Long-term memory and synapse-like dynamics of ionic carriers in two-dimensional nanofluidic channels

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One Sentence Summary: Electrolytes in 2D nanochannels develop long-term memory, allowing to implement Hebbian learning on a nanofluidic chip.

Fine-tuned ion transport across nanoscale pores is key to many biological processes such as information processing in the brain. Recent experimental advances have enabled the confinement of water and ions down to two dimensions, unveiling specific transport properties unreachable at larger scales and triggering hopes to reproduce the advanced ionic machinery of biological systems. Here we report experiments demonstrating the emergence of memory in the transport of aqueous electrolytes across (sub-)nanoscale channels. Our study unveils two types of ionic memristor responses, depending on the type of channel material and confinement, with long-term memory – from minutes to hours. We rationalize these behaviors in terms of self-assembly or surface adsorption of ions and show how arbitrarily large timescales can emerge from coupling ion transport to interfacial processes. Such behavior allows us to implement Hebbian learning with nanofluidic systems using ions in water as charge carriers, similar to the way that neurons work. This lays the ground for biomimetic neuromorphic computations on aqueous electrolytic chips.
Over the past decade, research in nanofluidics has shed the light on many unconventional phenomena arising in the transport of water and ions through nanometric channels [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. The field has grown at a fast pace, driven by the discovery of new fundamental behaviors of aqueous transport at nanoscales, but also by their potential for a wealth of applications, from water desalination to energy harvesting [2]. Most notably, the recent development of two-dimensional (2D) channels made by van der Waals assembly of various materials (graphite, hexagonal boron nitride, MoS$_2$, etc.) has enabled the study of ionic transport at the smallest scales, with unmatched versatility in terms of geometry or surface properties [11, 12, 13, 14]. Specifics of 2D interactions offer a new asset to fine-tune the properties of electrolytes, at odds with their bulk response. A recent, noticable prediction is that two-dimensional ionic self-assembly should be at the root of memory effects associated with conductance hysteresis under electrical forcing [15], a phenomenon known as memristor effect. It serves as a guide for neuronal computation in the brain using ions in water as charge carriers, but artificial systems capable of mimicking this behavior have eluded experimental inquiry in aqueous electrolytes until now.

A memristor – short for memory resistor – is a resistor with an internal state that is susceptible to change depending on the history of voltage seen by the system, thereby modifying its conductance [16, 17]. As this makes them the analogues of biological synapses, memristors have drawn considerable attention for their potential use as building blocks of bio-inspired, neuromorphic computers [18]. However, most of existing examples are based on solid-state devices (like the metallic-insulator-metallic, or MIM architecture) and function with coupled ion and electron dynamics [19]. While a handful of fluidic memristors were also designed [20, 21], they require high voltage to operate, well above the water splitting threshold (1.23 V with respect to normal hydrogen electrode), use non-aqueous environments or far exceed the nanoscale dimensions of biological systems. More generally, a challenge is to replicate the mechanism found in biological systems, where the transport and accumulation of solvated ions (notably calcium) in water are used for signalization, information processing and the building of memory [22, 23]. Developing such bio-inspired memristors would notably allow to design artificial nanofluidic chips for neuromorphic computation, build an interface between artificial nanofluidics and biological systems, and explore possible gains in efficiency from using solvated ions as charge carriers. Here we report in a series of experiments that 2D nanofluidic channels do open this avenue towards neuromorphic iontronics.

**Experimental demonstration of nanofluidic memristors**

**Pristine channels vs. activated channels**

In this work, we investigate two types of 2D nanochannels, of similar geometry but different surface properties (Fig. 1A). “Pristine” channels are made of two atomically smooth flakes of 2D material (here MoS$_2$) separated by an array of multiple layers of graphene nanoribbons used
as spacers. On the other hand, “activated” channels consist of two graphite flakes, in which a nanoscale trench is milled into the bottom flake using electron-beam-induced etching (EBIE) [14]. In both cases, the bottom wall of the channel is pierced and deposited on the aperture of a SiN membrane. Further details regarding the fabrication of activated and pristine channels can be found in [11] and [14] respectively, and recalled in Supplementary Information (Fig. S1-2). While similar in design, these channels differ on a few key properties. The height of pristine channels can be precisely controlled in increments of 0.34 nm, and here down to 0.7 nm – the channel’s depth corresponding to the spacers’ thickness. Conversely, the depth of activated channels is controlled by EBIE with a resolution limited to a few nanometers. As recently evidenced by Emmerich et al. [14], the latter carries a much stronger surface charge compared to pristine walls, due to the exposure of their bottom wall to the electron beam. Here, we use activated devices with channel height between 4 and 13 nm, and pristine devices with height between 0.7 and 86 nm.

Once fabricated, the 2D channels are embedded in a fluidic cell connected to two reservoirs filled with electrolyte (KCl, NaCl, LiCl, CaCl₂, NiSO₄, AlCl₃). Concentrations between 1 mM and 3 M were tested. A patch-clamp amplifier (KEITHLEY 2400 or 2600 Series) connected to Ag/AgCl electrodes allows for ionic current measurements under imposed time-dependent voltage drop $V(t)$ of various frequencies (0.1 – 200 mHz), shapes (sinusoidal, triangular), and amplitude (0.1 – 1 V). In each case, the channel’s conductance $G(t)$ is determined from current measurements from an instantaneous Ohm’s law $G(t) = I(t)/V(t)$. Further details regarding current measurements are reported in Supplementary Information. Typical ionic responses are shown in Fig. 1.

**Two types of memristors**

Our first, central result is that 2D nanofluidic channels do exhibit a memristive effect (Fig. 1B-E): when probed by a time-varying voltage, they display a non-linear current-voltage characteristics which is pinched at zero voltage, associated with a conductance hysteresis. This pinched loop is the hallmark of memristors. Such behavior is found in both types of channels – pristine and activated – for all tested salt and at all concentrations; see Supplementary Information for exhaustive results. This memristive effect was found to take place at frequencies between 0.1 and 200 mHz, well below frequencies where capacitive effects can introduce hysteresis. This corresponds to dynamical timescales from seconds to hours.

Secondly, from experimental results, one can identify two types of memristors, depending on whether the current-voltage characteristics does, or does not self-cross at the origin, see Fig. 1B (pristine MoS₂ channel) versus 1D (activated carbon channel). This fundamental difference between self-touching and self-crossing loops is best illustrated by looking at the curve of conductance as function of voltage: it either displays a twisted or open loop (see Fig. 1C and 1E, respectively). This effect was found to be robust to parameter changes, and notably in concentration or in the electrolyte (Fig. S9-11 and Fig. S13-14 for pristine and activated channels, respectively).
A key aspect of memristors is their ability to cycle between different internal conductance states; we observe that self-touching memristors change state depending on the absolute magnitude of applied voltage only (Fig. 1C), while crossing memristors also reacts to the sign of voltage (Fig. 1E). In addition, the conductance of self-crossing memristors seems to “saturate” for large voltage, with the lowest and highest values differing from a factor usually around 3. On the other hand, in the case of self-touching memristors, the conductance continuously increased for the tested voltage range, and can vary by up to two orders of magnitude. Together, these facts show that the possible internal states of crossing and touching memristors are fundamentally different.
Lastly, thinner pristine systems (channel height $h < 10 \text{ nm}$) could display either kind of behaviour depending on salt concentration (with touching loops at 0.1 M or higher). Thicker pristine channels, on the other hand, only displayed crossing-type loops; however, the memory effect is not as significant as that observed in thinner channels implying that the 2D confinement is essential for attaining memory effects. All corresponding data are provided in the supplementary information.

This comparison sheds light on a possible explanation. Crossing loops are predominant for high surface charges (as found in activated systems) and low concentration – in other words, for surface-dominated conduction. Instead, touching loops exist for moderate surface charge (pristine channels), high concentration and very strong confinement: this corresponds to a ‘confinement-dominated’ regime. In both cases, a prerequisite for memory effects is the system’s ability to display non-linear ion transport. Accordingly, we now focus on the description of the system’s various conductance states as function of applied voltage.

