Capillary condensation under atomic-scale confinement

Capillary condensation of water is ubiquitous in nature and technology. It routinely occurs in granular and porous media, can strongly alter such properties as adhesion, lubrication, friction and corrosion, and is important in many processes used by microelectronics, pharmaceutical, food and other industries. The century-old Kelvin equation is frequently used to describe condensation phenomena and has been shown to hold well for liquid menisci with diameters as small as several nanometres. For even smaller capillaries that are involved in condensation under ambient humidity and so of particular practical interest, the Kelvin equation is expected to break down because the required confinement becomes comparable to the size of water molecules. Here we use van der Waals assembly of two-dimensional crystals to create atomic-scale capillaries and study condensation within them. Our smallest capillaries are less than four ångströms in height and can accommodate just a monolayer of water. Surprisingly, even at this scale, we find that the macroscopic Kelvin equation using the characteristics of bulk water describes the condensation transition accurately in strongly hydrophilic (mica) capillaries and remains qualitatively valid for weakly hydrophilic (graphite) ones. We show that this agreement is fortuitous and can be attributed to elastic deformation of capillary walls, which suppresses the giant oscillatory behaviour expected from the commensurability between the atomic-scale capillaries and water molecules. Our work provides a basis for an improved understanding of capillary effects at the smallest scale possible, which is important in many realistic situations.

The Kelvin equation predicts that capillaries become spontaneously filled with water at the relative humidity

\[ \text{RH}_c = \exp(-2\sigma/k_B T \rho_N) \]  

where \( \sigma = 73 \text{ mJ m}^{-2} \) is the surface tension of water at room temperature \( T, \rho_N = 3.3 \times 10^{28} \text{ m}^{-3} \) is the number density of water, \( k_B \) is the Boltzmann constant and \( d \) is the diameter of the meniscus curvature. For a two-dimensional (2D) confinement created by parallel walls separated by a distance \( h, \ d = h/\cos \theta \) where \( \theta \) is the contact angle of water on the walls’ material. For capillary condensation to occur at relative humidity (RH) considerably below 100%, equation (1) dictates that \( d \) must be comparable to \( 2\sigma/k_B T \rho_N = 1.1 \text{ nm} \). For example, under typical ambient RH of 40–50%, water is expected to condense in slits with \( h < 1.5 \text{ nm} \) and cylindrical pores with diameters \( <3 \text{ nm} \), if \( \theta \) is close to zero. Even stronger confinement is required for capillaries involving less hydrophilic materials. So far, a broad consensus has been reached that the Kelvin equation remains accurate for menisci with \( d \geq 8 \text{ nm} \) (refs. 1–4, 8–11) and can also describe condensation phenomena in hydrophilic pores as small as 4 nm in diameter. To achieve agreement with the experiments at this scale, the Kelvin equation is usually modified to account for ‘wetting films’ that are adsorbed on internal surfaces before the condensation transition and effectively narrow the capillaries. For the smallest capillaries, the thickness of the wetting films was used as a free parameter. In the real world, pores, cracks and cavities obviously do not terminate at the scale of several nanometres but extend even below 1 nm or \( 2\sigma/k_B T \rho_N \), the fact that makes condensation phenomena omnipresent under ambient conditions. The latter scale is comparable to the diameter of water molecules, which makes it challenging to study experimentally because of difficulties in creating the required atomic-scale confinement. The varying thickness of wetting films and huge capillary pressures that can cause considerable deformations and the description in terms of homogeneous macroscopic thermodynamics becomes questionable. The capillary devices that we studied are shown schematically in Fig. 1a. Their most important part is atomically flat 2D channels made

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by van der Waals (vdW) assembly following the fabrication procedures described in the Methods. In brief, two atomically flat crystals were exfoliated from bulk muscovite mica or graphite to become the top and bottom walls of our capillaries. Separately, narrow strips of multilayer graphene were fabricated to serve as spacers between the two mica or graphite crystals. Stacking the crystals and spacers on top of each other resulted in the 2D channels shown in Fig. 1 and Extended Data Fig. 1. We used graphene spacers without the top crystal cover for several values of RH. All the AFM measurements were carried out in the non-contact PeakForce mode (Methods, ‘AFM topography under controlled humidity’).

As shown in Fig. 1a and Extended Data Fig. 1c, our capillary devices were assembled on top of a silicon nitride membrane. It had a rectangular opening that was extended into the bottom crystal by dry etching. The Si chip supporting the entire assembly was used to separate two miniature gas chambers that were integrated into an AFM set-up as shown in Extended Data Fig. 2a. The bottom chamber provided variable humidity so that one entrance of the 2D capillaries was exposed to a chosen RH. The opposite entrance was facing the top chamber, which was assembled on top of a silicon nitride membrane. It had a rectangular opening that was extended into the bottom crystal by dry etching. The Si chip supporting the entire assembly was used to separate two miniature gas chambers that were integrated into an AFM set-up as shown in Extended Data Fig. 2a. The bottom chamber provided variable humidity so that one entrance of the 2D capillaries was exposed to a chosen RH. The opposite entrance was facing the top chamber, which was assembled on top of a silicon nitride membrane.

Examples of transmission electron microscopy imaging of our capillaries are provided in Fig. 1b and Extended Data Fig. 1d. Mica and graphite were chosen as archetypal strongly and weakly hydrophilic materials. Their contact angles are known to be in the range of 0°–20° and 55°–85°, respectively.28,29 For surfaces exposed to air, θ is close to the above upper bounds.28,29 (Methods).

