

Probing Liquid Surfaces under Vacuum Using SEM and ToF-SIMS

Supplementary materials

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Part S1. Methods and Materials

S1.1 Fabrication of the microfluidic interface

The PDMS microfluidic device was fabricated using a soft lithography method. First, a template for casting was made on a silicon substrate, with SU-8 photoresist (Microchem, Newton, MA). This made features about 8 μm high using standard photolithography technique (See Figure 1B). The microchannel is 80 μm wide, 1.97 mm long and the narrow part of the channel in the middle is 10 μm wide, 30 μm long. The depth of the whole channel is 8 μm . The photomask was designed using the IntelliCAD software (IntelliCAD Technology Consortium, Portland, OR), and printed with 50,800 dpi resolution at Fineline Imaging (Colorado Springs, CO). A 10:1 ratio (w/w) of PDMS prepolymer and curing agent (Sylgard 184, Dow Corning Co., Midland, MI) were then thoroughly mixed, degassed under vacuum, poured onto the patterned template to a thickness of 1 cm, and cured in an oven at 75 °C overnight. After removing the patterned PDMS substrate from the template, two 1 mm diameter through-holes were made at the end of the microchannel by punching the substrate with a manually sharpened syringe needle (NE-301PL-C; Small Parts, Miramar, FL). The flow channel was enclosed using a silicon nitride (SiN) window (window: 100 nm thickness silicon nitride membrane, 0.5x0.5 mm²; and frame: 200 μm thickness silicon, 7.5x7.5 mm², Norcada Inc., Canada). The irreversible sealing between PDMS and SiN membrane was generated by oxidizing them both in an oxygen plasma (PX-250; March Plasma Systems, Concord, CA) for 1 min and immediately bringing them into conformal contact¹ under a stereomicroscope (SMZ-U, Nikon, Japan). The assembly was then placed in an oven at 75 °C for 2 h to form an irreversible bond. Above the channel on the SiN window, a hole approximately 2.5 μm in diameter was drilled through the membrane by the focused ion beam (FIB) (See Figure 1C). Alternately, the aperture was fabricated by using the TOFSIMS depth profiling feature.

S1.2 Reagents

Various liquids, including deuterium water (Aldrich, 99.9%), mixed sodium chloride, NaCl, (Aldrich, 99.0%) and sodium iodide, NaI, (Aldrich, 99.99) aqueous solutions, and DI water, were filled in the system by a syringe pump (Harvard apparatus, Holliston, Massachusetts), respectively.

S1.3 Instrumentation

An FEI Helios Nanolab dual-beam focused ion beam/scanning electron microscopy (FIB/SEM) was used to form the holes in the SiN film. The optical imaging of the channel and the hole was obtained with a Zeiss, Axioskop Routine Microscope. An FEI XL30 digital field mission gun Environmental Scanning Electron Microscope (ESEM) was used in this work. The microscope could be used in the “environmental” mode with up to 10 Torr of water vapor for hydration studies or under high vacuum SEM mode for chemical and morphological studies. For these studies it was not used in the high-pressure “environmental” mode, but rather in the high vacuum mode, basically like any conventional SEM. The energy dispersed X-ray spectrometer (EDX) was an EDAX 136-10 with Si(Li) detector of an active area of 30 mm² and a light element ATW2 window, which allows X-ray detection from elements higher than beryllium ($Z > 4$). The operating vacuum pressure was 3×10^{-6} mbar. A ToF-SIMS V spectrometer (IONTOF GmbH, Münster, Germany) was used to study the liquid interface in this work. A pulsed 25 keV Bi⁺ ion beam with an incident angle of 45 degree off the normal was used as the primary ion beam for all measurements. The Bi⁺ beam was focused into a diameter of about 250 nm and was rastered over a $10 \times 10 \mu\text{m}^2$ area for imaging acquisition. The focused Bi⁺ beam was also used to directly drill a hole on the SiN membrane with a circular raster area with a diameter of about 3 μm . The main chamber operating vacuum pressure in these experiments was 2.5 to 5.5×10^{-7} mbar. The interface device is normally preconditioned in a vacuum chamber to check leaks before using in SEM/EDX or ToF-SIMS. The instrument can be easily run on other Bi ions (Bi⁺² or Bi⁺³), which would give higher sensitivity, but at some expense in beam resolution.

