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The surface tension of ultrapure water in its pure vapour

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Abstract

The surface tension of pure water has been measured for more than a century using a wide range of experimental techniques. Despite this long history, reported surface tension values are not always in agreement; instead, they are distributed over a wider range than would be expected based on the stated accuracies of individual measurements. This discrepancy suggests the presence of systematic effects, such as contamination, that may be responsible for the observed deviations. Another unresolved issue in this context is the explanation of the Jones–Ray effect; the decrease of the surface tension of water for low concentrations of added salt. While some researchers attribute this effect to surface-active impurities, others argue that it represents a fundamental property of water itself. To gain more insight into these questions, an ultra-high vacuum (UHV) system for surface tension measurements was built in the surface-science group at TU Wien. Pendant drop tensiometry was selected as the measurement technique because it doesn't require any correction factors to calculate the surface tension and is well suited for operation in a UHV system. The aim of this diploma project is to use this system to perform highly accurate surface tension measurements of ultra-pure water in its own vapour. To enhance measurement accuracy, pneumatic vibration isolators were installed and the optical system was calibrated. Surface tension measurements were conducted over a range of temperatures, and after carefully selecting the results from the most stable pendant drops, the measured surface tension was found to be approximately 0.25 mN/m higher than the value generated from historical data. This result could indicate a contamination with surfactants in many historical experiments and can provide new insights into the Jones-Ray effect.

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A. Ovivo certificate of analysis

1. Introduction

There are a great number of experiments that measure the surface tension of pure water using various methods in different temperature ranges. The individual data accuracies reported for these experiments are as low as $0.01 \text{ mN} \cdot \text{m}^{-1}$ and generally below $0.3 \text{ mN} \cdot \text{m}^{-1}$ [1]. However, the values of surface tension reported by different authors at the same temperature are spread over an interval of about $2 \text{ mN} \cdot \text{m}^{-1}$ [1]. This spread is much larger than the accuracy estimations would allow. This points towards some kind of systematic influence that causes the different results between the studies. Since the data originates from a variety of experiments with different methods, the most likely cause of this discrepancy is contamination. The surface tension of water is very sensitive to small amounts of surface active chemicals[2, 3]. The main sources of contamination in surface tension measurements are contamination from surfaces of the instrument, contamination of the water itself, and contamination from the air.

It is becoming clearer that contaminations play a large role in water interfacial phenomena. A prime example for this is the Jones-Ray effect. The Jones-Ray effect[4] is the observation that small concentrations of added salt seem to decrease the surface tension of water instead of increasing it, as larger concentrations do. There is much debate about the mechanism of this effect and it could be an artifact caused by trace contaminants or a fundamental property of water. Here more accurate surface tension measurements in a very clean system could provide some new insights.

Undertaking the experiment in an ultra-high vacuum (UHV) system allows the ambient contaminants to be completely removed from the experiment. Moreover, the thorough cleaning and baking procedures of the UHV chamber and equipment ensure that surface active contaminants such as detergents aren't present in the experiment. The method best suited for a UHV system is the pendant drop method. Here a drop of water is condensed on the tip of a coldfinger from its pure vapour, allowing the complete exclusion of contamination. An image of the drop is fitted to numerical solutions of the Young-Laplace equation to determine the surface tension.

The surface science group at TU Wien has been using a UHV system with a coldfinger to dose water onto single-crystal surfaces. After some successful tests on this system, an instrument dedicated to measuring the surface tension of ultra-pure water in its own vapour was built.

The goal of this diploma project was to use this UHV system to gather accurate and reproducible surface tension data of ultra-pure water in its own vapour at various temperatures ranging from 30 ° to below the freezing point. In order to do that the optical system was calibrated using a calibration ball and a optical grid. To improve the accuracy further the system was mechanically decoupled from the building with pneumatic vibration isolators.

We found that the measured surface tension value of ultra pure water in our system was consistently higher than the literature value when the most stable drops were selected. This may indicate the successful removal of contaminants in the UHV surface tension instrument. In turn, this is interesting because it might give more insight into the cause for the Jones-Ray effect which could be investigated further in our system.

2. Theory

2.1. Jones-Ray effect

The Jones-Ray effect was first reported by Jones and Ray in 1937 [4] when they were measuring the relative surface tension of aqueous solutions of potassium chloride, potassium sulfate, and cesium nitrates with a capillary rise method. In large concentrations, these salts increase the surface tension of the solution with an approximately linear relationship between the salt concentration and the relative surface tension. This was in agreement with the theory at the time [5]. Jones' and Ray's experiments showed that for small concentrations however, the presence of salts seems to decrease the relative surface tension of the solution with a minimum at 2 ± 1 mM. This effect has been confirmed multiple times with different methods, different salts and even for solutions in heavy water [6, 7, 8].

A possible explanation for the Jones-Ray effect is the presence of trace amounts of charged surface-active impurities. Uematsu et al. [2] created an exactly solvable mean field model based on ion-surface interactions that can simultaneously explain experimental surface tension data for salt, base and acid solutions. In this model it is assumed that charged surface-active impurities are present in the water. The accumulation of these impurities at the interface is limited by electrostatic repulsion. A low concentration of salt shields this electrostatic repulsion and therefore causes more impurities to accumulate on the surface which reduces the surface tension.

Another explanation is that the Jones-Ray effect is in fact a fundamental property of water that would also occur in 100% pure H_2O . Okur et al. [9] proposed that the Jones-Ray effect originates from bulk ion-induced water-water correlations. To test this they measured the surface tension of the solution with and without the purposeful addition of nanomolar concentrations of a negatively charged surfactant. The salt solution with the added surfactant had a lower surface tension than the pure salt solution, but after removing the surfactant via stirring and aspiration the surface tension value returned to the value of the pure solution. The Jones-Ray effect however persisted and the surface tension of the solution stayed below the surface tension of pure water, even after multiple stirring/ aspiration cycles.

To gain more insight into the mystery of the Jones-Ray effect surface tension measurements need a high relative accuracy and a very controlled environment free

of contaminants. Both of these requirements can hopefully be provided by our UHV system. While most modern surface tension measurements try to employ measures to reduce contamination as much as possible to this date no one has undertaken a pendant drop tensiometry experiment under such clean conditions.

2.2. Supercooled water

Due to its unique molecular structure water exhibits many anomalous thermodynamic phenomena [10]. Similar to the very well known density maximum at 4° other thermodynamic response functions such as the isothermal compressibility and the heat capacity show an anomalous behavior at low temperatures[11, 12] . The most prevalent hypothesis to explain these anomalies predicts a liquid–liquid phase transition [13]. The theory describes liquid water as a locally heterogeneous mixture of two different phases, low density liquid (LDL) and high density liquid (HDL) water. At the liquid–liquid critical point a phase transition to a metastable homogeneous phase is predicted. This phase transition has not been observed experimentally, because in most experimental settings the water will spontaneously nucleate and form ice before a sufficiently low temperature can be reached. Different molecular dynamics models predict different temperatures for this phase transition.

Similarly an anomalous behavior of the surface tension was also expected. This so called second inflection point (SIP) was originally measured in 1951 at -8° by Hacker [14]. Later experiments also showed a significant increase in surface tension at lower temperatures, but the temperature of the (possible) SIP was much lower than -8° [15].

With our system we could provide very clean surface tension measurements of supercooled water where it can be ensured that contaminations are removed as much as possible and the water is not in contact with the ambient air.

2.3. Methods to measure surface tension

There are various different methods to measure the surface tension of a liquid. The liquid has to be in a state where there is a balance between some external force (for example gravity or buoyancy) and the internal force of the liquid which is responsible for the surface tension. In force pull experiments this force can be measured directly, in other methods another physical quantity associated with that force is measured. The surface tension is then calculated from the measured quantity utilizing a formula including empirically determined correction factors that relate to the experimental setup. Therefore methods that need these corrections

are not very suitable to measure the absolute value of the surface tension, they can however provide very high relative accuracy. The pendant drop method is different as here the physical quantity that is measured is the profile of a pendant drop and there are no corrections needed once the optical system is calibrated. In the following I will go through the various methods to measure surface tension expanding on this idea. In the end, I will provide arguments for why the pendant drop tensiometry method was used for the measurements in this thesis.

2.3.1. Capillary rise

Classical

The classical capillary rise method [16] to measure surface tension makes use of the phenomenon of capillary action. When a vertical tube is placed in a liquid, the liquid will rise up into the capillary and form a meniscus. Depending on the balance of the cohesion of the liquid and the interfacial interaction on the inner surface of the capillary this meniscus can be concave or convex. The height of the liquid in the capillary is then directly proportional to the surface tension:

$$h = \frac{2\gamma \cos \theta}{\rho g r} \quad (2.1)$$

Where h is the height of the meniscus, γ is the surface tension of the liquid, θ is the contact angle between the liquid and the inside surface of the capillary, ρ is the density of the liquid, g is the gravitational acceleration and r is the inner radius of the capillary. For water in a glass capillary the contact angle can be assumed to be zero, but it can also be measured separately with an optical system to reduce errors in the surface tension measurement. Other possible sources of errors are deviations of the ideal geometry of the capillary and contamination from the contact with ambient air. Moreover, in using the height of the meniscus as the measurement of the hydrostatic pressure in the capillary, the contribution to the hydrostatic pressure from the liquid wetting (or de-wetting) the capillary tubes is excluded. This naturally leads to inaccuracies[17].

