

Surface Tension, Minimal Surfaces, and Coffee Stains

Keywords:

VAN DER WAALS forces, specific surface energy, surface tension, minimal surfaces, capillarity, contact angle, cohesion, breaking-off method, bubble pressure method.

Measuring program:

Observation of minimal surfaces, observation of mass transport during the evaporation of a liquid drop, measurement of the surface tension with the breaking-off method and the bubble pressure method, pressure within gas bubbles.

References:

- /1/ DEMTRÖDER, W.: „Experimentalphysik 1 - Mechanik und Wärme“, Springer-Verlag, Berlin among others
- /2/ EICHLER, H. J., KRONFELDT, H.-D., SAHM, J.: „Das Neue Physikalische Grundpraktikum“, Springer-Verlag, Berlin among others.
- /3/ WALCHER, W.: „Praktikum der Physik“, Teubner Studienbücher, Teubner-Verlag, Stuttgart

1 Introduction

Many of you may still remember a childhood experiment: a pin was laid onto a water surface and did not submerge. Or maybe you remember observing insects which are able to run over the water surface of a pond without sinking. Both phenomena are explained by the surface tension of liquids. The following experiment deals with their quantitative measurement.

2 Theory

Various interaction forces are effective between the molecules within a liquid, the most important ones being the VAN DER WAALS forces, which originate from electrostatic forces. These interaction forces are effective at very short distances of about 10^{-9} m and cause the molecules to hold together (cohesive forces). They are considerably stronger than the interaction between the molecules of a liquid and those of gases (adhesive forces) above the surface of the liquid (e.g. air). This leads to the situation represented in Fig. 1: equally strong forces act on the molecules within the liquid in all directions and neutralize one another, the resultant force \mathbf{F}_R being zero. However, within a thin layer at the surface of the liquid a net force $\mathbf{F}_R \neq 0$ remains directed towards the interior of the liquid, perpendicular to the surface.

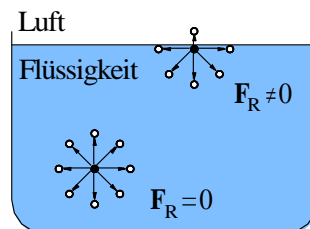


Fig. 1: On the origin of the surface tension of liquids; here, at the interface between a liquid and air. \mathbf{F}_R : resultant force acting on a liquid molecule.

If the surface of a liquid is to be increased by driving liquid molecules from the interior of the liquid to its surface, this force \mathbf{F}_R has to be overcome; the potential energy of the molecules is increased. From this we can immediately draw an important conclusion: Since a state of equilibrium is characterized by a minimum of potential energy, liquid surfaces cover *minimal surfaces* without the impact of external forces. Impressive minimal surfaces are easy to demonstrate by dipping differently shaped wire and plastic frames into soapsuds and then removing them. The soap film lamellae formed between the wires or fins represent minimal surfaces.

The energy required to increase the surface of the liquid by the amount ΔA is ΔW . The quotient of both values

$$(1) \quad w = \frac{\Delta W}{\Delta A}$$

is called the *specific surface energy* or *surface energy density*, the unit is $[w] = \text{J/m}^2$.

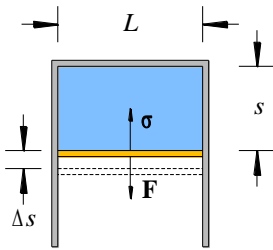


Fig. 2: On the definition of the surface tension.

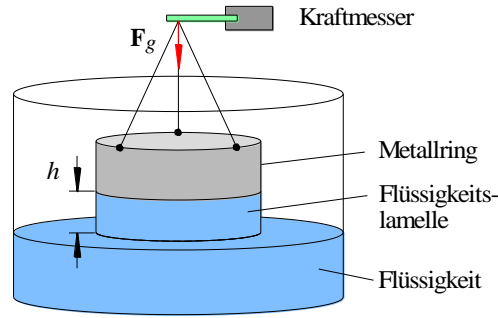


Fig. 3: Measurement of the surface tension using the breaking-off method.

