Materials and methods

Graphene on mica samples were prepared from highly oriented pyrolytic graphite (HOPG, grade ZYA, Momentive Performance Inc.) by the tape-free mechanical exfoliation method ¹ in a glovebox (LABmaster, M. Braun InertgasSysteme GmbH) filled with dry nitrogen and less than 5 ppm of water and 700 ppm of oxygen. Single layer graphene (SLG) pieces were optically detected inside the glove box.² They were confirmed with Raman spectroscopy to be single layers after atomic force microscopy (AFM) imaging. Double layer graphene pieces were confirmed with AFM imaging: the step height between single- and double-layer graphene pieces was confirmed to be 0.34 ± 0.02 nm. The samples were imaged with either Multimode 8 (Bruker), or with Cypher-ES (Asylum Research/Oxford Instruments). The imaging of wetting and dewetting with Multimode was done in a home-built environmental control box located within the glovebox. For imaging of wetting and dewetting with Cypher-ES, the samples were sealed inside the glovebox into a sample cell. Then the sealed sample cell was transferred to the Cypher instrument, and then exposed to dry nitrogen flow. With both AFM instruments, the samples remained unexposed to ambient, i.e., they remained dry, before imaging commenced with an exception of one sample. The sample shown in Figures 3A, and Figure 10S (E-H) has been briefly exposed to ambient for about 2 minutes for cantilever replacement after exposure to humid nitrogen but before dewetting experiments. For Raman spectra acquisition, the samples prepared in the Lab-Master glove box were sealed in a plastic box inside the glove box and transferred to a different glove box described in details further below such that the samples remained unexposed to ambient. The concentrations of H₂O and D₂O vapors were controlled by mixing dry nitrogen with the dry nitrogen bubbling through the respective liquids: H₂O (either Protegra CS Systems, CEDI Technology > 10 MOhm·cm; or bottled LC-MS grade, Sigma-Aldrich, the results for both were identical), D₂O (99.9 atom % D, Sigma-Aldrich). The mixing was done with a home-built setup for the imaging with Multimode 8 and Raman measurements, and the relative humidities (RH) were measured with Testo 625 (Testo Inc.). The mixing was done with a gas mixer GB 3000 (MCQ Instruments) for the imaging with Cypher-ES, and RH was measured with a built-in humidity sensor. The AFM images were processed with SPIP (Image Metrologies) by subtracting a first order polynomial. Fractal dimensions were estimated with Fractalyse software (ThéMA Laboratoire) using box counting method.
Raman spectra were acquired with a confocal Raman microscope (XploRa, Horiba Ltd) located inside a glove box. The glove box was initially purged with dry nitrogen, and then it was purged with dry nitrogen bubbling through washing bottles containing either H₂O or D₂O described above. Single- and bi-layer graphene pieces were optically detected inside the glove box. The samples were first equilibrated in H₂O or D₂O vapors at about 40% RH for one hour before the experiments with mica bending commenced. RH values inside the glove box were measured with an RH sensor (Testo 625, Testo Inc.) with the calibration fidelity of ± 2.5% RH, as provided by manufacturing company. A 532 nm excitation laser was used with the illumination intensity less than 1.4 mW on the sample surface under 100x objective (Olympus M Plan N 100X/0.90na). A neon lamp was placed close to the sample such that the spectra acquired on the samples contained the Ne-spectral lines. The Ne-spectral lines were used as references for Raman spectra calibration. The calibration was detailed in 3. The calibration method using neon lamp was used to measure the samples shown in Figure 2 of the main text and in Figure 6SC, D. For all other samples we used a standard instrument calibration implemented by the instrument manufacturer using a silicon line at about 520 cm⁻¹. Mica substrate was bent in a four-point bending setup inside the glove box. The setup was described in details previously.4 The mica surface strain was estimated as mica slab thickness divided by two times the bending radius. The uncertainties of graphene strain induced by mica bending were detailed previously.4 In brief, the uncertainties were propagated from the uncertainties of mica slab bending radius, mica slab thickness and positioning precision of laser spot position. The 2D peak position scattering, for when the laser spot was repositioned, was estimated to be 0.5 cm⁻¹.

