Forces, structures and ion mobility in nanometer-to-subnanometer extreme spatial confinements: Electrochemistry and ionic liquids

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Being able to probe electrolyte structures and ion mobility in nanometer confined cavities/pores is central for the fundamental understanding and steering of various processes in biologic and material systems. Here, we review how force probe experiments were utilized for studying interfacial physics at solid/liquid/solid interfaces. We discuss recent technological achievements, and show how micro-to-nano and ultimately subnanometer confinement can be achieved and probed using the Surface Forces Apparatus. We discuss ion-mobility and structuring in confined spaces during reactive and non-reactive conditions. This includes ion-layering and confinement induced effects, such as enhanced reactivity, decreased ion-mobility, electric double layer overlapping and more. We limit the discussion to electrochemical and ionic liquid systems, yet we discuss the broader perspective how to develop the technique further, and how recent advances can already find new exciting applications, across sometimes unexpected fields. These range from studying physiologic processes, to technologic application in catalysis, microfluidics or geology.

Keywords: forces, structures, ion mobility, ionic liquids, nano confinement, electrochemistry, atomic force microscope, surface forces apparatus

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I. INTRODUCTION

In recent years molecular scale probing of solid/liquid interfaces in electrochemical systems has seen an increased interest due to high demand for viable electrochemical energy storage and conversion technology. In electrochemical devices both ion structures at extended open interfaces as well as structuring in restricted geometries play an important role for optimizing performances and enabling technological breakthroughs.

As indicated in figure 1a, the structure of solutes and solvent on a charged (or polarized) surface is characterized by the formation of the so-called electric double layer (EDL). The EDL balances any surface charging by screening this charge via adsorption and/or accumulation of oppositely charged ions at the solution interface. Several EDL models evolved over the last century. There is consensus that the Stern-model, which has been modified and upgraded several times, captures the qualitative essence. It describes the EDL comprising of an inner layer with specifically and non-specifically adsorbed ions and preferentially oriented solvent molecules (Stern layer), and an outer layer with a "diffuse" Poisson-Boltzmann distribution of ions (Gouy-Chapman layer). While the diffuse ion distribution can be predicted well, in particular for low concentration electrolytes ranging from 0.1 mM to 100 mM, the inner layer structure and ion mobility remain experimentally challenging to assess. Yet, and we will see, these are accessible to force and simulation probe experiments.

Specifically, at gap sizes larger or equal to the Debye screening length, $\lambda_D$, the ion distributions is governed and well-described by continuum physics, i.e. Poisson-Boltzmann equations, using constant charge or potential, or more sophisticated charge regulation models such as the charge regulation approach. Here, recently discovered and unexpected diffuse contributions in highly concentrated salt solutions, such as ionic liquids or aqueous solutions used e.g. in water electrolysis, remain challenging in terms of a quantitative description.

Interesting aspects arise when EDLs of two apposing surfaces overlap at molecular separation distances. As shown in figure 1b, already a simple macroscopic experiment - i.e. confining millimeter sized balls between two flat surfaces - reveals that the mere presence of confining walls results in peculiar structural arrangements at separation distances approaching the diameter of the spheres. In this case, the marked triangular features form due to a tendency to minimize the volume occupied by the spheres in the confined space.

The physical picture of overlapped sub-Debyelength - i.e. molecularly - confined double layers,
and how this influences molecular structure, charging dynamics and electrochemical processes is less well understood. Yet, this is central to many electrochemical applications, including battery charging, nano-fluidics, corrosion processes and electrocatalysis. Figure 1d shows typical force versus distance characteristics recorded in molecular fluids, in this case ionic liquids with varying tail length. This data reveals a highly unusual oscillatory behaviour, indicative of a distance dependent layering of the confined ions during approach to molecular dimension. Solvation dynamics in such restricted spaces can be considerably slower compared to bulk solvation$^5$, ion diffusion and migration may be enhanced or limited depending on the chemistry$^{21}$ or reactivity of confining walls.

Force probe experiments emerged as a powerful tool for probing EDLs and structure of ions.
at surfaces with high lateral resolution. Atomic force microscopy based molecular scale imaging in 2D, and recently also in 3D,\textsuperscript{11} is becoming the exciting state-of-the-art to image structures at non-confined solid/liquid interfaces. It is now possible to record force maps representing positions of surface atoms, and electrolyte molecules with sub-Å resolution in all three dimensions. As shown in figure 1c, with its unprecedented resolution, this technique will continue to provide deep insight into processes at solid/liquid interfaces, but will not be reviewed extensively in this work.

