Politechnika Wrocławska
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Laboratorium
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EXERCISE 33	MEASUREMENT OF SURFACE TENSION

Exercise Objective: Familiarization with the description of intermolecular interactions and simple methods of measuring the surface tension of liquids.

Topics: The nature and character of intermolecular interactions in liquids, surface tension of liquids, pressure under a curved liquid surface, concave and convex meniscus, methods of measuring surface tension.

1. Introduction

The forces that bind molecules in liquids are different from those that form chemical bonds. Intermolecular forces in liquids act between electrically neutral atoms or molecules. These forces are called van der Waals forces. When the distance r between two electrically neutral molecules is sufficiently small, the electric charge distributions in these molecules undergo deformation and associated polarization. Then, a net force acts between the particles, which is the sum of two forces: an attractive force, F_1, acting between unlike charges, and a repulsive force, $\boldsymbol{F}_2$, acting between like charges:

$$\vec{F} = \vec{F}_1 + \vec{F}_2 \qquad (1)$$

A complete description of the forces acting between particles requires the use of quantum mechanics.

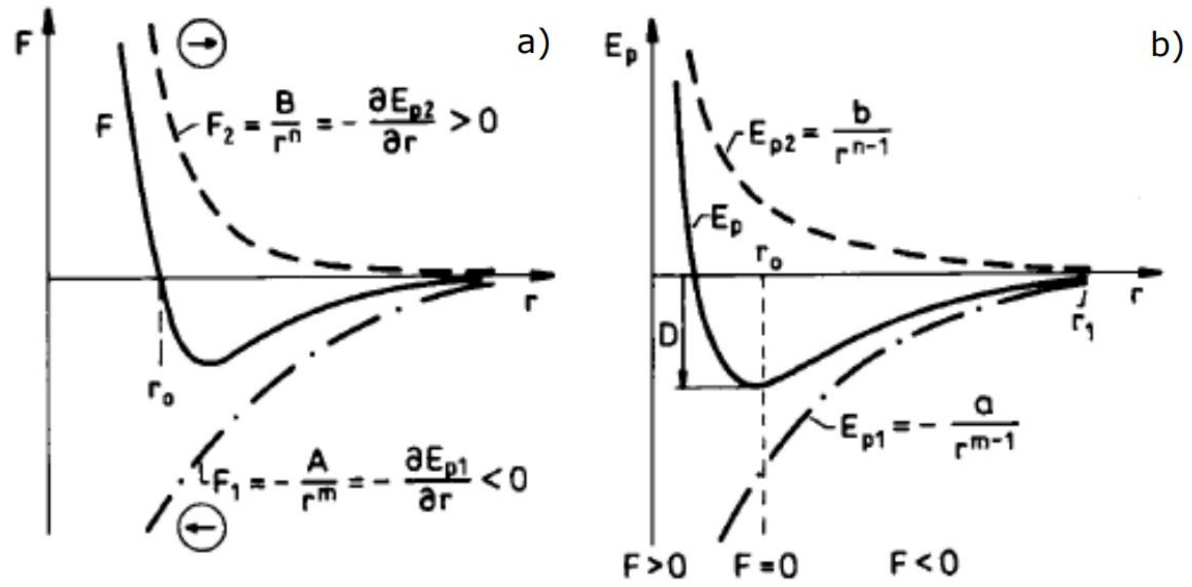

Fig. 1. Van der Waals interaction: a) dependence of the force and b) potential energy on the distance between two molecules

For large distances between particles, the attractive force $\boldsymbol{F_1}$ dominates, and as the distance between these particles decreases, repulsive forces $\boldsymbol{F_2}$ begin to dominate. Therefore, there is a distance r_0 between two particles at which the attractive and repulsive forces balance each other. These forces correspond to the potential energies E_{p1} and E_{p2}. The resultant potential energy E_p is their algebraic sum:

$$E_p = E_{p1} + E_{p2}. \tag{2}$$

At the distance of r_0, an equilibrium state occurs in which the potential energy reaches its minimum and the force $F(r_0) = 0$. At distances smaller than r_0, repulsive forces dominate, while at distances greater than r_0, attractive forces dominate. Then, the interaction energy of both molecules reaches a minimum D (Fig. 1). Van der Waals forces become vanishingly small for distances greater than 1 nm.

