Molecular transport through capillaries made with atomic-scale precision

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Nanometre-scale pores and capillaries have long been studied because of their importance in many natural phenomena and their use in numerous applications1. A more recent development is the ability to fabricate artificial capillaries with nanometre dimensions, which has enabled new research on molecular transport and led to the emergence of nanofluidics2–4. But surface roughness in particular makes it challenging to produce capillaries with precisely controlled dimensions at this spatial scale. Here we report the fabrication of narrow and smooth capillaries through van der Waals assembly5, with atomically flat sheets at the top and bottom separated by spacers made of two-dimensional crystals6 with a precisely controlled number of layers. We use graphene and its multilayers as archetypal two-dimensional materials to demonstrate this technology, which produces structures that can be viewed as if individual atomic planes had been removed from a bulk crystal to leave behind flat voids of a height chosen with atomic-scale precision. Water transport through the channels, ranging in height from one to several dozen atomic planes, is characterized by unexpectedly fast flow (up to 1 metre per second) that we attribute to high capillary pressures (about 1,000 bar) and large slip lengths. For channels that accommodate only a few layers of water, the flow exhibits a marked enhancement that we associate with an increased structural order in nanoconfined water.

Our work opens up an avenue to making capillaries and cavities with sizes tunable to ångström precision, and with permeation properties further controlled through a wide choice of atomically flat materials available for channel walls.

There are two principal routes for making pores and capillaries with nanometre dimensions7. The top-down approach uses micro- and nano-fabrication techniques and has realized channels down to 2 nm in average height8, but is fundamentally limited by surface roughness that is hard to reduce below a few nanometres using conventional materials and techniques9. The alternative bottom-up approach uses chemical synthesis with many advantages for scalable manufacturing, but which offers limited flexibility—especially for making capillaries with dimensions larger than several ångströms. Notable exceptions are nanotubes of carbon and other materials, which offered opportunities for studying mass transport through channels with nanometre diameters and atomically smooth walls10–12 and promised new kinds of membrane and nanofluidic systems. But it has proved extremely difficult to integrate nanotubes into macroscopic devices, which perhaps explains the continuing controversy about fast water transport through carbon nanotubes (CNTs): conflicting findings from the very few experimental groups who succeeded in studying their permeation properties13–15,16 have been discussed intensively in theoretical literature13,14,17, but with little further input from experiment. Graphene has also attracted considerable attention as a core material for making ultra-short nanopores18–21, and gas, liquid, ion and DNA transport through such pores has been reported. But the fundamental restrictions inherent to top-down and bottom-up techniques also limit the ability to control the diameters of graphene nanopores precisely. We overcome such problems by exploiting both the atomic flatness of graphene (which allows for relatively long channels with atomically smooth walls, somewhat similar to CNTs) and its atomic thinness (which, through stacking, provides atomic-scale control of the channel’s principal dimension, height). Our approach also preserves much of the flexibility offered by microfabrication techniques.

Figure 1a explains the basic idea behind our nanocapillary devices: they consist of atomically flat top and bottom graphite crystals that are separated by an array of spacers made from few-layer graphene. Such structures are fabricated by van der Waals (vdW) assembly using dry transfer techniques2 and a free-standing Si nitride membrane with a rectangular hole as mechanical support for the assembly. Figure 1b–d shows micrographs of some of our devices. For details of their fabrication, we refer to Methods section ‘Making nanocapillary devices’ and Extended Data Figs 1 and 2. We denote our devices by the number $N$ of graphene layers used as spacers. The height $h$ of the cavity available for molecular transport can then be estimated as $N_h$, where $a \approx 3.4$ Å is the interlayer distance in graphite, that is, the effective thickness of one graphene layer. All the capillaries reported here had the same channel width $w \approx 130$ nm, and 200 of them were incorporated within each device to increase molecular flow (Fig. 1). Their length $L$ varied from $<2\mu$m to $\sim 10\mu$m. Despite the large aspect ratios $w/L$, we found no sagging of the graphite walls, which would cause capillary closure (Fig. 1d and Extended Data Fig. 3).