To detect RH at which capillary condensation occurred in the 2D capillaries described above, we exploited the fact26,30 that the suspended thin crystals exhibited noticeable sagging caused by their vdW adhesion to sidewalls (Fig. 1c). In our experiments we found that, when the capillaries became filled with water, the sagging depth δ diminished (Fig. 1d), presumably because intercalating water molecules ‘screen’ the adhesion.23,30 To make the resulting changes in δ detectable by atomic force microscopy (AFM), it was important to choose the thickness H of the top crystal and the channel width w carefully (see Fig. 1a). As described in Methods (‘Remnant sagging above the condensation transition’), these two parameters define the stiffness of the top crystal and, hence, how deeply it bends inwards. We found that, for W = 150 nm, the top crystal should be ~50–70 nm thick to exhibit a sagging depth δ of several ångströms. If either w or H were changed only by a factor of 2, the strong dependence δ ∝ w3/H4 resulted in either collapsed channels (the top crystal attached to the bottom one) or such a small δ (<1 Å) that the condensation transition was impossible to discern by AFM.

The capillaries studied here were typically 5–10 μm long.

For example, no condensation occurred at the AFM tip during scanning.28,29 Examples of AFM imaging for mica and graphite devices are given in Fig. 1c, d and in Extended Data Fig. 3. They reveal pronounced sagging under dry conditions, which disappeared in high humidity. Typical evolution of the top crystal’s profiles with changing RH is shown in Fig. 1e and Extended Data Figs. 4 and 5. In these measurements, we increased RH inside the bottom chamber in steps of 5%, waited for an
condensation transition under extreme 2D confinement. a. Relative humidity \( R_{HC} \) required for water condensation in mica channels of different heights \( h \). Blue circles indicate experimental observations, their size reflects the 3.5% experimental uncertainty in determining \( R_{HC} \). Methods, ‘AFM topography under controlled humidity’. Two solid curves indicate \( R_{HC} \), given by equation (1) with bulk water’s characteristics for the range of possible \( \theta \) for mica (colour-coded). The upper curve (open black circles), with its own \( x \)-axis, shows our MD calculations for changes in \( \gamma_{SL} \) caused by restructuring of water inside 2D channels (\( \theta = 10^\circ \)). The arrows mark the energy minima that correspond to the integer number of water monolayers that can fit inside the 2D capillaries. Red symbols (connected by the dashed curve) are the expected behaviour calculated using the oscillating \( \gamma_{SL} \) shown in the upper curve and equation (2). Black dashed curve, same analysis but assuming fully flexible capillary walls allowing relaxation into the energy minima at commensurate \( h \). Green dashed circles, same analysis but for a finite rigidity of the confining walls. b. Same as a, but for graphite capillaries. The simulated curves are for \( \theta = 85^\circ \).

The temperature was kept at 294 ± 1 K. For the device in Fig. 1e, the sagging remained practically constant for \( RH \leq 75\% \) and then exhibited a pronounced jump at \( R_{HC} \), which we attribute to the condensation transition (another example is shown in Extended Data Fig. 5). Further increase in \( RH \) led to a gradual decrease in \( \delta \) such that the top crystal became practically flat at \( RH > 95\% \) (Fig. 1). The remnant sagging at \( RH > R_{HC} \) is well described by the negative capillary pressure which keeps the top crystal bent inward even after water has filled the 2D channels, suppressing the adhesion of the top crystal to the sidewalls. Indeed, for \( RH > R_{HC} \), \( \delta \) is evolved proportionally to \( \ln(RH) \) and reach zero at 100% humidity23,24, in agreement with the observed behaviour in Fig. 1e and Extended Data Fig. 6 (Methods, ‘Remnant sagging above the condensation transition’). If we repeated the same measurements but with decreasing \( RH \), a reverse jump occurred at the same \( R_{HC} \), that is, the condensation transition was non-hysteretic (Extended Data Fig. 4a; Methods, ‘Non-hysteretic behaviour of the condensation transition’). Note, however, that it could take up to several days for capillaries exposed to high \( RH \) to dry out completely and return to their original state (Extended Data Fig. 4b). On the other hand, for measurements with increasing \( RH \), no difference in \( R_{HC} \) was observed after either an hour or days of equilibration. Accordingly, our experiments were normally carried out with increasing rather than decreasing \( RH \), as in Fig. 1e.

Figure 2 summarizes our results for the condensation transitions observed in mica and graphite 2D capillaries. To allow more accurate comparison between data collected from different devices, we have accounted for the fact that capillaries with the same \( N \) of ten exhibited different sagging in their dry state, \( \delta_0 \). For capillaries with large \( \delta_0 \), we observed consistently lower \( R_{HC} \) than for those with small initial sagging and same \( N \). Moreover, comparing capillaries with different \( N \) but similar channel heights \( h = Na - \delta_0 \), we found close values of \( R_{HC} \) (Extended Data Fig. 5). This implies that it was the narrowest, central region of the 2D channels that determined the onset of condensation, in agreement with general expectations22 (Methods, ‘Effect of initial sagging’). Accordingly, to account for the effect of different \( \delta_0 \), Fig. 2 plots \( R_{HC} \) as a function of \( h \) rather than of \( N \). For mica capillaries, the experimental data are well described by equation (1) using \( \theta \) and \( \sigma \) of bulk water. Because \( R_{HC}(h) \) depends little on the exact value of \( \theta \) for strongly hydrophilic capillaries (Fig. 2a), the comparison of \( R_{HC} \) for mica with equation (1) is straightforward. This is not the case for weakly hydrophilic graphite, for which relatively small variations in \( \theta \) lead to considerable changes in \( R_{HC}(h) \) as per equation (1). Nonetheless, the values of \( R_{HC} \) observed for our graphite capillaries fall well within the range expected from the Kelvin equation using the contact angles \( \theta = 80 \pm 5^\circ \), typical for graphite surfaces under ambient conditions29.

