at the end of the capillary, its weight is more than balanced by the surface tension.
- A drop falls off when the gravitational force mg, determined by the mass m of the drop, is no longer balanced by the surface tension.
- The surface tensional
- force is equal to the surface tension multiplied by the circumference.

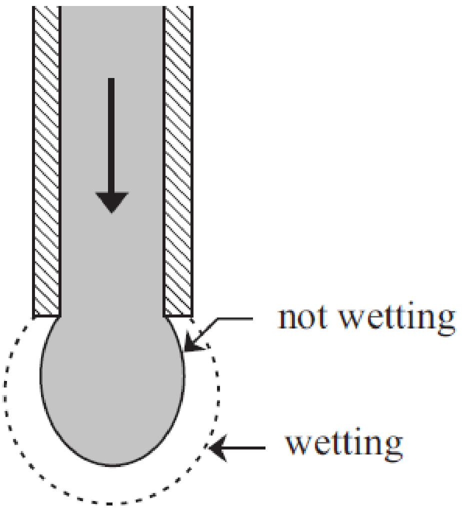


$$mg = 2\pi r_C \gamma$$

Surface tension measurement techniques

DROP-WEIGHT METHOD

- Thus, the mass is determined by the radius of the capillary.
- Here, we have to distinguish between the inner and outer diameter of the capillary.
- If the material of which the capillary is formed is not wetted by the liquid, the inner diameter enters into the equation).
- If the surface of the capillary tube is wetted by the liquid, the external radius of the capillary has to be taken.
- Up to 40% of the drop volume may be left on the stalagmometer tip. Therefore a correction f has to be introduced



$$mg = 2\pi r_C \gamma$$