In recent year we, and other groups started to introduce force probe techniques based on the surface forces apparatus (SFA) principle (sometimes also called the surface forces balance, SFB) as sensors for ion structuring, and ion dynamics in nano-confined spaces and in extreme small spatial confinement, opening up exciting new possibilities. Here we review these recent technological achievements and discuss ion layering and confinement induced effects, as probed using the SFA technique. While necessarily focusing the discussion on a limited, yet by no means complete set of results, we intend to provide a broader perspective about how the developed techniques can find new and exciting applications across sometimes unexpected fields. Therefore we start with a short definition and overview of the broad range of phenomena where confinement, and processes in confinement play a central role.

II. CONFINED SOLUTES AND SOLVENTS AND THEIR IMPORTANCE IN NATURE AND TECHNOLOGY

Extreme spatial confinement is characterized by limiting the space between two more or less rigid walls to separation distances, \( D_S \) or \( D \), which are in the range of molecular and ionic diameters. Such extreme confinement is central to many phenomena and processes in nature and technology including clay swelling, battery charging, micro-fluidic devices, localized and crevice corrosion, self-assembly and self-organized assemblies, oil recovery, biomineralization, friction as well as charge and material transport across bio-membranes.

How electrolytes structure and flow in restricted geometries has been, more or less, realized as potentially central aspect for driving functionality in all of these areas. Yet, experimental success and evidence are scarce and often limited to specific techniques and applications. Confined structure and dynamics are considered to be a result of combined effects of purely spatial limitations, i.e. the physical presence of confining walls (see again figure 1b), and chemical/physical interactions of confined matters with the confining walls. These can include Coulomb interactions,
specific or non-specific interactions, and hydrogen bridging among others. In general, confinement effects are manifested in (1) modified ion/solvent migration and diffusion rates, (2) by molecular structures evolving in confined interaction, and (3) by the repulsive/attractive forces generated in confined spaces. This results in a variety of phenomena across all disciplines, that are caused or controlled by these effects.

a. Materials science and geology. For instance in corrosion science it is central to understand how halide ions and proton diffuse in/out of a charged crevice or crack tip, where they can induce localized accelerated materials degradation. Such a confinement induced degradation is often detrimental to applications. It is possible that forces generated by ions diffusing and layering into a crack tip, generate an additional repulsive EDL force that drives fast crack-tip propagation rates during stress corrosion cracking. Similarly, in geochemistry, the effect of confinement controls processes such as dissolution/reprecipitation of contacting rocks, playing a central role in rock-metamorphosis. Concrete hardening and plasticity can be modulated effectively by controlling inter particle forces of closely confined calcite particles.

Confinement induced first order phase transitions from a fluid to a solid state were observed during sliding and during approach of simple organic liquids into molecular confinement (e.g. cyclohexane or silanes). Similar effects were seen for aqueous systems where the viscosity increased dramatically upon electrochemical polarization on a confining surfaces. Such confinement induced phase changes, and the close overlap of hydrated surfaces can have a profound effect on friction forces and damage/wear during sliding.

b. Biologic and soft matter systems. Also, water and hydration exhibits a surprisingly slow dynamic in confined self-organized surfactant assemblies. Ultrafast laser spectroscopy revealed a bimodal fast bulk-like response in the sub-picosecond range, followed by a much slower component with hundreds to thousands of picoseconds. This has been related to the disruption of the 3D hydrogen bond network of water in restricted geometries.

Confinement effects were also seen in simulation of molecular association of cavity-ligand pairs, which primarily interact in the hydrated state. Water-water interactions of approaching cavity-ligand pairs, concerted by the interactions of water adsorbed to the confining/interacting entities, can be an active player in enabling or rejecting ligand binding. Confined water (and presumably also ions) may hence determine the subtle balance among driving forces for molecular association of bioactive molecules, broadening the array of levers a biologic system utilizes for molecular control and precision.
c. Applications relying on confinement effects. Finally, confinement effects are already utilized in potential technologic applications, including micellar catalysis, electrocatalysis and nanofluidics. For instance, when apposing electric double layers overlap, e.g. in solvated nano-channels, the confined ion layering can be tuned for gating. By tailoring and switching the charge of a confining wall it is possible to tailor specific transport of ions and charged molecules based on both, size and electronic polarity exclusion. How ions flow and structure in such confined nanofluidic channels is central to tailoring such devices. In micellar catalysis and electrocatalysis confinement is recognized as a special compartmentalized environment, with beneficial properties for steering these processes, and enhancing material stability under reactive (catalytic) conditions.