Under ambient conditions, all surfaces are covered with various adsorbates including water and hydrocarbons22, and it is not unreasonable to expect that nanocapillaries could be blocked by contamination introduced during fabrication or adsorbed from the air. Accordingly, we first checked whether our devices were open for gas and ion transport. Extended Data Fig. 4 shows that this was the case and that He permeated through the capillaries. We carried out such He tests for practically all the devices and found them normally open, except for monolayer capillaries ($N=1$), which never exhibited any detectable permeation. Devices with larger $N$ gradually deteriorated and, after several days of measurements, often became blocked. We attribute this to a build-up of hydrocarbon contamination that creeps along surfaces and is present even under oil-free vacuum conditions in our He tests. On the other hand, if immersed in water, the capillaries showed much greater resilience. All the tested devices were found open (except for $N=1$, again) and exhibited ionic conductance scalable with their dimensions (see Methods section ‘Ionic conductance’ and Extended Data Fig. 5). Capillaries kept in water did not get blocked for months and could be repeatedly measured. The fact that such artificial channels with a height down to the ångström scale allow studies of molecular transport under normal (not ultra-high) vacuum conditions is perhaps the most surprising finding of this work.
Fig. 1 | Graphene capillary devices. a, General schematic of devices. The arrow indicates the flow direction used in all the experiments. b, Scanning electron microscopy (SEM) image of a trilayer device (top view). The spacers that are clearly seen in the area not covered by the top graphite can also be discerned underneath, running all the way to the hole etched in the bottom graphite. Three of the spacers are indicated by dotted lines and the edge of the hole by the dashed line. c, SEM micrograph of a cross-section of another device showing an array of capillaries with cavity height \( h \approx 15 \text{ nm} \). d, Cross-sectional bright field image of a bilayer capillary (\( h \approx 7 \text{ Å} \)) in a scanning transmission electron microscope (STEM). e, High-angle annular dark field (HAADF) image of the edge of the channel. The lamellae for cross-sectional imaging were made by focused ion beam milling (see Methods section ‘Visualization and characterization of graphene capillaries’).

Given the intense interest in nanoconfined water and the high stability of our devices in water, we explored their properties with respect to water permeation using precision gravimetry. As sketched in Fig. 2a and described in full in Methods, we measured weight loss from a miniature container that was filled with water and sealed with a Si nitride chip incorporating a nanocapillary device (Fig. 2a inset and Extended Data Fig. 6). An example of such measurements is shown in Fig. 2a. The slope of the measured curve yields the water evaporation rate, \( Q \). Because the total cross-section of our devices is typically \( <0.1 \text{ μm}^2 \), measurements with microgram precision over several days were required to achieve accurate determinations of \( Q \). Figure 2b shows \( Q \) observed for six devices with the same height (\( N = 3 \)) but different \( L \). Within our accuracy, \( Q \) was found to vary proportionally with \( 1/L = (1/L) \), where \( L \) is the effective average length with respect to a viscous flow, and \( (1/L) \) denotes averaging over contributions from channels with different \( L \) (see equation (1)). This dependence on \( L \) unambiguously indicates that the observed evaporation rate was limited by water flow through capillaries, in agreement with additional experimental observations described in Methods section ‘Gravimetric measurements’. The reproducibility of our gravimetry results can be judged from the scatter in the inset of Fig. 2b where \( Q \) values for the \( N = 3 \) devices are normalized by their \( L \). All the trilayer capillaries show practically the same \( Q \approx 10^{-8} \text{ g} \text{s}^{-1} \) normalized for 1 \( \mu \text{m} \) length, which translates into a flow velocity of \( \sim 0.1 \text{ m s}^{-1} \) for the shortest device in Fig. 2b (\( L \approx 4 \mu \text{m} \)). As a control, we fabricated devices following exactly the same fabrication procedures but without graphene spacers (\( N = 0 \)), in which case no weight loss could be detected. In addition, we tested our gravimetry set-up using micrometre apertures made in Si nitride membranes and found evaporation rates that agree well with those expected from theory (see Methods section ‘Gravimetric measurements’).

Having proved the accuracy and reproducibility of our measurements using trilayer devices, we investigated how the capillary flow depended on \( N \) using more than 30 different devices. Figure 3 shows that, as \( h \) decreases from \( \sim 10 \text{ nm} \) (maximum height in our gravimetry experiments), \( Q \) also decreases, as generally expected. However,
for $h < 2\,\text{nm}$, $Q$ unexpectedly shoots up by more than an order of magnitude with respect to the trend exhibited by large-$N$ capillaries, and a strong peak appears at $N = 4–5$ (Fig. 3b). Devices with monolayer spacers exhibited no detectable weight loss, similar to the case of $N = 0$ and in agreement with our He and ion-conductance tests.