Fig. 2 depicts a possible setup for measuring the specific surface energy. An U-shaped wire (grey) of width L with a movable piece of wire across its legs (yellow) set at an initial distance s from the bend is used. Let the surface between the wires be covered by a liquid film of area $2A = 2Ls$, for example, a soap film lamella (factor 2 because of front and back of the surface). The application of a force \mathbf{F} will move the moveable wire by a distance Δs , thus increasing the surface by $\Delta A = 2L\Delta s$. With $F = |\mathbf{F}|$, the energy ΔW required for this is:

$$(2) \quad \Delta W = F \Delta s$$

With Eq.(1), it follows for the *specific surface energy*

$$(3) \quad w = \frac{\Delta W}{\Delta A} = \frac{F \Delta s}{2L \Delta s} = \frac{F}{2L}$$

Considering the vector property of the force \mathbf{F} , we obtain the vector quantity *surface tension* $\boldsymbol{\sigma}$:

$$(4) \quad \boldsymbol{\sigma} = -\frac{\mathbf{F}}{2L}$$

with the unit $[\boldsymbol{\sigma}] = \text{N/m} = \text{J/m}^2$ ¹. As can be noted from Fig. 2, the surface tension is directed tangential to the surface. The magnitude of the surface tension, $\sigma = |\boldsymbol{\sigma}|$ is identical with the specific surface energy w : $w = \sigma$. The common term is „surface tension” for the magnitude σ , which will therefore be used in the following.

2.1 Measurement of the Surface Tension with the Breaking-Off Method

A commonly used set-up for measuring the surface tension of liquids against the air is shown in Fig. 3. A thin-walled cylindrical ring of radius r , wall thickness d and mass m is fixed on a dynamometer and dipped into the liquid. Then the ring is removed from the liquid by lowering the container (of the liquid). This creates a liquid lamella between the ring and the liquid’s surface. In order to keep the ring at height h the force $F(h)$ is required. Let us assume that, proceeding from the height h , we can withdraw the ring by an additional small distance Δh from the liquid to the height h_0 , such that the lamella just does not cut into itself and finally break off. The required work to achieve this is

$$(5) \quad \Delta W = F(h_0) \Delta h$$

by which the surface is enlarged by:

$$(6) \quad \Delta A = 2 \times 2 \pi r \Delta h$$

For the surface tension we thus get:

¹ The unit for surface tension is N/m. Mechanical tension, such as the strain effective on a staff is, in contrast, defined as force F per area A , hence $\sigma = F/A$ with the unit $[\sigma] = \text{N/m}^2$.

$$(7) \quad \sigma = \frac{\Delta W}{\Delta A} = \frac{F(h_0)\Delta h}{2 \times 2 \pi r \Delta h} = \frac{F(h_0)}{4\pi r}$$

By means of this *breaking-off method* it is possible to determine the surface tension σ of liquids against the air by measuring the maximum force $F:=F(h_0)$, at which the lamella just does not cut into itself and finally break off, and the ring radius r . It should be noted that the dynamometer indicates the total force F_g

$$(8) \quad F_g = F + mg$$

m being the mass of the ring including suspension and g the gravitational acceleration. Thus, the force F to be inserted into Eq. (7) is:

$$(9) \quad F = F_g - mg$$

That is the theory so far. In practice, the value determined with Eq. (7) has to be multiplied by a correction factor f which we give here without deduction and which we assume to be error-free ²:

$$(10) \quad f = 0.725 + \sqrt{\frac{0.3607}{r^2 \rho g} \sigma + 0.04534 - 0.839 \frac{d}{r}}$$

where σ is the raw value of the surface tension from Eq. (7) and ρ the density of the liquid. The corrected value σ_k of the surface tension is:

$$(11) \quad \sigma_k = f \sigma$$

2.2 Measurement of the Surface Tension with the Bubble Pressure Method

Another method for measuring the surface tension is presented in Fig. 4. A sharp-tipped capillary K with a small interior radius r is dipped vertically into a liquid (immersion depth h), the surface tension of which is to be measured against the air. The capillary is connected to an apparatus for measuring changes in air pressure that was previously detailed in the experiment “*Sensors...*”. The air pressure inside the capillary can be measured with the pressure sensor D.

