Measurement of the surface tension utilizing high-precision MEMS

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The surface tension of different liquids was successfully measured utilizing a high-precision microprobe. It is shown that surface tension can be measured at high repeatability (± 0.25 mN/m) and at a remarkable absolute accuracy higher than 95% over a broad range of liquids in comparison to literature values. Due to the very small and compact dimensions of the measurement system, only small sample volumes ($\ll$ 10 µl) are required. The measurement is carried out by fully automated measurement system utilizing a positioning system based on a step motor and a microcontroller.

1. Introduction

The measurement of the surface tension of liquids is getting more important, since it can be used to indirectly measure the purity, investigate adsorption processes at interface or monitor ageing phenomena[1].

Demands on modern tensiometers are[2]:

- high absolute and repeatability accuracy;
- short measurement time;
- fully automated and cost-effective measurement system;
- broad measurement range.

One main group of measurement systems determine the surface tension by means of a force measurement. In that case, the force is exerted on geometrically well-defined test objects such as plates, rings or rods. The crucial advantages are the simple measurement systems and their cost-efficiency. One disadvantage is that the minimum volume of required liquid is dependent on the dimensions of the test object. Thus, it is necessary to minimize the size of the test object if tiny sample volumes are to be investigated. For macroscopic systems this requirement is contradictory to the demand of a high accuracy because the wetting force decreases with decreasing dimensions of the test object.

We present a MEMS tensiometer featuring a miniaturized cylindrical probe tip[3]. Due to the small size of the probe tip even smallest amounts of liquids ($\ll 10$ µl) are sufficient to determine their surface tension. At the same time, small forces ($\ll 1\mu N$) can be detected at remarkable accuracy. The decrease in size of the test object does not lead to a loss of accuracy. This provides the opportunity to examine interesting surface physics on the micro scale. For example, the dependency of the surface tension on the droplet size can be investigated which can only be observed for very small droplets[4]. Additionally, the utilization of standardized micromachining processes keeps the overall system simple and cost-effective.

2. Design and characteristics of the MEMS tensiometer

For surface tension measurements, a uniaxial microprobe is utilized. This microprobe is an electrostatic MEMS actuator that comprises passive suspension consisting of four serpentine springs, two differentially evaluated electrostatic sensors and a stylus. At the tip of the stylus a small rod made of platinum/iridium is mounted by gluing (Fig. 1). All parts of the microprobe are integrated in a shared silicon-on-insulator (SOI) substrate. Therefore, the number of expensive assembling and packaging processes can be minimized, and the number of soft coupling elements such as joints or glues is reduced to a minimum.

The stiffness of the suspension differs in the single cartesian directions. A low stiffness is provided for the main deflection direction parallel to the stylus (z-direction). The stiffness of the

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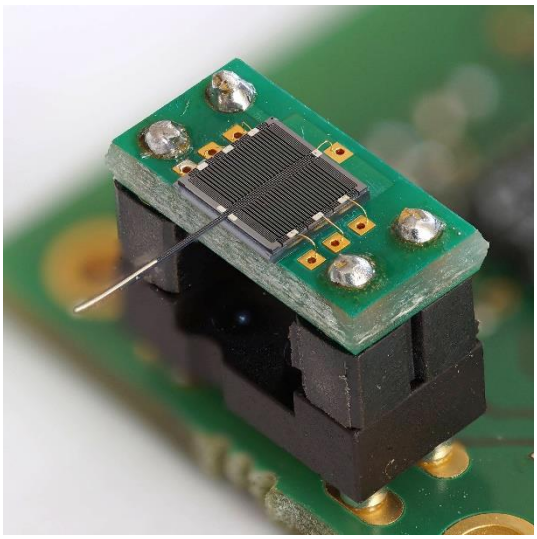

Fig. 1: Microprobe mounted on a dip socket for easy exchange; the attached platinum/iridium rod has a length of approximately $L = 3\ mm$ and a radius of $R = 50\ \mu m$

