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Anomalous ionic transport in tunable angstrom-size water films on silica

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Liquid and ionic transport through nanometric structures is central to many phenomena, ranging from cellular exchanges to water resource management or green energy conversion. While pushing down towards molecular scales progressively unveils novel transport behaviors, reaching ultimate confinement in controlled systems remains challenging and has often involved 2D Van der Waals materials. Here, we propose an alternative route, which circumvents demanding nanofabrication steps, partially releases material constraints, and offers continuously tunable molecular confinement. This soft-matter-inspired approach is based on the spontaneous formation of a molecularly thin liquid film onto fully wettable substrates in contact with the vapor phase of the liquid. Using silicon dioxide substrates, water films ranging from angstrom to nanometric thicknesses are formed in this manner, and ionic transport within the film can then be measured. Performing conductance measurements as a function of confinement in these ultimate regimes reveals a one-molecule thick layer of fully hindered transport nearby the silica, above which continuum, bulk-like approaches account for experimental results. Overall, this work paves the way for future investigations of molecular scale nanofluidics and provides novel insights into ionic transport nearby high surface energy materials such as natural rocks and clays, building concretes, or nanoscale silica membranes used for separation and filtering.

Nanofluidics | Ionic transport | Water film

Transport of liquids and ions at the nanoscale, referred to as nanofluidics, has attracted tremendous attention for its wide applications in desalination and filtration (1), clean energy extraction (2), design of new concepts of fluidic semiconductors (3) and biomolecular diagnosis (4). From a fundamental point of view, nanofluidics plays a key role in many fields of science, from the nanoscale communication mechanisms involved in cell biology (5) to macroscopic geological systems, involving for example transport of water and ions in soils, natural rocks, and clays. Conventional continuum descriptions have been challenged for ions and liquid transport in sub-nanometric slits or tubes (6), with original phenomena arising from confinement such as anomalous ion mobility (7, 8), ultra-fast flows in nanotubes (9, 10) or giant osmotic energy conversion (11).

One particular property of the nanoscale is a diverging surface-to-bulk ratio. Complex behaviors have often been attributed to enhanced surface effects. The most classical one concerns ionic conductivity, as its value is critical to determine the yield of energy conversion processes in nanofluidic membranes (11, 12). The ionic conductivity of a channel has generally at least two contributions; one originates from the bulk and is directly linked to the number of charge carriers that have been added in the solution (such as a fixed salt

concentration or pH), and the other originates from surface charges (for example from the ionization of the surface and the release of counter-ions, among other possible mechanisms). Experiments at low salt concentrations give access to the surface conductivity contribution. Indeed, a plateau of the conductance of the channel as a function of salt concentration (11, 13, 14) is observed provided that the so-called Dukhin number, $Du = |\sigma|/ehc$ (with σ the surface charge density on the channel walls, c the bulk salt concentration, e the elementary charge, and h the channel thickness), that compares the number of surface and bulk charge carriers, is larger than one. Deviations from this simple picture have been observed experimentally, for transport in carbon or boron nitride nanotubes (11, 14, 15), hydrophobic nanopores (16), graphene nanoslits (7) or proteinic channels (17).

On the one hand, continuous descriptions suggest that these deviations can be due to complex charge dissociation mechanisms at the interface (18), hydrodynamic slip and charge mobility along the interface (7, 19), or a subtle interplay between electronic properties of the material and ionic transport at the interface (6). In any cases, such surface mediated mechanisms involve molecular scale static or dynamical properties (20, 21).

On the other hand, these deviations can also originate from ultimate molecular confinement, resulting in the failure of the macroscopic continuum constitutive laws. For example, basic

Significance Statement

Nanoscale transport of ions and liquids is crucial for many geological and biological processes, but also for the design of efficient membranes for desalination, filtration, or osmotic energy harvesting. While the most salient behaviors arise at the molecular scale, such ultimate confinement has so far been achieved on a limited number of geometrical designs restricted to specific materials. To bypass previous technological limitations, we investigated transport in molecular-thick water films that spontaneously form onto fully wettable substrates surrounded by water vapor. We observed that ion transport is hindered nearby silica within a molecular layer of $\sim 3\text{ \AA}$, above which continuum models successfully capture our observations. Our approach opens up a new route to explore ultimate nanofluidic transport on various surfaces.

A.-L.B., C.Y., and L.J. designed research, A.-L.B., C.Y., O.V., M.Z. and A.A. designed the experiments, A.A. and M.Z. performed the experiments and analyzed the data, A.-L.B., C.Y., L.J., and A.A. derived the model, R.F. carried out electrode deposition, A.-L.B., C.Y., L.J., O.V., A.A. and M.Z. wrote the paper.

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51 physical constants known for the bulk are challenged, such as
 52 the dielectric constant of water (22), reported to drastically
 53 decrease from 80 to 2 for a 1 nm-confined water film in a
 54 graphene slit; similarly, viscosity can strongly increase for
 55 aqueous electrolyte of thickness below 3 nm (23, 24).

