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Measuring surface charge: Why experimental characterization and molecular modeling should be coupled

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Surface charge controls many static and dynamic properties of soft matter and micro/nanofluidic systems, but its unambiguous measurement forms a challenge. Standard characterization methods typically probe an effective surface charge, which provides limited insight into the distribution and dynamics of charge across the interface, and which cannot predict consistently all surface-charge-governed properties. New experimental approaches provide local information on both structure and transport, but models are typically required to interpret raw data. Conversely, molecular dynamics simulations have helped showing the limits of standard models and developing more accurate ones, but their reliability is limited by the empirical interaction potentials they are usually based on. This review highlights recent developments and limitations in both experimental and computational research focusing on the liquid-solid interface. Based on recent studies, we make the case that coupling of experiments and simulations is pivotal to mitigate methodological shortcomings and address open problems pertaining to charged interfaces.

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Introduction

When a solid surface meets an aqueous electrolyte, physical or chemical mechanisms can generate an electric surface charge [1−4]. Ions in the liquid reorganize to form a nanometric layer to balance the surface charge, the electrical double layer (EDL). Surface charge governs the stability and dynamics of soft matter systems, and as such it is a key property to characterize. Surface charge also drives the response of nanofluidic systems to thermodynamic gradients [5]. The development of new membranes to harvest e.g. blue energy (the osmotic energy of sea water) [6−8] has led to a renewed interest for finding new functional interfaces with optimal surface charge.

In that context, however, it is not clear that all interfacial properties governed by surface charge can be described with a single, well-defined quantity. For instance, equilibrium

interactions between colloids depend on the static distribution of ions in the EDL, but their electrophoretic motion also depends on interfacial hydrodynamics [9•,10••]. Similarly, different types of osmotic flows [5] and surface conductivity [11] might be controlled by a differently defined surface charge. Consequently, the results of standard characterization methods might not be easily used to simultaneously predict all properties governed by surface charge.

In this short review, we will first discuss the difficulty in defining surface charge. We will then give a brief overview of standard models and experimental tools (detailed descriptions can be found in textbooks or reviews, e.g. [1–4]), and discuss their limits. Next, we will give an overview of recent developments in experimental characterization, and show how progress in molecular modeling has transformed our understanding of the EDL. Finally, we will discuss benefits of coupling state-of-the-art experimental tools with molecular modeling to obtain a comprehensive picture of the interfacial structure and dynamics, necessary to accurately predict all surface-charge-related properties of liquid-solid interfaces. A complementary point of view can be found in a recent review focused on water at interfaces [12•].

Surface charge: an ill-defined concept

The concept of surface charge cannot be defined without ambiguity because liquid-solid interfaces are globally uncharged, with any surface charge being compensated by an oppositely charged EDL. It is therefore a question of separating charges between the surface and the liquid. However, both the charged species at the surface and those in the EDL can have complex structure and dynamics. For instance, interfacial charged species can be strongly bound to the solid, or free to diffuse along the surface [13]. Furthermore, ions in the EDL can have a reduced mobility, or belong to a hydrodynamic stagnant layer.

From this complex atomistic picture, different effective surface charges can be defined and measured, which quantify different physical phenomena at a larger scale. First, interactions between solid surfaces in solution result from the long-range distribution of ions between the surfaces. This can be used to define a static surface charge, which will for instance control the stability of colloidal systems. One can also define dynamic surface charges. In particular, the electroosmotic mobility can be used to define an electrokinetic charge [9•,10••]. However, it is not clear that the same electrokinetic charge can also describe other osmotic flows, e.g., diffusioosmosis and thermoosmosis. Finally, surface conductivity [11] can be used to define yet another surface charge.

Therefore, a suitable characterization method has to measure the relevant effective surface charge corresponding to a given phenomenon, or to provide a detailed enough description of the interface, which can be used to evaluate the adequate effective surface charge. In the second case, an accurate model of the interface is also needed. The discrepancy between surface charge measurements, and the

use of macroscopic theories – which are not a priori justified at the nanometer scale – to interpret them, underline the needs of coupling experimental measurements to molecular modeling in order to take proper account of the concept of surface charge. In the following section, we will review the standard models of the EDL, the standard characterization tools based on these models, and highlight their limits.