Counterpressure

The problem of a variation of the inner diameter along the capillary can be eliminated by using an inert gas to pressurize the open end of the capillary and keeping the meniscus at the same height. The surface tension can then be determined via the Young-Laplace equation for the meniscus by measuring the pressure needed to keep the meniscus at the same level. This method can reach a very good relative accuracy and is particularly well suited for the study of supercooled water. Another

advantage of the counterpressure capillary rise method is a shorter equilibration time and therefore a faster measurement.

This method has been used to study the surface tension and a (theoretical) second inflection point of supercooled water by Vins et al. [18, 15].

2.3.2. Force pull methods

Force pull methods are setups where a probe object of well defined geometrical proportions is dipped into the liquid to be investigated. The force exerted on the probe object is then measured by a precise scale. This can be done statically where a equilibrated force is measured or dynamically where the force is measured during the process of pulling the probe out of the liquid or dipping it into the liquid. One of the biggest advantages of these methods is that they don't require any optical measurements. However, the geometry of the object must be known in detail.

Wilhelmy plate

Wilhelmy-balance tensiometry [19, 20] also called the Wilhelmy plate method is one example for a force pull method. A vertical plate is dipped into the probe liquid and the force exerted on the plate is measured using a microbalance. This force is given by the following formula:

$$F = u\gamma \cos \theta \quad (2.2)$$

Where u is the length of the contact line of the liquid with the plate, γ is the surface tension and θ is the contact angle. As with other methods some corrections have to be applied to this formula to achieve accurate measurements [21].

In order to perform surface tension measurements the plate is usually made of a material like roughened platinum that ensures complete wetting of the plate (contact angle $\theta = 0$) for the liquid being investigated. The force is then directly proportional to the surface tension of the liquid.

The geometry of the sample has to be very uniform and precise because knowledge of the length of the contact line is also important for the accuracy of the measurement [22].

Due to the specific requirements on the sample it would be difficult to acquire and characterize usable samples as most surface science samples have only one well characterized polished side. Moreover the fact that a large amount of liquid is needed makes this method not ideal for experiments in a UHV system.

This method is not the best option for absolute surface tension measurements but it can still be used with careful consideration of the correction terms.

Du Noüy ring

The Du Noüy ring method [23] is also a force pull method, but it has two major differences to the Wilhelmy plate. Firstly the probe object is a thin ring usually made from a platinum-iridium alloy for its great chemical stability and high wettability. Secondly the force is not measured in an equilibrated state, but during the process of removing the ring from the liquid.

When this is done a thin film of the liquid is pulled up by the ring due to the adhesive force. The maximum force measured before the liquid film collapses can then be related to the surface tension.

In principle equation 2.2 holds here as well, where u is again the length of the contact line (for the ring this is the sum of the inner and the outer circumference). There are however some additional factors to consider. The ring itself has a finite thickness, so the maximum force will be slightly different for the inner and outer diameter of the ring. The weight of the liquid film itself also contributes to the measured force and has to be considered.

These deviations can be considered in the calculation of the surface tension by including a correction factor that has to be determined experimentally [24] by referencing another measuring method, for example the capillary height method. This makes the Du Noüy ring method practically useless for accurate absolute surface tension measurement as it will always rely on another method and therefore never reach a higher accuracy than that measurement. For this reason Patek et al. excluded surface tension values obtained by the Du Noüy ring method in their analysis [1].

2.3.3. Maximum bubble pressure

When a capillary is inserted into a liquid and a gas is pushed through the capillary a bubble of gas will form at the end of the capillary. This bubble will increase in size and pressure until the diameter of the bubble is equal to the diameter of the capillary. In this case the shape of the bubble will be hemispherical. For a spherical interface the Young-Laplace equation can be solved analytically to determine the surface tension:

$$\Delta P_{max} = \gamma \left(\frac{2}{R_{cap}} \right) \quad (2.3)$$

Where ΔP_{max} is the maximum pressure difference, R_{cap} is the inside radius of the capillary and γ is the surface tension. If more gas is added after the maximum pressure is reached the pressure will decrease again and finally the bubble will detach.

The maximum bubble pressure method is well suited to measure the surface tension of a freshly created interface as well as monitoring the surface tension of this interface over time [25]. This is particularly interesting for solutions of surface active molecules, as these will accumulate at the interface over time and change the surface tension. However, such a method is not suited to pure-vapour measurements of water inside an enclosed chamber, due to complications with pumping pure water vapour to create a bubble.

2.3.4. Drop weight

The drop weight method uses a drop of liquid hanging from the bottom end of a vertical capillary. The hanging drop is balanced by the gravitational force and the adhesive force due to the surface tension. As more liquid is added to the drop the contact angle will increase until it reaches 90° when the drop will detach from the capillary and fall. The theoretical maximum drop weight is given by Tate's Law[26]:

$$\gamma d\pi = m_{max}g \quad (2.4)$$

Where d is the inner diameter of the capillary, m_{max} is the maximum drop weight, g is the gravitational acceleration and γ is the surface tension. In reality this equation has to be modified, because some amount of liquid will always stay attached to the capillary. Equation 2.4 can be modified with a correction factor that depends only on the capillary diameter and the drop weight/ volume [27]. There are different methods to calculate these correction factors and the correct mathematical model has to be chosen according to the liquid to be examined. Additional correction factors that depend on different parameters such as the liquids kinematic viscosity and the drop formation time may also be necessary depending on the liquids characteristics [28].

Due to the large number of necessary correction factors and the resulting ambiguity in the results, the drop weight method is not suited for highly accurate absolute measurements of the surface tension.

2.3.5. Pendant drop

The pendant drop method [29] also uses a drop of liquid hanging at the end of a tip, but instead of the drops weight the shape of the drop is used to determine the surface tension. The shape of a hanging drop is a solution of the Young-Laplace equation 2.10. In modern experiments the shape of the drop is captured via a specialized optical setup and then fitted to theoretically calculated drop profiles.

The proper calibration of the optical system and the edge detection algorithm are very important.

One advantage over other methods is that the geometry and surface properties of the tip where the drop is created does not have a direct influence on the calculation of the surface tension. The only parameters that appear in the Young-Laplace equation 2.10 are the density difference between the liquid and the gas phase and the gravitational acceleration, both of which can be determined with more than sufficient accuracy.

A very important parameter for the measurement precision in pendant drop tensiometry besides the Bond number (see Section 2.1) is the Worthington number [30]. The Worthington number is defined as the ratio of the current drop volume to the theoretical maximum drop volume:

$$W_o = \frac{V_d}{V_{max}} \quad (2.5)$$

With the maximum drop weight (see Equation 2.4) this can be expressed as:

$$W_o = \frac{\Delta\rho g V_d}{\pi\gamma d} \quad (2.6)$$

Where $\Delta\rho$ is the density difference between the liquid and the gas phase, g is the gravitational acceleration, V_d is the drop volume (which can easily be calculated from a drop image in case of axisymmetric drops), γ is the surface tension and d is the diameter of the pendant drops support (usually the diameter of the needle that is used to create the drop). Berry et al. [30] have found in their pendant drop experiments that the Worthington number strongly correlates to the measurement precision and is better suited to characterize the quality of a pendant drop image than the Bond number.

As with all surface tension measurement techniques cleanliness of the equipment and measures against airborne contaminants are necessary. Usually pendant drop tensiometry is performed in some kind of temperature controlled environmental chamber. The liquid is then pushed through a syringe to create a drop at the end of the tip.

In surface science the usual approach to avoid contamination is to perform the experiment in ultra-high vacuum. For experiments with water this is a bit more difficult, because inside a UHV system that is being pumped the water will evaporate rather quickly. It is however possible to pump the system to a pressure of $\approx 10^{-10}$ mbar and then introduce the water so that the system contains only water and pure water vapour. The pendant drop can then be grown via condensation on the tip of a coldfinger.