**Two sources of non-linearity: collective ionic transport and ionic rectification**

The above observations suggest the existence of two distinct mechanisms behind the memristive behavior of nanofluidic channels. Touching-type memory only exists in thin channels ($h < 10 \text{ nm}$) and at high concentration ($c \geq 0.1 \text{ M}$) and the corresponding experimental results directly echo the theoretical mechanisms discussed in [15]. In this picture, a non-linear response can be accounted for by the formation of tightly bound Bjerrum pairs of ions if confinement is sufficiently strong (and the solution not too diluted), preventing conduction (Fig. 2A). The application of a sufficiently strong electric field can either break these pairs or assemble them into an arc-like polyelectrolyte, allowing electrical current to flow, a process known as the second Wien effect. As a result, the system’s conductance $G$ is a strongly non-linear function of voltage $V$ that almost vanishes in absence of voltage, behaving as

$$G(V) \propto |V|^\alpha$$ (1)

with a predicted exponent $\alpha$ larger than 1, and usually around 2 (see Supplementary Information and [15] for the derivation); note that imperfect pairing can be taken into account by adding a small constant term $G_0 = G(V = 0)$ into the above equation. This mechanism is independent of voltage sign, and thus does correspond to a self-touching loop in the IV curve, defining what is sometimes called a unipolar memristor. It also allows the conductance to vary continuously over a large range of values, accounting for experimental observations. In theory, this process can only take place in thinner channels – less than 2 nm in thickness – as Bjerrum pairs only exist under strong confinement. In practice, the transition from touching to crossing behavior was found to take place around a thickness of 10 nm. A possible explanation for this robustness is that ion pairs could still exist in the few water layers next to the channel’s wall, even in slightly larger channels.
On the other hand, crossing-type systems change state depending on the sign of applied voltage, and their memory should therefore stem from an internal asymmetry. However, some pristine systems do display this kind of hysteresis despite their internal surface being atomically smooth and controlled. Therefore, we attribute the source of asymmetry to entrance effects. By construction, the SiN membrane is present on one side of the device only (see Fig. 1A) and the two mouths of the channel do not have the same access resistance (Fig. S7). Coupled with the exclusion of anions from the channel (due to its strong negative surface charge), this is expected to result in ionic rectification (Fig. 2B): when cations flow from the side with lower access resistance, ions will accumulate inside the channel as entry is ‘easier’ than exit, resulting in a conductance increase. If voltage is reversed, cations will flow from the side of higher resistance, the channel will instead be depleted and conductance will drop. This mechanism is analogous to that of a PN junction, and results in a diode-like current-voltage characteristic [24] with two distinct possible values of conductance, defining a rectification factor $\beta_{\text{Rect}}$:

$$\frac{G(V > 0)}{G(V < 0)} \simeq \beta_{\text{Rect}}$$

Taking our specific geometry into account, we predict that this asymmetry should give rise to a rectification factor $\beta_{\text{Rect}} = 3$ (see Supplementary Information and Fig. S6), in good agreement with experiments. Because this type of non-linearity depends on voltage sign, it is referred as a bipolar memristor.

While any system presenting the same diode-like non-linearity could in theory display a memristive behavior, it can only do so on a frequency range fixed by the time it needs to switch between the conducting and the insulating states. However, such timescales are normally too short to be accessible in nanoscale systems, and this phenomenon requires peculiar transport processes to take place to be observed.

**Stop-and-go transport as a source of long-term memory**

For both self-touching and crossing loops memristors, memory timescales are found to reach extremely large values, in the range of minutes to hours. Such long-term memory can be accounted for by taking ion pairing or surface adsorption into account in the dynamics of confined ions. In the theoretical framework of Ref. [15], the electrolyte is indeed predicted to retain its conductance state through the formation of ion clusters, which was estimated to typically take a few milliseconds. More generally, one expects a nanofluidic channel to retain a conductance state (defined by the number of charge carriers present inside the channel) over a typical diffusion timescale, roughly $L^2/D$, with $L$ the channel length and $D$ a typical ionic diffusion coefficient in the channel. For channels of length around 10 $\mu$m, this would yield a maximum memory time of 0.1 s, still orders of magnitude lower than experimental values. However, this picture changes if interfacial processes, rather than diffusion, govern ion transport. Consider a particle diffusing through a channel with chemically-active walls, such that it may adsorb on the surface (see Fig. 2D). If the adsorption rate is much larger than the diffusion rate across the
Figure 2: Theory of nanofluidic memristors. A Wien effect as a source of non-linear ion transport. Under very strong confinement, ions assemble into non-conducting Bjerrum pairs. Conduction can then only occur through the breaking of pairs (Wien effect) or their clustering into conducting arcs (polyelectrolytic Wien effect), under the action of a strong electric field (regardless of sign). B Entry effects as a source of self-crossing memristors. The two mouths of the channel are asymmetric, resulting in ionic rectification depending on the side from which charges enter the system. If they enter from the side of low resistance, ions accumulate and conductance rises. Otherwise, the channel is depleted and conductance is lowered. C-D ‘Stop-and-go’ transport and long-term memory. In both mechanisms (Wien effect or geometrical asymmetry), the system’s conductance state can be retained over large timescales if transport is governed by a stop-and-go motion, induced by repeated pairing/depairing or adsorption/desorption events.
channel, then the particle will spend most of its time bound to the surface. As a result, the time it needs to escape the pore is the sum of the durations of all adsorption events. Let us define $\tau_{\text{diff}}$, the time needed to escape through diffusion alone and $\tau_d$ the time a particle bound to the surface takes to desorb. Then, if the particle is adsorbed every $\tau_a \ll \tau_{\text{diff}}$, there will be $\tau_{\text{diff}}/\tau_a$ such events along the particle’s trajectory as it escapes the channel. As a result, the survival time of the particle inside the pore reads:

$$\tau_m = \frac{\tau_{\text{diff}}}{\tau_a} \frac{\tau_d}{\tau_{\text{diff}}} \gg \tau_{\text{diff}}$$

(3)

In other words, the memory time of the system is the diffusion timescale times a ratio $\tau_d/\tau_a$ measuring the strength of surface effects. At chemical equilibrium, this corresponds to the ratio of particle numbers on the surface and in the bulk of the channel, as quantified by a Dukhin number $D_u = \Sigma/\varepsilon hc$, which compares the surface charge $\Sigma$ to the charge density in the bulk of the electrolyte, $\varepsilon c$. Putting numbers, activated systems typically have $D_u \sim 10^2 - 10^3$, showing that surface effects strongly dominate the bulk. Eq.(3) then predicts a memory time in the range $\tau_m \sim D_u \times \tau_{\text{diff}} \sim 100$s. This estimation is in agreement with experimental values, which are found to be in the range $\tau_m \sim 50 - 400$s (Fig. S12 and 14). A similar argument can be formulated for the other type of memristors, associated with touching loops. This time, the conduction state of the system is encoded in the number of ions which are not part of tightly bound pair (and can therefore contribute to current) – according to the Wien effect. Similarly to surface adsorption, one expects that successive pairing-unpairing events will create a stop-and-go motion of ions through the system (Fig. 2C). The memory time is then again found to be given by diffusion times a ratio of pairing and unpairing times, potentially reaching minute- or even hour-long timescales.

Building on this qualitative picture, one may propose a minimal model, accounting for the memristor effect over minute-long times for both touching and self-crossing memory types, as detailed in Supplementary Information (Fig. S7). We find that the system’s conductance at time $t$ is given by the convolution of its quasistatic conductance, as given by Eqs (1) and (2) depending on memristor type, with an exponential memory kernel:

$$G(t) = \int_0^\infty G_{qs}[V(t-s)]e^{-s/\tau}/\tau \, ds$$

(4)

where $G_{qs}$ is quasistatic (non-linear) conductance and $\tau$ a timescale of the order of the memory time $\tau_m$. The resulting prediction is in good agreement with experimental data, as shown in Fig. 3A-B. According to this simple model, measuring the loop in the IV curve allows to characterize the memristive effect, as shown on Fig. 4C. The curve of area as function of voltage frequency exhibits a maximum when the frequency matches the intrinsic memory time $\tau_m$, akin to a resonance. The comparison to the prediction of the model shows again a good agreement and provides a direct measurement of $\tau_m$ (Fig. 3C).
Figure 3: **Comparison of theory and experimental results.** A-B Fit of experimental data using the minimal model of nanofluidic memristor. For self-touching loops (A), the quasistatic conductance is taken to be a power law of applied voltage (here with exponent $\alpha = 2$), and a sign-dependent constant for crossing loops (B), see insets. The experimental curves are then fitted using the delay time $\tau$ as single free parameter, see Eq. (4). Datasets correspond to devices presented in Fig. 1B-E: 3 M KCl in pristine MoS$_2$ channel (height 1 nm) or 1 mM CaCl$_2$ in activated channel (height 13 nm). C Normalized loop area as function of voltage frequency. Data correspond to 100 mM CaCl$_2$ in 4 nm activated channel and 3 M KCl in 1 nm pristine MoS$_2$ channel. The memory timescale $\tau_m$ can be extracted from experimental data by looking for the frequency where the loop is the largest. The curve of loop area as function of frequency is well described by that of the minimal model (solid lines). See Fig. S8 for the normalization process.

