

## Iontronic dynamics: general discussion

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DOI: 10.1039/d3fd90032k

**Sanli Faez** opened discussion of the paper by Tanja Vidaković-Koch: In the reported measurements, for example in Table 1 of your paper (<https://doi.org/10.1039/d3fd00030c>), the specific energy consumption is increasing with increasing frequency, but all values are still lower than the steady state value. What explains the change between DC and AC at the lowest frequency? Which other mechanisms are involved and which frequency is expected to be the optimum of required specific energy?

**Tanja Vidaković-Koch** replied: The reason for the difference between the steady state (DC response) and the AC response for high amplitude inputs at low frequencies and other frequencies is the DC-component, a nonlinear non-periodic term. The DC-component is not time dependent (*i.e.*, non-periodic), but it is frequency dependent. The model we use has no frequency dependence of this term for the potential as input. The reason for this is the assumption that the potential is not affected by the ohmic drop (which is not the case in practice, so the DC-component is actually a frequency dependent term). When current is the input, the DC-component shows a frequency dependence, so this example is used to illustrate the effect of frequency (please note that the DC-components for potential and current as inputs are expressed by different terms, however the trend should be qualitatively the same (see the main manuscript; <https://doi.org/10.1039/d3fd00030c>)).

Based on eqn (22) (main manuscript), the specific energy consumption for current as input is defined as:

$$W_{\text{sp,i,dyn}} = \frac{E_{\text{mean}}}{FE_{\text{i,dyn}} M_i / (n_{\text{e,i}} F)}$$

where  $E_{\text{mean}}$  is the mean potential value under dynamic conditions,  $FE_{i,\text{dyn}}$  is faradaic efficiency of component  $i = \text{CO}$  or  $\text{H}_2$  under dynamic conditions and  $M_i$  and  $n_{e,i}$  are molecular weight of component  $i$  and number of exchanged electrons and  $F$  is the Faraday constant.

In Fig. 1 here, we show how the CO partial current,  $E_{\text{mean}}$ , CO faradaic efficiency and specific energy consumption change with respect to frequency at different amplitude values of input current. The zero amplitude values correspond always to steady state conditions. As one can see at high frequencies there is no improvement due to dynamic conditions. The improvement is observed only at low frequencies. We can see that specific energy consumption is decreasing with a decrease in frequency, which is here due to a decrease in mean potential and an increase in faradaic efficiency. In the experiment we observe that specific energy consumption is decreasing with a decrease in frequency. In the experiment we do not observe a plateau at low frequencies but a further decrease. The reason can be the influence of mass transport, which is not considered in the model. Our recent experiments (not shown here) demonstrate that under conditions like in Table 1 of the main manuscript, the hydrogen reaction is more influenced by the

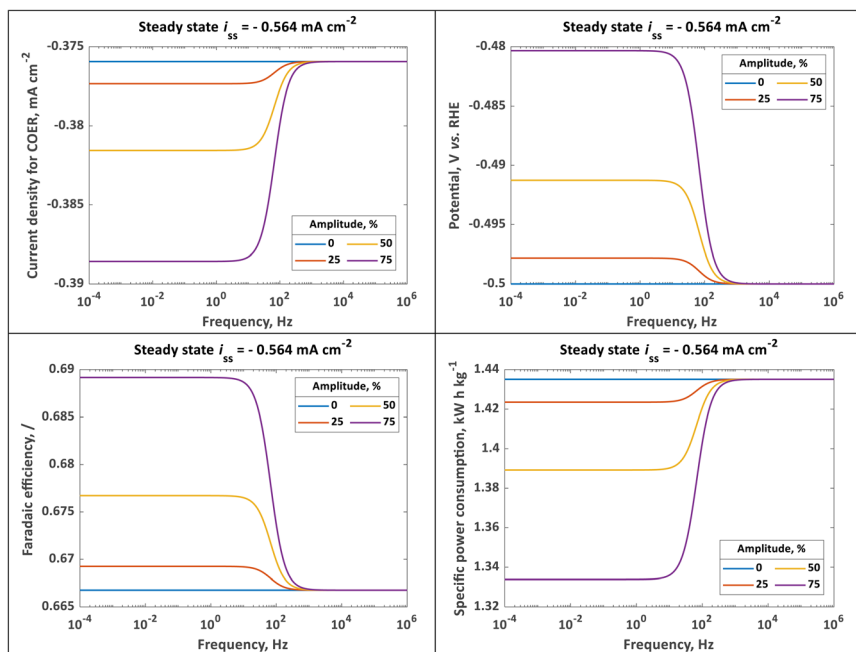


Fig. 1 Upper panel left: partial CO current densities at steady state (0%) and different input amplitudes (25–75% of  $i_{\text{SS}}$ ) showing an increase in partial CO current densities with increasing input amplitude; upper panel right: mean potential values at steady state (0%) and different input amplitudes (25–75% of  $i_{\text{SS}}$ ) showing a decrease in overpotential (the potential becomes more positive) under dynamic conditions; lower panel left: faradaic efficiency at steady state (0%) and different input amplitudes (25–75% of  $i_{\text{SS}}$ ) showing an increase in faradaic efficiency at dynamic conditions; lower panel right: specific energy consumption at steady state (0%) and different input amplitudes (25–75% of  $i_{\text{SS}}$ ) showing a decrease in the specific energy consumption under dynamic conditions compared to steady state conditions.

mass transport, while the CO reaction less. Mass transport limitations usually result in a decrease in hydrogen partial current, which then will result in an increase in CO faradaic efficiency (for input current mean current value is constant). Therefore in the present case low frequencies are more favorable. This is not always the case, for example if there is only a single reaction, which is mass transport limited, the DC-component will be maximum in the middle frequency range (see for example ref. 1).

1 L. A. Živković, S. Kandaswamy, M. Petkovska and T. Vidaković-Koch, Evaluation of electrochemical process improvement using the computer-aided nonlinear frequency response method: oxygen reduction reaction in alkaline media, *Front. Chem.*, 2020, **8**, DOI: [10.3389/fchem.2020.579869](https://doi.org/10.3389/fchem.2020.579869).

**Serge G. Lemay** requested: In the quasi-steady-state model discussed here, the enhanced performance originates from the electrode being biased part of the time at a more favourable potential. Under the same assumptions, the model would predict even better performance if the electrode was simply biased at a DC potential corresponding to the most favourable potential explored during AC actuation. Could you comment on this?

**Tanja Vidaković-Koch** responded: The origin of enhancement under high amplitude AC actuation is the nonlinearity of the electrochemical process. If the electrochemical process would behave linearly with respect to potential, no enhancement would be observed (this is the case in linear AC actuation (electrochemical impedance spectroscopy)). Therefore the origin of the improvement is not the condition that the electrode is being biased part of the time at a more favourable potential.

In Table 1 here we present faradaic efficiencies and specific energy consumption at a steady state value of  $-0.5$  V and two other steady state values which correspond to lower and upper bounds of the potential during a dynamic experiment at the amplitude of  $0.2$  V ( $-0.3$  and  $-0.7$  V respectively). In the steady state experiment the faradaic efficiency is increasing with an increase in overpotential (from  $-0.3$  V to  $-0.7$  V), as you also expected. The faradaic efficiency under dynamic conditions (mean potential  $-0.5$  V) is higher than under steady state conditions (steady state potential  $-0.5$  V). If we see how the values of the specific energy consumption are changing under different conditions than we see that the lowest specific energy consumption is obtained under dynamic conditions. Fig. 2 here displays two graphs showing the effect of dynamic conditions at different steady state values and different amplitudes. The effect of dynamic conditions is always positive, but it is more significant at lower overpotentials (e.g.

**Table 1** Faradaic efficiencies and specific energy consumption under steady state and dynamic conditions

Operation mode	Steady-state			Dynamic
Voltage, V	$-0.5$	$-0.3$	$-0.7$	$-0.5, A = 0.2$ V
$FE_{CO}$ , —	0.667	0.347	0.883	0.789
$W_{sp,CO}$ , kW h kg <sup>-1</sup>	1.435	1.653	1.518	1.213

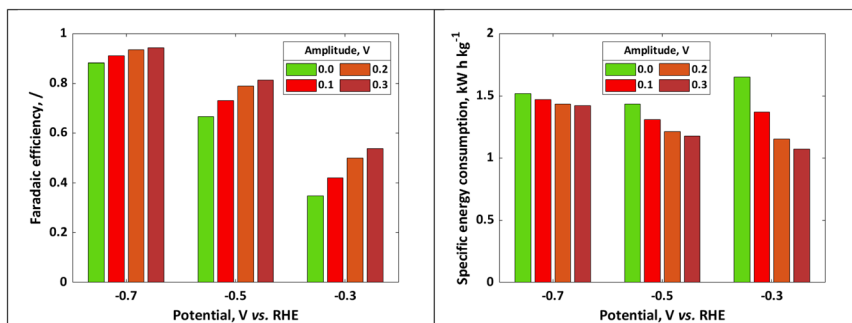


Fig. 2 (Left) Faradaic efficiencies at different mean potential values and different amplitudes (amplitude value of 0.0 V corresponds to the steady state condition, while amplitude values higher than zero indicate dynamic conditions) and (right) specific energy consumption under same conditions.

–0.3 V steady state potential). The main reason to perform experiments dynamically is to reduce the energy requirement of the process, and to achieve higher product selectivity/productivity at lower overpotentials and this is demonstrated in Fig. 2 here.

**Frédéric Kanoufi** asked: If I understood correctly you are comparing the FE of sinusoidal pulse modulated electrolysis with that of regular electrolysis. I wonder if you have considered other pulsed methods such as pulsed rectangular waveform or pulsed triangular waveforms? In this respect the question is about: to what extent is it important to explore the whole potential region of the kinetics or is it just related to renewing the electrode surface (pulse rectangular waveform)?

Moreover, to maybe better visualize the response of the device I wonder if you could present the  $i$ - $E$  response of the system for example in Fig. 3 of the main manuscript (<https://doi.org/10.1039/d3fd00030c>) (instead of  $i$ - $t$  and  $E$ - $t$ ) which is more visual for electrochemists.

**Tanja Vidaković-Koch** replied: We have used sine waves, both theoretically and experimentally. In Fig. 2 of the main manuscript (<https://doi.org/10.1039/d3fd00030c>), we also show experimental results for triangular waveforms. Square (rectangular) waveforms can also be implemented. Triangular and square waves are combinations of sine waves with different frequencies. From the point of view of the method, any of these waves can be explored. The derived theoretical functions are independent of the waveform. In terms of the potential range, we were interested in how dynamic operation affects CO selectivity in different potential ranges. Which potential range to investigate depends on the particular application. In general, the goal is to show that one can improve the selectivity and specific energy consumption by dynamic operation, so low overpotentials are of more interest. The observed effect also occurs in the regions where the catalyst surface does not change, so it has nothing to do with the renewal of the catalyst surface (although this can be also a beneficial effect, depending on the potential range). The data in Fig. 3 of

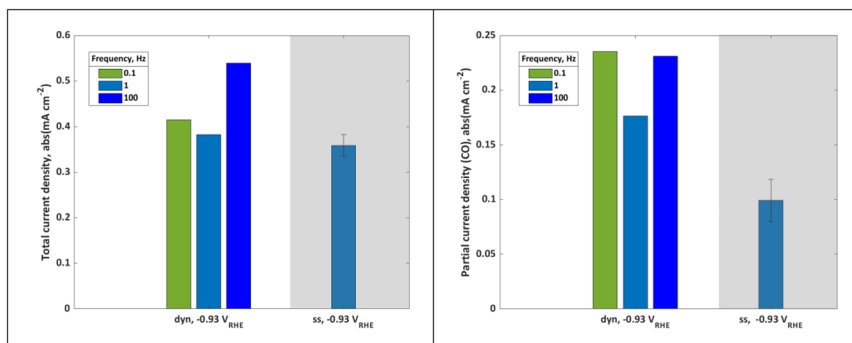


Fig. 3 (Left) Absolute total current density values under dynamic conditions and amplitude of 0.2 V as a function of frequency and under steady state conditions and (right) absolute partial CO current density values under dynamic conditions and amplitude of 0.2 V as a function of frequency and under steady state conditions. As can be seen for the same mean potential value under dynamic conditions/steady state potential under steady state conditions ( $-0.93$  V vs. RHE), total and partial CO current densities are always enhanced under dynamic conditions.

the main manuscript refer to only one potential value, so we present it in the form of a bar graph in Fig. 3 here. I hope this presentation is helpful.

**Sophie Marbach** enquired: Could you please tell me why did you call this method “pulsed” electrolysis since the input signal is sinusoidal and not in short pulses?