In order to press the air to the outlet of the capillary, the hydrostatic counter pressure p_F in the liquid must be overcome, it is given by

$$(12) \quad p_F = \rho g h$$

ρ being the density of the liquid and g the gravitational acceleration. If the air pressure in K is further increased, air bubbles of radius R slowly form at the outlet of the capillary (Fig. 5), whose inner pressure is reciprocally proportional to R . With increasing pressure, the air is further pressed out of the capillary and the radius R of the bubbles therefore continues to decrease. In the case $R = r$ the radius is minimal and the pressure in the bubble, which is then hemispherical in shape, is maximum. After exceeding this pressure the bubble grows and finally breaks off from the outlet. The pressure in the capillary collapses and the process of bubble formation starts again.

Let Δp be the overpressure against the hydrostatic pressure at the capillary outlet at which the pressure in the bubbles is maximal and their radius is r . If ρ_m is the density of the liquid in the manometer (here water) and h_m the height displayed by the manometer, we obtain for Δp :

$$(13) \quad \Delta p = (\rho_m h_m - \rho h) g$$

With that the surface tension can be calculated approximately by:

² according to KOSE, V. [Ed.]; WAGNER, S. [Ed.]: “Kohlrausch – Praktische Physik Bd. 1“, Teubner, Stuttgart, 1996

found at the drop's margin than inside the drop. The light centre of the coffee spot is therefore surrounded by a dark edge.

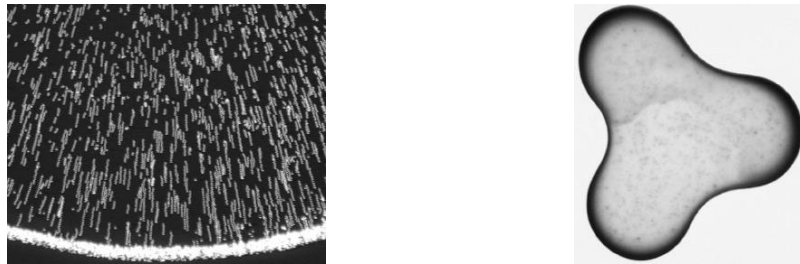


Fig. 6: Left: Radial capillary flow in a liquid drop on a glass surface⁵. The flow was made visible by multiple exposure of small micro spheres (diameter 1 μm), which were added to the liquid. Right: dried coffee stain with higher coffee concentration at its margin caused by such a flow.

3 Experimental Procedure

Equipment:

Ring ($r = 30,0 \text{ mm}$, $d = 0,6 \text{ mm}$, both error-free) with suspension, vertically adjustable platform, force sensor using strain gauge technique (U-OL, measurement range 100 mN), measurement amplifier for force sensor (U-OL), set of weights for calibrating the force sensor, capillary tube (inner diameter $d = (2,07 \pm 0,01) \text{ mm}$) in suspension at unit for vertical adjustment (reading accuracy 0.02 mm), pressure sensor (SENSETECHNICS HCLA12X5DB) on base plate with valves on mount, ERLENMEYER flask with smoothed plug on table, U-tube manometer (filled with water) with holder and reading scale, stand with adjustable pointers, beaker glasses, flexible tubes, tube couplings, taps, scissor jack, thermometer (accuracy 0.1° C), distilled water, soap suds, plastic frames, glass tube stand with two inlets and two outlets, microscope slides, toothpick, Aluminium plate, red wine, ethanol bath, bath with distilled water, hair-drier, nitrogen gas flask, kitchen paper roll, power supply (PHYWE (0 - 15 / 0 - 30) V), PC with data acquisition device (NATIONAL INSTRUMENTS myDAQ) and BNC-Adapter box.