56 To test these ultimate regimes, experimental systems have
 57 been developed, including nanopores (25), 1D nanotubes
 58 (11, 14, 15), or 2D nanoslits (7, 8, 26), and rich physical
 59 phenomena have been revealed. But up-to-date investigations
 60 are still restricted to very specific systems, such as carbon-
 61 based channels (graphene (27), graphite (28, 29)), and simi-
 62 lar van der Waals material systems (hBN (22), MoS₂ (25)),
 63 and with geometrical confinement down to one monolayer of
 64 graphene (6, 28, 30). Despite showing remarkable and promi-
 65 sing behaviors, these systems constitute a very specific class of
 66 materials, which consists of layered smooth individual atomic
 67 planes. Some extensive studies reported transport properties
 68 across proteinic nanopores (31), but restricting the analysis
 69 to the complex nature of the biological nanopores. On the
 70 contrary, studies in the vicinity of oxide substrates are limited
 71 to larger scales (13, 32, 33), with minimum confinement to
 72 2 nm so far. In sharp contrast to the loose molecular inter-
 73 actions on carbon-based or van der Waals materials, silicon
 74 dioxide is hydrophilic, with strong adhesion to adjacent water
 75 molecules (34–36). One may wonder how liquids and ions are
 76 transported in such a strong liquid/solid interacting channel
 77 with a size comparable to a few molecules, and if additional
 78 effects need to be addressed. Moreover, most existing fine-
 79 thickness-controlled nanochannels are too delicate to fabricate
 80 and leakage/blockage may pose a strong issue for practical
 81 applications (28). A cheap, yet easy-to-fabricate nanoscale
 82 channel is needed.

83 To tackle the above-mentioned questions, we have developed
 84 an experiment that takes advantage of surface wettability of
 85 silicon dioxide, which allows us to deposit a thin water layer,
 86 whose thickness can be continuously tuned from 0.3 to 2 nm.
 87 To achieve this, our device with a silicon dioxide interface was
 88 placed in a vacuum chamber with controlled humidity, which
 89 resulted in predictable water condensation on the silica surface.
 90 In this situation, the water film is free of contamination from
 91 the surroundings, in sharp contrast to most other nanofluidic
 92 devices (6, 30) where liquid reservoirs are connected to air.
 93 We then detected the conductance within this ultra-clean
 94 liquid film by applying an external electric field, and further
 95 deduced the magnitude of ion transport in the liquid. We
 96 discovered a non-linear response of conductance as a function
 97 of film thickness. A modified PNP (Poisson-Nernst-Planck)
 98 theory based on continuum mechanics successfully captures
 99 our observations, when taking into account that the transport
 100 of a monolayer of ions adjacent to the wall is totally hindered.

101 This result contrasts with the singular mobility reported
 102 for 2D materials, stressing out the critical impact of the nature
 103 of the substrate on nanofluidic ionic transport.

104 Experiments and results

105 **Tunable angstrom-size water films for nanofluidics.** To date,
 106 ultimate molecular confinement has been reached either in
 107 biological pores (31) or through advanced nanofabrication
 108 strategies (8). In the spirit of previous proposals for obtaining
 109 confinements of tens to hundreds of nanometers (37, 38), we
 110 extend soft-matter approaches to nanofluidics towards the

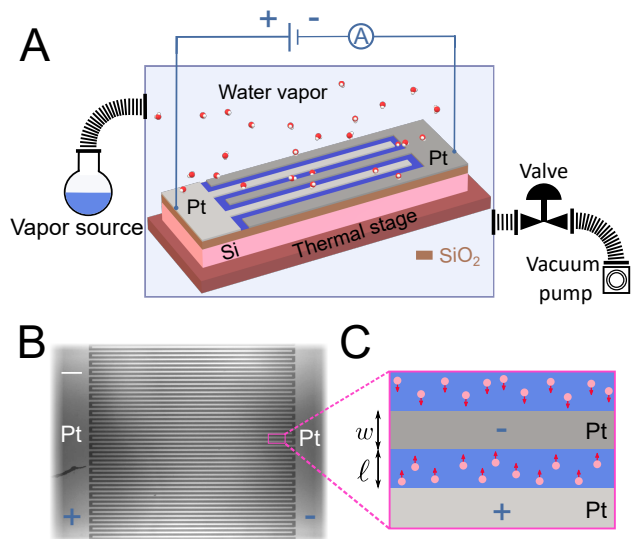


Fig. 1. Scheme of the experimental setup and picture of the substrate. (A) The substrate is placed in a vacuum chamber that eliminates airborne contaminants and oxidation. Water vapor with controlled pressure, set by the vapor source temperature T_b , flows into the chamber and is adsorbed onto the silicon dioxide surface between the electrode pads, forming a thin liquid film. The silicon dioxide temperature T is tuned by the underlying thermal stage, which determines the saturation vapor pressure of the electrode, and changes the thin film thickness. A sinusoidal voltage bias is applied to the liquid film and the current response is recorded to estimate its conductance. (B) Microscopic view of the sample under reflection light. Scale bar: 1 mm. The gray-shined part on the sample corresponds to the platinum electrode and the dark-shaded part corresponds to the SiO₂ surface between the electrodes. The interlaced design of the platinum deposition amplifies the electrode total length to 1.49 m. (C) Zoom-in of the patch framed in (B). Protons (pink circles) migrate (red arrows) between the two electrodes. Both the gap, ℓ , between two platinum branches and the width, w , of each platinum branch are 100 μm .

111 building of molecular-thick liquid films. Indeed a liquid film
 112 spontaneously assembles onto fully-wettable surfaces when
 113 exposed to its vapor (34, 35). Such a condition can be met
 114 with a clean silica surface under water vapor atmosphere, the
 115 pressure of which can be used to continuously tune the liquid
 116 film thickness in the angstrom to nanometer range (39–42).