**Tanja Vidaković-Koch** responded: The term “pulsed” is used here because it is widely used in the literature (water electrolysis, CO<sub>2</sub> electrolysis, electrodeposition). We also refer to this as forced periodic operation (which is more common in chemical engineering). The pulse is not single, but a pulse wave. The frequency of pulsing can be high or low. Pulsing can use different types of waves, such as square, triangular, or sine waves. The first two types are combinations of sine waves with different frequencies. In the model, the sine wave was used because it makes the mathematical treatment easier. However, the derived functions do not depend on the type of input.

**Martin Z. Bazant** questioned: The experiments nicely show how nonlinearities lead to rectified DC current in pulsed electrolysis, but I am skeptical of the theoretical interpretation, since it does not account for liquid–gas phase transformations. What is the role of bubbles in your experiments, and how can it be captured by models? I view this as one of the most difficult, fundamental problems in the field, since there is no simple model for the nucleation, growth and release of gas bubbles generated by faradaic reactions from liquids at an electrode. This is a very complicated, fully coupled problem as the electric fields and ionic currents must circumnavigate nucleating bubbles, and bubbles that cover the surface shut down the reaction temporarily. Nucleation is not describable here by simple classical theories, since it occurs far from equilibrium on a surface producing dissolved gas molecules that coalesce to form bubbles.

**Tanja Vidaković-Koch** answered: The theoretical framework we propose generally explains the origin of the current rectification under forced periodic conditions. It shows that the DC component is caused by nonlinearities of the process. In any electrochemical process, there are several causes of nonlinearities, of which nonlinear electrochemical kinetics is the most obvious. This effect has been accounted for in the simple model we have presented. The reason is that this effect is the most important. Other contributions to the nonlinear behavior could be nonlinearities related to mass transfer effects in reaction kinetics, nonlinearities related to double layer capacitances, or nonlinearities related to ohmic resistances. These effects were not considered because they would require a more complex model and it would be difficult to derive analytical expressions in such a case. But in general, our proposed theoretical framework can account for these effects. The effect of gas bubbles could probably affect mass transfer, double layer, or ohmic resistance. Indeed, it is difficult to describe this with classical theories. However, mathematical models are always an approximation to reality. Therefore, the effects mentioned can probably be captured by models with lower complexity, but these have the disadvantage that fitting parameters have to be introduced. It should be also noted that the bubbles are also causing the noise in the measurements. In the present experiments, mass transport conditions were optimized to remove bubbles efficiently, therefore no significant bubble growth was observed.

**Yan Levin** enquired: For ionic capacitors the charge is a nonlinear function of the potential difference. So one usually discusses a differential capacitance, while in your model you seem to use fixed capacitances. Can you please clarify this?

**Tanja Vidaković-Koch** replied: Yes, that is correct. We assumed that the capacitance does not change with the potential or composition of the electrolyte. This assumption was justified because we wanted to derive an analytical expression for the current rectification. The dependence of the capacitance on the potential theoretically leads to additional nonlinearities in the response. These effects have not been sufficiently studied in the literature, but it would be interesting to explore this direction.

**Alexei A. Kornyshev** asked: When measuring transient currents, have you done calibration, using different kinds of surfaces to teach your method to distinguish different materials?

**Tanja Vidaković-Koch** responded: In the method we apply we do not record or analyse transient currents. What we record and analyse is the periodic steady state part of the response. It is not clear what was meant with calibration to distinguish different materials. The focus is on different reactions, therefore the response will be dependent on reaction kinetics and the type of material. This means that theoretically different responses will be obtained for different kinetics on different materials.

**Alexei A. Kornyshev** opened discussion of the paper by Benjamin Rotenberg: Your theoretical approach and results touch upon very fundamental issues in physical chemistry. For a long time people tried to understand the mechanism of

motion of ions in water and how it is coupled with the orientational fluctuations of water dipoles (see, *e.g.*, ref. 1 and 2). Could you summarize what new light the findings of your analysis bring on this phenomenon?

- 1 P. G. Wolynes, Dynamics of electrolyte solutions, *Annu. Rev. Phys. Chem.*, 1980, **31**, 345–376, DOI: [10.1146/annurev.pc.31.100180.002021](https://doi.org/10.1146/annurev.pc.31.100180.002021).
- 2 B. Bagchi and R. Biswas, Ionic mobility and ultrafast solvation: control of a slow phenomenon by fast dynamics, *Acc. Chem. Res.*, 1998, **31**, 181–187, DOI: [10.1021/ar970226f](https://doi.org/10.1021/ar970226f).

**Benjamin Rotenberg** replied: Thank you for your suggestion. Solvent fluctuations play indeed a crucial role in ion diffusion and can be introduced in an implicit-solvent description *via* a generalized Langevin equation (as in the examples you cite) *via* a frequency-dependent memory kernel, which is the (projected) autocorrelation function of the force exerted by the solvent on the ion. Analytical models (including earlier works by Hubbard and Onsager, see, *e.g.*, ref. 1 and 2) have been proposed to describe the collisional and electrical contributions to the force on the ions, hence to the friction kernel. In particular, the mode-coupling theory (MCT) approach of Bagchi and co-workers allows description of this kernel, which depends on the evolution of the relative positions of ions and water and on the orientation of the latter, using structure factors such as the ones discussed in our contribution. These kernels can be introduced in MCT to capture the coupled effects of ion–solvent and ion–ion relaxations in electrolyte solutions (see, *e.g.*, ref. 3).

However, the analytical models for these so-called hydrodynamic and dielectric frictions have rarely been tested against molecular simulations, with some notable exceptions for the static (zero-frequency limit) friction,<sup>4</sup> usually under the assumption of an infinitely heavy ion where the memory kernel reduces to the force autocorrelation function. Recent studies have also emphasised the role of correlations between the van der Waals and electrostatic forces in ion diffusion.<sup>5,6</sup> In the last decade, new algorithms have been developed to extract the memory kernel from molecular dynamics trajectories, in order to go beyond the estimate from the force autocorrelation function. They have been used to investigate diffusion in bulk liquids<sup>7</sup> and to make the link with hydrodynamic descriptions,<sup>8</sup> as well as to study the diffusion of ions confined in clay nanopores.<sup>9</sup> Using more efficient algorithms,<sup>10</sup> we are now coming back to the case of the diffusion of ions in bulk water in order to assess the assumptions of continuous theories, and hopefully also provide insights into the microscopic mechanisms.

A recent illustration of the link between electrical fluctuations and diffusion can be found in ref. 11, where we analysed the electric field gradient fluctuations (EFG) for Na<sup>+</sup> ions in aqueous salt solutions to predict the quadrupolar NMR relaxation rate, which we validated by direct comparison with experiments. We showed that these fluctuations occur on the same time scale as that of the stress, which indicates that the models traditionally used to interpret the experimental quadrupolar NMR relaxation rate, such as the Stokes–Einstein–Debye model based on (rotational) diffusion, are not appropriate, since they rely on a decoupling of time scales between the considered process and the relaxation of the stress necessary to define the viscosity. However this does not imply the breakdown of the proportionality between the NMR relaxation rate and the viscosity, which is observed both in experiments and in simulations, because they are

proportional to the time integral of the EFG and stress autocorrelation functions, respectively. While additional efforts are still needed to pinpoint the microscopic mechanisms responsible for diffusion, this work highlights the role of the collective (sub-picosecond) fluctuations in the first two solvation shells of the ion in the EFG relaxation and the possibility to use NMR relaxation as a complementary tool to analyze electrolyte dynamics in the THz domain.

- 1 J. Hubbard and L. Onsager, *J. Chem. Phys.*, 1977, **67**, 4850.
- 2 J. B. Hubbard, *J. Chem. Phys.*, 1978, **68**, 1649.
- 3 J. F. Dufre che, *et al.*, *Phys. Rev. Lett.*, 2002, **88**, 095902.
- 4 S. Koneshan, *et al.*, *J. Am. Chem. Soc.*, 1998, **120**, 12041.
- 5 T. Samanta and D. V. Matyushov, *J. Chem. Phys.*, 2022, **156**, 204501.
- 6 D. V. Matyushov, *J. Chem. Phys.*, 2022, **157**, 080901.
- 7 A. Carof, *et al.*, *J. Chem. Phys.*, 2014, **140**, 124103.
- 8 D. Lesnicki, *et al.*, *Phys. Rev. Lett.*, 2016, **116**, 147804.
- 9 A. Carof, *et al.*, *Mol. Simul.*, 2014, **40**, 237.
- 10 H. Vroylandt, *et al.*, *Proc. Natl. Acad. Sci. U. S. A.*, 2022, **119**, e2117586119.
- 11 I. Chubak, *et al.*, *Nat. Commun.*, 2023, **14**, 84 (ref. 58 in the paper).

**Paul Robin** said: In the limit of low frequency, you said that you recovered some known results: in particular that the structure factors of the electrolyte resemble somewhat the predictions of the Debye–H ckel (DH) model, with some noticeable corrections.

In a recent paper,<sup>1</sup> Yael Avni, David Andelman and co-workers showed in a similar situation that deviations from DH theory often originate from the finite size of ions (which is neglected in DH). This leads to problems when considering correlations on length scales comparable to the physical size of ions. They proposed to use a simple model based on DH but where the coulombic interaction is cut to 0 for distances below the ionic size.

They were interested in the conductivity of electrolytes, but I was curious and using their method you can show that cutting off interactions in this way amounts to changing the static charge–charge structure factor from:  $S = k^2 / (k^2 + \kappa_D^2)$  ( $\kappa_D$  is the inverse Debye length) to:  $S = k^2 / (k^2 + \kappa_D^2 \cos ka)$  ( $a$  is the ionic size). In your paper (<https://doi.org/10.1039/d3fd00026e>) you use a concentration of 1.23 M and I guess your ions are typically like sodium ( $a \sim 0.3$  nm). Using that, I can compare the structure factor you measure to the expression above, and I get (nearly) quantitative agreement without a fitting parameter (see Fig. 4 here).

Does the above analysis bring anything new to the table/help modelling the behaviour of electrolytes? Is getting a simple and accurate closed-form for the structure factor useful beyond ascertaining that deviations from DH theory are due to finite size effects?

- 1 Y. Avni, R. M. Adar, D. Andelman and H. Orland, *Phys. Rev. Lett.*, 2022, **128**, 098002, DOI: [10.1103/PhysRevLett.128.098002](https://doi.org/10.1103/PhysRevLett.128.098002).

**Benjamin Rotenberg** responded: The fact that deviations from Debye–H ckel (DH) theory arise in particular from the finite size of the ions has been well known for decades and several liquid state theories have been developed to capture the combined effects of hard-core repulsion at short range and electrostatic interactions, as well as hydrodynamic interactions for transport. Notably, the Debye–H ckel–Onsager (DHO) route was also followed using the static correlations of the



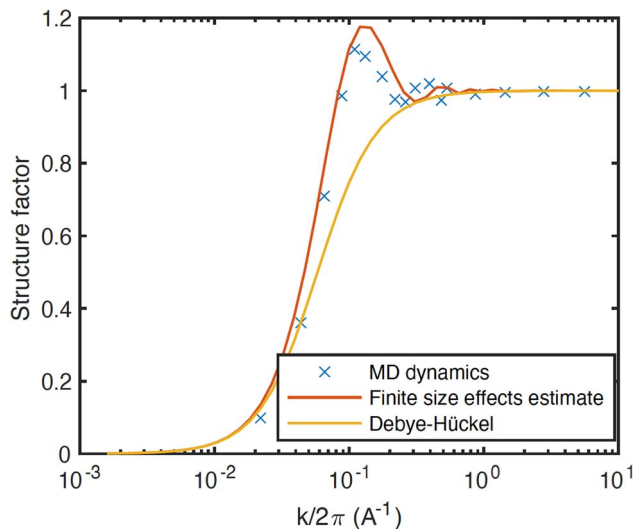


Fig. 4 Static charge–charge structure factor.

Mean Spherical Approximation (MSA), instead of that of DH theory, to predict analytically the transport properties of electrolytes (see, *e.g.*, ref. 1, which includes a summary of earlier results). The predictions of this MSA approach are in good agreement with experiments up to several mol L<sup>-1</sup>, including in the presence of multivalent ions, and are often used in chemical engineering (even though the sometimes lengthy analytical expressions seem to have discouraged the physics community, they can be easily computed numerically).