III. THE SURFACE FORCES APPARATUS: A DEVICE WITH ULTIMATE SENSITIVITY FOR EXTREME SPATIAL CONFINEMENT EFFECTS

As we have seen, forces, ion and solvent dynamics and structures in confined space are essentials and often determining drivers for processes in diverse fields. Probing confined structures in a well controlled system is experimentally challenging. Many experimental results involve probing bulk systems that consist of a high density of internal interfaces that confine solvent and solutes. For instance self-assembled architectures, or nano-porous systems are such systems, and can be studied with the arsenal of available bulk probe experiments, including e.g. X-ray probes. Other approaches involve pure simulations probes, which are currently computationally feasible at the ab initio level for gap sizes up a few nanometers. Again other approaches probe confined surfaces simply after a process in confinement occurred (e.g. in corrosion science) using post-experimental analysis tools.

Probing a single confined nano-pore, ideally with an in-situ variable pore size and in-situ tunable wall properties is much more challenging. In this respect the surface forces apparatus, SFA, evolved as a unique and powerful method for making well controlled 100-1000 µm² extended confined contact zones with sub-nanometer thickness accuracy, for probing ion layering and ion dynamics.

The inset in figure 2a shows the main feature of an SFA measurement, which is the direct and absolute measurement of the separation distance, D. This is achieved by setting up a pair of macroscopic surfaces (typically crossed cylinders) as an interferometer cavity by back-silvering transparent interacting surfaces, so that white light passing through such a cavity interferes con-
structively/destuctively. The interference pattern depends on the absolute distance between the surfaces, providing the possibility to in-situ control gap thicknesses with Å resolution. How SFA works in practice and theory was discussed extensively in our recent work.\textsuperscript{35}

![Image of graph](image_url)

**FIG. 2.** a) Force versus distance characteristic as a function of the applied potential, recorded between a polarized gold surface and a positively charged self-assembled monolayer (reprinted with permission from the American Chemical Society\textsuperscript{45}). b) In-situ SFA force spectroscopy of a solid electrolyte interface taken on different depths of discharge allow both mechanical and thickness characterisation. A sketch of a typical SEI is shown (reprinted with permission from Wiley\textsuperscript{30}).

Here we want to limit the discussion to the essentials: White light multiple beam interferometry (MBI) provides absolute distance control in an SFA; and lateral contact areas diameters are typically in the 10-100 μm range. This practically means SFA generates an extended extreme contact confinement by approaching two molecular smooth surfaces to small separation distances, and practically down to direct contact with D = 0. The distances are tracked with Å precision by analyzing wavelength shifts of white light interference spectra in transmission or reflection mode. With reflection mode it is possible to confine any metallic surfaces.\textsuperscript{28,35}

SFA was initially quite restricted to muscovite surfaces. Recent developments, including new analytical\textsuperscript{35} and experimental ideas,\textsuperscript{28,47} enable us now to use almost any surface combination. Specifically, electrochemically polarizable ultra-smooth and real surfaces have been studied in great detail over the last decade.\textsuperscript{27,32,36,42,46}
In the following subsections we will highlight a number of remarkable recent SFA-based experimental results that drive our understanding of structure and dynamics of ions in confinement and during approach of two EDLs in systems with relevance for electrochemical technology.

A. Surface structuring and electric double layer forces in nano-confined gaps during reactive and non-reactive electrochemical polarization.

a. Electric double layer forces and confined ions during potentiostatic polarisation. Figure 2a shows the first experimental force versus distance profile recorded during approach of a molecularly smooth positively charged amine-terminated surface, and a molecularly smooth polarizable gold electrode, at pH = 3. The approach curves follow the expected trend; switching from attractive to repulsive with the increasing electrochemical potential of the gold surface, given that the apposing surface is positively charged. The long-range repulsion forces from D = 40 to D = 5 nm are due to the overlap of the approaching diffuse EDLs, and can be fit well with standard EDL models.