117 In practice, we use substrates that consist of SiO₂ layers
 118 grown on silicon wafers. The surface was characterized by
 119 AFM and found to be smooth at the atomic scale (43), with a
 120 rms roughness of ≈ 0.2 nm and absolute value of the average
 121 of profile height deviations from the mean line $R_a \approx 0.17$ nm
 122 (see material and methods for details). This silica substrate is
 123 treated by oxygen plasma prior to the experiment and then
 124 introduced in a low-pressure experimental chamber where its
 125 temperature T can be controlled (Fig. 1A). The chamber is
 126 put under vacuum conditions and then connected to a water
 127 vapor source dipped in a regulated thermal bath at a fixed
 128 temperature T_b , so that the relative humidity (RH) in contact
 129 with the substrate can be finely controlled with the substrate's
 130 temperature T . Low-pressure conditions help to maintain the
 131 physio-chemical properties of the silicon dioxide surface, for
 132 example by removing airborne contamination and oxidation.

133 The thickness of the liquid film is measured by a spectro-
 134 scopic ellipsometer that is adapted to our vacuum chamber
 135 (Fig. 2A). The measurement of the attenuation and polariza-
 136 tion of the reflected light signal on the sample gives access
 137 to the water film thickness h , considering an optical model
 138 with three material layers (silicon at the bottom, thin silica

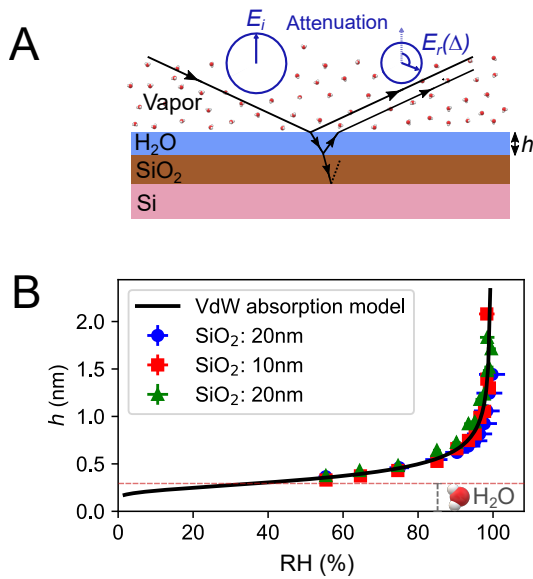


Fig. 2. Ellipsometric measurements of liquid film thickness. (A) Principle of ellipsometry measurements. (B) Thickness of the water film as a function of relative humidity in the chamber on three SiO₂ surfaces: 20 nm-thick (blue circles), 10 nm-thick (red squares) and 20 nm-thick (green triangles). Black solid line corresponds to the van der Waals adsorption model. Best fit gives the Hamaker constant $A_{slv} = (-6.79 \pm 0.07) \times 10^{-20}$ J.

thus evidencing negligible effect from the silicon base.

Probing Conductance. The conductance of the condensed film is measured by using platinum electrodes deposited on the silicon dioxide surface (Fig. 1A). The two facing electrodes are fabricated in an interlaced comb-shaped design (Fig. 1B) to increase the electrode total length and thus the signal magnitude.

A sinusoidal electrical voltage (1 V, 10 Hz) is applied between the two platinum electrodes, and the corresponding current circulating across the liquid film between the electrodes (Fig. 1C) is detected by a homemade amplifier. AC actuation avoids ion accumulation and depletion near the electrodes, and maintaining the signal amplitude below 1 V prevents water hydrolysis (redox potential of water is 1.23 V). A typical measurement of the imposed voltage and the induced current is reported in Fig. 3B, for a humidity of RH = 99.1 %. From an analysis of the amplitude of the signal and the phase shift, taking into account the system leakage thoroughly characterized under vacuum conditions (see SI appendix for details), we extract the film properties and in particular the conductance in the liquid, denoted G and reported in Fig. 3C.

By continuously varying RH, the nanometric film conductance, G , as a function of film thickness is summarized in Figures 3(C). We report two different experiments performed at two vapor source temperatures, $T_b = 6.01 \pm 0.02$ °C shown by the green data set (case I) and $T_b = 15.81 \pm 0.03$ °C shown by the blue data set (case II). In both cases, we performed loading measurements of G associated with gradual increase of RH (open symbols in Fig. 3C), and unloading measurements upon RH decrease (solid symbols in Fig. 3C). Overall, data show amplitude variability between samples but also a hysteretic behavior for G , which is smaller upon loading than upon unloading.

Such a hysteresis is reminiscent of water uptake hysteresis observed in porous materials during humidity cycles (46). Note however that in the present system, the liquid film itself does not display any hysteretic behavior with a thickness independent of the loading or unloading cycle. A possible origin for back-and-forth differences in conductance values could be attributed to the film–electrode connection, which involves water menisci. Indeed contact line pinning is a well-known and unavoidable source of hysteresis that will change the geometry of the connection with the water film depending on water uptake or release.