Wetting of graphene-mica interface with D₂O and H₂O films

Figure 1S shows AFM images of H₂O and D₂O wetting graphene-mica interface. Wetting with water has been addressed in details before.5 The initially dry samples (not shown here) were exposed to controlled mixtures of dry nitrogen with nitrogen bubbling through either D₂O or H₂O. As the relative humidity (RH) increases, islands of a water film start emerging from the graphene edges. The islands grow inwards and form labyrinthine patterns (Fig. 1S). Eventually, if we increased RH to 40%, the labyrinthine patterns combine to form a homogeneous film (Fig. 1S B and D)). We do not find any difference between wetting behavior with water and heavy water. Wetting with heavy water started within the same RH range. The wetting patterns with heavy water appear to be identical to water ones, i.e., they exhibited labyrinthine shapes with roughly same width (Fig. 1S). Heavy water and normal water both form homogeneous films at around 30 % RH.

The formation of labyrinthine patterns by water during the initial intercalation into the graphene-mica interface was explained by an equilibrium between electrostatic repulsion of water dipoles ordered normally to the interface, and the line tension at the boundaries between dry and wetted areas.5 Dipoles of D₂O and H₂O molecules are rather similar,6 therefore it is reasonable to expect similar electrostatic repulsions between the molecules and correspondingly similar labyrinthine patterns.
Figure 1S. AFM height and phase images (the insets) of SLGs exposed to A) H₂O and C) D₂O vapor at about 17% and 16% RH, respectively. The phase images show no significant contrast difference between wetted and dry areas. This indicates that both liquids intercalate into the graphene-mica interface. Both liquids form similar labyrinthine wetting patterns. B) and D) are the height images of the same areas acquired at higher RH, i.e., 40% for H₂O and 30% for D₂O.
Figure 3, non-colored version

Figure 2S shows the images of Figure 3 of the main text without coloring of the dewetting patterns.

Figure 2S. The figure is identical to the figure 3 in the main text, yet with all coloring, labelling and highlighting removed. The coloring possibly hides important features. For instance, with no coloring, one can see from the cross section in B), that the bottom of the dewetting patterns within double layer graphene (purple area in the cross section) is higher to compare with the neighboring top of the water filled single layer graphene (area I). We conclude from this that the height of the dewetting layer is smaller than the single layer graphene height, i.e., it is smaller than roughly 3.4 angstrom.7
Dewetting of H₂O filled mono- and bi-layer graphene-mica interfaces

Figure 3S shows dewetting patterns formed during relatively slow dewetting of mono-, bi- and few-layer graphene – mica interfaces filled with H₂O, i.e., RH was decreased from 40% to 13% in 2 minutes, and then it was kept constant. An overview image (Fig. 3S.A) shows both single- and double-layer graphene covered areas. The single layer graphene stripe is rather narrow, therefore also dewetting patterns are rather small laterally. Nevertheless, one can clearly recognize the fractal shape of the dewetting pattern (Fig. 3S.C). The dimension of the fractal is roughly 1.7. The dewetting patterns in bilayers (Fig. 3S.A and B) are more compact with fractal dimension around 1.85.

Figure 3S. AFM height images of single- and few-layer graphene flakes on mica filled initially with H₂O and then slowly dried with N₂ gas. RH was decreased from 40% to 13% in 2 minutes, and then it was kept constant for at least an hour before the images were made. A) An overview image. B) Magnification of graphene bilayer covered area. C) Magnification of SLG covered area.

Fast dewetting of single layer graphene-mica interface initially filled D₂O and H₂O films

Instantaneous drying from 40% to ~ 0% within less than a minute by purging the AFM sample cell with dry nitrogen caused growth of dewetting patterns that are highly ramified fractal structures for both D₂O and H₂O filled single layer graphene-mica interfaces (Fig. 4S).
Figure 4S. AFM topography images of single layer graphenes on mica. Similar fractal patterns formed in about one minute during fast dewetting of A) H₂O and B) D₂O intercalated single layer graphene – mica interfaces. Here RH was decreased from 40% to roughly 0% within less than a minute by direct purging of the AFM sample cell with dry N₂.