It is surprising that the macroscopic Kelvin equation using the characteristics of bulk water describes condensation in our mica capillaries so well and also provides qualitative agreement for the graphite capillaries. As mentioned in the introduction, strong discrepancy is expected for the ångström-scale confinement where only one or two layers of water fit inside capillaries. Before trying to explain the unexpected agreement between the experiment and the macroscopic Kelvin equation, we note that \( R_{HC} \) values in Fig. 2a are notably lower than the RH values required to achieve condensation in the previous studies for \( d \geq 8 \) nm. At our low RH, no continuous wetting layer is expected even on fresh mica surfaces22,33, and a partial coverage by monolayer water is probably suppressed further by adsorbates from air, which are responsible for the relatively large \( \theta \) close to 20°. The same consideration about the apparent absence of wetting films also applies for the graphite capillaries in which the wetting transition is even less likely22,38. Second, to avoid the macroscopic variables \( \sigma \) and \( \theta \) that are poorly defined under our extreme confinement, the Kelvin equation can be rewritten as22,38

\[
R_{HC} = \exp\left[-2(\gamma_{SV} - \gamma_{SL})/h k_B T \rho_h \right]
\]  

(2)

where \( \gamma_{SV} \) and \( \gamma_{SL} \) are the surface energies for solid–vapour and solid–liquid interfaces, respectively, and \( \gamma_{SV} - \gamma_{SL} = \sigma \cos \theta \). The energy \( \gamma_{SV} \)
is largely independent of $h$ because the interaction of gas molecules with surfaces should depend little on confinement. Also, $\rho_c$ changes relatively little for nearly incompressible water$^{20,34}$. Therefore, the dominant effect of extreme confinement is likely to come from $y_{\text{sa}}(h)$, which is governed by vdW interactions of liquid water with solid surfaces. Because these interactions are short-range, it is predominantly the first near-surface layer of water that determines $y_{\text{sa}}$. If this layer changes little under confinement, then $\Delta y = y_{\text{sa}}(h) - y_{\text{sa}}(\infty) = 0$, and capillary condensation should closely follow equation (1) even at the nanoscale$^{20,21}$. Substantial changes in $y_{\text{sa}}$ and, hence, $\rho_c$, are expected only in the limit of few-layer water where its near-surface structure is notably altered$^{20,34}$ (Extended Data Fig. 7).

For further analysis, we used molecular dynamics (MD) simulations (Methods) to evaluate $\Delta y$ and the resulting corrections to the macroscopic Kelvin equation, which are given by the factor $\exp(2\Delta y / h k_B T_\rho h)$ according to equation (2). Examples of the calculated $\Delta y(h)$ are shown in Fig. 2a and Extended Data Fig. 8. There are pronounced commensurability oscillations$^{20,21,34}$ in $y_{\text{sa}}(h)$ such that energy minima appear if 2D channels accommodate exactly one, two, three or four molecular layers of water. The oscillations practically disappear for $h > 15$ Å where $\Delta y$ becomes almost zero, which also implies that the macroscopic Kelvin equation should be valid in this regime. For smaller $h$, changes in $y_{\text{sa}}$ are comparable to $\sigma$, which means that the above correction factor is comparable to $\rho_c$ itself. Consequently, the simulated $RHC(h)$ dependences shown in Fig. 2 (red dotted curves and symbols) exhibit giant oscillations such that, for incommensurate $h$, water condensation becomes unfavourable and should not occur even at 100% humidity. No such oscillatory behaviour could be detected in our experiments.

We attribute its absence to elastic adjustment such that 2D channels tend to accommodate an integer number of molecular layers of water$^{20,34}$. Indeed, the energy minimization should be applied to the entire system, including the elastic energy of confining walls$^{21,35}$. For an extremely soft confinement, 2D channels would adjust their $h$ to reach the commensurate states at minima of $\Delta y$. The condensation behaviour in this case should follow the step-like black dashed curves shown in Fig. 2.

A finite rigidity pushes the equilibrium conditions away from the commensurability minima. To estimate a likely elastic response of our 2D channels, note that the capillary pressure above $RHC_{\text{el}}$, which is defined by $\sigma$, keeps the top crystal bent inwards typically by several ångströms (Fig. 1c; Extended Data Figs. 4–6). Similar elastic adjustments can be expected in our capillaries because changes in $\Delta y$ are comparable to the absolute value of $\sigma$. Accordingly, our confinement should be considered as rather soft. To illustrate the likely condensation behaviour in such a case, the green curves in Fig. 2 show the $RHC(h)$ dependences expected if the walls’ finite rigidity allows their deformations to reach within 0.5 Å of the commensurability minima in $\Delta y$. The latter curves are in good agreement with the experiment and, in the case of graphite capillaries, also exhibit the same trend towards lower RH for $h \sim 10$ Å as observed experimentally in Fig. 2b. In principle, the elastic response of 2D confinement could be included in the simulations self-consistently, but the scatter in the experimental data and different $H$ used for different capillary devices make this effort beyond the rationale of the present study.

