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DISCUSSIONS

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Electrotunable wetting, and micro- and nanofluidics: general discussion

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David Schiffrin opened discussion of the introductory lecture by Serge Lemay: After listening carefully to your challenging presentation I was left wondering if you believe in the validity of modeling as a reasonable approach to solving scientific issues?

Serge Lemay responded: It appears that I may have taken an overly pessimistic tone during the presentation! Yes, I believe that modeling is an important tool for disentangling complex transport processes involving diffusion, convection and electron transfer. In our work on electrochemical nanofluidics, for example, we have strived to account quantitatively for experimental observations using a combination of analytical calculations, simplified one-dimensional transport models and three-dimensional finite-element calculations. In practice, however, new effects are usually first encountered in the form of unexpected results to an experiment. For the case of concentration polarization, for example, we only came to the realization that it is necessary to account for the differences in diffusion coefficients between redox states after observing cross-talk between different electrodes co-located in a nanofluidic channel. While this could have been first predicted *via* modeling, there was little motivation to attempt such modeling until an experiment exhibited behaviour that was not fully understood.

Andriy Yaroshchuk opened a general discussion of the paper by Frieder Mugele: In the paper, you mention a surface charge density of -32 mC m^2 estimated from a zeta potential of approximately -40 mV at the salt concentration of 10^{-6} mol L^{-1}. According to my estimate, the charge density, should actually be about two orders of magnitude lower. To what extent could this change your conclusions?

Frieder Mugele replied: This comment is fully correct. There was clearly a mistake in the conversion of the complementary zeta potential measurements (Fig. 10 in the paper) into charge density in the original accepted version of the manuscript. We have rectified this in the final published version. In doing so, it turns out that the trapped charge density after many hours becomes a substantial fraction of the one extracted from the zeta potential. This suggests that a large fraction of the spontaneous surface charge at the Teflon–water interface eventually ends up in a trapped state. This picture is in fact much simpler than the one resulting from the original erroneous calculation. As a consequence, some aspects of the original discussion in the paper have become obsolete and were eliminated.

Alexei A. Kornyshev asked: Why it is only negative charges that adsorb into your solid matrix. Is it specific to the nature of the surface and the electrolyte used?

Frieder Mugele responded: There is a wide body of literature that reports negative surface charges for the vast majority of hydrophobic polymers (including Teflon) upon immersion into water. This is consistently found in various types of electrokinetic measurements, as well as force measurements and works on colloidal stability. All of these experiments probe the charge in the diffuse part of the double layer – which is equal and opposite to the charge that sits either directly on the solid surface or in a Stern layer. Generally, this negative surface charge is found to increase strongly with increasing pH, however, it decreases and eventually reverses below the isoelectric point, which is frequently found around pH 2–4 for this type of surface. This strong pH dependence in combination with the comparatively rather weak dependence on the presence of (weakly adsorbing) salt ions is the basis for the widespread conviction that the negative surface charge is caused by the adsorption of hydroxyl ions. A nice review on this topic was given by Zimmermann *et al.*[1] It should be added though, that research from the community of vibrational spectroscopy – *e.g.*, Sylvie Roke at EPFL – criticize this interpretation because they do not find the expected strong OH^- stretch signal in their non-linear optical sum frequency generation experiments.

1 R. Zimmermann, U. Freudenberg, R. Schweiß, D. Küttner and C. Werner, *Curr. Op. Coll. Interf. Sci.*, 2010, **15**, 196–202.

Carlos Drummond enquired: You have reported the time/history dependence of the properties of the fluoropolymer coatings commonly used in electrowetting applications. Have you found any correlation of this evolution with structural changes in the material? (*e.g.* local elastic modulus, morphology...)

Frieder Mugele answered: We have not studied these aspects in great detail. We did a few tests *via* AFM by comparing the surface structure before and after aging. In general, we did find similar spontaneous nano-structuring to that you reported earlier for polystyrene[1] if we age in degassed water at very high or very low pH. Yet, the data shown in the paper all refer to aging in normal aerated water, which does not show the spontaneous nanostructuring, but still displays trapped charge. Therefore, it seems that both phenomena co-exist, but there is no obvious and strong correlation. However, it may be worthwhile exploring this question in more detail.

1 I. Siretanu, J. P. Chapel and C. Drummond, *ACS Nano*, 2011, **5**, 2939–2947.

Mark Rutland remarked: The dynamics of the charge trapping observation is reminiscent of the migration of polar groups to the surface in response to exposure to a high dielectric constant medium. Is there a possibility that the trapped charges are associated with residual polar groups originating from the polymeric initiator during synthesis? In which case, there should be a molecular weight dependence on the trapped charge density, and possibly the dynamics of the trapped charge build up.

Frieder Mugele responded: This is an interesting thought. Some dependence of the charge trapping capability of fluoropolymers on molecular weight, composition (fractional composition of co-polymers) and initiators has been reported in the context of their use as electret materials. We have not explored this aspect in detail. This might indeed be an interesting candidate mechanism to explain the slow evolution of the trapped charge. At this stage, we do not have any microscopic insight into the nature of the trapped states.

Mark Rutland remarked: As a supplement to my previous question; while the presence of trapped charges seems unambiguous, the argument that hydroxides are responsible because hydrophobic surfaces such as air are negatively charged is not strictly tenable. The usual argument is that such surfaces are negatively charged because hydroxide ions are depleted less than hydronium ions, not because there is an intrinsic affinity.

Frieder Mugele replied: I agree that preferential hydroxyl adsorption cannot be deduced directly from our measurements. We simply find the same pH dependence of the trapped charge as usually reported for allegedly adsorbed hydroxyls in electrokinetic experiments. The rest is inferred from there using models such as those in ref. 14, 17–19 in the paper. I agree that “preferential adsorption” in the context of Teflon–water interfaces might also be phrased as “less depletion” in some way.

David Schiffrin said: The generally used electrowetting (EW) eqn (2) in your paper considers that the electrical energy associated with charging of the dielectric layer between the metal contact and the conducting droplet translates into a change of the interfacial tension of the solid–liquid drop interface and, hence, through the Young equation, to the electrical potential induced changes in the contact angle. Earlier in this discussion, Professor Mugele has clarified the role of the dependence of EW on liquid–vapour surface tension. Although the thermodynamic analysis of the EW system is still controversial, the relevance of surface stress for describing the forces acting at the interface between a solid and a liquid cannot be disregarded. Lipkowski *et al.*[1] recognised that interfacial tension and surface stress for a liquid metal in contact with an aqueous electrolyte have the same value, but that this is not the case for a polarised solid metal–solution interface. This distinction for electrified interfaces was extensively discussed by Haiss.[2] Electrochemical research has concentrated on the metal–solution interface, whereas, in the EW experiments, the “interfacial region” comprises a solid polymer with widely different mechanical properties than those of a metal–solution interface. In this respect, do you think it is correct to employ, for the former, the Lippmann formalism in the whole potential range usually studied? Ibach and others[3] demonstrated that the interfacial stress differs from the specific surface free energy and from the electrical energy supplied to the interfacial capacitance when the potential is changed (see, for instance, pages 114–116 of ref. 3). Do you think that the mechanical properties of the polymer dielectric could have a bearing on the contact angle saturation and subsequent hysteresis observed in EW measurements if the electrostatic tensile stress goes beyond the elastic limit of the polymer dielectric material? If this were the case, dielectric polymer crystallinity would determine the onset of contact angle saturation.

1 J. Lipkowski, W. Schmickler, D.M. Kolb and R. Parsons, Comments on the thermodynamics of solid electrodes, *J. Electroanal. Chem.*, 1998, **452**, 193–197.
2 W. Haiss, Surface stress of clean and adsorbate-covered solids, *Rep. Prog. Phys.*, 2001, **64**, 591–648.
3 H. Ibach, C. E. Bach, M. Giesen and A. Grossmann, Potential-induced stress in the solid-liquid interface: Au(111) and Au(100) in an HC104 electrolyte, *Surf. Sci.*, 1997, **375**, 107–119.

Frieder Mugele replied: Indeed, in the early 2000's there were vivid debates about the physical origin of the contact angle reduction in electrowetting-on-dielectric (as we discuss in our contribution), in particular whether it should be described using the same physico-chemical approach as in Lippmann's electrocapillary effect or whether what has been termed the "electromechanical" picture based on the distribution of Maxwell stresses would be more appropriate. In the end it became clear that the latter picture is more appropriate. From an energetic point of view, this is clear because the electric double layer and the dielectric layer can be viewed as two capacitors in series, where the double layer capacitance is approximately 1000× higher than that of the dielectric layer. Under such conditions, basic high school electrostatics tells us that the majority of the energy is stored in the smaller capacitance, *i.e.* in the dielectric layer. One of the early publications in the EW literature pointing out this aspect was by Fokkink and various co-workers in a series of articles published in *Langmuir* (1994, 1998)[1,2] and also *J. Electroanal. Chem.* (1994).[3] Later, Jones (*e.g.* in *J. Micromech. Mircoeng.*, 2005)[4] and my own group (Buehrle *et al.* in *Phys. Rev. Lett.*, 2003, and *J. Phys. Cond. Matt.*, 2007)[5,6] demonstrated that the microscopic contact angle at the contact line is actually not altered in electrowetting-on-dielectric, only the macroscopically apparent one on a length scale beyond the thickness of the insulating layer. The experimental verification of this claim provided[6] the ultimate proof of the dominance of the delocalized electrostatic field (and thus the Maxwell stress) distribution in electrowetting-on-dielectric rather than any microscopic effect on the scale of the electric double layer. The origin of contact angle saturation is, obviously, still one of the mysteries in electrowetting. According to models that implement the insulating layer and the ambient medium as perfect dielectrics and the drop as a perfect conductor, there should not be any contact angle saturation. Yet, these same models predict a divergence of the local electric field upon approaching the contact line, as already pointed out by Bruno Berge and co-workers in their work in *Eur. Phys. J. B* (1999).[7] Even if the Debye screening length is used as a natural cut-off for this divergence on small scales, this still predicts enormously strong electric fields close to the contact line that exceed the dielectric strength of typically used materials. So, it seems more or less clear that the origin of contact angle saturation can be traced back to some kind of non-linear material response beyond some critical voltage – preferentially in the vicinity of the contact line. The exact microscopic mechanism that eventually leads to failure is difficult to identify, amongst others, because it probably varies from system to system and depends a lot on the specific experimental conditions. In particular, the preparation and quality of the dielectric layers. Most people starting in electrowetting initially struggle with the poor quality of the dielectric layers, which break down at relatively low voltages. Once you improve the quality of the layers (or use very thick ones) other instabilities can arise, such as a breakdown of the ambient vapor, or the ejection of highly charged satellite drops from the contact line in a process that is similar to electrospraying (or a Rayleigh-like coulomb instability of charged drops). I am not aware of evidence that the electric field generates mechanical stresses exceeding the elastic limit of the substrate. But depending on the materials properties of the polymer, I can imagine that this could happen as well in certain systems (in our lab, we are currently looking at the response of soft rubbery substrates to the electric stresses in the spirit of something that can be called elasto-electro-capillarity. However, these experiments stay within the elastic limit of the substrate.) My personal conviction regarding contact angle saturation is that it is caused by the diverging electric fields – but that there is no universal mechanism for different systems.

1 C. Schoenenberger, J. A. M. Sondag-Huethorst, J. Jorritsma and L. G. J. Fokkink, *Langmuir*, 1994, **10**, 611–614.
2 W. J. J. Welters and L. G. J. Fokkink, *Langmuir*, 1998, **14**, 1535–1538.
3 J. A. M. Sondag-Huethorst and L. G. J. Fokkink, *J. Electroanal. Chem.*, 1994, **367**, 49–57.
4 T. B. Jones, *J. Micromech. Mircoeng.*, 2005, **15**, 1184.
5 J. Buehrle, S. Herminghaus and F. Mugele, *Phys. Rev. Lett.*, 2003, **91**, 861011–861014.
6 F. Mugele and J. Buehrle, *J. Phys. Cond. Matt.*, 2007, **19**, 375112.
7 M. Vallet, M. Vallade and B. Berge, *Eur. Phys. J. B*, 1999, **11**, 583–591.

Robert Dryfe asked: Your data (*e.g.* Fig. 4 in the paper) suggests that hydroxide ions "age" the Teflon dielectric layer, with the ageing effect more pronounced as the solution pH is increased. My question is whether this effect is reversible, *i.e.* if the Teflon, following ageing, is subsequently immersed in acidic solution, is the ageing attributed to the hydroxide reversed?

Frieder Mugele answered: We tried to remove the trapped charge by thermal annealing, as reported in the paper. Yet, this was not successful. Aging again in very acidic solution is a possibility that we have not explored. I agree that it would be worthwhile to try.

Roland Bennewitz enquired: Does the interaction of between droplet and trapped charged also influence the trapped charges, for example by redistributing them? Could the temporal development of the contact angle after application of a voltage step be used to probe dynamics in trapped charges?

Frieder Mugele answered: In principle, it is conceivable that the EW measurement affects the distribution of the trapped charge. Yet, for the majority of our experiments, we don't think that this plays an important role. First of all, the formation of the trapped charge takes place on a typical time scale of several hours as shown by the data in Fig. 2–5, whereas the time scale of probing the trapped charge is only a few minutes (see Fig. 2 in the paper). Secondly, the aging takes place upon direct immersion of the polymer surfaces into water, whereas the trapped charge measurements by EW in Fig. 2–5 are carried out with water drops in ambient oil. Immersing the system into ambient oil is a common practice in EW for several reasons, one of them is because it tends to minimize the interaction of the (typically aqueous) drop phase with the hydrophobic substrate and thereby improves the lifetime of the samples (and actual commercial devices). Having said this, the experiments shown in Fig. 6 and 7 were carried out upon aging the surface in direct contact with water under EW conditions, as explained in the paper. The difference in the aging behavior for positive and negative drop bias in Fig. 7 clearly shows that the formation of trapped charge can indeed be controlled to some extent by EW. I agree with you, that it should be possible to extract kinetic information from experiments such as the ones shown in Fig. 6 and 7. We plan to do this in upcoming experiments.

Konstantin Kornev remarked: These experimental results are very interesting and convincing that the fluoropolymer acquires an additional negative charge, which you called the trapped charge. I think that electrowetting is a great tool to distinguish the two processes of charge deposition: from the drop interior (bulk) or from the drop surface. There is a hot debate on interface charging by OH groups, see for example, ref. 1 and 2. Looking back at your data, do you see any evidence supporting the idea that the charges get deposited on the polymer surface during spreading/contraction of the droplet? Do you believe that the main mechanism of charging is the OH diffusion from the bulk?

