Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Vapour permeation measurements with free-standing nanomembranes

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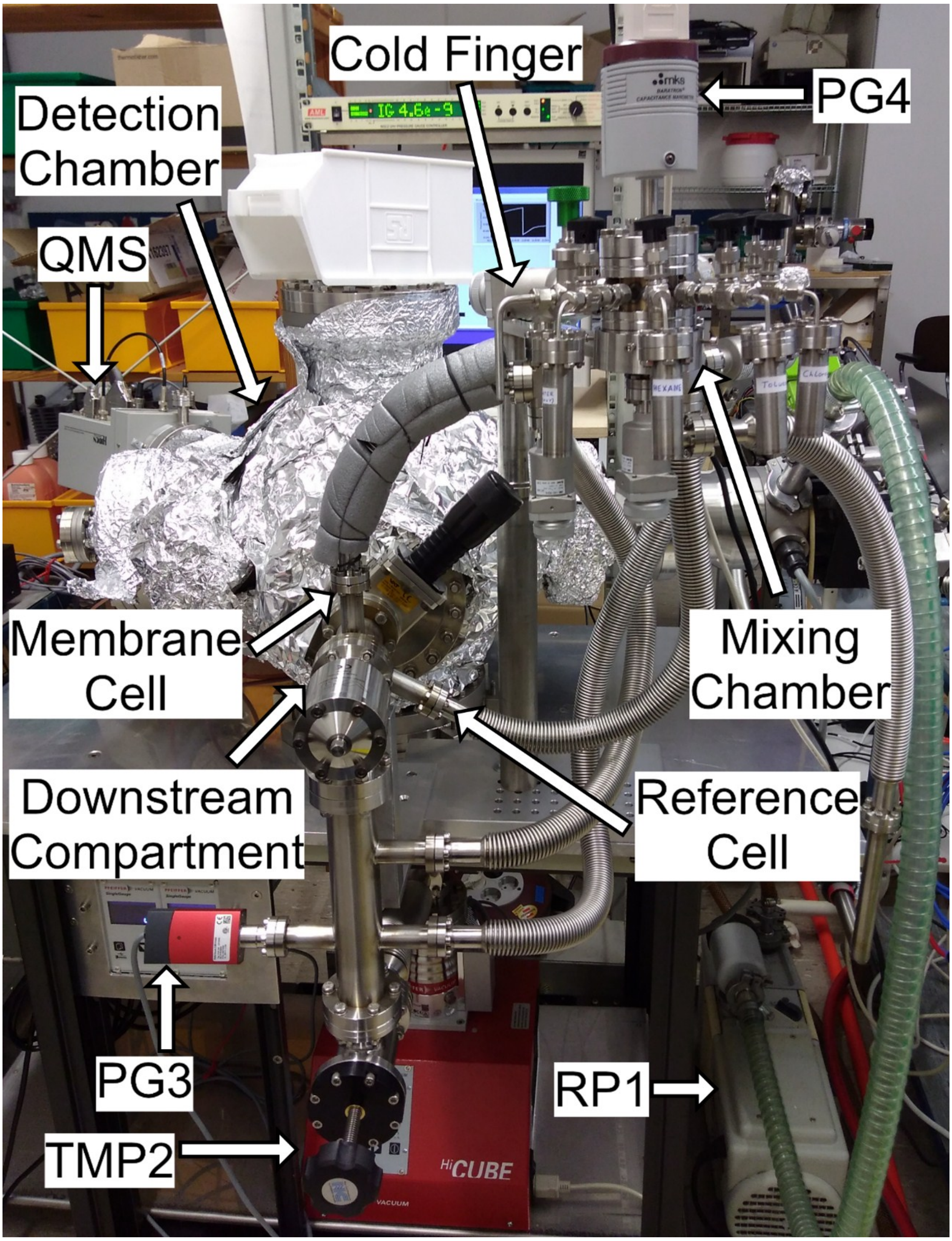

Fig. SM1. Photograph of the high-vacuum permeation setup. To navigate the reader, some of the system components are indicated similar to Fig. 1.

