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Some notes on surface tension measurements of supercooled water

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Abstract. The number of methods for the surface tension measurement of liquid in the supercooled state is limited. The capillary elevation method operates with a very small volume of liquid, which enables to measure below the freezing point. The height of the water column in the capillary is growing when the temperature is decreasing. In order to increase the precision of measurement, it is necessary to use a capillary of a very small inner diameter. But the smaller the diameter is, the longer time to reach the steady (stabilized) state of the liquid column in the capillary is necessary. This paper brings a theoretical approach to the velocity of motion of the liquid column in the capillary to the stable position in dependence on the capillary inner diameter. Theoretical results are compared with experimental data with water.

1 Introduction

The surface tension of supercooled water is a property important for a chemical and biological research or for an exploration of atmospheric phenomena. For instance, the surface tension at the interface between liquid and ice influences the formation of ice on aircrafts. The surface tension between a vapor and liquid phase is important for modeling of precipitation forming in clouds. The surface tension of supercooled water was measured in several experiments [1-10].

In our experiments [6, 8, 10], the surface tension of supercooled demineralized water in a liquid state was measured using the elevation capillary method. Glass capillaries with an inner diameter from 0.35 mm to 0.20 mm were used. From the equilibrium between the gravity force of the liquid of the density ρ in the capillary with the inner diameter d

$$F_g = \rho\, g\, H \frac{\pi\, d^2}{4} \qquad (1)$$

and the force caused by surface tension

$$F_\sigma = \pi d \sigma \cos\theta \qquad (2)$$

the surface tension σ is

$$\sigma = \frac{\rho\, g\, d}{4\cos\theta} H\,, \qquad (3)$$

where H is a height of the liquid in the capillary in an equilibrium state and θ is the contact angle of the meniscus. The angle θ is assumed to be zero if the inner surface of the capillary is carefully cleaned.

The result from equation (3) is that to increase a precision of experimental results it is necessary to use capillaries of a very small inner diameter. But it has its own limitations. One of it is the time that is necessary to reach a steady state of the meniscus in the capillary, i.e. relaxation time. The smaller the diameter is, the longer time we should wait for the column of liquid in the capillary to stabilize. The capillary of the inner diameter 0.05 mm was initially also considered to be used for surface tension measurements. But it was experimentally found out that it would be very difficult because of a very long relaxation time. Therefore we tried to derive a mathematical description of the velocity of the motion of the liquid column in the capillary, and consequently we derive an expression for the necessary time for the meniscus to fall from one position to another.

2 Experimental stand

All experiments were processed at ambient temperature and ambient pressure in the laboratory. The upper end of the capillary was tightly fixed in a short cylindrical vessel with a tight plug and a hose connected to an evacuating pump. It enabled to lift up the liquid in the capillary in order to get out possible bubbles from the capillary and also to suck acid in the capillary when it is necessary to clean its inner surface. During the measurements it is also necessary to move the liquid in the capillary a bit up and down to assure a smooth motion of the liquid in the capillary. The lower end of the capillary was immersed down to the vessel with the liquid. The cover of this

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vessel has a small leakage to assure the act of the ambient pressure at the surface of the liquid in this vessel. The lay-out of the arrangement is shown in figure 1. The details of the upper and lower vessels are given in figure 2 and figure 3.

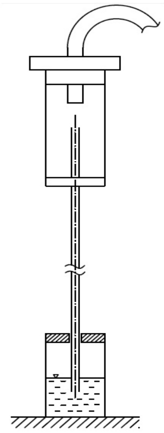

Figure 1. The lay-out of the capillary with the vessels.

Figure 2. The upper vessel with the fixed capillary.

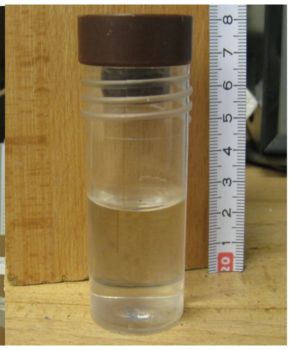

Figure 3. The lower vessel with the immersed capillary.

The change of the meniscus position was measured using the cathetometer Lomo KM-6 with an accuracy of 0.01 mm. The cathetometer is shown in figure 4. Time at which the meniscus was passing the predetermined positions was registered with a digital stop-watch.

3 Experimental method

All measurements of the surface tension were always made with a descending meniscus, similarly as it is written in [2]. Instead of overpressure in the lower vessel we applied depression in the upper vessel. The similar method was used also when we measured the relaxation time. The column of liquid was moved to a position a few millimeters higher than the equilibrium position, to the position marked with letter A at figure 5. After opening the hose to the atmosphere the meniscus started to fall to the equilibrium position marked as E.

