

Quick “easy?!” determination of the diameter of nanocapillaries

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ABSTRACT

Precise measurements of the inner diameter (ID) of nanocapillaries are of interest to many areas of study due to the high sensitivity of gas and liquid flows with respect to the radius of the capillary. Applications ranging from biological transport to electronics manufacture require knowledge of fluid transport properties through passages with nanoscale dimensions. In the microscale, volume flow and fluid velocity are quadratic and squared functions of the capillary radius, respectively. While these relationships hold for most fluids in the nanoscale, the dependence on the ID is extreme with small variations in diameter leading to significant variations in flow properties.

The current approach for measuring nanocapillary ID (i.e., FESEM) is time consuming and typically requires a conductive coating. A simple, nondestructive test to accurately determine the diameter of nanocapillaries based on bubble point was developed. The apparatus consists of a high pressure gas source connected to a nanopipette where the tip is located under the surface of a liquid. Bubble rate is determined as a function of pressure using an optical microscope. By using the Laplace relationship between surface tension induced pressure and capillary radius one can define inner diameter of nanocapillaries.

Keywords: nanocapillary, bubble

1 INTRODUCTION

There are a lot of techniques to evaluate inner diameter of nanocapillaries, for instance: microscopic methods, and SEM/TEM analysis [1]. But they have limitations and disadvantages. Due to wave length restrictions the microscopic method is useless for radii less than ~200 nanometers. Scanning Electron Microscopy can be used, but it involves coating the capillary with gold which drastically changes the outer diameter, especially when working with diameters of capillaries below 50 nm. The thickness of coating can be up to 30-40 nm. Additionally, it is important to know not only the outer, but also the inner diameter of nanocapillary. Another disadvantage of SEM technique is cost. That is why an easier and cheaper technique to determine the inner diameter of capillaries, the Bubble point apparatus, was developed.

2 EXPERIMENT

A bubble point apparatus was developed to accurately evaluate the inner diameter of the nanocapillary and predict the behavior of gas flow inside the nanocapillary quickly and without the need for ongoing SEM studies.

The setup consists of five main parts (see Fig. 1 and 2):

1. Gas supply - Dry Nitrogen (99.998%)
2. Pressure/flow regulator with Ashcroft digital Pressure gauge – 0.05% FS accuracy
3. Olympus BX 60 Microscope – 50-1000x magnification
4. Nano-capillary encased in PEEK tubing
5. Liquid reservoir

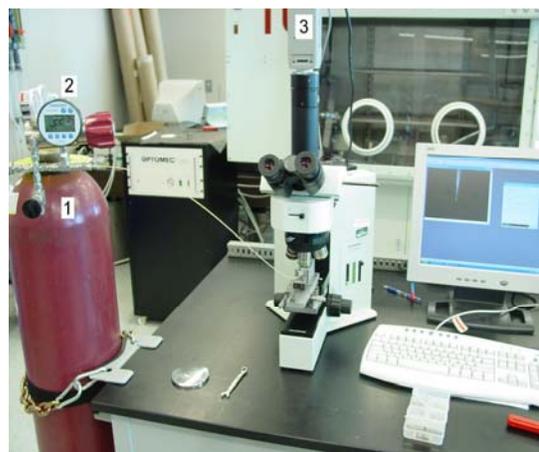


Figure 1: The parts of bubble point apparatus.

2.1 Background

The apparatus works by submerging a nanocapillary in a liquid, in this case, water. Initially, capillary forces draw water into the nanocapillary. As pressure is applied to the nanocapillary, the water is forced out.

The critical pressure is defined as the pressure at which all water is pushed out and a hemisphere of gas with a radius of curvature equal to the inner radius of the nanocapillary is formed at the nanocapillary tip. When critical pressure is reached, the bubble is stable, neither growing nor collapsing. If the applied pressure is slightly

higher than the critical pressure, the bubble will begin to grow.