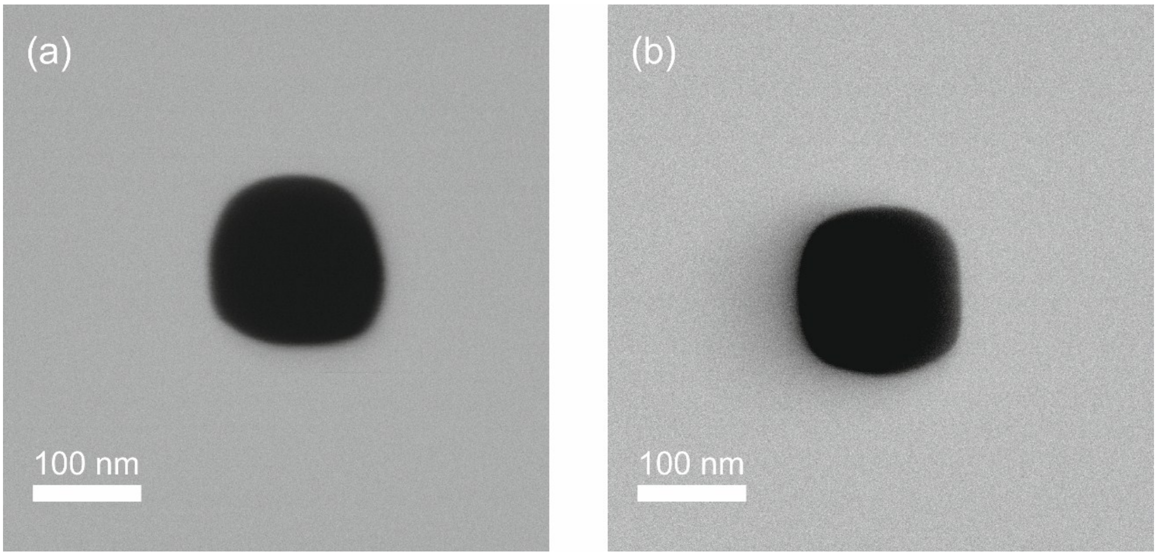

Fig. SM2. (a) Helium ion micrograph of the calibration nanoaperture. It was drilled in a 100-nm-thick silicon nitride window (Silson Ltd.) by a focused helium ion beam [1]. The area of the opening is determined from the image to be 19400 nm^2. The gas transmission probability α is calculated using the approximation for short circular ducts as follows [2]:

$$\alpha = \frac{1}{1 + 3l'/8r}; \qquad \frac{l'}{l} = 1 + \frac{1}{3 + 3l/7r}$$

where l is the length of the duct, and r is the radius. Deducing the effective r from the area of the aperture, one obtains α equal to 0.62.

(b) Helium ion micrograph of the nanohole which was placed into the membrane cell to verify the equality between the sample and the reference inlets. Its area equals to 18300 nm^2 and the transmission probability is obtained to be 0.61. The two apertures were compared by recording QMS signals for different gases as a function of applied feed pressure. The discrepancy in corresponding intensity/flow rate slopes was found to be less than 10% indicating the accuracy of the system.

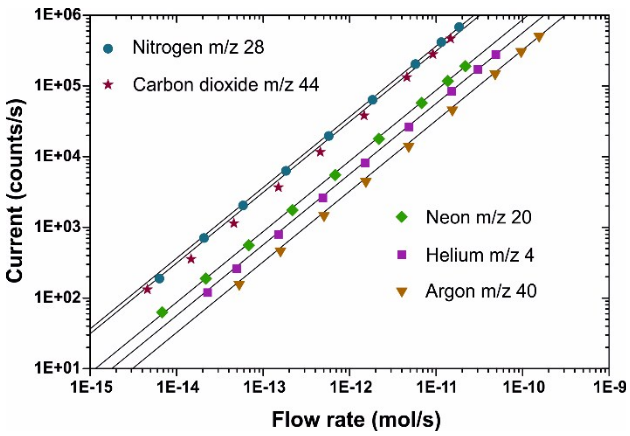

Fig. SM3. QMS response as a function of the gas flow rates. The measurements were done with the aperture depicted in Fig. SM2a upon increasing the upstream pressure. The flow rate is determined in accordance with the above described gas transmission probability.