This approach not only ensures the highest possible cleanliness but it also provides the opportunity to examine samples of the water after the experiment and

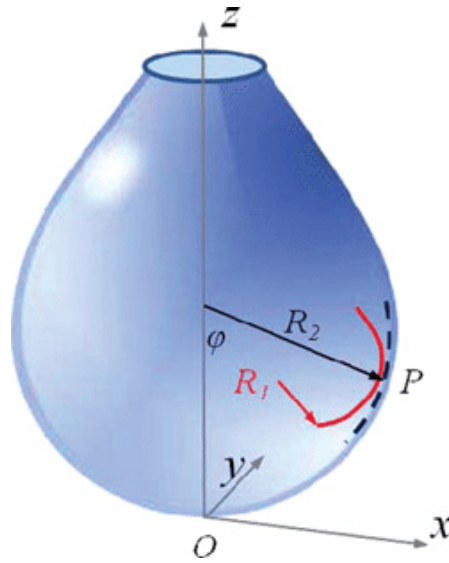


Figure 2.1.: Illustration of the principal radii R_1 and R_2 at point P on the surface of a drop (image from [33]).

perform a mass spectrometer analysis to detect and quantify possible trace contaminants.

2.4. Young-Laplace equation

Pendant drop tensiometry requires a mathematical model of the drop to determine the surface tension. The profile of a drop of fluid is determined by a balance of intermolecular forces and external forces. The profile of a pendant drop can be used to accurately measure the surface tension by fitting it to a calculated drop profile. The mathematical description of the normal stress balance across an interface separating two fluids is given by the Young-Laplace equation[31, 32]:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.7)$$

Where ΔP is the pressure difference at the surface, γ is the surface tension and R_1 and R_2 are the principal radii of the drop surface. An illustration of the principal radii of a drops surface is given in figure 2.1. The simplest possible solution to this equation is a sphere. This implies that ΔP is constant across the surface. The spherical approximation can still produce reliable results for small drops where gravity is negligible, but in general numerical methods have to be used to calculate drop profiles.

In the case of an ideal drop where the only external force is gravity ΔP follows a linear equation in z :

$$\Delta P = \Delta P_0 - \Delta \rho g z \quad (2.8)$$

Where ΔP_0 is the pressure difference at some reference point, $\Delta \rho$ is the density difference between the two fluids and g is the free-fall acceleration. Since ideal drops are axisymmetric, the curvature at the apex (R_0) is equal in all directions. This can be used as a reference point to express ΔP_0 by inserting $R_1 = R_2 = R_0$ into equation 2.7:

$$\Delta P_0 = \frac{2\gamma}{R_0} \quad (2.9)$$

The Young-Laplace equation for axisymmetric drops is then:

$$\frac{2\gamma}{R_0} - \Delta \rho g z = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.10)$$

Collecting some constants in the Bond number $Bo = \frac{\Delta \rho g R_0^2}{\gamma}$ and scaling each length by R_0 (indicated by a bar) yields the dimensionless equation:

$$2 - Bo\bar{z} = \frac{1}{\bar{R}_1} + \frac{1}{\bar{R}_2} \quad (2.11)$$

Since the drop is axisymmetric this equation can be expressed in cylindrical coordinates with the tangent angle φ (see Figure 2.2):

$$2 - Bo\bar{z} - \frac{\sin \varphi}{\bar{r}} = \frac{d}{d\bar{r}} \sin \varphi \quad (2.12)$$

Equation 2.12 can be parameterized by the arc length s measured from the apex of the drop to obtain a coupled set of dimensionless differential equations:

$$\begin{aligned} \frac{d\varphi}{d\bar{s}} &= 2 - Bo\bar{z} - \frac{\sin \varphi}{\bar{r}} \\ \frac{d\bar{r}}{d\bar{s}} &= \cos \varphi \\ \frac{d\bar{z}}{d\bar{s}} &= \sin \varphi \end{aligned} \quad (2.13)$$

Besides the spherical solution which would correspond to $\gamma \rightarrow \infty$, Equations 2.13 do not have an analytical solution and were first solved numerically by Bashforth and Addams [34]. Before computers were available, tables of these numerical solutions could be used to analyze drop profiles and determine surface tension

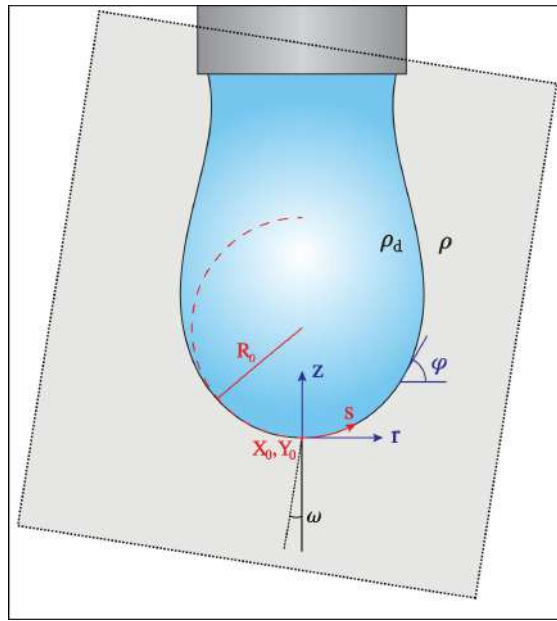


Figure 2.2.: The coordinate system used to parameterize the Young-Laplace equation for the pendant drop (from [30]).

values. Today, drop profiles are analyzed using computer algebra systems that use numerical integration of the Young-Laplace equation or other numerical methods to determine the surface tension.

2.5. Historical data

Accurately measuring the surface tension of pure water has been a pursuit of scientists since about 150 years. Therefore there is a large amount of data available for values of the surface tension of water at various temperatures spanning the usual liquid range of water and beyond, especially in the supercooled region. This data has been acquired with different methods, the most widely used ones are described in section 2.3.

A plot of the historical data can be seen in Figure 2.3. There it can be seen, that the measured values for the surface tension at a given temperature vary by more than ± 1 mN/m while the reported accuracies of the individual experiments are often in the range of 0.1 mN/m. There also seems to be a cluster of datasets that reproduce the temperature gradient of the complete data, but with surface tension values ≈ 0.3 mN/m higher.

Since there is no easy way to calculate the surface tension of water at a given temperature theoretically, an empirical formula needs to be derived from the exper-

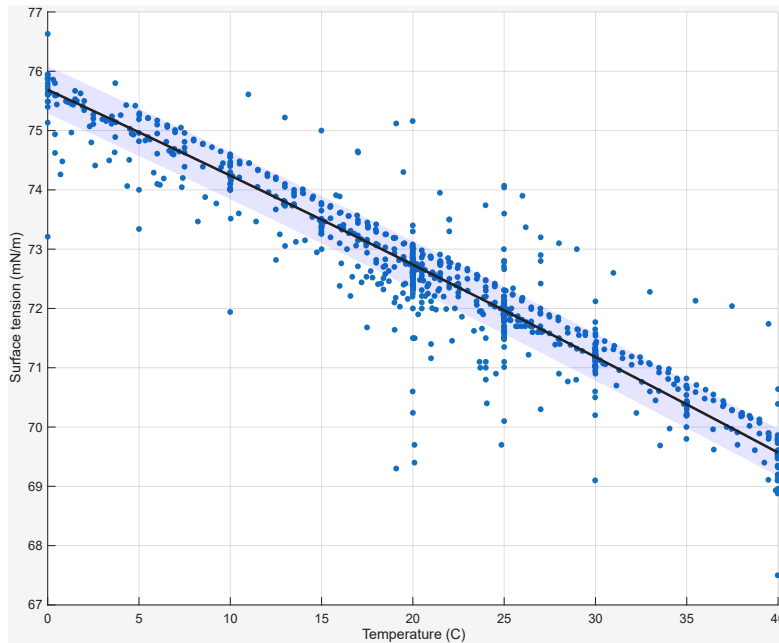


Figure 2.3.: Plot of the historic data used by Patek et al. [1] to generate recommended surface tension values

imental data. Since 1975 the former International Association for the Properties of Steam (now: International Association for the Properties of Water and Steam, IAPWS) has published the "Release on Surface Tension of Ordinary Water Substance" [35] where recommended values for the surface tension of water in a table are given. They also developed an interpolation equation that can provide surface tension values from the temperature of triple point of water (0.01 °C) to the critical temperature of water ($T_c = 647.096$ K):

$$\gamma = a\tau^c(1 + b\tau) \tag{2.14}$$

$$\tau = 1 - \frac{T}{T_c}$$

$$a = 235.8 \text{ mN/m}$$

$$b = -0.625$$

$$c = 1.256$$

Where γ is the surface tension and T is the absolute temperature.

The experimental data used for this interpolation needs to be selected very carefully, especially in the case of surface tension where so many different methods exist and the estimated accuracy and details about the experimental setup such

as cleaning procedures are often not stated explicitly by the researchers.

In 2016 Patek et al. developed a procedure to generate surface tension values from existing data that doesn't rely on a single correlation function [1]. In a first step they used a function similar to 2.14 to generate surface tension values based on all of the available data sets. Then the single data set with the largest mean absolute deviation from that equation was excluded and the procedure repeated until only a minimum number of data sets required to span the selected temperature range remain. This results in n surface tension equations where n is the difference between the total number of data sets and the minimum number of data sets plus one. The recommended surface tension value can then be calculated as the mean of these values.