The recent works of Avni *et al.*<sup>2–4</sup> exploit for the conductivity an idea from the same group<sup>5</sup> to tame the unphysically strong attraction between anions and cations by introducing a cut-off distance at short range (for all ion–ion interactions, not only between unlike charge). As you correctly point out, this modified Coulomb potential provides a significant improvement in the description of the static charge–charge structure factor with respect to DH theory. Introducing it in stochastic Density Functional Theory (sDFT) allows the making of analytical predictions (which reduce to the DHO prediction in the limit of vanishing cut-off distance, as expected) for the conductivity in good agreement with experiments. This work is particularly elegant, but the modified Coulomb potential only provides an approximate treatment of the interplay between excluded volume and electrostatics. In addition, in these works the effect of the finite size of the ions on hydrodynamic interactions is not taken into account. Together with colleagues in my lab, in particular Pierre Illien, over the last few months we have exchanged with David Andelman and his collaborators to compare the predictions of this new approach with the earlier ones of MSA, in particular the relative contributions of hydrodynamic interactions and ionic cloud relaxation on the conductivity. It turns out that while their sum is well described by sDFT with the modified Coulomb potential, at moderate concentrations they deviate from the MSA predictions (which had previously been validated against Brownian dynamics simulations with and without hydrodynamic interactions between ions). It is

possible to improve this description by also including the effect of the finite size in the hydrodynamic interactions *via* the Rotne–Prager tensor (instead of Oseen corresponding to point-like particles). One should note however that the constant value of the modified Coulomb potential inside the core also has an influence on the results (and the hard-core limit of an infinite value cannot be recovered, because it is not compatible with some of the approximations of the theory). We are currently finalizing a manuscript<sup>6</sup> that summarizes the above analysis, with additional results at the same level of description on the self-diffusion coefficient of the ions, which had not been considered previously. With all these caveats in mind, it is indeed a good suggestion to introduce this model of static correlations, which provides a significant improvement over DH theory at virtually no additional cost (and without the need of the static structure factor from the simulations), in the approximation of the dynamic correlations discussed in our contribution (eqn (33); <https://doi.org/10.1039/d3fd00026e>). We will try and can keep you informed of the result if you are interested.

- 1 J.-F. Dufrière, *et al.*, *J. Phys. Chem. B*, 2005, **109**, 9873, DOI: [10.1021/jp050387y](https://doi.org/10.1021/jp050387y).
- 2 Y. Avni, *et al.*, *Phys. Rev. Lett.*, 2022, **128**, 098002, DOI: [10.1103/PhysRevLett.128.098002](https://doi.org/10.1103/PhysRevLett.128.098002).
- 3 Y. Avni, *et al.*, *J. Chem. Phys.*, 2022, **157**, 154502, DOI: [10.1063/5.0111645](https://doi.org/10.1063/5.0111645).
- 4 Y. Avni, *et al.*, *J. Chem. Phys.*, 2023, **158**, 179901, DOI: [10.1063/5.0153878](https://doi.org/10.1063/5.0153878).
- 5 R. M. Adar, *et al.*, *Phys. Rev. E*, 2019, **100**, 042615, DOI: [10.1103/PhysRevE.100.042615](https://doi.org/10.1103/PhysRevE.100.042615).
- 6 O. Bernard, *et al.*, *arXiv*, 2023, preprint, arXiv:2306.16737, DOI: [10.48550/arXiv.2306.16737](https://doi.org/10.48550/arXiv.2306.16737).

**Sanli Faez** remarked: This is a suggestion. The calculations seem to be focusing on charge correlations because of the measurement signal from a micro-electrode. Some other methods, such as optical or ultrasonic measurements, can also probe density fluctuations. It would be helpful if density correlations are also calculated on the side.

**Benjamin Rotenberg** replied: Thank you for your suggestion. Indeed other fluctuations can be probed by other experimental techniques and estimated from molecular (and depending on the considered observables, also mesoscopic) simulations. Density fluctuations are particularly interesting, because they are related to interfacial thermodynamics. For example, Chandler and co-workers showed how water density fluctuations in a probe volume next to a substrate are related to the hydrophilicity/hydrophobicity of the latter, and developed the corresponding simulation strategies to estimate these (rare) fluctuations.<sup>1,2</sup> More recently, we investigated the microscopic origin of the effect of substrate metallicity on interfacial free energies by considering the spatial correlations in the electrode charge, which reflect that in the interfacial liquid.<sup>3</sup> In the ERC project SENSES, we also explore the possibility to interpret surface force balance experiments by considering the coupled charge and density fluctuations. Optical and ultrasonic measurements are very good illustrations. In particular, correlating spectroscopic and electrochemical measurements can provide complementary information (even though generally on different time scales).

- 1 D. Chandler, *Nature*, 2005, **437**, 640, DOI: [10.1038/nature04162](https://doi.org/10.1038/nature04162).
- 2 A. J. Patel, *et al.*, *J. Phys. Chem. B*, 2010, **114**, 1632, DOI: [10.1021/jp909048f](https://doi.org/10.1021/jp909048f).
- 3 L. Scalfi and B. Rotenberg, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **118**, e2108769118, DOI: [10.1073/pnas.2108769118](https://doi.org/10.1073/pnas.2108769118).

**Derek Stein** asked: I am interested to hear your perspective on whether certain noise mechanisms are currently within the purview of simulations or if they remain goals for future work: from my experimental perspective, the main noise sources that keep me up at night involve changes in the fluid boundary, like gas evolution at an electrode or the nucleation of nanobubbles at a surface with less-than-perfect wetting properties. How far away are we from numerically addressing multiscale problems like these?

**Benjamin Rotenberg** answered: The important practical issues of gas evolution and nucleation of bubbles indeed require simulation approaches beyond the molecular scale. I would recommend mesoscopic models able to deal with multiphase reactive interfacial flows, also taking into account electrostatic effects, such as the lattice Boltzmann method. Another challenge from the modelling point of view is that these processes are non-linear.

**Yan Levin** commented: The problem with field theoretical approaches is that the hard-cores are included simply as cut-offs on integrals. This is not correct for strongly repulsive systems. This often results in predictions which are qualitatively wrong. One dramatic demonstration of this is the behavior of critical parameters of asymmetric primitive models as a function of charge asymmetry – see for example the discussion in ref. 1. In this respect the liquid state theories, such as integral equations of classical DFT, are much more reliable than field theoretic approaches.

1 Y. Levin, *Rep. Prog. Phys.*, 2002, **65**, 1577.

**Martin Z. Bazant** asked: You have developed an elegant statistical theory of fluctuations mostly applicable to dilute, bulk electrolytes at low voltages, but one could argue that the most important properties of electrolytes for iontronics, biological and electrochemical systems arise in concentrated solutions, at interfaces, and (in some cases) at large voltages. How could the analysis be extended to some such situations?

(i) The analysis begins with the Poisson–Nernst–Planck (PNP) equations in the form of eqn (21) and (22) in the paper (<https://doi.org/10.1039/d3fd00026e>) suitable only for dilute electrolytes (typically <10 mM) and briefly considers extensions for dynamical density functional theory (DDFT), which leads to nonlocal terms that extend validity to higher concentrations. Still, there are clear departures from PNP or DDFT at typical concentrations for electrochemical and biological systems (>0.5 M), for example in the fact that the Nernst–Einstein relation between conductivity and diffusivity in dilute electrolytes breaks down. This is normally resolved and fitted (without any microscopic theory) using Stefan–Maxwell (SM) coupled flux models, *e.g.* in battery electrolyte models developed by John Newman and recently integrated with electrochemical nonequilibrium thermodynamics.<sup>1</sup> In the SM approach, there is a diffusivity tensor with new off-diagonal terms relating thermodynamic driving forces and their corresponding fluxes, where each coefficient has strong dependence on concentration, in addition to the complicated concentration dependence of chemical potentials (or activities) of ions. While the theory of fluctuations depends on linearization, these nonlinearities affect the base state

and will lead to results that depend on electrolyte composition in nontrivial ways. What are the prospects of applying the present method to SM electrolyte models?

(ii) Even for dilute electrolytes, the present analysis focuses on bulk properties, whereas interfaces can play more important roles in applications. How can the analysis be extended for spatially resolved fluctuations within interfacial double layers, or confined nanochannels, and are analytical results still possible? Of course, the results will depend on boundary conditions (fixed charge, fixed potential, reactions...).

(iii) The analysis of electrode charge fluctuations is a step in this direction, which considers instead the simpler problem of integrated charge fluctuations. The connection to external fields is mentioned with ref. 2 (ref. 140 in the paper), but this topic has a long history in electrochemistry and generally leads to a mixed “*RC*” time scale (geometric mean of the Debye and diffusion times), which has often been overlooked by theorists and experimentalists alike.<sup>3</sup> Since *RC* effects are noted in the paper, does this time scale, expressed as  $\lambda L/D$ , appear in the time scale “ $\tau$ ” defined after eqn (20)?

(iv) The connection of fluctuations with Marcus theory is tantalizing, since this opens the possibility of understanding electrolyte effects on electrochemical reaction kinetics, which of course is most important at electrode interfaces. To some extent this has been done in cited papers, *e.g.* by Limaye and Willard who computed reorganization energy within the double layer as a function of position from fluctuations in MD simulation, but this falls short of the analytical insights originated by Marcus and which might result from the present approach. Is it possible to predict the reorganization energy *versus* position up to an electrode surface from these sorts of theories?

1 R. B. Smith and M. Z. Bazant, *J. Electrochem. Soc.*, 2017, **164**(11), E3291–E3310.

2 K. Takae and A. Onuki, *J. Chem. Phys.*, 2015, **143**, 154503 (ref. 140 in the paper).

3 M. Z. Bazant, K. Thornton and A. Ajdari, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **70**, 021506.

**Benjamin Rotenberg** responded: Thank you for your questions. Indeed the model used to provide analytical results (PNP) for the charge structure factors is limited to dilute solutions, and the comparison with (molecular and implicit-solvent) simulations presented in our contribution confirms the expected limitations of the PNP predictions. However this does not affect the main message, namely the fact that seemingly unrelated experiments reflect different facets of the same underlying dynamics, with observables that can be expressed by considering various types of electrical fluctuations, so that it is beneficial to combine these experiments as complementary sources of information on ionic fluids. At least in principle, molecular simulations allow computing of the relevant quantities even in the complex cases involving concentrated electrolytes, interfaces, and large voltages. In practice, of course, this will be limited to relatively small systems and short time scales compared to many experimental situations.

(i) As you correctly point out, in order to make analytical predictions (or numerical predictions without simulations) one needs to go beyond PNP to deal with more concentrated electrolytes (and in the case of electrochemical systems, large voltages) relevant to most applications. One possibility, which we briefly discuss in our contribution, is dynamical density functional theory, which in principle allows capturing of the effect of interactions (in particular excluded-

volume) *via* the excess free energy. Your question is also related to that of Paul Robin (please refer to my corresponding earlier answer, including the recent preprint<sup>1</sup>). This is however not the only possibility, and the ones you mention are indeed relevant.

(ii) The case of confined fluctuations is indeed more complicated since the confinement breaks the translational invariance in some directions. The description in reciprocal space is then less straightforward than in the bulk case, even though it is possible to use the bulk structure factors and cut-off wavevectors as a first approximation (neglecting interfacial effects) of the confined fluctuations, see, *e.g.*, ref. 2. The correlation functions in the confined case are more easily expressed by combining reciprocal and real space (depending on the direction), as done, *e.g.*, in ref. 3 and 4. It is also possible to consider, *e.g.*, the response of the total current/polarization of the confined electrolyte to compute the frequency-dependent conductivity (see, *e.g.*, ref. 5 for a recent example where Brownian dynamics simulations were used to analyze the interplay between diffusion, confinement, migration and adsorption on the field- and frequency-dependent conductivity).

(iii) In the reference where eqn (20) was introduced,<sup>6</sup> the system chosen as an illustration consisted of a nanocapacitor with pure water (modelled with a rigid classical force field, without H<sup>+</sup> or HO<sup>-</sup> ions) as the liquid confined between the two electrodes. As a result, the characteristic time did not correspond to a time scale related to the ionic Debye relaxation time, *i.e.* to the Debye length  $\lambda$ , but rather to the Debye mode corresponding to collective dipole fluctuations. We have since been working on the (electrochemically more relevant) case of aqueous electrolytes, and indeed the presence of ions introduces slower charge fluctuation modes, reflected in an overall longer characteristic time scale “ $\tau$ ”. This time scale can be related to the one you mentioned ( $\lambda L/D$ , or more generally to the time scales that you discussed in ref. 7) but the assignment to ionic and solvent contributions requires some care, as they are correlated, as discussed for the bulk case in our contribution to this *Faraday Discussions* meeting

(iv) As you correctly point out, the link between electron transfer and solvent fluctuations around the solute, which has been clarified by Marcus who could even propose a simple analytical description for bulk solutes, is another fundamental example of where electrical fluctuations play a key role in experimental observables (electron transfer reaction rates in that case). This link has already been explored to investigate redox reactions in molten salts or electrolyte solutions at electrochemical interfaces using molecular simulations (see, *e.g.*, ref. 8–10). Such molecular insights can then be used to develop (semi-)analytical models.<sup>11,12</sup> Another promising approach, that we are currently exploring with my colleague Guillaume Jeanmairet, is molecular density functional theory, which can be combined with the molecular description of constant-potential electrodes<sup>13</sup> and for which we showed how to compute the quantities relevant to electron transfer in the Marcus picture.<sup>14</sup> Combining these two recent developments of molecular density functional theory (MDFT) allows for example to compute the reorganization energy as a function of position with respect to an electrode surface, as you suggest, in a much more efficient manner than with molecular simulations (some are nevertheless necessary to validate the MDFT predictions on a limited number of cases, since this is an approximate theory). With MDFT, a systematic investigation of the effects of the ion position or its

radius should also provide insights into how to improve analytical descriptions, whose simplicity is also key to the success, *e.g.*, of Marcus theory.