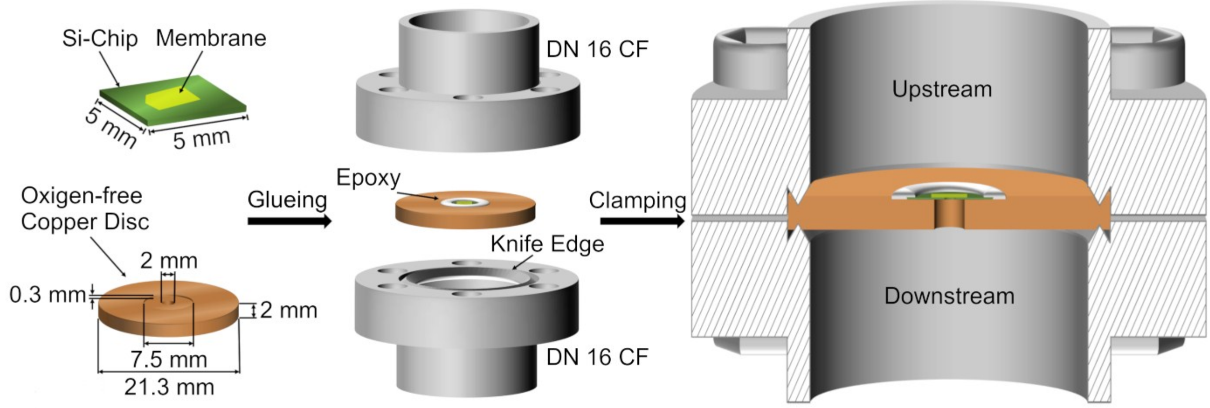

Fig. SM4. Schematic of the sample assembly. The fixture is analogous to that used in [3]. A nanomembrane is suspended over a holey silicon nitride window and is kept tightly by van der Waals forces [4]. The silicon chip is fixed onto a copper disc with an epoxy glue, and the leak-tight connection is achieved by securing the disc between two conflat flanges. The reference nanoaperture is mounted alike.