Now concentrating on the generic features displayed by these measurements, we evidence that the film conductance G non-linearly increases with the film thickness h . At small thicknesses comparable to the size of a single water molecule ($h \leq 0.3$ nm), G is undetectable, suggesting a significant hindering of proton mobility at this length scale (see hereafter for a detailed discussion). The conductance then increases, before reaching a plateau at moderate thicknesses $h \simeq 1.2$ nm. Interestingly, this plateau is reminiscent of the so-called surface conductance regime evidenced upon confinement, when the thickness h becomes smaller than the so-called Dukhin length (6, 11, 13, 33). In fact, below such a confinement scale, the concentration of ionic species in the channel becomes dominated by the number of counter-ions needed to balance the surface charge. If this surface charge is constant, this yields a fixed conductance independent of further confinement or bulk electrolyte concentration. A more adequate description

layer, adsorbed water layer at the top). In situ experiments performed on SiO₂–Si sample under vacuum (no water) give access to the reference parameter for silicon and silica for the interpretation of ellipsometry data. An additional water layer is then incorporated into the model structure (Fig. 2A) and the water film thickness h is then estimated with an accuracy of 0.3 nm. As expected, h increases with RH, to diverge at RH=100% (Fig. 2B). Optical monitoring of the surface was carried on to ensure that no signature of microscopic droplets or dry patches could be detected, as expected for a fully-wettable substrate. Considering the surface roughness and this observation, the liquid film is assumed to be homogeneous. However, droplets or patches below the microscopy resolution, 1 μm, can not be detected due to the optical limitations of the set-up.

Quantitatively, balancing the water chemical potential in the vapor and in the film allows us to write down the $h(\text{RH})$ relation in terms of the disjoining pressure (44), $\pi(h) = -\rho_l k_B T \ln(\text{RH})$, with ρ_l the liquid density, k_B the Boltzmann constant and T the temperature. For Van der Waals (VdW) interactions, the disjoining pressure classically reads $\pi(h) = -A_{slv}/(6\pi h^3)$ with A_{slv} the solid-liquid-gas Hamaker constant, which quantifies interaction energy between water vapor and solid through the water film. In principle other interactions may contribute to the disjoining pressure atop the VdW ones, such as electrostatics or specific surface adsorption (34, 44). In the present situation, however, VdW contribution turns out to be dominant as evidenced by the scaling law $\pi(h) \propto h^{-3}$ exhibited by experimental measurements (see SI appendix). Best fit to experimental data yields in $A_{slv} = -(6.79 \pm 0.07) \times 10^{-20}$ J, in good agreement with computed values (45). Note that substrates with various SiO₂ layer thicknesses show similar quantitative results (Fig. 2B),

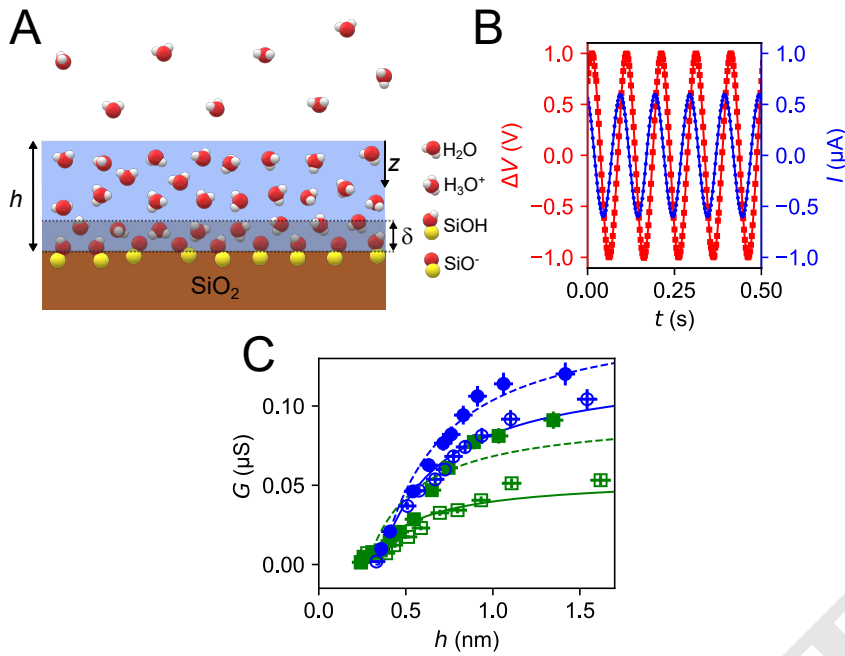


Fig. 3. Conductance measurements in a liquid film. (A) Schematic of the hindered diffusion layer model. The z direction is perpendicular to the external electric field, with $z = 0$ being the liquid-vapor interface and $z = h$ the liquid-solid interface. A hindered layer of thickness δ is represented next to the solid. (B) Typical voltage input (red) and raw current response (blue) of our experimental system. The input voltage is a 1 V AC sine wave with a frequency of 10 Hz. Scattered points correspond to experimental data and fitting curves are shown as lines. (C) Liquid film conductance, G , as a function of water film thickness h . Scattered points represent experimental data with open and full symbols for a loading and unloading cycle, respectively. Solid and dashed lines show model predictions for a loading (increase of the humidity) and unloading (decrease of the humidity) cycle, respectively. Green and blue colors indicate a vapor source temperature of $T_b = 6.01 \pm 0.02^\circ\text{C}$ (case I) and $T_b = 15.81 \pm 0.03^\circ\text{C}$ (case II), respectively.