- 1 O. Bernard, *et al.*, *arXiv*, 2023, preprint, arXiv:2306.16737, DOI: [10.48550/arXiv.2306.16737](https://doi.org/10.48550/arXiv.2306.16737).
- 2 M. Zorkot and R. Golestanian, *J. Phys.: Condens. Matter*, 2018, **30**, 134001.
- 3 S. Mahdisoltani and R. Golestanian, *Phys. Rev. Lett.*, 2021, **126**, 158002.
- 4 S. Mahdisoltani and R. Golestanian, *New J. Phys.*, 2021, **23**, 073034.
- 5 T. Hoang Ngoc Minh, *et al.*, *J. Chem. Phys.*, 2023, **158**, 104103.
- 6 G. Pireddu, *et al.*, *Phys. Rev. Lett.*, 2023, **130**, 098001.
- 7 M. Z. Bazant, *et al.*, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **70**, 021506.
- 8 S. K. Reed, *et al.*, *J. Chem. Phys.*, 2008, **128**, 124701.
- 9 A. P. Willard, *et al.*, *Faraday Discuss.*, 2009, **141**, 423.
- 10 M. A. Pounds, *et al.*, *Mol. Phys.*, 2015, **113**, 2451.
- 11 A. M. Limaye and A. P. Willard, *J. Phys. Chem. C*, 2020, **124**, 1352.
- 12 A. M. Limaye, *et al.*, *J. Chem. Phys.*, 2020, **152**, 114706.
- 13 G. Jeanmairet, *et al.*, *J. Chem. Phys.*, 2019, **151**, 124111.
- 14 G. Jeanmairet, *et al.*, *Chem. Sci.*, 2019, **10**, 2130.

**René van Roij** enquired: Your analysis has a (fully justified) focus on the charge–charge correlation, which is actually only one of many other possible correlations of linear combinations of density modes in multicomponent electrolytes. Can your analysis be generalised and/or extended to other correlators, and if so which of these (apart from the number–number correlations) contain specific (experimentally accessible) information?

**Benjamin Rotenberg** replied: Thank you for emphasising this important point. Indeed, the charge–charge dynamic structure factor is only one of the many possible combinations of individual species-wise structure factors. As mentioned in our contribution (<https://doi.org/10.1039/d3fd00026e>), other experiments also provide complementary information, since the contribution of each element can be very different from one experiment to another: combining neutron and X-ray scattering is particularly useful in the case of water, since the measured signal in these experiments is dominated by the contributions of H and O atoms, respectively. Other experiments are related to the cross-correlations between different types of currents. For example, the electrokinetic response corresponds to the coupled mass and charge fluctuations and the relevant quantities have been obtained in molecular simulations in the case of pure water by Sedlmeier *et al.*<sup>1</sup> The purpose of the ERC project SENSES (making Sense of Electrical Noise by Simulating Electrolyte Solutions, Grant Agreement No. 863473) and of our contribution to this *Faraday Discussions* meeting is precisely to make links between seemingly unrelated experiments and to combine various points of view on the same microscopic dynamics in electrolytes.

- 1 F. Sedlmeier, *et al.*, *J. Chem. Phys.*, 2014, **140**, 054512, DOI: [10.1063/1.4863444](https://doi.org/10.1063/1.4863444).

**Alexander Schlaich** asked: In your paper in Fig. 2(a) (<https://doi.org/10.1039/d3fd00026e>) you calculate the dynamic structure factor. I wonder why the results for the Brownian dynamics simulations seem to follow the one for the MD, rather than the Langevin dynamics results? Both should follow the Poisson–Nernst–Planck behavior...

**Benjamin Rotenberg** answered: Thank you for pointing this out. Indeed if the ionic current is sampled “sufficiently frequently” in both simulations, the

underdamped (Langevin) and overdamped (Brownian) simulations should provide the same power spectral density (PSD) for frequencies smaller than the inverse relaxation time of the underdamped dynamics (*i.e.* timescales longer than the corresponding relaxation time). We have checked that this is indeed the case when using, *e.g.*, the same time step and sampling frequency for both dynamics. However, the advantage of Brownian dynamics is that one can use a significantly larger time step to explore longer time scales. The frequency at which the ionic current is sampled is then limited, which results in a departure from the expected (Lorentzian) PSD with a plateau at high frequencies. This is an (easily controlled) artefact of the discrete Fourier transform, arising from the undersampling of the time series: when the sampling frequency decreases (fewer points to describe the current over same total trajectory length), the departure from the Lorentzian PSD occurs at lower frequencies and the plateau value (at high frequency) is larger. This numerical artefact is also present for the LD and MD cases but only at higher frequencies, since the corresponding sampling frequencies are larger. The apparent better agreement of BD with the MD results (compared to the underdamped case) is thus coincidental.

**Paul Robin** opened discussion of the paper by Sophie Marbach: If I understand correctly, here hyperuniformity is more or a less a consequence of electrolytic systems preferring global electroneutrality over large distances. Could the same type of noise you are describing be observed in systems that are not ionic? If so, under what conditions can I observe hyperuniformity?

Side question: In systems without charge, is there a “physical interpretation” of the origin of hyperuniformity (like electroneutrality in ionic systems)?

**Sophie Marbach** responded: This is a correct albeit shortened reasoning of why hyperuniformity emerges in electrolytic systems. In my understanding, the fact that ions interact over large distances is also crucial, in a system at equilibrium, to obtain hyperuniform behavior.

In colloidal systems with purely steric interactions, we have observed that fluctuations scale with the observed area (not volume, so if  $L$  is the size of the observation volume, they scale as  $L^{d-1}$  where  $d$  is the dimension of the system), a typical hyperuniform signature, for small boxes.<sup>1</sup> For large boxes, however, these short-range correlations fade out and we recover that the fluctuations scale with the observed volume ( $L^d$ ). These systems are thus not hyperuniform, within the strict mathematical definition which says that hyperuniformity corresponds to a lower scaling for infinite volumes ( $L \rightarrow \infty$ ).

In out-of-equilibrium systems, however, a lot of interesting hyperuniform behavior can be observed, for example in chiral active matter.<sup>2</sup>

1 E. K. R. Mackay, S. Marbach, B. Sprinkle and A. Thorneywork, The countscope: self and collective diffusion coefficients by counting particles in boxes, in preparation.

2 M. Huang, W. Hu, S. Yang, Q. X. Liu and H. P. Zhang, Circular swimming motility and disordered hyperuniform state in an algae system, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **118**(18), e2100493118.

**Sanli Faez** asked: The reported simulations are done for water as solvent. Which results can be applicable to apolar solvents with (controllable) low ion concentrations? Do you expect the results in Fig. 3 of the paper (<https://doi.org/>

[10.1039/d3fd00031a](https://doi.org/10.1039/d3fd00031a)) to overlap, for polar and apolar solvents, if they are rescaled by the Bjerrum length or a combination of that and the Debye length?

**Sophie Marbach** answered: In the case of apolar solvents, or more generally in the case where one accounts for ion pairing in solution, the Bjerrum length comes into play. Since there is a new length scale, associated with a new timescale corresponding to ion pair breakdown, I expect there might be other phenomena or scalings at play, according to the size of the observation box. It would definitely be interesting to perform simulations in this latter case.

**Yan Levin** enquired: Why did you say that Torquato introduced the idea of area scaling of charge fluctuations? As far as I know it was first done by Joel Lebowitz.

**Sophie Marbach** replied: I'm sorry for this shortcut. Indeed Joel Lebowitz and co-workers introduced the idea of superhomogeneous systems (area scaling of charge fluctuations), both in the context of charges but also starting from the one component plasma (e.g. uniform charged background, and only 1 species of counter-charges).<sup>1,2</sup> There is at least also one remarkable predating derivation for the one component plasma.<sup>3</sup> Salvatore Torquato then did considerable studies in this field, and named the behavior hyperuniformity, a term that eventually persists in the literature. I refer the reader to a recent and relevant review.<sup>4</sup> Following this discussion on hyperuniformity, I must stress that this is still an open area of research in mathematics and that there is still considerable ongoing work to understand which conditions are required in terms of pair-wise interactions to guarantee hyperuniformity; according to the specifics of the system, its dimension (2D, 3D,  $ND$ ) and its temperature.<sup>5</sup>

1 J. L. Lebowitz, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1983, 27, 1491.

2 D. Levesque, J.-J. Weis and J. Lebowitz, *J. Stat. Phys.*, 2000, 100, 209–222.

3 P. A. Martin and T. Yalcin, *J. Stat. Phys.*, 1980, 22, 435–463.

4 S. Torquato, *Phys. Rep.*, 2018, 745, 1–95.

5 T. Leblé, *arXiv*, 2021, preprint, arXiv:2104.05109, DOI: [10.48550/arXiv.2104.05109](https://doi.org/10.48550/arXiv.2104.05109).

**Yan Levin** remarked: Just a comment to say that short range interacting systems in a stationary out of equilibrium state have long range correlations, so this may explain why they show hyperuniformity.

**Martin Z. Bazant** said: As noted in eqn (12) of the manuscript (<https://doi.org/10.1039/d3fd00031a>), there are various ways to define time scales that could describe the data, starting from the fundamental Debye time,  $\lambda^2/D$ , and diffusion times,  $L^2/D$ . The Debye time is also the inverse Maxwell–Wagner frequency and describes charge relaxation, or charge–charge correlations. There is also an important mixed time scale,  $\lambda L/D$ , which is the geometric mean of the other two, and describes capacitive charging processes. It can be viewed as the “ $RC$  time” for charge buildup driven by conduction over the length scale  $L$ , and it plays a central role in electrochemical systems, especially near electrode boundaries.<sup>1</sup> Is there any evidence that this time scale plays a role in scaling of the charge correlation functions? This could become more clear if the observation box size  $L$  is varied. Also, how do the results change near boundaries of fixed charge or fixed potential, or under confinement? The mixed



time scale should become important near ideally polarizable electrode boundaries with fixed potential, at scales larger than the Debye length.

1 M. Z. Bazant, K. Thornton and A. Ajdari, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **70**, 021506.

**Sophie Marbach** responded: When the box size  $L$  is varied, we notice that the relaxation of the charge number in a box of size  $L$  depends strongly on the box size. For very small boxes, the timescale is the diffusion time across the box,  $\tau_{\text{diff}} = L^2/D$ , while for large boxes, the timescale corresponds to the Debye time, or time to diffuse across the Debye layer,  $\tau_{\text{Debye}} = \lambda_{\text{D}}^2/D$ . This phenomenon is because for large boxes, the dominant fluctuations come from a thin layer of thickness typically equal to the Debye length  $\lambda_{\text{D}}$ . Of course, for all the in-between box sizes, the typical relaxation time spans intermediate regimes, and we refer to Fig. 6a of the manuscript (<https://doi.org/10.1039/d3fd00031a>). Excited by this finding, we have checked carefully, and looked for a possible emergence of intermediate times, such as the  $RC$  times, with minimal models of relaxation in the bulk. However, likely because here there are no interfaces, the  $RC$  time does not appear to play a role. The results would most certainly change close to an interface, and we look forward to probing these new phenomena in the future.

**Christian Holm** asked: In a paper by Lee *et al.*,<sup>1</sup> local ionic fluctuations were postulated to give an explanation for the observed unusually long range screening lengths in dense electrolytes. I wonder if your formalism would be applicable to investigate this issue. Could you comment on this?

1 A. A. Lee, *et al.*, *Phys. Rev. Lett.*, 2017, **119**, 026002.

**Sophie Marbach** replied: My understanding is that one possible explanation of this effect is the presence of ionic clusters. I indeed believe that using our Counting in boxes formalism (to be called Countoscope) and analyzing the statistics of number of ions and number of charges within a box, at different scales, could help us describe and understand clustering effects and dynamics. We can hypothesize that small boxes probe individual dynamics while on larger clusters we would see the emergence of collective effects from these clusters. However, when it comes to the specific long-range screening lengths, the question is, on which system could we actually do the counting, *i.e.* is there a model simulation we could start from?

**Paul Robin** enquired: Here, you described particle number fluctuations in given samples of an electrolyte at equilibrium. In practice, we cannot measure this quantity: the only way to infer the number of ions in a system is generally to measure a conductance, for which you need to apply a voltage, driving the system out of equilibrium. Conductance is also a “convoluted” quantity, in the sense that fluctuations in conductance could be fluctuations in ion number, ion mobility, or system volume. So, what would be a “typical” experimental system to test your theory? Did you have a particular experiment in mind?