1 J. K. Beattie, A. M. Djerdjev and G. G. Warr, *Faraday Discuss.*, 2009, **141**, 31–39; K. Hänni-Ciunel, N. Schelero and R. von Klitzing, *Faraday Discuss.*, 2009, **141**, 41–53.
2 M. Liu, J. K. Beattie and A. Gray-Weale, *J. Phys. Chem. B*, 2012, **116**, 8981–8988.

Frieder Mugele responded: What we see experimentally is that negative charge does accumulate at the polymer–water interface (or possibly slightly below that interface). The magnitude of that charge increases substantially with increasing pH, as we report in Fig. 4 of our paper. The strong pH dependence and weak dependence on the presence of other (non-adsorbing) ions is generally seen as a key argument in support of the hydroxyl-adsorption scenario for the charging of the polymer–water interfaces. Of course, our macroscopic experiments lack chemical sensitivity and hence do not provide direct proof of the nature of the adsorbed anionic charge carriers. Yet, all of our observations are consistent with the idea of OH^- adsorption. And yes, the fact that the EW curve shifts implies that a substantial fraction of these adsorbed OH^- ions actually become permanently adsorbed in energetically very deep trap states. The latter is an additional aspect in our observations that is usually not captured in conventional electrokinetic measurements.

Evgeny Smirnov opened a general discussion of the paper by Robert Dryfe: When we are talking about electrotunable wetting there are two main question raised:

(1) How pure are the solvents and materials (like the wires and external substrates used)?

(2) Can impurities, if they are present in the system, significantly influence the electrowetting phenomena?

Robert Dryfe answered: With respect to question 1: the counter electrode is in contact with the droplet and could contaminate it, but this does not seem to be a problem, based on our work so far. If this were a problem, the approach of Kornyshev, Kucernak and Urbakh, based on the ITIES could be pursued – this means that the auxiliary electrode(s) are not in direct contact with the droplet.

For question 2: yes, certainly, in the case of adsorbates on the graphitic surface, which was discussed in the present paper.

Frieder Mugele commented: Of course, impurities are always an issue in surface science experiments and it is hard to 100% exclude them. The care that we take in cleaning the materials, the generality of the phenomenon reported (different fluoropolymers, several fluids) make us very confident that the results reported in our work are not caused by such artifacts. Working cleanly, we demonstrated in the past that we could use the EW response of various rather complex fluids (ranging from surfactant solutions to gelatin solutions and even to milk) to reproduce the oil–water interfacial tension otherwise measured in macroscopic tensiometry measurements (see Banpurkar *et al.*)[1]. Amongst others, this requires that the non-polar phases are cleaned using adsorption columns to remove polar components until the bare water–oil interfacial tension is constant.

1 A. G. Banpurkar, K. P. Nichols and F. Mugele, *Langmuir*, 2008, **24**, 10549–10551.

Anthony Kucernak added: We used ultra pure materials, substrates and liquids. I agree with Dryfe that the cleanliness of the system is of utmost importance. It is clear from our own work, that the template stripped surfaces would only show good results for relatively short periods (hours) after being cleaved. We took extensive steps to make sure our systems are clean and are able to track how dirty systems are by following the underlying electrochemistry of the substrates.

Susan Perkin remarked: You discuss the fortuitous adsorption of contamination from the atmosphere. This seems relatively uncontrolled; yet it opens the interesting idea of "electrowetting on monolayer" (EWOM), which could have the advantages of both EWOD (thick dielectric layer) and EWOM. Is this possible (*i.e.* is it possible to adsorb or graft a controlled monolayer or few-layers)?

Robert Dryfe answered: This is an interesting idea: in our paper, we refer to other work we reported in 2016 in *Langmuir* (ref. 27 in the paper)[1] on the effect of ambient contaminants on the capacitance of HOPG electrodes. We show in the present paper that these contaminants also reduce the wetting effect on these substrates. It is difficult to control the rate of adsorption of such "adventitious" carbons: a number of studies (including our own capacitance work) have suggested that substantial contamination occurs within one hour. Some more recent work (Li *et al.*, in ref. 23 of our *Faraday Discuss.* paper (DOI: 10.1039/c6fd00252h)[2] has suggested that immersion of the freshly cleaved graphite surface in aqueous solutions can slow down the surface contamination process. This method could be combined with addition of (for example) a diazonium solute to achieve rapid modification of the graphite surface before substantial fractions of adventitious carbon had adsorbed. The only drawback would be the relatively uncontrolled nature of the diazonium functionalisation process: without due care, oligomeric species can form, however it may be possible to use this approach to form a reasonable fractions of a monolayer with some control over its thickness.

1 Y. Zou, A. S. Walton, I. A. Kinloch and R. A. W. Dryfe, *Langmuir*, 2016, **32**, 11448–11455.
2 Z. T. Li, A. Kozbial, N. Nioradze, D. Parobek, G. J. Shenoy, M. Salim, S. Amemiya, L. Li and H. T. Liu, *ACS Nano*, 2016, **10**, 349–359.

Alexei A. Kornyshev asked: When you speak about aging of the surface, what do you mean exactly? Which properties change and what is the underlying mechanism?

Robert Dryfe replied: I would refer to the previous reply I have given to Susan Perkin's question: essentially, there has been a large body of work recently which has shown that the physicochemical properties of graphite surfaces are modified over quite fast timescales (one hour or less) on exposure to ambient atmospheres. This timescale represents the adsorption of "adventitious carbon", mainly derived from anthropogenic sources. We have seen the effect of this adsorption on basal plane graphite on the capacitance of the graphite electrode (ref. 27 of our *Faraday Discuss.* article, which was published in *Langmuir*[1]). Other groups have seen similar effects on the water contact angle: the identity of the adsorbates is unclear, essentially because they are airborne hydrocarbons, but it is possible to control this “unknown” factor by exposing the surface to a single volatile liquid, which will preferentially adsorb.

1 Y. Zou, A. S. Walton, I. A. Kinloch and R. A. W. Dryfe, *Langmuir*, 2016, **32**, 11448–11455.

Evgeny Smirnov asked: What do you think happens with the highly oriented pyrolytic graphite (HOPG) surface upon aging? You mentioned that oxygen content on the surface increased that is an indication of surface oxidation (sp^2 carbon to sp^3). Can those cites pin the contact line?

Also, the surface of the fresh HOPG contains terrain steps as shown by AFM. Can Li-ions from the 6M LiCl solution intercalate at such edges, deform the structure and, thus, form pinning points for the contact line, increasing θ closer to 90 degrees?

Robert Dryfe replied: With regard to the question about the ageing process, I would refer the questioner to the answers I gave to S Perkin and A Kornyshev. We do indeed see a reduced wetting effect (shown in this paper) on aged surfaces, but we attribute it to the reduction in capacitance of the surface – given that capacitance drives wetting – rather than the effect of localised pinning, although this point probably requires further study. We do not think that the lithium ions intercalate under the conditions we employ. Lithium intercalation is, of course, the basis of the lithium ion battery anode, but it requires larger potentials than we can access in aqueous solution.

Irena Kratochvilova enquired: From a physical chemistry point of view, what if you have a graphene surface instead? What would happen in principle?

Robert Dryfe responded: Despite the different electronic structure of graphene, it should be possible to reversibly "dope" the material (in this case electrochemically), and thereby change the contact angle in the same way as we have done for graphite. In fact, some articles reporting related phenomena have appeared very recently (see, for example, Hong *et al.*).[1]

[1] G. Hong, Y. Han, T. M. Schutzius, Y. Wang, Y. Pan, M. Hu, J. Jie, C. S. Sharma, U. Müller and D. Poulikakos, *Nano Lett.*, 2016, **16**, 4447–4453.

Irena Kratochvilova asked: What would happen to the contact angle for graphene when you apply a potential?

Robert Dryfe answered: We only have preliminary data on this phenomenon, but the contact angle should decrease either side of the potential of zero charge, such a response has been observed (although not systematically explored I would say) in the work of Hong *et al.*[1]

[1] G. Hong, Y. Han, T. M. Schutzius, Y. Wang, Y. Pan, M. Hu, J. Jie, C. S. Sharma, U. Müller, and D. Poulikakos, *Nano Lett.*, 2016, **16**, 4447–4453.

Alexei A. Kornyshev said: Why has the reversibility of electrowetting not been achieved on graphene? What was the nature of droplet pinning there? Defects, some “energetic inhomogeneity of the surface”, is this a polite name for adsorbed dirt?

Robert Dryfe answered: Good question. The best graphene sample to use would be one derived from mechanical exfoliation, but the inherent limitation there is the size of the graphene flakes (normally 100 microns or less), which makes observation of droplet spreading and contraction difficult. The alternative is to use graphene derived from chemical vapour deposition. These samples are larger, however there are two problems, which to date we have not been able to overcome. The first is that the samples often have a degree of heterogeneity: they are not always exclusively monolayer samples and (more seriously than the effect of atomic steps) contain pinholes and other defects from growth. The other problem is that the CVD samples are transferred to an insulating substrate by depositing a polymer overlayer, and etching the underlying growth substrate (normally copper). It is difficult to remove the polymer completely, thus the residues act as defect sites which “pin” droplet motion. We are working on this problem!

Alpha Lee commented: There have been recent studies (*e.g.* Bozym *et al.*[1]) showing that the differential capacitance near the point of zero charge is a non-monotonic function of ion concentration. This has been explained in terms of effects of strong ion–ion electrostatic correlations in concentrated electrolytes. Electrowetting measurements, in principle, could probe interfacial capacitance. I wonder whether you have performed the electrowetting experiment at different concentrations of lithium chloride? If so, is the electrowetting number (at a particular voltage) non-monotonic?

[1] D. J. Bozym, B. Uralcan, D. T. Limmer, M. A. Pope, N. J. Szamreta, P. G. Debenedetti and I. A. Aksay, *J. Phys. Chem. Lett.*, 2015, **6**, 2644–2648.

Robert Dryfe answered: This is an interesting question: we did not look at the effect of ion identity or concentration on the wetting effect in the present work, but we did explore these points (to some extent) in our initial paper – ref. 17, published in *Soft Matter*.[1] In that paper, we show that there are quite strong effects of ion identity on the strength of the wetting phenomenon, but they are more apparent at larger absolute potentials where we start to run into the effects of electrolysis (see the question from Prof Mugele below) so it is difficult to deconvolute an electrolyte-specific capacitance (and hence wetting effect) from an electrolyte dependent electrolysis effect. We chose to perform our concentration dependent experiments with KF, because that electrolyte showed the most symmetric wetting effect with respect to the potential of zero charge, again see the response to Prof Mugele, the wetting effect is a function of concentration, but only at higher potentials (in the range before electrolysis begins) and only weakly so for concentrations above 1 millimolar. You are correct: it would be very interesting to correlate the wetting effect we see with the concentration-dependent capacitance. The latter is complicated by graphite's semi-metallic nature, meaning (see the works of Gerischer *et al.*) that the capacitance is strongly potential dependent.

1 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.

Frieder Mugele remarked: Following up on the previous question, which was about the concentration dependence of the electrowetting response in your systems, I think that it is also important in such electrowetting experiments without dielectric to worry about equilibrium *vs.* non-equilibrium effects. As Serge Lemay stressed in his introductory lecture, Faradaic reactions are very often present – and it is always important to worry about the role of non-equilibrium effects. So, remembering from your *Soft Matter* paper in 2016 that Faradaic reactions do occur at higher voltages, my question is, by how much do you think it will be realistically possible to change the contact angle before the onset of substantial chemical reactions and do you think that this is going to limit the applicability of dielectric-free electrowetting?

Robert Dryfe replied: This is an important question. The data we have so far (see the *Soft Matter*, 2016, article you refer to, which is ref. 17 of our *Faraday Discuss.* article)[1] for KF suggests that for potentials less then 0.5 V either side of the potential of zero charge (pzc), the concentration dependence of the wetting effect is actually quite weak. We see a stronger potential dependence for more positive potentials (between 0.5 and 1 V positive of the pzc) although it is more difficult to define on the negative side, because we impinge on the zone of electrolysis. With regard to your point about the extent of the change, we do see a strong contact angle change (30 degrees) within the electrolysis window, at least for positive potentials, although the effect is weaker for negative potentials.

1 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.

David Schiffrin asked: The very large difference in electrowetting behaviour between a pyrolysed photoresist film (PPF) and the HOPG basal plane is puzzling. The pristine PPF sample shows a very uneven structure at the nanoscale as you show in Fig. 4a of your paper. Although this may lead to the facile adsorption of organic impurities from air as you suggest, the possibility of chemical surface oxidation by oxygen should also be considered. Your XPS results indicate that this is the case. This would lead to a high population by quinoid groups in the surface region and, as you argue, sp^2 surface features will be lost when the surface is functionalised employing diazonium chemistry. This will result in large differences between the PPF and HOPG samples, with the former having a large dipolar component and hence stronger interaction with the solution employed in your experiments.

Did you measure oxygen reduction on the PPF surface in alkaline solutions? This will indicate clearly the presence of quinod groups.

In addition, the relative dielectric permittivity of the 6M LiCl solution investigated at 25 °C is 31.4,[1] a low value, close to the range of non-aqueous solvents and related to the high solvation energy of LiCl in water, leading to a stronger interaction between the surface and both the free and ion-paired components of the solution.[2] Finally, why did you use such a concentrated LiCl solution?

1 J. M. Mollerup and M. P. Breil, Modeling the Permittivity of Electrolyte Solutions, *AIChE J.*, 2015, **61**, 2854–2860.

2 M. B. Singh, V. H. Dalvi and V. G. Gaikar, Investigations of clustering of ions and diffusivity in concentrated aqueous solutions of lithium chloride by molecular dynamic simulations, *RSC Adv.*, 2015, **5**, 15328–82158.

Robert Dryfe answered: We did not explicitly look at the effect of the surface state on oxygen reduction (or other electrolytic processes) because we are generally trying to avoid the zone of electrolysis. It is, however, a good point and, in fact, our data (Supporting Information of the paper, Fig. 1) does suggest that the reductive potential limit occurs earlier on the PPF substrate than on the other electrodes, which is in line with your suggestion. The point about the permittivity of the concentrated LiCl is a good one: we had not considered this, but it may be the explanation for the rather low capacitance values we have observed, when attempting to fit our electrowetting data to the classical capacitance model, see Fig. 2c of ref. 17 in the paper. Finally, the choice of this concentrated solution was purely pragmatic: such concentrated electrolytes do not evaporate, so we are able to use small (100 microns diameter) droplets without substantial changes in volume over a timescale of several hours.

Konstantin Kornev opened a general discussion of the paper by Anthony Kucernak: Your results are very interesting and challenging. Can you please comment on the accuracy of measurements of the drop profile after voltage application? Is the camera resolution sufficient to observe distortion of the drop profile at the contact line? Is there any indication of the drop profile bending under voltage?

