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DISCUSSIONS

Iontronics under confinement: general discussion

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Lydéric Bocquet opened a general discussion of the paper by Markus Valtiner: These are very nice and important experiments (**https://doi.org/10.1039/d3fd00038a**). Can you comment on the dynamics? The dynamics in the experiments seems to be substantially faster than the diffusion time scale (among others). Did you study this more exhaustively?

Markus Valtiner replied: Thank you very much for this comment. We have indeed checked on the time scales using a simplified diffusion model (see eqn (5)–(9) in our paper), which matches well with the measured velocities defined in eqn (9) in our paper. It should be emphasized that we are not measuring diffusion rates directly, instead we are tracking the rate of the equilibrated ion concentration front. Indeed dynamics should be further studied both experimentally as well as theoretically for this experiment, with different ions, confinement distances and potential steps.

Alexei A. Kornyshev asked: In order to check that your estimate for the relaxation time obeys the RC-time law, $\tau = LL_D/D$ (where L is the size of the gap, L_D is the Debye length, and D is the diffusion coefficient), it may be good to vary L in your experiments and see that the law is satisfied. Did you check that? Such a law, however, would only work for small voltage jumps, so that the voltage dependence may also be worth checking.

Markus Valtiner replied: We have not checked this aspect so far, due to instrumentation limitations. This is indeed an intriguing experiment however, which requires very stable distance control over long time scales, and at large and short distances. A typical Surface Forces Apparatus (SFA) setting has limited

feedback control at larger distances, where drift results in larger distance changes (at a rate of some Å min^{-1}). At small distances, as in our reported experiments, drift results in lower absolute distance changes, due to stabilization by electric double layer repulsion. As such, with current equipment we cannot easily scan across a suitable range of L. We have made further developments in this direction,[1] to enable long-time drift free constant distance experiments at all distances. Such a measurement can hence be realized now with such equipment, and will be reported in future work.

1 K. A. Schwenzfeier and M. Valtiner, Design and testing of drift free force probe experiments with absolute distance control, *Rev. Sci. Instrum.*, 2022, **93**, 073705.

Serge G. Lemay commented: In your article it is stated that "This suggests that diffusion is the main mechanism for ion equilibration in an electrochemically modulated nano-pore." However, given the high surface-to-volume ratio, it seems surprising that migration would not play a role during charging. Could you please comment?

Markus Valtiner answered: Understanding the dynamics of the local electrochemical potential/field is not trivial. It is unclear to us, which local potential gradient establishes during charging (*e.g.* considering time-variant potential drops into the gap). At this point in time, our very simplified diffusion model appears to match with the measured time scales. We have of course also tested adding migrative flux with reasonable potential drops, which increased the estimated 'front velocities' significantly above the measured velocities. However, a much more rigorous simulation will be needed, in addition to experiments that can track the local electrochemical potential in the gap experimentally (*e.g.* scanning Kelvin probes).

Susan Perkin said: Thank you for presenting such interesting observations. I am curious about the asymmetry in the response, comparing the switch from positive to negative and *vice versa*. Do you have any insight into this? Does it relate to your choice of salt; does the double layer charge differently when the counterion is different?

Markus Valtiner responded: Thank you very much for this comment. Indeed this asymmetry, and in particular the observed 'distance overshoot' seen in Fig. 2b in our article is interesting, and we have observed differences with different ions. We hypothesize that overscreening, as well as different diffusion coefficients of anions/cations, and gap size to ion radius relations, may play a role in such dynamic phenomena.

Benjamin Rotenberg highlighted: You mentioned that ion exchange proceeds by diffusion of ions, but the results are reported to correspond to an ionic front with a constant velocity. This comes in particular from a straight line fit of the data in Fig. 4a in your article.

Couldn't the data reported in this figure be better fitted with a square-root dependence on time (rather than linear), as expected for a diffusive process? From the distance and time ranges, the crude estimate $\Delta R^2/2\ \Delta t$ gives a diffusion

coefficient of the order of 10^{-9} m^2 s^{-1} which seems consistent with typical diffusion coefficients for the ions. Even though other processes might play a role, this would support your conclusion of a diffusive mechanism.

Markus Valtiner answered: Thank you very much, this is indeed a good suggestion for the analysis of the data. Having proceeded to do such a fit ($\Delta R^2/2\,\Delta t$), we have indeed found that the data shown in Fig. 4a can be fitted well with a diffusion rate in the region of 3×10^{-9} m^2 s^{-1}. As you also state, one should further point out that diffusive processes appear to be a major driving force, but we are not measuring the diffusion of single ion species. Instead, this experiment tracks the equilibrated ion concentration front, and this fit further supports this argument.

Martin Z. Bazant commented: The visualization of "ion waves" in dynamical surface force apparatus measurements is very interesting and frankly, to be expected, in a model that accounts for the nonlinear drift due to electromigration in the lateral direction under confinement between charged surfaces. This is an example of an ion concentration "shock wave", analogous to the "deionization shock waves"[1] which were first observed and modeled by Mani, Santiago and Zangle (2009) in nano/microfluidic devices with charged surfaces,[2,3] and applied to desalination in shock electrodialysis.[4,5] There can also be effects of nonlinear absorption as well as nonlinear drift, leading to ion concentration shock waves, in fields such as ion exchange chromatography and capillary electrophoresis, as pioneered by Neal Amundsen starting in the 1940s and widely advanced [see ref. 6 – and references therein]. The new aspect here could be considering the effects of polarizable metal surface, and this should lead to nonlinear "transmission line" charging with propagating shocks as well. The experiments may also be affected by lubrication "squeeze flows" which can lead to slow lateral mass flow in response to surface force changes, coupled to these nonlinear ionic effects.

How might these dynamical effects influence surface force measurements which are normally interpreted in terms of 1d models of electrolyte double layer structure? Is it possible that some of the data interpreted this way are affected spurious dynamical forces resulting from lateral ionic relaxation by "ion waves"?

1 A. Mani and M. Z. Bazant, Deionization shocks in microstructures, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2011, **84**, 061504.
2 T. A. Zangle, A. Mani and J. G. Santiago, Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces, *Chem. Soc. Rev.*, 2010, **39**(3), 1014–1035.
3 A. Mani, T. A. Zangle and J. G. Santiago, On the propagation of concentration polarization from microchannel–nanochannel interfaces Part I: analytical model and characteristic analysis, *Langmuir*, 2009, **25**(6), 3898–3908.
4 S. Schlumpberger, *et al.*, Scalable and continuous water deionization by shock electrodialysis, *Environ. Sci. Technol. Lett.*, 2015, **2**(12), 367–372.
5 M. A. Alkhadra, *et al.*, Electrochemical methods for water purification, ion separations, and energy conversion, *Chem. Rev.*, 2022, **122**(16), 13547–13635.
6 E. V. Dydek and M. Z. Bazant, Nonlinear dynamics of ion concentration polarization in porous media: the leaky membrane model, *AIChE J.*, 2013, **59**(9), 3539–3555.

Markus Valtiner replied: Thank you very much for the interesting literature references. Let me answer your two questions as follows:

(1) "How might these dynamical effects influence surface force measurements which are normally interpreted in terms of 1d models of electrolyte double layer structure?" We have indeed measured the force change of the 3D slit pore system in response to the slit charging. The SFA used in this work can independently measure force and distance at the same time. As you can see in Fig. 4b in our article, the force response appears spontaneous with the experimental time resolution. It will indeed be interesting to increase the experimental resolution (time and force) in order to directly measure potential non-linear dynamic force responses.

(2) "Is it possible that some of the data interpreted this way are affected spurious dynamical forces resulting from lateral ionic relaxation by "ion waves"?" The 1D interpretation of force *versus* distance in Fig. 7 in our article, compares the thermodynamically expected distance change at a constant applied load, with the experimentally measured distance (both after ion equilibration). Here, we do not expect an influence of the ion dynamics/ion waves. It will however be intriguing to improve the experimental resolution further to explore such effects experimentally.

Siretanu Igor said: The significant layering of ions (ClO_4^- and Li^+) observed in your MD simulation (Fig. 6 in your article) has also been observed in experiments. Are the dots, protrusions, and small islands in the AFM figures shown in Fig. 5a and b related to adsorbed ions? Are they Li ions? What is the origin of the clustering of Li ions in islands? Is it due to the lateral interaction of another origin? Do you eventually see Li ions covering the whole surface?