**Sophie Marbach** responded: Thank you for this important question. We are currently conducting experiments with colloids sedimented in 2D, whose position

we can track with time, and onto which we can apply counting on observation boxes of varying sizes. We have found perfect agreement between experiments, simulations, and theory in that case.<sup>1</sup> Namely, we have observed the subdiffusive scaling of particle number fluctuations in boxes and other exciting behavior associated with steric and hydrodynamic interactions. We look forward to sharing these results as soon as possible.

We could extend this experiment with charged colloids with long-range interactions or possibly other colloids with different interactions to mimic an ionic system. Currently, we are exploring colloidal motion and particle number fluctuations under an applied flow field, which plays the role of the electric field in the case of ions. And on the other side, we also hope to extend the theory to driven systems.

1 E. K. R. Mackay, S. Marbach, B. Sprinkle and A. Thorneywork, The countscope: self and collective diffusion coefficients by counting particles in boxes, in preparation.

**Susan Perkin** asked: Have you considered applying a similar analysis for electrolytes with asymmetric charge, *e.g.* 2 : 1 salts?

**Sophie Marbach** replied: We would very much like to, since this is a relatively easy step following up on what we've done: in fact, analytically, one needs to extend the description of the structure factor, and then integrate it in the proper volume. Numerically we can start with implicit water Brownian dynamics as well. In the case of asymmetric salts, both in charge and in mobility, we expect nontrivial behavior to occur, and we are eager to see what comes out.

**Joan Montes de Oca** enquired: Do you have an estimation for the total correlation length of the system in the bulk? I imagine that if the total size of the simulation box is smaller than the correlation length, the fluctuations will not only scale with the subdivision of the volume inside the box, but also with the total size of the simulation box.

**Sophie Marbach** answered: At the densities we investigate here, the correlation length, or at least the Debye length, is much smaller than the size of the simulation box. However, we can wonder when the effect of having a finite simulation box comes into play, since for a box = simulation box, the fluctuations should simply vanish. In all our analysis, we have kept the analysis box at most 1/2 of the size of the simulation box (in side length), and found that we could get enough statistics for these box sizes that agreed with a model that supposed infinite bulk. It would be interesting to probe larger boxes, however they often come with lesser statistics (since we can fit fewer larger boxes and eventually just one).

**Frédéric Kanoufi** asked: I wasn't aware of this hyperuniformity concept and your contribution is very inspiring. I wonder how hyperuniformity would be detected in the case of particle/ion adsorbed onto a surface? Do you know of experimental examples of hyperuniform behaviour at colloidal particles immobilized on surfaces?

**Sophie Marbach** replied: It would be interesting to probe this on particle/ion adsorbed to surfaces. For example, if the adsorption happens at specific loci of

the underlying surface structure, we could expect that the crystalline structure of the surface is reflected on the adsorbed particles. In that case, then we might expect some hyperuniform signatures. In fact, the “most hyperuniform” structure, is a crystal. And a crystal actually has “uniform” particle number fluctuations (the number fluctuations are none). We are investigating these days colloids near surfaces, in 2D. According to the packing fraction, the number fluctuations on finite box sizes can indeed be hyperuniform, reflecting a local structure of the colloids. This hyperuniform signature occurs increasingly at higher density.<sup>1</sup>

1 E. K. R. Mackay, S. Marbach, B. Sprinkle and A. Thorneywork, The countscope: self and collective diffusion coefficients by counting particles in boxes, in preparation.

**Frédéric Kanoufi** remarked: As a follow-up comment, your work, adapted to 2D situations, should be inspiring for single entity electrochemistry, as you mentioned in your manuscript (<https://doi.org/10.1039/d3fd00031a>). Particularly for what is known as single nanoparticle electrochemical collision, when the collision of a nanoparticle on a micrometric electrode is detected from an electrochemical current. Recent interest in this field, from Y.-T. Long,<sup>1,2</sup> is to elucidate the near-surface dynamics of the electron transfer (and associated ion transfer), and how the presence of nanoparticles near an electrode surface can affect its potential. Definitely your work will help understand such processes.

1 F. T. Patrice, *et al.*, *Annu. Rev. Anal. Chem.*, 2019, **12**, 347–370, DOI: [10.1146/annurev-anchem-061318-114902](https://doi.org/10.1146/annurev-anchem-061318-114902).

2 S.-M. Lu, *et al.*, *J. Am. Chem. Soc.*, 2021, **143**, 12428–12432, DOI: [10.1021/jacs.1c02588](https://doi.org/10.1021/jacs.1c02588).

**Sophie Marbach** responded: Thank you for this interesting comment. Indeed, our work can easily be extended to 2D, at least analytically, since the formalism would mean doing an integral over just a 2D area instead of a 3D volume. Of course here there is surface chemistry to be taken into account, which is an exciting perspective!

**René van Roij** opened discussion of the paper by Ehud Haimov and Alexei A. Kornyshev: In your energy-harvesting device the capacitance changes periodically because of shape changes of a droplet induced by a periodic mechanical force. Do you solve the Young–Laplace equation for the droplet shape? And have you considered, perhaps in the spirit of the paper by Janssen *et al.*,<sup>1</sup> a time-dependent rather than a constant voltage to optimize the harvested energy? This way one should expect a considerable additional gain, especially at slow mechanical vibrations compared to the (cycle-averaged) *RC* time.

1 M. Janssen, *et al.*, *RSC Adv.*, 2016, **6**, 20485–20491.

**Ehud Haimov** answered: We simplified the approach. In the main text (<https://doi.org/10.1039/d3fd00056g>), we considered a cuboid shape for the droplet, and will include a new appendix A that shows the (negligible) effect of the droplet’s meniscus non-zero curvature caused by a wetting angle larger than 90°. It should be noted that for our application, the shape of the droplet is primarily relevant for determining the contact length in the droplet–electrode interface, which directly influences the capacitance. To obtain the contact length for each given pressure, we calculated the free energy of the system and minimised it with respect to the contact length. We

have not considered the effects of AC bias voltage. Using a constant voltage allowed us to have an analytical solution for the charge and current which provided a further insight into how the different system parameters would affect the generated current. Furthermore, with a view of using a rapidly rechargeable back-up capacitor in a “shoe” as a source of bias voltage, we would not want to complicate the system by any externally controlled and energy consuming electrical devices.

**Derek Stein** asked: Could you comment on the efficiency of this concept? The definition of efficiency that interests me is the fraction of net mechanical work performed over one full cycle (one step) that is converted into useful electrical energy that can drive an external load. With this definition, the most efficient energy harvester is the one that minimizes dissipative mechanical process live viscous fluid flow (and by placing the *net* mechanical work performed over one cycle in the denominator, this efficiency is unaffected by any elastic energy that may be stored and recovered with each step). Could you also say how the system returns to its original state after each step? In other words, what stretches the shoe sole back to its original shape after it has been compressed?

**Ehud Haimov** replied: In our proposed devices, the working substance is assumed to be a hydrophobic ionic liquid. Upon exerting external pressure, the liquid tends to spread across the electrodes, thereby increasing the lateral dimensions of the double-layer, and when external pressure is lifted, the hydrophobicity drives the liquid back to its original spatial shape distribution as discussed in the paper (<https://doi.org/10.1039/d3fd00056g>). The percentage of mechanical power input that's converted into electrical power output is quite small (~5%). The reason for this relatively low yield, is due to the limitations of the restoring force which originates in the liquid's hydrophobicity. In the case of the porous electrode setup, the pores were limited in length (capped) so that the hydrophobic forces of the liquid would be enough to clear the pore once the external pressure is lifted.

**Derek Stein** said: This concept involves fluid being squeezed through tiny channels. It would be interesting to know how much energy is dissipated by such viscous flows.

**Ehud Haimov** responded: In our proposed devices, the percentage of mechanical power input that's converted into electrical power output is very small (~5%). For that reason, we have not investigated heat dissipation effects. However, heat dissipation could become important for the regulation of the devices' working temperature.

**Sophie Marbach** asked: The 8 watts measure what does it correspond to, what's the duration of the energy impulse from feet pressing? In my understanding the time where a foot is on the ground whereas in the air is quite different, how long does the system take to re-equilibrate once it is pressed?

**Ehud Haimov** replied: In ref. 1, it was estimated that 10 watt average power can be harvested from the kinetic energy of a 68 kg individual walking at a pace of 2 steps per second when only considering the striking of the heel.

In our paper (<https://doi.org/10.1039/d3fd00056g>) we were mainly interested in the average power over a period of foot press. To that end, it was enough to consider a harmonic external pressure (sinusoidal) instead of a more precise pressure profile of footfall. As for re-equilibration, as mentioned in the paper, we assume that: (i) in the case of flat electrodes, the rate of droplet shape-change is much faster than the rate of change of applied pressure, thus the shape of the droplet readjusts itself to equilibrium immediately, and, (ii) in the case of porous electrodes, the displacement rate of liquid penetration length is determined by the Washburn equation, which, if assumed applicable, gives the parameter-dependent description of the liquid penetration of the pore for any mode of pressure variation. We considered the latter sinusoidal, but of course other modes of periodical variation of the pressure could be considered within the same formalism.

1 T. Starner, Human-powered wearable computing, *IBM Syst. J.*, 1996, 35, 618–629.

**Martin Z. Bazant** said: There is another challenge for the porous shoe design to be added to the list at the end: How can you ensure that the electrolyte reversibly, reliably and fully wets the electrode in each step, especially over large numbers of cycles? Displacing one fluid with another immiscible fluid in a porous medium is a notoriously difficult problem in many fields, ranging from secondary oil recovery to lab-on-a-chip medical devices. There are fundamental hydrodynamic instabilities for which there is no perfect solution. For random porous structures, there are both dynamical viscous fingering instabilities and thermodynamical capillary instabilities, which lead to incomplete wetting, trapped fluid, and hysteresis in every cycle.<sup>1</sup> This is true even under gentle forcing, as in mercury porosimetry, which has strong hysteresis if the fluid is withdrawn after penetrating.<sup>2</sup> It is tempting to neglect this and assume that the model behind mercury porosimetry is always valid, namely by using parallel arrays of pores, but again there can be fluid instabilities having to do with spontaneous permeability variations and droplet breakup as the fluid seeks the path of least resistance. This has been shown for bubbles in microfluidic devices, even in the limit of identical parallel pores.<sup>3</sup> The instability can be suppressed in one direction (*e.g.* the more violent compression step of fluid penetration) by using tapered converging channels (analogous to auto-inhibitory reactions), but then the reverse process will be unstable (analogous to auto-catalytic reactions).

Of course, these effects are most pronounced in small channels where capillarity is important, below the capillary length (2 mm in water), but there will always be a tendency for incomplete wetting that may interfere with efficient operation over many cycles.

- 1 Z. Gu and M. Z. Bazant, Microscopic theory of capillary pressure hysteresis based on pore-space accessivity and radius-resolved saturation, *Chem. Eng. Sci.*, 2019, 196, 225–246.
- 2 Z. Gu, R. Goulet, P. Levitz, D. Ihiawakrim, O. Ersen and M. Z. Bazant, Mercury cyclic porosimetry: measuring pore-size distributions corrected for both pore-space accessivity and contact-angle hysteresis, *J. Colloid Interface Sci.*, 2021, 599, 255–261.
- 3 S. Protière, M. Z. Bazant, D. A. Weitz and H. A. Stone, Droplet breakup in flow past an obstacle: A capillary instability due to permeability variations, *Europhys. Lett.*, 2010, 92, 54002.

**Ehud Haimov** responded: You are right, all these problems can emerge and undermine the device performance. So it makes sense to try first experimenting

with mm-sized pores. Of course, increasing pore size will reduce the overall surface area accessibly to the electrolytic solution, and thereby diminish the maximal capacitance. Nevertheless, the proof of the principle experiments should start with such systems, and only after success down this line, we may try to see how the system would function with electrodes of finer porosity.

**Gilad Yossifon** asked: Can you elaborate on your considerations in choosing ionic liquid, and discuss why electrowetting and what are the limitations of this effect?

**Ehud Haimov** answered: There are several advantages and disadvantages for using ionic liquid compared to an electrolyte solution. I summarise some of them here. Ionic liquids, in contrast to electrolytes, are not volatile, which directly affects the robustness and longevity of the harvester device. Moreover, ionic liquids are better at preventing shortcuts. On the other hand, ionic liquids are very much viscous, which can be rectified to some degree by mixing it with organic solvents. Moreover, it's hard to find ionic liquids that are non-wetting on a metallic surface (although we cite one such option in the paper). It should also be noted that with electrolytes, one can generally achieve much larger double layer capacitance (surface) density by increasing the ionic strength of the solution.

