In the field of nanofluidics, it has been an ultimate but seemingly distant goal to controllably fabricate capillaries with dimensions approaching the size of small ions and water molecules. We report ion transport through ultimately narrow slits that are fabricated by exfoliation of a single atomic plane from a bulk crystal. The atomically flat angstrom-scale slits exhibit little surface charge, allowing elucidation of the role of steric effects. We find that ions with hydrated diameters larger than the slit size can still permeate through, albeit with reduced mobility. The confinement also leads to a notable asymmetry between anions and cations of the same diameter. Our results provide a platform for studying the effects of angstrom-scale confinement, which is important for the development of nanofluidics, molecular separation, and other nanoscale technologies.


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whether, in addition to the found complete exclusion of large (>13 Å) ions, our angstrom-scale slits provide any size effect for common inorganic salts, as widely discussed in the literature and important for applications (1–3). To this end, several chloride solutions were chosen, with cations’ \( D_h \) values ranging from ~6.6 to 12.5 Å. Chloride’s \( D_h \) is 6.6 Å. Despite reaching the limit \( h < D_h \), our channels exhibited no abrupt steric exclusion (Fig. 2A and fig. S4B), contrary to what is often assumed when modeling ion transport. As reported above (Fig. 1), the conductivity \( \sigma \) of KCl, where both ions had \( D_h \), changed relatively little with respect to its bulk conductivity. The chloride solutions with larger cations exhibited a notable reduction in their \( \sigma \), which reached a factor of 4 for \( \text{Al}^{3+} \) and ~50 for tetramethylammonium (their \( D_h \) values are ~1.5 and 2 times larger than \( h \), respectively). These observations clearly show that ions under confinement do not act as hard balls but are able to partially shed or flatten their hydration shells (14, 23).

It is known that edges of nanopores and nanotubes have a profound effect on their ionic conductivity (10, 11, 13, 15, 18). To find out whether similar entry-exit effects contribute to ion transport through our angstrom-scale slits, we studied dependence of their \( G \) values on the channel length \( L \). An example is shown in Fig. 2B for two chloride solutions. The measured resistance 1/\( G \) increases linearly with \( L \) and, within our accuracy, the linear fits extrapolate to zero. This indicates little contribution from entry-exit barriers, proving that the conductance is dominated by ion diffusion inside the slits.

To gain more information about the influence of angstrom-scale confinement on ion transport, we performed drift-diffusion experiments (8, 13, 15, 17). The two reservoirs were again filled with various chloride solutions, but now in different concentrations. Specifically, we used 10 and 100 mM solutions in the permeate and feed reservoirs, respectively (Fig. 3A). Because cations and anions generally diffuse at different rates, a finite ion current arises even in the absence of applied voltage—consequently, \( I-V \) curves become shifted along the voltage axis (Fig. 3A). A positive current at zero \( V \) corresponds to higher mobility of anions, \( \mu^- \), compared to that of cations, \( \mu^+ \). For example, the curves in Fig. 3A show that \( \text{K}^+ \) and \( \text{Al}^{3+} \) diffuse through our angstrom-scale slits faster and slower than \( \text{Cl}^- \), respectively. The zero-current potential \( E_{0} \), allows us to find the mobility ratio, \( \mu^+ / \mu^- \) (13, 17), using the Henderson equation (24)

\[
\mu^+ / \mu^- = \frac{z_+}{z_-} \frac{\ln(\Delta) - \frac{z_+ F E_m}{RT}}{\ln(\Delta) - \frac{z_- F E_m}{RT}}
\]

where \( z_+ \) and \( z_- \) are the valences of cations and anions, respectively; \( F \) is the Faraday constant; \( R \) is the universal gas constant; \( T = 300 \, \text{K} \); and \( \Delta \) is the ratio of \( C \) in the feed and permeate containers. In our experiments, \( \Delta = 10 \) and \( z_+ = -1 \). Figure 3B plots \( \mu^+ / \mu^- \) obtained using Eq. 1. The mobility ratio changes by one order of magnitude with increasing \( D_h \) from \( \text{K}^+ \) to \( \text{Al}^{3+} \) but is indifferent to the wall material. We also used reference adsorption on capillary walls (8, 9). This agrees with our measurements of KCl conductance under pH values ranging from 2 to 10, which showed (22) that \( G \) was practically constant under acidic conditions but rapidly increased for high basic pH (fig. S6). Note that both constant and variable charge models yield the same intrinsic charge density. The small \( \Theta \) and little dependence on walls’ chemistry provide an opportunity to examine more subtle effects in ion transport. Because \( \Theta \) is comparable to \( D_h \) for small ions, we investigated