Standard approaches

Standard models

A comprehensive model of a charged interface in an aqueous electrolyte (but even pure water is one) needs to describe the distribution of charge, the dynamics of charged species, and interfacial hydrodynamics (see Fig. 1).

For the charge distribution, models generally separate the EDL into two regions. Beyond a few molecular sizes of the solid surface, ions can be considered as point charges and one commonly uses the mean-field Poisson-Boltzmann (PB) equation to describe their distribution, assuming that the dielectric permittivity of the solvent is local, isotropic and homogeneous [1]. This equation predicts that the electric potential and the local charge density decrease exponentially with the distance from the charged interface. The decay range is given by the Debye length λ_D, which scales as the inverse square root of the salt concentration (Fig. 1). The PB equation also predicts that the charge of the EDL can concentrate in a region thinner than the Debye length with a non-exponential decay. Specifically, this happens when the so-called Gouy-Chapman length ℓ_{GC}, which scales as the inverse of the surface charge, becomes smaller than λ_D. The charge of the EDL then concentrates in a region of thickness ℓ_{GC} (Fig. 1).

Very close to the surface (a few molecular sizes), the hypotheses underlying the PB equation are especially poorly justified. One generally introduces the so-called Stern layer to describe this region [14,15]. The Stern layer is usually assumed to consist of adsorbed ions – specifically or not, which may be partially or fully dehydrated. A number of planes and layers are defined accordingly, e.g., the inner Helmholtz plane (IHP), below which ions are specifically adsorbed and at least partially dehydrated, and the outer Helmholtz plane (OHP) separating the adsorbed hydrated ions and the diffuse layer obeying the PB equation (Fig. 1). It has also been recognized that the dielectric permittivity of the solvent below the IHP can deviate from that beyond the IHP, due to a preferred orientation of solvent molecules in response to surface charge [16]. Finally, theoretical models beyond the standard PB framework have been developed to account explicitly for, e.g., correlations, image charges, finite-ion-size effects, or specific adsorption in the Stern layer [1,2].

For hydrodynamics, a local and homogeneous viscosity is usually assumed, together with a no-slip boundary condition. A stagnant layer is often introduced, defining the shear plane where the hydrodynamic velocity vanishes (Fig. 1). While the stagnant layer does not participate to the flow, whether its diffusion dynamics is bulk-like, hindered or even
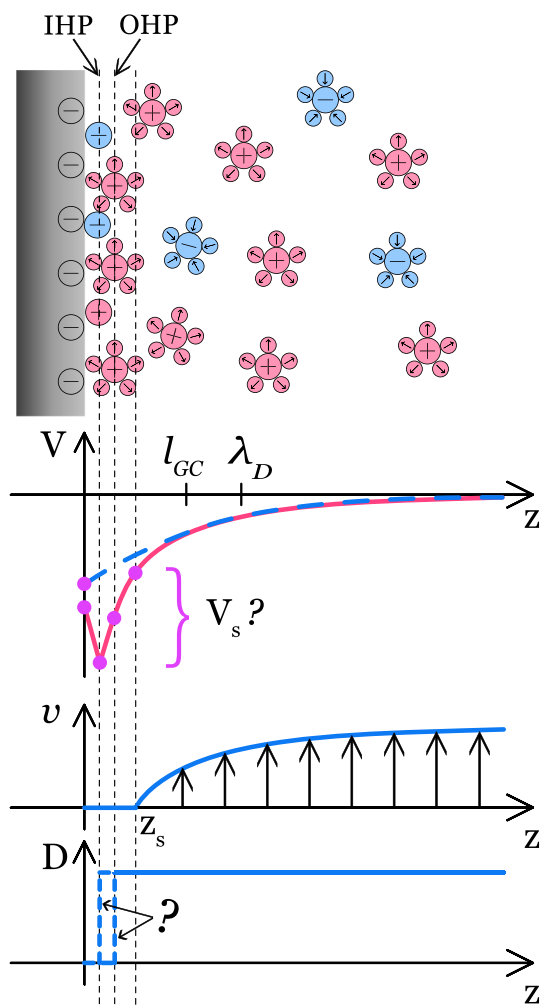
Fig. 1 Standard model of the electrical double layer. From top to bottom: ion distribution; electric potential profile V (full red line: true potential; dashed blue line: apparent exponential potential as seen far from the interface); velocity profile v; ion diffusion coefficient profile D. Even from this traditional description, a number of surface potentials V_s (represented by magenta points) and corresponding surface charges can be defined, see text for details.