It is most interesting to note that the absolute distance measurement in an SFA provides a direct view into the confined electrolyte at different potentials. The confined EDL thicknesses are labelled as hard walls in the figure. Specifically, at negative polarization of the gold surface the positively charged amine surface is only separated by a sub-nanometer thin water layer, which in this case is presumably hydration water of the two surfaces. Charge neutrality in this sub-nanometer gap is achieved by the opposite charging of the surfaces. At positive polarization of the gold, the positive amine surface is separated at a larger distance of about 2.5 nm, indicating the necessary confinement of counter ions in the gap between the two similarly charged surfaces.

This result is so far interesting as it provided a first proof-of-principle that confined EDLs can be modulated in-situ by electrochemical potential variation, and an SFA can track such changes with sub-Å accuracy.

b. Detecting the formation of reaction products during electrochemical polarization. Figure 2b shows a more recent SFA force versus distance experiment, recorded during consecutive approaches in a typical battery electrolyte (LiPF6 dissolved in organic ethers) between a mica surface and a gold surface. In this experiment a constant anodic current flow was applied to the gold surface. This results in the dynamic formation of decomposition products from the electrolyte that aggregated on the electrode surface, forming the so called solid-electrolyte-interface (SEI) which...
is essential to the stable operation of any commercial lithium ion battery anode.

Confining the SEI allowed to measure its thickness in-situ during growth as a function of the polarization time. At the same time the typical shape of the force versus distance characteristic during compression allowed to understand the mechanical properties of the formed SEI.

This is an experimental insight that is not accessible to other techniques such as AFM force probing, which lacks the absolute distance control. As such, with SFA it is possible to monitor dynamic reactions and interaction forces during polarization of a nano-meter confined electrochemical interface. Similarly, SFA was uniquely used for detecting surface changes during corrosive degradation in confined gaps.27

FIG. 3. Static force versus distance characteristic in an ionic liquid during application of four different electrochemical potentials, respectively. An unexpected long-range component was reported for these systems for the first time (reprinted with permission from the National Acedemy of Sciences of the U.S.A.16). b) Interference (= 445 nm, (a) and (b)) and fluorescence emission (= 525 nm, (c) and (d)) images electrolyte layering in a nano-meter confined gap (concentrations indicated). The dotted lines characterize the D = 030 nm region. (e) Schematic of the experiment and (f) scaling of the measured apparent Debye length with the solution concentration (reprinted with permission from the American Chemical Society12).

c. Unexpected electric double layer forces in highly concentrated solutions. Figure 3a shows the first force versus distance characteristic recorded in an EC-SFA across a neat ionic liquid as a function of the applied potential. In this study Gebbie et. al16 used the electrochemical SFA to measure forces evolving in such systems at nanometer distances. As can be seen, the structuring of the ionic liquid indicates confined, strongly ordered and adsorbed ion layers of 2 nm thickness at -500 mV, and thinner and less stable (lower repulsion) layering structures at +500 mV. Around the potential of zero charge the force profile indicates limited ion structuring between
the surfaces.

This was not unexpected and confirms potential dependent confinement of potential dependent cation/anions structures. Yet, the clearly visible long-range component of the force profile, i.e. the attraction starting at about 30 nm, was not expected at all, and it was not observed in similar measurements in previous studies. Based on expectations and previous results (see e.g. figure 1d, ionic liquids were considered to behave as highly concentrated solutions, with screening of the surface charge occurring in the inner electric double layer. I.e. the strongly structured ion layering was expected to screen any surface charge within a few nanometers of the interface. In his initial work Gebbie et. al\textsuperscript{16} interpreted this result as a low concentration of free ions in a matrix of an essentially neutral ion liquid bulk (defect model). This unexpected finding triggered controversial discussions, and many systems were remeasured and/or reanalyzed to confirm these long range forces.\textsuperscript{15} In subsequent work, other researchers also found this long range effects in other highly concentrated solutions such as $>$1 molar aqueous electrolytes,\textsuperscript{3,37,39} Several competing models emerged, explaining this long-range component, based on the Bjerrum length, charge-correlations or defect models in analogy to semi-conductors which are now tested rigorously.