**Hebbian learning with nanofluidic memristors**

**Reversible strengthening of a nanochannel**

This qualitative and quantitative rationalization of the ionic memristor effects paves the way for the implementation of learning algorithms using our nanofluidic devices. As a proof of concept, we now show that they can be used to emulate some basic functionalities found in biological synapses. Because their memory is not lost when voltage is reset to zero, we only focus on memristors that display self-crossing loops (e.g., ‘bipolar’ memristors), as exhibited here with activated nanochannels. We first confirm that their conductance can be increased or lowered through voltage sweeps of a given sign (Fig. 5A). Following a positive spike, the conductance is abruptly increased for a short period ($\sim 1$ min), before relaxing to a long-term value above its initial state (Fig. 5B). This shows that our device displays both short- and long-term memory, similar to biological synapses.

These neural connections act as resistors whose conductance can be tuned during learning processes, with reversible modifications both on short (milliseconds to minutes) and long (minutes to hours or more) timescales [25, 26]. The latter, known as long-term potentiation (or depression, when the conductance is lowered) enables the storage of information through the
Figure 4: Programing a nanochannel through reversible conductance strengthening. A. Evolution of the ionic current (red) under voltage pulses of constant sign (blue). Positive (resp. negative) pulses result in an increase (resp. decrease) of conductance. B. Conductance change following a positive voltage pulse, exhibiting both short- (< 2 min) and long-term (> 15 min) memory. The conductance is read by applying a weak square voltage wave that has no sensible impact on the state of the system, and modified through a strong voltage spike. Blue points are experimental data. The red solid line is a guide for the eye. Inset: applied voltage as function of time. The red arrow indicates the beginning of the voltage spike. C Long-term modification of a nanochannel's conductance. 30 write spikes (+1 V, 10 s) are applied, followed by 30 erase spikes (-1 V, 10 s) which bring back the system to its initial state. Between each spike, the conductance is let to stabilize during two minutes and is then measured with a read pulse (0.1 V, 5 s), see Fig. S3. All data correspond to activated channels with height $h = 5$ nm filled with CaCl$_2$ at 1 mM.

synapse’s conductance state as a form of in-memory coding. While the exact biological mechanisms are still debated, the transport and accumulation of calcium ions at specific places play a key role [23, 27]. Taking inspiration from these features, we design a protocol to implement in-memory computations with our nanofluidic channel, see Fig. 5C. We increment a nanochannel’s conductance by applying a ‘write’ voltage spike (+1 V during 10 seconds). It can then be accessed to via a ‘read’ pulse (+0.1 V during 5 seconds), which does not perturb sensibly its value. It can also be reset to its original value with an ‘erase’ spike (−1 V during 10 seconds). This allows for a versatile and reversible modification and access to the stored value for computational applications. As a proof of concept, we show in Fig. 4C that the modification process is indeed fully reversible and allows to store an analog variable over long timescales, by applying a series of 60 write and erase spikes. We thus demonstrate that nanoscale channels can be ‘programmed’ through the tuning of their conductance, enabling the implementation of in-memory operations with ion-based nanofluidic systems.
**Hebbian learning algorithm**

Building on the similarities between our nanofluidic system and synapses, we now implement a basic form of Hebbian learning. In biological neuron networks, this process consists in the modification of synaptic weights depending on the relative activation timings of two neurons connected by a given synapse, see Fig. 5A. If the presynaptic neuron repeatedly emits an action potential just before the activation of the postsynaptic neuron, the synapse is strengthened, as this suggests a form of causality between the two activation events. Conversely, the synapse is weakened if the firing order is reversed, as this would point at some anticausality relation. Importantly, these modifications occur even if the presynaptic neuron only causes a mild response (that is, too weak to initiate an action potential by itself) of the postsynaptic one. Altogether, this process implements a form of principal component analysis of the inputs received by the network [28], and is believed to play a major role in learning.

To mimic this mechanism, we designed the experiment presented on Fig. 5B: a nanochannel is connected via the electrodes to a ‘program’ which emulates the behavior of two neurons. Whenever the presynaptic neuron A emits a voltage spike, we mimic a flip-flop mechanism connecting the system to a generator $E_-$ that applies negative voltage spikes. This lasts until the presynaptic neuron B activates and the system is branched on another generator $E_+$ applying positive spikes instead. The opposite chain of events occurs if neuron B activates first. In both cases, the flip-flop resets if a given total amount of time has passed since its activation, allowing the process to start over. Further details regarding the implementation are provided in supplementary materials (see Fig. S4).

If neuron A activates just before neuron B, then the system receives a few negative spikes, followed by many positive spikes, see Fig. 5C, left panel. Its conductance is thus globally increased. When the firing order is reversed, conversely, more negative than positive spikes are applied on the system (Fig. 5C, right panel), whose conductance is therefore lowered.

We implemented this protocol in the experiments as follows: we first measure the system’s conductance, and run the program which consists in 8 successive activations of neurons A and B, with tuneable relative activation timing. Then, we measure any change in the conductance. The result is shown on Fig. 5D: when the presynaptic spike is followed (within a 40 seconds window) by a postsynaptic spike, the connection is strengthened. Otherwise, if the delay is too great or if the order is reversed, the connection is left unchanged or weakened, respectively. This phenomenology remarkably mimicks the one observed in biological synapses, where the accumulation of certain ionic species triggers the strengthening of connections between neurons through various mechanisms [29, 27]; here, the same accumulation of ions directly results in an increased conductance.

Two-dimensional nanochannels exhibit long-term memory, in the form of a memristor effect that can have two different physical origins - strong correlations between ions or entrance effects. In both cases, memory is retained over long timescales through interfacial processes that slow down advection-diffusion across the channel. We fully characterized experimentally and theoretically both of these mechanisms, showing they may be harnessed for ‘iontronics’
Figure 5: **Implementation of Hebb’s law using carbon nanochannels.** A Hebb’s law in biological synapses: a synapse’s conductance is increased (resp. decreased) when its presynaptic neuron fires just before (resp. after) the postsynaptic one, adapted from [29]. This implements a form of causality detection, known as spike-timing-dependent plasticity (STDP). Inset: rat hippocampal neuron (©ZEISS Microscopy from Germany, CC BY 2.0) B Hebb’s law with nanofluidic memristors: voltage spikes are applied to a nanochannel, mimicking the activation of two neurons A and B. After each spike from the presynaptic (resp. postsynaptic) neuron, a series of erase (resp. write) spikes is applied. C Example of voltage spikes series depending on whether the presynaptic (i) or postsynaptic (ii) neuron activates first. D Conductance change after 8 successive activations of the two neurons, in percentage of the initial conductance and as function of the relative activation timing of the neurons. Inset: SEM image of an activated nanochannel. Data correspond to an activated channel with height $h = 5 \text{ nm}$ filled with CaCl$_2$ at 1 mM. See also Fig. S5 for additional data.

applications. These systems reproduce the tuneability of synapses, through an accumulation (or depletion) of ions, and can implement basic learning algorithms such as Hebb’s rule within a simple nanofluidic architecture. More generally, our work illustrates how confinement-induced phenomena can be harnessed to build ionic machines inspired by biological systems. This paves the way for the development of more complex iontronic devices on nanofluidic chips with advanced circuitry. The use of water and ions in the nanofluidic memristors, which is shared by
biological systems, furthermore suggests the possibility to interface artificial with biological devices.

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**Acknowledgements**

**Funding:** L.B. acknowledges funding from the EU H2020 Framework Programme/ERC Advanced Grant agreement number 785911-Shadoks and ANR project Neptune. L.B. and A.S. acknowledge support from the Horizon 2020 program through Grant No. 899528- FET-OPEN-ITS-THIN. A.K. acknowledges Ramsay Memorial Fellowship, and also funding from Royal Society re-search grant RGS/R2/202036. B.R. acknowledges the Royal Society fellowship and funding from the EU H2020 Framework Programme/ERC Starting Grant number 852674 AngstroCAP. This work has received the support of Institut Pierre-Gilles de Gennes (program ANR-10-IDEX-0001-02 PSL and ANR-10-LABX-31).