Finally, we note that elastic adjustments should also play an important role in real-life capillaries responsible for condensation phenomena under ambient humidity. Indeed, capillary pressures at 1 mm scale typically exceed 1 kbar, and the resulting elastic response of even infinitely thick walls can exceed 1 Å for the case of 2D confinement (Methods; ‘Remnant sagging above the condensation transition’). This should force atomic-scale capillaries to elastically adjust their geometry$^{11,23,24}$ suppressing commensurability oscillations and resulting in the condensation transition at RH close to the values prescribed for a soft confinement. Accordingly, capillary condensation under ambient conditions can be expected to qualitatively follow the macroscopic Kelvin equation, as happened for the reported capillaries.

## Online content

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Methods

Fabrication procedures

The capillary devices studied here were fabricated following the procedures described in refs. 26,27 and shown in the flow chart of Extended Data Fig. 1a. First, a large crystal of multilayer graphene (number of layers N) was prepared on an oxidized Si wafer by mechanical exfoliation. Using electron-beam lithography and oxygen plasma etching, we patterned the crystal into a set of parallel narrow strips that had a width of ~150 nm and were separated by approximately the same distance (Extended Data Fig. 1b). These spacers were then put on top of a mica or graphite crystal of typically 20 nm in thickness. The latter crystal was prepared on a separate Si wafer and, in this work, is referred to as the bottom crystal (Extended Data Fig. 1a, stage I).

In parallel, we prepared a suspended silicon nitride (SiN) membrane with a rectangular hole in the centre (Extended Data Fig. 1a, stage 2). To this end, we used commercial Si wafers with 500 nm of SiN deposited on both sides. Using photolithography and reactive ion etching (RIE), we made a window of about 750 × 750 μm² in size in one of the SiN layers. The wafer was then placed in hot KOH to etch through the entire Si thickness and obtain a freestanding SiN membrane of ~70 × 70 μm² in size. After that, a rectangular hole (~3 × 20 μm²) was plasma-etched in the SiN membrane by means of another round of photolithography and RIE (Extended Data Fig. 1a, stage 2).

The two-layer assembly consisting of the bottom crystal and graphene spacers (Extended Data Fig. 1a, stage I) was transferred on top of the SiN membrane in such a way that graphene strips were aligned perpendicular to the long edge of the rectangular hole. This step was followed by RIE from the backside of the Si wafer to etch the hole through the bottom crystal (Extended Data Fig. 1a, stage 3). Finally, another mica (or graphite) crystal was placed on top of the two-layer assembly to form 2D channels (Extended Data Fig. 1a stage 4, Extended Data Fig. 1c).

After each crystal transfer, samples were cleaned in acetone, deionized water and isopropanol. This was followed by annealing at 400 °C in a hydrogen–argon atmosphere for 3 h. Such thorough cleaning was essential to remove polymer residues and other possible contamination, which could otherwise block the capillaries. In our experiments, we used only those capillaries that exhibited uniform sagging along their entire length, such as those shown in Fig. 1c and Extended Data Fig. 3.

The contact angle for muscovite mica and natural graphite used for making our devices was measured by Drop Shape Analyzer 100S (Krüss). We found θ = 80–85° for graphite and 15–20° for mica after exposure to ambient air for a few days, in agreement with previous reports (see, for example, refs. 26,27).

AFM topography under controlled humidity

Our set-up for AFM measurements is shown in Extended Data Fig. 2a. The SiN wafer containing a capillary device such as that shown in Extended Data Fig. 1c was placed to seal an airtight metal chamber with a volume of about 1 cm³. A continuous flow of nitrogen gas into this chamber was used to seal an airtight metal chamber. Fresh silica gel granules were usually placed inside the enclosure to provide low humidity in the top chamber.

All AFM images in our experiments were taken in the PeakForce mode using Dimension FastScan ( Bruker) and analysed with WSxM software. Selected capillaries were imaged at regular RH intervals of 5%, after stabilizing humidity in the bottom chamber for approximately an hour. As an example of our AFM measurements, Extended Data Fig. 3 shows three critical steps in the evolution of the topography for an N = 3 graphite capillary. The initial sagging in this case was ~4 Å as seen for RH = 55% in Extended Data Fig. 3a. With RH increasing in 5% steps, no change in the sagging profile was observed until we reached 70% RH. At the latter humidity, the top crystal was found to sag notably less (Extended Data Fig. 3b). On increasing RH further, the top crystal gradually lifted and became practically flat at 95% RH (Extended Data Fig. 3c). The flattening process is described in detail below. Because the rapid change in sagging happened somewhere between 65% and 70% RH, we assigned the condensation transition to RHc = 67.5 ± 2.5% with an additional error of ±1% because of the humidity sensor’s accuracy (as indicated by the symbol size in Fig. 2).