3.1 Minimal Surfaces

Sketch your expectations concerning minimal surfaces after dipping and withdrawing the available plastic frames⁶ from the soapsuds while preparing the experiment. Compare your expectations with the experimentally obtained minimal surfaces. Note that local minima may form in addition to the global (absolute) minimum (Fig. 7).

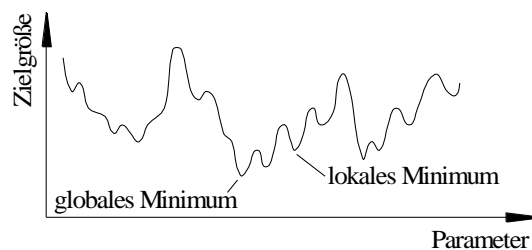


Fig. 7: Global minimum of a target value as a function of a parameter. Besides the global minimum, there are many local minima one of which has been marked exemplarily.

3.2 Red Wine Stains

Pour some drops of red wine on to a microscope slide. Draw the drops into interesting forms with a pipette and observe how the fruit flesh concentration changes by evaporation of the liquid within the drops during the laboratory course. To accelerate the evaporation of the liquid, the slides are put onto a thin Aluminium plate above a radiator.

3.3 Measurement of the Surface Tension Using the Breaking-Off Method

The surface tension of distilled water against air is to be measured using an experimental set-up according to Fig. 3. A bending rod is used as force sensor, which is already known from the experiment "Sensors...".

Hints:

- The suspension threads of the ring were adjusted by the technical assistant prior to the experiment so that the ring hangs horizontally. Do not change this adjustment without informing the technical assistant or supervisor!
- The ring must not be touched with bare hands in order to avoid grease and sweat traces which would falsify the measuring results. Therefore, hold the ring with suspension threads only!

⁵ cf. R. D. DEEGAN: „Capillary flow as the cause of ring stains from dried liquid drops“, Nature 389 (1997) 827 – 829.

⁶ Photographs of the plastic frames can be found on the GPR web site.

First, the force sensor suspended on a stand is calibrated using a set of weights. For at least five weights G in the range of (0 – 100) mN the output voltage U_M of the measurement amplifier (Damping / Dämpfung on) is measured. The measurement is carried out by means of a data acquisition board in a PC⁷ using the MATLAB-script `DatenEinlesen.m`. This is a more comprehensive and more comfortable version of the script which was used during the experiment „Data Acquisition and Processing with the PC...“. The graphic user interface created by the script is self-explaining.

$G = m g$ is plotted over U_M and a calibration curve (regression line) is determined by means of linear regression. For g , the value for Oldenburg is used: $g = 9.8133 \text{ m/s}^2$; it may be taken to be exact (error free)⁸.

The ring is cleaned (rinse in ethanol bath and wash thoroughly with distilled water; then rinse in distilled water for at least one minute, dry with hair-drier), fixed to the force sensor and its weight is determined (measure U_M , and determine G using the calibration curve).

Next, a beaker glass with distilled water is put on the vertically adjustable platform and raised such that the lower rim of the ring becomes submerged in the liquid to a depth of about 5 mm. The ring is to be held in this position for a few minutes, in order to ensure sufficient wetting. The temperature of the liquid is determined directly prior to the measurement; the thermometer must be cleaned prior to each measurement (rinse in distilled water).

The platform is now lowered carefully (without jerks!) until the lamella breaks off. During this process the output voltage of the measurement amplifier is recorded with the PC using a sample rate of 0.5 kHz. The number of measurement values to be recorded depends on the duration of the experiment. 10.000 measurement values, corresponding to a measuring time of 20 s, are a good choice to start.