Markus Valtiner responded: The data clearly shows the hexagonal lattice of the mica, with extra protrusions and bumps. We interpret these as hydrated ions which adsorb on the surface. In our view the clustering is due to the random distribution of charge in the mica lattice, which results in lines, and cluster-like structuring on the surface. We have shown similar intrinsic ordering of ions on mica, which was freshly cleaved in vacuum using nc-AFM.[1] We have measured topographies at higher concentrations, and so far never found what we would define as a full coverage for Li.

1 G. Franceschi, P. Kocán, A. Conti, S. Brandstetter, J. Balajka, I. Sokolović, M. Valtiner, F. Mittendorfer, M. Schmid, M. Setvín and U. Diebold, Resolving the intrinsic short-range ordering of K+ ions on cleaved muscovite mica, *Nat. Commun.*, 2023, **14**, 208.

Gilad Yossifon opened a general discussion of the paper by Zuzanna S. Siwy: Your experiments were obtained under steady state conditions (**https://doi.org/10.1039/d3fd00063j**). If you monitor the temporal change maybe you would obtain a more direct correlation with zeta potential? Secondly, your set-up is limited by aspect ratio; how does it compare to the more simple long straight channel set-ups. Finally, the surface charge can also be monitored by measuring the current under an imposed concentration gradient, *e.g.* reverse dialysis. Can you comment on this?

Zuzanna S. Siwy communicated in reply: Indeed, our experiments were obtained in steady state conditions. Measuring a temporal response is an interesting

possibility, which we have not yet considered. Concerning pores with a small aspect ratio, we believe the electrokinetic measurements can still inform us about the effective surface charge, however we are probing charges on the pore walls and the membrane surfaces in this case. We can indeed measure currents in conditions that are similar to reverse dialysis. We will look into this possibility using electrodes with very well controlled potential in organic solvents.

Sophie Marbach asked: Thank you for your talk. Could you give us a bit more insight on what vibrational sum-frequency-generation spectroscopy (VSFG) is and what it teaches you in the experiments?

Zuzanna S. Siwy replied: VSFG gives a unique insight into molecular properties of an interface between two centrosymmetric media. This is because within the electric dipole approximation, no VSFG signal is generated in an isotropic bulk medium. The VSFG signal informs us on the arrangement of solvent molecules at the interface and unravels its spatial organization.

Rene van Roij commented: We all know that the viscosity of a solvent gives rise to an ohmic resistivity, and a charged surface to a capacitive electric double layer, such that RC-type iontronic circuits can be realised. Is there any prospect that a chiral solvent could give rise to an inductive circuit element with LR or LCR characteristics?

Zuzanna S. Siwy responded: This is a very interesting point that we have not yet considered. We will definitely look into it.

Yan Levin said: What is the value of the dielectric constant of the solvent? Did the measured properties follow the Hofmeister series for different anions?

Zuzanna S. Siwy replied: The dielectric constant of propylene carbonate and acetonitrile is 64 and 37, respectively. We have not studied a sufficient number of anions to draw a conclusion whether the observed behavior followed the Hofmeister series.

Gilad Yossifon said: Why could you not use your nanopore to monitor diffusion flux; zeta potential under an imposed concentration gradient?

Zuzanna S. Siwy communicated in response: This is an excellent question. These measurements are currently being designed. Such experiments will allow us to quantify the magnitude of the effective potential of the silica/propylene carbonate interface.

Emer Farrell commented: I noticed in your paper that the enantiopure *R* form of the solvent is studied, have you tried studying the enantiopure *S* form, and if so, how did it impact the results? Do you expect the chiral form of the solvent (*R* or *S*) to affect the solvent ordering?

Zuzanna S. Siwy answered: The electrokinetic measurements were done only with the *R* enantiomer of propylene carbonate, while VSFG used both forms. We

expect the results of the electrokinetic measurements to be similar for *R* and *S* propylene carbonate, which will be checked in the future.

Yan Levin opened a general discussion of the paper by Christian Holm: Which water model did you use in your article (**https://doi.org/10.1039/d3fd00043e**)? Does it have the same dielectric constant as real water? In the case of DFT with solvent, what was the model of solvent and how was the dielectric constant included in the DFT?

Christian Holm replied: The employed water model was TIP4P/epsilon which matches the dielectric properties of real water almost perfectly. For the case of the DFT solvent we modelled it as a dumbbell containing opposite charges on its end. The relative dielectric constant of this solvent was about 2.4, but in addition to that we also used a background epsilon of 4.1, yielding an approximate effective dielectric constant of 10, estimated from a capacitor model by DFT. For the solvent free DFT we used the standard implicit solvent model and various values for epsilon, see our paper and the ESI for details.

Susan Perkin asked: In electrolytes in general there are multiple decay parameters describing interaction potentials (*e.g.* see ref. 1), and in your paper you use the parameter 'zeta' to refer to (at least) two different decay terms. In Fig. 1 zeta is the decay length of a monotonic exponential term; while in Fig. 2 and 3, in the regions marked with exponent *n*, zeta corresponds to the decay of a damped oscillatory function (like in eqn (14)). In the experiments that gave rise to the data in Fig. 1, the damped oscillatory term is also apparent and it is probably this decay which is more comparable to the results of the simulations in Fig. 3. Recent analysis by Härtel *et al.*,[2] showed that the oscillatory and monotonic contributions can indeed be observed simultaneously in the restricted primitive model (RPM), albeit in a region of phase space different to the experiments. It was shown that the amplitude of the longer, monotonic, contribution decreases in magnitude as salt concentration increases and is presumed to be below the noise level at high salt concentrations. Is it possible that the monotonic decay is below the noise in your simulations?

1 R. Kjellander, The intimate relationship between the dielectric response and the decay of intermolecular correlations and surface forces in electrolytes, *Soft Matter*, 2019, **15**, 5866–5895.
2 A. Härtel, M. Bültmann and F. Coupette, Anomalous Underscreening in the Restricted Primitive Model, *Phys. Rev. Lett.*, 2023, **130**, 108202.

Christian Holm answered: As mentioned in our previous works,[1,2] we followed the decay of the potential of mean force (PMF) down to an accuracy of $10^{-5}\ k_{\mathrm{B}}T$, showing no hint of monotonic decay and anomalously large decay lengths. Your suggestion that the data of your measured damped oscillatory regime could correspond to our results sounds interesting, and I would be keen on seeing a screening length emerging from that. The fact remains that our very precise measurements do not show any monotonic long decay length. The large decay lengths observed by Härtel *et al.* that you mention, are in the strong-coupling regime, where ions form clusters because of strong ionic interactions. In this regime, screening is due to a small amount of free ions and is reminiscent of the

Debye screening. This might be expected. Similar ideas have already been discussed by the Israelachvili group,[3] but instead of clusters, they spoke of ion pairs. It is unclear whether these effects survive in the weak coupling regime and at high ion concentrations. In our simulations of room temperature ionic liquids and aqueous NaCl, we do not see such (strong) clustering.

1 J. Zeman, S. Kondrat and C. Holm, Bulk ionic screening lengths from extremely large-scale molecular dynamics simulations, *Chem. Commun.*, 2020, **56**, 15635–15638.
2 J. Zeman, S. Kondrat and C. Holm, Ionic screening in bulk and under confinement, *J. Chem. Phys.*, 2021, **155**, 204501.
3 Gebbie, M. Valtiner, X. Banquy, E. T. Fox, W. A. Henderson and J. N. Israelachvili, Ionic liquids behave as dilute electrolyte solutions, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 9674–9679.

Susan Perkin asked: Are you able to calculate the activity coefficients of ions and/or water in your simulations, and do they match the experimental values for the relevant salt concentration? You mentioned that no aggregation is observed, but based on bulk activity coefficients wouldn't you expect to see at least some ion pairing or aggregation?

Christian Holm responded: This question addresses only the atomistic simulations. The used force-fields for the water (TIP4P/ε) and the ion force fields are thermodynamically consistent force fields, *i.e.* they have been parameterized to reproduce the experimental activity coefficients. I do not know how one would define ion pairing or clustering in dense electrolytes. You always have some pairs which come close to each other for some small amount of time. However, we never observed any long-lived aggregates or larger inhomogeneities in the fluid. I am also not sure how to infer ion pairing from the activity coefficients.

Rene van Roij asked: It is very comforting to see that relatively cheap implicit-solvent models and computationally much more expensive explicit-solvent models, give very similar and relatively short asymptotic decay lengths for the concentration profiles and for the force–distance curve between two planar electrodes. This agreement is to be expected (at least in equilibrium) provided the effective ion–ion interactions in the primitive models are a good representation of the explicit-solvent-mediated effective ion–ion interactions. However, the nice agreement between theory and simulation in some sense only confirms the theory, whereas the correctness of models can only be confirmed by comparison with experiments. With the observed long-ranged force–distance curves of a large number of carefully conducted SFA-experiments in mind, can you think of any physical ingredient that is missing or relatively poorly represented in your equilibrium simulations of explicit-solvent models? Or are you rather led to the conclusion that the interpretation of the SFA-experiments should involve a new ingredient, for instance extremely slow equilibration processes?