Electrowetting was considered in the model, taken into account in an approximative fashion. A full account of the electrowetting would require us to consider a voltage-dependent capacitance, which would greatly complicate the model. In the paper (<https://doi.org/10.1039/d3fd00056g>), we included the electrowetting effect for the approximative case of constant voltage (the battery voltage).

**Jenny Pringle** enquired: The size and type of the cation and anion of ionic liquids (ILs) can significantly change the properties, including possibly affecting how they align at the surfaces or if they enter the electrode pores. Have you looked at the effect of different ILs? It looks like the radii of the pores is included in your calculations but not the ionic radii – how is this variable accounted for?

**Ehud Haimov** replied: The type of IL and size of counterions will affect the equilibrium capacitance, viscosity, and ion diffusion coefficients. But all these are incapsulated in the input parameters of the theory. In the case of the flat electrodes, the time of recharging of the electrical double layers is much shorter than the period of change of external pressure, and thus the ion-transport limitations are insignificant here. In contrast, for the porous electrode design, with very long pores, the time to form the double layer following the flow of the electrolytic liquid into the pore may be significant. The effect of ion transport limitations here deserves further investigation. For a constant, voltage-independent capacitance and negligible electrical load, this effect has been considered by Kornyshev *et al.*<sup>1</sup>

1 A. A. Kornyshev, R. Twidale and A. B. Kolomeisky, Current generating 'double layer shoe' with a porous sole: ion transport matters, *J. Phys. Chem. C*, 2017, **121**, 7583–7595.

**Frédéric Kanoufi** said: As a follow-up question on the experimental chemistry or electrochemistry of the system, you used TiO<sub>2</sub> electrodes which are likely of

high surface energy on which the 90° contact angle liquid might be tricky to reach. I wonder if you are considering the use of a thin organic hydrophobic layer to expand the use to other liquids? Have you considered or evaluated the effect of wettability hysteresis?

**Ehud Haimov** responded: We have chosen to consider the specific mixture of Li doped IL and TiO<sub>2</sub> electrode following a study<sup>1</sup> showing that a large non-wetting contact angle was reached. As for the organic solvophobic layer, if it's very thin (down to ~1 nm) and its incorporation does not drastically reduce the capacitance, it might be interesting to explore this suggestion. Indeed, this measure could help suppress contact angle hysteresis, the possible effect of which on the reverse actuator performance was not considered in our idealized model.

1 C. Wang, *et al.*, Revealing the wetting mechanism of Li<sup>+</sup>-doped ionic liquids on the TiO<sub>2</sub> surface, *Chem. Eng. Sci.*, 2023, **265**, 118211.

**Serge G. Lemay** opened a general discussion: This is a question aimed at stimulating further discussion. While of fundamental interest, to what extent is understanding of these microscopic fluctuations relevant in interpreting experiments? What can be learned?

**Benjamin Rotenberg** replied: Thank you for encouraging further discussion on this topic. I see several aspects to this question.

(i) In many experiments, the fluctuations of the measured properties are considered as “noise” that is detrimental to the target “signal”. This is particularly true in small systems (nanopores, nanofluidic devices) where the number of charge carriers is small. However, as you are well aware since you have also worked on this in the context of nanoelectrochemistry, these fluctuations encode information on the dynamics of the system of interest – as summarized in the title of Landauer’s famous article:<sup>1</sup> “the noise is the signal”. In order to interpret the experimentally measured “noise”, *e.g.* the spectral density of current fluctuations, modelling and simulations are particularly useful to disentangle the microscopic mechanisms that contribute to these fluctuations.

(ii) For a specific recent example of how this approach can be useful to interpret experiments, I can suggest ref. 2 (ref. 58 of our contribution) on the NMR quadrupolar relaxation rate of Na<sup>+</sup> ions in aqueous NaCl solutions, in particular the effects of temperature and concentration. The predictions from the electric field gradient fluctuations, using a combination of DFT calculations and classical molecular dynamics (MD) simulations, are in excellent agreement with the experiments and the analysis of the MD trajectories allows discussion of the microscopic mechanisms leading to the measured relaxation rates. Please also refer to my earlier answer to Alexei Kornyshev’s question for more detail.

(iii) In our contribution (<https://doi.org/10.1039/d3fd00026e>), which illustrates the general approach we explore in the ERC project SENSES, we propose a unifying theoretical perspective on electrical noise (largely based on previous work by others, even though we also include some of our recent contributions and new results on aqueous electrolytes) and highlight the fact that seemingly unrelated experiments can be considered as complementary windows on the same underlying dynamics. We hope that this contribution will encourage

experimentalists from different fields to consider their favorite approach with this in mind – and of course you are all welcome to get in touch with me if you would like to discuss more about this.

1 R. Landauer, *Nature*, 1998, **392**, 658.

2 I. Chubak, L. Alon, E. V. Silletta, G. Madelin, A. Jerschow and B. Rotenberg, *Nat. Commun.*, 2023, **14**, 84 (ref. 58 in the paper).

**Kislou Voitchovsky** answered: The initial motivation for this work is to find a way to quantify the mobility of charges at the interface. Put naively, if the applied field is too fast, the charges between the probe and the surface should not be able to follow, resulting in a different force being measured (assuming we are able to differentiate local effect from global background). Achieving this would enable ion mobility mapping across many systems from bio-interfaces to energy-related systems, with implications for both fundamental understanding and applications/design in technology.

**Frédéric Kanoufi** addressed Tanja Vidaković-Koch and Benjamin Rotenberg: This session had a common interest in the understanding from experimental and theoretical approaches of ion dynamics in systems showing non-linear behaviour. A typical system with increased interest might be the understanding of electrochemical gas evolution reaction during, for example, hydrogen evolution reactions. The electrogeneration of gas nanobubbles (or microbubbles) is obviously a complex non-linear problem in electrochemistry but also for modelling/theoretical studies at triple interfaces. Are there some new challenges in describing ion organization near a gas nanobubble or considering them as a charged particle? Would your strategies allow to apprehend such gas nanobubble formation in electrochemical systems?

**Tanja Vidaković-Koch** answered: Thank you for your question. Yes, the issue of gas formation at electrode surfaces is of great interest. The development of gas bubbles leads to an additional limitation of mass transfer, so the effect could be captured by the method proposed here. To do this, it is necessary to formulate a nonlinear dynamic model of an electrochemical process that describes gas formation and its effects on reaction kinetics. I am not familiar with research activities on stabilization of nanobubbles in electrolyte solutions and electrochemical double layer formation on such nanobubbles, thank you for mentioning this.

**Benjamin Rotenberg** replied: Dealing with this practically important issue is very challenging for molecular simulations due to the length and time scales involved. Brownian dynamics simulations such as the one discussed in our contribution for bulk electrolytes are probably not the best strategy. I would rather recommend alternative mesoscopic approaches able to deal with multiphase reactive interfacial flows, also taking into account electrostatic effects. In that respect, even though to the best of my knowledge there are at present no reported studies capturing all features simultaneously, the lattice Boltzmann method seems a good way forward, since it has already been used in different studies to investigate multiphase flow at interfaces, reactive flows, electrokinetic effects at liquid/liquid interfaces taking into account the dielectric contrast and the



solvation of ions in both phases,<sup>1</sup> and more recently reactions coupled to electrokinetic effects,<sup>2</sup> or electrokinetics near metallic electrodes.<sup>3</sup> An additional challenge to apply the proposed strategy to investigate the electrical response from charge fluctuations to the situation you mention is that the nonlinear response corresponds to rare current fluctuations at equilibrium. Recent developments based on large deviation theory are nevertheless promising for investigating the nonlinear response to electric fields with simulations, as illustrated, e.g., for the field-dependent conductivity in electrolytes and molten salts.<sup>4,5</sup>

1 B. Rotenberg, *et al.*, *Faraday Discuss.*, 2010, **144**, 223, DOI: [10.1039/b901553a](https://doi.org/10.1039/b901553a).

2 I. Tischler, *et al.*, *J. Comput. Sci.*, 2022, **63**, 101770, DOI: [10.1016/j.jocs.2022.101770](https://doi.org/10.1016/j.jocs.2022.101770).

3 A. J. Asta, *et al.*, *J. Chem. Phys.*, 2019, **151**, 114104, DOI: [10.1063/1.5119341](https://doi.org/10.1063/1.5119341).

4 D. Lesnicki, *et al.*, *Phys. Rev. Lett.*, 2020, **124**, 206001, DOI: [10.1103/PhysRevLett.124.206001](https://doi.org/10.1103/PhysRevLett.124.206001).

5 D. Lesnicki, *et al.*, *J. Chem. Phys.*, 2021, **155**, 014507, DOI: [10.1063/5.0052860](https://doi.org/10.1063/5.0052860).

**Martin Z. Bazant** opened discussion of the paper by Frieder Mugele: The experiments comparing surface forces on rough amorphous silica and smooth mica surfaces are very interesting, but can the results showing molecular oscillations on the crystal mica surface be interpreted quantitatively in terms of a theory?

I would suggest comparing to the recently published Dipolar Shell Theory,<sup>1</sup> which extends the nonlocal hard-sphere models for ions (charge monopoles) reviewed in the introductory lecture by Yan Levin (<https://doi.org/10.1039/d3fd00062a>) for polarizable hard spheres, as the most basic model of solvent molecules. This approach has been shown to reproduce surface forces, layering, and molecular orientations in molecular dynamics simulations of ionic liquids<sup>2</sup> and also different pure polar liquids including water.<sup>3</sup> The last figure of ref. 3 has curves for surface forces from the theory and MD simulations of water, which could be compared to your experimental data directly. The theory paper<sup>1</sup> also predicts effects of mixtures of ions and solvent molecules (monopoles plus dipoles), going beyond the primitive model of electrolytes with a continuous solvent, which again could be tested experimentally.

These theoretical papers also suggest an interesting direction for your experiments: vary the solvent. The theory<sup>1</sup> predicts a very simple formula for the range of oscillating solvent forces (“hydration forces” for water), a “solvation length” equal to the molecular diameter  $\times \alpha \times \sqrt{\epsilon - 1}$  where  $\epsilon$  = relative permittivity, and the factor  $\alpha = \frac{1}{\sqrt{6}}$  in the linearized theory for spherical solvent, and is an O(1) constant for real solvents in MD simulations.<sup>3</sup> This prediction would be very interesting to test by varying permittivity and solvent size, e.g. with water, acetonitrile, ethylene carbonate, and other important electrolytic solvents.

1 J. P. de Souza, A. A. Kornyshev and M. Z. Bazant, Polar liquids at charged interfaces: a dipolar shell theory, *J. Chem. Phys.*, 2022, **156**, 244705.

2 J. P. de Souza, K. Pivnic, M. Z. Bazant, M. Urbakh and A. A. Kornyshev, Structural forces in ionic liquids: the role of ionic size asymmetry, *J. Phys. Chem. B*, 2022, **126**, 1242–1253.

3 K. Pivnic, J. P. de Souza, A. A. Kornyshev, M. Urbakh and M. Z. Bazant, Orientational ordering in nano-confined polar liquids, *Nano Lett.*, 2023, **23**, 5548–5554.

**Martin Z. Bazant** also asked: The experiments with nano AFM tips revealing true molecular surface forces are brilliant, and I especially appreciate the results

concerning attractive surface forces in multivalent electrolytes. While the interpretation of Fig. 7 in the paper (<https://doi.org/10.1039/d3fd00049d>) to explain attractive surface forces from ‘cooperative ordering’ of solvent could be playing a role for  $\text{Cs}^+$ , this should be checked against the predictions of recent theories and MD simulations for solvents under extreme confinement between oppositely charged plates.<sup>1–3</sup> In any case, I believe this hydration mechanism is unlikely to be as important as ion–ion correlation effects for  $\text{Ca}^{2+}$  and other multivalent ions. A recent continuum model of oscillating multivalent ion surface forces (including monotonic hydration interactions) was able to accurately predict the attraction of calcium silicate hydrate (CSH) layers on flat mica surfaces, which is the critical mechanism for cohesion of cement paste.<sup>4</sup> Could a model like this also be relevant for the multivalent ion data presented here? It would be worth checking quantitatively.

- 1 J. P. de Souza, A. A. Kornyshev and M. Z. Bazant, Polar liquids at charged interfaces: a dipolar shell theory, *J. Chem. Phys.*, 2022, **156**, 244705.
- 2 J. P. de Souza, K. Pivnic, M. Z. Bazant, M. Urbakh and A. A. Kornyshev, Structural forces in ionic liquids: the role of ionic size asymmetry, *J. Phys. Chem. B*, 2022, **126**, 1242–1253.
- 3 K. Pivnic, J. P. de Souza, A. A. Kornyshev, M. Urbakh and M. Z. Bazant, Orientational ordering in nano-confined polar liquids, *Nano Lett.*, 2023, **23**, 5548–5554.
- 4 R. P. Misra, J. P. de Souza, D. Blankshtein and M. Z. Bazant, Theory of surface forces in multivalent electrolytes, *Langmuir*, 2019, **35**, 11550.