1.1 Surface tension of a liquid at the boundary with another phase

The average distances between molecules in liquids are much smaller than in gases. Therefore, the forces of interaction between liquid molecules are much greater than those between gas molecules. A molecule inside a liquid is subjected to attractive forces from the surrounding molecules. Due to spherical symmetry, these forces compensate each other so that their resultant is zero (Fig. 2). At the surface of a liquid, the attractive forces from liquid molecules create a resultant directed into the liquid along the normal to its surface. The resultant force from gas or vapor molecules also acts on the molecule in question along the normal to the liquid-gas (vapor) boundary, but it is directed outward. However, the magnitude of this force is many times smaller than the attractive forces between liquid molecules. The resultant force acting on molecules at the liquid surface is therefore directed into the liquid and exerts a pressure of tens of thousands of atmospheres. As a result, the surface of the liquid shrinks.

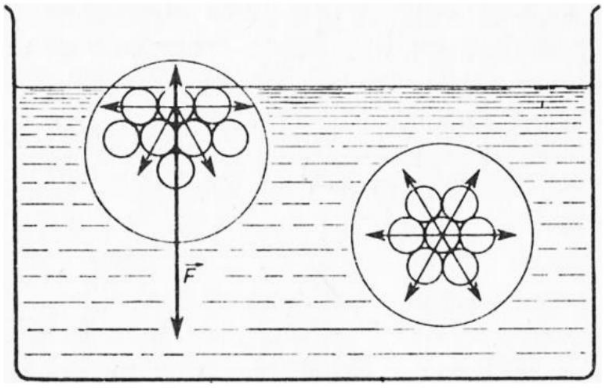

Fig. 2. The resultant of forces acting on a molecule inside and on the surface of a liquid.

When no external forces act on a liquid, it assumes a spherical shape. Transferring molecules from the interior of the liquid to its surface requires work against the resultant intermolecular forces. Molecules at the liquid's surface have higher potential energy than molecules inside the liquid.

The surface tension σ of a given liquid at the boundary with another phase is the work *W* required to isothermally increase the surface area by a unit value Δ*S*.

$$\sigma = \frac{W}{\Delta S}\,. \tag{3}$$

This definition may be better understood with an example. If we form a soap film on a wire frame (Fig. 3), a movable section of length l of which is immersed in a soap solution, surface tension will cause the film's surface area to decrease. Under the action of the weight of the movable section of the frame on one side and the surface tension forces of the film on the other, the movable section of the frame will come to an equilibrium position.

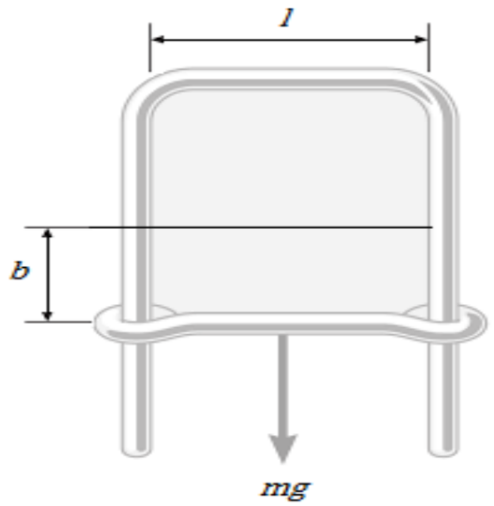

Fig. 3. Soap film stretched on a frame

When we hang an additional weight from the movable part of the frame, its weight *mg* will cause the movable part to shift by *b*. In this way, work $W = mgb$ will be performed, under the influence of which the film surface will increase by $2S = lb$ (because the film has two surfaces). Experiment shows that the ratio of work *W* to the surface 2*S* is a characteristic feature of a given phase boundary, so

$$\sigma = \frac{W}{2S} = \frac{mgb}{2lb} = \frac{mg}{2l} = \frac{F}{2l} \,. \tag{4}$$