233 is rather to consider that the ionization rate at the surface
 234 depends on the film thickness, thanks to a so-called charge
 235 regulation mechanism. However, that both the schematic constant
 236 charge and the charge regulation pictures may break
 237 down in ultimate confinement, with a progressive fading away
 238 of the conductance at a finite thickness is a novel feature that
 239 we discuss in the following.

240 Conductance model

241 **Continuum approach.** In order to rationalize the above mea-
 242 surements, we now discuss the theoretical modeling of the
 243 ionic conductance in our system. As the liquid film comes
 244 from water vapor condensation in a vacuum, ions in the water
 245 film result from water self-dissociation or ionization of silanol
 246 surface groups through: $\text{SiOH} = \text{SiO}^- + \text{H}^+$. At $\text{pH} = 7$ and
 247 for typical silica surface charges (13, 33, 47), ions concentra-
 248 tion is entirely dominated by protons H^+ from the surface
 249 reaction (44). In the following, we will therefore neglect water
 250 dissociation reaction together with the presence of hydroxide
 251 ions OH^- .

252 Next, we describe the electrostatic potential ψ and ions
 253 distribution c_+ in the film by adopting a continuum mean-
 254 field Poisson-Boltzmann (PB) equation, in the Gouy-Chapman
 255 regime (48, 49) for monovalent ions. We complement this
 256 equation by the boundary conditions along the direction z
 257 perpendicular to the surface (Fig. 3A). At the free surface
 258 $z = 0$, we assume no surface charge and sets the potential to
 259 zero so that $\phi'(z = 0) = \phi(z = 0) = 0$, with the dimensionless
 260 potential $\phi = e\psi/(k_B T)$. At the silica/water interface, the
 261 potential relates to the surface charge density σ according
 262 to $\phi'(z = h) = 4\pi\ell_B\sigma/e$ with $\ell_B = e^2/(4\pi\epsilon k_B T)$ being the
 263 Bjerrum length that compares Coulombic interactions with
 264 thermal energy (see SI appendix for details). Overall, this
 265 provides the z profiles for ϕ and c_+ as a function of the film
 266 thickness and of the yet-to-be-determined surface charge σ
 267 (see SI for complete derivation).

Finally, the water film conductance is obtained according
 to

$$G = \frac{I}{\Delta V} = \frac{1}{\Delta V} \iint_{\mathcal{S}} \mathbf{j}_e \cdot d\mathbf{S} \quad [1]$$

with ΔV the applied voltage between the two platinum elec-
 trodes, \mathcal{S} the cross section of the integration domain (here
 $\mathcal{S} = h \times L$ with L the total length of the electrode), \mathbf{j}_e the
 current density vector, $\mathbf{j}_e = ec_+(z)\mathbf{v}(z)$, with \mathbf{v} the velocity
 of ions. The velocity of ions has in principle two contributions
 (21, 50): one originating from their electrophoretic mobility,
 and the other one from the electro-osmotic flow generated at
 the interface. In practice, the electro-osmotic contribution is
 negligible when the channel size is smaller than the Debye
 length for a low surface charge density (51–53), and only the
 electrophoretic effect will be considered in the following (see
 SI appendix).

To close the description, we need to come back on the
 surface charge σ and specify its properties. A full descrip-
 tion would be to consider that the surface charge is fixed by
 an ionization ratio that results from a chemical dissociation
 mechanism (44), i.e., charge regulation mechanism. This is
 detailed in the discussion section and in the SI appendix, and
 results in the same quantitative description. However, as a
 first approach, we will simply consider that the ionization
 ratio of silanol groups is fixed, independent in particular of
 the film thickness, thus resulting in a constant surface charge.
 Accordingly, an equivalent number of charge carriers H^+ is
 released in the liquid, which can move under an electric field.
 If the mobility μ_+ of these ions is homogeneous across the
 water film (a second hypothesis), liquid film conductance will
 be a constant $G \propto e\mu_+|\sigma|$, referred to as surface conductance
 regime (11, 13, 21). This behavior is indeed consistent with
 what is recovered in our experiments for films thicker than
 1.2 nm. Nevertheless, it fails to account for the evolution of
 G down to molecular confinement, where the conductance
 eventually vanishes.

As is clear from the above discussion, within the present

Table 1. Fitting parameters for the hindered diffusion layer model at constant surface charge density σ

T_b ($^{\circ}\text{C}$)	Loading		Unloading	
	σ ($\mu\text{C m}^{-2}$), δ (\AA)		σ ($\mu\text{C m}^{-2}$), δ (\AA)	
6.01 ± 0.02	-9.50 ± 0.79	2.74 ± 0.19	-16.4 ± 1.6	2.78 ± 0.20
15.81 ± 0.03	-22.6 ± 0.8	3.45 ± 0.12	-28.9 ± 1.0	3.55 ± 0.11

continuum framework, conductance calculations are based on two assumptions on the surface charge and on the ions dynamics. As mentioned above, it is possible to relax the constant surface charge assumption, using a more adequate charge regulation mechanism (44). This approach is however not capable alone to account for our experimental results (see the SI appendix for full details).

Hindered diffusion layer. In the following, we relax the second assumption concerning the mobility of the ions. We then build a simple analytical model considering that ion mobility is not constant all over the film. For the sake of simplicity, we introduce a so-called hindered diffusion layer near the liquid-solid surface, where the mobility of counter-ions is fully inhibited. Such a molecular layer has been reported in other contexts, with the observation of decreased transport properties under confinement (23, 39, 54–59), or of an ice-like structure (41, 42, 60) in the vicinity of silica.