The entire evaporation process involves several steps, including transport of water vapour to capillary mouths inside the container, viscous flow through the graphene capillaries and subsequent diffusion and evaporation of transported water into air. To find out which steps affect the observed permeation, we carried out additional experiments. When the container was weighed upside down so that the liquid was in direct contact with the entries of the capillaries, exactly the same $Q$ was recorded as in the upright position (see Methods section ‘Gravimetric measurements’). This is not surprising because, at 100% relative humidity (RH) inside the container and the contact angle of water on graphite $\phi \approx 55^\circ–85^\circ$, the channels should be filled with the liquid owing to capillary condensation. Atomic force microscopy and Raman spectroscopy further confirmed that the water inside the capillaries was in a liquid state (see Methods). We also note that the water meniscus cannot reside inside the nanocapillaries, given that the observed $Q$ values require a water surface area of $\sim 1\,\mu\text{m}^2$ (as follows from the Hertz–Knudsen equation), that is, one to two orders of magnitude larger than the total cross-sectional area of the capillaries in our devices. Therefore, evaporation of the transported liquid must take place outside the mouths of the capillaries, and suggests an evaporating extended meniscus, which has been extensively studied in the literature for the case of macroscopic capillaries. For our nanoscale openings, the extended meniscus is likely to involve an atomically thin layer of absorbed water that extends over micrometre distances being driven by high spreading pressures (Extended Data Fig. 7a). To assess the role of this water film in our case, we measured $Q$ for different RH outside the container. Surprisingly, no difference was found with increasing external RH up to values close to the onset of capillary condensation (see Methods section ‘Gravimetric measurements’). This shows that $Q$ is not limited by diffusion and evaporation processes outside the container, and that the limiting process in our system is instead liquid flow through the graphene capillaries—in agreement with the finding that $Q$ depends only on the capillary parameters $L$ and $N$.

For long and wide rectangular channels with $w/h \gg 1$, liquid flow driven by pressure $P$ is described by

$$Q = \rho \frac{h^3}{12\eta} \left(1 + \frac{6\delta}{h}\right) \frac{Pw}{L},$$

where $\rho$ is the water density, $\eta$ its viscosity and $\delta$ the slip length. All these characteristics of nanofluidic water may depend on $h$. To find out whether equation (1) can explain the observed water transport behaviour, we performed molecular dynamics (MD) simulations using typical parameters for water–water and water–carbon interactions (Methods). Our analysis shows that $\delta$ is large ($\sim 60\,\text{nm}$) but does not vary much with $h$ (Extended Data Fig. 7), in agreement with previous MD results for flat graphene surfaces. Also, changes in $\rho$ are found to be relatively minor, reaching 4% for our smallest channels (Extended Data Fig. 8). The viscosity $\eta$ increases by a factor of 2 for $N < 5$, which reflects the fact that water becomes more structured under nanoc confinement. Using these parameters in equation (1), we find that $Q$ detected for our smallest capillaries requires $P$ of the order of 1,000 bar. This is consistent with supporting transport measurements using containers pressurized at $\sim 1.5$ bar (close to the maximum pressure that our membranes could withstand), which revealed no difference in $Q$ (see Methods section ‘Gravimetric measurements’).

It is difficult to perform MD simulations of the capillary pressure exerted by evaporating an extended meniscus because the low density of vapour necessitates a prohibitively large simulation volume. Therefore, we introduce the following simplification. The extended curvature of the meniscus is determined by two spatial scales, its height $h$ and length outside the capillary mouth (Extended Data Fig. 7a). The length is expected to depend on RH but this was not the case experimentally, which allows us to approximate the extended meniscus using only $h$. With reference to Extended Data Figs 7a and 8a, both extended and internal menisci should have approximately the same height and involve the same interaction of water with graphite. Therefore, in both cases, $P$ can be approximated as $P_0 + \Pi \approx 2\sigma \cos(\phi)/h + \Pi$, where the first term describes the pressure due to a curved meniscus (with $\sigma \approx 72\,\text{mN}\,\text{m}^{-1}$ the surface tension of water). Even for our largest channels, $P_0$ exceeds 10 bar. The second term $\Pi$ refers to the so-called disjoining pressure, which describes the water–surface interaction, which can dominate at the nanoscale but rapidly decreases with increasing $h$. Our MD simulations (see Methods section ‘Capillary pressure’) show that, for large $N > 10$, $P$ roughly follows the classical dependence $P_0$ with $\phi \approx 80^\circ$; but the disjoining pressure becomes dominant at smaller $N$, reaching above 1,000 bar (Extended Data Fig. 8b). Combining the simulated $P$ with the other flow characteristics found in our MD analysis, equation (1) yields the $Q(N)$ dependence shown in the inset of Fig. 3b. It qualitatively reproduces our experimental findings, including the peak at small $N$ and even its absolute value. The physics behind the non-monotonic dependence $Q(N)$ can be understood as follows. At large $N$, the classical contribution $P_0 \propto 1/h$ dominates and equation (1) yields the linear dependence $Q \propto h$, in agreement with the trend observed in Fig. 3b for $h > 3\,\text{nm}$. Evaluating equation (1) numerically in the classical limit ($P = P_0$), we find $Q \approx 10^{-10}\,\text{g}\,\text{s}^{-1}\mu\text{m}$ for $h = 10\,\text{nm}$,
in agreement with the values in Fig. 3b. The marked increase in Q for small N is due to the rapidly rising disjoining pressure, whereas the final fall in Q for smallest N occurs due to a combined effect of decreasing h and increasing η, which both reduce Q, overtaking the rise in pressão at small h. Note that, if it were not for the large enhancement factor 6hδ due to the low friction of water against graphene walls, the simulated flow would be well below our detection limit.