Christian Holm answered: Rene, thank you very much for bringing up this question, since it highlights the important first part of any theory, namely the importance of the model used for describing the experiments, aka reality. We are dealing here basically with three different models: firstly the fully atomistic one with an explicit water model and realistic ion parameters or models of fully

atomistically resolved ionic liquids within a polar atomistic solvent; secondly primitive ions, living in a solvent environment modeled by simple dumbbell-like polar solvent molecules having otherwise only hardcore interactions; and thirdly the primitive model with ions modeled as charged spheres living in a solvent represented as a dielectric continuum. Basically, all these three models agree in their outcome for the screening lengths values (small) and the scaling with n between 1 and 2, showing a crossover behavior to the hardcore dominated regime. The latter type model is also the starting point for most analytical work on this problem, so no other outcome will be expected. The universal behavior seen in the experiments of Smith *et al.*,[1] make me strongly believe that the model should not be more refined, since we could still make it more complex by including electronic polarizability and charge transfer, making it more and more specific to the actual materials and liquids used. However, I tend to believe that this is highly unlikely to play a role in order to understand the observed experimental data. Your point of saying that the SFA might measure non-equilibrium effects is tempting, since from our simulations I conclude that within our model no large long-range screening lengths and no cubic scaling exist in equilibrium.

1 A. M. Smith, A. A. Lee and S. Perkin, The electro-static screening length in concentrated electrolytes increases with concentration, *J. Phys. Chem. Lett.*, 2016, **7**, 2157–2163.

Benjamin Rotenberg asked: Firstly, in the simulations where you determine the composition of the confined electrolyte by imposing the chemical potentials of water and of the salt, how much does the composition of the confined electrolyte differ from that of the reservoir?

Secondly, you advocated more experimental work. Are there features of the experimental system that still haven't been taken into account in the models? For example, for mica surfaces with which this anomalous underscreening is reported, someone mentioned yesterday the fact that there are lateral heterogeneities. Could this play a role on the decay of the measured force?

Christian Holm replied: Concerning the first point, we show in our paper in Fig. 8 that, both the atomistic MD simulations and the solvent-explicit DFT calculations, have a significant (negative) surface excess that increases strongly with salt concentration. As can be inferred from Fig. 6, both the ion pair and the water number need to be adapted sensitively. For the smallest separation (1 nm) and highest concentration (2 mol l^{-1}) studied, the composition differs by about a factor of 2 from the reservoir (Fig. 8c), *i.e.* drastic effects are expected due to changing composition.

In our atomistic approach we used one of the best available models from the InterfaceFF package, showing no unexpected deviations from the solvent-explicit primitive model. Since mica is used experimentally because it is known for its remarkable homogeneity, I tend not to make strong conclusions as a theorist here – however, experimental investigations of different surfaces seem a logical next step to me.

Monica Olvera de la Cruz commented: Regarding the fact that your simulations are computing the same forces as in the experiments, I want to stress that

indeed, you are assuming thermodynamic equilibrium but the experiments are done on a surface. In electrostatics all boundary conditions matter, and your system is a thin slit in contact with the bulk, so all ions have different hydration depending on the layer in the bulk.

Christian Holm answered: Thank you for this comment, let me start with the latter part regarding electrostatic boundary conditions and layering. In our models this is included and in line with my previous reply, I see no reason how charge transfer or chemical reactivity should resolve this puzzle. Regarding non-equilibrium effects, again, this might play a role, but as far as possible the experiments carefully try to make sure (by extrapolating to zero speed) that they measure equilibrium effects.

Sophie Marbach asked: The scales you can probe in the numerical simulation differ from those in the experiments. But maybe more importantly, the geometry is different as well, with the SFA configuration being 2 cylinders. Even if we do a Derjaguin approximation to model the forces between the 2 plates, they have to be integrated for different distances. Can you comment on that?

Christian Holm replied: In our DFT model the walls are simple hard charged walls, but due to the periodic boundary conditions infinitely extended and all long-range forces are captured in this infinite plate geometry. Any possible curvature effects would only diminish the forces, and not enhance them. However, due to the macroscopic size of the 2 cylinders in the millimetres range, I believe that no curvature effects should be visible in the experiments.

Derek Stein said: The reduced mobility of ions in the high-density limit is reminiscent of the reduced mobility of counterions near highly charged surfaces, where the ion density is also very high. Are these phenomena related in any way? The ion mobility can be easily obtained from the trajectories of the ion obtained in the simulations presented here. It would be interesting to know the dependence of ion mobility on density. That could be compared with the author's own calculations of the counterion mobility near highly charged surfaces, like DNA.

Christian Holm responded: Thank you for your interesting suggestion. Our focus so far was purely on the static properties like screening, but it would be very interesting to look into the ionic transport properties of dense electrolytes as a function of density. The all-atom simulations would indeed provide us with all necessary data, so one could investigate effects like the one we observed in ref. 1. However, our employed DFT can unfortunately only probe static quantities.

1 S. Kesselheim, W. Müller, and C. Holm, Origin of Current Blockades in Nanopore Translocation Experiments, *Phys. Rev. Lett.*, 2014, **112**, 018101.

Serge G. Lemay remarked: In the article by Fung and Perkin (**https://doi.org/10.1039/d3fd00042g**), time scales on the order of hours are reported for the appearance of anomalous underscreening. Is it correct to believe that your simulations are fully equilibrated?

Christian Holm answered: I am not sure about Fung and Perkin's experiment, they measure over hours, since I vaguely remember that they control their surface force balance with about 1 Angstrom per second. We checked carefully that our atomistic simulations, which were run for the aqueous systems over more than a microsecond, are definitely in thermal equilibrium by looking at decays of autocorrelation times *etc.* We are fully convinced that our simulations are measuring quantities in thermal equilibrium.

Alexei A. Kornyshev commented: In a detailed, comprehensive analysis that combined simulation and theory, performed with comparison to experiments,[1] we found that between 15–20% of ions in the studied ionic liquids are free to move, all others are in clusters, the mobility of which is much slower if not zero, moreover most of them are uncharged. There is an intensive interchange between the two states, with the activation energy of ion 'excitation' from the bound to free state being close to the thermal energy, k_BT. This approved the proposed concept of an ultra-narrow band 'ionic semiconductor',[2] where the 'valence band' is the clustered state, and the 'conduction band' is the free state. This observation was also confirmed by the fact that the ionic conductivity in the ionic liquids is well reproduced by the Nernst–Einstein equation with the mobilities and the concentrations of free ions only.[2] All looks well, but such concentrations of free ions are still too large to explain the underscreening paradox.

1 G. Feng, M. Chen, S. Bi, Z. A. H. Goodwin, E. B. Postnikov, N. Brilliantov, M. Urbakh and A. A. Kornyshev, Free and bound states of ions in ionic liquids, conductivity, and underscreening paradox, *Phys. Rev. X*, 2019, **9**, 021024.
2 M. V. Fedorov and A. A. Kornyshev, Ionic liquids at electrified interfaces, *Chem. Rev.*, 2014, **114**, 2978–3036.

Christian Holm responded: Thank you Alexei for the enlightening comment.

Paul Robin asked: In Fung and Perkin's experiment, I believe that forces can be measured even at quite large distances, say 20 nm. At these scales, do you also measure something in simulations (but with a different scaling)? Or just thermal noise? Generally, simulation boxes are very small due to computation time issues. I believe that the data presented in the figures you showed, correspond to a distance of 3 or 4 nm between the two surfaces. How do you make sure that you are "measuring at the right distance"?

Christian Holm answered: Let me start out with the atomistic simulations. At 20 nm we only measure thermal noise. For the explicit water simulations in Zeman *et al.*[1] we are already at 3 nm in the noise level of $10^{-5}\ k_BT$ in the potential, although we used box lengths of over 40 nm. For the coarse-grained ionic liquids we were in the noise level at 14 nm with a box length of 50 nm and the largest screening length we have been measuring was about 1.4 nm for the coarse-grained ionic liquid, all other liquids had a lower screening length below 1 nm. For the DFT simulations we used slits of various distances, making sure we see the full decay of the pressure curves until they convergence to a constant value. This normally happened at length scales of $10/\sigma$, corresponding to roughly 5 nm.