Anthony Kucernak replied: This is an interesting comment. All of our results were obtained by imaging the entire droplet (about 0.5–1 mm wide), and we did not perform experiments where we zoomed in to the contact line at high resolution. Thus, although we did not see any indication of distortion near the contact line, such a distortion is not precluded, especially if it occurred within ~10 μm of the contact line.

Alexei A. Kornyshev said: In our previous joint work, for a set of benefits, we added organic electrolyte into the droplet (both in theory[1] and experiments[2]). Among other benefits, this allowed us to avoid electric-field-induced distortions of the droplet, which made it possible for the droplet to acquire the ideal truncated sphere shape. Why now, in this new round of studies have you preferred not to do it?

1 C. W. Monroe, L. I. Daikhin, M. Urbakh and A. A. Kornyshev, Electrowetting with electrolytes, *Phys. Rev. Lett.*, 2006, **97**, 136102 (1–4); C. W. Monroe, M. Urbakh and A. A. Kornyshev, Double-Layer Effects in Electrowetting with Two Conductive Liquids, *J. Electrochem. Soc.*, 2009, **156**, 21–28.

2 A. A. Kornyshev, A. R. Kucernak, M. Marinescu, C. W. Monroe, A. E. S. Sleightholme and M. Urbakh, Ultra-low voltage electrowetting, *J. Phys. Chem. C*, 2010, **114**, 14885–14890; M. Marinescu, M. Urbakh, T. Barnea, A. R. Kucernak and A. A. Kornyshev, Electrowetting dynamics assisted by pulsing, *J. Phys. Chem. C*, 2010, **114**, 22558–22565.

Anthony Kucernak responded: This was driven by experimental observation. We noted that the degree of pinning seemed strongly associated with the electrolyte concentration (both in the aqueous phase, and the oil), so we decided to look at systems without electrolyte in the organic phase. To our surprise these seemed less susceptible to pinning. We assessed the shape of the droplets, and saw little deviation from the ideal spherical shape (indeed, deviation from the ideal shape was more obvious in pinned droplets). Although we did not note any deviation, there very well might have been deviation from the ideal shape, but only observable at distance scales below that easily probed with our optical microscope.

Susan Perkin asked: Presumably you are finding that addition of water to the droplet, to improve (reduce) the pinning, also leads to a reduced refractive index contrast between the drop and surrounding liquid and this may be not ideal for applications. Could agitation of the contact line, such as small amplitude mechanical vibration, serve to reduce pinning?

Anthony Kucernak answered: Yes, it is true that the properties of the two fluids converge as their composition become more similar. Thus properties such as density, viscosity and index of refraction are liable to be quite similar. It is still possible to see the interface between the two liquids, so there still is some difference in refractive index, although clearly the greater the difference the better for an optical device. In contrast, having a similar density is quite useful as it means that the system is unaffected by orientation. Also, the amplitude of capillary waves may become quite large as the densities approach each other – this may contribute to de-pinning of the system.

Martin Bazant commented: The data in Fig. 5 of the paper look like the thermodynamic (quasi-equilibrium) response of a bistable system in the limit of low salt concentration, rather than a kinetic effect of random remnants of aqueous solution from the electrowetting cycles. Is there a possible thermodynamic interpretation, where some mixture of the two liquids "phase separates" into a well-defined quasi-equilibrium surface layer at a low salt concentration, which alters the advancing contact angle, while the addition of more salt keeps the water in solution and prevents the formation of this layer thermodynamically? In this context, the pinning effect could also be viewed as one of nucleation and the growth of this surface phase.

Anthony Kucernak responded: This is an intriguing and useful suggestion. It would also explain the strange concentration dependence – *i.e.* that the effect occurs over a very small concentration range and is not related to the logarithm or even square root of the concentration of the electrolyte.

Alpha Lee said: In your paper, you mentioned that the high free energy of transfer of ions into the dichloroethane (DCE) phase explains the reluctance of ions to desorb from the surface and, hence, the hysteresis in the electrowetting. Out of the many chloride salts, only lithium chloride produces a reversible response. I wonder whether you have some insight into why Li^+ is particularly good? Does Li^+ have the lowest free energy of transfer amongst the cations that you tried? One might perhaps expect organic cations (*e.g.* alkylammonium cations) to have a lower free energy of transfer than Li^+?

Anthony Kucernak answered: This is an interesting point. Sabela *et al.*[1] have determined the values for the free energy of transfer from water to 1,2-dichloroethane, and lithium has the highest free energy of transfer of the common univalent cations – so it seems the reason is not as simple as just the free energy of transfer.

[1] A. Sabela, V. Mareček, Z. Samec and R. Fuoco, *Electrochim. Acta*, 1992, **37**, 231–235.

Hubert Girault remarked: In the last part of your work, you have used salting out as a strategy to create a liquid–liquid interface. Usually, this method generates rather diffuse interfaces with poor optical properties. Do you think you will be able to develop optical applications with such a system?

Anthony Kucernak replied: It is true that close to the critical (plait) point the properties of the two phases become quite similar, but the benefit of utilising a salted out system (or indeed, any other two or three component liquid system with high solubility of each component in each of the two liquid phases), is that the system can be tuned – that is, it is possible to vary the index of refraction or density change of the two different phases by choosing the initial total composition of the system. See the below figure (Fig. 1) in which we can either choose the two different phases to be very similar by varying the total composition of the system to be composition 1, or we can choose the two different phases to be much more dissimilar (composition 2).

Hubert Girault asked: Recently, the group of Katano in Japan has shown it was possible to use decafluoropentane to carry out ITIES.[1] Do you think that fluorinated solvents could be used for your application?

[1] H. Katano, Y. Kuroda and K. Uematsu, Applicability of a fluorous solvent 1,1,1,2,3,4,4,5,5,5-decafluoropentane for the non-aqueous medium in liquid–liquid electrochemistry, *J. Electroanal. Chem.*, 2017, **788**, 232–234, DOI: 10.1016/j.jelechem.2017.01.060.

Anthony Kucernak responded: We did try to use some perfluorinated solvents (more specifically FC40 – which judging by it’s average molecular weight must be mostly perfluorododecane), but found the system to be heavily pinned. The fact that the decafluoropentane is not totally fluorinated must allow some electrolyte solubility. However, our limited experience using fluorinated solvents indicates that they are not so promising for performing electrowetting in our system, which lacks a dielectric barrier.

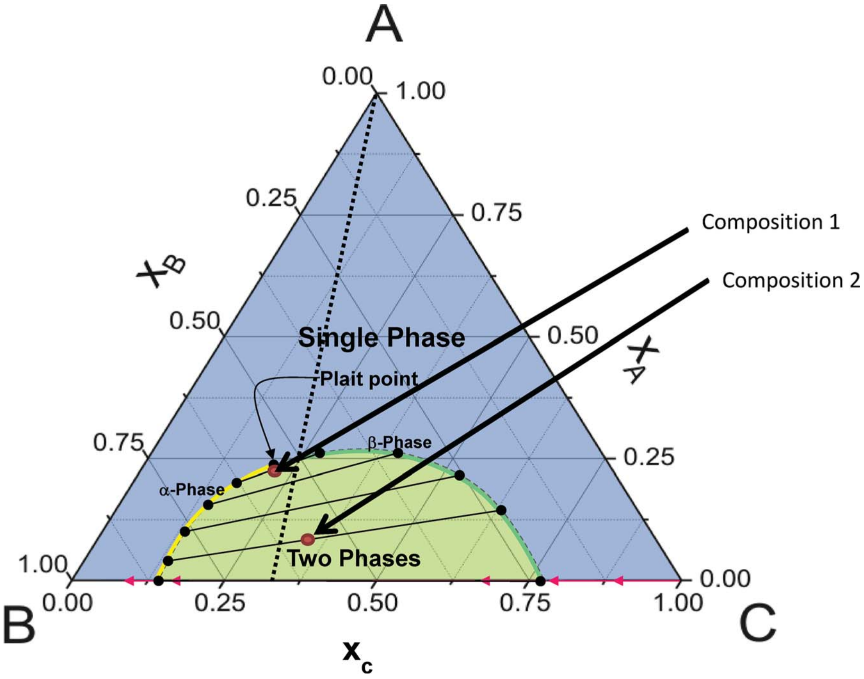

Fig. 1 Cartoon of the phase diagram for a three component, two phase system showing how the choice of overall system composition can lead to two phases which are either very similar on composition (composition 1); or a system in which the two different liquid phases have quite different compositions (composition 2).

Ranabir Dey enquired: Can the hysteresis, as stemming from the mechanism explained with the help of Fig. 4 in the paper, be quantified in terms of the difference between the advancing and the receding contact angles?

Anthony Kucernak replied: This is an interesting suggestion, and would involve an attempt at developing a theory associated with pinning. I worry that any such model may be over-parameterised for the experimental results we have. At a very coarse level, we show in the paper that as the solubility of water in the oil phase increases, the amount of hysteresis decreases, leading to the concept behind Fig. 4. In order to validate this hypothesis it would be useful to quantify the surface coverage of water at the electrode interface under the droplet. Although difficult, it may be possible to do this using a spectroscopic imaging method where we probe the metal/liquid interface.

Ranabir Dey remarked: Can the classical contact line dynamics models relating the contact angle to the contact line velocity, like the Cox–Voinov model, be applied to such liquid–liquid systems?

Anthony Kucernak answered: I think the system is somewhat more complicated than those studied by Cox–Voinov type models. In those models, the surrounding phase (air) is mostly ignored as its density and viscosity are almost inconsequential in comparison to the droplet. For a liquid–liquid system the surrounding phase has a density and viscosity which is not so different from the droplet, and so cannot be ignored when studying the kinematics of such systems.

Alexei A. Kornyshev opened a general discussion of the previous 3 papers on Electrotunable Wetting with a general question to all speakers of this session and the audience: what is the future of electrowetting in general, and ultra-low voltage electrowetting in particular, first of all in terms of applications? There has been some decline in interest for this subject, which seemed to be hot a decade ago. Now, there are more publications in the area of reverse electrowetting for energy harvesting, what we will hear *e.g.* in the work of Professor Krupenkin (DOI: 10.1039/c6fd00253f) during the session on Electroactuators, whereas the electrowetting-based lenses and displays do not seem to have massively taken off. On the other hand, there is a strong resistance in the EWOD community against further exploration of electrowetting on conductors, presented in the brilliant papers of the Dryfe and Kucernak groups. Like our first joint paper on ultra-low voltage electrowetting, it is very hard to publish this work in the highest profile journals. What are your thoughts about this?

Frieder Mugele responded: Let me say first of all that I would not really agree with the idea that there is a decline of interest in EW. The number of publications with EW in the title has been steady at around 150 per year for almost 10 years (see Web of Science). Yet, this implies that fundamental scientific interest has not been increasing. From my perspective, this reflects the fact that the basic principles have been sorted out. Except for specific issues such as contact angle saturation, it is not clear what *the* fundamental question would be. As a consequence, the focus is on new application areas (such as reverse EW by Prof. Krupenkin or our own MALDI mass spectrometry enhancement,[1] in which the flexibility of EW is used to do new things.

At the same time, commercial interest has been increasing – yet without an excessively big market. EW lenses are sold by the 100 000 per year not by the tens of millions as originally hoped, lab-on-a-chip devices are commercially available by Illumina and a few other smaller players. Most of the use is in academic labs. Displays fight issues with long term stability and fierce competition with LCD technology, which has been optimized through probably thousands of man years of engineers' work. It is still out there, and the fact that Amazon bought Liquavista demonstrates that people still expect something from the technology in this area. Yet, it is a mass market. And you have to demonstrate the ability to make things by the millions and with reliable performance for years.

The fact that long term reliability seems to be *the* key bottleneck for applications is probably also the reason for the reluctance of people to pick up EW directly on conductors for applications. After all, electrocapillarity with direct electrode–electrolyte contact did not make into anything that came close to a product for more than a century – until Bruno Berge pushed the use of the dielectric layers, which made the systems all of a sudden (largely) independent of the specific chemistry. Don't forget that all these applications come with their own very diverse requirements regarding salt content (both species and concentrations), pH, specific solvent properties, *etc*. EW on dielectric is much more forgiving and flexible in this respect than the classical EW on conductor. Whether the operating voltage is 20 V (as can be easily achieved if a company invests into the proper fabrication of dielectric layers) or 2 V is a lot less of practical issue than this flexibility.

1 O. Kudina, B. Eral and F. Mugele, *Anal. Chem.*, 2016, **88**, 4669.

Robert Dryfe answered: I think the conductor approach is still capable of addressing applications that the presence of dielectrics precludes. The graphite surface should be more chemically and physically stable, over the long term, than many dielectrics, and the extension of the approach to graphene (which we are working on – see my previous responses) will offer the advantages of substrate flexibility and transparency that cannot readily be achieved using the conductor approach. I also think that the possibility of electrolysis (on a conductor) could be turned into an advantage rather than a disadvantage: if an electrochemical reaction produces a highly coloured product from a transparent starting material (many reduction processes, *e.g.* of quinone type species, do this), then it will be possible to achieve wetting based pixelation. Another very interesting prospect with conductor-based electrowetting, is the idea of using this approach to fill very small channels, *e.g.*, the 1–2 nm height channels Radha *et al.* have recently made using graphene “spacers”.[1] I think the field should drop its apparent conservatism, and let electrowetting on (graphite and other related) conductors develop, then applications will surely follow.

1 B. Radha, A. Esfandiar, F. C. Wang, A. P. Rooney, K. Gopinadhan, A. Keerthi, A. Mishchenko, A. Janardanan, P. Blake, L. Fumagalli, M. Lozada-Hidalgo, S. Garaj, S. J. Haigh, I. V. Grigorieva, H. A. Wu and A. K. Geim, *Nature*, 2016, **538**, 222.

Anthony Kucernak remarked: For technological applications, it is clear that longevity is of prime concern. But I think there are already some interesting suggestions that have been put forward for new and novel systems, such as those based on SLIPS or the reverse electrowetting discussed in the question. Certainly, the passage of liquids through porous media *via* an electrowetting type process is an area which might prove fruitful in the future.

Alexei A. Kornyshev continued the discussion of the paper by Robert Dryfe: Am I right to understand that you see dewetting of water droplets at large voltages? Usually you have dewetting of the oil droplet in an aqueous environment as the latter tends to go underneath the oil droplet, due to having a higher dielectric constant. But why should the water droplet leave the surface at a large electrode polarization? Have I mixed up something?

Robert Dryfe replied: No, so far, we only see wetting of the graphitic surfaces by aqueous droplets, either surrounded by air or an immiscible (organic) solvent.

Alexei A. Kornyshev opened a general discussion of the paper by Robert Hillman: I did not find contact angle curves in your paper, neither have they been shown in your presentation slides today. How large is the contact angle variation. Is there a hysteresis in the electrowetting response. Without such information it is hard to judge how your electrodes perform electrowetting-wise? Can you tell us something about it?