**Competing interests:** The authors declare no competing interests.

**Data and materials availability:** All data are in the main text or supplementary materials.
Supplementary materials for:
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1 Methods

1.1 Nanofabrication of pristine channels

We fabricated the pristine nanochannels via van der Waals assembly following the protocol reported in our previous work [1]. Briefly, the process has two major parts: I) the preparation of the top-spacer layers, II) the assembly of the resulting top-spacer layers with the bottom layer to form tri-crystal (top-spacer-bottom) stack. Graphene and MoS$_2$ flakes were prepared by the mechanical exfoliation of their bulk layered forms, Graphenium graphite and natural MoS$_2$ crystals (purchased from Manchester Nanomaterials). On a Si/SiO$_2$ substrate, an exfoliated graphene flake with a specific thickness between 0.7 and 86 nm, is searched using an optical microscope, and the thickness is confirmed by atomic force microscopy (AFM) (Fig. S1A). Parallel strips (width of $\sim$120 nm, spacing $\sim$150 nm) are etched on this graphene layer using e-beam lithography (EBL) and dry etching using oxygen plasma (Fig. S1B). The spacing between the graphene strips will be the channel width $w$ in the final device, while the thickness of the graphene will be the channel height $h$. Fig. S1B (bottom panel) shows the AFM height profile of a three layer thin graphene spacer, showing channel width of $\sim$150 nm, and a channel height of $\sim 1.2 \pm 0.1$ nm. Following this, a MoS$_2$ crystal (thickness of 150 to 200 nm) was transferred on top of the graphene spacer (Fig. S1C). This MoS$_2$ layer will serve as a top wall of the channel.

The nanofluidic chip fabrication process begins by drilling a microhole ($\sim 3 \mu m \times 50 \mu m$) in a SiN$_x$ membrane (thickness of 500 nm) on a silicon wafer, using photolithography and dry etching (mixture of SF$_6$ and CHF$_3$ gases). A thin MoS$_2$ layer (thickness of 20 to 40 nm) is then transferred on top of the microhole on SiN$_x$ membrane to act as the bottom layer of the channel, using polymethylmethacrylate (PMMA) based wet transfer method (Fig. S1D). Then, the bottom layer is etched from the back of the SiN$_x$ membrane via dry etching with CHF$_3$ and O$_2$ gases, to protrude the microhole onto MoS$_2$. Following this, the previously prepared stack of top MoS$_2$-graphene spacer is wet-transferred onto the bottom MoS$_2$ layer on SiN$_x$ (Fig. S1E). During this transfer, the spacer is oriented in such a way that the channels are perpendicular to the rectangular microhole. Then, the graphene spacer is dry etched (O$_2$ gas) from the back of SiN$_x$ membrane to further open the microhole into the channels. At this stage, the resulting channels have variable lengths determined by the shape of the top MoS$_2$ flake, and any thin edges of the top layer could lead to its sagging into the channels thus blocking the channel entries. To address this, a final step of gold deposition is done over the tri-crystal stack, where a Cr/Au strip (thickness 5 nm/70 nm, respectively) is deposited after photolithography to open the channels (Fig. S1E). The gold layer will aid the device stability by minimizing the lifting of the MoS$_2$ top layer during measurements at high voltages. Moreover, the gold strip serves as a mask to create uniform and desired channel length for all channels across the device. Regions of the tri-crystal stack not masked by the Au strip are etched away, hence only the channel region underneath the gold strip remains (Fig. S1H). Throughout the device fabrication process, after each flake transfer, the device is placed in a furnace under H$_2$:Ar (1:10) gas for annealing (300$^\circ$C for 3 hours and 400$^\circ$C for 4 hours) to clean the polymer contamination. The
optical images of the final channel devices on SiN are shown in Fig. S1I, both in reflection mode and transmission mode, with the channel length $L$ (from the microhole to the end of the Au strip) indicated.

1.2 Nanofabrication of activated channels

We briefly recall here the nanofabrication process of activated carbon nanochannels. A more detailed description can be found in Ref. [2]. Bidimensional graphite crystals are obtained from commercially available graphite (GRAPHENIUM) by mechanical exfoliation on a Si/SiO$_2$ substrate using cleanroom tape. A first graphite flake (‘bottom layer’) is pierced using electron beam induced direct etching (EBIE) in water vapor inside a scanning electron microscope, and then several trenches are dug from the hole using the same technique (Fig. S2, step 1). A second graphite crystal (‘top layer’) of roughly 50 nm in thickness is deposited above the hole and covers partially the trenches, closing them into channels (Fig. S2, step 2). This first transfer is realized using the dry-transfer techniques with a droplet-shaped polydimethylsiloxane (PDMS) stamp spin-coated with polypropylene carbonate (PPC). Finally, this bi-layer heterostructure is transferred above a Si/SiN window with a circular aperture in its middle, by making sure that the hole in the bottom layer lands above the aperture (Fig. S2, step 3). This second transfer is realized by wet transfer using a polymethylmethacrylate (PMMA) sacrificial layer.

In typical cases, activated channels are $5 - 10 \mu$m long, $100 \text{nm}$ wide, with a height ranging from 5 to $15 \text{nm}$.

1.3 Current measurements

Devices are placed into nanofluidic measurement cells separating two reservoirs filled with electrolyte solutions of various salt concentrations and ionic species (KCl, CaCl$_2$, AlCl$_3$, NiSO$_4$, NaCl, LiCl). We use Ag/AgCl electrodes to apply a potential drop across the channels and measure the resulting ionic current. Our electrodes are connected to KEITHLEY amplifiers (models 2636B and 2401). We use AC voltage of various frequencies (0.1 to $200 \text{mHz}$) and waveform (sinusoidal or triangular) with a sampling rate of 2 Hz.

2 Bio-inspired algorithms

In this section, we detail how we performed basic neuromorphic operations with activated channels. In all cases, input voltage was generated via MATLAB and exported as a text file, and then applied on the system by a LABVIEW program with a sampling rate of 2 Hz.
2.1 Long-term potentiation

Reversible, long-term modification of a nanochannel’s conductance is achieved by applying positive “write” pulses (+1 V during 10 s), or negative “erase” pulses (−1 V during 10 s). After each pulse, the conductance relaxation is tracked by applying 10 weak “read” pulses (ΔV_{\text{read}} = +0.1 V during 5 s), every 5 s (see Fig. S2A-B), and computing for each of these pulses the conductance from:

\[ G = \frac{I}{\Delta V_{\text{read}}} \quad (1) \]

The conductance was found to stabilize after roughly two minutes of relaxation.

We then check that these modifications were incremental and reversible by applying 30 write pulses, followed by 30 erase pulses, see Fig. 5C from main text. After each pulse, the system was let to relax for two minutes to let the conductance stabilize.

2.2 Hebbian learning

The algorithm used to implement Hebbian learning is detailed in main text but we recall it here for the sake of clarity. A nanofluidic device is connected to a single generator that emits a voltage emulating the behavior of two neurons. Whenever the presynaptic neuron A emits a voltage spike (0.3 V, 5 s), we mimic a flip-flop mechanism connecting the system to a generator \( E_- \) that applies negative voltage spikes (−1 V, 5 s each). This lasts until the presynaptic neuron B emits a spike (−0.3 V, 5 s) and the system is branched on another generator \( E_+ \) applying positive spikes (+1 V, 5 s each) instead. The opposite chain of events occurs if neuron B activates first. In both cases, the flip-flop resets if a total amount of time \( \tau \) has passed since its activation, allowing the process to start over.

To mimic Hebbian learning, we assume that neuron B always activates with a delay \( \Delta t \) compared to neuron A. \( \Delta t \) can be negative, implying that B actually fires before A. Then, for a given value of \( \Delta t \), we apply the above procedure 8 times, and measure the conductance change of the channel at the end (see Fig. S4).

If A activates just before B, the system will be subject to a few negative spikes followed by many positive ones, increasing its overall conductance (see Fig. S4D). On the other hand, if \( |\Delta t| \) is comparable to \( \tau \), the channel will receive an almost equal amount of positive and negative spikes, leaving its conductance unchanged.

Additional data measured on different systems than the ones presented in Fig. 5-6 from main text are displayed in Fig. S5 for robustness.

In all cases, we prepared the channel in an intermediate conductance state so that saturation to the state of maximum or minimum conductance is not a problem during the learning process.
3 Theory of the nanofluidic memristor

In this section, we detail an analytical model of the nanofluidic memristor, highlighting two distinct mechanisms. The most illustrative difference between the two is the shape of the IV curve under a sinusoidal excitation, which either self-touches (Wien effect mechanism, section 3.1) or self-crosses (ionic rectification, section 3.2) at the origin.

If considered in a vacuum, both these effects only yield a memory time on the timescales of milliseconds at best. In the last part of this section, we therefore provide a minimal model explaining the emergence of long-term memory from the coupling of surface processes to bulk transport between two reservoirs.