**Frieder Mugele** replied: This is a simultaneous answer to the previous two questions from Martin Bazant. This is a very interesting and justified remark. The primary point of our paper is to stress the universality and robustness of the phenomenology in the experiments, *i.e.* the presence of oscillatory forces with a characteristic separation between force maxima close to the diameter of the water molecules and the presence of a monotonic tail with an (approximately) exponential decay on the scale of a few molecular layers, independent of the substrate (crystalline mica *vs.* amorphous silica).

I fully agree that the microscopic interpretation in terms of an oscillatory solvation force (originating from packing) and a monotonically decaying hydration force is not unique. The interpretation in the suggested very recent publications by Bazant and Kornyshev and colleagues is certainly interesting. It is for us one of the most interesting insights of this *Faraday Discussions* meeting that different interpretations of our experiments in terms of these models are possible. There will be two main challenges: (a) the details of the oscillatory forces are most certainly affected by the geometry of the specific tip in the experiments. We will have to revisit the details of our data analysis procedures to see how confident we can be about interpreting minor variations that we deliberately ignored so far. (b) Suppose we can trust the experimental data regarding these small effects, there is still a question to the theorists of how one should distinguish oscillatory forces due to polarization correlations from oscillatory forces arising from excluded volume correlations. After all, the discreteness of water molecules is also undisputed. I look forward to follow-up discussions with our theory colleagues Bazant, Kornyshev and others to identify whether an alternative interpretation of our data can be given.

**Alexei A. Kornyshev** said: If you take the Landau–Ginzburg functional with higher order gradient terms then the theory will give you oscillations in hydration forces, which will, however, survive only if the interface is sharp.<sup>1</sup> It might be very

interesting to do experiments with cut tips with the cut surface area larger than all characteristic correlation lengths in the solution, and in one case have that surface very polished and in another case rough, and then to check the prediction of that theory. Of course it may be difficult to keep that cut surface parallel to the surface of the plane being probed, which is not the issue in the Surface Force Apparatus.

1 J. G. Hedley, H. Berthoumieux and A. A. Kornyshev, The dramatic effect of water structure on hydration forces and the electrical double layer, *J. Phys. Chem. C*, 2023, **127**, 8429–8447, DOI: [10.1021/acs.jpcc.3c00262](https://doi.org/10.1021/acs.jpcc.3c00262).

**Frieder Mugele** responded: I agree with the comment, this would be interesting to do. The challenge to guarantee a good alignment between the flattened tip and the solid surface can be met if the tip is not cut *ex situ* with a focus ion beam (as some others have done in the past) but if the tip is instead flattened at the bottom by rubbing it on the same sample, on which the AFM measurements are carried out. This can be done by taking AFM scans in so-called contact mode with a controlled normal load. In this manner, one can wear off the top of the tip and generate a flat bottom, which is by the nature of the process parallel to the substrate. Subsequently, one moves a few (or a few tens or hundreds) of micrometers to the side on the same sample and records the force–distance curves. This procedure has been used in our present paper (<https://doi.org/10.1039/d3fd00049d>) and is described in some more detail in ref. 1.

1 D. Ebeling, *et al.*, *Nanotechnology*, 2011, **22**, 305706.

**Y. K. Catherine Fung** asked: The paper (<https://doi.org/10.1039/d3fd00049d>) mentioned the hydration force of NaCl at different concentrations was measured on a mica surface. However, these graphs are not shown in the paper. Can you comment on the behaviour of the hydration force with NaCl at different concentrations on mica?

**Frieder Mugele** replied: Thank you Catherine. Indeed, the paper does not show any NaCl data. NaCl data were shown in our earlier publication.<sup>1</sup> The result is that NaCl displays very similar behaviour to LiCl and KCl regarding the oscillatory hydration force component. The monotonically decaying component is intermediate between LiCl and KCl, as one might expect.

1 S. R. van Lin, K. K. Grotz, I. Siretanu, N. Schwierz and F. Mugele, Ion-specific and pH-dependent hydration of mica–electrolyte interfaces, *Langmuir*, 2019, **35**, 5737–5745.

**Zuzanna S. Siwy** enquired: Your AFM experiments have revealed the structure of interfacial water. Could your measurements also inform us on the distribution of ions? Do your measurements probe properties of the Stern layer?

**Frieder Mugele** answered: One of the remarkable observations of this paper (<https://doi.org/10.1039/d3fd00049d>) as well as our earlier one<sup>1</sup> is that ions have a rather limited effect on the oscillatory part of the observed hydration forces – with the exception of Rb<sup>+</sup> and Cs<sup>+</sup>, the most weakly polarizable alkali cations that destroy the oscillatory hydration structure. For these ions, Prof. Voitchovsky and co-workers (see, *e.g.*, ref. 2) reported that individual

immobilized ions can be visualized at the mica–water interface for concentrations beyond approximately 10 mM. We also reported the visualization of ions in the Stern layer at the gibbsite water interface.<sup>3</sup> This study provided deep insights into how the complex composition of the Stern layer produces the ‘effective’ surface charge measured on the colloidal scale of, say, 1–2 nm and beyond.

- 1 S. R. van Lin, K. K. Grotz, I. Siretanu, N. Schwierz and F. Mugele, Ion-specific and pH-dependent hydration of mica–electrolyte interfaces, *Langmuir*, 2019, **35**, 5737–5745 (ref. 34 in the paper).
- 2 M. Ricci, P. Spijker and K. Voitchovsky, Water-induced correlation between single ions imaged at the solid–liquid interface, *Nat. Commun.*, 2014, **5**, 4400.
- 3 I. Siretanu, D. Ebeling, M. P. Andersson, S. L. S. Stipp, A. Philipse, M. C. Stuart, D. van den Ende and F. Mugele, Direct observation of ionic structure at solid-liquid interfaces: a deep look into the Stern Layer, *Sci. Rep.*, 2014, **4**, 4956 (ref. 55 in the paper).

**Susan Perkin** said: You show small oscillations in force which are attributed to ‘hydration forces’ and water layering. The wavelength doesn’t appear to change, despite adding salt at different concentrations, and there has been some discussion about why that is the case. It seems to me helpful to interpret these oscillations as arising from the water–water correlation contribution to the total interaction potential; this is the dominant term at low salt concentration. Beyond a certain critical concentration the wavelength of oscillations might be expected to shift to a different value determined by the ion correlations. Did you see this?

**Frieder Mugele** responded: I am not sure if I understand the first part of the comment completely. But it is closely related to a very interesting issue that I start to appreciate thanks to this meeting. When we attribute the oscillatory part of the forces to water layering, then I would call this a contribution from the water–water correlation, specifically from its entropic part as in a hard sphere liquid. This is what we discuss in our paper and try to describe in the final sketch in Fig. 7 of the paper (<https://doi.org/10.1039/d3fd00049d>). Based on the work of Professors Kornyshev and Bazant and co-workers and discussions throughout this meeting, I understand that such force oscillations may also arise from the oscillatory part of the orientational correlations of water (related to non-local water polarization). At present, I would not know how to tell these two possible origins apart. This will be the subject of follow-up discussions with Professors Kornyshev and Bazant.

Regarding the transition to a different characteristic spacing of force oscillations: as described in our paper, we do not observe this. In fact, we never saw such a transition in measurements for concentrations up to 4 M. To our knowledge, this is consistent with all other work in the AFM literature, with one notable exception,<sup>1</sup> which also reported a transition to ion-related periodicities of increasing correlation length. However, we understood from the first author of that work that those measurements were done in an evaporating drop close to crystallization. Therefore, the actual concentration at the moment of the measurement is not known and not well defined. Having said this, the observation nevertheless qualitatively supports the very plausible idea of the existence of such a transition upon approaching crystallization. Our measurements are all performed in closed cells and never displayed any such transition within the range of concentrations studied (*i.e.* up to 4 M).

1 D. Martin-Jimenez, E. Chacon, P. Tarazona and R. Garcia, Atomically resolved three-dimensional structures of electrolyte aqueous solutions near a solid surface, *Nat. Commun.*, 2016, 7, 12164.

**Monica Olvera de la Cruz** asked: The diagrams of the water dipoles show some correlation different in positive and negative. Can you extract the range? In negatively charged domains in proteins dipoles are correlated over 1.7 nm, a larger distance than in positively charged domains which is 1.2 nm and this may affect their solubility.<sup>1</sup> Is this range similar to what can be observed?

1 B. Qiao, F. Jiménez-Ángeles, T. D. Nguyen and M. Olvera de la Cruz, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, 116, 19274–19281.

**Frieder Mugele** replied: As shown in Fig. 2–4 and 6 of our paper (<https://doi.org/10.1039/d3fd00049d>), the range over which we can detect oscillatory forces is approximately 1 nm. The monotonic contribution can sometimes extend up to 1.5 nm, as also shown in our earlier paper.<sup>1</sup> We cannot tell possibly positively or negatively charged domains on the surface apart. As we explain in our paper, we also don't believe that charge (on a colloidal scale) is important for the observed water oscillations. Instead, we believe that the hydration forces are dominated by the local anchoring of water to the substrate (hydrogen bonding) in combination with short-range packing effects.

1 S. R. van Lin, K. K. Grotz, I. Siretanu, N. Schwierz and F. Mugele, Ion-specific and pH-dependent hydration of mica–electrolyte interfaces, *Langmuir*, 2019, 35, 5737–5745 (ref. 34 in the paper).

**Tim M. Kamsma** opened discussion of the paper by Elalyaa Mohamed: The transistor keeps its memory over a long time scale, for which your hypothesis was that it is difficult for ions to permeate the membrane. If that is the case then one would expect it to slowly equilibrate if you leave it for a while, is that what you also observe in your experiments?

**Elalyaa Mohamed** responded: Yes. This is what I observe when I leave it for a while. As we decrease the size of the membrane's pores the time to equilibrate will increase.

**Tim M. Kamsma** asked: What is the typical switching time of the device?

**Elalyaa Mohamed** answered: Thank you for your question. The typical time for switching is around 20 s.

**Paul Robin** enquired: If I understand correctly, your device is a nanofluidic transistor with a memory, let us say a “memtransistor”. I know about memristors, but is a “memtransistor” a thing in the electronic literature? If so, for what kind of applications is it used?

**Elalyaa Mohamed** replied: Thank you for your question. The ionic voltage effect soft triode (IVEST) is not a nanofluidic device. It is an electrochemical device in the macro range. Recently we have been trying to decrease the size to

micro by printing or sputtering the bottom electrodes. The construction of the IVEST allows different ways of construction.

I would like to call it a “triode” as it is a more general name not restricted to specific function or design. Can we use it as a memtransistor? Yes. It has a memory function and a controllable resistance. We think that it can be a base for new computational systems and can be a building block for neuromorphics. Likely it can be used in applications related to memory.

**Fabio Cicoira** asked: Why did you choose TiO<sub>2</sub> for your device?

**Elalyaa Mohamed** responded: The construction of the IVEST was inspired by the DSSC. Titanium dioxide proved to work very well with the electrolyte and the other parts of the device. We wanted to have a semiconductor layer that can desorb ions and be compatible with the used electrolyte.

**Fabio Cicoira** enquired: Why do you need to have first the compact layer and then the nanoparticles?

**Elalyaa Mohamed** answered: We used the compact layer to reduce the back flow of the electrons and reduce the possibility of the reaction of the electrode and the electrolyte. It is also important for making interconnection between the TiO<sub>2</sub> layer and the metal mesh.

**Igor Siretanu** asked: Are the memory effects of ionic devices (ionic voltage effect soft triodes) displaying any ion-specific effects? Does the illumination and activation of UV light change its properties?

**Elalyaa Mohamed** replied: Thank you for your question. Actually, we did not investigate yet the specific ionic effects that the memory effect of the IVEST can display. For the effect of illumination, we already started investigating these effects.

**Yujia Zhang** queried: How is the memory effect related to the size of the device?

**Elalyaa Mohamed** answered: Thank you for your question. We expect that the memory effect will be improved when we decrease the size.

**Bee Hockin** said: In your paper (<https://doi.org/10.1039/d3fd00020f>) you mention that the stability of the device was “monitored over days up to 200 days, as shown in Fig. 6B”, and that the observed changes in performance are moderate and likely connected with solvent loss. You go on to say that after the technical improvement of the construction method, the devices show better stability. Could you please comment firstly on what methods were used to improve the construction of the device, and secondly how this “better” stability was quantified? It appears that the TiO<sub>2</sub> recipe was changed, could you comment briefly on this change and how it affected the device please?