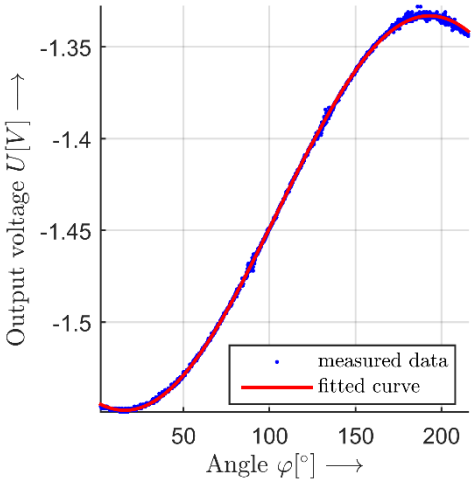

Fig. 2: Measurement data and the fitted curve $U(\varphi) = a \cdot cos(b \cdot \varphi + c) + d$ for the determination of the proportionality factor c_U; the determined coefficients are: $a = -0.1075\ V, b = 1.0148, c = -15.9723°, d = -1.4405\ V$

springs in x- and y-direction is much higher, respectively. Therefore, the deflection can be regarded as purely parallel to the z-direction.

Details regarding the manufacturing process and the evaluation electronic can be found in references [5-7].

The overall stiffness of the springs in z-direction was determined by the shift of the resonance frequency caused by the attachment of the platinum/iridium rod. For this purpose, the amplitude-frequency characteristic of the microprobe with and without the glued rod was measured. The resonance frequency without the rod $f_{r,1} = 1180\ \mathrm{Hz}$ and the frequency with the attached rod $f_{r,2} = 820\ \mathrm{Hz}$ was determined. With the overall mass change Δm the stiffness k is calculated by:

$$k = \left(2\pi f_{\mathrm{r},2}\right)^2 \cdot \frac{\Delta m}{\left(\frac{f_{\mathrm{r},2}}{f_{\mathrm{r},1}}\right)^2 - 1} \qquad (1)$$

The mass change is equal to the sum of the masses of the glue m_G and the attached rod m_R. The mass of the applied glue was neglected. This leads to an underestimation of the mass change Δm and thus the stiffness k. However, the induced error is small due to the small amount of applied glue and the significant difference between the density of the glue and the platinum/iridium rod. The length $L = 3\ \mathrm{mm}$ and the radius $R = 50\ \mu\mathrm{m}$ are determined from microscopic images (Fig. 1) in order to calculate the mass of the rod. The mass m_R is calculated by $m_\mathrm{R} = \pi R^2 L \cdot \rho_\mathrm{R}$ where $\rho_\mathrm{R} = 21560\ \mathrm{kg/m^3}$ is the density of the platinum/iridium rod[8]. This leads to a mass of $m_\mathrm{R} = 0.5080\ \mathrm{mg}$. The resulting stiffness is $k = 27.345\ \mathrm{N/m}$. Finally, the mass of the microprobe m_P without the attached rod can be calculated to be $m_\mathrm{P} = \frac{k}{\left(2\pi f_{r,1}\right)^2} = 0.4975\ \mathrm{mg}$.

In addition to the stiffness k the proportional factor c_U between the sensor output voltage U and the microprobe deflection must be known to determine the arising forces. This parameter is determined by measuring the deflection of the probe due to gravitational forces. For this purpose, the microprobe is mounted on a rotatable device, and the output voltage U is measured as a function of the angle φ between the stylus and direction of the gravitational force. The rotation was achieved using a stepper motor with an angular resolution of 1.8° per step. The resulting cosinusoidal function is fitted by

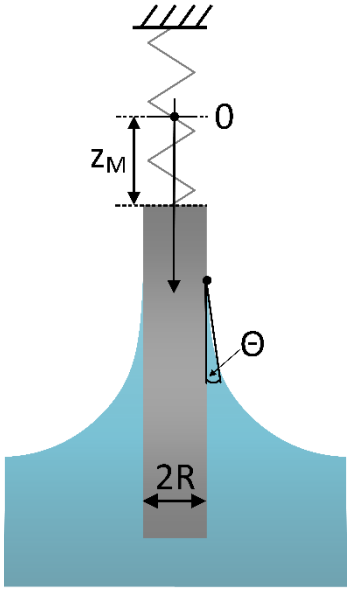

Fig. 3: Schematic side view of the platinum rod at the tip of the microprobe immersed in a test liquid