The moving part of the frame, and therefore the free edge of the frame, moves under the action of a force tangential to the film surface and normal to its free edge. This force can be balanced by a weight. As it can be seen from formula (4), **surface tension *σ* can also be defined as the force *F* tangential to the liquid surface, acting per unit length of the liquid surface edge.** In the SI system, the unit of surface tension *σ* is J/m² (according to the first definition) or N/m (according to the second definition).

1.2 Surface tension at the different media interface

At the boundary of a liquid, gas, and solid, a **curvature of the liquid surface, called a meniscus**, is observed. The meniscus is the result of the distribution of forces acting on liquid molecules located near the boundaries of three phases: liquid, gas, and solid. **Cohesive forces** are the forces acting between molecules of the same body. **Adhesive forces** are the forces acting between molecules of different bodies. A molecule located on the surface and near the wall of a container (solid body) will be subjected to forces from other liquid molecules, solid molecules, and gas molecules (Fig. 4). The force F_3 acting on the molecule in question from the container wall, will be directed along the normal to the wall and toward the wall. The force F_1 acting from the liquid molecules will be directed into the liquid, and the force F_2 will be directed into the gas (or vapor). Force $F_{1,2}$ is the resultant of forces F_1 and F_2. The value of force F_2 is significantly smaller than the other two. If the resultant force *F* is directed downward and toward the solid (as in Fig. 4), the liquid meniscus will be concave because the free liquid surface must be perpendicular to the resultant force acting on the liquid molecules on its surface (Fig. 5a). If the resultant force *F* is directed downward and toward the liquid, a convex meniscus is observed (Fig. 5b).

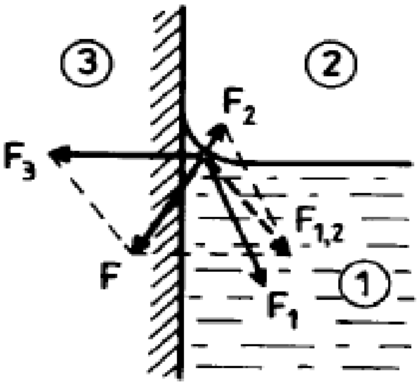

Fig. 4. Distribution of forces acting on a liquid molecule located on the liquid surface near the vessel wall.

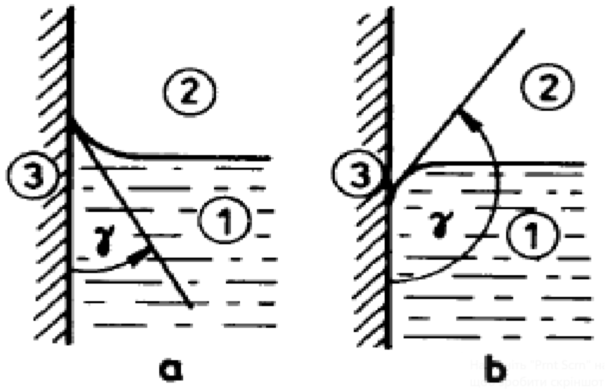

Fig. 5. Meniscus of the liquid: a – wetting, b – non-wetting vessel wall, where γ is the angle between the vessel wall and the tangent to the liquid surface.

Due to the existence of surface tension, additional pressure acts under the curved surface of a liquid. According to Laplace, this additional pressure is

$$\Delta p = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) , \tag{5}$$

where R_1 and R_2 are the radii of curvature of the normal cross-sections perpendicular to each other, for which the radii of curvature assume extreme values. These radii correspond to the case of a meniscus of non-spherical shape (e.g. an ellipse or a cylinder). These radii are considered positive when the centers of curvature of the normal cross-sections are on the liquid side, and negative if they are on the opposite side. Therefore, for a concave meniscus, $\Delta p < 0$, and for a convex meniscus, $\Delta p > 0$. The additional pressure Δp is always exerted toward the center of curvature of the meniscus. For tubes with a very small internal diameter, called capillaries, we can assume that $R_1 = R_2 = R$ (segment of the spherical surface), then:

$$\Delta p = \frac{2\sigma}{R} \ . \tag{6}$$

This is also the additional pressure inside a gas bubble of radius R when it is just below the liquid surface. The pressure inside a soap bubble will be twice as great because it has two surfaces: an outer and an inner. In thin capillaries, the additional pressure under the curved surface causes the liquid to rise when the meniscus is concave (wetting, Fig. 6a) and to sink when the meniscus is convex (no wetting, Fig. 6b). This phenomenon, called capillarity, plays a significant role in nature. It allows sap to rise in plants.

Equation (6) can be derived as follows: per unit edge of the free surface of the liquid (Fig. 7), a surface tension force F acts, tangential to the liquid surface. Its horizontal component F_r is balanced by the elastic action of the capillary wall, while the vertical component F_h causes the liquid level to rise.

$$F_h = F\cos\gamma, \quad \cos\gamma = \frac{r}{R}, \quad F_h = F\frac{r}{R}, \tag{7}$$

where *r* is the radius of the capillary and *R* is the radius of curvature of the meniscus. The force acting on the entire circumference of the edge of the liquid surface of radius *r* is

$$F = \frac{2\pi\sigma r^2}{R}. \tag{8}$$

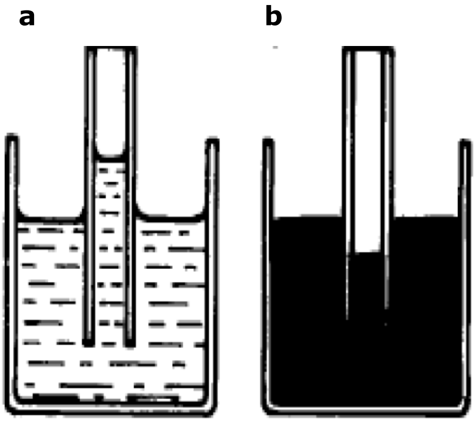

Fig. 6. Liquid level in the capillary:
a) "rising" of the liquid in the capillary wetting the capillary walls, b) "falling" of the liquid in the capillary not wetting the capillary walls

The additional pressure Δp is equal to the ratio of this force to the cross-sectional area passing through the circumference of the liquid edge, therefore

$$\Delta p = \frac{F}{\pi r^2} = \frac{2\sigma}{R}. \tag{9}$$

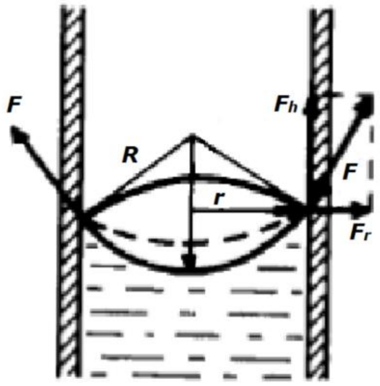

Fig. 7. Schematic diagram for calculating the pressure under a curved surface

Another effect of surface tension is the difficulty in immersing objects that are not susceptible to wetting by the liquid or in detaching objects that are wetted by the liquid from the liquid's surface. These effects are insignificant for large objects, because their weight, proportional to the cube of their size, is much greater than the surface tension forces, which are directly proportional to the object's size. However, small objects can be buoyed by surface tension, even though they would sink if submerged. For example, a water strider (insect) stays afloat on the surface of a liquid thanks to surface tension. This allows it to move much faster than if it were immersed in water.

Surface tension depends significantly on temperature and the phase a liquid is in contact with. Therefore, when specifying specific surface tension values, the phase a given liquid is in contact with and the liquid's temperature should be specified. Generally, surface tension decreases linearly with increasing temperature. Everything described above applies to the case where the liquid is a so-called pure phase, i.e., a single-component liquid. When dealing with two- or multi-component liquids, the phenomena occurring are more complex. There are cases where the liquids are immiscible and where two substances are miscible. In the first case, the less dense liquid will flow to the surface as individual droplets, or in the case of a larger quantity, it will spread evenly across the entire surface. The case where the liquids are miscible is further divided into two, depending on the forces between the solvent and the solute.