1 J. Zeman, S. Kondrat and C. Holm, Ionic screening in bulk and under confinement, *J. Chem. Phys.*, 2021, **155**, 204501.

Lydéric Bocquet asked: The explanation of the anomalous screening effect still remains evasive and one may explore other leads. For example, at high concentrations, one is close to saturation, and the transition may be shifted in confined systems. Did you explore the phase behavior, *e.g.*, looking for other phases and signatures of phase transitions? For example, one may envision the presence of larger size clusters which may modify the screening, *etc.*

Christian Holm responded: We did not explicitly explore the phase behavior of the liquid in confinement, but we also did not observe any signature in the liquid structure that alerted us to believe that we were anywhere close to a transition. As already mentioned in the answer to Susan Perkin, long lived clusters or fluid inhomogeneities were not observed. In the previous extensive atomistic works of Zeman *et al.*[1] we were actively looking for these effects with no success in any of the investigated models.

1 J. Zeman, S. Kondrat and C. Holm, Ionic screening in bulk and under confinement, *J. Chem. Phys.*, 2021, **155**, 204501.

Yujia Zhang opened a general discussion of the paper by Fabio Cicoira: Please clarify the mechanism of the higher performance of the hydro–organogel device your report (**https://doi.org/10.1039/d3fd00065f**).

Will the vertical design work in flexible working scenarios without significant performance decrease?

Fabio Cicoira replied: Good morning. The hydro–organogel gating medium leads to higher performance, likely because of the higher ionic conductivity. However, the ion gel gated devices can be operated at higher voltage, since the water electrolysis threshold would not be an issue.

We did fabricate flexible vertical devices but with a quite low success rate. The main issue is that plastic substrates are more irregular and not as flat, with respect to glass. However, we are confident the issue will be solved soon.

Daniel Felipe Duarte Sánchez commented: In your paper, the performance differences between vertical and planar electrochemical transistors are attributed exclusively to the channel lengths obtained. However, it has been shown[1] that the charge carrier mobility of organic semiconducting polymer thin films can differ even over two orders of magnitude, because of the orientation (edge-on, face-on, end-on) of the polymer molecules with respect to the substrate. Shouldn't this orientation be considered to establish the extent of the length channel dependence on the performance of the described organic electrochemical transistors (OECTs)?

1 J. Ma, K. Hashimoto, T. Koganezawa and Keisuke Tajima, End-On Orientation of Semiconducting Polymers in Thin Films Induced by Surface Segregation of Fluoroalkyl Chains, *J. Am. Chem. Soc.*, 2013, **135**, 9644–9647.

Fabio Cicoira replied: It is a very good point which could be the object of further investigations, since we haven't studied the molecular orientation with respect to the substrate. I expect this contribution to not be very important, given the high film thickness.

Serge G. Lemay queried: It is stated in the article that "In vertical structures, the reduced channel length increases the charge carrier concentration", I do not understand this statement. Is it tied to band bending at the contacts?

Fabio Cicoira replied: This statement is not correlated to band bending at contacts. The charge carrier concentration/density is inversely proportional to the area of the channel material that is in contact with the electrolyte. In the vertical structure the area of channel material that is in contact with an electrolyte is smaller than in the planar structure. This leads to a higher charge carrier density for vertical structures.

Martin Z. Bazant said: It is quite interesting to modulate electronic currents with ions in OECTs with conducting polymers. You provide a nice summary of the field with comparisons between devices of this type, but it would also be helpful to compare to other types of solid-state iontronic memristors.[1] There has been a lot of recent work on using ions in battery-like intercalation materials to modulate electronic currents. For Li-ion battery materials in 'lithionics" this is particularly effective for materials such as LTO[2] and LCO[3] which undergo metal–insulator phase transitions as a function of intercalated lithium concentration, but the main problem is the switching time, which cannot be much smaller than milliseconds, even if the device takes advantage of surface phase transformations on electrode surfaces.[4] This is considered too slow for current hardware in neuromorphic computing and AI, but protonic devices can be much faster than lithionic devices.[5] This field is progressing quickly toward memristor devices that may be integrated in new hardware for fast neuromorphic computation.[6]

By contrast, liquid/polymer iontronic devices like yours and others in this *Faraday Discussion*, which are closer to biological neurons gating ion transport, are far slower, harder to integrate in large-scale computation, and seemingly lacking in models of active ion pumps and synaptic interfaces between neurons, which are essential for the brain to operate. What is your view on bio-inspired *versus* solid-state neuromorphic computing? What is the limit of switching times in your system, and how do the performance characteristics compare to solid-state iontronic devices?

1 A. Sood, A. D. Poletayev, D. A. Cogswell, P. M. Csernica, J. T. Mefford, D. Fraggedakis, M. F. Toney, A. M. Lindenberg, M. Z. Bazant and W. C. Chueh, Electrochemical ion insertion from the atomic to the device scale, *Nat. Rev. Mater.*, 2021, **6**, 847–867.
2 J. C. Gonzalez-Rosillo, M. Balaish, Z. D. Hood, N. Nadkarni, D. Fraggedakis, K. J. Kim, K. M. Mullin, R. Pfenninger, M. Z. Bazant and J. L. M. Rupp, Lithium-battery anode gains additional functionality for neuromorphic computing through metal–insulator phase separation, *Adv. Mater.*, 2020, **32**, 1907465.
3 N. Nadkarni, T. Zhou, D. Fraggedakis, T. Gao and M. Z. Bazant, Modeling the metal–insulator phase transition in Li_xCoO_2 for energy and information storage, *Adv. Funct. Mater.*, 2019, **29**, 1902821.
4 H. Tian and M. Z. Bazant, Interfacial resistive switching by multiphase polarization in ion-intercalation nanofilms, *Nano Lett.*, 2022, **22**, 5866–5873.
5 X. Yao, K. Klyukin, W. Lu, M. Onen, S. Ryu, D. Kim, N. Emond, I. Waluyo, A. Hunt, J. A. del Alamo, J. Li and B. Yildiz, Protonic solid-state electrochemical synapse for physical neural networks, *Nat. Commun.*, 2020, **11**, 3134.
6 M.-K. Song, *et al.*, Recent advances and future prospects for memristive materials, devices, and systems, *ACS Nano*, 2023, **17**, 11994–12039.

Fabio Cicoira responded: Martin, thanks a lot for this question.

To be honest, I am not yet into the neuromorphic field. However, the advantage I see for organic devices is the ease of fabrication and the possibility to obtain flexible-stretchable devices. The switching speed limit is considered to be in the rage of milliseconds. However, high speed devices have been recently obtained *via* the optimization of device engineering. I will definitively look into the lithionics. Thanks a lot!

Serge G. Lemay commented: The impedance plot in Fig. 2(a) of your article, exhibits behaviour reminiscent of a constant phase element, which is often associated with diffusive processes. Could you comment on the origin of this behaviour?

Fabio Cicoira answered: Please see ref. 1 for a discussion of impedence.

1 M. Azimi, A. Subramanian, J. Fan, F. Soavi and F. Cicoira, Electrical and mechanical stability of flexible, organic electrolyte-gated transistors based on iongel and hydrogels, *J. Mater. Chem. C*, 2023, **11**, 4623–4633.

Gilad Yossifon asked: Are you sure the transistor works in depletion mode? Can you get your voltage from negative to positive? Do they work in both modes?

Fabio Cicoira communicated in reply: The transistors based on PEDOT:PSS do work in depletion mode. The applied voltage would dedope the channel and gradually switch the device from the ON to the OFF state, as shown in several publications. It is however still possible to observe a small increase in current upon application of a negative gate bias, due to doping of the channel by electrolyte ions. See for instance the following publication: C. Kim, M. Azimi, J. Fan, H. Nagarajan, M. Wang and F. Cicoira, All-printed and Stretchable Organic Electrochemical Transistors Using a Hydrogel Electrolyte, *Nanoscale*, 2023, **15**(7), 3263–3272.

Amritha Janardanan commented: What is the minimum length of PEDOT/PSS channel you tried? Do you observe any decrease in transconductance after a certain point, after initially increasing, as you decrease length? I am thinking of parallel to silicon transistors where reducing the length causes off current to increase.

Fabio Cicoira answered: This is an important point. The printer we used for this experiment cannot go below 200 microns of lateral resolution, which is probably above the channel length at which contact effects become predominant. So, we did not observe a decrease of the transconductance upon decrease of the channel length.

Zuzanna S. Siwy opened a general discussion of the paper by Paul Robin: How could you reconcile what you propose in your article (**https://doi.org/10.1039/d3fd00035d**) with the previous work by Bezrukov and Winterhalter, on the importance of conformational changes of biological channels to the formation of 1/*f* noise? Could your model propose ways to mitigate 1/*f* noise?