$U(\varphi) = a \cdot \cos(b \cdot \varphi + c) + d$, where a, b, c and d are fit parameters. The parameter c_U is calculated with the overall mass of the microprobe $m = m_P + m_R = 0{,}1006\ \mathrm{mg}$, the stiffness k and the fit parameter a:

$$c_U = \frac{m \cdot g}{k} \cdot \left|\frac{1}{a}\right| \tag{2}$$

An example of measured and fitted curve is shown in Fig. 2. The measurement was repeated six times, and the calculated values of c_U for each measurement were averaged. The resulting value is $c_U = 3.389\ \frac{\mu m}{V}$. Afterwards, the force can simply be calculated:

$$F = k \cdot z_M = k \cdot c_U \cdot U \tag{3}$$

where z_M is the deflection of the microprobe.

3. Physical background of surface tension measurement

Surface tension as physical quantity can be interpreted either as energy per unit area or as force per unit length. As a consequence, numerous different measurement methods were developed. One main group of methods determines the surface tension of liquids indirectly via a measurement of the force due to wetting at a test object. Most widely known methods are the Wilhelmy plate[9], the Du-Noüy ring[10] and the Du-Noüy-Padday[11] method. The method described here is a variation of the Wilhelmy plate method combined with the Du-Noüy-Padday method: A thin platinum rod is utilized as test object that is fixed at the tip of the microprobe. The rod is immersed into the solution perpendicular to the liquid surface. The force due to wetting F_W acting vertically on the microprobe (see Fig. 3) is calculated by[9]:

$$F_W = \gamma_{lv} \cdot L_W \cdot \cos(\Theta) \tag{4}$$

where γ_{lv} denotes the interfacial tension between the liquid and the surrounding medium, L_W denotes the length of the wetted perimeter of the rod and Θ is the contact angle between the platinum rod and the liquid. The length L_W is given by $L_W = 2\pi \cdot R$ where R is the radius of the rod. In equilibrium, the wetting force is compensated by the force F_S resulting from the deflection of the springs of the microprobe and the force F_b due to buoyancy. The force equilibrium is therefore written as:

$$\begin{aligned} F_W = \gamma_{lv} \cdot 2\pi \cdot R \cdot \cos(\Theta) &= F_S + F_b \\ &= k \cdot z_M + \rho_F \cdot g \cdot V \end{aligned} \tag{5}$$

where ρ_F is the density of the liquid, $g \simeq 9.8107\ \mathrm{m/s^2}$ is the constant of acceleration due to gravity and V is the volume of liquid displaced by the platinum rod. The exact value of the force due to buoyancy is hard to measure because the immersion depth is unknown. One possibility to avoid an error due to buoyancy is to slowly withdraw the rod from the liquid and simultaneous measure the deflection of the microprobe. At a specific height no volume is displaced by the rod and the force due to buoyancy vanishes. This is noticeable as a maximum in the force deflection curve. This procedure is known

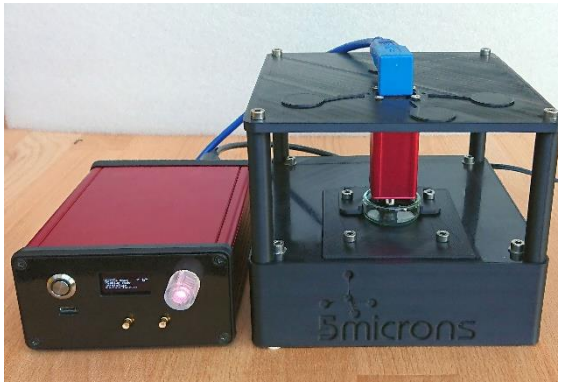

Fig. 4: Measurement system for the determination of surface tension

as the Du-Noüy-Padday method. Therefore, the interfacial tension γ_{lv} is given by:

$$\gamma_{\mathrm{lv}} = \frac{F_{\max}}{2\pi \cdot R \cdot \cos(\Theta)} = \frac{k \cdot \Delta z_{\mathrm{M}}}{2\pi \cdot R \cdot \cos(\Theta)} = \frac{k \cdot c_{\mathrm{U}} \cdot \Delta U_{\mathrm{M}}}{2\pi \cdot R \cdot \cos(\Theta)} \quad (6)$$