Until recently, the only evidence for long range electric double layer effects in highly concentrated solutions originated from force probe experiments. Ducker et. al\textsuperscript{12} developed an interesting complementary approach to evaluate the ion concentration into a crack tip. As shown in figure 3b they utilized a fluorescent dye as electrolyte and measured its intensity into a crack. At the same time the crack thickness was evaluated using reflection interference pattern. In this work, the apparent Debye length in concentrated electrolytes was found to scale with the inverse concentration, which is qualitatively in line with models and force measurements. Yet, no quantitative agreement could be reached, remaining subject to further research and discussion.\textsuperscript{12}

What is interesting in a broader perspective is, that SFA is capable to precisely detect a weak (and in this case unexpected) long-range force during overlap of electric double layers in confinement. Yet this force was completely missed e.g. in AFM measurements of neat ionic liquids. The reason for this is again related to the contact geometry and general setup of an SFA experiment. The SFA generates a considerably larger contact areas in the 100-1000 $\mu$m range, hence in terms of area or radius normalized forces the SFA is considerably more sensitive compared to an AFM. Only in colloidal probe experiments, where the force/area is equally sensitive compared to SFA, AFM results were able to also detect these weak electric double layer forces in neat ionic liquids,\textsuperscript{15} and recently also highly concentrated multivalent electrolytes.\textsuperscript{39} This comes as no surprise, but it
highlights the necessary appreciation of the complementary nature of these two techniques; in particular when studying surfaces with low surface charge often found in biologic systems (e.g. amphoteric surfaces), or when studying highly concentrated electrolytes.

B. Ion and surface dynamics during dynamic electrochemical polarization of micro-to-nanometer confined gaps

So far we have seen that SFA provides an absolute distance measurement and superior force sensitivity for small integral forces, and it provides direct insight into molecular layering at confined interfaces during static conditions. With these specifications it is possible to design and perform unique dynamic polarization experiments to reveal ion dynamics in micro-to-nanometer confined gaps, that are impossible to achieve with other techniques.

a. Electrochemical polarization at constant separation - nanometer scale effects

Figure 4a shows the recorded absolute distance change as a function of time during the potentiostatic oxidation of molecularly smooth platinum surface in 50 mM sulfuric acid. Upon stepping the potential from 400 mV to 1400 mV a significant attractive force moves the surfaces closer by up to 6.5 nm during the first 4 seconds. Afterwards the distance change levels at 3 Å. These 3 Å correlate with the thickness of a monolayer of platinum, that was consumed during oxidation of the surface. Again, SFA proves to be sensitive to electrochemical surface reactions at the monolayer level.

The more surprising result of this study was the initial transient force response after the oxidation. These time dependent forces were related to the ion migration/diffusion out of the confined contact zone. Specifically, during oxidation of platinum protons are generated, resulting in an unbalanced electric double layer at the platinum surface and the counter electrode in the experiment. Ion migration and diffusion must equilibrate this charge imbalance of the EDL.

The measured displacement increased significantly with decreasing surface separations down to about 30 nm. It is interesting to realize that this suggests that unbalanced electric double layers generate significant transient forces that are comparable with van der Waals and equilibrated electric double layer forces. This may have important implications for electrocatalyst stabilities and corrosion processes in confined spaces in general. Spontaneous release of charge can generate potentially degrading forces, and fields at unbalanced EDL interfaces may enhance dissolution reactions. At the same time this result suggested that it is possible to quantitatively analyze the observed ion migration/diffusion in confined gaps in-situ with the EC-SFA.
FIG. 4. Electrochemical SFA force probe experiments at constant separation during dynamic change of the surface potential. In a) a platinum surface was oxidized, resulting in the formation of an oxide and the release of protons. The release of protons and subsequent charge regulation at the interface dominates the initial response ($\Delta D_{ERF}$). Simultaneously the nanometer scale surface oxidation ($\Delta D_M$ can be tracked (reprinted with permission from the American Chemical Society\textsuperscript{36}). In b) this concept was extended to quantitatively analyze and simulate ion migration into a charging nanopore with dimensions of $D > 30$nm (reprinted with permission from NPG\textsuperscript{42}).

In this direction Tivony et. al\textsuperscript{42} utilized the same constant separation approach to measure the charging of a similar nanoslit during stepping the potential in the EDL charging regime. Figure 4b shows the transient distance change during potentiostatic polarization between -200 mV and +200 mV at surface separations from between some 100 nm and 30 nm.

Here, no reaction occurs and simple EDL charging was studied. Specifically, during negative polarization cations are driven into the gap in this polarization window, charging the EDL. And during positive polarization cations are driven out of the confined gap. This study found that the nanoslit charging time is on the order of seconds, which is far slower than the time for charging a non-confined surface. The time for charging increases at smaller gap sizes, and it decreases with the ion concentration.