By assuming the ion motion is totally inhibited in a hindered diffusion layer of thickness δ next to the solid interface (see Fig. 3A), the electrophoretic velocity along the surface reads (i) $v(z) = \mu_+ \Delta V / \ell$ for $z < h - \delta$, with ℓ the distance between the electrodes and μ_+ the ionic mobility of protons, (ii) $v = 0$ for $h - \delta \leq z \leq h$ in the hindered diffusion layer. Recalling that in our present case, the electro-osmotic contribution is negligible, the conductance then reads:

$$G = \frac{L}{\ell} 2\epsilon k_B T \mu_+ K \tan [K(h - \delta)]. \quad [2]$$

where K^{-1} is a characteristic length satisfying $Kh \tan(Kh) = 2\pi\ell_B h |\sigma| / e$ (see SI appendix for details). Note that when the hindered diffusion layer δ is small compared to the film thickness and in our conditions (see SI for details), this expression can be reduced to $G \simeq G_s \times (1 - \delta/h)$, with G_s the expected surface conductance for an homogeneous film without any hindered diffusion layer. For a constant surface charge, G_s is expected to be independent of the film thickness, and a plateau should be reached where a surface conductance is recovered (8, 11, 13). This is indeed the behavior we recover for large h .

Discussion

Fig. 3C shows the comparison between experimental data and the hindered diffusion description as given by Eq. (2). Overall this simple model captures well all the features of our experiments using the surface charge σ (assumed fixed) and the hindered layer thickness δ as free parameters. Values obtained for different substrates and for the loading/unloading branches are summarized in Table. 1.

First, the hindered diffusion layer thickness δ is found to be 0.31 ± 0.04 nm for all the data set, which is comparable to the size of one single water molecule and in good agreement with experiments reporting a structured stagnant layer of water

adsorbed at an oxide interface. In the literature, the thickness of this layer however varies (from one to three molecular layers) with the type of properties that is considered (41, 42, 61). On a dynamical point of view, such stagnant layers have been observed experimentally when looking directly at hydrodynamic boundary conditions, with a fixed thickness of one molecular layer (62, 63). Second, the surface charge density σ is found to be around $-20 \mu\text{C}/\text{m}^2$. In absolute value, it appears to be lower than measurements in the vicinity of silica in macroscopic systems (64). However, when considering charge regulation mechanism as discussed below, this value is in good agreement with expected ionization rate in such confined conditions (64).

Despite the good agreement between the model and the experiments, several hypotheses can be discussed. Concerning transport properties, we account for confinement and in particular friction at the water/silica interface by introducing the hindered diffusion layer, a first step towards more complex mobility profiles for the ions due to the presence of the surface. We also assume that the water-vapor interface is frictionless, which seems reasonable if the amount of adsorbed impurities is low (65).

Concerning our modeling of the ion distribution in the film (PB formalism), we have assumed that the dielectric permittivity of water was not modified by the confinement. Recent work suggests a decrease of the normal permittivity due to confinement (22, 24). Taking this effect into account, using $\epsilon_r \simeq 2.1$, does not significantly modify the results (see SI appendix). For example, the surface charge extracted from the experimental data for the unloading cycle at $T_b = 6.01 \pm 0.02$ $^{\circ}\text{C}$ is shifted from $16.37 \mu\text{C m}^{-2}$ to $16.42 \mu\text{C m}^{-2}$ (the dashed green curve in Fig. 3C), a difference of one order of magnitude below the error bar of the measurements.

In addition, we note that to tune the relative humidity, we vary the temperature of the substrate. If we consider film thicknesses above 0.3 nm, the temperature variation is of around 15 $^{\circ}\text{C}$, more precisely between $T = 6.0$ $^{\circ}\text{C}$ to $T = 20$ $^{\circ}\text{C}$ for case I, and $T = 15.9$ $^{\circ}\text{C}$ to $T = 30$ $^{\circ}\text{C}$ for case II. This could affect also our results as proton mobility has been shown to be dictated by a Grotthus mechanism and to increase with temperature, with a change of more than 10% for a 10 $^{\circ}\text{C}$ variation (66, 67). This effect could explain the discrepancy between measurements performed at the two different temperatures that we have considered, the coldest one (case I) resulting in a lower conductance. However, this effect cannot be at the origin of the conductance collapse at low humidity (low film thickness), because low humidity is obtained by increasing the temperature, which can only increase the proton mobility and hence the conductance.

We also considered the liquid/vapor interface to be neutral, which is somewhat controversial. Specific charge adsorption at the water/vapor interface has been attributed either to impurities (68), or to specific anion adsorption. However, impurities should be very scarce here under low pressure environment. Moreover, in this water condensed film, the amount of anions is limited to spontaneous water dissociation, leading to a maximum surface density (if all the ions adsorb at the free surface) of 10 nC m^{-2} , which is very small compared to the surface charge density at the silica surface.