The use of low humidity in the top chamber notably improved the stability of AFM imaging but was not essential. Indeed, if we simply connected the top and bottom chambers so that both sides of the studied capillaries were exposed to the same RH, the condensation transition was found to occur at the same RHc as in the case of low RH in the top chamber. This shows that the condensation transition is determined by the RH at the entrance side (that is, the highest RH) (Extended Data Fig. 2b). This observation is consistent with the fact that no difference in sagging was observed along the entire length of the capillaries, even when their exits were at low RH (Fig. 1d; Extended Data Fig. 2b), which indicates no detectable gradient in negative capillary pressure along the 2D channels. The constant capillary pressure can be attributed to a very fast flow of liquid water through our atomically flat capillaries26, which allows essentially the same meniscus curvature at both entrance and exit sides, as shown schematically in Extended Data Fig. 2b. If the top chamber is kept at low humidity, such an equilibrium state is stabilized by a slightly retracted exit meniscus and slow Knudsen diffusion of vapour near the capillary exit26, which provides the required RH gradient. This is different from the case of nanoporous media with rough internal surfaces and tortuous capillaries, where both liquid and vapour transport are slow, allowing large pressure gradients to build up along the liquid flow direction26.

Non-hysteretic behaviour of the condensation transition

Capillary condensation in nanochannels is often accompanied by hysteresis such that RHc required to reach the transition depends on whether external RH is increased or decreased4,11,12,23,34. This was not the case for our capillaries, which exhibited no hysteresis within our experimental accuracy. This behaviour is illustrated in Extended Data Fig. 4a, which shows the profiles of the top crystal for a four-layer graphite capillary where RH was changed in a small loop around the transition observed at RHc = 77.5 ± 2.5%. The capillary’s sagging was constant for RH ≤ 75%. Then we increased RH to 80% and equilibrated for 1 h, following the experimental procedures described above. The 5% change in RH led to a pronounced jump in the sagging depth δ, indicating the condensation transition (compare black and red curves in Extended Data Fig. 4a). The capillary profile remained stable while RH was maintained at 80%. When we decreased RH back to 75%, the capillary did not return to the initial dry state after 4 h (blue curve). Nonetheless, the top crystal continued to sag gradually with time (Extended Data Fig. 4a). The dry state was eventually reached (after more than 9 h but less than 16 h). Therefore, the condensation transition occurred at the same RHc with either increasing or decreasing humidity, although long equilibration times were needed for 2D channels to dry up.

The slow recovery of the initial dry state is further exemplified by Extended Data Fig. 4b. It shows the case of a graphite capillary with N = 6, where the condensation transition was found to occur between 60% and 65% RH. In Extended Data Fig. 4b, we first increased RH from 60% directly to 95%, well above the transition (black and red curves, respectively). Then RH was reduced to ~30%, well below RHc = 62.5 ± 2.5%.
As seen in Extended Data Fig. 4b, the top crystal regained its original profile very slowly, and the capillary returned to its dry state only after several days. After this the sagging remained stable. The reason for such a slow drying process remains to be understood.

It is also worth mentioning that our capillary devices did not show any discernible change in sagging with changing RH below the condensation transition, as seen, for example, in Fig. 1e. This is in contrast to the usual elasto-capillary response of nanoporous media, in which adsorption of water molecules on internal surfaces leads to notable strain, usually referred to as the Bangham effect. Its apparent absence in our experiment is perhaps not surprising. First, as discussed in the main text, we expect only a small partial coverage of internal walls by adsorbed water molecules before the transition. Second, if there were notable adsorption, the adsorption-induced strain is typically of the order of 10^-4 for materials with high Young's modulus. Therefore, for our top crystals with \( h \) and \( w \) of ~100 nm, this strain would translate into sagging of the order of 0.1 Å, below our experimental accuracy.

**Effect of initial sagging**

For 2D channels with the same \( N \), their heights \( h = Na - \delta_0 \) could vary considerably because of different \( H \) and slightly different \( w \), which control the initial sagging \( \delta_0 \). This resulted in different RH, observed for capillaries with the same \( N \). This behaviour is illustrated in Extended Data Fig. 5, which shows the condensation transition in two capillaries with \( N = 5 \) but different \( \delta_0 \). The capillary in Extended Data Fig. 5a had a top layer with \( H = 70 \) nm and exhibited initial sagging of ~4 Å. The transition in this device occurred at \( RH_c = 82.5\% \). The other capillary (Extended Data Fig. 5b) had a thinner (~45 nm) top crystal and, accordingly, its \( \delta_0 \) was larger (~8.5 Å). The latter device exhibited \( RH_c = 72.5\% \), considerably lower than that in Extended Data Fig. 5a. This implies that \( N \) was not the critical determinant of the onset of water condensation. The importance of \( h \) rather than \( N \) is even better exemplified by the results of Extended Data Fig. 4: the capillary with \( N = 4 \) in Extended Data Fig. 4a exhibited the condensation transition at 77.5% RH, whereas the nominally larger capillary with \( N = 6 \) in Extended Data Fig. 4b showed the transition at lower RH = 62.5%. This obviously contradicts the expectation that the smaller-\( N \) capillary should exhibit lower RH. However, because of different \( \delta_0 \), the smaller \( (N = 4) \) capillary in Extended Data Fig. 4a had \( h = 7 \) Å, which was larger than \( h = 3.5 \) Å for the larger \( (N = 6) \) capillary in Extended Data Fig. 4b. The smaller RH for 2D channels with smaller \( h \) agrees with the general expectations.