We start by recalling that a memristor is a resistor with a hysteretic conductance. In terms of elementary electronics, it is described by a set of two equations:

\[ I = G[n(t)] \Delta V(t), \]  
\[ \dot{n} = f(n, \Delta V(t)) \]

where, \( I \) is the electrical current flowing through the device under a time-varying voltage drop \( \Delta V(t) \), \( G \) is the conductance that depends on an internal parameter \( n \), which can be seen as the system’s memory. It evolves according to a dynamical equation (3), where the dot represents the time derivative.

The goal of this section is to detail, for the two mechanisms, what \( n \) physically represents and to derive its evolution equation from the underlying physics. In other words, to explain the memristor effect observed in confined electrolytes, we need to first show that they possess several internal conductance states, and then that they are able to retain such states over long periods.

3.1 Second Wien effect under 2D confinement

In this section, we discuss equation (1) from main text, which corresponds to the first possible memristor mechanism. The full derivation can be found in Ref. [3], and we only state and discuss the various results for the sake of clarity. In this mechanism, \( n \) represents the proportion of ions which are able to move under an electric field, the others forming neutral (and therefore non-conducting) ion pairs, also referred to as Bjerrum pairs [4]. If the field is strong enough, it will tear some pairs apart, increasing \( n \) and the global conductance, in a process known as the second Wien effect. If the field is turned off, pairs will eventually form again; however this process takes some time, allowing for a memristor effect, akin to an electric arc in a discharge tube: an external voltage is required to ionize the gas and make it conduct current, but the gas will stay conducting for a short time after the voltage is removed [5].

The second Wien effect is a well-known phenomenon observed in weak electrolytes. It was extensively studied by Onsager for bulk electrolytes [6], resulting in an approximate law for the
conductance $G$ under an external field $E$:

$$G(E) \approx G(0) \left[ 1 + \frac{\beta e^2}{4\pi\epsilon\ell_E} + \ldots \right] \approx G(0) \left[ 1 + \frac{\ell_B}{\ell_E} + \ldots \right]$$  \hspace{1cm} (4)$$

with $\beta = 1/k_B T$ and $\ell_E = k_B T/e E$ a lengthscale defined by the external field, and $\ell_B$ the Bjerrum length. Here, $G(0)$ corresponds to the conductance of ions that are already free at thermal equilibrium (i.e. with no external field). This results in a slightly non-linear IV curve:

$$I = G(E) \Delta V \approx G(0) \Delta V \left[ 1 + \alpha \Delta V \right]$$  \hspace{1cm} (5)$$

$\Delta V$ being the voltage drop associated with the field $E$. Without detailing the (mathematically involved) exact derivation by Onsager, the critical point is that ion pairs form according to a chemical equilibrium given by:

$$\dot{n}_p = \frac{1}{\tau_a} n_f^2 - \frac{1}{\tau_d} n_p$$  \hspace{1cm} (6)$$

with $n_p$ the proportion of ion pairs, $n_f$ the proportion of free ions, $\tau_a$ and $\tau_d$ the ion pair association and dissociation times, respectively. One has $n_f + n_p = 1$ and the conductance is simply given by:

$$G[n_f] = n_f G_\infty$$  \hspace{1cm} (7)$$

where $G_\infty$ is the conductance in the fully dissociated case. Overall, the system is able to remember the application of an electric field in its recent past over a timescale $\tau_a$, and paired electrolytes can be used to create memristors.

This cannot be achieved in bulk water, which fully dissociates all commonly used salts. However, as noted by Ref. [3], ionic interactions are greatly increased under confinement. This results in the formation of non-conducting Bjerrum pairs, sometimes to the point that there are no ‘free’ ions left at thermal equilibrium. In this case, the conductance vanishes in absence of an electric field, $G(0) = 0$, and it can be shown that:

$$G(E) \propto \ell_E^\alpha$$  \hspace{1cm} (8)$$

with $\alpha > 1$ scaling like the strength of ionic interactions. In typical cases, one has $\alpha \sim 2$. In many experimental examples, however, a non-zero conductance remains even in the absence of voltage. Taking into account the fact that there may actually be a few free ions left at equilibrium, we then write:

$$G(E) = G_0 + G_1 \left( \frac{|E|}{E_0} \right)^\alpha$$  \hspace{1cm} (9)$$

with $G_0 \ll G_1$. This corresponds to equation (1) of main text. The number of ion pairs play the role of an internal state variable governing the system’s conductance. It should be noted, however, than the value of $G_0$ was found to vary from device to device (even with similar dimensions), although the general shape of the IV curves was preserved, see Fig. S11.
3.2 Ionic rectification

The above mechanism, based on Wien effect, can only produce self-touching loops in the IV curve, and only the absolute magnitude of voltage, and not its sign, governs the dynamics of ion pairs. In experiments, however, we often observe loops that cross themselves at the origin, with a conductance difference between positive and negative voltage. As this means that the system also reacts to the sign of voltage (see Fig. S8), this points out to another mechanism behind the nanofluidic memristor effect, that would stem from some internal asymmetry in the nanofluidic devices.

Here, we detail another mechanism, based on entry effects caused by spatial asymmetry. While the channel itself is symmetrical, it is connected on one side directly to a reservoir, and on the other side to the hole in the SiN membrane (see Fig. 1 from main text), which is much thicker than the graphite flakes: typical membranes have a thickness of 500 nm, compared to less than 100 nm for graphite flakes. Due to this, there is less available space for ions to enter the channel from the membrane’s side than from the other side. Additionally, as the channel walls bear a strong negative surface charge, conduction is governed by the motion of cations. This combination of charge exclusion and geometrical asymmetry results in what is called ionic rectification: if the current flows from the membrane’s side, cations will face a large entry resistance, and a small exit resistance, causing the channel to be depleted. In the opposite case, however, ions will accumulate inside the channel, resulting in a conductance increase. In addition to this purely geometric effect, the SiN membrane also bears a lower surface charge than the wall of activated channels. This can reinforce the asymmetry between the two access resistances of the channel.

As a consequence, the system’s conductance will depend on the sign of applied voltage in a diode-like manner:

\[ G = G_+ \quad \text{if } \Delta V > 0 \]  \hspace{1cm} (10)
\[ G = G_- \quad \text{if } \Delta V < 0 \]  \hspace{1cm} (11)

where \( G_+ \) and \( G_- \) are two constants. This process was extensively studied in various configurations (asymmetry in surface charge, in channel height, etc.) \([7, 8, 9]\). In what follows, we propose a simplified theory enabling us to quantify this phenomenon, without resorting to the complex Poisson-Nernst-Planck equations. We consider only the motion of cations, which we assume behave like tracer particles subject to an electrostatic potential \( V \). We also reduce the channel to a single point located at the origin on an \( x \) axis (as the interior of the channel is symmetric, it does not play a role here). Due to the membrane’s thickness, only a quarter of free space is available to ions on the membrane’s side (see Fig. S7). On the other side, they can freely diffuse in a half space. To take these remarks into account, we model both reservoirs by channels whose size diverges quickly. We describe the reservoirs in polar coordinates by (see
with \( h \) the height of the nanochannel. Let \( c(x) \) be the concentration of particles, \( D \) their diffusion coefficient and \( l \) the transverse lengthscale. We impose the following boundary conditions:

\[
c(x = \pm \infty) = c_0
\]

\[
V(x = \pm \infty) = \mp \frac{V_0}{2}
\]

We then have to solve the Poisson equation:

\[
\frac{1}{R(x)} \partial_x (R(x) \partial_x V) = 0
\]

as well as the conservation of particle flux:

\[
DR(x) \partial_x c - \frac{eD}{k_B T} cR(x) \partial_x V = \frac{I}{el}
\]

with \( I \) the electrical current. Defining \( \gamma = R_+/(R_- + R_+) \) the asymmetry factor and \( \beta = 1/k_B T \), we obtain:

\[
\frac{I}{elD} = \frac{2c_0 R_+ \beta e V_0 (1 - \gamma) e^{(1-\gamma)\beta e V_0} (1 - e^{-\beta e V_0})}{e^{(1-\gamma)\beta e V_0} + R_+ \frac{1-\gamma}{\gamma} (1 - e^{-\gamma \beta e V_0}) - 1}
\]

In this last equation, the current \( I \) should be thought of as a function of the applied voltage \( V_0 \). We obtain, in the \( |V_0| \to \infty \) limit:

\[
I(V_0 \to +\infty) = \beta e^2 V_0 (1 - \alpha) D c_0 R_+ l
\]

\[
I(V_0 \to -\infty) = \beta e^2 V_0 \frac{\alpha}{1 - \alpha} D c_0 R_- l
\]

Therefore, the rectification factor of the IV curve is:

\[
\frac{I(+\infty)}{I(-\infty)} = \frac{R_-}{R_+ + R_-}
\]

Since the channel opens up on one side on a half 3D space, and a quarter of 3D space on the other side, we assume that \( R_+ = 2R_- \), resulting in a rectification factor of 3, as measured in experiments.