As already mentioned, another important restriction concerns the fixed surface charge hypothesis. A more accurate

charge regulation mechanism can be considered instead (44). In the SI appendix, we investigate different possible charge regulation models; here we will only briefly discuss a so-called single pKa model. In short, the surface charge density is controlled by the fraction φ_i of ionized groups at the surface: $\sigma = -e\varphi_i/a^2$, with a the average distance between each silanol sites. The fraction φ_i can be related to the constant K_a of the silanol dissociation reaction, and to the local proton concentration $c_+(z = h)$ at the surface (determined from the PB equation):

$$K_a = \frac{[\text{SiO}^-] c_+(z = h)}{[\text{SiOH}]} = \frac{\varphi_i}{1 - \varphi_i} c_+(z = h). \quad [3]$$

The surface charge density and surface potential can then be obtained by combining Eq. (3) and the electrostatic boundary condition. None of the charge regulation mechanisms that we have tested can properly account for experimental results, and in all cases a further hindered diffusion description is needed for protons mobility (see SI appendix). Within this hindered diffusion framework, both fixed charge and charge regulation perform well. Assuming a typical silanol mean distance of $a = 0.47 \text{ nm}$ (69), the corresponding surface charge can be estimated through the ionization fraction and the reaction constant as $\text{pKa} = 8.37 \pm 0.11$, in good agreement with the literature where a value of $\text{pKa} \simeq 9$ has been reported (47).

Finally, we used here a simple Gouy-Chapman model for the ions distribution near the substrate, neglecting the possible presence of a so-called Stern layer (70), in which the potential drops. It was experimentally shown that the magnitude of this layer is directly linked to the radius of adsorbed counter ions at the interface (71, 72). In our case, the amount of counter ions (here small protons) is limited and neglecting this contribution seems reasonable.

A natural extension would be to go beyond standard PB framework, to account for correlations and molecular steric repulsion (44, 48). But these two effects appear negligible in our situation. Indeed, a typical surface charge density, $-20 \mu\text{C}/\text{m}^2$, results into sparse adsorption sites on the silica surface, with a mean distance d_i of 89 nm between each other. Then, the so-called plasma parameter, ℓ_B/d_i (49, 73, 74), which determines if correlations are important, is far smaller than one, meaning that correlations can be safely neglected. Note that extreme confinement can extend the range of electrostatic interactions and hence favor correlations (6); however, even considering the more stringent criterion imposed by the confinement, the mean inter-ionic distance d_i is large enough so that correlations can be neglected. Likewise steric effects are also negligible because d_i is by two orders of magnitude larger than the ion size, even considering the ion hydration shell (75, 76).

As a conclusion, we have presented a new approach towards exploring ionic transport in regimes of ultimate – molecular – confinement. Based on the spontaneous condensation of a liquid film atop a fully wettable substrate, our method allows us to continuously tune the liquid film thickness from 0.3 to 2 nm in an ultra-clean environment. For the largest film thicknesses $h \geq 1.2 \text{ nm}$, our conductance measurements on silica substrates recover the well-established surface conductivity regime (11, 13), whereas a strong departure is evidenced when reaching molecular confinement, which shows a non-linearly fading conductance. Strikingly, this effect can still be captured within a continuum description, provided that variations of the

ion mobility in a monolayer of ions close to the wall, where protons motion is fully inhibited, are accounted for. These results are in contradiction with the existence of a highly conductive Stern layer in the vicinity of substrates (77, 78), or with observations of mobility enhancement in ultra-confinement (8, 14, 15, 79) in the vicinity of specific surfaces where the origin of charges is different. But they support well recent results in 2D water confined in graphene slits, that suggest that proton mobility is reduced by a factor of 20 (26) or, more generally, the existence of a stagnant hydrodynamic layer at the molecular scale in the vicinity of surfaces as observed for alkanes (62, 80) or water (54, 81). How phoretic and pressure driven transport are coupled in this molecular layer near an oxide surface remains an open question. Further studies could consider other types of liquids or substrates, such as van der Waals materials to test how the so-called Grotthus transport mechanism (57) is modified in ultra-confinement, for example. Finally, investigating the full film structure and its dynamical fluctuations in these regimes of ultraconfinement would be required to show the limits of continuous modelling.

Materials and Methods

Electrode Fabrication And Preparation. Commercially available silica substrates were used (WWD4 0525 250X 1618 S301, MicroChemicals). The SiO_2 layer was thermally grown on Si wafer by the dry/wet/dry way, with a thickness of 300 nm to minimize the current leakage. The Si bulk of the wafer is undoped. The roughness of the silica surface was characterized by an atomic force microscope (AFM, Asylum Research, MFP3D), and quantified by both the rms value (random mean square) and the profile height deviations from the mean line Ra , defined as $Ra = \frac{1}{L} \int_0^L |z(x)| dx$, with $z(x)$ the difference of altitude from the mean value. We fabricated the platinum electrodes following standard lithography methods as briefly detailed below (see SI appendix for additional elements). To efficiently detect the current in the liquid film, the electrode was designed in an interlaced comb-shaped geometry so that its total length went up to 1.49 m on a 300 mm² area. The width of the electrode beam and the spacing between each electrode branch is of the same size, 100 μm . The deposition pattern was achieved thanks to photolithography of a 1.5 μm photosensitive resin 409 type AZ5214 and lift-off. A first binding 10 nm-thick Titanium layer was first deposited, followed by the Platinum deposition. For this, we used an electron gun evaporator from Alliance Concept (model EVA300). The total deposited thickness is checked by profilometry (Dektak 150 model, from Bruker) and found to be 30 nm \pm 1 nm.