After completing the data acquisition the data is stored in ASCII format (Button Save Data) and imported into Origin. There the conversion of the output voltage $U_M(t)$ of the force sensor into a force signal $F(t)$ is done using the calibration function. The parameters of the calibration function (regression line) may be assumed to be without error. $F(t)$ is plotted and the maximum force F_g before the lamella breaks off is read. Fig. 8 shows a typical course of $F(t)$. For reading off the maximum force, the Origin-Tool „Data Reader“⁹ can be used.

The measurement is carried out at least 5 times. One exemplary force curve is enclosed with the report. The surface tension σ of water is calculated for every measured value of F_g by means of Eqs. (7) to (11). An error statement for the individual values of σ is not required. The density ρ of water, needed calculate the correction factor (Eq. (10)) is given in Appendix 4.1 as a function of temperature.

Finally, both the mean of σ and its standard deviation are calculated and compared to the value for water given in the literature (Eq. (18) in appendix 4.2).

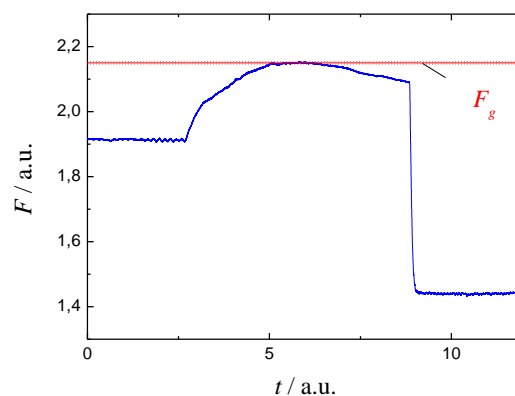



Fig. 8: Exemplary course of the force F as function of time t during the measurement of the surface tension with the breaking-off method. F_g is the maximum force before the lamella breaks off. The dotted red lines mark the range of the maximum error $\pm \Delta F_g$ of F_g , which is determined by the noise of the force sensor's signal. "a.u." stands for *arbitrary units*.

⁷ Output of the measurement amplifier connected to the BNC jack of input channel AI 0 or AI 1; AGND switch next to the BNC connector is off.

⁸ Value according to <http://www.ptb.de/cartoweb3/SISproject.php> (15.10.18); the error of $2 \times 10^{-5} \text{ m/s}^2$ is neglected.

⁹ The graphic symbol of the tool Data Reader is 

3.4 Measurement of the Surface Tension Using the Bubble Pressure Method

The surface tension of distilled water against air is to be measured by means of the experimental set-up according to Fig. 4. The U-tube of the manometer is filled with water, to which some drops of a detergent are added for better wetting the U-tube. The beaker glass B has been already cleaned by the technical assistance and filled with distilled water to 1 cm below its upper edge. The temperature of the water is measured. Before the measurement the thermometer must be cleaned (as described in chapter 3.3).

The capillary is fixed in its mount, adjusted vertically, and dipped into the distilled water using the unit for vertical adjustment ($h \approx 30$ mm). The position of the vertical adjustment, at which the capillary tube is just dipped into the liquid can be determined with an accuracy of ± 0.05 mm by simultaneously observing the capillary outlet and its image mirrored by the water, so that the immersion depth h can be adjusted with the same accuracy.

Hint:

Prior to the experiment the capillary tube was cleaned with ethanol, then rinsed in distilled water and dried in a stream of nitrogen. The metal area must not be touched with bare hands in order to avoid grease and sweat traces which would falsify the measuring results. Therefore, touch the capillary tube only at the upper PVC holder!

At first the pressure sensor is calibrated. This is done following the same procedure used in the experiments “Sensors...” and “Data Acquisition and Processing with the PC...”. During the calibration the tap between the ERLLENMEYER flask E and the capillary is closed, the tap to the U-tube manometer is opened. For at least five height differences h_m in the manometer in the range of (0 – 80) mm the output voltage U of the pressure sensor is measured, the pressure $p(h_m)$ is calculated, p is plotted over U , and the parameters of the regression line are calculated.