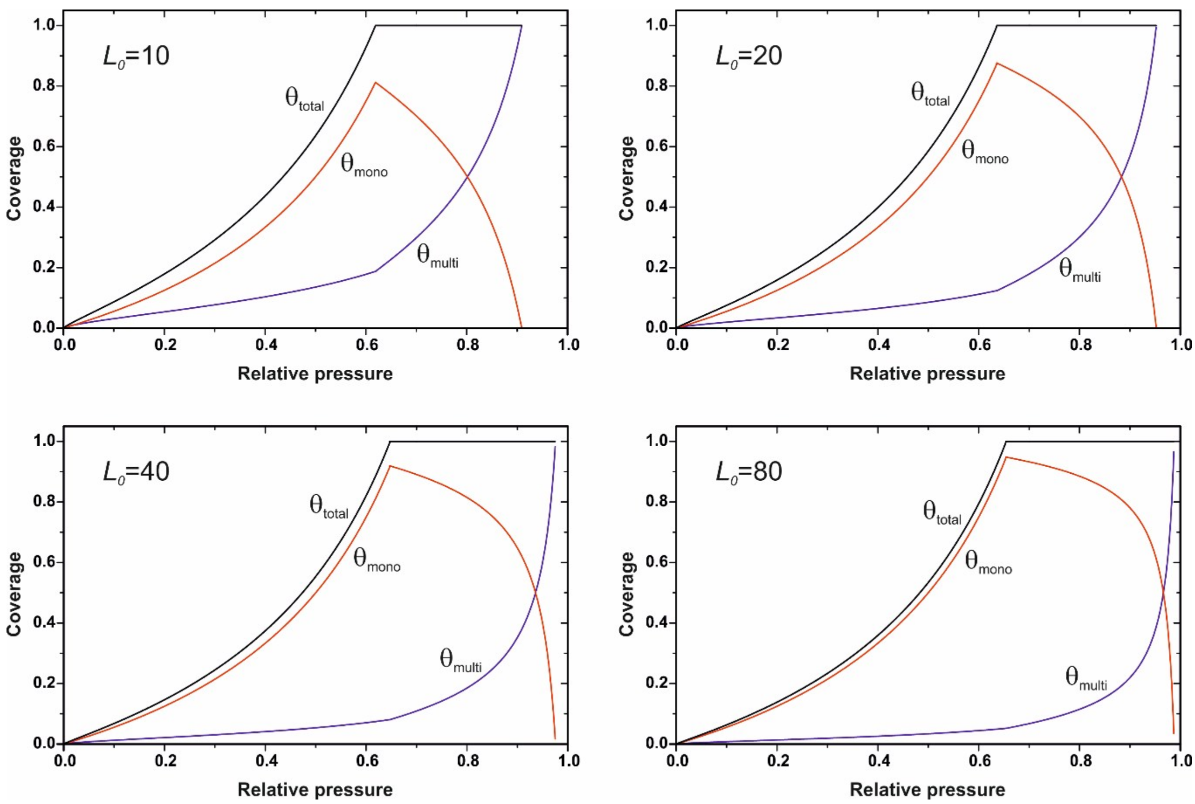

Fig. SM5. Water coverage as a function of relative pressure. θ_{mono} and θ_{multi} were calculated within the developed model for the indicated values of L_0. θ_{total} stands for the total surface coverage, i.e. $\theta_{mono} + \theta_{multi}$.

Table SM1. System components. Designations are identical to those shown in Fig. 1.

	Designation	Description	Supplier	Model
Vacuum Pumps	RP1	Oil Sealed Rotary Vacuum Pump	Edwards, UK	RV8 (>10 years old)
	RP2	Chemical Resistant Scroll Pump	Edwards, UK	nXDS15iC (brand new)
	TMP1	Turbomolecular Pump	Leybold-Heraeus, Germany	TURBOVAC TMP-150 (>10 years old)
	TMP2	HiCube 80 Eco Pumping Station incorporating Turbomolecular Pump and Backing Pump	Pfeiffer Vacuum Technology AG, Germany	HiPace 80 (brand new) MVP 015-4 (brand new)
Valves	V1-V5	Chemical Resistant Angle Valve	SMC Corporation, Japan	XMH-16C-XQ1A (brand new)
	V6-V10	Stainless Steel Integral Bonnet Needle Valve	Swagelok, USA	SS-ORS3MM (brand new)
	V11	Stainless Steel High Flow Metering Valve	Swagelok, USA	SS-6L-MM (brand new)
	GV	Ultra-High Vacuum Gate Valve	VAT Group AG, Switzerland	A571030 (>10 years old)
	AV1	Easy Close All-Metal Angle Valve	VAT Group AG, Switzerland	54032-GE02 (brand new)
	AV2	Copper Seal Angle Valve	Nor-Cal Products, Inc., USA	CSV-S04400 (brand new)
Pressure Gauges	PG1	Ion Gauge	Arun Microelectronics Ltd, UK	AIG17 (>10 years old)
	PG2	Pirani/Cold Cathode Gauge	Pfeiffer Vacuum Technology AG, Germany	PKR 360 (brand new)
	PG3	Pirani/Capacitance Gauge	Pfeiffer Vacuum Technology AG, Germany	PCR 280 (brand new)
	PG4	Baratron Capacitance Manometer	MKS Instruments, USA	626C52MCE9 (brand new)
Detector	QMS	Quadrupole Mass Spectrometer	Hiden Analytical, UK	HAL V RC PIC-RGA 1001 (>10 years old)

Solution of the Eqs. 10 and 11

1) Rearranging

$$n_0\frac{L^3}{L_0^2} = n_0\frac{x}{2(1-x)},$$

one obtains:

$$L = \left(\frac{L_0^2}{2}\frac{x}{(1-x)}\right)^{\frac{1}{3}} = \left(\frac{L_0}{2}y\right)^{\frac{1}{3}},$$

where *y=x/(1-x)*.

2) The equation

$$n_0 + n_0\frac{L^2}{L_0^2}(L-1) = n_0\frac{x}{(1-x)}$$

can be written in the form

$$L^3 - L^2 = L_0^2\left(\frac{x}{(1-x)} - 1\right) = L_0^2(y-1),$$

where *y=x/(1-x)*.