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**Fig. 1. Ion transport under angstrom-scale confinement.** (A) Schematic of our measurement setup. (B) \( I-V \) characteristics of a device with 200 channels in parallel; \( w = 0.13 \, \mu \text{m}, L = 7 \, \mu \text{m} \). 1L MoS\(_2\) spacers, KCl concentrations vary from \( 10^{-3} \) to \( 10^{-5} \) M. For clarity, the curves for low \( C \) are magnified by the color-coded factors. (C) Conductance for two representative devices with 2L graphene and 1L MoS\(_2\) as spacers (symbols). For KCl concentrations \( \leq 10^{-4} \) M, the measured \( G \) was comparable to typical electrical leakage, as indicated in gray. (D) Conductance of slit devices made from graphite, hBN, and MoS\(_2\), using 2L graphene spacers: \( L = 7 \, \mu \text{m} \). In (C), the dashed curve is a fit assuming a constant surface charge, whereas the solid curves in (C) and (D) represent fits using the variable charge model. Error bars indicate the accuracy of determining \( G \) for individual \( I-V \) curves. Insets show schematics of the used slits.

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**Fig. 2. Size effect in ionic conductivity.** (A) Conductivity of various 0.1 M solutions for a device with graphite walls and 1L MoS\(_2\) spacers (blue circles). Chlorides’ cations are listed along the top \( x \) axis, and their \( D_h \) values are shown along the bottom \( x \) axis. The solid curve is a guide for the eye. Open squares denote \( G \) for a device with 1L MoS\(_2\) spacers. (B) Conductance of slit devices made from graphite, hBN, and MoS\(_2\), using 2L graphene spacers; \( L = 7 \, \mu \text{m} \). In (C), the dashed curve is a fit assuming a constant surface charge, whereas the solid curves in (C) and (D) represent fits using the variable charge model. Error bars indicate the accuracy of determining \( G \) for individual \( I-V \) curves.

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capillaries with size > D± where no steric effects were expected (22). The latter devices exhibited µ+/µ− values very close to those reported in the literature for bulk solutions, confirming the accuracy of our analysis for angstrom-scale slits (figs. S7 to S9).

It is more informative to find µ+ and µ− rather than their ratios. To this end, we measured conductivity of various chloride solutions (as in Fig. 2A) using relatively high C = 1 M so that the surface-charge contribution could be neglected. The conductivity can then be described as \( \sigma = \frac{F(c_+ \mu_+ + c_- \mu_-)}{2} \), where c+ and c− are the concentrations of anions and cations, respectively. Combining the latter equation with the found µ+/µ− value, we obtained µ+ and µ−. Their values are plotted in Fig. 3C. The mobility of Cl− varies little for different salts (within ±15%), but its absolute value under the confinement becomes about three times smaller than in bulk solutions (Fig. 3C). In stark contrast, the cations exhibit a decrease in mobility by a factor of ~10 with increasing diameter increases. Our results imply that any feasible confinement is unlikely to provide high selectivity between small ions, and living and artificial systems must rely on strategically placed electric charges inside channels or at their entries.

Our atomically flat angstrom-size slits exhibit, in the first approximation, little chemical interaction with ions and act purely as a geometric confinement. The observed changes in small ions’ mobility can be explained by distortions of their hydration shells, which become progressively more costly in terms of the energy if the ion diameter increases. Our results imply that any feasible confinement is unlikely to provide high selectivity between small ions, and living and artificial systems must rely on strategically placed electric charges inside channels or at their entries.

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**SUPPLEMENTARY MATERIALS**
www.sciencemag.org/content/358/6362/s11/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S10
References (31–35)
30 April 2017; accepted 7 September 2017
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Fig. 3. Ion mobility under angstrom-scale confinement. (A) Examples of I-V characteristics for various chloride solutions under the concentration gradient Δ = 10 (device with graphite walls and 1L MoS2 spacers). The inset shows a schematic of the drift-diffusion measurements. (B) Mobility ratio µ+/µ− as a function of cations’ D± value for slits made from graphite, hBN, and MoS2 (color coded), using 2L graphene spacers. Open squares represent the ions’ hydration energy. (C) Ion mobility under the confinement as a function of D± (circles). The most complete data set (graphite walls) is shown. Other walls yielded similar values. Diamonds represent literature values (25) for µ+ and µ− in bulk solutions. Curves in (B) and (C) are guides for the eye. Error bars indicate SDs in our measurements of the zero-current potentials.
Size effect in ion transport through angstrom-scale slits

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Squeezing through a hole
Transport of an ion is usually directly related to its hydrated radius and assumed to be nonflexible. Either a hydrated ion fits through an aperture or it does not, and shape should play a dominant role rather than charge. Esfandiar et al. created nanofluidic devices by stacking structured bulk materials, including graphite, boron nitride, and molybdenum disulfide. They investigated the transport of ions in aqueous solutions through the nanochannels in the devices. Unexpectedly, they observed different behavior for ions of similar hydrated size but opposite charge. Science, this issue p. 511