A) If the forces between the solute and solvent molecules are weaker than the forces acting solely between the solvent molecules, the solute molecules are pushed to the surface layer, where their concentration increases. This phenomenon is called adsorption, and the substances accumulating in the surface layer are called surface-active substances, or adsorbates. A solvent, or a material that collects another material on its surface, is called an adsorbent. In this case, the surface tension decreases (e.g., a small amount of detergent added to water).

B) If the forces between the solute and solvent molecules are greater than the forces between the solvent molecules themselves, a phenomenon called negative adsorption occurs, in which the concentration of solute molecules in the surface layer is lower than in the rest of the solution. Substances such as electrolytes or aqueous sugar solutions have a higher surface tension than pure water.

2. Measurement principles and systems for determining surface tension

In the Laboratory of Fundamental Physics, Faculty of Fundamental Problems of Technology at Wrocław University of Science and Technology, surface tension measurements are made using the following methods: detachment, capillary, stalagmometer and bubble.

2.1 Tear-off method (Exercises 33a and 33e)

Surface tension is measured using the tear-off method, using metal plates that are well wetted by the liquid being tested. The measurement involves determining the force required to separate a plate of known circumference from the liquid surface (Fig. 8). The plate's weight Q and the force F required to separate the plate from the liquid can be measured using a suitably designed balance. The force F required to separate the plate from the liquid surface is equal to the sum of the plate's weight Q and the surface tension force F_n.

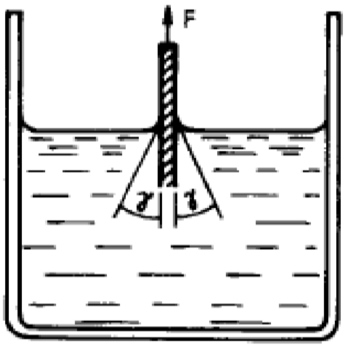

Fig. 8. Wetting of a metal plate by a liquid

$$F = Q + F_n \tag{10}$$

$$F_n = 2\sigma\,(l + d)\cos\gamma \tag{11}$$

In equation (11) l is the length of the edge of the plate immersed in the tested liquid at the moment of its detachment and d is its thickness, the angle γ is between the surface of the plate and the plane tangent to the liquid surface (Fig. 8). In the case of a liquid wetting the plate, due to the action of adhesion forces, the liquid molecules adhere to the metal and the angle γ is approximately equal to zero, then $\cos\gamma \approx 1$. Therefore, we have

$$^{(12)}\sigma = \frac{F-Q}{2(l+d)}\ .$$

If the plate thickness *d* is small compared to the edge length *l*, it can be neglected. A torsion balance (Fig. 9) is used to measure forces *F* and *Q*. A torsion balance operates on the following principle. The gravity of the weighed body creates a primary torque that acts on one end of the spring. Turn knob 8 counterclockwise until the movable pointer 4 aligns exactly with the red line 5, indicating equilibrium. This creates a compensating torque (in the opposite direction to the primary torque), which acts on the other end of the spring. The value of force *Q* can be read on the movable scale 7 at the point indicated by pointer 11. When the immersed plate is lifted from the liquid surface, the value of force *F* is read at the moment of its separation. The process of measuring surface tension on the torsion balance and the analysis of the results can be found in the instructions for Exercise 33a.