**AFM topography images of single- and bilayer-graphenes after strain measurements**

All graphene pieces used for the strain relaxation measurements were imaged with AFM under ambient conditions to determine their lateral dimensions. Figure 5S shows a few example images. The single layer graphenes in A) and B) were exposed to D₂O and H₂O vapors respectively during strain relaxation measurements. The lateral size of SLG in A) is larger to compare with the one in B) (note the different image scale); nevertheless, the SLG piece in A) relaxed the strain much faster to compare with the one in B), see the main text for the details.

Figure 5S. AFM height images of SLG pieces after strain transfer measurements done in a glove box filled with N₂ gas enriched with A) D₂O and B) H₂O vapors. C) A bilayer-graphene piece after strain transfer measurements done in a glove box filled with N₂ gas enriched with H₂O vapor. Their Raman data acquired during strain transfer measurements are shown in Figure 2 of the main text. The green spots indicate roughly the laser spot positions on the samples during Raman measurements. The black arrows indicate the direction of strain induced by the bending.
More examples of strain relaxation in graphene with intercalated H$_2$O and D$_2$O layer

Here we show Raman results from another 4 SLG samples. Two of them were measured in H$_2$O vapor while the other two were measured in D$_2$O vapor. The experiments were performed in the similar way as we did on samples shown in Figure 2. In all cases the RH was high enough to form molecular layers at the graphene-mica interface. We can find significant difference of strain relaxation behaviour in samples measured with H$_2$O and D$_2$O. The results are always similar to the data shown in Figure 2.

![Graph showing 2D peak position dependency on time from A, B) SLGs lying on H$_2$O film and C, D) another SLGs lying on D$_2$O film. The strain steps of mica for each sample are shown, and the vertical arrows indicated the expected shift for SLGs if it would follow the surface strain of mica.](image)

**Figure 6S.** 2D peak position dependency on time from A, B) SLGs lying on H$_2$O film and C, D) another SLGs lying on D$_2$O film. The strain steps of mica for each sample are shown, and the vertical arrows indicated the expected shift for SLGs if it would follow the surface strain of mica.

**Strain relaxation in graphene on layers of H$_2$O and D$_2$O mixtures**

We performed the strain transfer measurements on graphene samples exposed to mixed vapors with different ratio of H$_2$O and D$_2$O. For mixing ratios of D$_2$O: H$_2$O of 7:3 and 3:7 we found the same behaviour of the 2D peak position as for pure D$_2$O. Only for mixing ratio of 1:9 D$_2$O:H$_2$O
we observed 2D peak changes with time due to strain relaxation. However, in that case the relaxation time was lowered (2 Minutes) compared to pure water (8 Minutes).

Figure 7S. strain relaxations in a SLG exposed to vapor with mixing ratio D$_2$O:H$_2$O of 1:9.

Bilayer graphene spectra on flat and bent mica

Figure 9S. Raman spectra from the bilayer graphene samples in Figure 2C, exposed to H$_2$O vapor acquired before and after bending of mica.
Development of D$_2$O and H$_2$O dewetting patterns at SLG-mica interfaces

Figure 10S shows the evolution of D$_2$O and H$_2$O dewetting patterns of two SLG samples. The RH was decreased within 2 minutes from 40% to about 13% and then kept constant. Figure 10S A) and E) are the first images acquired when RH reached 13%. Then AFM imaging under tapping mode was repeated on the zoomed areas on both SLGs (Figure 10S, areas marked by green boxes).

Figure 10S. development of the A-D) D$_2$O and E-H) H$_2$O dewetting patterns at two graphene-mica interfaces. The time interval between each two adjacent images are about 30 minutes.

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