To build the electrical connection for the current detection, two circuit pin sites were stuck to the electrode by a silver conductive paint (RS 186-3600, RS PRO) and epoxy adhesive (EA 9492, Henkel) that are inert to the electrode cleaning. Each time prior to experiments, electrode was cleaned in the clean room according to the following protocol: the electrode was wiped multiple times with clean room tissues, respectively soaked with distilled water, ethanol and acetone, to remove visible surface contaminants; then it was placed into ethanol ultrasonic cleaning bath (Elma S100H, Elmasonic) to remove organic chemical groups for 5 minutes; after the ultrasonic bathing, it was dried with compressed air and further placed into oxygen plasma cleaner (PDC-002, Harrick Plasma) under high power for 3 minutes to further remove surface foreign chemical groups and enhance the surface wettability. Once the electrode was out of plasma cleaner, it was conserved into a petri dish and would be instantaneously brought to the vacuum chamber for conductivity measurements.

Experimental Control And Data Acquisition. The thickness of the liquid film was tuned by changing relative humidity in contact with the electrode SiO_2 interface. To achieve this purpose, the electrode

537 was placed on a thermal stage (Mk2000, Instec) of high precision
538 $\pm 0.001^\circ\text{C}$ so that the saturated vapor pressure at the SiO_2 inter-
539 face could be controlled by setting the stage temperature.
540 To keep physico-chemical properties of the SiO_2 interface during mea-
541 surements, for example to avoid the airborne contamination, the
542 electrode was placed inside a vacuum chamber (TS102V-F2, Instec)
543 that was depressurized by a scroll vacuum pump (XDS10, Edwards).
544 To stabilize the vapor pressure present on the electrode, the vacuum
545 chamber was further connected to a vapor source filled with distilled
546 water (18.2 M Ω -cm, PURELAB flex, ELGA) whose temperature
547 was strictly set by a thermal bath (200F, Julabo) at 6 or 15.8 $^\circ\text{C}$.
548 This temperature was lower than the ambient temperature so that
549 the system was free of condensation on all tube walls. Thus the
550 vapor pressure, P , obeys the Clausius–Clapeyron relation under
551 thermally quasi-equilibrium state and is computed thanks to the
552 the IAPWS formulation 1995 (82). The whole system’s leakage rate
553 was 1.5 Pa/min. To eliminate the accumulating effect of leakage
554 and minimize the surface aging due to contamination, the vacuum
555 pump continued to be rolling during conductance measurements and
556 the suction flow rate inside the vacuum chamber was set at a small
557 value by a metering valve (NY-2M-K6, Swagelok) with an opening
558 of 5 μm to limit temperature variations in the liquid film. During
559 the experiments, the vapor pressure inside the vacuum chamber
560 was detected by a capacitance gauge (CMR362, Pfeiffer Vacuum).

561 To measure the liquid film thickness as a function of relative
562 humidity, a spectro-ellipsometer (J.A Woolam M-2000) was adapted
563 to the same vacuum apparatus. The beam angle was set at 70° and
564 the reflected signal was measured for various wavelengths ranging
565 from 300 to 1000 nm. The polarized incident light was reflected by
566 the substrate, and its intensity and polarization were detected and
567 analyzed. The Si wafer with a 10 nm to 20 nm-thick SiO_2 layer on
568 top was cleaned with the same cleaning protocol as described for the
569 electrode. The reason for using a thinner SiO_2 layer is that the con-
570 densed liquid film thickness, typically of 1 nm, is two orders smaller
571 than a 300 nm SiO_2 layer such that the thickness measurement of
572 the liquid film is drowned into the noise according to the three layers
573 model to extract water film thickness. The thin SiO_2 layer was de-
574 posited by Plasma Enhanced Chemical Vapor Deposition technique
575 at INL on a p-type (Boron) Si wafer (WSD2 0279 250B 1314 SNN1
576 MicroChemicals). As it consists in amorph SiO_2 layers and only
577 water/ SiO_2 interface is considered, it is reasonable to assume that
578 thick thermally grown SiO_2 layer and thin deposited SiO_2 layer are
579 equivalent. Moreover, it was shown that varying the SiO_2 thickness
580 did not change our experimental results. One-minute ellipsometer
581 scanning for liquid film thickness and 3 minutes waiting gap before
582 the next run were maintained all throughout and three-times run
583 for each case was performed to reduce the statistical errors and
584 ensure measurement reproducibility.

585 For the conductance measurements, a home-made I/V converter
586 was developed to convert small currents to detectable voltages.
587 The voltage sent out to the electrode and that received after the
588 I/V converter were obtained through a digital-analogic card (NI
589 USB-6216, National Instruments) controlled remotely by a python
590 script. The applied voltage to the electrode was a sinusoidal wave
591 of 10 Hz with the magnitude of 1 V. The choice of a periodic wave
592 is to avoid the accumulation of ions and possible electrode aging or
593 polarization in our system. Voltage of 1 V is below the hydrolysis
594 voltage so that no hydrolysis is expected during measurements. The
595 sampling rate of the acquisition was set to 2000 Hz. The complex
596 conductance was then calculated based on the applied voltage and
597 measured current. Each measurement lasted 30 s and was repeated
598 three times to minimize statistical errors. Recovery time was kept at
599 least 3 minutes before the next measurement when the experimental
600 condition changed so that the system had enough time to reach its
601 equilibrium. All the data were analyzed with python codes.

602 More details on data analysis and apparatus details can be found
603 in SI appendix.

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