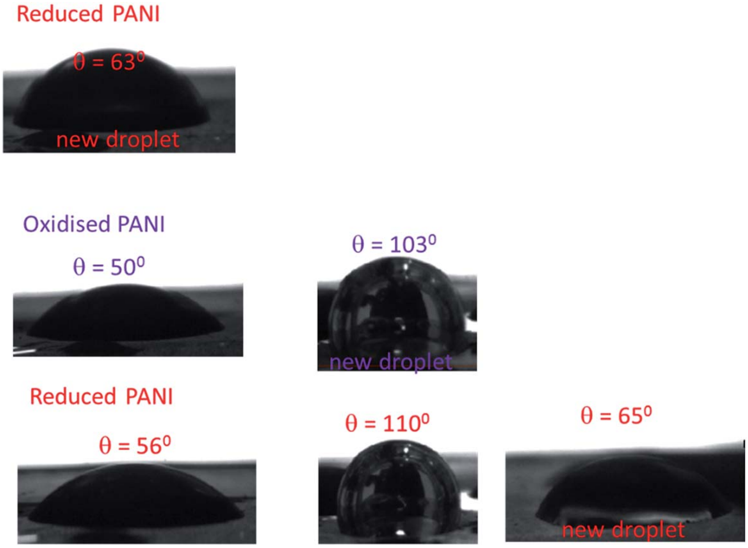

Fig. 2 Contact angle measurements for chloroform droplets deposited on a horizontally oriented polyaniline film immersed in aqueous 0.1 M H_2SO_4. Data were acquired using a Theta Lite Optical Tensiometer (model: Thetalite 101), in conjunction with OneAttension software (version 2.5, r5128, Biolin Scientific). The working electrode was an Au film (sputter coated on a glass slide, with a 3-mercaptopropyl)trimethoxysilane bonding layer) onto which polyaniline was potentiodynamically polymerised (20 cycles at scan rate 10 mV s^{-1}, in the potential range −0.2 V to 1.0 V) from a solution of 0.01 M aniline (Sigma Aldrich, ≥99.5%) in aqueous 0.1 M H_2SO_4. The film was then transferred to monomer-free background electrolyte and maintained under potentiostatic control (Ivium potentiostat) for the measurements shown. Coulometric assay gave a polymer coverage, Γ = 152 nmol cm^{-2}. In both cases, a standard 3-electrode cell configuration was used, with an Ag/AgCl (saturated KCl) reference electrode and an iridium oxide coated titanium mesh counter electrode.

Robert Hillman responded: As indicated above, pronounced hysteresis effects prevented us acquiring dynamic real time *in situ* contact angle measurements during film redox switching. We were restricted to determination of contact angle measurements between droplets placed on a polymer film whose charge state was fixed potentiostatically. Such observations were made for a range of solvents and are illustrated in the figure below for the case of a polyaniline film (deposited from and exposed to bulk aqueous sulfuric acid solution), onto which were placed chloroform droplets. The top row (single panel) shows a droplet placed on a reduced polyaniline film. When the film is oxidised (second row), the same droplet (left panel) shows relatively little variation in shape (contact angle). However, if a second droplet (second row, second column) is placed on the surface, then the contact angle is very different, *i.e.* responds to the change in film charge state. Re-reduction of the polymer (third row) results in very little change in the contact angles for *either* of these droplets; certainly, they do not uniformly respond to the film charge state. However, deposition of a third droplet (third row, third column) shows behaviour essentially the same as for the initial droplet on the oxidised surface.

We deduce that, while the majority of the polymer film is undergoing redox state switching in response to changes in applied potential and accessing the bulk solution as the source/sink of charge neutralising ions to satisfy this, the small portion of the film beneath the droplet is not. This is most likely due to charge transport limitations laterally beneath the droplets (over mm distances), as compared to the more rapid charge transport vertically across sub-micron distances. Consequently, droplets deposited under a different potential constraint are sampling an unrepresentative (unconverted) part of the polymer in terms of charge state.

Frieder Mugele commented: The surfaces that you present are very heterogeneous in nature. The chemical and topographic heterogeneity that is introduced by the incorporation of nanofibers, -platelets, or -particles in your films should give rise to substantial contact angle hysteresis. The question is: did you measure the contact angle hysteresis by inflating and deflating the droplets (at fixed electrochemical conditions)? It would be very useful to have an idea about how close the measured angles are to equilibrium. I am afraid that the receding contact angle in these systems might be really low.

Robert Hillman replied: Your identification of the interplay of chemical and physical (morphological and topographical) factors is very important. We agree that this will introduce a range of complications, including the expectation of hysteresis in contact angle measurements as one changes the interfacial characteristics, *e.g.*, the film redox state and thus hydrophilicity/hydrophobicity (see response to later question, below). We did attempt the type of inflation/deflation experiments you describe, but the results were not conclusive as a consequence of an apparent “drift” of contact angle values, upon which were superimposed relatively small changes in absolute values. Although these observations do not permit any definitive conclusions, we attribute these effects to extreme hysteresis, such that we do not (on the timescale of our measurements) approach equilibrium.

Elisabeth Smela enquired: Polyaniline typically has two pairs of redox peaks, as shown in Fig. 2a in the paper, going from leucoemeraldine to emeraldine and then pernigraniline. Whether these transitions are associated with anion ingress or egress depends on the pH. Under some conditions, you observe additional peaks. For example, the addition of MWCNTs to the aqueous aniline + H_2SO_4 solution during deposition results in three pairs of peaks (Fig. 3a), and the positions are shifted. Are you able to correlate these various peaks with particular ion ingress/egress processes and to account for the shifts?

In Fig. 8b in the paper, the CV goes from two pairs of peaks in 2EG : ChCl to four pairs in H_2SO_4. Do these new events indicate that both anion and cation transport are occurring? What are your thoughts on the loss of electroactivity upon returning the film to 2EG : ChCl? It is interesting that in Fig. 8e going into 2EG : ChCl again results in a loss of electroactivity, which is then recovered in H_2SO_4.

Regarding the gradual loss of electroactivity in H_2SO_4, we have shown that PANI can be stably cycled in methanesulfonic acid, and others have shown stability in CSA and NSA.[1]

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[1] E. Smela and B. R. Mattes, Polyaniline actuators: Part 2. PANI(AMPS) in methanesulfonic acid, *Synth. Met.*, 2005, **151**, 43–48.

Robert Hillman answered: As you indicate, the voltammetric response of Fig. 2a in our paper is entirely typical of that reported by many authors for polyaniline films. While not a structural method, this gives some confidence that the polymer (*cf.* composite) films we study are a representative "baseline" from which to explore composite properties. The presence of additional peaks in the voltammetric response when MWCNTs are incorporated (Fig. 3a) is reproducible, so we do not attribute this to polymer degradation; by restraining the upper potential limit we have tried to minimise this widely acknowledged problem. We are therefore driven to suggesting that these are attributable to MWCNT-influenced redox energetics. The additional peaks are within *ca.* 0.1–0.2 V of the features seen in Fig. 2a, so the energetics would be shifted by *ca.* 10–20 kJ mol^{-1}. Since iVt techniques are not structural probes, we are not able to be more specific on the basis of the data available. The data of Fig. 8 in the paper relate to a more complex physical situation, in which the medium of exposure is varied. The issue here is the rate of exchange of electrolyte/solvent between the film and the ambient medium. Slow kinetics result in voltammetric peak broadening, so deconvolution of the multiple peaks is impractical; nonetheless, consideration of their origin is worthwhile. The interior of a polymer film on an electrode is heterogeneous: there will be cracks, fissures and pools of electrolyte, whose rate of exchange with the ambient medium will vary. In particular, there will be some solvent pools that are effectively trapped within the film interior and that exchange only slowly. Thus, while some parts of the film may show a voltammetric response that reflects the ambient medium almost immediately, there will be other parts of the film that are effectively unaware of the change and respond as though still exposed to the previous solution. This will generate multiple peaks, each associated with different anion/cation exchange processes. Returning a film to 2EG : ChCl (after exposure to aqueous medium) requires penetration of larger ions (irrespective of whether it is the anion or cation that transfers). This will diminish film capacity. Transfer back to H_2SO_4 might be expected to remove this constraint. Superimposed on these effects are slow structural relaxations that may restore film performance, but on much longer timescales.

Michael Urbakh asked: Have you measured dissipation using Quartz Crystal Microbalance experiments? What additional information can be obtained from these experiments?

Robert Hillman replied: In the further development of this work[1] we have measured the acoustic admittance spectra of polyaniline and polyaniline/MoO_2 films during deposition and subsequent redox cycling. Representative data for polyaniline deposition (under the conditions employed in this study) are shown in Fig. 3, below. The upper panel shows the variation of QCM resonant frequency as a function of charge. The dotted line is a guide to the eye for a linear response that would be characteristic of an acoustically thin ("rigid") film. The lower panel shows admittance spectra acquired for the bare Au electrode in solution prior to film deposition (blue trace) and after five successive deposition cycles (brown, grey, yellow, blue, green, respectively). The shifts to lower frequency (increasing mass) and lower admittance are clear; the point of departure from linearity in the upper panel is indicated by the vertical dashed line in the lower panel. In the case of polyaniline/MoO_2 films, the departure from $\Delta f - Q$ linearity is at approximately

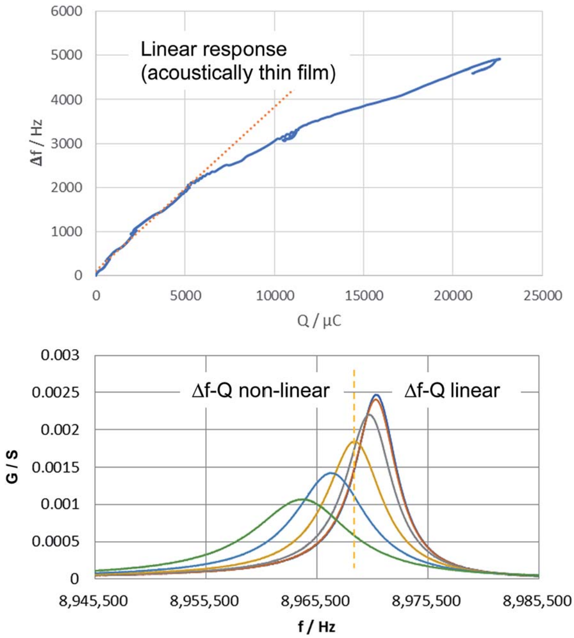

Fig. 3 Acoustic admittance data acquired during the potentiodynamic deposition (10 mV s^{-1}, in the range -0.2 to 0.95 V) of polyaniline on Au. The working electrode was one of the Au electrodes (area 0.23 cm^2) of a 9 MHz AT-cut quartz crystal resonator (Seiko QCM922A). A standard 3-electrode cell configuration was used with an Ag/AgCl (saturated KCl) reference electrode and a Ti mesh counter electrode. The deposition solution was 0.1 M aniline (Sigma Aldrich, ≥99.5%) in aqueous 1 M H_2SO_4. The upper panel shows the variation of peak admittance frequency with charge throughout the course of 5 deposition cycles. The lower panel shows selected full admittance spectra prior to deposition (highest resonant frequency and peak admittance) and at the end of each cycle (progressively shifting to lower peak frequency and peak admittance).

twice the charge, suggesting "stiffening" of the film by the particulates. This is consistent with the notion of solid particulates retaining film structure and performance over longer intervals of cycling.

[1] R. Burrell, University of Leicester, private communication.

Andy Mount said: You are making large compositional and structural changes to the entire film, cycling it between completely oxidised and reduced. We previously showed for poly(indole-5-carboxylic acid) conducting polymer films that there are gross changes in deposited films that occur as a result of the dynamic and repeated injection and removal of ions from the layer as formed.[1] These ions move in and out of the coat, bringing in solvent and progressively opening up pores in the film over timescales up to days, which leads to a different mean chemical and physical structure. This seems consistent with the observations in your work. It seems that in order to change interfacial properties, for a conducting polymer such as polyaniline with highly conductive electron transfer, as with polyindole, conversion may occur from the outside of the coat in, and you may be able to cause the interfacial change whilst minimising global structural changes by only changing the outside of the layer (*e.g.* through rapid pulsing) rather than the inside, and reversing prior to any longer term re-equilibration. Have you observed such effects? What would be the likely minimum distance from the surface where redox change would produce the desired electrowetting effect?

1 A. R. Mount and M. T. Robertson, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5169–5177.

Robert Hillman responded: The experiment we ultimately wished to perform was very much along the lines you describe, with the intention of correlating film external physical properties (contact angle at the outer surface) with internal composition (measured as a spatial average *via* injected/removed charge). The goal of this was to distinguish "inside/outwards", "outside/inwards" and spatially uniform compositional changes. Simplistically, these might be consequences of rate limiting electron transport from the electrode across the film, rate limiting ion transport from the solution across the film, and electron/ion transport rates of similar magnitude, respectively. In the case of "inside/outwards" change the contact angle would not change until the end of the redox conversion, while in the case of the "outside/inwards" change the contact angle would be complete very early in the conversion. There is the complication that diffusionally driven solvation changes are likely to lag these charged species transfers, thereby introducing further hysteresis,[1] but this does not negate the general concept. However, as you suggest, the practical difficulty – which prevented us from making definitive measurements – is that there are likely to be slow structural relaxation processes that extend the timescales beyond those over which the measurements are made. These coupled chemical processes generate film history-dependent mechanistic changes that are manifested[1] as apparently irreproducible behaviour during repetitive redox cycling.

With regard to the last part of your question, about the distance from the surface at which redox state changes would drive electrowetting effects, there are two answers, according to where one defines the surface to be. In the simplest situation of a perfectly smooth film of uniform composition, we would estimate the distance to be on the order of a few molecular diameters, *i.e.*, 1–5 nm. If the surface is not smooth, though still compositionally homogeneous, the same argument would apply, but the plane in question would be contoured ("rippled") in the same manner as the physical surface of the film. In the case we have, where the chemical and physical inhomogeneities are of larger scale and are more irregular, delineating a plane that defined the threshold for interaction is not practical.

1 A. R. Hillman and S. Bruckenstein, *J. Chem. Soc., Far. Trans.*, 1993, **89**, 3779–3782.

George Schatz remarked: What is the fraction of carbon nanotubes (CNT) used in this work? Is it of interest to study the variation of the results with respect to this fraction? Conductivity of CNT/polymer composites is often quite good even for volume fractions of 1%.

Robert Hillman replied: We do not have a quantitative value for the CNT content of the composite films. The problem is that the nanotubes that are incorporated will be wrapped in polymer and thus not visible morphologically (*e.g.*, by SEM) and that compositionally they are not unduly different from the polymer (largely carbon) so cannot be distinguished by elemental probes (*e.g.*, EDAX). The MoO_2 particulates discussed later in our paper are advantageous in the latter respect. Intuitively, we believe that the films contain a few percent of nanotubes and we agree that even such low levels are likely to have substantive impact on properties.