When the meniscus appeared in the preselected positions, the corresponding time was registered. With capillaries of the inner diameter 0.2 mm and 0.3 mm it was easy to find also the equilibrium position. But it was difficult with a capillary of a diameter 0.05 mm. The velocity of the meniscus was very low and the experimentally located equilibrium state is doubtful. Its experimentally determined position could be also influenced by many factors that can appear during a very long relaxation time.

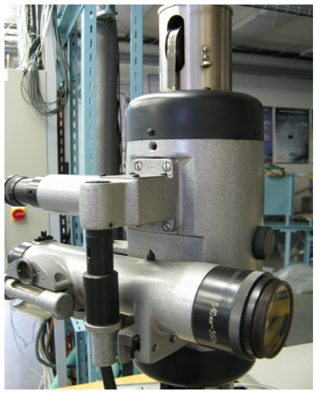

Figure 4. Lomo KM-6 cathetometer.

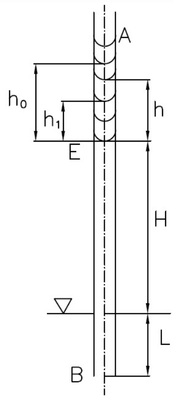

Figure 5. Capillary with the dimensioning.

4 Mathematical modelling

The velocity of the liquid motion in the capillary is very small. Therefore we tried to apply the laminar flow hypothesis.

Applying the equation of a specific energy conservation between positions A and B (figure 5) at the capillary we get

$$g(h+H+L)+\frac{p_0}{\rho}+\frac{w^2}{2}-gH = \\ =\frac{p_0+\rho\, g\, L}{\rho}+\frac{w^2}{2}+\zeta\,\frac{w^2}{2}\,. \tag{4}$$

The term $(-g\,H)$ on the left side of the equation (4) represents the specific energy done by the surface tension at the equilibrium position of the meniscus. The last term on the right side of the equation (4) represents the specific energy losses caused by a friction inside the liquid. For the laminar flow it is expressed as

$$\zeta=\lambda\,\frac{l}{d}\;=\frac{64}{\mathrm{Re}}\,\frac{l}{d}\;, \tag{5}$$

where l stands for the total length of the tube filled with liquid, d means its diameter. In our case the length is

$$l = h + H + L \,. \tag{6}$$

The Reynolds number for the flow inside the tube with liquid is defined by the expression

$$\mathrm{Re} = \frac{wd}{\nu}\,, \tag{7}$$

where w stands for the mean velocity and ν stands for the kinematic viscosity coefficient of the liquid.

Substituting equations (5) and (7) to the equation (4) we get

$$g\,h = \frac{64\,\nu}{w\,d}\left(h + H + L\right)\frac{w^2}{2}\,. \tag{8}$$

And finally for the velocity we get

$$w = \frac{g\,h\,d^2}{32\,\nu\left(h + H + L\right)}\,. \tag{9}$$

In an elemntary interval dt the column of the liquid falls by elemntary lenght dh. It could be expressed as

$$-\,\mathrm{d}h = w\,\mathrm{d}t\,. \tag{10}$$

Then the time of the meniscus falling from the position h_0 to h_1 (figure 5) could be derived by integrating

$$t_{01} = -\int_{h_0}^{h_1}\frac{\mathrm{d}h}{\mathrm{w}}\,. \tag{11}$$

Using the equation (9) we get

$$t_{01} = \frac{32\,\nu}{g\,d^2}\left[\left(h_0 - h_1\right) + \left(H + L\right)\ln\frac{h_0}{h_1}\right]. \tag{12}$$

It should be noted that this equation was derived for the time of the meniscus motion from the position h_0 over the equilibrium position E to the position h_1 that is also situated over the equilibrium position E. Taking this rule in account we can calculate the time corresponding to the motion of the meniscus between any two positions.

5 Results of measurements

5.1 Measurements with capillary d = 0.2 mm

Our measurements were carried out at the temperature $t = 24$˚C. The value of the surface tension at this temperature was interpolated from tables [11]. It is $\sigma = 72.15\ 10^{-3}$ N/m. The lengths were measured and they are $H = 136.05$ mm and $L = 28$ mm. The inner diameter of the capillary can be calculated from the equation (3). The results are shown in Table 1.

Table 1. Measured and calculated time for the meniscus falling.

Position	Measured data [mm]	Measured time [s]	Calculated time [s]
h_0	6.68	0	0
h_1	3.57	7.15	6.71
h_2	0.89	23.03	21.32
Close to E	Stated 0.01	-	68.04

It is possible to conclude that a good agreement was achieved between calculated values and measured data. The second finding is that the time necessary for the quasi-equilibrium state (0.01 mm over equilibrium point) is longer than one minute with the examined capillary of the inner diameter of about 0.2 mm as it was calculated from the equation (12).