This ionic rectification causes the build-up of concentration inhomogeneities, with an accumulation or a depletion of ions inside the channel, depending on the sign of voltage.
3.3 Minimal model of a nanochannel with long-term memory

In this section, we complement the above analysis by showing how long-term memory can emerge from interfacial processes in 2D nanochannels. We first show how the rectification mechanism can be slowed down considerably if there is adsorption of ions on the channel's walls. This allows us to derive a minimal model with analytical solutions, which can then be extended to more complex cases, like that of the second Wien effect. However, we start by taking a step back to analyze the nature of nanofluidic memory.

3.3.1 What does it mean for a nanochannel to have memory?

In this section, we discuss what we really measure in a memristor experiment, and how we can quantify a system’s memory, with the help of a simplistic advection-diffusion model.

We first focus on channels exhibiting ionic rectification. Rather than taking the model presented in previous section, with geometrical asymmetry, we simplify the problem even further. We assume that the channel has a concentration \( c \) of ions. The channel itself is connected to two reservoirs. We introduce an ad hoc asymmetry by assuming than the reservoir on the left of the channel has concentration \( c_L \), and the reservoir on the right \( c_R \), to mimick ionic rectification while keeping mathematical complexity at a minimal level. Lastly, we assume that there is an external forcing \( f \) driving particles from the left to the right. For the sake of simplicity, we work with units such that the diffusion time across the channel, \( L^2/D \), is equal to \( 1/2 \).

In a continuous problem, the particle flux would be:

\[
 j(x, t) = -\frac{1}{2} \partial_x c + f(t)c(x, t) = j_{\text{diff}} + j_{\text{adv}} \quad (22)
\]

Note that the diffusive part \( j_{\text{diff}} \) is an artefact of the way we introduced spatial asymmetry in this model; it is irrelevant in actual experiments. The real physical quantity of interest is therefore \( j_{\text{adv}} \). In practice, we measure this flux at the electrodes, i.e. at both ends of the channel, without access to the full spatial dependence of \( j \). In a time-independent problem, flux is conserved and this does not matter; we obtain \( j_{\text{measured}} = f \langle c[f] \rangle_{\infty} \), where \( \langle c[f] \rangle_{\infty} \) is the spatial average of \( c \) when the channel is subject for a forcing \( f \) for a very long time. In the quasistatic limit, one would replace \( f \) by a slow-varying forcing \( f(t) \):

\[
 j_{\text{quasistatic}} = f(t) \langle c[f(t)] \rangle_{\infty} \quad (23)
\]

where \( \langle c[f(t)] \rangle_{\infty} \) is now the spatial average of \( c \) when the channel is subject for a forcing “frozen” at a specific value \( f(t) \). A memory effect is any deviation from the above equation; it translates the fact that the forcing is varying faster than the time needed to equilibrate the system quasistatically. In other words, memory is stored in the number of particles that can contribute to conduction.

However, when the system is not in the quasistatic limit, flux is not conserved across the system. It is then hard to make exact sense of what is being actually measured at the electrodes;
in the following, we admit we may still assume we measure a spatial average of the advection flux, but that this average is now instantaneous:

\[ \dot{j}_{\text{measured}} \simeq f(t) \langle c(x, t) \rangle_x = f(t) \frac{1}{L} \int c(x, t) \, dx \]  

(24)

Assuming the forcing is sinusoidal \( f(t) = f_0 \cos \omega t \), one can then compute the area of the hysteretic loop in the conductance-voltage curve:

\[ A(\omega) = \left| \oint \langle c(x, t) \rangle_x \, df \right| = \int_0^{2\pi/\omega} \omega f_0 \langle c(x, t) \rangle_x \sin \omega t \, dt \]  

(25)

The bigger \( A \) is, the more memory the system has of its recent past. We thus define the memory timescale as \( \tau_m = 2\pi/\omega_m \) such that \( A(\omega_m) \) is maximum.

There is, however, no simple way to solve the advection-diffusion equation under periodic forcing, even in 1D, so we simplify the problem further by writing an approximate equation for the mean \( \langle c \rangle \) only, see Fig. S7A:

\[ \dot{\langle c \rangle} + \langle c \rangle \simeq \frac{c_L + c_R}{2} + f(t) \frac{c_L - c_R}{2} \]  

(26)

This model is summed up in Fig. S7. In all what follows, we drop the \( \langle \cdot \rangle \) for the sake of simplicity. This yields:

\[ c(t) = \frac{c_L + c_R}{2} + f_0 \frac{c_L - c_R \cos \omega t + \omega \sin \omega t}{1 + \omega^2} \]  

(27)

so that the loop area is:

\[ A(\omega) = f_0 \frac{c_L - c_R}{2} \frac{\omega}{\omega^2 + 1} \]  

(28)

This yields \( \tau_m = 2\pi \), or, in dimensional terms:

\[ \tau_m = \pi \frac{L^2}{D} \]  

(29)

This is perfectly intuitive: since information is encoded in the particle number, it cannot be retained for more than the diffusion time. However, nanochannels have \( L < 10 \mu m \), meaning that the diffusion time cannot exceed a second, contrary to what is observed in experiments (\( \tau_m \sim 1 \) hour).

Before we move on to a slightly modified version of this model to account for this, let us make the following remark. The quasistatic solution to the above problem is:

\[ c_{qs}[f] = \frac{c_L + c_R}{2} + f \frac{c_L - c_R}{2} \]  

(30)

The instantaneous solution we obtained can be rewritten into the following form:

\[ c(t) = \int_0^{+\infty} c_{qs}[f(t - s)] e^{-s/\tau} \, ds \]  

(31)

where \( \tau = 1 \), equal to \( \tau_m \) up to a factor of order unity. This equation will allow us to model more complex situation, where analytical solutions do not exist.
3.3.2 Adsorption-desorption model

To complement the above model, which does not account for long memory times observed in experiments, we consider the possibility of ion adsorbing on the channel’s walls, and denote the number of adsorbed particles by $\sigma$. Introducing $k$ and $\lambda$, the adsorption and desorption rates, respectively, we obtain (see Fig. S7B):

\[
\dot{c} + c = \frac{c_L + c_R}{2} + f(t) \frac{c_L - c_R}{2} - kc + \lambda \sigma \tag{32}
\]

\[
\dot{\sigma} = kc - \lambda \sigma \tag{33}
\]

It again can be solved analytically:

\[
c(t) = \frac{c_L + c_R}{2} + f_0 \frac{c_L - c_R}{2} \left[ \frac{\lambda^2 + (1 + k) \omega^2}{\lambda^2 + [(1 + k)^2 + 2 k \lambda + \lambda^2] \omega^2 + \omega^4} \right] \tag{34}
\]

\[
A(\omega) = f_0 \frac{c_L - c_R}{2} \omega \left[ \frac{\lambda (k + \lambda) + \omega^2}{\lambda^2 + [(1 + k)^2 + 2 k \lambda + \lambda^2] \omega^2 + \omega^4} \right] \tag{35}
\]

The memory timescale is then given by:

\[
\{ \lambda (k + \lambda) + 3 \omega^2 \} \left[ \lambda^2 + \left\{ (1 + k)^2 + 2 k \lambda + \lambda^2 \right\} \omega^2 + \omega^4 \right]
\]

\[
\ldots = \omega \left\{ \lambda (k + \lambda) + \omega^2 \right\} \left[ 2 \left\{ (1 + k)^2 + k \lambda + \lambda^2 \right\} \omega + 4 \omega^3 \right] \tag{36}
\]

There is no closed-form solution to this last equation, but we can extract an approximate solution when surface effects strongly dominate ($k \gg \lambda$ and $k \gg 1$):

\[
\omega_m \sim \frac{\lambda}{k} \ll 1 \tag{38}
\]

In other words, the memory time reads in this case:

\[
\tau_m = \frac{2 \pi \sigma_\infty L^2}{c_\infty D} \tag{39}
\]

where $\sigma_\infty$ and $c_\infty$ are the values of $\sigma$ and $c$ at chemical equilibrium. The ratio $\sigma_\infty/c_\infty$ appearing in the above equation is the analogue of the Dukhin number [10], which measures the importance of the surface charge of a channel with respect to the bulk concentration in ions. This number can reach several hundreds, so $\tau_m$ can be of the order of several minutes.