Looking at the individual experiments in detail reveals that the higher surface tension values often originate from experiments where special measures to keep the sample clean were employed. Gittens et al. [36] performed capillary rise and drop volume experiments under a nitrogen atmosphere and measured a higher surface tension value than the recommended value. Gaonkar et al. [22] also measured higher surface tension values (72.91 mN/m at 20°) using the Wilhelmy plate method.

The fact that presumably cleaner experiments measure higher surface tension values could be an indicator that there are trace surfactants present in the majority of the other experiments, as these surfactants could decrease the surface tension significantly even at very low concentrations [37].

3. Experimental Methods

3.1. UHV system

The UHV system consists of the main experimental chamber, the water reservoir and a pumping chamber that is connected to a turbomolecular pump via a gate valve. A schematic of the system can be seen in Figure 3.1. The experimental chamber and the water reservoir are encased in a temperature controlled box (for details see Section 3.1.3). The experimental chamber has inlets to introduce gasses, salts or other compounds into the system in a controlled manner in order to investigate the Jones-Ray effect (see Section 2.1). The whole system can be baked to about 180°C for several days to remove any adsorbates from the chamber walls. To introduce the water into the chamber a secondary reservoir (the pre-cleaning chamber) can be connected to the main reservoir. The pre-cleaning chamber can be baked separately.

3.1.1. Coldfinger

The temperature of the coldfinger tip is controlled by two heating elements (tip heating and counterheating) connected to a PID controller and a nitrogen cooling system. Initially the nitrogen cooling was planned to flow liquid nitrogen directly into the tip with a custom made valve, but this was problematic as the valve would easily get jammed due to condensation and freezing. The solution was to use nitrogen gas instead. The nitrogen gas flows through a coiled copper pipe submerged in liquid nitrogen and is pumped through the coldfinger by a venturi pump. The flow has to be controlled manually by a flow controller.

The shape of the coldfinger tip should not influence the results of the drop shape measurement directly as the tip is cropped out before the fitting. It does however affect the growing procedure of the drop. A sharp tip is better suited for depositing water onto a surface, a blunt tip with a square cross section can produce larger pendant drops. The problem with a square cross section is, that it produces additional drops on the side of the tip that won't flow into the main drop due to the sharp edge around the circumference of the tip. To alleviate that issue this edge was slightly rounded off before the bakeout.

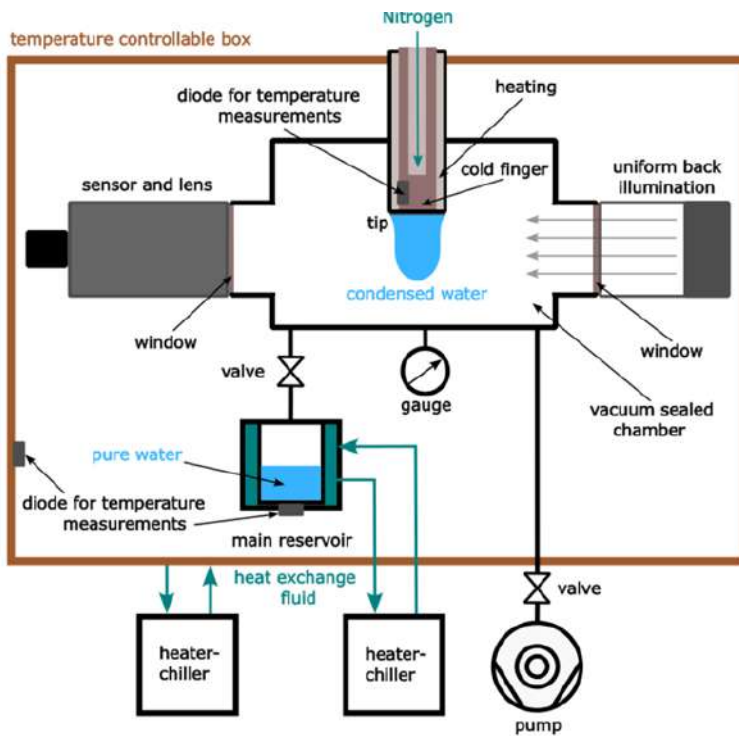


Figure 3.1.: Schematic of the drop chamber

3.1.2. Pressure gauges

To measure the pressure of the water vapour in the experimental chamber during drop experiments a "MKS Baratron Type AA09A Absolute Pressure Transducer" is used. This is a capacitance manometer that converts pressure to a linear DC output voltage. Additionally a "MKS Type 660B Power Supply Digital Readout" is required to as a power supply and readout unit.

The Baratron gauge has a metal diaphragm that is exposed to the experimental chamber on one side. On the other side there is a high vacuum reference cavity that is kept at $\sim 10^{-7}$ mbar by an integral chemical getter system. The diaphragm is deflected according to the absolute pressure in the chamber. Since the diaphragms mechanical properties are temperature dependent there is a temperature dependent pressure offset that needs to be taken into account. Similarly the electronics unit also has a temperature dependent offset. Both of these contributions are linear in temperature so it is possible to determine the parameters of an equation describing the pressure offset by pumping the system to UHV and taking measurements at different temperatures.

3.1.3. Temperature control

To precisely control the temperature of the experiment the entire experimental chamber as well as the water reservoir is encased in an environmental box made of temperature isolating foam and aluminum panels for stability in such a way that there is as little heat transfer as possible from the inside to the outside. The box is connected to a "LAUDA PRO RP 290 E" heater-chiller via multiple heat exchangers attached to the inside aluminum panels. To ensure an even temperature distribution inside the box there is a small fan attached to the heat exchanger on the bottom panel of the box.

A second heater-chiller of the same type is connected directly to the water reservoir. Separate control of the reservoir temperature is necessary to grow and shrink the drop and most importantly to remove the water from the experimental chamber by condensing it in the reservoir.

The heater-chillers have a operating temperature range of -90 to 200°C and a temperature stability of ± 0.05 K.

Both heater-chillers use silicone oil as a heat transfer fluid, which was chosen because it has a large stable temperature range, it is non-flammable, chemically inert and non-toxic.

To measure the temperature there are multiple calibrated diodes (inside the coldfinger, higher up on the coldfinger to control the counterheating, on the bottom of the water reservoir and directly on the chamber).

3.1.4. Vibration dampening

The dampening of vibrations is very important in surface science as vibrations can and will significantly influence the results of many techniques. At the same time vibrations are also unavoidable, especially when using UHV systems where the pumps will always cause vibrations frequencies. Additional sources of vibrations in the pendant drop experiment are the heater-chillers, the cooling water, the bubbling of the liquid nitrogen in its reservoir and of course vibrations from the building. Especially low frequencies of ~ 4 Hz are problematic for the pendant drop experiment as the water drop has a resonant frequency around that value [38].

Initially the drop chamber as well as all the scroll pumps and the heater-chillers were placed on thin pieces of relatively dense foam. Soon it became apparent that this would not be sufficient to get a good image of the pendant drop.

Different kinds of softer foam were ordered and tested individually with vibration measurement device and frequency analyzer to see which frequencies resonate. A combination of a soft foam and a harder foam was chosen. To further isolate the scroll pumps from the experiment the hoses connecting the pumps to the chamber

were weighed down with steel blocks (about 15 kg), the same was done to the hoses for the heater chillers.

The biggest achievement in reducing vibrations however was reached by mounting the chamber on a system of three pneumatic vibration isolators of the "S-2000A Stabilizer" series purchased from Newport. This system significantly reduced the vibrations of the system and it has the additional benefit, that the chamber can be precisely leveled.

3.2. Ultra-pure water

In order to measure the surface tension of pure water it is important to ensure that the substance in the experimental chamber is pure water. Since surface tension is a phenomenon that occurs at an interface very small amounts of surface active chemicals can have a large effect on the measurement[3].

3.2.1. Milli-Q

Milli-Q ultra-pure type 1 water is used in the surface science group at TU Wien for rinsing glassware and other equipment, sonication of samples and for analysis techniques such as inductively coupled plasma mass spectrometry (ICP-MS). It is provided by a water purification system located in another lab in the same building, which means it is not possible to bring the water into the experimental chamber without exposing it to ambient air. Milli-Q ultra-pure water is certified according to the ISO 3696 [39] norm for water for laboratory and analytical uses. The trace contaminants are given in table 3.1. The Milli-Q water is only tested for total organic carbon, sodium, chloride and silica. All of their concentrations are in the order of parts per billion, which corresponds to micrograms of contaminant per liter of water.

Total Organic Carbon (TOC)	< 5 ppb
Sodium (Na)	< 1 ppb
Chloride (Cl)	< 1 ppb
Silica (SiO ₂)	< 3 ppb

Table 3.1.: Trace contaminants of Milli-Q type 1 ultra-pure water.