The above observations strongly suggest that \( h \) is the size parameter that best describes the condensation transition in our atomic-scale capillaries. This means that it is the central region between the sagged-top and flat-bottom crystals where the condensation process is effectively initiated. This is not entirely unexpected because MD simulations have previously shown that corner menisci in narrow channels were unfavourable for condensation. Furthermore, note that the mean free path of water molecules in air is about 65 nm, which is comparable to the channel width \( w = 150 \) nm. This implies that the entire channel should present a single entity from the standpoint of thermodynamics, allowing only one condensation transition over the channel's cross-section. To this end, it is important to note that although our capillaries contained only a few monolayers of water, there were still millions of molecules inside each capillary, which should be sufficient for the thermodynamic description, unlike in the case of nanometre-scale droplets containing a small number of molecules.

**Remnant sagging above the condensation transition**

As seen in Extended Data Fig. 4b, the top crystal regained its original profile very slowly, and the capillary returned to its dry state only after several days. After this the sagging remained stable. The reason for such a slow drying process remains to be understood.

This explanation is supported by MD simulations. They showed that capillaries with monolayer spacers (\( N = 1 \)) always collapsed (independently of \( H \)) because of vdW interaction between the top and bottom crystals. The collapsed capillaries could be opened by intercalating water, because the attraction rapidly diminishes at distances more than a few Ångströms so that even a monolayer of water provided sufficient ‘screening’ of the vdW attraction.

In all our measurements, the sagging depth \( \delta_0 \) became abruptly smaller at the condensation transition but did not completely disappear. Only if RH was increased further did the remnant sagging gradually decrease, approaching zero at 100% RH, so that the top layer became essentially flat (Fig. 1d, e; Extended Data Fig. 3). The remnant sagging at the transition and its gradual changes with further increases in RH can be explained by the negative pressure \( P \) caused by the condensed water meniscus. Let us consider our typical mica capillary with \( w = 150 \) nm and top-layer thickness \( H = 50 - 60 \) nm (Extended Data Fig. 6a). After the condensation transition occurred at a certain RH (which depended on channel height \( h \)), the top layer remained sagged typically by several Ångströms. At the condensation transition, the capillary pressure is given by \( P = 2\sigma \cos \theta/\gamma h \). Using the contact angle \( \theta = 20^\circ \) for mica and the surface tension of bulk water, \( \sigma = 73 \) mN m^-1, the Young–Laplace equation yields \( P = 700 \) bar for \( h = 2 \) nm.

The negative pressure \( P \) forces the top crystal to bend downwards, resulting in its sagging given by

\[
\delta = \frac{5Pw^4}{32EH^3}.
\]

where \( E = 60 \) GPa is Young’s modulus of mica in the out-of-plane direction. Similar agreement is found for graphite capillaries, although there is a larger uncertainty in the estimates (a factor of 2) because \( P \) strongly depends on \( \theta \). As RH is increased beyond the condensation point, the meniscus extends outside capillaries, and its curvature becomes progressively smaller to match the external RH. Accordingly, the negative capillary pressure above RHc evolves with RH and is given by the other Kelvin equation

\[
P = k_BT \ln(RH).
\]

According to this equation, the pressure that bends the top crystal should decrease logarithmically with RH, in good agreement with our observations (Extended Data Fig. 6b). Note that, close to 100% RH, \( \delta \sim P \sim \ln(RH) \sim (RH - 1) \) is expected to approach zero linearly, as indeed observed in Fig. 1e and Extended Data Fig. 6b.

The condition of partially sagged but open capillaries (that is, few Ångströms < \( \delta_0 < Na \), as in our devices) is rather difficult to satisfy experimentally. Indeed, if we were to decrease \( H \) or increase \( w \) by only a factor of 2 with respect to the optimal design found, \( \delta \) in equation (3) would increase by an order of magnitude because of the high powers. On the other hand, the capillary pressure \( P \) in equation (4) depends on RH only logarithmically, which means that even at very low humidity (for example, 5%), it would be thermodynamically favourable for the top layer with the non-optimal \( w \) or \( H \) to bend all the way down and reach the channel’s bottom. Therefore, such non-optimized 2D channels are unstable with respect to spontaneous water condensation under low-humidity conditions. If we were to do the opposite and increase the top crystal’s stiffness (by halving \( w \) or doubling \( H \)), \( \delta \) in equation (3) becomes so small (<1 Å) that changes in the sagging would be immeasurable to detect by AFM. The above consideration shows that there is a subtle interplay between materials parameters and the design of 2D channels, and stringent rules should be followed in order to detect the
condensation transition in experiment. Following this insight, we usually increased $H$ by $\sim 50\%$ for our smallest 2D channels with $N = 2$ and 3, which ensured that they remained open. Also, when making graphite capillaries, we used top crystals slightly ($\sim 20\%$) thicker than in the case of mica capillaries with the same $N$ because mica has a higher Young’s modulus than graphite.