where $F_{\max}$ is the maximum force, Δz_{M} is the maximum deflection of the microprobe and $\Delta \mathrm{U_M}$ is the corresponding sensor output voltage. The error due to neglection of buoyancy is small because of the favorable scaling of the forces, for example: If a rod with a radius of $50\ \mu\mathrm{m}$ is immersed $1\ \mathrm{mm}$ in water $\left(\rho = 1000\,\frac{\mathrm{kg}}{\mathrm{m}^3}, \gamma_{\mathrm{lv}} \cong 0{,}072\,\frac{\mathrm{N}}{\mathrm{m}}\right)$, buoyancy is in the order of $F_{\mathrm{B}} \simeq 80\ \mathrm{nN}$ whereas the wetting force is in the order of $F_{\mathrm{W}} \simeq 23\ \mu\mathrm{N}$. The error resulting from buoyancy neglection is much smaller than $1\ \%$. Thus, the microprobe can also be considered similar to a Wilhelmy plate and equation (4) is still valid.

Equation (3) shows that the measurement of surface tension γ_{lv} generally requires the simultaneous measurement of the contact angle Θ. This can be circumvented by utilizing a test object made of a material featuring a high free surface energy, thus enforcing nearly perfect wetting and therefore a contact angle $\Theta \cong 0° \rightarrow \cos\Theta = 1$. Hence, a platinum/iridium rod (90/10) is fixed on the microprobe.

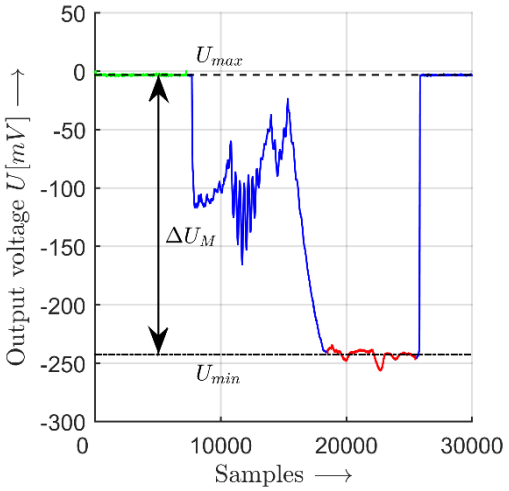

Fig. 5: Blue curve shows measured values of the output voltage U during one measurement for DI water; green/red dots show the used values for the calculation of U_{max}/ U_{min} due averaging

4. Measurement System

For surface tension measurements, the platinum/iridium rod is immersed into the liquid and slowly retracted afterwards. Simultaneously, the output voltage of the electrostatic sensors is captured. Accordingly, the measurement system comprises a positioning system, an electronic evaluation unit and a user interface (cf. Fig. 4). An additional temperature sensor is integrated to determine the temperature of the liquid. For positioning, a stepper motor is mounted on a linear stage that moves the liquid reservoir up and down ($\approx 70\ \mathrm{nm}$ per step). The mechanical system is housed in a 3D-printed case together with the control unit for the stepper motor, the mount for the microprobe and the temperature sensor. The electronics assembly and the user interface are housed in a second case. Stepper motor control and sensor voltage evaluation is carried out utilizing a *Teensy 3.2* microcontroller. The respective parameters can be adjusted, the measurement can be started, and the results are displayed either directly via an integrated user interface or utilizing an additional Java program on an external PC. An LCD display and a control

knob are integrated in the electronic case as direct user interface. Thus, no PC or additional hardware is needed to perform a measurement. Retracting speed, immersion depth of the rod and the number of measurement cycles need to be specified as measurement parameter, only. After a measurement is started, the stepper motor slowly lifts the liquid reservoir beneath the probe tip until a deflection of the microprobe of approximately $50\ \mathrm{nm}$ is detected. Thus, the location of the liquid surface is found automatically. Afterwards, the reservoir is lowered by a fixed distance. This position serves as initial position for the actual measurement and for sampling of sensor voltage and stepper motor position. At the next step, the reservoir is lifted again until the specified immersion depth is reached. After a small rest in this position, the reservoir is lowered at specified speed until the initial position is reached again. This hole procedure is repeated for the user specified number of repetitions. This means that the location of the liquid surface is determined during each single measurement. The advantage of this procedure is that the conditions for each measurement are kept equal, especially in terms of the immersion depth, even for rapidly evaporating liquids.