The agreement between our model and the experiment is striking, especially if we consider the approximation used for calculating P and the unresolved experiment-theory dispute concerning water permeation through CNTs. Further work is required to fully understand the mechanisms involved, and, in particular, to model extended menisci with nanoscale dimensions. Finally, the observed closure of monolayer capillaries (N = 1) seems to be not an accidental effect. Our MD analysis reveals that such narrow cavities are intrinsically unstable and collapse due to vdW attraction between opposite graphite walls (Extended Data Fig. 9).

Our fabrication approach allows capillary devices to be prepared in which the channel height can be controlled with true atomic precision by choosing spacers of different two-dimensional crystalline materials (such as graphene, boron nitride, molybdenum disulphide) and their combinations. One can also alter the chemical and physical characteristics of these capillaries (for example, change their hydrophilicity) by using different atomically flat crystals for channel walls. Furthermore, the availability of highly insulating materials such as boron nitride and mica allows the design of nanofluidic systems in which ionic or mass transport can be controlled by gate voltage. Our current devices transfer minute amounts of liquid, typical for nanofluidics, but it is feasible to increase the flow by many orders of magnitude using dense arrays of short (submicrometre) capillaries covering millimetre-sized areas, which could be of interest for nanofiltration, for example.

**Online Content** Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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METHODS
Making nanocapillary devices. Our fabrication procedures are explained in Extended Data Fig. 1. First, we prepare a free-standing Si nitride membrane of approximately $100 \times 100 \mu\text{m}^2$ in size using commercially available Si wafers with 500 nm thick Si nitride. A rectangular hole ($3 \times 200 \mu\text{m}$) is made in the membrane using the standard photolithography and reactive ion etching (step 1). Then a relatively thick (>10 nm) graphene crystal is deposited on the hole by electron beam lithography and oxygen plasma etching to create an array of parallel stripes of ~130 nm in width and separated by the same distance (Fig. 1a). These dimensions are chosen to obtain sufficiently narrow channels (to prevent them from collapsing; see below) and, at the same time, to ensure full reproducibility using our lithography facilities. The graphene stripes are then transferred onto the bottom graphite so that they are aligned perpendicular to the long side of the rectangular opening (step 3).

Oxygen plasma etching is employed to drill through the graphite–graphene stack using the hole in Si nitride as a mask (step 4). Finally, another graphene crystal (approximately 100 nm in thickness) is ‘dry-transferred’ to serve as the capping layer. This completes a set of graphene capillaries, such that their entries and exits are accessible from the opposite sides of the Si wafer (step 5). After each transfer, the assembly is annealed at 400 °C for 3 h to remove possible contamination.

Visualization and characterization of graphene capillaries. In addition to Fig. 1, Extended Data Fig. 2 provides further examples of imaging of our graphene capillaries including their optical, atomic force microscopy (AFM), SEM and STEM micrographs. We used SEM and optical images such as in Fig. 1b and Extended Data Fig. 2a to measure lengths of our devices and calculate their average length with respect to the fractional error $\sigma = 1/10L$.

Oxygen plasma etching to create an array of parallel stripes of $\approx 130 \text{ nm}$ in width and a probe current of $21 \text{ mrad}$, a HAADF inner angle of $48 \text{ mrad}$ were introduced into two reservoirs separated by a Si wafer incorporating a graphene device under investigation. Possible air bubbles were even greater than those found for 10 times higher channels (Extended Data Fig. 4b), contrary to general expectations. A similar enhancement of He flow was previously reported for sub-2-nm CNTs and attributed to the atomic smoothness of graphene walls.

For the case of a water vapour driven by the difference in RH (differential pressure of 23 mbar), equation (2) yields evaporation rates of $\approx 5 \times 10^{-14} \text{ g s}^{-1} \text{ cm}^{-2}$ for 50 nm to avoid their collapse. On the other hand, smaller capillaries ($N < 5$) are found to exhibit leak rates that are nearly two orders of magnitude higher than the rates expected from equation (2). Moreover, their $Q_{\text{water}}$ were even greater than those found for 10 times higher channels (Extended Data Fig. 4b), contrary to general expectations. A similar enhancement of He flow was previously reported for sub-2-nm CNTs and attributed to the atomic smoothness of graphene walls.

Ionic conductance. We also tested a number of capillary devices using the electrochemical set-up shown in Extended Data Fig. 5a. KCl solutions of different concentrations with low ionic charges (approximately 5) were introduced into two reservoirs separated by a Si wafer incorporating a graphene device under investigation. Possible air bubbles were removed by extensive flushing from both sides of the Si wafer. Current–voltage ($I$–$V$) characteristics were recorded using Keithley 2636 A SourceMeter and Ag/AgCl electrodes. Extended Data Fig. 5b, c shows examples of our measurements for two devices with $N = 2$ and 17. The $I$–$V$ curves are linear at low biases and exhibit little hysteresis. At high $C$, the observed ionic currents for a given voltage differ approximately by a factor of $\approx 8$, in good agreement with the ratio between the channel heights. Devices with $N = 0$ and 1 exhibited no detectable ionic conductance.