Note that one part per billion of a contaminant in water corresponds approximately to one $\mu\text{g/L}$.

3.2.2. Ovivo

Ovivo Switzerland AG is a company that specializes in ultra-pure water treatment systems for various industrial and research applications such as semiconductor production. The ultra-pure water that was bought from Ovivo is tested much more rigorously than the Milli-Q water available in the lab. For example the TOC content of the Ovivo water is at 0.56 ppb which is ten times lower than what is given as TOC value for the Milli-Q system under ideal operating conditions. The Ovivo water is also analyzed for the amount of various trace metals and anions. The amounts of these contaminants was in the order of single digit ppt or lower for all contaminants except for Fluoride ions which were detected at a concentration of 35 ppt. The full certificate of analysis can be seen in Appendix A. Since this water is much cleaner than the Milli-Q water we decided to use the Ovivo ultra-pure water exclusively for our experiment.

3.3. Optical system

3.3.1. Camera

The camera used for the measurements in this diploma project is an Alvium G5 - 5GigE Vision camera from Allied Vision with a Sony IMX183 sensor with a resolution of 20.2 megapixels.

Telecentric lens

A telecentric lens is a lens that has its entrance pupil at infinity. As opposed to the perspective projection of normal lenses a telecentric lens provides an orthographic projection of the object. The advantage is that the size of objects is not distorted when moving along the optical axis. A telecentric lens has a working distance - where objects are in focus - which cannot be changed. Therefore the camera has to be focused by moving either the camera or the object to the correct distance.

The telecentric lens used in this project is a TECHSPEC large format telecentric lens #62-901 from Edmund Optics with a primary magnification of 0.9x, a working distance of 11 mm, telecentricity $< 0.1^\circ$ and a distortion $< 0.1\%$.

3.3.2. Optical calibration

Besides the steps taken to reduce the possibility of contamination in the UHV system or the water used in the experiment the tuning of the optical setup is one of the most important steps to ensure accurate and reproducible surface tension measurements.

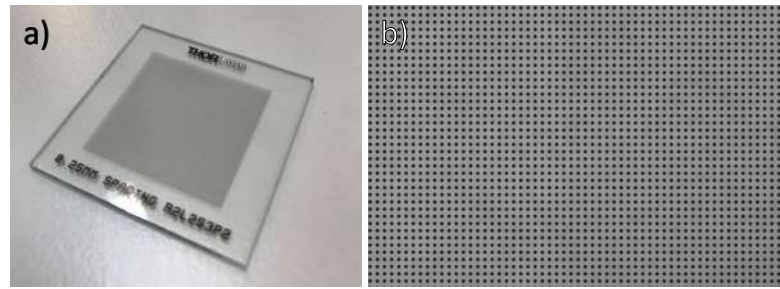


Figure 3.2.: a) The calibration grid used to determine the image distortion, b) Image used for fitting the dot grid

All lenses, no matter how precisely they are made have some deviations from the manufacturer's ideal specifications. This can be some image distortion as well as some deviation from the given value of magnification. These deviations of the lens in combination with the optical sensor needs to be measured, so it can be removed from images of the drop or the calibration ball. To measure the real characteristics of the lens some images of an optical grid with precisely spaced dots were taken (see Figure 3.2). Since the spacing of these dots is supposed to be even, any local difference in the distances between the dots must be the result of image distortion, while a global deviation of the distances between the dots would indicate a deviation in the given magnification value. During this testing we found that the camera sensor moves as it gets hotter during operation. To avoid the shifting of the camera sensor a custom camera cooling was produced, consisting of an aluminum block that can be mounted to the sensor with a hole to flow lab cooling water. This setup kept the camera sensor at a stable temperature of about 8°C during operation. With the watercooling of the camera the distortion of the value and direction of the image distortion can be determined (see Figure 3.3) and the image can be undistorted by applying the opposite of those values to the respective pixels in the image. In this step the magnification of the lens was found to deviate slightly from the manufacturer specification at 0.8979x 0.9x.

After the image undistortion the optimal operating parameters of the camera (focus distance, aperture, illumination and exposure time) have to be determined in combination with the edge detection algorithm, especially the sigma value of the gaussian filter used for smoothing the image.

To do this a precisely manufactured calibration ball ($6\text{mm} \pm 1\mu\text{m}$) was placed in the air chamber in the same location where the drop would be. The radius of the ball was then measured with the same edge detection algorithm that would be used for the pendant drop. The illumination voltage of the uniform back illumination and the exposure time are the least critical parameters as long as the image is not overexposed or underexposed. In terms of vibrations a shorter exposure time does

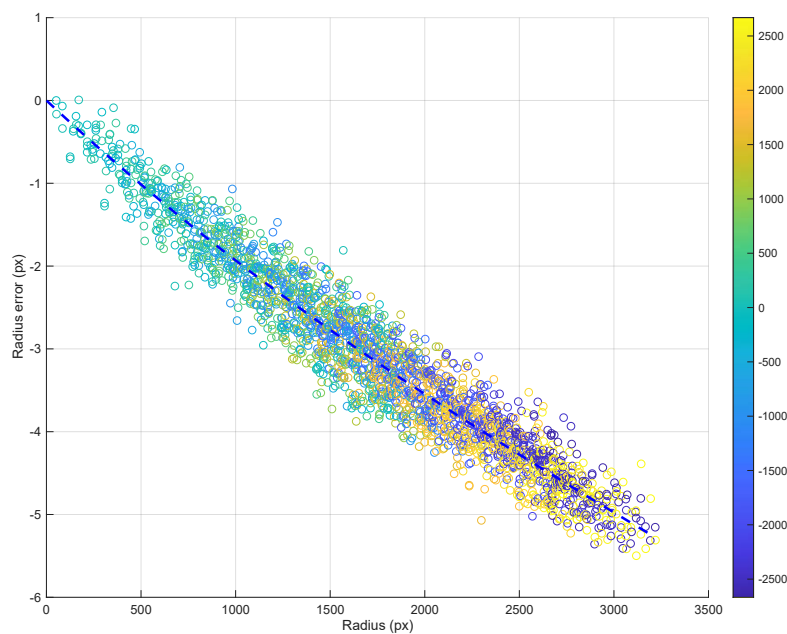


Figure 3.3.: The deviation of the optical grid imaged by the telecentric lens. The color represents the vertical position of the pixels in the image. If the yellow and dark blue dots were distributed unevenly this would indicate that the grid is not perpendicular to the optical axis. This was also checked in the horizontal direction.

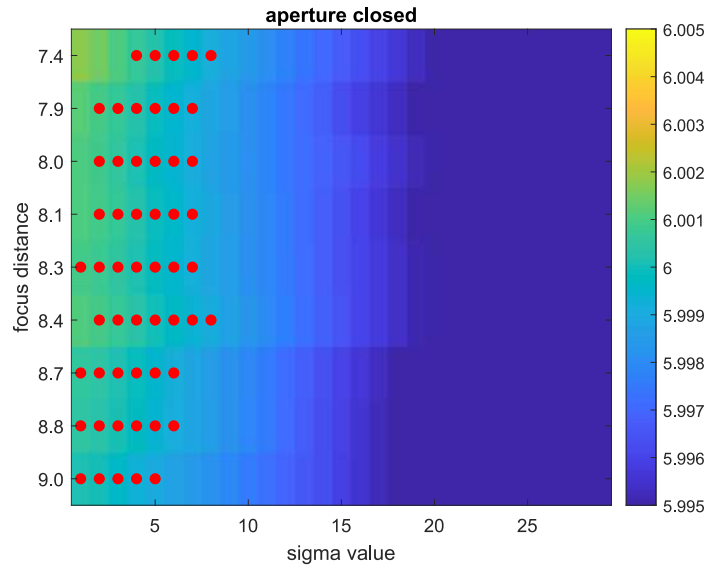


Figure 3.4.: Plot of the measured size of the calibration ball with different focus distances and sigma values. The red dots represent parameters where the measured diameter of the calibration ball deviates $\leq 1\mu\text{m}$ from its nominal diameter.

not really bring any benefits as an image of a drop that is moving will not yield an accurate surface tension value anyway.

Before the edge detection it is necessary to apply a gaussian smoothing to the image. Without a smoothing filter the image will be too rough and it is not possible to detect a continuous edge. The sigma value given in Figure 3.4 corresponds to the width of the gaussian used in this smoothing. A very high sigma value results in underestimating the radius of the calibration ball and is therefore not desirable. We have found that a sigma value of 3 is the smallest reasonable value to use which should give the most accurate results for the radius of the calibration ball.