Alexei A. Kornyshev asked: What about the applications of your findings? How are you going to use them for electrowetting devices for fundamental studies?

Robert Hillman answered: The data presented in our paper include measurements of capacitance, relevant to charge storage applications. Here, the *internal* wetting of the electroactive material is central to its accessibility for redox conversion. Greater wetting by the ambient medium enhances the rate of transport of charge neutralising ions to/from the external solution.

Another goal (on which we do not report here) that relies on *external* wetting relates to an aspect of forensic science, namely the visualization of latent (non-visible) fingerprints. A common feature of many reagents, whether generic or specific, used for this purpose is that they react with some component (*e.g.*, amino acids, lipids) of the deposited fingerprint residue and thereby generate a coloured (visible) substance. Practically, despite a large number of reagents and processes, the recovery rate for latent fingermarks is surprisingly low. In many cases, a limiting factor is the availability or accessibility of the target substance in the fingerprint residue. The strategy we envisaged recognised that the fingerprint residue, which is present in lines on the surface, may be considered as an extended "droplet", subject to contact angle variation. The concept was that repeated flexing of the droplet shape would have a stirring action that would bring additional target molecules to the "droplet" surface, thereby enhancing sensitivity. The work reported here was designed to provide fundamental insights to underpin the more applied aspects.

Himani Medhi communicated: Your work reported on the electrical behaviour of different polymer composites of PANI. Among the eight varieties, *i.e.*, PANI, PANI/MoO_2, PANI/Gr and PANI/MoO_2/Gr prepared from both oxaline electrolyte and aqueous electrolyte, which one demonstrated the best electrochemical behavior?

Graphene materials usually have excellent electrochemical behavior. So does the modification enhance the electrochemical behavior of PANI compared to that of graphene?

Robert Hillman communicated in reply: Evaluation of optimal film performance is a combination of the highest charge storage capacity and its longevity. Under the conditions used here, composite films prepared from an Oxaline medium and containing both MnO_2 and graphite performed best in both respects (and thus overall). Polyaniline films (containing no composite components) showed fairly rapid decline in charge storage/recovery performance; absolute values did vary with medium of exposure (aqueous *vs.* ionic liquid), but the trend in any given medium was downwards. Inclusion of MoO_2 alone did relatively little to arrest this decline. Inclusion of graphite alone significantly improved stability of response and inclusion of both graphite and MoO_2 particulates enhanced this further.

Our choice of inclusions into the polymer film represents entities that are essentially 1-dimensional (carbon nanotubes), 2-dimensional (graphite flakes) and 3-dimensional (MoO_2 particulates). Graphene sheets would be interesting in that they represent the extreme of the 2-dimensional category.

We have not undertaken experiments using graphene (*cf.* graphite), so we are unable to comment on how this might affect performance. If, as we speculate, much of the beneficial effect of the graphite is associated with irregular packing that generates free volume through which ion transport is enhanced, then graphene might do this more efficiently provided that it had the mechanical rigidity to retain structure during redox-driven film morphological changes.

Nikolay Brilliantov opened a general discussion of the paper by Konstantin Kornev: Does the porous film play a significant role in the process? Can it trap charges inside?

Konstantin Kornev responded: Yes, it does. The porous film is crucial to screen any flow and to provide uniform removal of metal along the wire. We never measured the charge on this porous film, therefore, we cannot comment on the charge trapping effect.

David Schiffrin asked: This is a rather difficult system to model and the use of dimensionless numbers for transport phenomena is a very sensible approach for establishing the main parameters to be considered, in your case, the Bond number, which establishes the importance of surface tension compared with gravitational forces. Although you conclude from its value for the geometry that you are investigating, that the surface effects are the most important, you propose that the driving force determining the flow pattern is convection due to the high density of the tungsten solution formed.

However, the surface tension isotherm that you measured: $\sigma = 73.26 - 24.98\ [WO_4^{-2}]$, demonstrates that the surface tension of the aqueous tungstate solution, the product of the dissolution of tungsten, has a lower surface tension than that of the KOH solution. The flow pattern you present in Fig. 3 in the paper indicates that there is a process at the aqueous solution–tungsten air boundary driving the convective flow. I suggest that this is an example of a Marangoni convective flow driven by the surface tension gradient at the above mentioned boundary. The flow direction corresponds to your Fig. 3, *i.e.*, from a region of low to another of high surface tension due to electroassisted flow of the tungstate solution product of the electropolishing reaction. This would give a physical reason to your comments about the Bond number, surface tension beats gravity! This analysis only addresses the potential where convective flow dominates, but not the precipitation limited electropolishing observed at lower electropolishing potentials. Can you comment on the origin of this difference in behaviour?

Konstantin Kornev responded: Thank you for this very interesting idea about the Marangoni effect as a driving force for flow. It definitely makes sense to look into this effect more carefully. The schematic in Fig. 3a in our paper is based on our observation of electropolishing for very thick, 0.5 mm in diameter, wires (see ref. 23 in the paper). The flow visualization and discovery of an immiscible film enriched with tungstate have been conducted on thick wires. The amount of the resulting reaction products produced by these wires is much greater than that produced by thin wires. Therefore, we cannot say with certainty about the flow caused by the anodization of thin wires. We did not study the flow pattern in detail, the vortex is hidden under the meniscus making such an investigation very difficult. The flow pattern was suggested in ref. 23 in our paper to support our explanation of the flow of thin immiscible film. At that time, we did not have data regarding the surface tension.

In the present paper, the Bond number was calculated for the tubes where any flow is essentially damped. Relative to the wire anodization in the Petri dishes or large vessels where the flows are visible, we do not see any flow in the tubes. The meniscus shape is perfectly described by the nodoid model suggesting that any deflection of the meniscus profile caused by any flow in the tube is insignificant. Our interpretation of the measured contact angle is based on the assumption that the tungstate concentration in the tube has reached equilibrium.

A thin immiscible film enriched with tungstate may, however, flow, but it is not visible. Therefore, we cannot say anything about the contact line region where the Marangoni effect is expected to be the strongest. Consequently, the Marangoni effect on the observed change of the contact angle cannot be ruled out at this moment. The Marangoni flow is expected to show up long before the formation of an immiscible film. Therefore one expects to see this effect at a low tungstate concentration, *i.e.*, in the precipitation limited electropolishing. We look forward to systematically studying the flow patterns to see whether the Marangoni flow is indeed the main player here.

Martin Bazant asked: The results are very interesting and also counter-intuitive, if one thinks in terms of equilibrium electrowetting phenomena. The main results Fig 5d in the paper show that the increased contact angle is perfectly correlated with the tungstate anion concentration, which increases after the voltage is turned on and electropolishing and oxidation of tungsten proceeds. This production of tungstate ions is relatively fast (a few seconds), then it slows down and causes the dewetting phenomenon to occur over minutes, as tungstate ions are gradually removed. The effect is independent of the voltage applied, and depends only on the relatively low tungstate ion concentration. These observations suggest that the phenomenon is not directly related to electrocapillarity, or the lowering of the solution/electrode surface tension by capacitive charging of the double layers. Instead it seems more like alteration of the zero-voltage contact angle by a weakly hydrophobic surface product, which responds quickly to tungstate ions resulting from the reactions.

The apparent suppression of the electrowetting effect and lack of explicit voltage dependence may be related to the non-capacitive charging of the double layer during Faradaic reactions. The applied voltage which oxidises/dissolves the metal may also drive electrodeposition of anions/complexes that cover the surface with a saturated constant surface charge. Since the overall salt concentration is high ($C_{\mathrm{KOH}} = 1\mathrm{M}$), the voltage drop across the diffuse part of the double layer that contributions to capacitive charging and electrowetting is relatively small compared to the compact/surface layer. Therefore, if the voltage is large enough to saturate the adsorbed surface charge, there will be no dependence on voltage, but still a dependence on the tungstate ion concentration.

What do you think of this hypothesis? To test these ideas, it could be interesting to vary the supporting electrolyte concentration, and to perform *in situ* AC impedance analysis of the double layer capacitance under DC bias.

Konstantin Kornev replied: Thank you for this interesting note. The argument in favour of the classical treatment of the electrowetting effect originated from a traditional view of the metal/electrolyte surface suggesting that the tungsten surface is always covered with a non-conductive native oxide film. Therefore, as a voltage is applied, a thin precursor wetting film should spread over the oxide surface. As the oxide film grows, the potential drops. Also, the 3D Pourbaix diagram suggests that some other oxides and hydrates can be formed at the surface (see ref. 26 and 30 in the paper for a detailed discussion of these effects). Therefore, the lack of direct dependence of the contact angle on applied voltage does not necessary imply that the voltage remains the same. We agree that the interpretation of these experiments would be easier if one could separate the electrowetting scenario from the electrochemical features of metal anodization. Thank you for the suggested experiments.

Mohit Kulkarni commented: My question is, is the gel-like structure reversible? I suspect if you can reverse the voltage and use proper electrolyte, the gel-like structure formed can be reversed. This technique may be useful in future for purifying conducting materials (at least their surfaces) by supplying alternating positive and negative voltage with a controlled duty cycle.

Konstantin Kornev answered: Thank you for your suggestion. We did not study this effect and hence cannot comment on it.

Kelsey Hatzell asked: Do you observe the same kinetics for the gel-like bridge formation during optical and X-ray experiments? At the energy levels you are imaging with during tomography did you see any artifacts or bubbles during the experiments?

Konstantin Kornev responded: We did not observe the gel-like bridges connecting the wire and electrolyte surface through the microscope, but we did observe them inside the electrolyte. However, we did not study the kinetics of their formation systematically. When one uses a single tube with an immersed tungsten electrode (anode) and a stainless steel electrode (cathode) below it, the stainless steel electrode produces bubbles disturbing the tungsten anodization and *in situ* observations. This problem was addressed in the two tube microfluidic setup reported in the paper. We did not see any bubbles in the tube with the tungsten wire. No bubbles were formed at the 8960 eV X-ray beam. This X8C beamline of the Brookhaven National Laboratory was chosen purposely to avoid any artifacts of this kind (see the experimental details in Ref. 24, 26 and 31 in the paper).

Andriy Yaroshchuk remarked: Can you pierce anything with your nanoneedles? Are their mechanical properties good enough?

Konstantin Kornev answered: We have used the precipitation limited electropolishing (PLE) needles to pierce cells (ref. 25 in the paper). Recent experiments show that these long needles can be used to make ~10 μm diameter holes in 100 μm thick non-woven membranes. The length of the thin part of the PLE needle can be varied from hundreds of microns to a few centimeters, therefore, the flexural rigidity of these needles can be adjusted for a particular application.

Himani Medhi communicated: The position of the tungsten wire connected to the copper wire should be pointed out in Fig. 1b in the paper for clear visualization of the schematic model.

Konstantin Kornev communicated in reply: The following explanation has been added to the legend in Fig. 1: The copper wire was attached to the tungsten wire far away from the meniscus.

Himani Medhi communicated: As mentioned in the conclusion, this study is able to evaluate the surface tension of the electrolyte (here, KOH) and the concentration of the reaction product (here K_2WO_4). Is it applicable for another electrolyte and metal couple?

Konstantin Kornev communicated in response: We believe that the proposed methodology can be generalized to any metal/electrolyte couple.

Himani Medhi communicated: Fig. 5d in the paper explains that with contact angle the interaction of the metal and the electrolyte increases leading to an increase in tungstate ion concentration. But from Fig 5a and 5b, it is clear that with the decrease in surface tension, the tungstate ion concentration increases, then with the increase in surface tension, the tungstate ion concentration decreases. Will you please elaborate about these facts?

Konstantin Kornev communicated in reply: The effect of the concentration of tungstate ions on the surface tension and contact angle is indirect. Due to complexation and adsorption of tungstate at the air/electrolyte interface, the surface tension changes. In the presented series of experiments corresponding to the PLE, the concentration of tungstate ions did not exceed 0.01 mol L^{-1}: as the tungstate concentration increased, the tungstate ions were prone to form different compounds with the ions that were present in the solution. These compounds precipitated out forming a solid porous shell. Therefore, in the PLE regime, the electrolyte cannot contain tungstate in greater amounts. However, a tungstate concentration greater than 0.01 mol L^{-1} can be obtained for convection limited electropolishing (CLE), see Fig. 5d in the paper. The tungstate ions are concentrated at the wire surface and oversaturate the surrounding electrolyte to form a film with a distinguishably different density. The resulting film is immiscible with the surrounding electrolyte (see ref. 23 and 31 in the paper). Following the evolution of the contact angle as the tungsten anodization progresses, one observes that, initially, the meniscus probes the same wire surface for both PLE and CLE regimes. As the tungstate concentration increases and the CLE regime takes over, the contact angle increases. This implies that the meniscus probes a surface made of some different, more hydrophobic, compound. We believe that the wetting precursor film enriched with tungstate ions extends beyond the visible contact line. The working hypothesis is that the tungstate, potassium, and hydroxyl ions strongly interact in this film to change the contact angle.

Ranabir Dey opened a general discussion of the paper by Sunny Kumar: What you observe is a highly dynamic phenomenon; I do not think it is correct to use a simplistic energy balance formalism to explain the observed phenomenon. The energy balance approach does not consider the dissipative mechanisms or the other dynamic effects (like the dynamic contact angle) which are very important for your case.

Sunny Kumar responded: We never modelled the dynamics of the process in this work. We provided a qualitative explanation for the spreading of the droplet under an applied field. The contact angle is changing in the presence of the electric field and in the absence of the same field, it returns back to its initial state. This observation is very similar to electrowetting on solid surfaces, where electrical forces are routinely brought in together with the surface tension force to provide a qualitative explanation for the contact angle variation. Of course, the entropy changes associated with the process in the presence of an electric field is controlling the kinetics of the process. Thus, the problem requires a lot more attention in that direction, which is perhaps beyond the scope of the work. The use of the word “anomalous” in the title of the paper was employed because of this reason. There is lot more to understand than what is understood up until to now.

Nikolay Brilliantov commented: When the rotating droplets break in your experiments, what is the physics behind this? Do they break owing to the centrifugal force, which becomes large at high rotation frequencies, or do they break due to the electrostatic instability?

Sunny Kumar answered: The centripetal force helps in spreading the drop. In this type of system there is a possibility of electrolysis, which also nucleates a trace amount of gas bubbles inside the system. The droplet starts breaking from the points where some gas bubbles are present and also when the droplet thins a lot due to spreading. The rotational motion helps in accelerating the break up.