For nanoscale 2D capillaries such as cracks or slits inside bulk materials ($H \gg \delta$), their elastic deformations caused by large capillary pressures can notably shift the condensation transition with respect to that expected for the rigid confinement$^{33,34}$. To estimate the magnitude of such adjustments, let us consider the deformation of a half-space elastic medium subject to the uniform load $p$ over a suspended strip with the width $\omega = 2\delta a$ in the range of $-\delta a \leq x \leq \delta a$. The vertical deformation is given by$^{44}

$$u_a(x) = -\frac{(1-v)p}{\pi G}a \left( \frac{x}{a} + 1 \ln|x/a| - \frac{x}{a} - 1 \right) \ln|x/a| - 2,$$

(5)

where $v$ is Poisson’s ratio and $G$ is the shear modulus. This equation yields the sagging

$$\delta = u_a(0) - u_a(\pm a) = \frac{\ln(2)(1-v)p\omega}{\pi G}.$$  

(6)

If we take as an example the elastic properties of graphite with $G = 10$ GPa and $v = 0.34$, equation (6) yields $\delta \approx 2.3 \text{ Å}$ for capillary pressures of about 1,000 bar. Such $P$ are typical for cavities of 1–2 nm in height (see above). This indicates that elastic deformations can not only be a contributing factor during the condensation transition$^{23,24,36}$, but also allow atomic-scale cavities in bulk materials to adjust their size so that an integer number of water layers can fit inside, similar to our case where the top crystal was intentionally made sufficiently flexible.

**Molecular dynamics simulations of water–surface interaction under strong confinement**

To investigate the dependence of the solid–liquid surface energy $\gamma_{SL}$ on $h$, MD simulations were performed using LAMMPS simulation code$^{45}$ and the SPC/E model for water molecules$^{46}$. The interaction between water and confining walls was modelled by the Lennard–Jones potential with parameters taken from ref.$^{47}$. Flat rigid graphene sheets were used to mimic the confining walls. For simplicity, to account for surfaces with different $\theta$, we varied the interaction energies of carbon with hydrogen, $\epsilon_{HC}$, and oxygen, $\epsilon_{OC}$. These energies were multiplied by a factor of $k$ that was varied from 0.7 to 1.3 in steps of 0.2 to find the water–wall interaction that would approximate the experimental contact angles. The MD angles $\theta$ were estimated by using water droplets containing 4,000 molecules. Our simulations yielded $\theta = 85^\circ$, $63^\circ$, $30^\circ$ and $11^\circ$ for $k = 0.7$, 0.9, 1.1 and 1.3, respectively. The insets of Extended Data Fig. 7 show the profiles for the water droplets found in the case of $\theta = 11^\circ$ and $85^\circ$. We used these two $\theta$ and the corresponding $k$ to model $\gamma_{SL}(h)$ for our mica and graphite capillaries, respectively. Note that the former value lies in the middle of the contact-angle interval observed for mica$^{48}$ and, importantly, our MD results exhibited little sensitivity to the exact $\theta$ for strongly hydrophilic capillaries, as expected from the $\cos \theta$ dependence.

Having established parameters for the desired contact angles, we proceeded to another simulation set-up that consisted of two flat four-layer graphene sheets immersed in a water box containing 40,000 molecules. The dimension of each graphene sheet was $102.2 \times 100.9 \text{ Å}^2$ whereas the water box was $140.0 \times 140.0 \text{ Å}^2$ in size, which allowed water molecules confined between the rigid graphene sheets to exchange easily with outside molecules. After an equilibrium run of 1.0 ns, the two sheets were brought progressively closer in steps of 0.2 Å. Each time the system was equilibrated for 0.1 ns and its total potential energy was calculated for further analysis. Periodic boundary conditions were imposed in all three directions. All the simulations were carried out with the isothermal–isobaric ensemble at 298 K. The density profiles found in our simulations are shown in Extended Data Fig. 7. The confined water exhibits a pronounced layered structure that extends over two intermolecular distances from each surface, before the water density converges to its bulk value, in agreement with the earlier literature (see, for example, refs.$^{39,40,44,45}$).

The deviations $\delta\gamma$ in the solid–liquid surface energy $\gamma_{SL}$ from its bulk value may be considered as extra work spent to rearrange water molecules into the strongly layered structures shown in Extended Data Fig. 7. If $h$ is sufficiently large, the extra work is negligible because the opposite surfaces do not ‘feel’ each other, and their near-surface water structures remain unchanged with respect to the case of infinite $h$. However, as the walls are getting closer, the layered structures overlap (see the density profiles for $h \leq 10$ Å in Extended Data Fig. 7). As a result, the total energy and, hence, $\delta\gamma$ exhibit pronounced oscillations (Extended Data Fig. 8).

Using equation (2) and the numerically found $\delta\gamma$, it is straightforward to calculate the RH required for water condensation inside atomic-scale capillaries. The results are plotted in Fig. 2 of the main text and reveal giant oscillations in $\gamma_{SL}$, which emerge when the structured layers of water near the two confining surfaces start overlapping. Note that the confining walls in the MD simulations were made rigid, disallowing elastic deformations considered separately in our analysis in Fig. 2.

**Data availability**

All the mentioned data to support this study and its conclusions are available upon request from Q.Y.

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Author contributions A.K.G. suggested the project and directed it together with Q.Y. and P.Z.S. fabricated devices. Q.Y. performed measurements and carried out data analysis with help from L.F., Y.V.S., S.I.H. and Z.W.Z. F.C.W. provided theoretical support. A.K.G., Q.Y., F.C.W. and I.V.G. wrote the manuscript. All authors contributed to discussions.