This study was further able to provide a quantitative comparison of the observed transient force with the transmission line model, that explains pore charging. Fitted charging times were within the order of magnitude comparable to classical transmission line calculations. These two pioneering studies showcase how SFA can be utilized to generate stable nanometer confinement for evaluation of dynamic processes such as pore charging and reactivity in confinement.
b. **Electrochemical polarization at constant separation - micrometer ranged effects.** Interestingly, transient force responses are not limited to nano-pore charging experiments and potentiostatic experiments. Recently, Perez-Martinez et al.\textsuperscript{32} demonstrated that AC variations across a micrometer thick gap of an ionic liquid can generate a distance independent force response with extremely slow equilibrium times of up to 1000 seconds. Figure 5a shows attractive and repulsive force responses as a function of time caused by an alternating electric field at frequencies above the characteristic charging time of an EDL. How this result relates to the "unexpectedly" long electrostatic decay length and bulk characteristics of ionic liquids is an interesting and open question.

![Fig. 5](image-url)

**FIG. 5.** F from micrometer to sub-nanometer pores. a) Measured force between mica surfaces across [C$_2$C$_1$Im][NTf$_2$] as a function of time during switching on/off an electric field across the fluid. Data indicates a very slow $10^3$ s evolution towards a (1) repulsive or (2) attractive steady state in an AC field (reprinted with permission from RSC\textsuperscript{32}.) b) MD simulation of charging dynamics in sub-nanometer pores. The schematic shows a typical snapshot of the simulated systems featuring a 5.3 Å pore connected to an ionic liquid reservoir. The simulation result illustrates the typical charging time of an ionophobic and an ionophilic pore, illustrating that wall/ion interactions can drastically accelerate charging dynamics (reprinted with permission from NPG\textsuperscript{21}).
IV. APPROACHING THE LIMITS - REAL-TIME VISUALIZATION OF ION MIGRATION IN SUB-NANOMETER CONFINED SPACES

So far we have seen charging dynamics and charging effects at surface separation in the tens of nanometer-to-micrometer range. The ultimate limit of a pore charging experiment will be to approach dimensions that are accessible to MD simulations, where pores of about 1 nm, or less, can be simulated easily.\textsuperscript{21} Figure 5 shows the result of an MD study by Konrat et al.\textsuperscript{21} A nanopore with 0.53 nm height, shown in the inset, was simulated in an MD experiment. Tuning of the wall/ion interactions allowed to make the charging pores ionophilic or ionophobic. As can be seen in the figure, results indicate a considerably increased charging dynamic of ionophobic pores, suggesting new routes for materials engineering.

In this direction a number of experimental efforts indicate the feasibility of the SFA approach to also study and detect ion dynamics in such sub-nanometer pores.

FIG. 6. Probing dynamic processes in nanometer and sub-nanometer confined spaces with the SFA. a) An initially only 0-2 Å thick sub-nanometer sized pore filed with water was monitored during ion diffusion (NaCl and added 30 mM CaCl\textsubscript{2}) into , resulting in a swelling to 8 Å and 13Å nanopore, respectively (reprinted with permission of Elsevier\textsuperscript{2}). b) shows the (1) initial dehydration of a single water layer confined between two hydrophilic mica surfaces, followed by the (2) wetting and separation of the gap to 12 Å (reprinted with permission from NPG\textsuperscript{29}).

Figure 6 shows a set of experiments that approached ion dynamics in nanometer-to-subnanometer confinement in an SFA. Figure 6a shows a study by Anzalone et. al\textsuperscript{2}, where Na\textsuperscript{+} and Ca\textsuperscript{2+} diffusion into a sub-nanometer sized pore was studied. Transient EDL swelling upon exchanging water in the confined initial gap was recorded. Ion exchange time scales were found to be in the range

\begin{align*}
\text{FIG. 6. Probing dynamic processes in nanometer and sub-nanometer confined spaces with the SFA. a) An initially only 0-2 Å thick sub-nanometer sized pore filed with water was monitored during ion diffusion (NaCl and added 30 mM CaCl}_2) \text{ into, resulting in a swelling to 8 Å and 13Å nanopore, respectively (reprinted with permission of Elsevier\textsuperscript{2}). b) shows the (1) initial dehydration of a single water layer confined between two hydrophilic mica surfaces, followed by the (2) wetting and separation of the gap to 12 Å (reprinted with permission from NPG\textsuperscript{29}).}
\end{align*}
of 20-100 seconds, indicative of slow ion diffusion rates in such small gaps.