Ranabir Dey asked: The Neumann’s construction gives the balance of the surface tension forces at the contact line of a liquid droplet floating on an immiscible liquid. The surface tension forces act over a length scale comparable to the interfacial length scale, which, at the most, is of the order of $10^{-}9$ m; while the electrical stress is distributed over a length scale comparable to the dielectric thickness (which in your case is at the least 80×10^{-6} m). Hence, I see no reason why the electrical stress should alter the typical Neumann’s construction at the droplet contact line. I strongly feel that the Neumann’s construction will still be valid for your case.

Sunny Kumar responded: We assume that you meant thickness of the dielectric layer in the experimental setup. The term “dielectric thickness” has a separate meaning, which is in general in the nanometer domain – important for many nanoelectronic applications such as MOSFET where dielectric strength is computed near the junctions.

We appreciate your suggestions and viewpoints. However, we feel that the arguments here are rather one sided and the following points also need consideration. The question is if the Neumann's construction is still valid then why in the presence of an electric field does the droplet spread? Furthermore, after removal of the same field we get back the initial configuration, as shown in Fig. 1a in the paper. The experiments confirm that the electric field is at work near the contact line. One must note that, experimentally, no two fluids are completely immiscible. Immiscibility is more of a theoretical paradigm. Thus, in the experimental situation, the thickness of the interfaces are rather diffused. Furthermore, when a droplet forms a lens on another immiscible liquid, the contact line is on a deformable liquid. In this situation, the thickness of the interface can be anticipated to be much more than the typical atomistic length scale. This ensures that the manifestation of the surface tension force is from both sides of the diffused interface near the contact line – one side water and the other side oil. It is well known that these interactions are rather long-range as the van der Waals force also contributes to the magnitude of the surface tension force (*e.g.* the relationship between the Hamaker constant and the interfacial tension). Since the magnitude of surface tension takes care of these colloidal effects we keep the surface tension part of the force balance the same as the macroscopic one. In addition, although a high intensity electric field is applied across the setup, the manifestation is mainly observed at the contact line, where we focus. In this type of experimental setup there is every possibility that a leakage current is present in the underlying water layer and the potential difference is manifested only across the droplet. Thus, we used the potential difference as applied to calculate the variation in the contact angle. We argue that the induced dipoles accumulate near the diffuse interface to develop additional EHD stress for spreading, which relaxes upon removal of the electric field to again form the lens.

Nikolay Brilliantov asked: Rotation of a charged droplet implies an electric current, which gives rise to a magnetic field. Could this magnetic field be measurable and important for the maximal rotation frequencies in your experiments?

Sunny Kumar answered: For the rotation experiments we have already used an external magnetic field. It is the interaction between the leakage current due to the trace amount of free charges in the dielectric oil droplet and the externally applied magnetic field that leads to a Lorenz force, which cause the rotation.

David Schiffrin said: The assumptions made in the analysis of the deformation of the organic droplet do not reflect the geometry of the system under study due to the complexity of the electric field distribution. We have here two charged metals, one a cylindrical probe immersed in an oil drop at the surface of water and the other a flat copper tape covered with a PTFE insulating layer. Potential was applied between the two metals and the changes in geometry of the oil drop were observed. This configuration is unsatisfactory for investigating electrowetting processes due to the lack of uniformity of the electric field. Neither the drop nor the supporting medium is conducting and, therefore, the field distribution is very complex. A central assumption in the calculation of EW effects is based on the changes of the solid-conducting drop interfacial tension due to the field across the insulating layer of the metal conductor. This is estimated from the charging energy of the corresponding capacitance. In your proposed EWOL setup, no such interface is present and the capacitance between the different components is undefined and variable as the field changes. The deformation and atomization of droplets in electric fields has been known for many years (see ref. 1 below and the many citations from this reference) and has found applications in industrial processes such as electrostatic painting.

1. G. Taylor, Disintegration of Water Drops in an Electric Field, *Proc. Royal Society London A*, 1964, **280**, 383–397.

Sunny Kumar replied: Thank you for the query and we fully agree with the views that the electric field associated with the system is fairly complex. In fact, in the present scenario, this can be resolvable only when a three phase computational fluid dynamic framework is developed where an expanding and disintegrating droplet under the said conditions can be performed.

Our calculations were based on a force balance at the three-phase contact point where the surface tension force competed with the electric field force to change the wettability properties. A free energy minimization at the contact line (or a point!) between the oil droplet and the water surface gave an idea about the variation in the contact angle with increase in the electric field potential. This is to explain the change of the wettability with help of the Neumann's triangle for an oil floating on an oil–water interface. In our case, the drop is spread, then transiently oscillated, and then ejected out of the applied electric field as a measure of stress relaxation, which is very different from the seminal work of Taylor.

It may be noted here that even in the EWOL setup there is some leakage current through the water layer under the oil (ranging from a mA to a few μA), which enables the separation of the induced dipoles perhaps near the droplet base. Thus, the interface is expected to be the base of the dielectric droplet.

Also, please note that the droplet showed a rotational motion apart from getting disintegrated at high speed in presence of the Lorenz force. Thus, although the deformation and atomization of droplets under electric fields are commonly studied systems, the one presented here is very different from these systems owing to the use of the Lorenz force.

Roland Bennewitz opened a general discussion of the previous 3 papers on Electrotunable Wetting with a general question to all speakers of this session and the audience: Is the electrowetting of an omniphobic system (as proposed by the research group of Joanna Aizenberg)[1] of interest? Has anyone attempted to perform experiments with these surface systems?

1 T.-S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity, *Nature*, 2011, **477**(7365), 443–447.

Frieder Mugele answered: I suppose what you mean are not so much omniphobic surfaces (*i.e.*, surfaces that repel both aqueous and non-polar liquids in ambient air), but so-called SLIPS (Slippery Liquid-Infused Porous Surfaces) that were originally described by David Quéré and became well-known under the name SLIPS by the Aizenberg group. For those samples, oil actually wets a porous medium and thereby prevents drops of polar fluids such as water from coming into touch with the solid matrix. The oil lubricates the contact between the drop and the substrates and thereby enables very low contact angle hysteresis (say, 1 degree or less) even for moderate absolute values of the contact angle (*e.g.*, around 90 degrees). The function of the porous matrix is to hold the oil in place. The required wetting conditions to enable SLIPS performance were summarized by Smith *et al.*[1]

SLIPS surfaces are interesting for EW applications, too. Yet, the problem is that the Maxwell stress that pulls the aqueous phase towards the substrate tends to thin the lubricating oil layer leading to stronger drop–substrate interaction (and hence pinning) than in conventional SLIPS systems. I am aware of one publication (Hao *et al.*)[2] illustrating some of these possibilities. Yet, in my view this work leaves important questions open and there is room for further studies. Preliminary tests in our experiments two years ago primarily highlighted the risk of enhanced contact angle hysteresis.

1 J. D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R. E. Cohen, G. H. McKinley and K. K. Varanasi, *Soft Matter*, 2013, **9**, 1772.
2 C. Hao, Y. Liu, X. Chen, Y. He, Q. Li, K. Y. Li and Z. Wang, *Sci. Rep.*, 2014, **4**, 6846.

Robert Dryfe responded: The short answer is yes, this approach is of interest. I am not aware of any electrowetting studies using the "patterned" approach of Aizenberg *et al.*, which relies on a fluorinated lubricant layer to provide low contact angle hysteresis, where the wetting occurs directly on a conductor. I am, however, aware of work which uses an approach similar to Aizenberg *et al.* (*i.e.* a porous substrate infused with a fluorinated liquid layer) to achieve rapid, reversible electrowetting - albeit using the conventional dielectric (and therefore high voltage) configuration – Hao *et al.*[1] The key question would be: can this approach be extended to the electrowetting on a conductor configuration? Although I think the electrowetting performance of the conductors (graphite) may already equal that described by Hao *et al.*, circumventing the need for the porous structure and lubricating layer.

1 C. Hao, Y. Liu, X. Chen, Y. He, Q. Li, K. Y. Li and Z. Wang, *Sci. Rep.*, 2014, **4**, 6846.

Anthony Kucernak replied: These systems may well be of interest. One issue for liquid–liquid systems in the SLIPS configuration is finding a suitable liquid, which is not soluble in either of the two liquid phases. Maybe a liquid metal and two "normal" liquids would suffice, although in this case I think this would not produce a good SLIPS surface.

Frieder Mugele opened a general discussion of the paper by Lydéric Bocquet: In your presentation, you make use of the Gibbs–Thompson relation to explain on the one hand how favorable interfacial energies induce the formation of a solidified bridge despite the fact that the system is in the fluid phase according to bulk thermodynamics. On the other hand, you argued when modeling the interfacial energy of the crystal by introducing mirrors as solid boundaries as top and bottom, confining the surface makes the system basically infinite in the direction perpendicular to the slit. This should make the system more bulk-like. I wonder whether the latter argument is consistent with the (undoubtedly correct) assertion of the Gibbs–Thompson relation. If metallic walls make the system more bulk-like than dielectric ones – why does the system then solidify more easily for the metallic ones than for the dielectric ones, given the fact that bulk thermodynamics favors the liquid state. What is it that I am missing?

Lydéric Bocquet replied: In our view, the picture of the image charges of the confined ionic crystal extending the system to infinity is, in actuality, merely a sketch so rather caricatural and may be misleading. The surface energy of an ionic crystal at a perfect metal substrate is actually non-vanishing, simply because the image charges do not interact with each other. This is discussed in the paper in section 3.2, see eqn 29–30. But as we discuss in the article, what is important is that the surface energy of the ionic liquid–metal interface is higher than the ionic crystal–metal interface. And the difference between the two increases with metallicity. See also the supplementary materials for J. Comtet *et al.*[1]

1. J. Comtet, A. Niguès, V. Kaiser, B. Coasne, L. Bocquet and A. Siria, Nanoscale capillary freezing of ionic liquids confined between metallic interfaces and the role of electronic screening, *Nat. Mater.*, 2017, **16**, 634–639.

Alexei A. Kornyshev asked: I had some conceptual difficulty in understanding the physics of your results. Positioning liquid between the conducting plates will exponentially screen electrostatic interactions between ions, be it repulsive interactions of ions of one sign or attractive interactions of the opposite sign. The screening range is proportional to the gap thickness divided by π in a slit pore or a larger number in a cylindrical one. This effect has actually led to the formation of a superionic state in the nanostructured electrodes of supercapacitors.[1] This is an established fact, as well as we know that if the conducting plates are not ideal "mirrors", and there is electric field penetration into a metal, like in your Thomas–Fermi media, the screening length will be renormalized, effectively increasing the gap thickness.[2] So weakening of Coulomb forces will be slightly less pronounced. But how, generally, can the weakening of the Coulomb forces stimulate freezing? I would expect that it should make the liquid even more liquid-like, if not gas-like? At least moving it towards a liquid of hard spheres? Of course the effect I am speaking about must be pronounced only in very narrow gaps. In a wide multilayer gap the ions in the middle part of it will hardly ever feel it. But, in the first layers near the conductive surfaces interionic interactions will be weakened by image forces: instead of Coulomb law, they will follow quasi "ion–dipole" law. So freezing can hardly be due to renormalized ion–ion interactions, but rather by image–force determined attractions of ions to the electrodes. But again this will be felt just by the first couple of layers. How this could affect the bulk of the gap, remains a mystery to me. Can you unravel it?

1 S. Kondrat and A. A. Kornyshev, Superionic state in double-layer capacitors with nanoporous electrodes, *J. Phys. Cond. Matter*, 2011, **23**, 022201; Corrigendum, 2013, **25**, 119501; M. V. Fedorov and A. A. Kornyshev, Ionic liquids at electrified interfaces, *Chem. Rev.*, 2014, **114**, 2978–3036.
2 C. Rochester, A. A. Lee, G. Pruessner and A. A. Kornyshev, Interionic interactions in conducting nanoconfinement, *ChemPhysChem*, 2013, **14**, 4121–4125.

Lydéric Bocquet responded: The physics of our experimental results (published in Comtet *et al.*, *Nat. Mater.*, 2017)[1] is interpreted as a shift of the liquid-crystal phase transition due to confinement, as summarized by the Gibbs–Thomson description. Such an approach was followed in various contexts: for the confinement-induced crystallization of liquids in porous media (see, *e.g.* Warnock *et al.*[2]), or for the so-called capillary condensation of liquids in confinement in humid environments (see *e.g.* Coasne *et al.*[3]). Physically, such a phase change occurs because of a thermodynamic competition between the bulk and surface contributions to the free energies of the different phases (liquid and solid in the context of our study). This introduces, accordingly, a length scale as a bulk-to-surface ratio, usually denoted as a Kelvin length. For confinement larger than the Kelvin length scale, the bulk term dominates over the surface terms and the thermodynamically stable phase in confinement is similar to that of the reservoirs. Now, for confinements below the Kelvin length scale, the surface terms dominate over the bulk contribution and the thermodynamically stable phase in confinement is the one favored by the surfaces. This argument can be rationalized in terms of a change in the Helmoltz free energies, comparing the difference in the bulk free energy between the two phases, in terms of the chemical potential of the bulk phase, and the surface free energy, which introduces the difference in surface tension between the two thermodynamic phases over the surface. For confinement-induced freezing, the Kelvin length resulting from this argument is given according to the celebrated Gibbs–Thomson equation (eqn (1)):

$$\lambda_{\mathrm{s}} = \left(\frac{2T_{\mathrm{B}}\Delta\gamma}{\rho L_{\mathrm{h}}(T_{\mathrm{C}} - T_{\mathrm{B}})}\right), \tag{1}$$

where L_{h} is the latent heat of melting, ρ the liquid density, and $\Delta T = T_{\mathrm{C}} - T_{\mathrm{B}}$ is the shift in transition temperature between freezing in confinement T_{C} and bulk freezing, T_{B}; $\Delta\gamma = \gamma_{\mathrm{wl}}–\gamma_{\mathrm{wc}}$ is the change of surface tension between the liquid–wall and crystal–wall interfaces.

In the context of our paper, we have shown that:

(i) due to electrostatic interactions, the surface energy of a crystal phase is lower when in contact with a metal wall as compared to an insulating wall;

(ii) the surface free energy of a crystal phase on an imperfect metal is expected to be lowered compared to the insulating case to a lesser extent than for a perfect metal (with the surface tension increasing continuously between the perfect metal and insulating material).

We have derived these results on the basis of an analytical 1D model for a crystal–metal interface, see eqn (35) in the paper, whose conclusions are generalized to 2D and 3D using numerical estimates of interfacial energies. Furthermore, while calculating the liquid–metal interfacial energy is a challenging task, we argue based on a detailed analysis of the main contributions to the surface energy for the 1D model, see eqn (41) and (42), that the surface energy is mainly dominated by the direct (attractive) interaction of ions close to the surface with their direct images (the remaining contributions, involving 2-body contributions, being negligible). Based on this analysis, we show that below the Kelvin length, confinement induced freezing is expected. It would be highly interesting to perform Molecular Dynamics simulations of an ionic liquid confined between (imperfect) metal walls. Up until now, we could only perform simulations of an ionic liquid (molten salt) confined between insulating walls, see the supplementary materials from Comtet *et al.* published in *Nat. Mater.* (2017).[1] These simulations not only confirm that crystallization occurs in nanometric confinement even for insulating surfaces, but also that the shift in the freezing temperature (or, equivalently, the threshold confinement) is properly predicted by the Gibbs–Thomson formula given above.