Extended Data Fig. 5d shows that the ionic conductance, $G$, increases linearly with $C$ for ions concentrations higher than $10^{-2} \text{ M}$, and its absolute value agrees well with the values expected from the known bulk conductivity of KCl solutions. In the low concentration regime ($< 10^{-3} \text{ M}$), $G$ saturates to a constant value, the same for both devices. Such saturation is typical for nanocapillaries and attributed to the surface charge effect. In our case, the saturation value is very small and, taking into account electro-osmotic and finite-$C$ contributions, we find a surface charge density of $\approx 3 \times 10^{10} \text{ cm}^{-2}$, orders of magnitude lower than the values observed for other nanocapillaries including CNTs. This serves as another indication that graphene walls of our channels are impurity-free, in agreement with low charge densities usually found in graphene-based vdW heterostructures.

Gravimetric measurements. The set-up used in our studies of water permeation is shown in Extended Data Fig. 6a, b. The assembled capillary device was mounted on top of a container partially filled with deionized water. The container was then placed on a microbalance (Mettler Toledo XPE26) and weighed in an enclosure with a constant temperature (typically, 21 ± 0.1 °C) and at near 0% humidity that reacted to high RH in such a way that the sagging disappeared and the top graphite layer became flat in the AFM images. For example, for capillaries with $N = 5$ this straightening of graphene walls happened at ~70% RH, indicating the onset of capillary condensation. This allows an estimate for the contact angle $\phi \approx 55^\circ$, in agreement with $\phi$ observed for water on clean graphite surfaces. No changes with increasing RH were observed for sufficiently thick top layers that exhibited no initial sagging and were used in the studied devices.

Helium permeation. To ensure that the fabricated capillaries are not blocked by sagging or contamination, we checked gas permeation through them using a helium-leak detector (INFICON UL200). A principal schematic of our experimental set-up is shown in Extended Data Fig. 4a. In short, a Si wafer with a capillary device is clamped between O-rings and separates two oil-free vacuum chambers. One of them is equipped with pressure gauges and a pump to allow control of the applied helium pressure $P_h$ at the capillary entry. The other chamber is connected to the leak detector. We have found our graphene–Si nitride membranes sufficiently robust to withstand $P_h$ up to 2 bar. Examples of our tests are shown in Extended Data Fig. 4b. For N = 0 and 1, all other nanocapillaries allowed He permeation.
was maintained using molecular sieves. The weight of the container was recorded at regular intervals (typically, 1 min) using a computer.

To verify the accurate operation of the gravimetric set-up, we prepared reference devices with round apertures of different diameters, D, etched in Si nitride membranes. Using the same sample mounting and measurements procedures as for our graphene devices, we measured water evaporation through the apertures (Extended Data Fig. 6). The Knudsen numbers for our apertures are small and the evaporation can be described by diffusion of water molecules through air. The molecular flow \( F \) is given by

\[
F = \frac{1}{3} \langle v \rangle \frac{dN}{dx}
\]

where \( \langle v \rangle \) is the average velocity of molecules in air, \( t_{\text{air}} \approx 60 \text{ nm} \) is the mean free path, and \( dN/dx \) the concentration gradient. To leave the container, water molecules have to diffuse through air over a distance of about \( D \), which allows an estimate \( dN/dx \approx 2 \pi D/\langle v \rangle \) where \( \Delta n = \Delta P/(\rho k_B T) \) is the difference in water concentrations at large distances from the aperture and \( \Delta P \) the difference in their partial pressures. The diffusion problem can be solved exactly for the case of infinitely thin orifices, which is a reasonable approximation for our 500-nm-thick Si nitride membranes and yields:

\[
\frac{dN}{dx} = \frac{4 \Delta n}{\pi D} \approx \frac{4 \Delta n}{D}
\]

The resulting weight loss is given by

\[
Q = \frac{\rho m_{\text{H}_2\text{O}}}{4} \pi D^2
\]

where \( m_{\text{H}_2\text{O}} \) is the molecular weight of water. This equation yields \( Q \propto D \), in agreement with the observed behaviour in Extended Data Fig. 6d. The counterintuitive linear dependence arises because the available area for diffusion increases proportionally to \( D^2 \) whereas the diffusion length decreases as \( 1/D \). Using \( \Delta P = 23 \text{ mbar} \), the above equation yields \( \sim 1.7 \times 10^{-6} \text{ g s}^{-1} \text{ Å} (\text{m}_{\text{inum}}) \), which is within 15% from the best fit in Extended Data Fig. 6d. Importantly, the measurements for our aperture devices cover approximately the same range of \( Q \) as that found for graphene capillaries (Fig. 3). The excellent agreement between the experiment and theory confirms reliability of our gravimetry set-up.