The measurement of the output voltage of the sensor is carried out in the same manner as done in the breaking off method (chapter 3.3) by means of a DAQ device and a PC using the MATLAB-script `DatenEinlesen.m`.

After completion of the calibration the tap to the U-tube manometer is closed and the one to the capillary is opened. The scissor jack S below the storage vessel V is then raised slowly and carefully (if possible no jerks), until the gas bubbles breakoff from the capillary outlet. During this process the output voltage of the sensor is recorded with a sampling rate of 1 kHz. Also in this measurement the number of recorded measurement values depends on the duration of the experiment. 20.000 measurement values (corresponding to 20 s) are a good choice to start.

After completing the data acquisition the data is stored in ASCII format (Button Save Data) and imported into Origin. There the conversion of the output voltage $U(t)$ of the pressure sensor into a pressure signal $p(t)$ is done using the calibration function. The parameters of the calibration function (regression line) may be assumed exact (error free) for this purpose. $p(t)$ is plotted and the maximum pressure p_m just before the first bubble breaks off is read. Fig. 9 shows a typical course of $p(t)$. For reading the maximum pressure the Origin-Tool „Data Reader“ can be used.

The measurement is carried out at least five times. One exemplary pressure curve is enclosed with the report. The mean \bar{p}_m , and its standard deviation are calculated from the data for p_m . From \bar{p}_m , the immersion depth h and the literature data for g and ρ the overpressure Δp including maximum error is determined by Eq. (13):

$$(16) \quad \Delta p = (\rho_m h_m - \rho h) g = \bar{p}_m - \rho h g$$

ρ is calculated by means of Eq. (17) (Appendix 4.1) and is assumed to be exact. For g , the value for Oldenburg is used: $g = 9.8133$ m/s²; it may also be taken as an exact value. Thus, the only values determining the maximum error of the pressure difference Δp are the maximum error Δh of h and the standard deviation of \bar{p}_m .

Finally, the surface tension σ is calculated according to Eq. (14). The error of σ is determined with the aid of the approximation solution given in Eq. (15). The result is compared with the data stated in the literature (Eq. (18)) as well as with the results obtained by means of the breaking-off method.

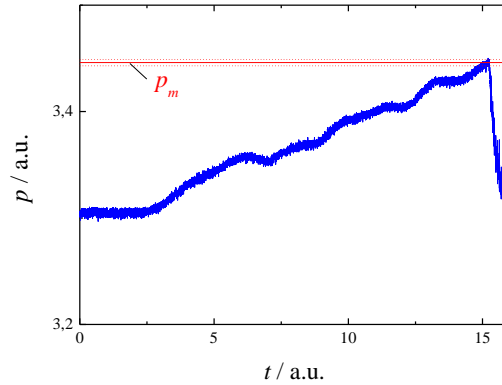


Fig. 9: Exemplary course of the pressure p as function of time t during the measurement of the surface tension using the bubble pressure method. p_m is the maximum pressure before the bubbles break off. The dotted red line indicates the interval of the maximum error $\pm \Delta p_m$ of p_m , caused by the noise of the signal from the pressure sensor. The waviness of the rise in pressure is caused by non-uniform raise of the scissor jack.

3.5 Interior Pressure in Gas Bubbles

A glass tube stand like the one in Fig. 10 is dipped into soap suds with both outlets and then taken out. By aeration at the inlets and by appropriately opening and closing the cocks at the two outlets, two different sized soap bubbles can be created. Subsequently the connecting cock between both bubbles is opened.

Question 1:

- Which bubble grows at the cost of the other one and why? (Hint: Note Eq. (15)).
- How high is the interior pressure p in gas bubble with the radius r , surrounded by a soap-suds lamella (surface tension of the soap solution: σ)?¹⁰

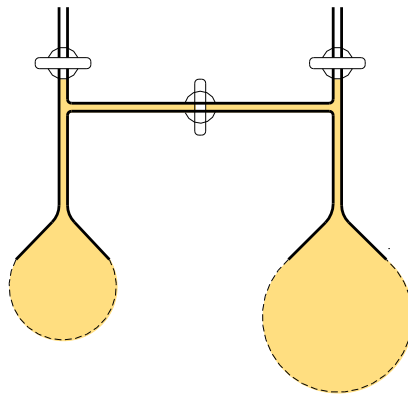


Fig. 10: Glass tube stand for demonstration of the interior pressure in gas bubbles.