To summarize, the mechanism at stake is a thermodynamic surface-induced phase change, with no specific limitation on the values for the confinement threshold. Accordingly, it does not rely on the comparison of confinement with molecular extension for the (electrostatic) interactions. Let us make a last comment on the experimental side: we remark that in our experimental work (Comtet *et al.*, *Nat. Mater.*, 2017)[1], the tip radius is in the range of microns, to compare with the confinement at which freezing is measured, *i.e.* the Kelvin length (up to 100 nm). There is, accordingly, a separation of length scales between the confinement and lateral length scales in these experiments. We note that the radii of standard AFM tips are much smaller. This raises the question of freezing in a situation where the lateral tip size is in the same range or smaller than the Kelvin length, since lateral inhomogeneities in confinement are expected to strongly perturb the freezing transition.

1 J. Comtet, A. Niguès, V. Kaiser, B. Coasne, L. Bocquet and A. Siria, Nanoscale capillary freezing of ionic liquids confined between metallic interfaces and the role of electronic screening, *Nat. Mater.*, 2017, **16**, 634–639.
2 J. Warnock, D. D. Awschalom, and M. W. Shafer, Geometrical Supercooling of liquid in porous glass, *Phys. Rev. Lett.*, 1986, **57**, 1753–1756.
3 B. Coasne, A. Galarneau, R. J. M. Pellenq and F. Di Renzo, Adsorption, intrusion and freezing in porous silica: the view from the nanoscale, *Chem. Soc. Rev.*, 2013, **42**, 4141.

Alexei A. Kornyshev enquired: Will the freezing trend be maintained if the gap is very narrow?

Lydéric Bocquet answered: We expect so, but we did not perform experiments up to now in this range. The abundant literature on freezing in the confinement of simple fluids shows that Gibbs–Thomson remains valid for very narrow gaps (a few molecular diameters). Interestingly, for such very small pores, while the scaling of the shift in freezing temperature ΔT with 1/H remains (H being the pore size), the freezing temperature becomes a function of the number of confined molecular layers rather than the pore size itself. However, since the number of layers is a linear function of the pore size, the scaling as 1/H remains, but with sharp increases in ΔT as the number of confined layers changes. For more details, the reader is referred to typical review papers such as Alba-Simionesco *et al.*[1] In the context of the present study, the molecular simulations on nanoconfined salts discussed above (see supplementary materials for J. Comtet *et al.*, *Nat. Mater.*, 2017)[2] also suggest that the Gibbs–Thomson equation holds for these non-molecular liquids and remains valid down to pores of a few molecular diameters.

1 C. Alba-Simionesco, B. Coasne, G. Dosseh, G. Dudziak, K. E. Gubbins, R. Radhakrishnan and M. Sliwinska-Bartkowiak, *J. Phys.: Condens. Matter*, 2006, **18**, R15–R68.
2 J. Comtet, A. Niguès, V. Kaiser, B. Coasne, L. Bocquet and A. Siria, Nanoscale capillary freezing of ionic liquids confined between metallic interfaces and the role of electronic screening, *Nat. Mater.*, 2017, **16**, 634–639.

Martin Bazant commented: The capillary freezing of a room-temperature ionic liquid (RTIL) under confinement, influenced by surface energy, is a fascinating phenomenon to shed light on the thermodynamic properties of electrified double layers. The modeling approach of Thomas–Fermi (Debye-like) screening by electrons in the metal is clever and novel as a means to understand the role of metallicity, where the solid effectively screens the discrete large ions in the liquid. The analysis of the effect of density on the electrostatic energy of the interface based on simple configurations of ions is interesting, but also limited in its applicability. The results only apply at zero temperature for the electrostatic contribution to enthalpy. Naturally, the surface energy depends on the density of ions, and their attractive ion–image force, and the density of the crystal is somewhat larger than the liquid, thus promoting "wetting" nucleation and stabilization of the crystal under confinement. However, this analysis is incomplete (as the authors acknowledge) and raises several questions:

(1) Can a relatively small density difference between crystal and liquid explain the experimental shift of freezing point, using the formulae in the paper? This, by itself, does not seem to be such a large effect.

(2) How can the effect of entropy at finite temperature be neglected, which tends to favor the liquid over the crystal and might dominate the density-dependent electrostatic screening from the TF analysis? After all, ordering is the primary difference between crystal and liquid, and none of the calculations in the paper can distinguish the thermodynamic properties of liquid and crystal interfaces, beyond their surface concentration difference. I do appreciate the simplicity of the authors' theoretical approach, which is self-contained and does not appeal to MD simulations, but perhaps there are simple ways to include entropy in the model, *e.g.* using hard-sphere or lattice-based approximations which abound in the liquid statistical mechanics and electrolyte literature.

(3) What could be the role of ionic screening in the liquid/solid *versus* electronic screening in the metal? This is usually considered to be more important in RTIL and is also strongly affected by Coulomb correlations. As simple calculation based on the Bazant, Storey and Kornyshev (BSK) model for RTIL (applied in ref. 37 in the paper to electrolytes) could be helpful to make estimates: see Bazant *et al.*[1] This model also takes into account density constraints in a simple way, following Kornyshev (2007) and Bikerman (1942).[2–4]

1 M. Z. Bazant, B. D. Storey and A. A. Kornyshev, *Phys. Rev. Lett.*, 2011, **106**, 046102; Erratum: *Phys. Rev. Lett.*, 2012, **109**, 149903.
2 A. A. Kornyshev, Double-layer in ionic liquids: paradigm change?, *J. Phys. Chem. B*, 2007, **111**, 5545–5557.
3 J. J. Bikerman, Structure and capacity of the electrical double layer, *Philos. Mag.*, 1942, **33**, 384.
4 M. Z. Bazant, M. S. Kilic, B. D. Storey and A. Ajdari, Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions, *Adv. Colloid Interface Sci.*, 2009, **152**, 48–88.

Lydéric Bocquet responded: The change in surface energy is typically a density difference times an interparticle interaction, as highlighted by eqn (41) and (42) in the paper. Thus, due to the large magnitude of electrostatic interactions (*e.g.*, as compared to thermal energy), even a relatively small change in density between the crystal and liquid phase can lead to an important change in surface free energy. The predicted order of magnitude for the shift in the freezing point is consistent with the experimental data, see eqn (6) in ref. 11 in the paper. Concerning the modeling *per se*, our model aims to capture the basic mechanisms at the origin of a metallicity-dependent surface tension favoring the crystal over liquid. As a first step, we indeed omitted entropic effects, since these are expected to be small as compared to direct electrostatic contributions which are predominant here. But we fully agree that there is a need now to account properly for entropic effects. The type of models suggested by our colleague are indeed very good leads to go beyond the present analysis. In the 1D model developed in our paper, the ions are organized in a crystal and fully correlated. Ionic screening is implicitly taken into account when summing up the interaction energies to calculate the surface energies. Now, going into more detailed models of the disordered phase will require us to account more systematically for the ionic screening. Again, the BSK type of model is certainly an excellent lead towards this goal. In general, a systematic statistical modeling of the surface free energies of RTIL is needed, taking properly into account the role of the nature of confining surfaces. We hope that our results will motivate further work in this direction.

Carlos Drummond said: As ionic liquids are often composed of bulky polarizable ions, it seems likely that ion–substrate electrodynamic dispersion forces will be significant (for metal or dielectric surfaces). Wouldn't it be important to consider this factor in your theoretical description?

Lydéric Bocquet answered: While polarizability for species containing a larger number of electrons is indeed expected to contribute to the total energy of the system, electrostatics between ions is a far more dominant term which rules the physics at play. Therefore, while the role of polarizability has often been put forward, it seems that this corresponds rather to a correction than a contribution that would significantly affect the effects induced by the direct, electrostatic contributions. It should be emphasized that specific ion–ion contributions such as dispersive and repulsive interactions (which are important to accurately describe the physicochemical properties of these ionic liquids including their low melting temperature compared to simple molten sales) are expected to be far more important than the polarizability in our analysis of the surface energies.

George Schatz asked: How important are the higher multipoles? Are there situations where the simple image model is adequate in describing the problems you are considering?

Lydéric Bocquet replied: In the 1D model introduced to calculate the surface energy of a ionic crystal close to a metallic wall, it is interesting to note that all terms contribute individually, but due to an overall cancellation of terms, the main contribution stems from the direct interaction of charges close to the wall with their image.

Susan Perkin enquired: In your discussion of eqn (37) in your paper you remark upon the apparent van der Waals-like term. Can you say anything about the extent to which the analogy applies, or comment on what we can understand from this term? For example, classical Hamaker constants can be positive or negative, whereas this term seems to be purely attractive. Are there any conditions in which it might be repulsive?

Lydéric Bocquet answered: This expansion is associated with a multipole expansion of the total interfacial energy. Accordingly, it is expected that a dipolar term results in a van der Waals-like contribution with a proper Hamaker constant. What is more striking is the 1/D term scaling like the inverse film thickness and, therefore, dominant over the van der Waals contribution. While here we consider a geometry involving a metal/ionic crystal/dielectric interface, it would be of high interest to consider a more relevant configuration with a metal/ionic crystal/ionic liquid interface. For now, we do not have predictions in this case. But the expansion of the interface energy in terms of film thickness and the sign of the terms may be expected to change in this instance. In view of the difficulty of accordingly estimating the electrostatic contributions to the free energy of the ionic liquid interfaces, we expect that Molecular Dynamics simulations could be a proper tool to answer to this question. We leave this point for future work.

Alexei A. Kornyshev commented: If the solvent permittivity is higher than the background dielectric constant of the Thomas–Fermi medium, at short distances the image force will be repulsive, but not attractive.[1] You might not see this for pure ionic liquids, but what will happen if you mix them with a highly polar liquid? Will you still see the freezing effect, or will the result change?

1. A. A. Kornyshev, A. L. Rubinshtein and M. A. Vorotyntsev, Image potential near a dielectric/plasma like medium interface, *Phys. Status Solidi B*, 1977, **84**, 125–132.

Lydéric Bocquet responded: It would indeed be highly interesting to explore the influence of adding solvent in these experiments. This will modify strongly the image charge contributions, as suggested in the question. We did not perform these experiments up to now.

Note however, that the strong impact of metallicity on the phase behavior explored in our contribution and Comtet *et al.* in *Nat. Mater.* (2017)[1], also results from an “ideal” matching of the molecular length scales with the Thomas–Fermi screening length in the metal, both being in the range of Angstroms (a regime in which image charges contribute strongly to the interfacial energies). Adding solvent will dilute the ionic liquid, making the inter-ion distance larger and weakening the effects of image charges. This is expected to reduce the effect explored here.

1 J. Comtet, A. Niguès, V. Kaiser, B. Coasne, L. Bocquet and A. Siria, Nanoscale capillary freezing of ionic liquids confined between metallic interfaces and the role of electronic screening, *Nat. Mater.*, 2017, **16**, 634–639.

Andriy Yaroshchuk said: In the sample calculations presented in the paper, you use a Thomas–Fermi length of 1 Angstrom. This implies that deviations from the ideal metallic behavior shouldn’t occur at essentially larger distances. At the same time, the neighboring phase is modeled as a dielectric continuum. This seems okay in the case of a vacuum, but you also mentioned potential applications of your analysis involving solvents. In this case, for example, non-local dielectric screening may be important, and it manifests itself at distances essentially exceeding 1 Å. Isn't this a considerable limitation of your analysis in the case of solvent-containing fluids?

Lydéric Bocquet replied: At this stage, we can not draw such a conclusion. What is indeed expected is that an effect of metallicity will occur whenever the Thomas–Fermi length is in the range of the inter-ionic distance (as a side note this matching condition is definitely not to be considered as stringent and is merely a rule of thumb; see, furthermore, the 2D and 3D calculations in Fig. 6 of our paper). So, if a solvent dilutes the ions considerably, the effects of image charges and metallicity are indeed expected to decrease.

Now, when this image charge effect disappears remains to be assessed and requires specific detailed estimates with, *e.g.*, Molecular Dynamics simulations. Indeed, in the presence of a solvent, some of the molecules will indeed solvate the ions and modify the interfacial structure close to the wall (in some situations, possibly leading to a depletion of ions close to the walls). However, the local structure will depend on a number of factors which are difficult to predict without a dedicated study at the molecular scale: *e.g.*, the value of the effective local dielectric permittivity and the consequences this has for the solvation energy of ions, their distribution close to the metal (are they solvated or attracted by their images?), possible non-local dielectric effects, the effect of dissymmetry between the ion and solvent sizes, *etc.* Many of these details and the competition between them are not known. In a different situation involving the adsorption of ions at hydrophobic interfaces, the interfacial structure of the ions is the result of a complex balance between a combination of all these effects (in line with the Hofmeister series), which cannot be simply predicted; see for example Huang *et al.*[1] So the effect of solvent is definitely an interesting question which remains open at this stage. It is not a limitation of the analysis, rather an extension.

1 D. M. Huang, C. Cottin-Bizonne, C. Ybert and L. Bocquet, *Phys. Rev. Lett.*, 2007, **98**, 177801.

Michael Urbakh asked: In your rheological experiments you studied the response to oscillations perpendicular to the surface. Have you studied a response to shear oscillation (oscillations parallel to the surface)? Have you observed the same threshold length for freezing in both cases?

Lydéric Bocquet answered: This is definitely a direction to follow and we are currently doing experimental work along these lines.

Martin Bazant opened a general discussion of the paper by Alpha Lee: This work raises the interesting possibility of controlling turbulent drag by the application of voltage at blocking electrodes. The electrokinetic phenomenon that could cause this effect is called "induced charge electro-osmosis" (ICEO). It would be helpful to make this connection, and a significant amount of literature exists that should be discussed, as reviewed in *Curr. Opin. Colloid Interface Sci.* (2010)[1] and *Adv. Colloid Interface Sci.* (2009).[2] Most theoretical work on ICEO has considered simplified thin double layer models for charging and flow generation, but recently a direct numerical simulation has been reported by Davidson, Andersen and Mani,[3] which reveals chaotic vortices and advection, even around blocking electrodes as considered in this work. However, this is not turbulence caused by inertia, but rather ICEO-driven electroconvection at high voltages, which is related also to the Rubinstein–Zaltzman instability in electrodialysis, due to the common feature of strong concentration polarization and salt depletion.