1 S. M. Bezrukov and M. Winterhalter, Examining Noise Sources at the Single-Molecule Level: 1/*f* Noise of an Open Maltoporin Channel, *Phys. Rev. Lett.*, 2000, **85**, 202.

Paul Robin replied: Bezrukov and coworkers measured current fluctuations across a biological channel that is known to switch between different states (open/closed). They observed step-like fluctuations in the current, which they attributed to this switching effect, and they saw 1/*f* noise in this case. When they subtracted these step-like fluctuations by hand in the initial signal, 1/*f* noise disappeared, so they concluded that 1/*f* noise was created by the switching mechanism alone.[1]

However, other experiments on biological channels (*e.g.*, ref. 2) showed that 1/*f* noise can be observed even when the channel is "locked" into the open state (this can be done *e.g.* by single-channel measurements, and excluding from the statistical analysis, measurements where the channel switched to the closed state during the experiment). 1/*f* noise also seems to be a general behavior anytime one measures a charge current across a small sample connected to a large "reservoir". It has been reported in solid-state nanopores made of material much stiffer than biological channels, and in metallic or semi-conducting junctions. In these cases, no switching mechanism can account for 1/*f* noise.

Taking a step back, we can try to reconcile these observations:

– It is very possible that in the experiment by Bezrukov *et al.*, several sources of noise superimpose due to the switching mechanism.

– Or it could be that the way the authors filtered their data to "remove" the step-like fluctuations, prevent them to observe "regular" 1/*f* noise.

The former is highly probable, as a minority of other experiments on biological channels did not observe 1/*f* noise at all; probably because some other, stronger source of noise was also present.

Presently I cannot predict how any given pore will fluctuate when immersed in water during a conductance measurement; our work simply allows to extract pore fluctuations (denoted S_W in the paper) from the current fluctuations (denoted S_I). It is therefore difficult to suggest a precise way of reducing noise.

However, one can suggest general mechanisms that would lead to a lower noise level. We can plug-in different models of fluctuating pores in our theoretical framework and see how they impact the noise level – basically, the prefactor of 1/*f* noise. This is not reported in the paper, but noise is reduced when transport of ions across the pore is "anti-collective": this occurs when several ions cannot cross the pore at the same time, or that there is a finite recovery time between two passages of ions across the pore. This phenomenon is known as "refractoriness", and it can reduce the value of the 1/*f* noise prefactor (usually denoted α).

How to design a nanopore such that it exhibits such "anti-collective" transport in practice is, however, another matter, and I do not have a concrete solution. Biological channels probably achieve this through the use of molecular-scale pores with filters and ion-binding sites that only allow the passage of ions one at a time. We could try to copy this idea, but it would be quite challenging from an experimental point of view.

1 S. M. Bezrukov and M. Winterhalter, Examining Noise Sources at the Single-Molecule Level: 1/*f* Noise of an Open Maltoporin Channel, *Phys. Rev. Lett.*, 2000, **85**, 202.
2 F. Wohnsland and R. Benz, 1/*f*-Noise of open bacterial porin channels, *J. Membr. Biol.*, 1997, **158**, 77–85.

Sophie Marbach commented: I have a practical question: when you fit the experimental data, did you notice if the fits were sensitive to the range you were fitting? What is your fitting procedure? In particular what is your fitting procedure for the systems for which it appears that there are 2 regimes, yet in Fig. 2I in your article, only one exponent is reported. Could you please clarify?

Paul Robin answered: For the fitting of the exponents in Fig. 2, we used in most cases a frequency range of 5–50 Hz. Data points around 0.1 Hz have poor statistics due to the way the power spectra are computed, and the signal contains spurious peaks above 50 Hz due to electrical equipment.

That being said, the obtained exponents were quite robust and represent the data in the entire frequency range well, as can be seen in Fig. 1 and 2 (except in the few cases where the noise level was very low, where other sources of noise probably blur the data).

On Fig. 2I we report exponents that correspond to the low frequency regime. In that case, the fitting was done using only data points below 20 Hz. The high frequency range was then well described by a simple $1/f$ scaling, see Fig. 1D in our article, but we did not perform a precise fitting due to the above limitation for data points above 50 Hz. We apologize for the confusion.

Sophie Marbach remarked: In the distribution of trapping times you assume, you are fitting with an exponent $(1 + \alpha)$. For dimensional reasons, it is clear that there should be a timescale in there, does this timescale mean anything physically and how may this physical process affect the amplitude of the noise?

Paul Robin replied: We indeed need to introduce some typical timescale T in the formal definition of the trapping time distribution. This timescale serves as an infrared cut-off (as a "pure" power law distribution would not be integrable at short times).

For the sake of argument, we use the following trapping time distribution:

$P(t) = 0$ if $t < T$, otherwise $P(t) = \alpha T^{\alpha}/t^{(1+\alpha)}$ (note that the precise form of this distribution is not physically relevant, we chose this simple cut-off at t).

Tim M. Kamsma said: You seem to confirm a previous hypothesis as to why the surface chemistry results in a long-term memory timescale, which can be set in a short time. You state that ions stay in the channel for a long time due to the stop-and-go behaviour, but to me it would then seem that they also enter slowly, thus also requiring an equally long write pulse.

If the change in surface charge due to ion accumulation or depletion then is to blame, this would also be confusing to me since Langmuir processes relax as a single exponential in either direction, *i.e.* charging and discharging of the surface would also take equal time, unless you take surface-to-ion coulomb interactions into account which I believe you do not.

So to me the evidence you now find for this stop-and-go process does not yet explain why this then would translate to a long-term memory effect. I understand how the stop-and-go process can effect conductance, but I don't see yet which process exactly, is happening quickly during the write pulse yet then decays slowly over a long retention time. I would be very grateful if you could share some additional thoughts on this.

Paul Robin replied: This question I believe concerns the results presented in an earlier work,[1] where we showed that voltage pulses could be used to update the conductance of a nanochannel with long-term memory.

What matters for the modification of the surface charge is, in my interpretation of the process, not the duration of the voltage pulses, but the total charge that goes through the pore. A short, albeit strong enough, voltage pulse can therefore modify the surface charge. Note that it does not mean that the modification itself is fast (one must still wait a fair amount of time for the conductance to stabilize after the voltage pulse is applied).

I am not sure I fully understand your remark on Langmuir processes: in the previous paper, we did postulate that there where two microscopically relevant timescales (adsorption and desorption times, the latter being much longer), and the memory model was based on a Markov process which is identical to the one described in our present paper (Section 4.4) – except that here we looked at fluctuations around a steady state, rather than the response to an unsteady external field.

Note that in the limit where desorption time $\gg$ adsorption time, fluctuations around the steady state only allows access to the adsorption time (see eqn (41) and (42) and the following paragraph in our article). Maybe that is the source of confusion between short- and long-timescales.

1 P. Robin, T. Emmerich, A. Ismail, A. Niguès, Y. You, G.-H. Nam, A. Keerthi, A. Siria, A. K. Geim, B. Radha and L. Bocquet, Long-term memory and synapse-like dynamics in two-dimensional nanofluidic channels, *Science*, 2023, 379, 161–167.

Frédéric Kanoufi said: As a follow-up to Sophie Marbach's question, did you consider the case of surface diffusion? Is it included in the sub-diffusion regime or in the adsorption–desorption one? I also wonder if the adsorption regime can show some cooperative form or local influence. To be more explicit, do you think that a preferred adsorption on one 2D surface might induce a local charge (or chemistry) change and why not a preferred later adsorption on the opposite 2D surface? One could then see succession of adsorption/desorption between opposite plates.

Paul Robin answered: The short answer to these questions it that, currently, we do not know how to discriminate between one scenario or another.

Our paper should be seen as a first step towards deciphering these current fluctuations. Up until now, a lot of attention has been drawn to $1/f$ noise, which had a very unclear origin, and could not easily be attributed to any given physical process. We showed that it was possible to extract the "meaningful" part of the noise, as the $1/f$ scaling seems to originate from diffusive motion in the reservoirs. With that "out of the way", deviations from simple diffusive motion can be analyzed in more detail.