**Elalyaa Mohamed** responded: To improve the construction of the device new parts were added to the fabrication method. We used a plastic ribbon with a defined shape to have a known geometry of the device. This ribbon made it easier to fix the bottom electrode. The device was also fixed on an electronic

breadboard and the connection to the measuring setup was through metal pins as shown in Fig. 1A of the paper (<https://doi.org/10.1039/d3fd00020f>). This decreased the possibility of mechanical destruction of the device and decreased the fluctuation of the measured  $R_{BB}$  by the known fixed geometry. In our previous publication<sup>1</sup> another recipe was used for the TiO<sub>2</sub> suspension. This suspension resulted in a thick layer of TiO<sub>2</sub> on the top electrode containing dead material that is not in contact with the top electrode. To get the optimized performance we had to change the suspension. The used recipe was then improved to result in a smooth layer with no dead material on the top electrode as shown in Fig. 5 here, copied from ref. 1: (b) is the old recipe and (c) is the improved one used in this *Faraday Discussions* paper. The performance of the IVEST improved with the new TiO<sub>2</sub> recipe.

1 S. Josten, T. Koehler and F. Marlow, *Sol. Energy*, 2022, **247**, 346–354, DOI: [10.1016/j.solener.2022.10.036](https://doi.org/10.1016/j.solener.2022.10.036) (ref. 21 in the paper).

**Mark Aarts** asked: Concerning the use of separators with different pore sizes, how does this affect for example the setting and/or retention time of the transistor?

**Elalyaa Mohamed** answered: Thank you for your question. When we decrease the size of the pore starting from 600 nm and below the injection of the electrolyte inside the device becomes more difficult. For the retention time, it increases, as the ions will need more time to diffuse through the membrane.

**Igor Siretanu** opened discussion of the paper by Robert A. W. Dryfe: How are the solutions of 5–6 M prepared, making sure that the salts have fully dissolved? Did you quantify the conductivity of the solution? Is the graphene deposited on a Si wafer? Have you tried different substrates and observed any differences?

**Robert A. W. Dryfe** replied: The graphene is deposited on an oxide-covered Si wafer, as stated in the Experimental section of our paper. I agree that it would be extremely interesting to look at the effects of other substrates but we have not had an opportunity to do so yet.

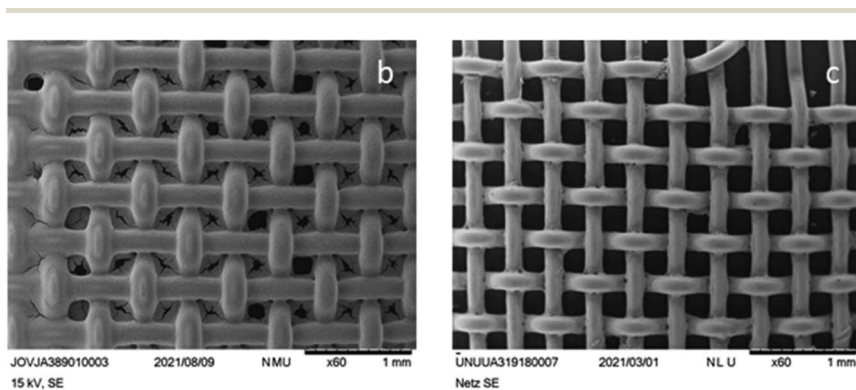


Fig. 5 (b) SEM image of TiO<sub>2</sub> coated working electrode (old recipe) and (c) improved TiO<sub>2</sub> coating. Reproduced from Josten *et al.*, *Sol. Energy*, 2022, **247**, 346.<sup>1</sup>

Regarding the solutions, we work with salts that have high solubility, about 15 *m* in some cases, and have taken care to measure the basic physical properties of these concentrated electrolyte phases, including their conductivity (see the supporting information of our 2022 paper).<sup>1</sup>

1 A. A. Papaderakis, K. Polus, P. Kant, F. Box, B. Etcheverry, C. Byrne, M. Quinn, A. Walton, A. Juel and R. A. W. Dryfe, *J. Phys. Chem. C*, 2022, **126**, 21071–21083, DOI: [10.1021/acs.jpcc.2c06517](https://doi.org/10.1021/acs.jpcc.2c06517) (ref. 16 in the paper).

**Lydéric Bocquet** asked: For such graphitic surfaces, there is the risk of pollution by hydrocarbons or other components in the air. Do you prepare the surface in a clean room? Or any specific procedure to prepare fresh surfaces? Do you monitor the changes over time?

**Robert A. W. Dryfe** responded: The short answer is “no” and this is a difficulty with our graphene experiments, which complicates the direct comparison with the (electro)wetting response of graphite.

In our earlier work on graphite,<sup>1</sup> we are able to obtain a strong and entirely reproducible electrowetting response, but the effect does require the graphite basal plane to be as clean as possible. This does not mean the use of clean room conditions, rather we cleave the graphite sample and immediately contact the surface with the droplet. Leaving the sample open to the surface indeed allows for ambient contamination, as we and others have seen, which indeed weakens the wetting response. The difficulty we have for graphene is that the sample cannot be cleaved in the same way so although we take care to work under “clean” conditions, we cannot be so sure about the surface state of the sample, particularly as the sample is prepared *via* chemical vapor deposition (CVD) methods in a separate laboratory. That said, the strongest wetting effects we have seen on graphene (*e.g.* see Fig. 3(a) of our manuscript; <https://doi.org/10.1039/d3fd00037k>) relate to ions which we believe intercalate, rather than merely “adsorbing”. The observation of a weaker change with respect to graphite for these intercalation anions does suggest that the system can less easily and reversibly accommodate the potential-induced change – an effect which may be independent (to some extent) of sample contamination.

1 A. A. Papaderakis, K. Polus, P. Kant, F. Box, B. Etcheverry, C. Byrne, M. Quinn, A. Walton, A. Juel and R. A. W. Dryfe, *J. Phys. Chem. C*, 2022, **126**, 21071–21083, DOI: [10.1021/acs.jpcc.2c06517](https://doi.org/10.1021/acs.jpcc.2c06517) (ref. 16 in the paper).

**Alexei A. Kornyshev** enquired: What do you think may be the effect of quantum capacitance of graphene<sup>1</sup> on electrowetting?

1 T. Fang, A. Konar, H. Xing and D. Jena, Carrier statistics and quantum capacitance of graphene sheets and ribbons, *Appl. Phys. Lett.*, 2007, **91**, 092109.

**Robert A. W. Dryfe** answered: This is a good question. Our work focusses mainly on the wetting effect, but this is, of course, dictated by the capacitance. The work cited shows the “bottom-gating” configuration which has been extensively used by the solid-state physics community, however the benefits of “top-gating” (*via* the electrolyte) have been realised more recently – for a discussion of the pros and cons of these approaches, see ref. 1.



In either case, the “gating” phase (the dielectric solid, or the electrolyte) provides a capacitance in series with the intrinsic capacitance of the electrolyte. In the case of our electrowetting experiments, we use as high a concentration of electrolyte as possible (for other experimental reasons, see earlier papers<sup>2,3</sup>), but this has the spin-off benefit of maximising the contribution from the 2D material. Despite this, there is not a strong correlation between predicted and measured wetting responses (or capacitive responses that would be inferred from those wetting responses). As other questions have indicated, this is probably because of the sensitivity of the substrate to ambient contamination. In other words, further efforts are required to clean the graphene *in situ* (if possible) immediately prior to the wetting experiments – in line with what we have been able to achieve by cleavage of graphite materials.

1 M. Velický, *J. Phys. Chem. C*, 2021, **125**, 21803.

2 Z. Li, Y. Wang, A. Kozbial, G. Shenoy, F. Zhou, R. McGinley, P. Ireland, B. Morganstein, A. Kunkel, S. Surwade, L. Li and H. Liu, Effect of airborne contaminants on the wettability of supported graphene and graphite, *Nat. Mater.*, 2013, **12**, 925–931, DOI: [10.1038/nmat3709](https://doi.org/10.1038/nmat3709).

3 C. A. Amadei, C.-Y. Lai, D. Heskes and M. Chiesa, Time dependent wettability of graphite upon ambient exposure: The role of water adsorption, *J. Chem. Phys.*, 2014, **141**, 084709, DOI: [10.1063/1.4893711](https://doi.org/10.1063/1.4893711).

**Paul Robin** said: Your experiment, where you measure a “slow” decay of the contact angle of a droplet on graphene, made me think of another one by Mischa Bonn and co-workers.<sup>1</sup> In their experiment, they measure through sum-frequency generation (SFG) the orientation of water next to a graphene surface acting as an electrode, itself deposited on a chemically-active material that can react with protons. Depending on the voltage of the electrode, they measured a “slow” re-orientation of water molecules. They attributed that to the fact there was a chemical reaction in the substrate below the graphene, which was limited by proton transfer through graphene.

Could there be some link with what you measure; *i.e.*, maybe the “intercalation” of ions that you mention could be something similar to the proton transfer they suggest? Maybe this could be tested by looking at different substrates?

For the details of the experiment, you can find them in ref. 1. I believe that in this specific paper they don't mention the “slow” reorientation effect (which is unpublished I think, probably in preparation).

1 Y. Wang, Y. Nagata and M. Bonn, *Faraday Discuss.*, 2024, DOI: [10.1039/d3fd00107e](https://doi.org/10.1039/d3fd00107e).

**Robert A. W. Dryfe** responded: Thank you, this is a very interesting comment. I was not previously aware of the pre-print by this group,<sup>1</sup> in the forthcoming *Faraday Discussions* volume on Water at interfaces, but I have consulted it and the earlier work by this group<sup>2</sup> (ref. 10 of their *Faraday Discussions* pre-print<sup>1</sup>). The work of Bonn and co-workers is indeed interesting, although as you correctly state, the dynamic measurements are not (yet) reported. Without knowing more about the details of the Bonn work, it is difficult to comment further, but I would add that the effect that we see is specific to “larger” anions such as the TFSI anion (bis(trifluoromethanesulfonyl)azanide) and the perchlorate anion, which are known to intercalate within graphite layers (see our recent work<sup>3</sup>). This specificity to larger anions suggests that the anions themselves are responsible, although one could argue for an intercalation step that allows for proton transfer.

It would certainly be interesting to look at the effect of different substrates on graphene electrowetting, not least because wetting “transparency” of graphene and the associated role of the substrate has been a rather controversial topic (see for example: ref. 4).

- 1 Y. Wang, Y. Nagata and M. Bonn, *Faraday Discuss.*, 2024, DOI: [10.1039/d3fd00107e](https://doi.org/10.1039/d3fd00107e).
- 2 Y. Wang, T. Seki, X. Liu, X. Yu, C.-C. Yu, K. F. Domke, J. Hunger, M. T. M. Koper, Y. Chen, Y. Nagata and M. Bonn, *Angew. Chem., Int. Ed.*, 2023, **62**, e202216604, DOI: [10.1002/anie.202216604](https://doi.org/10.1002/anie.202216604).
- 3 A. A. Papaderakis, A. Ejigu, J. Yang, A. Elgendy, B. Radha, A. Keerthi, A. Juel and R. A. W. Dryfe, *J. Am. Chem. Soc.*, 2023, **145**, 8007–8020, DOI: [10.1021/jacs.2c13630](https://doi.org/10.1021/jacs.2c13630).
- 4 C.-J. Shih, Q. H. Wang, S. Lin, K.-C. Park, Z. Jin, M. S. Strano and D. Blankshtein, *Phys. Rev. Lett.*, 2012, **109**, 176101, DOI: [10.1103/PhysRevLett.109.176101](https://doi.org/10.1103/PhysRevLett.109.176101).

**Zuzanna S. Siwy** asked: Would the reversibility of the wetting–dewetting transition observed in your experiments depend on the size of anions? In other words, did you see a difference between fluoride and chloride salts?

**Robert A. W. Dryfe** replied: To a first approximation, at low potentials, we do not see a strong difference between fluoride and chloride, at least for graphite electrodes. Our earlier work has investigated these anions to some extent (see ref. 1 and 2). At more extreme positive potentials, above approx. 1 V vs. Ag/AgCl, we do see a change that is specific to the fluoride, which we attribute to the (known) formation of fluoride intercalation compounds and partial fluorination of the surface.

- 1 A. A. Papaderakis, K. Polus, P. Kant, F. Box, B. Etcheverry, C. Byrne, M. Quinn, A. Walton, A. Juel and R. A. W. Dryfe, *J. Phys. Chem. C*, 2022, **126**, 21071–21083, DOI: [10.1021/acs.jpcc.2c06517](https://doi.org/10.1021/acs.jpcc.2c06517) (ref. 16 in the paper).
- 2 D. J. Lomax, P. Kant, A. T. Williams, H. V. Patten, Y. Zou, A. Juel and R. A. W. Dryfe, *Soft Matter*, 2016, **12**, 8798–8804, DOI: [10.1039/c6sm01565d](https://doi.org/10.1039/c6sm01565d) (ref. 17 in the paper).

## Conflicts of interest

There are no conflicts to declare.