The key difference here is that pressure-driven turbulent flow is imposed in the channel, and mixing prevents large changes in salt concentration. This allows some effects of interaction between “normal” ICEO flows and turbulent eddies, which could influence drag. As shown in the original paper[4] on ICEO microfluidic devices and related effects in the induced-charge electrophoresis of colloidal particles, the most important feature of ICEO flow is its strong dependence on broken symmetry, which has not been exploited here, since the work considers only parallel flat electrodes. I suggest doing simulations and an analysis of electrode arrays with non-electrode regions on the surface, or geometrical perturbations away from flat walls to engineered rough features, which will drive much stronger ICEO flows extending far from the double layer, set by the length scale of the geometrical or surface heterogeneity. As also shown in the original paper I mentioned, it is useful to consider AC voltages to fully exploit the non-linearity of ICEO without saturating the flow at steady state or triggering Faradaic reactions. So I suggest also applying AC voltages in asymmetric electrode channel geometries, and this could also be combined with the well studied effect of AC electroosmosis for periodic electrode arrays (although the frequency will typically be larger, the length scale smaller and the flow velocity weaker for that effect).

For the test case of charging flat electrodes, the authors compared with the response to a sudden DC voltage,[5] but they could also test their code and analysis for large AC voltages.[6]

1 M. Z. Bazant and T. M. Squires, *Curr. Opin. Colloid Interface Sci.*, 2010, **15**, 203–213.
2 M. Z. Bazant, M. S. Kilic, B. D. Storey and A. Ajdari, *Adv. Colloid Interface Sci.*, 2009, **152**, 48–88.
3 S. M. Davidson, M. B. Andersen and A. Mani, *Phys. Rev. Lett.*, 2014, **112**, 128302.
4 M. Z. Bazant and T. M. Squires, *Phys. Rev. Lett.*, 2004, **92**, 066101.
5 M. Z. Bazant, K. Thornton and A. Ajdari, *Phys. Rev. E*, 2004, **70**, 021506.
6 L. Højgaard Olesen, M. Z. Bazant and H. Bruus, *Phys. Rev. E*, 2010, **82**, 011501.

Alpha Lee answered: Many thanks for the suggestions and comments. We are indeed very inspired by the ICEO literature. We agree that AC effects as well as other symmetry-breaking mechanisms are important for affecting the flow, and we are in the process of implementing them in our code.

Lydéric Bocquet commented: The effects you are considering could be interesting also for the problem of drag crisis on a body, associated with the laminar to turbulent transition of the boundary layer. Here, electrochemical effects could be quite pronounced for surfaces with curved geometry.

Alpha Lee responded: We agree that electrokinetics could be an interesting handle to control external flows, although the mechanism would be quite different to the one we sketched out in our paper. At a sufficiently high Reynolds number, drag on a sphere is dominated by the separation of the boundary layer. This type of drag is known as pressure, or form drag, as opposed to skin-friction drag. While plasma actuators have been used to control form drag, the mechanism of control is very different. Boundary layer separation comes about when the boundary layer faces an adverse pressure gradient, which drains the momentum of the boundary layer. Eventually, the momentum close to the wall drops to such an extent that the viscous stress at the wall becomes zero, and the boundary layer separates. By injecting momentum parallel to the flow in the boundary layer, using methods such as blowing or electric forces in the case of the dielectric barrier discharge actuator, the separation can be delayed or even prevented, reducing form drag. The drag crisis in a sphere happens when the boundary layer transitions to turbulence, which is more effective in distributing momentum. Thus turbulence could reduce the form drag and, even when the skin-drag is increased by having a turbulent boundary layer, the total drag is reduced. In an analogous way, electrokinetics could be useful in reducing drag for external flows if a large enough force can be applied in a direction parallel to the flow, as this would delay boundary layer separation.

For drag in internal flows such as the Couette flow that we considered, the pressure drag does not exist as the boundary layers cannot separate, thus the only source of drag is the skin drag. In this case, we want to reduce the level of turbulence as far as possible, so the mechanism for drag reduction is different.

Nikolay Brilliantov asked: The Kolmogorov energy spectrum for turbulence implies the scaling $k^{\{-5/3\}}$, where $k \propto 1/\lambda$ is the wave vector and λ is the according space scale. This dependence covers a few length scales, down to scales comparable to the molecular scale length. You have an intrinsic length scale in your system, associated with the Debye screening length. Physically, I expect that the appearance of the new length scale would change the Kolmogorov spectrum. Do you observe this?

Alpha Lee replied: The 5/3 law holds for homogeneous isotropic turbulence. Even in the absence of the ion concentration field, the spectra in a channel would not scale as $k^{\{-5/3\}}$. There are some theories that postulate a mixed $k^{\{-1\}}$ and $k^{\{-5/3\}}$ scaling,[1] but the Reynolds numbers considered here are far from sufficient to obtain clean power laws. As a side note, Bolgiano[2] postulated that an alternative scaling for kinetic energy and temperature exists for buoyancy-driven turbulence as a modification to the original Kolmogorov scaling. While the existence of the Bolgiano scaling has been found in a particular system by Boffetta *et al.*,[3] it is suspected to be absent for most thermally driven turbulent flows.[4] One could imagine that similar modifications to the scaling could exist for ion-driven turbulence. Indeed, Druzgalski and Mani[6] observe a variety of spectra for ion concentration and kinetic energy, but the scaling relationships span less than an order of magnitude in k.

1 A. E. Perry, S. Henbest and M. S. Chong, *J. Fluid Mech.*, 1986, **165**, 163.
2 R. Bolgiano Jr., *J. Geophys. Res.*, 1959, **64**, 2226.
3 G. Boffetta, F. De Lillo, A. Mazzino and S. Musacchio., *J. Fluid Mech*, 2012, **690**, 426.
4 D. Lohse and K.-Q. Xia, *Annu. Rev. Fluid Mech.*, 2010, **42**, 335.
5 C. L. Druzgalski and A. Mani, *Phys. Rev. Fluids*, 2016, **1**, 073601.

Michael Urbakh commented: In your simulations you applied stick boundary conditions for fluid velocity at solid–liquid interfaces. However, our own simulations of friction in ionic liquids[1] demonstrated that variation of the surface charge density may strongly influence boundary conditions for velocity at the interfaces. In particular, they can be changed from stick to slip boundary conditions. This can provide an efficient mechanism for tuning friction by applying voltage in the systems considered in your simulations.

1 O. Y. Fajardo, F. Bresme, A. A. Kornyshev and M. Urbakh, *J. Phys. Chem. Lett.*, 2015, **6**, 3998–4004.

Alpha Lee responded: Many thanks for the comment. We agree that bridging the length scales and using insight from MD to parametrise the boundary conditions in continuum theory is an exciting direction, and we are currently pursuing it.

Alexei A. Kornyshev said: In any electrolytic medium the static voltage will translate into an electric field localized within the double layer near the electrodes. This could not directly affect the turbulence in a wide gap. And this is what you see: the effect of ion turbulence is very weak, if noticeable. Have you tested what happens when the gap becomes narrower and narrower? Of course, then the Reynolds number will get smaller and the turbulence itself might disappear. Is there still some range of distances within which the turbulence is still there, but the effect of the polarization of the walls becomes noticeable?

Alpha Lee answered: The main idea behind skin friction reduction in a turbulent channel is to mitigate the self-sustaining mechanisms, located near the walls, which generate the turbulence. This has been shown to be possible by using bubbles, small amounts of polymers (of the order of parts per million), or riblets deep inside the boundary layer. Du and Karniadakis[1] showed that travelling wave-like forces confined close to the wall are capable of reducing drag. Therefore, as long as the force is applied deep inside the boundary layer, the method should work, and the electrical double layer does not need to extend throughout the whole gap.

The work presented here is our first attempt at constructing forces which could potentially reduce drag by trying the simplest case: constant applied voltage with no spatial dependence. More sophisticated mechanisms will be investigated in the future, and the system could potentially be a physical realisation of the Du–Karniadakis travelling wave. Another potential mechanism is *via* the application of an AC field, which could excite electroconvective instabilities.

1 Y. Du and G. E. Karniadakis, *Science*, 2000, **288**, 1230.

Andriy Yaroshchuk asked: In the paper, you state that one of the principal purposes of your study was to develop methodology for the analysis of turbulent flows coupled to ion transfer. Ali Mani of Stanford University is working on similar problems. What are the principal differences between your approaches?

Alpha Lee answered: Our work is different to Ali Mani's work in several respects. First, Mani focuses on high Schmidt number active flows, whereas we are considering electrokinetic flows driven by turbulent forcing. In the problems that Mani considered, the velocity is linearly enslaved to the concentration field, and the numerical algorithms he developed are specialised to that case. In his earlier studies,[1] the simulations have a Reynolds number of effectively zero, and thus solves the Stokes equation. In Druzgalski and Mani, *Phys. Rev. Fluids* (2016),[2] the Navier–Stokes equations are solved, but again the non-linear inertia term is small, thus it can be considered as a perturbation. We focus here on turbulence driven by the plates, instead of by the concentration field, *i.e.* concentration is a passive scalar. In our case, a large Schmidt number does not linearly enslave the concentration field and make the simulations easier, but instead sharpens the concentration gradients making the simulations harder.

Second, a constant current boundary condition is used for most of Mani's work (although we are aware of his study of chaotic ICEO which considered a blocking electrode[3]). In general, a constant current boundary condition prevents the formation of extremely sharp double layers, thus reducing the need to enforce ion conservation to machine precision. If ion conservation is not enforced to machine precision, the finite-difference errors close to the walls become significant, and ions "leak" out of the system – a numerical artifact that caused us a lot of grief in our earlier attempts at this problem.

1 C. L. Druzgalski, M. B. Andersen and A. Mani, *Phys. Fluids*, 2013, **25**, 110804.
2 C. L. Druzgalski and A. Mani, *Phys. Rev. Fluids*, 2016, **1**, 073601.
3 S. M. Davidson, M. B. Andersen, and A. Mani, *Phys. Rev. Lett.*, 2014, **112**, 128302.

Martin Bazant opened a general discussion of the paper by Andriy Yaroshchuk: This effect is an interesting use of broken symmetry to achieve pumping with AC forcing, but in contrast to other schemes, such as AC/ICEO flows, the time scale here is that of diffusion, required to alter the concentration polarization layer, which is typically rather slow. For cooling or other the practical applications, what would be the minimum AC period required to achieve sufficient flow or heat transfer, and how would this depend on the size and material properties of the device? What is the most promising application, and it is feasible with existing materials?

Andriy Yaroshchuk responded: Thank you for this relevant question. Indeed, the development of the non-linear response takes some time in this system. So far, we have simulated only stationary conditions, so I cannot give a quantitative answer to your question. However, we can roughly estimate that quasi-stationary conditions are achieved when the convective flow has enough time to "sweep" the whole thickness of the nanoporous layer. Thus, in our opinion, the relxation here is primarily controlled by convection and not diffusion (because the Péclet numbers are typically not small). Typical linear velocities of convection in our simulations are tens of microns per second so for a thickness of one hundred micrometers the characteristic time is around or below 10 s. In the application we primarily target at present ("active" moisture removal in sports garments) we use capacitive electrodes that are capable of sustaining the required currents in one direction for longer periods of time (minutes). Thus, this application seems to be feasible with existing materials, although further improvement of the capacitive electrodes would be quite useful and is being worked on.

Martin Bazant asked: Besides the low AC frequency, which could be addressed possibly by miniaturization and integration, could you estimate the energy cost of the pump (and its scaling with size, materials, *etc.*), and thus the size and weight of the battery that would be required to power it for portable/wearable devices?

For personal cooling, the weight and size of the distributed heat exchanger and transport system for the liquid coolant would also need to be considered. Could a practical wearable system be designed around such a pump?

Andriy Yaroshchuk replied: Unfortunately, we are not, yet, that close practical systems to be able to answer this question in sufficient detail. Just as a rough estimate, typical current densities are around 100 A m^{-2} and the maximum voltage is around 1 V (because we cannot afford to have electrode reactions close to a human body). This gives us an estimate of the power density requirement of around 100 W m^{-2}. For the moment, the existing prototypes are not intended to cover the whole body, they just use "active windows" close to the most problematic body parts. The total area of such "windows" can be below 0.05 m^{-2}, which gives us a power requirement of less than 5 W. Sorry to say, but I'm not an expert in modern batteries, therefore, I am unable to tell you to what weight of battery this may correspond. One should also keep in mind that the materials are primarily intended for use during sports activities, which typically don't take a very long time. Accordingly, it would be enough to have a battery that can provide this power over a period of several hours, then be recharged afterwards.

With regard to the distributed heat exchanger and transport system for the liquid coolant please note that we're developing a system for moisture removal not cooling. We don't have any dedicated coolant in the system.

Himani Medhi communicated: This article describes theoretical aspects of asymmetric electro-osmotic pumping across porous media sandwiched with perforated ion-exchange membranes keeping some parameters (see Table 1 in the paper) fixed. Is this a simulation study that can be carried out for micro- and mesoporous materials as well as materials with inter layer spaces having high ion exchange capacities?

Trond Heldal communicated in reply: The porous layer could have a wide range of pore sizes (*e.g.*, 50 nm or 1 micron) "conjugated" with a permselective ion conductive layer with sparse perforations with large pore size (*e.g.*, 5 microns).

Nikolay Brilliantov opened a general discussion of the previous 3 papers on Micro and nanofluidics with a general question to all speakers of this session and the audience: Is it justified to remain on the Navier–Stokes level for these cases when a new, possibly, short-range scale length, associated with the Debye screening length appears? This short scale length implies larger gradients in the system. Therefore, may be one needs to use the Burnett or super-Burnett hydrodynamics, to account for terms with high-order gradients?

Lydéric Bocquet answered: It was shown by a number of works that the Navier–Stokes equations are valid down to length scales in the range of several atomic diameters (typically 1 nm for water under standard conditions), see discussion in ref. 1 below. Adding a molecular length scale (in the same range as molecular interactions) is therefore not expected to modify these conclusions.

1 L. Bocquet and E. Charlaix, *Chem. Soc. Rev.*, 2010, **39**, 1073–1095.

Alpha Lee answered: The Knudsen number (mean free path/characteristic distance) quantifies the validity of the Navier–Stokes equations. For the cases we consider, we are still within the limit of a Knudsen number smaller than one. As long as Kn <0.5, the viscous term in the Navier–Stokes equations have been shown to hold,[1] and only the no-slip condition needs correction due to the appearance of a Knudsen layer. For even smaller Kn <0.1, the slip-length correction vanishes. As the Debye length is still larger than the molecular or ionic diameter, we are safely within that limit. Surprisingly, the Navier–Stokes equations have been shown to work even for steep and small-scale gradients, such as shock waves.

1 Y. Sone, *Molecular Gas Dynamics: Theory, Techniques, and Applications*, Birkhäuser, 2007.