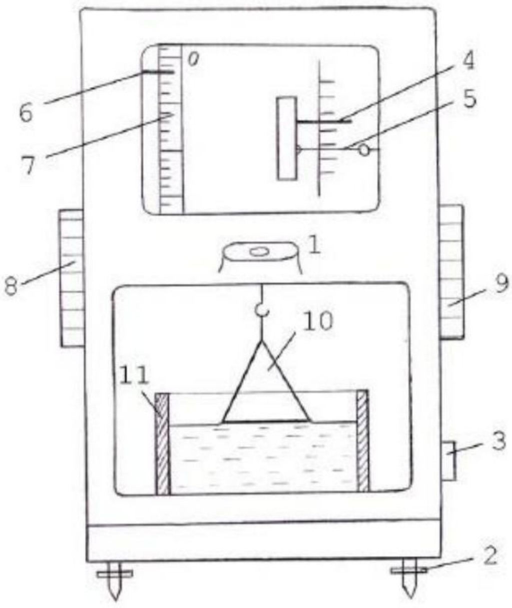

Fig. 9. Torsion balance

1. Level gauge
2. Adjusting screws
3. Protecting locking knob
4. Movable pointer
5. Red line – indicator of balance
6. Pointer
7. Movable scale
8. Knob causing rotation of the scale (7)
9. Knob causing shift of the pointer (6)
10. Metal plate
11. Measuring vessel with tested liquid

Surface tension measurement using the peel method can also be performed using a torsion balance (photo 1 - exercise 33e, along with the operating instructions). Its main part is a light, horizontal beam 5 suspended on a thin torsion thread 6 (a thin metal tape), from the end of which a plate 7 is suspended. Before immersing the plate in the tested liquid, its weight *Q* is compensated using a knob 1 attached to one end of the tape. The value of force F_n at the moment the immersed plate is peeled from the surface of the tested liquid is read 2 from the scale of the knob 3 coupled to the other end of the tape.

$$\sigma = \frac{F_n}{2(l+d)} \qquad (13)$$

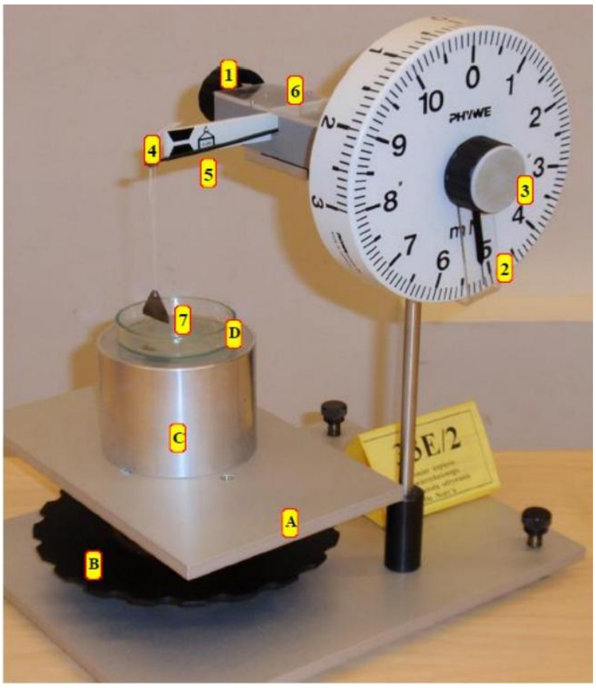

Photo 1. General view of the measuring station with a torsion balance:
A – height-adjustable table,
B – height adjustment knob,
C – extension,
D – vessel with tested liquid,
Torsion balance:
1 – zeroing knob,
2 – pointer,
3 – main knob,
4 – plate mounting point,
5 – arm scale,
6 – twisted wire,
7 – measuring plate.

If instead of a plate we use rings with a thin wall and a diameter D, then

$$\sigma = \frac{F_n}{2\pi D} \,. \tag{14}$$

This method of measuring surface tension was proposed by the French physicist Du Nouy.