Qualitatively, the above equation can be recovered from a semi-quantitative argument as follows. The memory time is given by the maximum time a particle can stay within the channel. It will reach one of the reservoirs if left free for more than $L^2/D$, by randomly diffusing along the channel. However, every $1/k \ll 1$, the particle is adsorbed and stops moving, only liberated after a time $1/\lambda$. Along its course through the channel, there will therefore be $kL^2/D \gg 1$.
such events of duration $1/\lambda$. The total time spent inside the channel is the sum of the “travelling time” and “resting time”:

$$\tau_m \sim \frac{1}{\lambda} \left( \frac{k L^2}{D} + \frac{L^2}{D} \right) \sim \frac{k L^2}{\lambda D} \quad (40)$$

The last approximation holds since we assumed that $k \gg \lambda$, such that the total resting time is much larger than the travelling time.

To complement the above minimal model, we also computed a numerical solution of the 1D advection-diffusion under periodic forcing and with adsorption, yielding similar results (not reported here).

### 3.3.3 Wien effect

In the previous model, long-term memory emerges from a stop-and-go mechanism of ions being adsorbed and desorbed. However, this process is more general than the specific physics of adsorption, and we can write a similar system taking into account a Wien effect mechanism:

$$\dot{c} + c = c_0 - \frac{1}{\tau_a} c^2 + \frac{1}{\tau_d[f(t)]} p \quad (41)$$

$$\dot{p} = \frac{1}{\tau_a} c^2 - \frac{1}{\tau_d[f(t)]} p \quad (42)$$

Here, $c$ is the concentration of ions that can contribute to conduction (free ions or polyelectrolytes), while $p$ represents the concentration of pairs. This system is, however, non-linear in both $c$ and $f$, and as such admits no analytical solution, but is qualitatively similar to the previous linear case. Rather than looking for an approximate solution of this already simplistic model, we instead use the ansatz derived above.

### 3.3.4 A simple ansatz - Determination of the memory time

Here, we detail how we fitted the curves presented in Figure 4 of main text. As per sections 3.1 and 3.2, we have two models describing the conductance of a 2D nanochannel under a constant electrical forcing. As shown by equation (31), this conductance becomes in the time-varying case:

$$G(t) = \int_0^{+\infty} G_{qs} [\Delta V(t-s)] e^{-s/\tau} ds \quad (43)$$

where $G_{qs}$ is the conductance in the stationary case (i.e. if the voltage was ‘frozen’ at the value $\Delta V(t-s)$ for an infinite amount of time). Depending on cases, we use the following expressions:

$$G_{qs}(\Delta V) = G_1 \Delta V^\alpha, \quad \alpha = 2 - 3 \quad (Wien \ effect) \quad (44)$$

$$G_{qs}(\Delta V) = \begin{cases} G_+, & \text{if } \Delta V > 0, \\ G_-, & \text{if } \Delta V < 0 \end{cases} \quad (Ionic \ rectification) \quad (45)$$
We first use these models to extract the quasistatic limit of experimental curves, and we then “turn on” memory effects by plugging the chosen model into equation (31). To assess the robustness of our approach, we can determine the memory time through two methods:

- By using \( \tau \) as a fitting parameter in equation (31).
- By noticing that, upon correct renormalization (see below), the area of the loop in the IV curve should take the form:

\[
A^*(\omega) \simeq K \frac{\omega \tau_m}{1 + \omega^2 \tau_m^2}
\]

with a theoretical value \( K = 1 \) in the adsorption-desorption model, and using \( \tau_m \) as a fitting parameter in this last equation. In the case of the pairing-depairing model, we cannot derive the exact expression of \( A^* \), but we use the above expression as an approximative ansatz, with \( K \) as a fitting parameter.

Both quantities \( \tau \) and \( \tau_m \) can be interpreted as memory timescales, being equal up to a factor \( \pi \) in the minimal model. In practice, both methods yield similar results (\( \tau \sim \tau_m \sim 100 \text{ s} \), see Figure 4 from main text), but we believe the second one (\( \tau_m \)) to be more robust as its determination uses from data over several frequencies.

Let us now detail how we normalize the loop area. Memristive devices cycle between different conductance states. The largest loop that could be observed would be in the case where the device switches abruptly between the lowest and the highest conductance states, \( G_{\text{off}} \) and \( G_{\text{on}} \), whenever it reaches \( \Delta V = \pm V_0 \) (for bipolar memristors) or \( \Delta V = 0 \) and \( |\Delta V| = V_0 \) (for unipolar memristors). The conductance-voltage curve then takes the shape of a rectangle of size \( 2V_0 \times (G_{\text{on}} - G_{\text{off}}) \). The IV curve then takes the shape of two triangles of total area \( V_0^2 \times (G_{\text{on}} - G_{\text{off}}) \), which we therefore use as a normalization. For each case, we determine \( G_{\text{off}} \) and \( G_{\text{on}} \) graphically using data with the lowest frequency for a given device and salt concentration. In the case of devices with mixed unipolar-bipolar behavior, we determined both extremal conductance for positive and negative voltage, and then used \( 0.5V_0^2 \times (G_{\text{on},+} - G_{\text{off},+}) + 0.5V_0^2 \times (G_{\text{on},-} - G_{\text{off},-}) \) as normalization. This normalization process is summed up in Fig. S8.

4 Additional experimental data

4.1 Pristine channels

We provide additional data to characterize the memristor effect in pristine channels, which is found to be robust when we vary salt concentration, channel height and the chemical nature of the electrolyte.

On Fig. S9, we show that the memristor effect can be observed in pristine devices regardless of the electrolyte used (KCl, NaCl, LiCl, CaCl\(_2\) or NiSO\(_4\)), asserting its robustness. Despite
variations in conductance, all these curves display the same non-linear general shape remindful of the Wien effect.

On Fig. S10, we provide additional data for the memristor effect in bilayer pristine channels with potassium chloride of various concentrations. In particular, we notice that the system behaves like a bipolar memristor at low salt concentration.

On Fig. S11, we show the evolution of loops in IV curve at fixed frequency and salt concentration, but with increasing channel height. We find that the effect is most visible in thin channels, and that the loop collapses to a straight line in larger channels. This shows that memory effects can only be observed if confinement is sufficiently strong so that ion-ion interactions are enhanced, allowing the formation of ion pairs.

Lastly, Fig. S12 shows the determination of the memory time of three different devices (and two concentrations) from the evolution of the loop area with frequency. We obtain values between 50 and 400 s.

4.2 Activated channels

Additional data characterizing the influence of salt concentration on memristive effects in activated channels are presented in Fig. S13. They notably include raw data for Fig. 2A of main text. We observe that concentration variations have little effect on the memory of thinner channels (Fig. S13A-B), while this influence is more visible for devices above 10 nm in thickness. This notably shows that, in more confined systems, interfacial processes are stronger than bulk effects.

In addition, the memristor effect can also be observed with salts other than CaCl$_2$, as shown on Fig. S14 for KCl and AlCl$_3$.