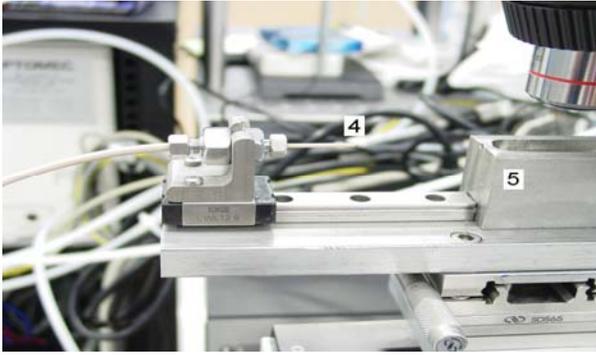


Figure 2: The parts of bubble point apparatus.

Bubble growth is a function of fluid flow rate, which in turn is a function of applied pressure, and the radius of the nanocapillary. The critical bubble radius is the radius of bubble when the buoyancy force on the bubble overcomes the surface tension force. At this point, the bubble will detach from the end of pipette and a new bubble will start growing.

At a given $P > P_{cr}$, bubble growth is a function of flow rate and bubbles will form and detach with regularity. The time between bubble detachment can be related to the flow rate when all else is constant. This in turn results in a mathematical relationship for the time between bubbles and the applied pressure. This data can be used to construct a plot of time versus applied pressure. As the applied pressure approaches the critical pressure, the time between bubbles goes to infinity, indicating P_{cr} has been reached.

The relationship between critical pressure P_{cr} and radius of capillary R_c is given by [2], [3]:

$$P_{cr} = \frac{2\sigma}{R_c}, \quad (1)$$

where σ is the surface tension (σ for water is equal to 0.07 N/m).

Figure 3 shows the range of pressures which must be overcome in order to see a bubble at the free end of the capillary. For instance, the applied pressure should be at least one hundred atmospheres to produce bubbles from nano-pipettes of 10 nm. In the future studies of different liquids with lower surface tension will be conducted to allow testing of smaller capillaries.

As previously mentioned, to detach a bubble from the capillary the buoyancy force must exceed the surface tension force, given in Equation (2):

$$F_\sigma = 2\pi R_c \sigma, \quad (2)$$

where R_c is the radius of capillary.

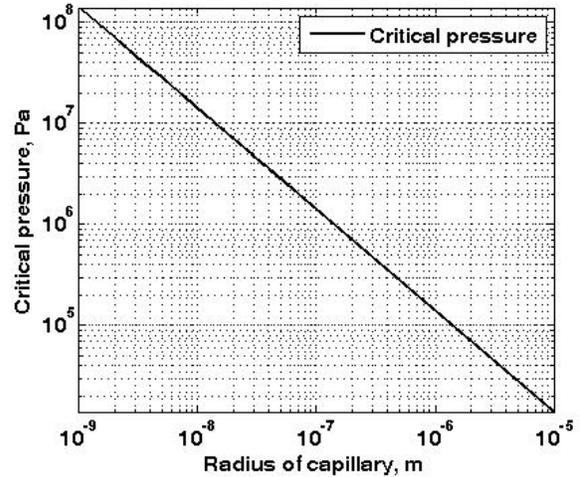


Figure 3: The critical pressure versus the radius of capillary.

At the same time buoyancy force given in Equation (3) also acts on the bubble:

$$F_g = \frac{4}{3}\pi R_b^3 (\rho_l - \rho_g)g, \quad (3)$$

where ρ_l and ρ_g are the liquid and gas density respectively, and R_b is the radius of bubble.

The critical bubble size can be calculated from the force balance of Equation (2) and (3). This relation is given in Equation (4):

$$R_{cr} = \sqrt[3]{\frac{3R_c \sigma}{2(\rho_l - \rho_g)g}} \quad (4)$$

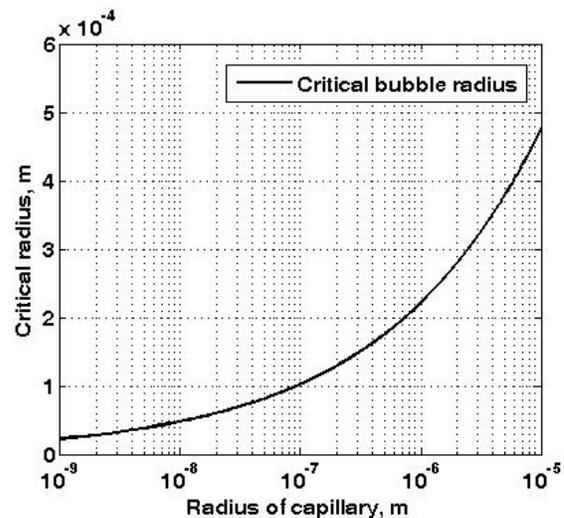


Figure 4: The critical radius versus the radius of capillary.