To determine the influence of the aperture setting and the focus distance a series of images were taken varying these parameters. The images were then used to measure the radius of the ball to determine sets of parameters where the size of the ball would be represented correctly by the algorithm. A set of such parameters is visualized in Figure 3.4. Additionally the edge profiles were extracted to compare them to the edge profile of the water drop. The derivative of the edge profiles was then fitted to a gaussian to determine the edge width and peak height which can be used to find the focus point of the lens. The peak widths of those derivatives can be seen in Figure 3.5. The fit to a gaussian is justified since diffraction phenomena are generally mathematically described by the Airy pattern which has a central maximum that can be approximated as a gaussian[40].

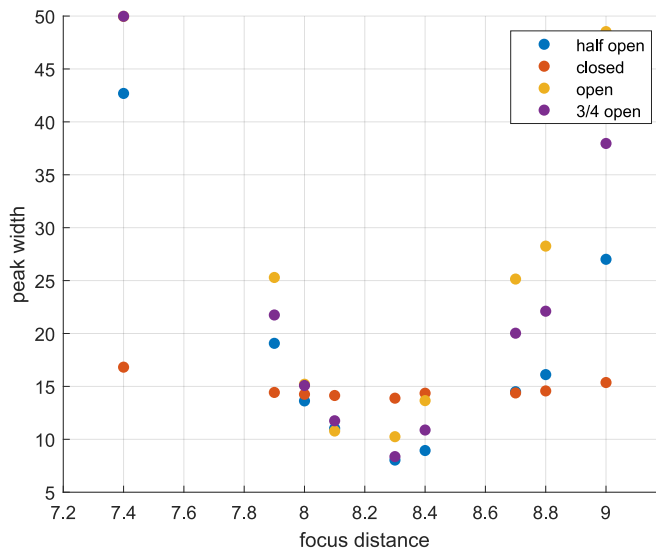


Figure 3.5.: The peak width of the gaussians fitted to the derivative of the edge at different aperture settings.

3.4. Measurement procedure

After the UHV chamber and the pre-cleaning chamber are baked to remove any adsorbates from the walls the system is ready and water can be inserted.

3.4.1. Inserting the water

A schematic of the water insertion process can be seen in Figure 3.6. The water purchased from Ovivo was stored in a laminar flow hood in the lab. The pre-cleaning chamber was also stored there and after the bakeout the water was poured directly from the container into the pre-cleaning chamber inside the flow hood. The pre-cleaning chamber was then closed and connected to a designated pumping station (the pump on the left in Figure 3.6). The water was then frozen by inserting the whole pre-cleaning chamber into a small container of liquid nitrogen. After the water was completely frozen the pumping station was started to evacuate the pre-cleaning chamber while the water was slowly warmed up to remove any gases dissolved in the water. This process was repeated a few times until the pressure settled at the vapour pressure of pure water. The pre-cleaning chamber was then connected to the drop chamber and the water was distilled to the water reservoir.

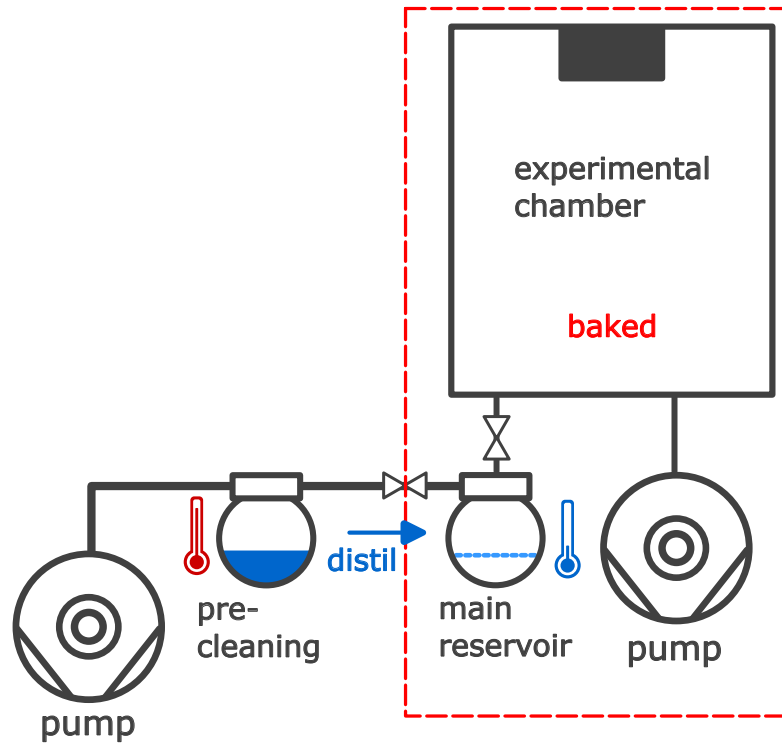


Figure 3.6.: Schematic of the water insertion process. The water is first cleaned via freeze-pump-thawing in the pre-cleaning chamber and then transferred to the main water reservoir by distillation.

3.4.2. Drop growth

The drop growth during the experiment is mainly governed by two parameters: The temperature setpoint of the tip of the coldfinger and the exhaust pressure of the venturi pump that pulls cold nitrogen gas through the coldfinger. The temperatures of the water reservoir and the box (the temperature of the chamber) should be set closed to the desired target temperature where the measurement is going to be performed. In the beginning the tip setpoint is set to a higher than the reservoir temperature. Once the tip temperature settles, the reservoir valve can be opened to introduce water vapour to the experimental chamber. The tip temperature can then be lowered to condense water on the tip and start growing a drop. A temperature difference of $\Delta T \approx 10^\circ\text{C}$ makes the drop grow within a couple of minutes, for $\Delta T \approx 5^\circ\text{C}$ the growth will take tens of minutes. The goal is to grow a pendant drop as close to the maximum size as possible without having the drop fall down. To slow down the growth the exhaust pressure is lowered and the tip temperature is brought up to equilibrium with the reservoir temperature. Ideally all temperatures should be in equilibrium so that the drop is neither growing nor shrinking as this would significantly change the surface tension value and an accurate measurement would be impossible.

Side drops

Due to the geometry and internal heat distribution of the coldfinger tip it is possible that additional drops form on the side of the coldfinger tip that don't connect to the main pendant drop. If this happens it can be a problem with the drop growth because at some point when the side drops become too big and finally fall into the main drop the main drop will also fall down in most cases. The solution to this is to grow the drop normally with a $\Delta T \approx 10^\circ\text{C}$ between the tip and the reservoir. Then when the drop size gets larger and the side drops start to cause the main drop to fall down the growth has to be slowed ($\Delta T \approx 2^\circ\text{C}$) and the drop can usually be grown to a size about 90% of the maximum drop size. This takes much longer than the drop growth without side drops so over the operation of the experiments the tip geometry was adjusted to avoid side drops as much as possible.

4. Results and discussion

Over the duration of the project a number of measurements were performed at different temperatures ranging from 20°C to 27°C. The results of all of these measurements can be seen in Figure 4.1. An example image of a drop with a reasonable Worthington number (the volume of the drop in relation to the maximum drop volume) $Wo \sim 0.80$ is shown in Figure 4.2.

An important value besides the absolute surface tension value at each temperature is the difference between the measured surface tension value and the recommended literature value (see Section 2.5) at the same temperature ($\Delta\gamma = \gamma_{measured} - \gamma_{lit.}$). It is expected that this value should have a small standard deviation across different temperatures. Mostly because there is no reason to expect the gradient of the surface tension with respect to the temperature to change. This gradient is defined by the entropy of the surface and is not expected to change significantly when trace amounts of molecules adsorb to the water interface [41, 42]. That is, when molecules adsorb at an interface, they shift the gamma values by equal amounts across a given temperature range. In temperature ranges larger than $\pm 10^\circ\text{C}$, changes in the gradient might be observed, but this is outside the scope of this work. The $\Delta\gamma$ values from our measurements however, have a high standard deviation of 0.5 mN/m and values both higher and lower than the literature value.

To address the scatter of $\Delta\gamma$, we must consider the quality of the collected data. The first indicator for the quality of a pendant drop image is a low temperature gradient in the system as this indicates a stable drop and therefore an accurate measurement. Drop images with the standard deviation of the 4 different temperatures measured in the system (coldfinger, counterheating, experimental chamber and water reservoir) $< 1^\circ\text{C}$ were selected for the experiment. The second selection parameter for high quality data is the residual error of the fitting algorithm. Drop images with a residual $< 1 \mu\text{m}$ were selected, since that is the accuracy of our calibration of the optical system (see Section 3.3.2). The third important metric for the data quality in pendant drop tensiometry is the Worthington number (see Equation 2.6), the drop size relative to the theoretical maximum drop size. Generally drops with a larger Worthington number produce a smaller standard deviation in measured surface tension values[30]. In our results we find that drops with $Wo > 80\%$ lead to a standard deviation $< 0.01 \text{ mN/m}$ inline with the results of Berry et al.[30].