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Extended Data Fig. 1 | Nanofabrication of 2D channels. 

(a) Simplified flow chart for our fabrication procedures. (1) Graphene spacers and the bottom crystal of either mica or graphite (shown in yellow) were assembled on top of an oxidized Si wafer. (2) A suspended SiN membrane with a rectangular hole was prepared separately. (3) The two-layer assembly was transferred from the Si oxide wafer onto the SiN membrane. The opening was extended through the assembly by RIE. (4) The top crystal of mica or graphite was placed on top of graphene spacers. 

(b) AFM micrograph of graphene spacers with \( N = 5 \). The colour scale is given by the height profile (blue curve). 

(c) Optical image of a final mica device used in our experiments. The bottom mica crystal shows up in purple on top of the square SiN membrane. Graphene spacers (\( N = 3 \)) and the top mica layer are outlined in blue and yellow, respectively. 

(d) Cross-sectional scanning transmission electron microscopy image of a graphite channel with \( N = 2 \). The blue ticks mark the channel's edges.
Extended Data Fig. 2 | Measurements of capillary condensation. a, Our AFM set-up. Humidified nitrogen gas flows through the bottom chamber made from an aluminium alloy. A silicon wafer of 15 × 15 mm² in size is seen to cover the chamber, flush with its top surface. The white rubber gasket was lowered during AFM measurements to seal the space above the Si wafer. Inset, cross-sectional schematic showing how capillary devices were mounted during AFM measurements. b, Schematic of a water plug inside our capillaries. For brevity, the layered structure of water is ignored in this sketch. When the top chamber is at low RH, the meniscus slightly retracts inside the capillary to create a vapour pressure gradient. The RH gradient stabilizes two menisci with the same curvature at both exit and entrance. The distance from the exit meniscus to the opening is expected to be short because, in our atomically flat capillaries, water moves much faster as liquid than vapour.\(^\text{26}\).
Extended Data Fig. 3 | Visualization of the condensation transition using AFM. a–c, Images of a graphite capillary with N = 3 at RH of 35%, 70% and 95% (a, b and c, respectively). The upper part of each image shows sagging of the top graphite crystal (H = 80 nm) into the 2D channel. The lower part shows the area immediately outside the channel, which is not covered by the top graphite. The black dotted lines mark a border between the two regions (edge of the top crystal). The colour scales for the lower and upper parts of the AFM images are given by the green and black curves, respectively. The profiles are averaged over ∼100 nm along the y direction, and the curves in the upper parts of all the panels are provided on the same scale given by the black arrows in panel a. A small number of horizontal scanning lines (x direction) around the black-dot dividing lines were removed for clarity because they contained numerous instabilities caused by the AFM tip moving along the edge of the top crystal and jumping up and down. Such instabilities are typical for AFM scanning close to edges.
Extended Data Fig. 4 | Non-hysteretic capillary condensation with slow dynamics. 

**a**, Sagging profiles for a graphite capillary (N = 4) with increasing and decreasing RH between 75% and 80%. Black curve, initial dry-state profile. Red curve, RH was increased to 80%. Then, RH was returned to 75% and maintained at this humidity. AFM profiles were taken after 4 h, 9 h and 16 h (colour coded).

**b**, The N = 6 graphite capillary was brought from the dry state (black curve) into the state filled with water and kept for an hour at 95% RH (red). The humidity was then decreased to ~30%, well below the condensation transition observed at 62.5 ± 2.5% for this device. The colour-coded curves show the time evolution towards the original dry state. Note that the sagging depths δ for such hysteretic loops were highly reproducible but details of sagging profiles could differ in different RH cycles. For example, the top crystal’s adhesion to the right wall was different in the original and final dry states, as seen in **a** (compare black and purple curves). This hysteresis is attributed to irreproducible vdW attachments of top crystals to channel sidewalls.
Extended Data Fig. 5 | Capillary condensation in 2D channels with different initial sagging. a, b. Sagging profiles for two N = 5 graphite capillaries with different δ₀. RH was increased in 5% steps (colour coded). The water condensation transition occurred between 80% and 85% RH in a and between 70% and 75% in b. The difference in RH for the same N is attributed to different h in the two cases.
Extended Data Fig. 6 | Remnant sagging above the condensation transition.

**a**, Schematic of top crystal sagging. **b**, Typical behaviour observed for the sagging depth $\delta$ as a function of RH, after the condensation transition occurred at RH < 60%. Symbols: Measurements for two different mica capillaries with $N = 8$. The solid curves are best fits using equations (3) and (4) (colour-coded). The grey symbol with error bars indicates the experimental accuracy.
Extended Data Fig. 7 | MD simulations of strongly confined water. **a**, Its density profiles at different distances $h$ between two rigid capillary walls with the contact angle $\theta \approx 11^\circ$. **b**, Same calculations but for contact angle $85^\circ$. The orange dashed lines mark positions of the surfaces that defined the 2D channels. Water exhibits a pronounced layered structure near each surface, and the structures start to overlap for $h < 15\,\text{Å}$. Top insets, cross-sectional profiles for water droplets placed on the surfaces with the given $\theta$. 
Extended Data Fig. 8 | Changes in the solid–liquid surface energy caused by atomic-scale confinement. Calculated \( \Delta \gamma(h) \) for several characteristic \( \theta \). The arrows indicate the number of molecular layers of water that fit inside the 2D channels.