4 Appendix

4.1 Density of Water

The temperature dependence of the density ρ of water can be described by the following polynomial (T in $^{\circ}\text{C}$, range of validity: $-20^{\circ}\text{C} < T < 110^{\circ}\text{C}$)¹¹:

$$(17) \quad \rho = 10^3 \cdot \left(\begin{array}{l} 0,99975 + 8,42492 \cdot 10^{-5} \{T\} - 8,82693 \cdot 10^{-6} \{T\}^2 \\ + 5,91004 \cdot 10^{-8} \{T\}^3 - 2,05642 \cdot 10^{-10} \{T\}^4 \end{array} \right) \frac{\text{kg}}{\text{m}^3}$$

¹⁰ Hint: For an air bubble in water there is *one* interface between air and water. For a soap bubble there are *two* interfaces between the soapsuds and air.

¹¹ Polynomial fit to data from WEAST, R. C. [Ed.]: „CRC Handbook of Chemistry and Physics“, 56th Ed., CRC Press, Boca Raton; errors negligible.

The graph of this function is shown in Fig. 11.

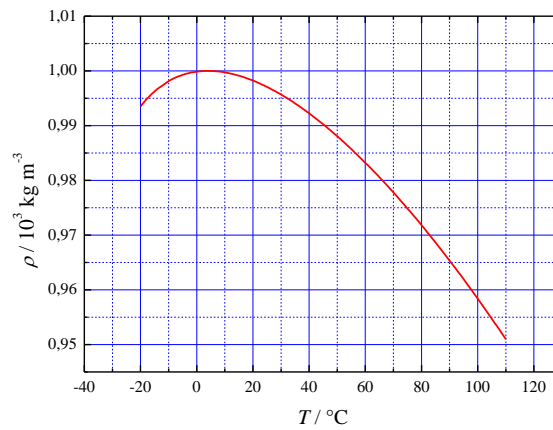


Fig. 11: Density of water as a function of temperature.

4.2 Surface Tension of Water

The temperature dependence of the surface tension σ of water against air can be described by the following polynomial (T in °C, validity range: $0^\circ\text{C} < T < 100^\circ\text{C}$)¹¹:

$$(18) \quad \sigma = \left(\begin{array}{l} 0,07569 - 1,49944 \cdot 10^{-4} \{T\} + 1,97712 \cdot 10^{-7} \{T\}^2 \\ - 8,34217 \cdot 10^{-9} \{T\}^3 + 4,57847 \cdot 10^{-11} \{T\}^4 \end{array} \right) \frac{\text{N}}{\text{m}}$$

The graph of this function is shown in Fig. 12.

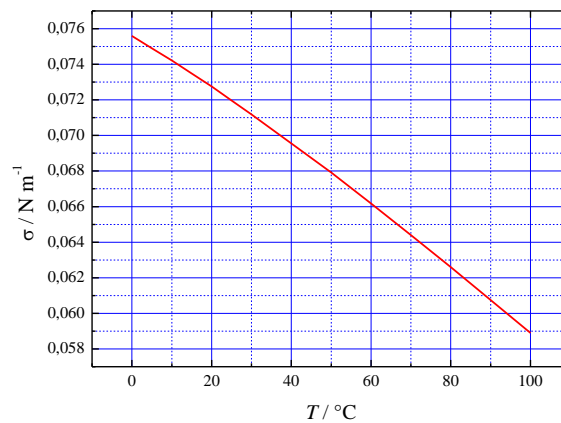


Fig. 12: Surface tension σ of water against air as a function of temperature T .