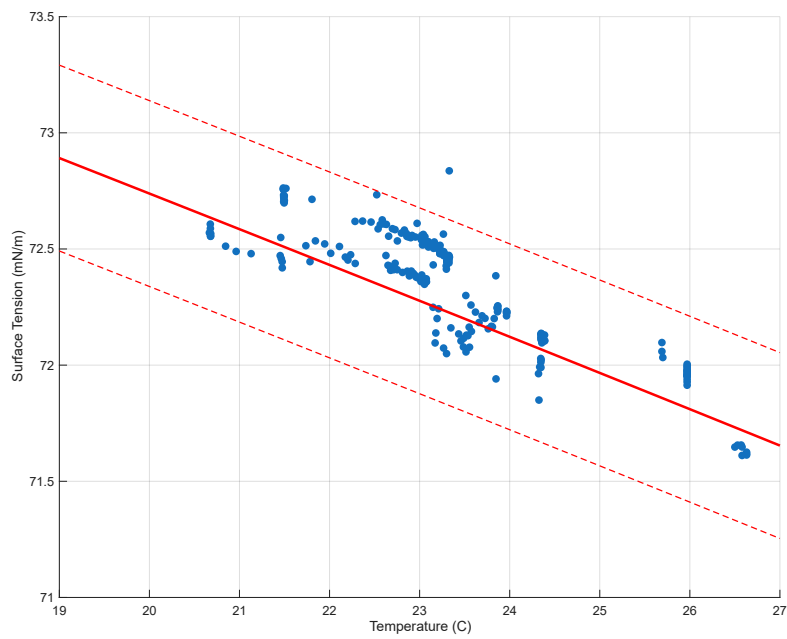


Figure 4.1.: Plot of all the surface tension data measured during this project. The solid red line represents the recommended surface tension values calculated by the Patek method (see Section 2.5) and the dashed red lines represent the standard deviation of the historical data used to calculate those values.

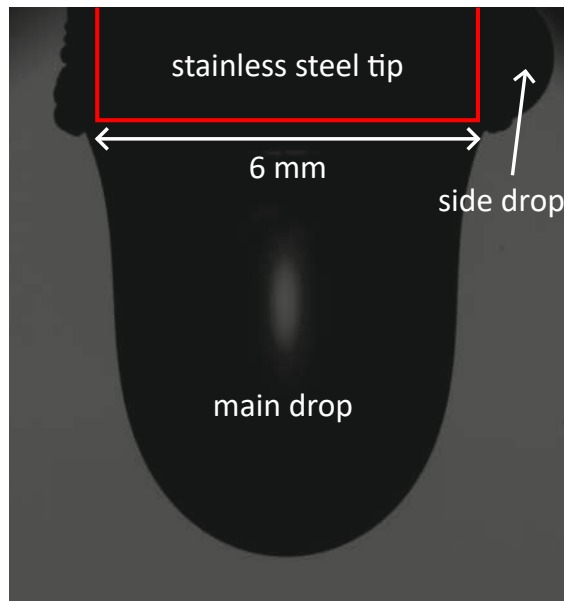


Figure 4.2.: An example image of a drop with a Worthington number $Wo \sim 0.80$

After this selection of the most reliable results the standard deviation of the $\Delta\gamma$ values has improved from 0.5 mN/m to 0.02 mN/m (see Figure 4.3). There is a clear trend as all of the results follow the same temperature gradient as the values generated from the historic data, but the values are about 0.25 mN/m higher. It is important to note that this reduced set of data still includes a number of different pendant drops from different days. The consistency of the data across different days excludes any systematic error occurring on any individual day e.g. from remounting the optics, or from changes in room temperature. A higher surface tension value in our data could mean that there is some contamination in the historical data that decreases the surface tension. A contamination that decreases the surface tension has to be caused by some compound that will preferably adsorb at the surface of the drop (surfactants) [37]. Since we are removing these surfactants in our experiment we measure a higher surface tension value.

Another explanation for our higher measured value for $\Delta\gamma$ is the presence of a contamination that increases the surface tension of the water in our experiment. A contamination with charged ions that preferably remain in the bulk of the water as opposed to the surface would increase the surface tension in our experiment [43, 44]. The Ovivo water used for the experiment has very high purity with respect to charged ions (see Section 3.2.2) so the water itself can be ruled out as the source of a possible charged ion contamination. However, it is well established that high purity waters when in contact with metals cause dissolution of metal ions into the water [45, 46]. In turn, it could be that the tip is a source of charged

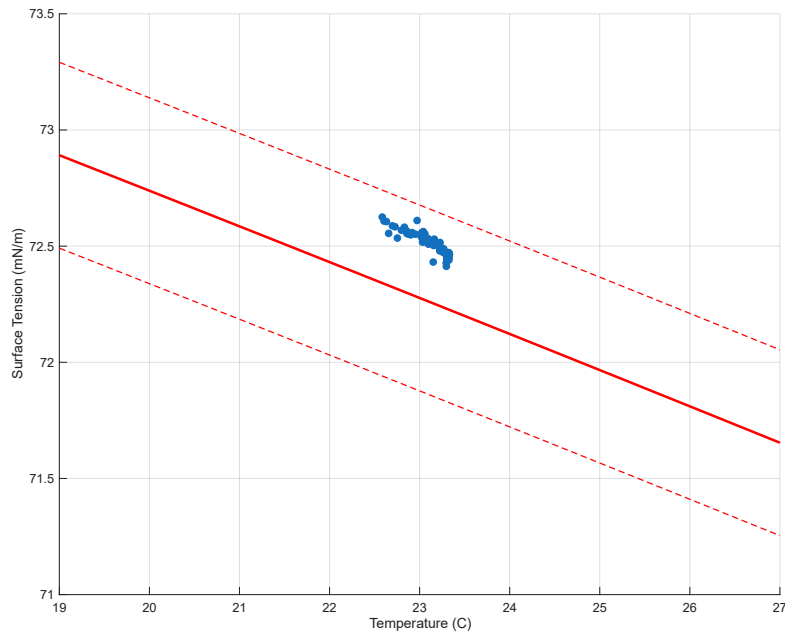


Figure 4.3.: Plot of the drop data after selection of the most reliable results

ion contamination in our experiment. To investigate this further a clean gold sample was inserted into the experimental chamber and 15 drops were condensed on the coldfinger tip and dropped onto the sample. The water was then evaporated and the gold sample was analyzed via X-ray photoelectron spectroscopy (XPS). The XPS spectrum was then compared to a previously recorded XPS spectrum of the clean gold sample. The only peaks that appeared in the XPS spectrum after the water drops were iron, nickel and chromium, this is inline with the expected dissolution of the stainless steel into the ultra-pure water (see Figure4.4). The amount of impurities was estimated to be around 1 ppb for iron and < 1 ppb for nickel and chromium. The ppb of Fe, Ni and Cr correspond to approximately nM concentrations. In the end, these concentrations will not appreciably effect the experiment, as metal ions require concentrations on the order of 1 mM to change the surface tension of water by ~ 0.01 mN/m [47, 48]. No other impurities that could possible cause a higher surface tension value were detected in the water drops.

The fact that we could not detect any contaminants that could increase the surface tension in our experiment points to the conclusion that there is a surfactant contamination in the previous experiments. The question is what kind of surfactants could cause such a contamination. Airborne hydrocarbons are known to contaminate all surfaces [49, 50], even in UHV environments [51] and can greatly influence surface properties such as wettability [52]. It is however unlikely that these compounds are the reason for a significant change in surface tension measure-

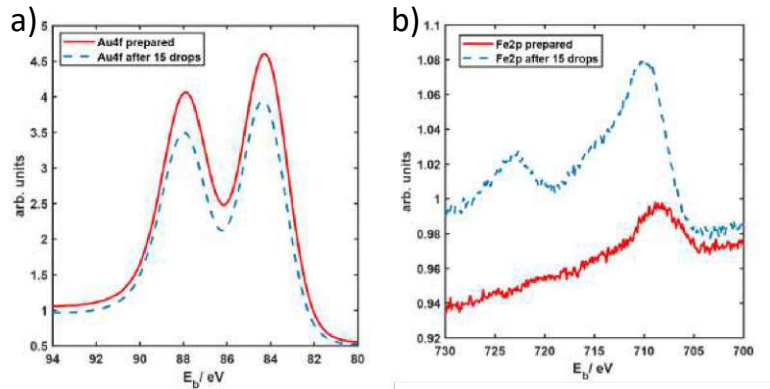


Figure 4.4.: Results of the X-ray photoelectron spectroscopy analysis of the gold sample before and after dropping 15 drops of water onto it in the experimental chamber. a) Gold 4f reference spectra before and after water deposition. b) Fe 2p core-level before and after water deposition. The most noticeable change can be seen in the iron 2p peak. The estimated amount of impurities was 1 ppb for iron and < 1 ppb for nickel and chromium.

ments as the most commonly occurring airborne hydrocarbons such as terpenes, hopanes and steranes are not known to be strong surfactants. Moreover, gases are also known to change the surface tension of water, almost always decreasing the surface tension with increases of pressure. This means in our measurements, where we have removed the gases, a higher surface tension value is to be expected. However, the measured value for $\Delta\gamma$ of 0.25 is too large to be completely explained by the removal of gases. The removal of 1 bar of air is expected to increase the surface tension by about 0.08 mN/m[53].