Part S2 Related Calculations

S2.1 Outgassing/Permeability of Materials

Of the materials used in the construction, the PTFE tubing and even more so the PDMS, have significant permeability to air and water vapor. In our case, the permeation of these two materials was calculated below:

Permeation of PTFE to water: $0.09 \text{g} \cdot \mu\text{m} / \text{m}^2 \cdot \text{day}^2$; the tubing size: OD: 0.0625” and ID: 0.03”, the total length used 2x21.9cm, the maximum experiment time 8hours.

$$W = 0.09 \text{g} \cdot \mu\text{m} / \text{m}^2 \cdot \text{day} \times 1/3 \text{day} \times 0.219 \text{m} \times 2\pi(0.03 \text{inch} \times 0.0254 \text{m/inch}) / (0.0625 - 0.03) \text{inch} \times 25.4 \times 10^3 \mu\text{m/inch} = 3.8 \times 10^{-8} \text{g}$$

Permeation of PDMS to water: $4000 \times 10^{-11} \text{cm}^3 \text{cmcm}^{-2} \text{s}^{-1} \text{mmHg}^{-1}$,³ the diameter at ends of the channel: 1mm, channel length: 2mm, the narrow channel part is 10 μm wide and 30 μm long, the

wide part is 80 μm wide and 1.97mm long, and the channel depth is 8 μm . Assuming the average thickness of PDMS is 1cm

$$V_{\text{H}_2\text{O}} = 4000 \times 10^{-11} \text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{mmHg}^{-1} \times 24 \text{mmHg} \times 8 \times 3600 \text{s} \times (0.05^2 \pi + 0.197 \times 0.008 + 0.003 \times 0.001) \text{cm}^2 / 1 \text{cm} = 2.8 \times 10^{-4} \text{cm}^3$$

$$n = PV/nRT = 1.01 \times 10^5 \text{Pa} \times 2.8 \times 10^{-10} \text{m}^3 / 298 \text{K} \times 8.314 \text{J} \cdot \text{K}^{-1} \text{mol}^{-1} = 1.1 \times 10^{-8} \text{mol} = 2.0 \times 10^{-7} \text{g}$$

Based on these calculations, only 3.8×10^{-8} and 2.0×10^{-7} g water went through tubing and PDMS block during the 8 hours. It is really small number comparing with the water in the self-contained system (200 μl , 0.2g). In addition, PDMS block was coated with a thin layer of gold to further limit the permeability of the water through PDMS. The coating gold film also prevents the PDMS from degassing. So PDMS and PTFE tubing are acceptable in our case.

S2.2 Temperature Drop

The net loss of water in this microfluidic interface will result in a local cooling of the water. In the water jet devices this cooling is extreme, cooling takes place on all sides, and the only thermal mass is the cylinder itself, whereas in our case, the aperture has fluid that on the substrate is thermally anchored to the semi-infinite solid. And the cooling is only from the small region of the aperture, which leads to greatly reduced cooling.

We assume the water is spherical, bowed inward to a hemisphere and it freely evaporates from this entire surface. This diffusion problem is covered by Crank,⁴ in Eq. (S-1):

$$\begin{aligned} D \nabla^2 C &= \frac{\partial C}{\partial t}; & \frac{\partial C}{\partial r} &= h(C_1 - C) \text{ at } r = R, \text{ for } h' \equiv h + 1/R: \\ \frac{C(r=R) - C_0}{C_1 - C_0} &= \frac{hR}{(1+hR)} \left[1 - \exp(h'^2 Dt) * \text{erfc}(h' \sqrt{Dt}) \right] \end{aligned} \quad (\text{S-1})$$