frozen remains unclear and may depend on the specifics of the interface. The hydrodynamic shear plane position z_s is not simply related to the "static" IHP and OHP. However, z_s is commonly confused with the IHP or OHP, i.e., the stagnant layer and the Stern layer are assumed to share the same boundaries.

Finally, regarding ion mobility, standard models assume bulk-like diffusion for ions in the diffuse layer [11,17], and immobile ions in the Stern layer, although a dynamic Stern layer is sometimes introduced to explain anomalies in surface conductivity [18–21].

Standard models provide an effective description of the interface, introducing a limited number of adjustable parameters with a simple physical interpretation. These models

can relate macroscopic experimental measurements to microscopic parameters such as surface potential or shear plane position. They can also be adjusted or extended to consistently describe different effective surface charges, for instance the electrokinetic charge or the surface conductivity. However, being fundamentally effective models, which are not based on an atomistic description of the interface, they cannot be expected to provide a comprehensive and consistent prediction of all the different effective surface charges.

Standard experimental tools

On standard basis, different methods are used to characterize surface charge. Some are based on transport properties (Fig. 2a–b), and in particular electrokinetic characterization of colloids, porous materials or surfaces. Others rely on probing static properties of the interface, such as electrostatic potentials (Fig. 2d).

Transport measurements

Electrokinetic methods have been widely used to investigate the mobile part of electrolyte solutions at the interface with suspended colloids or in micro/nanochannels. For example, the electrophoretic mobility is measured, from which an electrokinetic potential, or ζ-potential, is inferred [9•]. Alternatively, an electroosmotic plug flow in micro/nanochannels can be determined, using for example the all-electric current monitoring method [22] or some fluorescent probe [23]. According to Onsager reciprocal relations, the ζ-potential can also be determined from the streaming current [24••].

Within the standard description of the EDL, the ζ-potential can be identified with the value of the electric potential at the shear plane, separating the stagnant layer from the flowing liquid [9•], see Fig. 1. This electrostatic potential can in turn be related to the electrokinetic surface charge, i.e., the total charge contained behind the shear plane, thanks to the Grahame equation [15]. This equation is based on the mean-field PB description of the diffuse EDL, so that it relies on the assumptions that the shear plane is located outside the Stern layer and that the dielectric permittivity does not vary beyond the shear plane.

Another method is to probe the conductivity in porous materials or nanopores at low salt concentration [3,25,26]. In this regime, a so-called surface conductivity is measured, which is a signature of the electrostatic environment in the vicinity of the surfaces. However, surface conductivity also depends on ion mobility close to the surface, and can include contributions from the solid or from quantum charge transport at the interface, so that its relation to the bare surface charge is complex.

Generally, electrokinetic experiments provide no direct insight into the bare surface properties of a colloid or channel wall, to which ions are adsorbed. Moreover, despite the good match between results obtained from streaming current or electroosmosis experiments, a discrepancy with the surface charge obtained from surface conductivity

remains [20,27–29], underlining the complexity of the systems when transport properties are considered.

Static measurements

Static measurements typically either measure the electrostatic surface potential, or the number of ionized groups at the surface, to determine the surface charge.