2.2 Capillary method (exercise 33b)

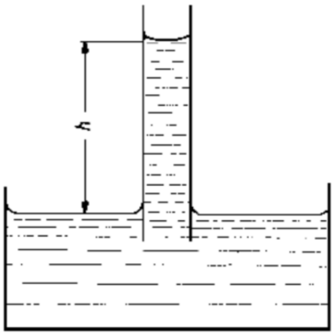

Fig. 10. Measurement of the surface tension of a liquid using a capillary

As described earlier, there is an additional pressure Δp in the capillary (Formula 9). For a wetting liquid, the angle γ between the liquid surface in the capillary and the capillary surface is approximately zero. This corresponds to a hemispherical meniscus, then $R = r$, where r is the capillary radius. This meniscus causes a pressure change of:

$$\Delta p = \frac{2\sigma}{R} = \frac{2\sigma}{r} \,. \tag{15}$$

For a liquid wetting the capillary walls, the liquid level in the capillary rises until the additional pressure is balanced by the hydrostatic pressure of the liquid column inside the capillary p_h

$$\Delta p = p_h = \rho\, g\, h \tag{16}$$

where: ρ - density of the liquid, g - acceleration of gravity, h - height of the liquid column in the capillary, measured from the liquid level in the vessel. Hence

$$\sigma = \frac{\rho g h r}{2} \,. \tag{17}$$

Calibrated capillaries are used for the measurement. The level difference between the liquid surface in the vessel and the capillary h (Fig. 10) is read from a millimeter scale. The liquid's density, after measuring its temperature, is read from the tables. A detailed description of the measurement process and the analysis of the results is included in the instructions for Exercise 33b.

2.3 Stalagmometer Method (Exercise 33c)

A stalagmometer (Fig. 11) is a vessel with a capillary at the end. Liquid flows slowly through the capillary under the influence of gravity, forming a drop at its tip. The liquid wets the lower base of the capillary and adheres tightly to it. As the drop grows, it narrows and then breaks off.

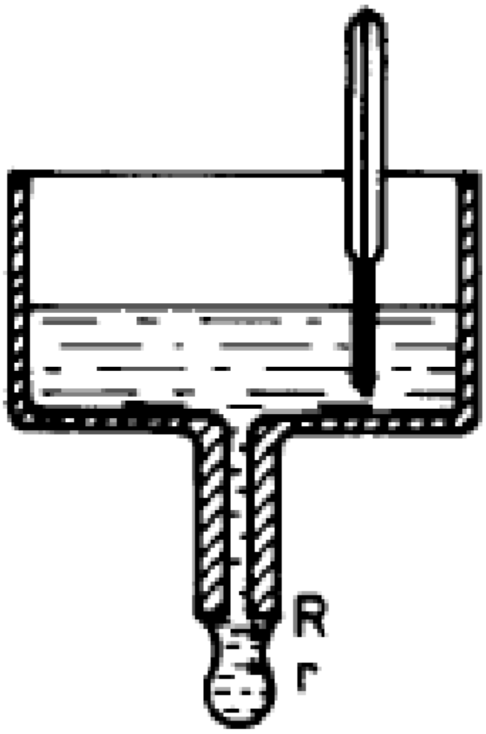

Fig. 11. Stalagmometer

The outer radius of the capillary is R, and the radius of the drop's narrowing at the moment of detachment is r. The weight of the drop mg acts on the entire circumference of the narrowing of the drop, balancing the force of surface tension. Therefore, we can write

$$\sigma = \frac{mg}{2\pi r} \,. \tag{18}$$

The measurement involves determining the throat radius r and the droplet mass. The throat radius can be measured directly using a microscope with an eyepiece equipped with a scale, or determined indirectly. The main difficulty with this measurement is that two throat edges (left and right) must be observed simultaneously. It is also difficult to determine the moment of measurement. Therefore, in the laboratory, the throat radius is determined indirectly. Indirect measurement of the droplet throat radius involves replacing the throat radius *r* with the outer capillary radius *R* and simultaneously introducing the coefficient $k = R/r$. Then

$$\sigma = \frac{mgk}{2\pi R} \ . \tag{19}$$

After introducing the new constant $K = k/(2\pi)$, we finally obtain

$$\sigma = \frac{mgK}{R} \ . \tag{20}$$

The numerical factor K is a function that depends on the expression

$$U = \frac{m}{\rho_T R^3} \ , \tag{21}$$

where m is the mass of one drop, and ρ_T is the density of the tested liquid at the temperature at the time of measurement. The mass of a single drop is assumed to be the average mass of, for example, 50 drops. The relationship between *K* and *U* is given in Table 1 of the instructions for Exercise 33c. It also provides a detailed description of the measurement process and the analysis of the results.