In practice, the mechanisms that you mention (surface diffusion and adsorption with cooperativity) could be fitted to our theory, which simply provides a link between fluctuations measured at the electrodes (denoted S_I in the paper) and fluctuations within the pore (denoted S_W). One problem is that from the graph of S_W alone one cannot really discriminate between one precise scenario and another, with no external information about how ions interact with the

surfaces of interest (NB: this is in part because the power spectrum alone does not contain all the statistical information about the fluctuations – it is just the modulus of the Fourier-transformed correlation function; the complex phase is lost). It is also not clear to me how to draw a well-defined line between surface diffusion and adsorption. In some cases, adsorbed ions are known to have a non-zero mobility, so that conduction can be seen as the sum of two effects: motion of ions in the bulk of the channel and on its surface (see *e.g.* ref. 1). While not reported in the paper, I initially include these two components of conduction in the model of adsorption–diffusion presented in the last section of the paper. It turned out to be unnecessarily complex for the general description of our experimental data, but could be relevant in other contexts, or for a more accurate description. The mechanisms you mention are of great interest, in particular because inducing "collective adsorption" could be a way of modulating the noise level. To ascertain whether they are relevant or not, however, we would probably need more experimental data and more information about the surface physico-chemistry (*e.g.* using spectroscopy techniques to complement the data).

1 B. Grosjean, M.-L. Bocquet and R.Vuilleumier, Versatile electrification of two-dimensional nanomaterials in water,*Nat. Commun.*, 2019, **10**, 1656.

Sophie Marbach added: I want to comment on Frédéric Kanoufi's question. From what Jean Comtet told me, in previous experiments,[1] the particles are either stuck on the surface, in which case they observe them; while in between jumps the particles move too fast for them to be resolved. So it could either be that getting out of the trap is a sub-diffusive process or diffusion on the surface itself is somehow sub-diffusive. Whether sub-diffusion comes from long adhesion times or friction with the surface on which they diffuse is therefore not clear.

1 J. Comtet, B. Grosjean, E. Glushkov, A. Avsar, K. Watanabe, T. Taniguchi, R. Vuilleumier, M.-L. Bocquet and A. Radenovic, Direct observation of water-mediated single-proton transport between hexagonal boron nitride surface defects, *Nat. Nanotechnol.*, 2020, **15**, 598–604.

Paul Robin answered: I completely agree with this point. The current analysis does not allow to discriminate between one scenario and the other. Since noise measurements only give access to global correlations, they would need to be complemented by other types of insight (simulations, spectroscopy, *etc.*) to obtain a more precise conclusion.

As a side note, I would add that we do not claim that the $1/f^{1+\alpha}$ power spectrum observed has the same microscopic origin as the subdiffusive transport reported by Jean Comtet and coworkers (which, I believe, is specific to protons on the hexagonal boron nitride surface). I merely used it as an example showing that power law waiting times do exist at the microscopic level in nanofluidic experiments.

Christian Holm asked: In your theoretical analysis you used the Poisson–Nernst–Planck (PNP) model to come up with a noise scaling $1/f^{(1+\alpha)}$. Would you get the same scaling if you start including hydrodynamics into the PNP model, or would you expect some new features?

Paul Robin answered: We currently do not know as we did not consider any effect of hydrodynamics in the model.

Qualitatively, I expect that two aspects could play a role:

– Hydrodynamic interactions between ions: in most cases (say at the Debye–Hückel level), they yield corrections that are similar to that of electrostatic correlations and are usually weaker. I do not expect them to be relevant here: they act on a length scale comparable to the Debye length, and thus matter only at very short timescales (∼100 ns) and very high frequencies, which we do not consider here.

– Electro-osmosis: electro-osmotic flows can generate additional conduction in nanochannels with charged walls. In that case, the electro-osmotic flow plays a role equivalent to an additional electric field within the channel. Therefore electro-osmosis should not modify the conclusion of the article.

In addition, hydrodynamics within the pore can easily be included in the model, mattering only for the "transport process" W, whereas our model is interested in linking this transport process to fluctuations at the electrodes.

Of course, one would need to carry out a more detailed and quantitative analysis to conclude that hydrodynamics can be safely neglected.

Frédéric Kanoufi queried: As you shared some optical images to illustrate your talk, I'm wondering if you are considering implementing single molecule fluorescence microscopy as a complementary observation? It would be interesting first to observe the diffusion/adsorption regimes discussed, but also to exploit and correlate the electrical noise analysis to another noise analysis (optical noise). Do you think this could be possible in the near future or could you explain what challenges should be addressed?

Paul Robin answered: The authors of the paper I briefly mentioned are already trying to use their single-molecule microscopy technique to visualize ion transport in nanofluidic channels. They recently submitted a preprint.[1]

This definitely would be of great help in the understanding of ion transport fluctuations. Indeed, our paper highlights the fact that ionic current measurements using electrodes in large reservoirs, far from the nanochannel, introduce $1/f$ noise which is not a signature of fluctuations of the pore itself, but a diffusive noise of ions in the reservoirs, so that the total signal has to be "decyphered" before being exploited to characterize the pore.

Optical techniques would provide direct access to ion fluctuations at the nanoscale, similar to what can be directly measured in MD simulations (where one can simply compute the velocity–velocity correlation function of all ions within the pore, with no need for electrodes, *etc.*). In a recent Perspective article we tried to suggest ways of using such complementary approaches to advance the knowledge of nanofluidic systems.[2] Optical techniques could also include SFG measurements for example. This is definitely within reach in the next few years of research. There are, however, a couple of challenges: first of all, most optical techniques come with certain set-up constraints, so that not all nanofluidic systems could be probed using them. Enclosed devices that are not transparent may prove a little hard to access… In addition, the technique reported above is based on the presence of chemically and optically active defects on the surface of boron nitride; it is not clear if similar results could be obtained using other

materials. 2D nanochannels made with boron nitride (which is transparent!) are, however, 'ideal candidates' for these kinds of experiments.

1 N. Ronceray *et al.*, Liquid-activated quantum emission from pristine hexagonal boron nitride for nanofluidic sensing, *arXiv*, 2022, Preprint, arXiv:2204.06287v3 [cond-mat.mes-hall], **https://arxiv.org/abs/2204.06287**.
2 P. Robin and L. Bocquet, Nanofluidics at the crossroads, *J. Chem. Phys.*, 2023, **158**, 160901.

Daniel Felipe Duarte Sánchez commented: If in order to achieve such deviations from Hooge's law, a device like the one you fabricated is required, what do you think are the general conditions for this behaviour to arise? For instance, in solid state devices, trap states are present as defects in the material, do you think such traps could be harnessed in the same way to obtain an absorption-like effect that would produce a Hooge's law deviation?

Paul Robin replied: From the model, deviations to Hooge's law are observed whenever ion transport within the channel is correlated (either in time or between ions). I would therefore expect that, as you suggest, traps and defects would result in such deviations. This is actually what we proposed to model the behaviour of channels made of activated graphite (we assumed that ions could adsorb on surface defects). Electrons in most solid-state devices actually have the same diffusive behaviour as dissolved ions (as long as the sample size is larger than their mean free path), so the same conclusions should apply in your example.

Serge G. Lemay remarked: In your discussion of heavy-tailed residence times, you introduce a cut-off time T in eqn (37) of your article, which would suggest significant correlations between events. Should one ascribe a physical meaning to this cutoff time?

Paul Robin responded: This time scale was introduced as a regularization parameter: no probability distribution can be a "pure" power law on the entire real axis (otherwise its integral would diverge and could not sum up to 1).

What to make of the specific value that we extracted from the fitting process is, however, unclear. We found $T = 100$ ns, which would correspond to some microscopic timescale; for example, it is comparable to the Debye time (time needed for an excess of charge to spread out due to electrostatic interactions).

Please note that the specific shape of the distribution that we used (with a sharp cut-off for waiting times below T) is unphysical at short times. We chose it for the sake of mathematical convenience: we were interested in capturing the long- rather than the short-timescale dynamics (the latter being inaccessible to noise measurements anyway, as noise from the electrical set-up makes the data for frequency above 100 Hz impossible to analyze).

Martin Z. Bazant asked: Your 1D toy model of pink noise is quite elegant, with a homogenous reaction term added to a diffusion equation to represent random noise. Such models are common in chemical engineering, and the scaling of the reaction term relative to the diffusion term is controlled by the Damkoller number, Da. Your model considers the high frequency limit where the reaction is effectively fast, Da $\gg$ 1, in which case boundary effects are screened over a distance 1/sqrt(Da). What happens in the opposite limit of t = low frequency? I

suppose geometrical effects become important, and perhaps the model loses validity?

Paul Robin answered: I am not familiar with the literature on chemical engineering, so I may not have fully understood your question.

In the toy model, we consider a diffusion equation with (1) a uniform source term (which may fluctuate and depend on time) and (2) a fully absorbing boundary condition on the electrodes. So, unless I misunderstood your point, we do not have a uniform reaction term in the model.