Surface potential measurements have been expended in the 1990s by measuring the forces involved between a sphere and a plane using AFM/SFA-like tools [30–34], see Fig. 2d.

The static surface charge can be measured in various ways. For example, potentiometric titration is commonly used to probe the bare charge of a solid surface [35]. Other seminal techniques involve specific adsorption of organic conjugated compounds onto the charged surface, which is titrated using UV−Vis spectroscopy [36]. Similarly, neutron reflectivity is a powerful tool to determine non-selectively species adsorption [37] or water structure [38] at interfaces.

Attempts to probe both electrokinetic transport properties and static properties for the same sample remain scarce due to the technical constraints of the different measurements [39•]. For colloids, the relation between static charge (obtained by titration) and electrokinetic charge depends on the nature of the surface charge [40]: while electrokinetic and static potentials are consistent for AgI, for which the charge results from an excess of the ionically bonded constituents, the electrokinetic potential is lower than the static potential for metal oxides, for which the charge arises from the dissociation of hydroxyl groups.

Latest innovations in experimental characterization

Recent innovations in determining the structure of liquid-solid interfaces focused on probing the chemical nature
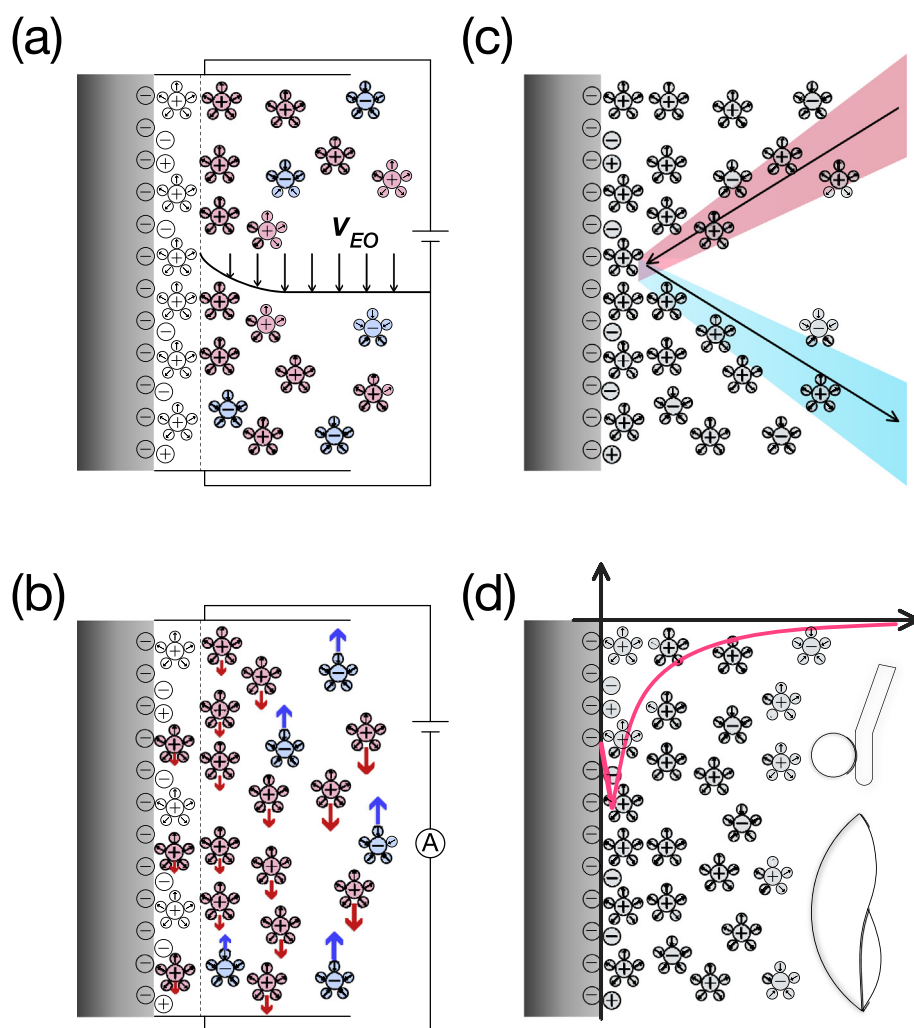