To narrow down the range of possible explanations for the observed fast water flow, two additional sets of experiments were carried out. First, using devices with \( N = 5 \) and 30, we increased RH outside the container up to 50% and \( > 70\% \), respectively, using increments of 20%. Surprisingly, no changes in \( Q \) could be detected. At even higher external RH, the evaporation completely stopped (at \( \approx 90\% \) for \( N = 30 \)), which is attributed to condensation at the output side of the channels. This shows that it was not necessary to maintain RH accurately at zero and confirms once again that it was not the differential vapour pressure that drove the water flow. Most importantly, these experiments indicate that water diffusion and evaporation outside the capillaries was not a limiting factor in our permeation measurements. Otherwise, the increase in external RH would significantly reduce \( Q \).

In the second set of experiments, we applied an additional pressure of 1.3 ± 0.3 bar to the water column inside our containers. This pressure was chosen to be close to the maximum pressure that our membranes could withstand. To create such pressures while keeping the container weight below \( \sim 15 \text{ g} \) (required for precision gravimetry), a chosen amount of NaBH\(_4\) was dissolved in water inside the container which resulted in a slow release of hydrogen (over several hours at room temperature). The pressure build-up inside a closed container was monitored in Extended Data Fig. 7a. The pressure build-up inside a closed container was monitored in Extended Data Fig. 7b. Unless specifically mentioned below, we used the SPC/E model for water\(^{47}\), and the carbon atoms were modelled as fixed neutral particles interacting with oxygen through the Lennard–Jones (LJ) potential with the standard values\(^{48,49,50}\) of the interaction parameters, \( \epsilon_{\text{CO}} \) and \( \sigma_{\text{CO}} \). For consistency, in all the presented simulations we used \( \epsilon_{\text{CO}} = 0.0927 \text{ kcal/mol} \) and \( \sigma_{\text{CO}} = 3.283 \text{ Å} \), and LJ interactions were truncated using a cut-off of 10 Å. The temperature of water was maintained at 300 K using the Berendsen thermostat. Long-range Coulomb forces were computed using the particle-particle-particle mesh method, and all the simulations were carried out in the canonical ensemble using LAMMPS\(^{51}\). The graphene capillary shown in Extended Data Fig. 7b was initially connected to two reservoirs that contained 5,000 water molecules each. A pressure of 1 bar was applied to the water reservoirs in Extended Data Fig. 7b to find \( \epsilon = \eta = \lambda \) which is given by the ratio of the shear viscosity \( \eta \) to the liquid–solid friction coefficient, \( \lambda \). Both \( \eta \) and \( \lambda \) were calculated through the Green–Kubo formalism using the simulated local structure of water\(^{45,46}\). We found that \( \eta \) was in the range of \((0.5–0.9) \times 10^{-5} \text{ Pa s}^{-1} \) and \( \lambda \) was about \( 10^{14} \text{ Pa}^{-1} \text{ s}^{-1} \), in agreement with the previous simulations for the water–graphite interface\(^{14,43}\). This yielded \( \lambda \approx 3 \pm 8 \text{ s}^{-1} \) for \( \eta \) ranging from 2 to 30 (Extended Data Fig. 7c). Note that CNVs are known to exhibit a strong dependence of \( \eta \) on their diameter\(^{14}\), which is attributed to the effect of curvature. No \( \eta \) dependence was found for planar graphene channels either in our simulations or previously\(^{14,47}\). For example, Falk et al.\(^{14}\) reported \( \eta \approx 80 \text{ mPa s} \) for \( h = 4 \text{ nm} \) and \( 4 \text{ nm} \) and Kannam et al.\(^{52}\) found \( \eta \approx 60 \pm 6 \text{ mPa s} \) for \( h < 4 \text{ nm} \). The relatively minor discrepancies can be attributed to details of MD simulations such as different interaction parameters and different thermostats.

Despite usual\(^{48,49}\), quantitative differences between NEMD and EMD simulations (Extended Data Fig. 7c), both show qualitatively the same behaviour with a rapid decrease in water flow with decreasing \( N \) (approximately, \( \sim h^2 \) as expected from equation (1) for a constant pressure \( P \)) and without any anomalies at small \( N \). This is in agreement with the previously reported simulations for flat graphene capillaries\(^{14,47}\). We also tried other models for water (TIP4P/2005\(^{53}\)) and its interaction with graphene\(^{48}\) as well as the use of a flexible graphene confinement. However, if a pressure \( P \) was assumed independent of \( h \), we found it impossible to obtain a peak in permeation at small \( N \).