5. Results

Liquid	***Mean value*** $\bar{\gamma}_{\mathrm{lv}}\ \left[\frac{\mathrm{mN}}{\mathrm{m}}\right]$	***Literature*** $\gamma_{\mathrm{lv}}\ \left[\frac{\mathrm{mN}}{\mathrm{m}}\right]$	***Error*** [%]
DI water	70.53 ± 0.2	71.80 @ 26 °C[12]	1.80
Isopropyl alcohol	20.99 ± 0.1	20.85 @ 26°C[13]	0.67
Propylene carbonate	42.07 ± 0.05	40.5 @ 25 °C[14]	3.88

Tab. 1: Measurement results for investigated liquids

The previously described measurement procedure was performed for the three liquids: DI water, isopropyl alcohol ($\mathrm{C_3H_8O}$) and propylene carbonate ($\mathrm{C_4H_6O_3}$). Surface tension was measured twenty times for each liquid. The complete measurement time for all twenty measurements was approximately five minutes. For each measurement the minimum value of the voltage U_{min} was determined by averaging over a specific deflection range (see Fig. 5). Additional the values of U during the narrowing process of the reservoir were averaged resulting in a value U_{max}. Afterwards, the value for ΔU_{M} was calculated by $\Delta U = U_{\mathrm{max}} - U_{\mathrm{min}}$. Averaging ensures that the influence of vibrations or small defects on the platinum/iridium rod are minimized.

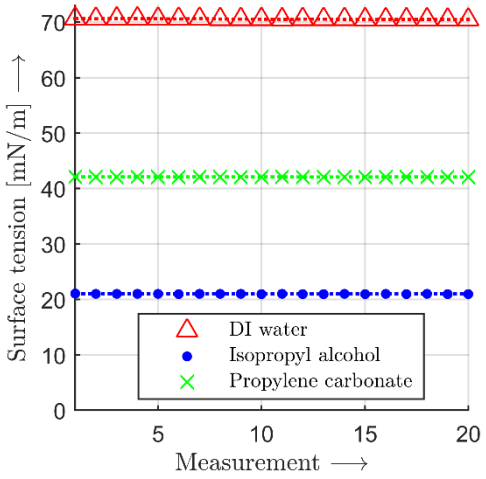

Fig. 6: Measurement results for the surface tension γ_{lv} of different liquids; the surface tension was determined twenty times consecutively for each liquid

The resulting values of γ_{lv} for each measurement liquid are shown in Fig. 6. The high repeatability accuracy of the presented tensiometer over the entire range of investigated surface tension values is proven. Additionally, the mean value of the twenty single measurements for each liquid was calculated. The resulting values for $\bar{\gamma}_{\mathrm{lv}}$ with maximum deviation, corresponding literature values and the errors are summarized in Table 1. The maximum deviation describes the difference between the maximum and the minimum value of γ_{lv} of all twenty measurements and is therefore calculated by $\max(\gamma_{\mathrm{lv},i}) - \min(\gamma_{\mathrm{lv},i})$ for each liquid. The small values for the maximum deviation demonstrate the high repeatability accuracy. Addition-

ally, it is shown that the measured surface tensions are in very good agreement with corresponding literature values. The absolute measurement error is smaller than 5% compared to the documented values. Discrepancies between the measured and the literature values are mainly caused by impurities of the liquids and shape deviations of the platinum/iridium rod. However, the reached absolute accuracy is comparable to state of the art tensiometers anyway.

6. Conclusion

A new tensiometer was presented utilizing a high-precision MEMS. The introduced system is applied to determine the surface tension in a fully automated procedure over a broad range of surface tension values. Surface tension measurements are in very good agreement with corresponding literature values. Additionally, it was proven that the repeatability accuracy is remarkably high. One main advantage of the presented system is that even smallest amount of liquids can be investigated.

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