Fig. 2   Different experimental tools: (a) electrokinetic transport; (b) surface conductivity; (c) X-ray reflectivity or nonlinear optics; (d) AFM/SFA-like tools. Methods illustrated in (a) and (b) only provide information on ions highlighted in color, while methods illustrated in (c) and (d) are non-specific.

and position of ions in the vicinity of the interface [41], see Fig. 2c. Among them, specific set-ups based on X-ray reflectivity represent a powerful tool to investigate the interfacial ion distribution, for example in the case of electrolytes in the vicinity of electrodes [42].

Thermodynamic adsorption energies have been measured using resonant anomalous X-ray reflectivity [43,44•], and specific adsorption of chloride versus iodide near hydrophilic surfaces has been observed with X-ray standing waves [45•]. A more sophisticated method based on X-ray photoelectron spectroscopy applied to a microjet containing silica nanoparticles was used to determine precisely the influence of ion specificity on the surface potential and on the Stern layer composition [46••]. This method has also been compared to other, more standard, surface potential determination [47]. However, most of the experimental results in the above-mentioned studies require support of modeling (density functional theory [43,44•], molecular dynamics [45•], analytical [46••]) to get a full picture of the processes taking place at the interface. Moreover, X-ray based techniques are limited because they can only identify the chemical nature of the ion and not its ionization state and electrostatic environment. For instance, these techniques are blind to hydroxide and hydronium ions, which have a strong impact on the structure and dynamics of charged interfaces.

The electrostatic potential of interfaces has also been probed using nonlinear optics, sum frequency generation (SFG) [48–50] — evidencing a cationic specific Stern layer structure — and second harmonic generation (SHG) [51]. Furthermore, surface potential measurements in recent ion-sensitive field-effect transistor (ISFET) studies have provided new insight into the effect of pH and salinity of various electrolytes on the EDL structure and found that standard complexation models cannot explain the observed behavior [52–54]. Here also, molecular simulations have been used to interpret the results [55,56].

More direct probing techniques have also been used to gain insight into the interfacial fluid structure. Following huge improvement of AFM resolution, it became possible to probe the structure of the interface [57•,58,59], and even the residence time of single ions in the Stern layer [60•,61].

Radically different approaches also focused on the determination of ion repartition at interfaces using transport property characterization. Beyond standard electrokinetic characterization, new electrokinetic properties have been investigated, and in particular the diffusiophoretic [62,63] and diffusioosmotic [6,64] response to ion concentration gradients in solution. Whereas the ζ-potential measured from diffusioosmotic and electroosmotic velocities coincide for KI, LiI and NaI salts in the vicinity of a silica interface [64], discrepancies are observed when considering the diffusioosmotic current of a KCl solution flowing through a membrane formed by boron nitride nanotubes [6]. In the latter, the surface potential is in good agreement with the one measured by surface conductivity, rather than the one calculated from electrokinetic mobility. A similar discrepancy between the ζ-potential and the thermophoretic mobility was recently highlighted for functionalized polystyrene particles [65].

To disentangle the couplings between static and transport properties of interfacial ions, a few attempts to measure both the electrokinetic response of the interface together with its structure have been documented [66]. For example, Jalil and Pyell [67] combined their own standard electrokinetic measurements with X-ray spectrometry data of Brown et al. [46••] to get a more refined picture of the EDL for monovalent electrolyte solutions in contact with silica nanoparticles. In a more direct approach, in situ SFG experiments at liquid-solid interfaces under flow have shown a signature of the flow on the surface potential [68••]. Conversely, SHG experiments performed at liquid-gas interfaces evidenced no modification of the signal when electroosmotic flow was generated [69]. Recent experiments coupling SHG and streaming potential at hydrophilic and hydrophobic solid-liquid interfaces also did not observe any effect of the flow [70]. These contradicting observations underline the complexity of the mechanisms involved and indicate that the relation between the EDL structure and dynamics depends on the chemical nature of the interface.