That being said, we did perform a few approximations, for example by saying that the electrode plays the role of a fully absorbing boundary condition: more realistically, we would need to model the redox reaction occurring at the electrode. Overall, I would expect that the high-frequency limit is more problematic that the low-frequency one, because for example we can no longer assume that the reaction on the electrode is instantaneous. This is consistent with experiments, where, $1/f$ noise disappears above say 50–100 Hz, but is quite robust at low frequency.

Alice Thorneywork added: Following on from the previous point, in an experiment, how far away from a channel does your probe need to be to observe a $1/f$ scaling in the noise with the origin you propose in your paper?

Paul Robin answered: Typically, measurements on $1/f$ noise are done on the frequency range 1–100 Hz. The model we have developed predicts that $1/f$ noise disappears at a very low frequency (say 1 μHz) corresponding to the diffusion time between the channel and the probe, which are separated by $\sim$1 cm in a typical nanofluidic experiment.

To raise this cut-off frequency up to 1 Hz, one would need to probe the channel at a distance of about 10 micrometers.

Christian Holm commented: I felt a little bit confused during your presentation about the $1/f$ noise induced by the reservoir, where the same noise can also be found in the channel. If I consider experimentally, let's say, a biological pore like α-hemolysin or aerolysine embedded in a membrane, so that I have rather macroscopic reservoirs and microscope pores: what can I learn about those pores from measuring the noise? Is the noise then not dominated by the reservoirs? If I would measure the noise in an atomistic simulation purely in the channel, could I predict then how the noise would look in the larger system (pore plus two reservoirs)? And what would I learn from such a measurement for the channel under consideration?

Paul Robin answered: The main take-away message of this work is that reservoirs seem to "deform" noise and can be responsible for $1/f$ noise. In your example, meaningful information about the biological pore could be extracted from the measured signal by removing this reservoir noise. In an atomistic simulation, one can directly compare the velocity–velocity correlation function of all ions within the pore (or in fact any correlation function of ions within the pore), as one has access to the full "molecular movie". There is thus no need to "disentangle" the fluctuations in the case of MD simulations.

Note, however, that one should be careful when comparing simulations and experiments, as similarly-named quantities are often not defined and computed in the same way. In experiments, one measures a global electrical current on an electrode. In simulations, one typically sums the velocity of all ions within the simulation box. In both cases this should give the ionic current across the pore, but there is no reason for the two quantities to fluctuate in the same way.

Robert Johnson highlighted: Noise in current–time measurement of ion flux through nanopores is a very interesting topic, and can sometimes tell us about analytes trapped within the nanopore itself. We have observed previously that dsDNA of differing base-pair compositions trapped inside the α-hemolysin nanopore results in different noise signals.[1] Specifically, noise in the current–time measurement increases as the stability of the duplex (as measured by the melting temperature, T_m, of the duplex decreases).

1 R. P. Johnson, A. M. Fleming, Q. Jin, C. J. Burrows and Henry S. White, Temperature and Electrolyte Optimization of the a-Hemolysin Latch Sensing Zone for Detection of Base Modification in Double-Stranded DNA, *Biophys. J.*, 2014, **107**, 924–931.

Paul Robin answered: Thank you for sharing this study, which I was unaware of. There were indeed a few examples where blockade events in a biological pore were successfully attributed to a microscopic structure (see *e.g.* ref. 1). The challenge here was to analyze current fluctuations which do not take the form of step-like blockade events, and whose physical interpretation is much less clear. However, in both cases the philosophy is the same: extracting meaningful physical information from current noise.

1 S. M. Bezrukov and M. Winterhalter, Examining Noise Sources at the Single-Molecule Level: 1/*f* Noise of an Open Maltoporin Channel, *Phys. Rev. Lett.*, 2000, **85**, 202.

Giovanni Pireddu opened a general discussion of the paper by Felipe Jiménez-Ángeles: Have you looked at conduction modes perpendicular to the material surfaces?

Felipe Jiménez-Ángeles responded: Thank you for your question. Indeed, it would be very interesting to investigate the conduction in the perpendicular direction. For that, one has to consider a time-dependent field. However, we have yet to look at it.

Paul Robin commented: I believe you said that you observe more ion pairs for monovalent ions (NaCl) than for multivalent ($CaCl_2$, *etc.*) ions, and more pairs at high field than at low field (**https://doi.org/10.1039/d3fd00028a**).

If ion pairs originate from strong interactions between ions, I would expect the opposite: multivalent ions attract one another more strongly and should form more pairs. And the electric field should tear pairs apart.

How do you make sense of this apparent paradox?

Felipe Jiménez-Ángeles answered: Thank you for the question. This is a very interesting point. We see that the anions around cations are located at three different separation distances: (1) a layer when they are in direct contact without

mediation of another ion/molecule; (2) a second layer, when the pairing is mediated by a water molecule; and (3) a third layer, when the pairing is mediated by more than two ions/molecules. Indeed, we see that the number of ion-pairs associated at the second and third layers decreases as the field strength increases (as you pointed out). However, the associated ions at direct contact increases as the field strength increases. We hypothesize that there is a decrease in the energy cost to remove a water molecule from in-between two ions as the field strength increases. Therefore, we see more direct association as the field strength increases. For our monovalent cations there is mostly direct association with the anions. Since more water is removed from in-between the ions there is also an increase as the field strength increases.

Please note that my co-author Ali Ehlen helped to respond to these questions.

Alexander Schlaich said: Firstly, in general, in a confined system, one obtains a local (or non-local) relation for the dielectric permittivity profile depending on the electrostatic boundary conditions (see *e.g.* ref. 1–3). That is, the parallel and perpendicular dielectric constants given in eqn (9) and (10) of your article, use volume averages – which volumes did you use here and why? Note, that there is a rigorous way to define a dielectric dividing plane similar to the Gibbs surface concept, see ref. 4.

Secondly, in your simulations, how did you determine the number of water molecules in the slit?

1 V. Ballenegger and J.-P. Hansen, Dielectric permittivity profiles of confined polar fluids, *J. Chem. Phys.*, 2005, **122**, 114711, DOI: **10.1063/1.1845431**.
2 H. A. Stern and S. E. Feller, Calculation of the dielectric permittivity profile for a nonuniform system: Application to a lipid bilayer simulation, *J. Chem. Phys.*, 2003, **118**, 3401–3412, DOI: **10.1063/1.1537244**.
3 D. J. Bonthuis, S. Gekle and R. R. Netz, Profile of the Static Permittivity Tensor of Water at Interfaces: Consequences for Capacitance, Hydration Interaction and Ion Adsorption, *Langmuir*, 2012, **28**, 7679–7694, DOI: **10.1021/la2051564**.
4 A. Schlaich, E. W. Knapp and R. R. Netz, Water Dielectric Effects in Planar Confinement, *Phys. Rev. Lett.*, 2016, **117**, 048001, DOI: **10.1103/PhysRevLett.117.048001**.

Felipe Jiménez-Ángeles replied: Thank you for sending these references; they are very useful. I am glad that you raised these questions. Indeed, the system's volume is a very important parameter in determining the dielectric constant. To calculate the system's volume we employed the center–center separation between the two graphene sheets, namely, $L_z = 1.38$ nm. Please notice that the water layer is $L_w = 0.97$ nm, approximately, whereas the slab is placed in a simulation box of $L = 8$ nm. We noticed that the results are different using L_w to calculate the dielectric constants. Based on the references that you provided I see potential lines of interest for future research.

For your second point, the number of water molecules in the slit channel is determined by equilibrating the channel with a reservoir using the configuration shown in Fig. S1 in the ESI of our paper (**https://doi.org/10.1039/d3fd00028a**). When the equilibrium number of water molecules is determined, we simulate the slit separately using periodic boundary conditions in the x and y directions.

Alexander Schlaich added: When you use conductive surfaces in your simulations, there should be a term corresponding to the surface polarization in the fluctuation–dissipation relation. Is this correctly included?

The formalism you apply to average over the perpendicular dielectric permittivity profile applies only to the case when no free charges are present, *i.e.* for a divergence-free displacement field perpendicular to the surface. How about the presence of salt in your simulations?

Felipe Jiménez-Ángeles replied: Thank you for your insightful questions. In our simulations we model the conductive surfaces by imposing a constant surface potential which leads to induced surface polarization charges that are calculated at every time step in the simulations. This polarization charge fluctuates in time and in space, and the total electrode's charge fluctuates around a mean value. The polarization fluctuations have a Gaussian distribution and the mean value is zero for grounded surfaces. These polarization charges affect the behavior of the confined molecules. We investigate the current form using the particle velocities and we observe a non-linear trend as a function of the applied field. The extra contribution and the deviation from the linear trend are consequences of the polarizable surfaces and the confinement. This contribution should be reflected in a generalized fluctuation–dissipation relation but we have not derived those relationships. We calculate the current based on the simulation velocities.