As seen in Figure 4 the radius of the bubble at the point of detachment is relatively large, in range of 0.1 mm. This allows the use of standard microscope with low magnification (100-200x) to visualize bubbles.

2.2 Experimental procedure

Pipettes used in all testing were fabricated with the shortest possible tip. This was done to obtain a more robust tip for the experiments. To pull nanocapillaries the Sutter instrument P-2000 was used. This instrument can be used to make nano-pipettes as small as 15 nm. In this initial stage, the inner diameter of the quartz capillary is relatively large, 75- 100 μm .

Once pipettes were fabricated, they were secured in the bubble point apparatus and placed under 100-200x magnification. The procedure for mounting the nanocapillary in Bubble point apparatus looks as follows:

- 1) Insert nanocapillary (NC) into PEEK tubing,
- 2) Place NC with PEEK tubing in the carriage of the apparatus,
- 3) Pore water in liquid reservoir and slide NC into liquid block by moving the carriage,
- 4) Apply pressure in range necessary for bubbles.

Pressure was gradually increased in increments of 25 kPa until bubbles were formed and detached. The time scale from when the bubble became visible to detachment was of the order of milliseconds. The time between bubbles was recorded for ten successive bubbles at constant pressure. The pressure was increased and the time for the next ten bubbles was measured.

During the experiment applied pressure is always a little bit more than the critical pressure in order to make bubbles grow. If applied pressure would be equal exactly to the critical pressure there would be no visible bubbles. The goal was to recalculate critical pressure from experimental data as precisely as possible.

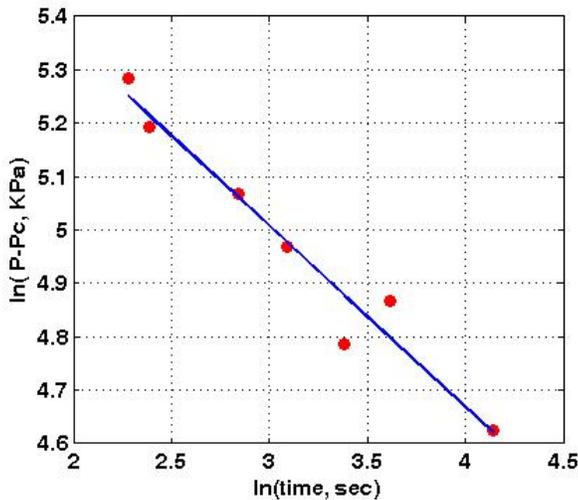


Figure 5: The sketch of power fitting.

To solve this problem two statistical methods are described below. A value for the critical pressure is assumed to be less than minimal applied pressure. For the first method the plot of the “ $\log(p - p_{cr})$ versus $\log(\text{time})$ ” relation is linearly fit with experimental data (see Fig. 5).

Here it is supposed that the relationship obeys the power approximation:

$$p - p_{cr} = \frac{A}{t^\alpha} = At^{-\alpha}, \quad (5)$$

where α is positive number, t is time.

Therefore: $\log(p - p_{cr}) = \log A - \alpha \log t$.