5.2 Measurements with capillary d = 0.05 mm

Measurements with such a thin capillary were performed to find an estimated necessary time for reaching the quasi-equilibrium state (0.01 mm over equilibrium point) and also to verify calculated values. They were compared with the measured data. The result is shown in figure 6.

Calculated time necessary to reach the mentioned quasi-equilibrium state from the position 10 mm over the equilibrium state takes 4482 seconds, i.e. one hour and 15 minutes. From the position 3 mm over the equilibrium state it takes one hour.

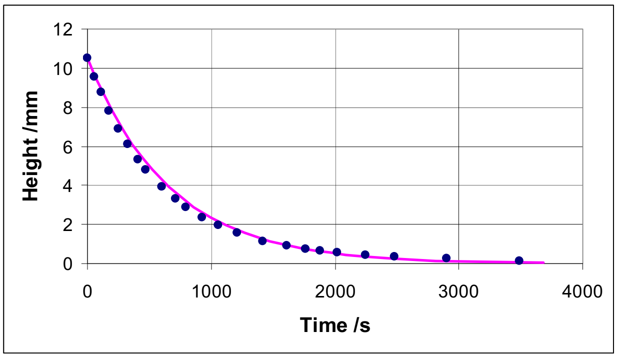

Figure 6. Capillary d = 0.05 mm, experimental data (circles) and calculated (line).

To shorten the time necessary for the attainment of the equilibrium state of the liquid column in the capillary, it can be achieved using the thin capillary in the measuring chamber only. Below the measuring chamber this capillary should be extended with a pipe of a larger diameter. But it requires a reconstruction of the experimental stand.

6 Discussions

6.1 Application of the Hagen-Poiseuille equation

Floriano and Angel [2] also measured the surface tension of water and they wrote: "With the very small diameter tubing, results were irreproducible because the movement of the meniscus in the long columns supported in the case of small-diameter tubings was very sluggish (partly because of the r^{-4} dependence of the Poiseuille flow times and partly for reasons unknown)."

This affirmation is correct with one exception, which is that the exponent should be -2 and not -4. It will be proven below.

The Poiseuille equation for the volumetric flow rate is

$$Q = \frac{\pi r^4 \Delta p}{8 \eta \Delta l} . \quad (13)$$

Here Δp is the pressure loss, Δl is the length of the pipe in which is liquid, and η is the dynamic viscosity coefficient.

The mean volumetric velocity is

$$w = \frac{Q}{\pi r^2} = \frac{r^2 \Delta p}{8 \eta \Delta l} . \quad (14)$$

The coefficient of the kinematic viscosity is defined as

$$\nu = \frac{\eta}{\rho} . \quad (15)$$

Then the expression for the velocity is

$$w = \frac{d^2 \Delta p}{32 \nu \rho \Delta l} . \quad (16)$$

The pressure increment caused by the vertical liquid column of the height h is

$$\Delta p = \rho g h . \quad (17)$$

Then the velocity is given as

$$w = \frac{g h d^2}{32 \nu \Delta l} . \quad (18)$$

The equation (18) is identical with the equation (9) considering that in our experiment is $\Delta l = h + H + L$.

6.2 Determination of the equilibrium state from experimental data

During the measurements of the surface tension of liquid each experimental data should be reached at the equilibrium state. The closer to the equilibrium state the meniscus is, the slower is its velocity. Therefore the experimental determination of the relaxation time is difficult particularly with a capillary of a very small diameter. It will be easier to determine an approximate position of the equilibrium point E from the measured distance between the positions of the meniscus h_0, h_1 and the corresponding time interval t_{01}. Using substitutions

$$h_1 = x, \quad h_0 = \Delta h + x , \quad (19)$$

the equation (12) becomes

$$t_{01} = \frac{32 \nu}{g d^2} \left[\Delta h + (H + L) \ln \frac{\Delta h + x}{x} \right] . \quad (20)$$

We can also observe that the relaxation time according to the equation (12) and also (20) is infinite.

7 Conclusions

A very long relaxation time was experimentally found out in an attempt to use a capillary of a very small diameter for the measurement of the surface tension by a so-called capillary elevation method. Then it was decided to analyze the motion of a liquid column in a vertical capillary and to find a functionality of the time necessary for the attainment of the equilibrium state of the liquid column in the capillary. On the assumption that the flow of the liquid in the capillary is laminar it was derived that that time is inversely proportional to the square of the capillary diameter. This result was checked with experimental data. A very good agreement was obtained. It was proven that it will be unrealistic to use capillaries of extremely small diameters constant over the entire length.

It was also shown how to calculate the equilibrium position of the meniscus from two positions of the descending meniscus and the corresponding time interval and how to calculate the relaxation time.

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