This cubic equation can be solved using the Cardano formula. For simplicity, we denote
$k = L_0^2(y-1)$
and obtain:

$$L^3 - L^2 - k = 0,$$

which corresponds to a general form

$$L^3 + aL^2 + bL + c = 0$$

with the coefficients $a = -1$, $b = 0$ and $c = -k$.

Substituting with *L=z-a/3*, we obtain the depressed cubic, where the quadratic term equals to zero:

$$\left(z-\frac{a}{3}\right)^3 + a\left(z-\frac{a}{3}\right)^2 + b\left(z-\frac{a}{3}\right) + c = 0$$

$$\left(z-\frac{a}{3}\right)\left(z^2-\frac{2}{3}az+\frac{a^2}{9}\right) + a\left(z^2-\frac{2}{3}az+\frac{a^2}{9}\right) + bz - \frac{1}{3}ab + c = 0$$

$$\left(z^3-\frac{2}{3}az^2+\frac{a^2}{9}z-\frac{a}{3}z^2+\frac{2}{9}a^2z-\frac{1}{27}a^3\right) + \left(az^2-\frac{2}{3}a^2z+\frac{a^3}{9}\right) + bz - \frac{1}{3}ab + c = 0$$

$$z^3 + \left(-\frac{2}{3}a-\frac{1}{3}a+a\right)z^2 + \left(\frac{1}{9}a^2+\frac{2}{9}a^2-\frac{2}{3}a^2+b\right)z + \left(-\frac{1}{27}a^3+\frac{1}{9}a^3-\frac{1}{3}ab+c\right) = 0$$

$$z^3 + \left(-\frac{1}{3}a^2+b\right)z + \left(\frac{2}{27}a^3-\frac{1}{3}ab+c\right) = 0$$

Inserting the coefficients leads to:

$$z^3 - \frac{1}{3}z - \frac{2}{27} - k = 0,$$

where $p = -\frac{1}{3}$ and $q = -\frac{2}{27} - k$.

Now, one can calculate the discriminant:

$$D = \left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3 = \frac{q^2}{4} + \frac{p^3}{27} = \left(\frac{-\frac{2}{27} - k}{2}\right)^2 + \left(\frac{-\frac{1}{3}}{3}\right)^3 = \left(\frac{\left(\frac{-2-27k}{27}\right)}{2}\right)^2 + \left(\frac{-\frac{1}{3}}{3}\right)^3$$

$$= \left(\frac{-2-27k}{54}\right)^2 + \left(\frac{-1}{9}\right)^3 = \frac{4 - 108k + 729k^2}{2916} - \frac{1}{729} = \frac{4 - 108k + 729k^2}{2916} - \frac{4}{2916}$$

$$= \frac{729k^2 - 108k}{2916} = \frac{27k^2 - 4k}{108}$$

Using the Cardano formula

$$z = \sqrt[3]{-\frac{q}{2} + \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}} + \sqrt[3]{-\frac{q}{2} - \sqrt{\frac{q^2}{4} + \frac{p^3}{27}}}$$

we obtain:

$$z = \sqrt[3]{\frac{2+27k}{54} + \sqrt{\frac{27k^2 - 4k}{108}}} + \sqrt[3]{\frac{2+27k}{54} - \sqrt{\frac{27k^2 - 4k}{108}}}$$

Undoing the substitution *L=z+1/3* , *L* is expressed as

$$L = \sqrt[3]{\frac{2+27k}{54} + \sqrt{\frac{27k^2 - 4k}{108}}} + \sqrt[3]{\frac{2+27k}{54} - \sqrt{\frac{27k^2 - 4k}{108}}} + \frac{1}{3}$$

where $k = L_0^2(y-1)$.

The final solution is written as following:

$$L = \sqrt[3]{\frac{2+27L_0^2(y-1)}{54} + \sqrt{\frac{27L_0^4(y-1)^2 - 4L_0^2(y-1)}{108}}} + \sqrt[3]{\frac{2+27L_0^2(y-1)}{54} - \sqrt{\frac{27L_0^4(y-1)^2 - 4L_0^2(y-1)}{108}}} + \frac{1}{3}$$

References

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4. S. P. Koenig, N. G. Boddeti, M. L. Dunn, and J. S. Bunch, Nat. Nanotech., 2011, **6**, 543.