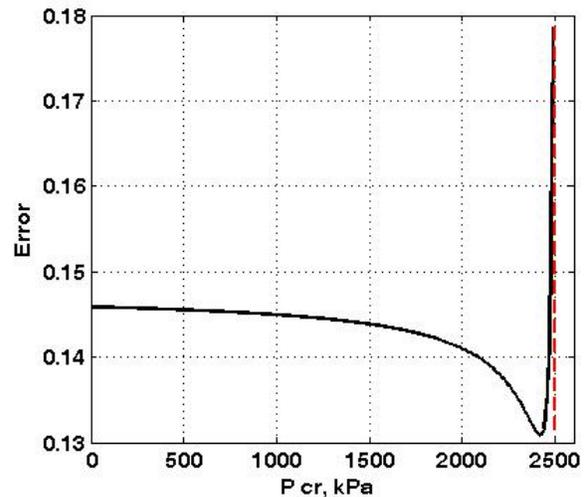


Figure 6: The Error in approximation versus the critical pressure.

By knowing equation for the fit line the error for this particular critical pressure can be obtained. The value for critical pressure is changed, and the errors between the fit line and experimental data are calculated for different critical pressures. This gives the “error versus critical pressure” relation curve. Based on the minimum of this curve, the critical pressure is selected (see Fig. 6).

For the second method the plot of “ $\log(p - p_{cr})$ versus time” relation is also linearly fit to experimental data. Here the pressure is assumed to obey an exponential approximation:

$$p - p_{cr} = A \exp^{-Bt}, \quad (6)$$

where B is positive number, t is time.

Therefore: $\log(p - p_{cr}) = \log A - Bt$. Finally a similar Error calculation as for the first approach is conducted.

Figure 6 shows “error vs. critical pressure” dependency in the power approximation. Relying on this curve the critical pressure is defined to be 2400 kPa. Then by using

the Laplace Equation (1) the inner radius is calculated at 58 nm.

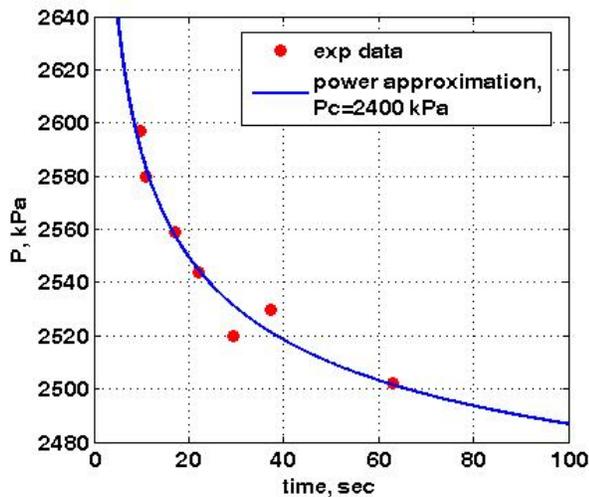


Figure 7: The experimental data and the best power approximation.

One challenge of the experiments was to minimize variations in the data sets. This apparatus is very sensitive due to scale of research. A small deviation in pressure, in properties of water, or in the ambient environment can cause large changes in the final result. The proposed causes of these variations are:

- Impurities inside of nanocapillary.
- Airborne particles plus contaminants. Experiments were done in ambient atmosphere. It is possible that dust or particles in the air contaminate the end of nanopipette.
- Particles in water. Deionized water was used in the Bubble point apparatus. This water was also passed through Acrodisc Sterile Syringe Filters from VWR with pore radius of 0.2 micron.

3 CONCLUSIONS

A simple apparatus to measure the inner radius of nanocapillaries was designed and created. The technique is inexpensive, simple and none destructive compared with others. The advantages of this method as well as disadvantages were discussed. All parts of apparatus and the whole procedure of work were shown and described. Several questions are still open, but up to now the Bubble point apparatus is very useful way of nanocapillary characterization.

REFERENCES

- [1] Scott Mittman, Dale G. Flaming, David R. Copenhagen, and Jack H. Belgum, "Bubble pressure measurement of micropipet tip outer

diameter," J. of Neuroscience Methods, 22, 161-166, 1987.

- [2] F.L. Roman, J. Faro, and S. Velasco, "A simple experiment for measuring the surface tension of soap solutions," Am. J. Phys, 69(8), 920-921, 2001.
- [3] Huai Z. Li, Youssef Mouline, Noel Midoux, "Modelling the bubble formation dynamics in non-Newtonian fluids," Chemical Engineering Science, 57, 339-346, 2002.