**Capillary pressure.** To analyse changes in the capillary pressure \( P \) with decreasing \( N \), we used the MD set-up shown in Extended Data Fig. 8a. As discussed in the main text, the internal meniscus was chosen as an approximation for the evaporating extended meniscus sketched in Extended Data Fig. 7a. Both have approximately the same height \( h \) determined by \( N \) and involve same interactions of water molecules with graphite. Note that the extended meniscus is driven by interactions with one graphite surface, which should result in a somewhat smaller \( \Pi \) with respect to the modelled internal meniscus. This should lead to better agreement with our experimental results but possible corrections are neglected below. Water was supplied into the graphene capillaries from a relatively large reservoir placed on the left. The reservoir was terminated with a rigid graphene sheet that was allowed to move freely from left to right. Capillary pressure sucked water inside the channel and forced the sheet to move to the right. We applied a compensating force in the opposite direction to keep the sheet stationary. From the found force and the known cross-sectional area of the channel, the pressure \( P \) was calculated.

The results are shown in Extended Data Fig. 8b (solid symbols). The simulated capillary pressure rises notably faster than that expected from the classical term due to the curved meniscus (red curve). The steeper increase in \( P \) can be understood as due to the disjoining pressure \( \Pi = \Pi_{\text{vdW}} + \Pi_{\text{ent}} \) of several contributions, including the vdw pressure \( \Pi_{\text{vdW}} \) and entropic terms. The latter appear because of different energies of states of water inside and outside graphene nanocapillaries\(^{27}\) as well as the enhanced structural order in nanofomed water\(^{29,32,41,42,49,50}\). In our case, changes in \( P \) are relatively minor (inset of Extended Data Fig. 8b) leading to the corresponding entropic pressure\(^{27,28}\) of \( \sim 0.02 \text{ bar} \) (magenta curve). Also, \( \Pi_{\text{vdW}} = \Pi = (6\pi h^2) \) presents a relatively small effect, where \( A \) is the Hamaker constant for water–graphite interaction\(^{29,32}\). The \( \Pi_{\text{vdW}} \) contribution becomes notable only for \( N < 3 \) because of the rapid \( h^2 \) dependence (blue curve). The total of the above three contributions is shown in Extended Data Fig. 8b by the green dashed curve. The remaining difference with respect to the MD-simulated dependence can be attributed to the entropic pressure due to the increased structural order in graphene layers\(^{21,23}\).
(Extended Data Fig. 9). We found that the walls of monolayer channels sagged already after several ps, independent of the thickness of graphite walls. In stark contrast, bilayer channels remained open. This behaviour is attributed to vdW attraction between capillary walls, which is sufficiently strong at short distances to deform the graphite bulk but rapidly vanishes with increasing the separation51.

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Extended Data Figure 1 | Microfabrication process flow. (1) A micrometre-scale hole is prepared in a silicon nitride membrane. (2) Bottom graphite is transferred to cover the opening. (3) An array of graphene spacers is transferred on top. (4) The hole is extended into the graphite–graphene stack by dry etching. (5) Top graphite crystal is transferred to cover the resulting aperture. The accompanying optical images (in natural colours) illustrate the results after each step for one of our devices. Graphene spacers are invisible in the photos and indicated by an opaque rectangle in (3). Steps 3 and 4 were often interchanged.
Extended Data Figure 2 | Additional images of graphene capillaries.

**a**, Optical image of a final device. The green region is the free-standing silicon nitride membrane. The Si wafer is seen in brown and the top graphite crystal (arrowed) in yellow. Red, yellow and grey contours indicate positions of the top graphite, bottom graphite and graphene spacers, respectively. The nearly-vertical dark lines are wrinkles in the bottom layer. **b**, AFM image of four-layer graphene spacers on top of a bottom graphite crystal (height profile along the dashed line is shown below the image). Inset, high-resolution scan (friction mode) from the region indicated by the arrow. The observation of the atomic lattice confirms that our assemblies have atomically smooth surfaces. Such smoothness is impossible to achieve using conventional materials and processes that invariably lead to the surface roughness exceeding the scale given by few-layer graphene spacers. Although the side walls of our channels are rough due to limitations of electron-beam lithography, we estimate that, because of the large ratios \( w/h \), the side wall contribution to the flow resistance cannot exceed 5% even for our 10 nm devices. **c**, SEM micrograph of a capillary device with \( h \approx 15 \text{ nm} \). **d**, Bright field STEM image of a graphene capillary with \( N = 4 \). Spacers and channels are arrowed in **c** and **d**.
Extended Data Figure 3 | Sagging of top graphite. a, Left, AFM image of trilayer channels, which are covered by a graphite layer of varying thickness. b, Left, partial sagging of the top graphite into wide channels. We can see that the top graphite bends down into the channels over their entire height $h \approx 5$ nm. Right, height profiles that correspond to the traces shown by the dashed lines in the AFM images at left.
Extended Data Figure 4 | He leak through graphene capillaries.