Figure 6b shows an initial dehydration of a monolayer of adsorbed water out of a contact formed between two mica surfaces. In this study by Moremans et. al\textsuperscript{29} dehydration was initiated by surrounding the contact with hygroscopic battery fluid. The first step (1) characterizes water diffusion out of the confined zone (2-3 Å confinement) and indicates dehydration time scale on the order of 20-30 seconds. The second step, (2) the rehydration of the dry interface by battery fluid occurs within a shorter time scale of 5-10 seconds for a graphene interface, while the gap does not wet with battery fluid for gold and mica surfaces. This is in line with the observations of the mentioned theoretical study,\textsuperscript{21} indicating that the wall/solute and wall/ion interactions are controlling the wetting process.

V. CONCLUSIONS AND PERSPECTIVES

Force probe experiments in an SFA evolved as a powerful tool for exploring ion structures, ion mobility as well as forces in a range of systems. We feel that these exciting developments, with new analysis and measurement approaches and protocols at hand, is starting a new era for probing confinement effects in electrochemical systems with EC-SFA.

The close approach of experimental probe and simulation dimensions (at least for the confinement height), will stimulate new synergistic research that aims at understanding ions and solvent dynamics in extremely confined spaces. With new surface designs it seems to become possible to generate nanometer and sub-nanometer confinements with tailored chemistry to study ionophobic/ionophilic gaps during dynamic charging.

A field were we see enormous room for further improvement is the coupling of the SFA technique with complementary methods such as fluorescence microscopy,\textsuperscript{22} X-ray scattering and reflectivity measurements,\textsuperscript{48} as well as vibration spectroscopies.\textsuperscript{22}

In this direction the results of Ducker et. al\textsuperscript{12} are exciting. It is possible to simultaneously extract complementary information from fluorescence and distance probes, this combined approach has yet to emerge in a productive SFA setup. First efforts are promising delivering proofs-of-principle,\textsuperscript{22} and we expect interesting results, in particular also in the bio direction, in the near future. With the emerging opportunity to combine force and fluorescence probe experiments it seems just a technicality to build a combined confinement SFA/high resolution microscopy setup for studying diffusion processes in confined spaces at the molecular scale.
Further, various approaches for delivering an X-SFA and *in-situ* combinations with neutron scattering methods have emerged over the last decades. This combined setup is extremely challenging, yet we expect more than just proofs-of principle in this direction. For instance, we could recently test a setup based on a flat-on-cylinder geometry to simultaneously measure scattering and X-ray reflectivity. Initial results are very promising, and open complementary paths to study pore charging mechanism.\textsuperscript{48}

Finally, the SFA community will need to deal with active feedback regulations in SFA. So far, constant distance experiments rely on very excellent temperature stabilisation, to limit any thermal drift on the time scale of the experiments. An active distance and force feedback regulations has not yet been build into an SFA setup.

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**COMPETING FINANCIAL INTERESTS**

The authors declare that there are no competing financial interests.

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*The authors measure and discuss interfacial forces evolving in a reactive system, with relevance to geochemistry.


**This reference provides an exciting path into complementing force probe techniques with fluorescence markers. It is noteworthy that this work is able to construct a Debye screening length based on measuring the fluorescence signal into a crack. This may find numerous applications complementing the SFA technique.


**In this work the authors discuss operating and analysis principle along with recent theoretical and technical advances of the SFA technique.

In this reference the authors developed the constant separation approach to uncover reactivity and ion mobility in nano-confined gaps during electrochemical polarization.


In this paper the authors use the constant separation approach to quantitatively fit ion mobility in a charging nanopore. The authors compare to the classic transmission line model and find nano-pore charging times that correlate to within the order of magnitude, laying the ground for further theoretical analysis of such experiments.


The authors developed and tested a rigorous charge regulation model during approach of electric double layers, that should find broad application in the field.


*The authors show how metal/metal contact can be realized in an SFA setup, and they demonstrate that this data can be analyzed accordingly. This will open up new possibilities for SFA.*


*In this work X-ray combinations with the SFA technique are reviewed and recent success with a novel X-SFA is discussed. A successful combination of SFA confinement and structural probes was achieved.*