2.4 The bubble method (exercise 33d)

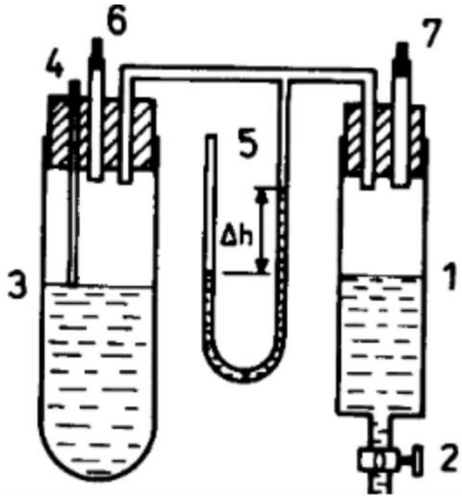

Fig. 12. Device for measuring surface tension using the bubble method
1. Vessel with water to create a vacuum
2. Drain valve
3. Vessel with the tested liquid
4. Capillary
5. Liquid manometer
6. Tube for replenishing the tested liquid
7. Tube for replenishing water

The device for measuring surface tension using the bubble method is shown in Fig. 12. If water flows out of vessel 1 through valve 2, the pressure in vessels 1 and 3 will decrease. At a certain moment, air bubbles will begin to form at the outlet of capillary 4, which is located just below the surface of the tested liquid. The lower end of capillary 4 is conical, so that the capillary opening and the cone generatrix form a sharp edge. The bubble radius *R* is equal to the capillary radius *r*. The pressure inside the bubble is equal to the atmospheric pressure p_a. This pressure is balanced by the pressure resulting from the surface tension of the liquid $2\sigma/r$ and the pressure p_w prevailing inside vessel 3, therefore

$$p_a = \frac{2\sigma}{r} + p_w \ , \tag{22}$$

$$\Delta p \ = \ p_a - p_w = \frac{2\sigma}{r} \ . \tag{23}$$

The value of $p_a - p_w$ can be calculated based on the difference in liquid levels Δh in the manometer 5

$$p_a - p_w = \rho_T g \Delta h \qquad (24)$$

where ρ_T is the density of the liquid in the manometer. Therefore,

$$(25)\ \frac{2\sigma}{r} = \rho_T g \Delta h\ ,$$

hence

$$(26) \qquad \sigma = \frac{1}{2}\rho_T g \Delta h r\ .$$

For the pressure equilibrium condition to be met, air bubbles emerging from capillary 4 should form slowly. The described method can be used to measure the surface tension of various liquids. In Exercise 33d, we measure the surface tension of water. A detailed description of the measurement procedure and the analysis of results can be found in the instructions for this exercise.

3 Questions:

1. What is the condition for equilibrium of forces acting between two liquid molecules?
2. Describe the distribution of forces acting on a molecule inside and on its surface. Why does the surface of a liquid shrink?
3. Define the concept of surface tension (unit). What does surface tension depend on?
4. Explain the phenomenon of meniscus. What determines its type?
5. What determines the Laplace pressure under a curved liquid surface?
6. Give examples of surface tension in everyday life.
7. Describe the method for determining surface tension using the peel method. What forces act on a plate immersed in a liquid?
8. Describe the method for determining surface tension using the capillary method. What determines the height of the liquid column in a capillary immersed in the liquid?
9. Discuss the method for determining surface tension using the stalagmometer method. How can the radius of a drop's throat be determined? 10. Explain how to determine surface tension using the bubble method. What is the pressure in an air bubble in a liquid?

Based on the textbook "Laboratory Exercises in Physics" edited by Ryszard Żuczkowski, Wrocław University of Science and Technology Publishing House, 1989.

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