The most plausible explanation for our large measured difference from the historical data are trace surfactants that are left on the surfaces of the instrument from detergents used in the cleaning process that we are able to remove in our experiment. The most commonly used surfactants in household and industrial anionic detergents are linear alkylbenzene sulfonates and alcohol ethoxysulfates [37]. These surfactants can have a very strong effect on the surface tension of water, even if there are only trace amounts present. Uematsu et al.[3] have proposed the presence of trace amounts of anionic surfactants as the explanation for different phenomena that occur in experiments concerning the air-water interface such as the conflicting results on the surface charge of water and the Jones-Ray effect (see Section 2.1). In particular, Uematsu et al. argue that the 5 ppb TOC in MilliQ water, a standard lab water source (see Section 3.2.1) could be a non-zero amount of trace surfactant. Assuming the surfactant has a mass of a typical alkylbenzene

sulfonate, 5 ppb TOC would equate to a concentration of 200 nM. Uematsu et al. demonstrate with their modeling that 200 nM is enough to produce the Jones-Ray effect. 200 nM of an alkylbenzene sulfonate surfactant would also be enough to cause the surface tension difference we measure with respect to the literature value for water [54, 55]. This consistency brings our results inline with those of Uematsu et al. and reinforces our surfactant hypothesis.

Our UHV system is cleaned with detergents that contain surfactants as well, but every surface that comes in contact with the ultra-pure water is heated to 180 °C for multiple days while under a vacuum of up to 1×10^{-10} mbar. The decomposition temperature of surfactants is typically 100°C – 200°C [56, 57] so this bakeout ensures there are no surfactants left in the UHV system. In the end, this bakeout, in addition to using the very clean Ovivo ultra-pure water, gives us the confidence in claiming that our experiment is more surfactant free than most prior historic data.

Our hypothesis, that prior historic data might be contaminated, is also supported by experiments from other groups. Gittens et al. [36] performed capillary rise experiments under a nitrogen atmosphere and washed their instruments with phosphoric acid. They measured a difference from the recommended value $\Delta\gamma = +0.3$ mN/m at 20°C. Gaonkar et al. [22] distilled their water in the presence of KMnO_4 to remove organic impurities and cleaned their glassware with a mixture of sulfuric acid and an inorganic oxidizer free of metallic ions. They measured a difference from the recommended value $\Delta\gamma = +0.17$ mN/m at 20°C. The difference between the measured surface tension value and the recommended value for our experiment $\Delta\gamma = +0.25$ mN/m matches well with results of these groups.

The attempts to measure the surface tension of supercooled water using pendant drop tensiometry were unfortunately not successful. The water would freeze at about -8 °C too quickly to stabilize the drop. Homogeneous nucleation of supercooled water usually occurs at much lower temperatures, close to -40°C [58]. However most of the experiments on supercooled water are performed with very small amounts of water. Since the probability for homogeneous nucleation is always dependent on the volume it is plausible that our drop would freeze at a higher temperature. The surface roughness of the coldfinger tip should not contribute to ice nucleation significantly [59]. The most likely reason for the freezing of the drop is an internal temperature gradient in the drop due to the cooling system being too strong.

5. Conclusions

During this project a self designed UHV system was prepared and used to perform highly accurate measurements of the surface tension of ultra-pure water in its own vapour using pendant drop tensiometry. To ensure measurement accuracy, sources of vibration that interfered with the system were systematically investigated. Pneumatic vibration isolators were subsequently installed to decouple the setup from vibrations originating from the building and nearby equipment. The optical system was carefully calibrated in combination with the drop-shape fitting algorithm.

Surface tension measurements were then conducted over a temperature range from 20°C to 27°C. After careful selection of drops exhibiting the smallest temperature gradients across the system, the lowest residual fitting errors, and the largest Worthington numbers, the measurements consistently indicated that the surface tension of ultra-pure water is higher than the recommended values derived from historical data. The most plausible explanation for this result is the presence of trace surfactants in many historical experiments, which were effectively removed in our setup during the bakeout process.

To further confirm this finding, additional measurements over a broader temperature range would be beneficial. Our results also allow for a new interpretation of previous data related to the Jones–Ray effect (see Section 2.1). If many reported surface tension measurements of pure water indeed contain trace surfactant contamination, this would support the hypothesis proposed by Uematsu et al.[2] that charged surfactants induce the Jones-Ray effect. Future experiments could directly investigate this phenomenon by introducing small concentrations of salts into the system and measuring the resulting changes in surface tension.

Another promising application of the UHV system are contact angle measurements of sessile drops under extremely clean conditions. The system is already equipped with a sample holder that can be positioned beneath the coldfinger tip, allowing sessile drops to be created by freezing water on the coldfinger and subsequently depositing it onto a sample. Such measurements are particularly relevant given the ongoing controversy surrounding the wettability of surfaces such as freshly exfoliated graphite[60] and graphene[61], and the extent to which airborne contaminants influence their wetting behavior[52].

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A. Ovivo certificate of analysis

Ovivo Switzerland AG

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Benkenstrasse 262 - 4108
Witterswil - Switzerland
Tel. +41 61 555 12 52



Worldwide Experts in Water Treatment

Certificate of Analysis

Product name: Ultrapure water (UPW)

CAS Number: 7732-18-5

Formula: H₂O

Lot: 20240716

Quality certificate release date: 19.07.2024

Test	Result
Online UPW data under pressure (2.1 bar; 21.1°C)	
Resistivity	18.2 MOhm.cm
TOC (Total Organic Carbon)*	0.56 ppb
Particles ≥50 nm **	≤50 particles/L
Metals by online ICP-MS/MS	
Aluminium (Al), total	< 1 ppt
Arsenic (As), total	< 1 ppt
Boron (B), total	< 10 ppt
Barium (Ba), total	< 0.5 ppt
Beryllium (Be), total	< 0.4 ppt
Bismuth (Bi), total	< 0.2 ppt
Calcium (Ca), total	6 ppt
Cadmium (Cd), total	<0.5 ppt
Cobalt (Co), total	<0.7 ppt
Chromium (Cr), total	<1 ppt
Copper (Cu), total	<1 ppt
Iron (Fe), total	2 ppt
Gallium (Ga), total	< 0.5 ppt
Mercury (Hg), total	< 5 ppt
Indium (In), total	< 0.1 ppt
Potassium (K), total	< 5 ppt
Lithium (Li), total	< 0.2 ppt
Magnesium (Mg), total	< 1 ppt
Manganese (Mn), total	< 0.5 ppt
Molybdenum (Mo), total	< 0.5 ppt
Sodium (Na), total	4 ppt
Nickel (Ni), total	< 2 ppt
Lead (Pb), total	< 0.2 ppt
Antimony (Sb), total	< 0.2 ppt
Tin (Sn), total	2 ppt
Strontium (Sr), total	< 0.2 ppt
Tantalum (Ta), total	< 0.1 ppt
Titanium (Ti), total	< 0.5 ppt
Thallium (Tl), total	< 0.1 ppt
Vanadium (V), total	< 0.2 ppt
Tungsten (W), total	< 1 ppt
Zinc (Zn), total	< 2 ppt
Zirconium (Zr), total	< 0.2 ppt

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*Measuring device: Sievers 500RLe TOC analyzer

**Measuring device: UDI-50 Liquid Particle Counter PMS

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Worldwide Experts in Water Treatment

Test	Result
Anions by online UPW-IC	
Fluoride (F ⁻)	35 ppt
Acetate (CH ₃ COO ⁻)	< 5ppt
Formate (HCOO ⁻)	< 5ppt
Chloride (Cl ⁻)	< 5ppt
Nitrite (NO ₂ ⁻)	< 5ppt
Bromide (Br ⁻)	< 5ppt
Nitrate (NO ₃ ⁻)	< 5ppt
Sulfate (SO ₄ ²⁻)	6 ppt
Oxalate (C ₂ O ₄ ²⁻)	< 5ppt
Phosphate (PO ₄ ³⁻)	< 5ppt

Comment:

UPW sampled under N₂ atmosphere.
Date of sampling: 16.07.2024
Operator: Sébastien Grand

Dr. Dimitriou-Christidis Petros
Head of Innovation Laboratory

Die approbierte gedruckte Originalversion dieser Diplomarbeit ist an der TU Wien Bibliothek verfügbar
The approved original version of this thesis is available in print at TU Wien Bibliothek.

*Measuring device: Sievers 500RLe TOC analyzer

**Measuring device: UDI-50 Liquid Particle Counter PMS