a, Schematic of our set-up. Two vacuum chambers are separated by the silicon nitride wafer incorporating a nanocapillary device. Valves connect the chambers to a pump, a He leak detector and a gas inlet. He atoms are represented by filled orange circles.

b, Leak rates normalized for 1 \( \mu \text{m} \) length and given per channel as a function of applied pressure for capillary devices with \( N = 5 \) and \( N \approx 45 \) (\( h \approx 1.7 \text{ nm} \) and 15 nm, respectively), and a control device without graphene spacers (\( N = 0 \)).
Extended Data Figure 5 | Ion transport through graphene nanochannels. **a**, Schematic of our measurement set-up. A nanocapillary device fabricated on top of a Si nitride wafer (SiN is shown in green) is clamped using O-rings (black) to separate two containers (indicated by magenta lines). The containers are filled with a KCl solution (blue), and silver chloride–silver wires (dark grey) are used as electrodes to measure ionic conductance. **b**, Examples of current–voltage ($I$–$V$) characteristics of the smallest capillary devices ($N = 2$) at different KCl concentrations (labelling the curves; $L$ ranges from 2.8 $\mu$m to 7 $\mu$m). **c**, Same as **b** but for a device with $N \approx 17$ of approximately the same average length $L$ ($L$ from 1.7 $\mu$m to 7.3 $\mu$m). **d**, Ionic conductance for these devices as a function of KCl concentration, $C$ (without normalizing for their slightly different $L$). Both blank Si nitride wafers separating the reservoirs and control devices with $N = 0$ (no spacers but otherwise prepared using the same fabrication procedures) exhibited leakage conductance of the order of 20 pS, which did not change with $C$ (olive symbols). The dashed lines show ionic conductance $G$ expected from the bulk conductivity of KCl for the given channel dimensions. The solid curves are fits taking into account an additional parallel conductance due to the surface charge.
Extended Data Figure 6 | Gravimetric measurements. a, Extended schematic of the experimental set-up. A small aluminium container filled with water is sealed with a Si nitride wafer containing a graphene capillary device (total weight should not exceed ~15 g to allow the required measurement accuracy). The container was weighed either upside down (water in contact with capillaries as shown in the sketch) or in the upright position as shown in the inset of Fig. 2a (capillaries are exposed to 100% RH). Both orientations resulted in the same Q. b, Photographs of our gravimetric set-up. Main image, microbalance with our miniature container being weighed (its position is indicated by a dashed square). Image to the right, the container is open and the Si nitride wafer (that is clamped between the O-rings during measurements) is removed. c, Examples of water evaporation through apertures of different diameters, D (colour coded) d, Dependence of the evaporation rate on D (error bars, s.d.). Red line, best linear fit. Inset, optical micrograph (natural colour) of an aperture of 30 μm diameter, which is etched in a Si nitride membrane.
Extended Data Figure 7 | Molecular dynamics simulations of water flow through graphene slits. a, Our capillaries are filled with water and the driving pressure is determined by evaporation of the extended meniscus that appears at the capillary mouth. The meniscus is sketched in the drawing, showing a thin film of water propagating along the graphite surface. b, MD set-up with the simulation box indicated by the black lines. The particular snapshot is for $N = 4$. Dark grey balls represent carbon atoms arranged into graphene planes. Red and light grey spheres show oxygen and hydrogen atoms of water molecules. c, Simulated slip length $\delta$ and water flux $Q$ as a function of $N$. In the case of NEMD, $\delta$ (blue symbols) was calculated from the simulated $Q$ (blue bars) using equation (1). Using $\delta$ found from the EMD simulations (grey symbols) and the pressure gradient of $10^{15}$ Pa m$^{-1}$, equation (1) yields $Q$ shown by the grey bars.
Extended Data Figure 8 | MD simulations of capillary pressure.

a, Our MD set-up for $N = 4$. Colour coding as in Extended Data Fig. 7b. Graphene planes to the right represent a graphite crystal with four atomic planes removed. The vertical graphene plane is used as a movable membrane to apply a compensating force to stop the water meniscus from propagating to the right. b, Main figure, simulated capillary pressures (symbols with s.d. error bars). The red curve shows the best fit for large $N$ using $P_0 = 2\sigma \cos(\phi)/h$, which yields $\phi \approx 80^\circ$. Blue and magenta curves show $\Pi_{vdW}$ with the Hamaker constant $A \approx 115 \text{ zJ}$ (ref. 53), and the entropic pressure due to changes in $\rho$, respectively. Dashed green curve, combined pressure from the three contributions. Inset, simulated density $\rho$ of water confined between graphene sheets under external pressure of 1 bar.
Extended Data Figure 9 | Micromechanical stability of graphene cavities. Shown are snapshots of mono- and bilayer capillaries (left and right columns, respectively) after 100 ps of MD simulations.

a–d. Capillaries with different thicknesses of graphite walls, respectively 2, 6, 20 and 40 graphene layers.