This is expressed in terms of molecular diffusion for a system initially at condition C_0 everywhere. This will be used later for estimating the effects of water loss on concentrations. We map this on to temperature as in Eq. (S-2). C is replaced by T , and D is replaced by κ/c , where κ is the thermal conductivity, c is the volumetric heat capacity, and h becomes $B(T_0)c/\kappa/(T_0-T_1)$, where $B(T)$ is the evaporative heat load per unit area. To use this as an estimate, we represent the actual evaporative heat loss versus T with a linearized version, with T_1 being the temperature where B extrapolates to zero.

$$\begin{aligned} \kappa/c \nabla^2 T &= \frac{\partial T}{\partial t}; & \frac{\partial T}{\partial r} &= \left(\frac{B(T_0)c}{\kappa(T_0 - T_1)} \right) (T_1 - T) \text{ at } r = R \\ T(r=R) &= T_0 + \frac{(T_1 - T_0)hR}{(1+hR)} \left[1 - \exp(h'^2 \kappa/c t) * \text{erfc}(h' \sqrt{\kappa/c t}) \right] \end{aligned} \quad (\text{S-2})$$

Based on this derivation, for a 3 μm diameter aperture, channel width/depth of 10 and 8 μm , and flow of 100 μL over 8 hrs, the water reaches the far side of the aperture in about 70 μs , and should cool from 298K to about 281.3 K, i.e., ~ 17 K.

S2.3 Concentration Change

The surface evaporation of the water will change concentrations of solutes. Considering cooling, assuming pure water (or dilute solutions) and the temperature is 281 K, the evaporation rate times the hole transit time of 70 μs gives a depth of water loss of 0.08 μm . But non-volatile solutes (NaCl, for example) within this 0.08 μm layers would definitely be left behind and diffuse away from the surface. According to Eq. (S-1) and (S-3):

$$\frac{\partial C}{\partial r} = \frac{1}{D} \rho_0(T) \sqrt{\frac{kT}{2\pi m}} \frac{1}{\rho_{liq}} (C) \quad \text{at } r = R \quad (\text{S-3})$$

where $\rho_0(T)$ is the vapor pressure of water at the time-dependent surface temperature of the water. D is the diffusion constant for the solute. Assuming $1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ (that for NaCl), the approximate diffusion distance after 70 μs is 0.32 μm . This is small compared to the aperture radius, and 4 times larger than the lost volume of water, i.e., 0.08 μm . With the vapor pressure and mean speeds fixed at 281 K, this yields surface concentrations of solute just before it reaches the far side of the aperture of 1.2 times the initial concentration. But note that this is not an indication of catastrophic drying, for solutions well below saturation. We should be able to alter the amount of drying just by changing the flow rate, and observe the effects directly via the analytical instruments that can now be brought to bear upon the liquid.

Part S3

Figure S1 shows the very dark secondary electron image in the hole, which indicates the absence of water behind the hole.

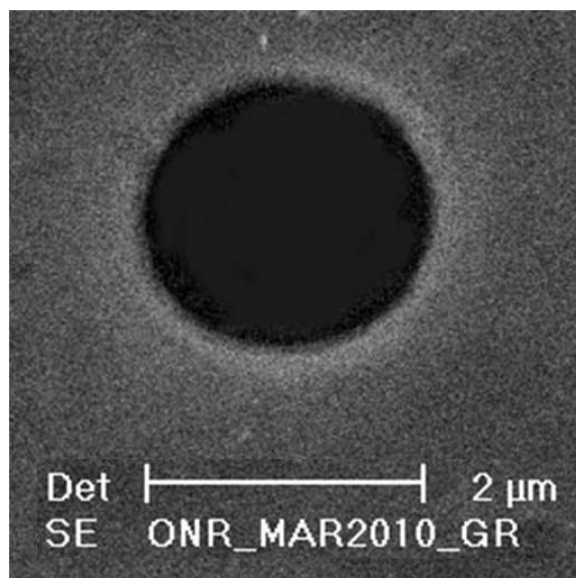


Figure S1. SEM/EDX image of the micron hole with no water behind it.

References

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