We also provide additional data regarding the effect of voltage frequency (Fig. S15), corresponding to Fig. 4C of main text. These data allow us to compute the memory time of each activated system, from the frequency at which the loop in the IV curve is the largest. We obtain values spanning from 50 to 400 s, in a similar range as pristine devices. Such variations may be explained by the variability of the surface state of activated systems following the etching in low pressure water vapor.
Figure S1: Schematic flow-chart in cross-sectional view and corresponding optical and AFM images. **Step I:** Preparation of the top-spacer layers on silicon/silicon oxide (SiO$_2$) wafer. A Graphene is mechanically exfoliated; the thickness of this graphene flake will determine the height ($h$) of the channel. Bottom panel: Optical image of a 3-layer graphene spacer. **B** Patterning of the spacer using electron beam lithography (EBL) and etching into parallel strips. Bottom panel: atomic force microscopy (AFM) image and height profile of the patterned graphene-spacer ($h \sim 1.2$ nm and $w \sim 150$ nm). **C** Transfer of MoS$_2$ flake as a top layer over graphene spacer. Bottom panel: Optical image of the top-spacer stack. **Step II:** Assembly of the tri-crystal (top-spacer-bottom) stack on silicon/silicon nitride (SiN$_x$) wafer. **D** Transfer of a MoS$_2$ flake onto SiN$_x$ membrane bearing a hole ($\sim 3 \times 50$ µm), to serve as bottom wall of the channel. **E** Dry etching of the MoS$_2$ bottom layer from the back of the SiNx. **F** Transfer of the top (MoS$_2$)-spacer (graphene) stack prepared in C over the bottom MoS$_2$ prepared in E. **G** Patterned gold (Au) deposition over the tri-crystal stack. **H** With the Au strip as a mask to protect the underneath channels, the surrounding regions are etched away. The gold strip thus determines the channel length ($L$). **I** Optical images (left: reflection mode, right: transmission mode) of the final channel device. The tricrystal device is underneath the gold strip on the SiN$_x$ membrane.
Figure S2: **Fabrication of activated nanochannels. Step 1: Patterning of the bottom layer.**
Up: 2D side view of a graphite bottom layer crystal after the patterning on a Si/SiO$_2$ substrate. Middle: 3D view of the patterning process. A square-shaped hole and four trenches connected to the hole are represented. Bottom layer graphite is dark grey and the Si/SiO$_2$ substrate is light pink. The electron flux, represented as a green tip, enables selective removal of matter. Down: AFM image of the bottom layer after etching. Scale bar represents 1 µm. **Step 2: Dry transfer of the top layer.** Up: 2D side view. A top layer crystal is added above the bottom layer. Middle: 3D view of the device after the transfer of the top layer, represented in glassy transparent grey. Down: SEM image of a device at that stage. Four channels are visible in white. The bottom layer hole remains visible through the top layer. Scale bar represents 5 µm. **Step 3: Wet transfer on the Si/SiN membrane.** Up: 2D side view. Middle: 3D view, with the SiN membrane in green. The circular aperture in the SiN membrane is visible by transparency. Down: Optical microscope image of a finished device. Scale bar represents 10 µm.
Figure S3: **Long-term modification of a nanochannel conductance using voltage pulses**  

**A** ‘write’ pulse (+1 V, 10 s), followed by ten ‘read’ pulses (+0.1 V, 10 s) to study the relaxation of the conductance.  

**B** An ‘erase’ pulse (−1 V, 10 s), followed by ten ‘read’ pulses (+0.1 V, 10 s).  

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**Figure S3:** Long-term modification of a nanochannel conductance using voltage pulses.  

A ‘write’ pulse (+1 V, 10 s), followed by ten ‘read’ pulses (+0.1 V, 10 s) to study the relaxation of the conductance. B An ‘erase’ pulse (−1 V, 10 s), followed by ten ‘read’ pulses (+0.1 V, 10 s).
Figure S4: **Algorithm for the implementation of Hebb’s rule with activated channels**

Voltage input emulating 8 successive activation of a pre-synaptic and a post-synaptic neuron with a relative spike timing $\Delta t = 10$ s. The conductance is read before and after with low amplitude ‘read’ pulses, highlighted by red circles. **B-E** Examples of input voltage for various relative spike timings of the two neurons.
Figure S5: Additional data for the implementation of neuromorphic computing with activated channels. The salt used is CaCl$_2$, 1 mM. A Evolution of the ionic current (red) under voltage pulses of constant sign (blue) (see Fig. 5A of main text). B Conductance change following a positive voltage pulse of 1 V in amplitude and a duration of 15 s (see fig. 5B of main text). The conductance is read with an alternating square voltage of 0.1 V in amplitude and a period of 20 s. C Reversible, long-term modification of a nanochannel’s conductance. 30 write spikes (+1 V, 10 s) are applied, followed by 30 erase spikes (-1 V, 10 s) which bring back the system to its initial state. Between each spike, the conductance is let to stabilize during two minutes and is then measured with a read pulse (0.1 V, 5 s), see Fig. 5C of main text. D Conductance change after 8 successive activations of the two neurons, in percentage of the initial conductance and as function of the relative activation timing of the neurons (see Fig. 6D of main text).
Figure S6: **Simplified model of ionic rectification.** A. Geometry of the experimental setup. The presence of the SiN membrane on one side of the device introduces spatial asymmetry. B. Schematics of the theoretical model. Reservoirs are modeled by quickly expanding channels, one being twice as large as the other.

Figure S7: **Minimal model of nanofluidic memory.** A. Minimal model of purely diffusive memory. The nanochannel is modeled by a single point that exchanges particles with two reservoirs. The concentration difference between reservoirs plays the role of geometrical asymmetry. Memory is stored in the concentration inside the channel \( c \), and the memory time is the diffusion timescale. B. Same minimal model, but with particle adsorption on the channel’s walls. Transport is now limited by a stop-and-go mechanism of particles adsorbing and desorbing from the walls, giving rise to a memory time orders of magnitude larger than diffusion. C. Memristor effect in the minimal model, as shown by the loop in the IV curve, in dimensionless units. The blue curve corresponds to the model described in panel A (section 3.3.1), and the red one in panel B (section 3.3.2). Memory effects are visible at low frequency only when surface effects are taken into account.
Figure S8: **Normalization of loop area.** A. Example of an experimental conductance-voltage curve for a bipolar memristor (see Figure 1C from main text), corresponding to an adsorption-desorption memory mechanism, with the graphical determination of $G_{on}$ and $G_{off}$. B. Idealized loop in the conductance-voltage curve, defining the normalization factor for a bipolar memristor.

C. Example of an experimental conductance-voltage curve for a unipolar memristor (see Figure 1B from main text), corresponding to a Wien effect memory mechanism, with the graphical determination of $G_{on,\pm}$ and $G_{off,\pm}$. D. Idealized loop in the conductance-voltage curve, defining the normalization factor for a unipolar memristor.
Figure S9: **Nanofluidic memristor effect in a pristine channel with various electrolytes.**

A-E Current-voltage characteristics of an activated channel with height under a voltage sweep of amplitude 0.75 V. Other parameters (salt, concentration, channel height and frequency) are specified on each panel.
Figure S10: **Evolution of the memristor effect with salt concentration.** A-D Current-voltage characteristics of a pristine nanochannel with height $h = 0.7 \text{ nm}$, filled potassium chloride at various concentrations, under a voltage sweep of amplitude 0.75 V and frequency 3 mHz. Orange curve indicates a self-crossing loop, and blue a self-touching one.
Figure S11: **Evolution of memristive effects with channel height.** Current-voltage characteristics of pristine channels of different heights filled with potassium chloride, under a voltage sweep (frequency $f = 3$ mHz). **A-B** Two different devices with height $h = 0.7$ nm (with concentration 3 M, voltage amplitude 1 V, and 1 M, 0.75 V, respectively). **C-E** Devices with height $h = 2.8, 8.5$ and 86 nm, respectively (concentration 1 M, voltage amplitude 0.75 V or 1 V).
Figure S12: **Memristor effect: influence of voltage frequency.** Current-voltage characteristics of different pristine-MoS\(_2\) devices with channel heights \(h = 0.7\) nm (A-B) and 7 nm (C-D), the electrolyte is KCl 1M for A, C and KCl 3M for B, D; applied voltage is sinusoidal with frequency ranging from 0.6 mHz to 200 mHz. The normalized loop area vs frequency of A is presented in main Fig. 4C of main text. Insets for B-D represent the corresponding normalized areas of the different current-voltage characteristics for that device. The error bars represent the area variation between three successive voltage sweeps.
Figure S13: Memristor effect: influence of salt concentration (raw data). Current-voltage characteristics of four different activated devices, with CaCl$_2$ and AC voltage oscillating between ±1 V at 1 mHz. The current is normalized by its maximum value for each salt concentration. **A** Raw data corresponding to Fig. 2A from main text. **B-D** Additional data for activated channels of different thickness. In each case, current is normalized by its maximum value, to allow easier comparison between different datasets.
Figure S14: **Nanofluidic memristor effect in an activated channel with various electrolytes.** Current-voltage characteristics of an activated channel with height \( h = 13 \text{ nm} \), under a voltage sweep of frequency 1 mHz and amplitude 0.8 V.  

- **A** Potassium chloride, 100 mM.  
- **B** Calcium chloride, 1 mM.  
- **C** Aluminum chloride, 1 M.
Figure S15: Memristor effect: influence of voltage frequency (raw data). Current-voltage characteristics of four different devices, with CaCl$_2$ 100mM (A-B) or 1mM (C-D). Inset: Normalized area versus frequency. Squares are experimental values and solid lines are theoretical model with memory time parameter, $\tau_m$, equals to 50 s (B), 100 s (C) and 400 s (D). The normalized area vs frequency of the 4nm device (A) is presented in main text Fig 4.C.
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