We used the formalism to calculate the dielectric constant based on the polarization fluctuations. Indeed, this formalism considers the fluctuations from dipoles and multipoles. Therefore, in our calculations we only included the fluctuations from the water molecules, not from the ions.

Alexei A. Kornyshev remarked: Schmickler's group in their DFT study[1,2] have shown that position of the 'image surface' in a pore; is outside the edge of a gold electrode, and inside for a graphite electrode; this may help to explain what you observe. On another point: our previous study[3] has shown very strong variation of the diffusion coefficient of ions in a nanopore of an electrode with the electrode potential, which has not been experimentally verified yet. Do you see any signatures of such effect in you studies?

1 A. Goduljan, F. Juarez, L. Mohammadzadeh, P. Quano, E. Santoz and W. Schmickler, Screening of ions in carbon and gold nanotubes – a theoretical study, *Electrochem. Commun.*, 2014, **45**, 48–51.
2 W. Schmickler, A simple model for charge storage in a nanotube, *Electrochim. Acta*, 2015, **173**, 91–95, DOI: **10.1016/J.Electacta.2015.04.177**.
3 S. Kondrat, P. Wu, R. Qiao and A. A. Kornyshev, Accelerating charging dynamics in subnanometer pores, *Nat. Mater.*, 2014, **13**, 387–393.

Felipe Jiménez-Ángeles answered: Thank you for the comments and for passing the references on the work by Schmickler's group and from your group. These are interesting and useful. In relation to the increased diffusion of ions with potential from the electrodes. This is certainly an important point that we have not investigated yet but we will certainly consider it in the future. Thanks for this question.

Christian Holm remarked: Thanks for your interesting talk. Do you have a physical picture of why the conductivity is enhanced for the case of a constant potential wall in contrast to the constant charge situation? Another question I had is why did you not consider comparing the difference in ionic diffusivity for the case of polarizable and non-polarizable surfaces? This would already hint at the

behaviour for the conductivity *via* the Nernst–Einstein relation without applying any field. The last question I have is related to the applied electric fields. Did those correspond to experimental values or are you applying very high fields that are outside the linear response regime?

Felipe Jiménez-Ángeles replied: The picture we have of the increased ionic conductivity in confinement by polarizable surfaces (conductors) is that the surfaces screen the electrostatic repulsion between equally charged ions. This is mainly observed for multivalent cations. We observe an enhanced correlation between the cations. The pair correlation functions g++(r) reveal that cations may approach other cations at high electric fields, E_x. This is only observed in confinement by conductors but not by non-polarizable surfaces. In the pair correlation functions we observe peaks that imply clustering is mediated by the anions. We observe that at low E-fields, divalent and trivalent cations tend to be apart from other cations, however, the tendency to approach between cations increases at high fields in the polarizable systems. The fact that we observe it only at high fields also indicates a contribution from the water polarization.

Your question about comparing ionic diffusivity is a very important point. At this time I do not have the precise comparison between the diffusivities but we will certainly investigate the differences. However, it is important to mention that the Nernst–Einstein relation gives a limiting constant value of the ionic conductivity. This relationship does not capture the non-linear behavior of the ionic conductivity. In our results, not only is the conductivity enhanced, but also the I–E curve is non-linear. This implies that the conductivity is not constant but it depends on the applied electric field. In our simulations the applied electric field goes beyond the linear regime. The higher differences between conductors and non-conductors are observed in the high field regime.

Susan Perkin said: Just like in many simulation works on related systems, in your work it is necessary to apply really large electric fields (above the dielectric break-down limit of the materials concerned) in order to observe the interesting features. Why is this?

Felipe Jiménez-Ángeles responded: Dear Susan, Thank you for your question. Indeed, our results show only little differences between the systems with polarizable surfaces and non-polarizable surfaces except at very high fields. This is due to the image plane position considered in this work, namely, the location of the polarization charges. In the model discussed in this paper, the polarization charges are located at the center of the electrodes' atoms. The result is that the effect of polarization is minor except at very high fields. In our later article (currently in revision, see ref. 1), we discussed the effect of placing the image plane at different locations. Depending on the material, the polarization plane has to be placed in different locations. This implies that two materials have different image plane locations, even if both are conductors. In this later work, we found that surface polarization has a significant effect by considering the plane on the electrode's surface not only at high fields but at all the fields.

1 P. Santos, F. Jiménez-Ángeles, A. Ehlen and M. Olvera de la Cruz, Modulation of ionic conduction using polarizable surfaces, *arXiv*, 2023, preprint, arXiv:2306.10214.

Paul Robin addressed Felipe Jiménez-Ángeles and Ali Ehlen: In your simulations, what does the conduction dynamics look like?

Pairs breaking up, clusters of ions moving together?…

Felipe Jiménez-Ángeles replied: For monovalent ions, we primarily see more "tighter" clusters and chains that move when they carry a net charge. For the higher valency ions (which we believe are more strongly solvated), the net non-natural clusters are loser and therefore qualitatively break and reform more easily.

PS: Ali Ehlen collaborated in this response.

Yan Levin said: What is the size of the ions that you are using. I would expect that smaller ions will be more strongly hydrated and that electric field will not be able to remove the water molecules from between cations and anions.

Felipe Jiménez-Ángeles answered: Dear Yan, thank you for your question, this is a very good point. The ions diameters are 3.3, 2.4, and 3.75 angstrom for the monovalent, divalent, and trivalent cations, respectively. The anion diameter is 4.4 angstrom. It is true that the cations dehydration would be more energy unfavorable but it would be more favorable for the Cl^- ion because is bigger. When they for pairs it is probably the anion that releases the water.

Paul Robin addressed Ali Ehlen and Felipe Jiménez-Ángeles: (In relation to Ali Ehlen's remark that, in the case of multivalent ions, they saw loosely connected "trains" of ions moving together) I believe this is similar to the behaviour I observed in simulations of 2D nanochannels (height 1 nm, made of dielectric material) some time ago. We eventually came up with a theory to model this kind of collective conduction, giving rise to a non-linear (∼power-law) relation between the applied electric field and the conductance. This seems to be (at least qualitatively!) in agreement with what you report.[1]

See in particular Fig. 2C (the "train" does seem tightly connected, but this was with a 2–2 electrolyte. I also looked at 2–1 electrolytes like $CaCl_2$ and the train was a lot "looser" – not reported in the article) and eqn (7) of main text. The model of the collective transport corresponds to Sections 3.4 to 3.7 of ESI.

Note that we also looked at the effect of the metallicity of the channel walls in a follow up study. Though we did not look at this collective behaviour in particular in this case, we measured numerically a conductance which seems to indicate the same non-linear effects.[2]

Side note: You might also be interested in a last paper, which was not centered on 2D nanochannels but on nanotubes, although in a similar spirit.

A common problem in simulation is "how many ions to put in the box", because in nanochannels the concentration may be different from the reservoirs due to entry energy barriers. We proposed a solution in the case of nanotubes;[3] similar results could easily be obtained for 2D nanoslits with metallic/dielectric/ *etc.* walls.

1 Robin, Kavokine and Bocquet, *Science*, 2021.
2 Kavokine, Robin and Bocquet, *J. Chem. Phys.*, 2022.
3 Robin, Delahais, Bocquet and Kavokine, *J. Chem. Phys.*, 2023.

Felipe Jiménez-Ángeles answered: Dear Paul, thank you for sharing these references and for your comments. Indeed, our results seem to agree qualitatively with your results. It is interesting that in our simulations the conductive walls enhance the non-linear ionic conduction more than the conductive materials. However, I see qualitative differences between our results and yours that could be due to the ionic valences and the channel separation distances. I think that there is room to extend this study.

Amritha Janardanan remarked: What is your explanation for why the electric field removes the hydration shell?

Felipe Jiménez-Ángeles responded: Dear A. Janardanan, Thank you for your question. The effect of the external field on water is the orientation in the direction of the field. It seems that the water orientation induced by the external field is competing with the orientation imposed at the hydration shell. Therefore, the ions release the water when the energy penalty of maintaining it is too high. The position of the released water is compensated by the counterions that form a close association with the ions. Therefore, we see a peak in the anion–cation pair correlation function while the cation–water pair correlation function peak decreases.

Conflicts of interest

There are no conflicts to declare.