Latest developments in molecular modeling

Whereas state-of-the-art experiments revealed new information on the structure and dynamics of the EDL, molecular simulations have highlighted the limits of standard models [71–78], and can help refining models using a bottom-up approach. Molecular dynamics (MD) simulation is a particularly powerful tool to explore the structure and dynamics of the EDL. MD provides an explicit description of the atomic structure of the liquid-solid interface, with its time evolution computed based on empirical interaction potentials between atoms. MD simulations provide accurate control over environmental conditions and full access to microscopic information that is inaccessible in experiments. As such, simulations can be used to explain experimental observations, or to improve models and assumptions for interpreting experimental measurements [79].

Indeed, the suitability of standard models becomes questionable when screening lengths compare with the molecular size, as well as typical values for surface roughness. In fact, both the Debye length and the Gouy-Chapman length can easily reach 1 nm for realistic salt concentrations ($>10^{-2}$ M) or surface charges (>40 mC/m^2). In that situation, standard models can fail to describe the EDL in many ways and a more sophisticated description is needed.

First, it is possible that the ion distribution does not follow the mean-field Boltzmann law, especially when only electrostatic interactions are taken into account. Here, MD can provide information on specific interactions that need to be included in the Boltzmann factor [80–82••,83–85•,86–89]. Furthermore, ion-ion correlations, which are particularly important with multivalent species and concentrated solutions, can strongly affect the ion distribution, and even reverse the apparent surface charge as seen far from the interface [90]. Also here, MD can help to refine the existing models [91–94•].

More importantly, the dielectric permittivity of the solvent can become inhomogeneous and anisotropic near the interface, or the local permittivity approximation can break down [89,95–97••,98–100]. Extended theories need to be used in those cases, although it has been shown that simple effective models, with just a step in permittivity at a given distance from the wall, can reproduce static and electrokinetic charges obtained by molecular simulations (which make no assumption on the dielectric permittivity) [97••]. Whether such simple models can also predict the surface response to other thermodynamic gradients (e.g. osmotic or thermal) remains to be explored.

The standard picture for hydrodynamics, with a stagnant layer followed by a liquid with constant viscosity, has also been questioned by MD simulations at the nanoscale [101•,102]. First, the no-slip boundary condition fails on some surfaces [103]. The electrokinetic mobility is then amplified by hydrodynamic slip for a given surface charge [104,105•,106]. In turn, the amplitude of slip depends on surface charge [83,107–109]. Corrected continuum descriptions [110,111] describe MD results well [105•,107], and the amplification effect of slip was confirmed by two independent experiments [39•,112]. Hydrodynamic slip is for instance key to understanding anomalous electrokinetic charge in foam films [113,114]. Other osmotic flows can be strongly affected by slip [115–117], and more generally by nanoscale dynamics [118].

Second, the stagnant layer concept has been questioned by MD results. For instance, no stagnant layer was observed on amorphous silica [94•], beyond a monolayer of strongly adsorbed water molecules, whose thickness was comparable to the roughness of the disordered surface. Zhang et al. [119] also did not observe a stagnant layer on silica, but instead they showed that viscosity increased smoothly near the surface. Smoothly increasing viscosity profiles were also observed by others near hydrophilic surfaces [87,97••,120••], but not near hydrophobic surfaces [97••]. More generally, various simulation studies have indicated that viscosity can be inhomogeneous [87,120••,121,122•,123] and even nonlocal [124]. Continuum theory taking the viscosity profile into account can predict electroosmotic flow rates [119]. The complex viscosity profiles can also be described through effective sharp boundary models, for instance by a constant viscosity combined with a few angstroms thick stagnant layer on silica [119], by a constant viscosity on slipping surfaces, or by the inclusion of a step in viscosity on non-slipping surfaces [97••]. Although such simple descriptions can be convenient, their parametrization hinges on detailed insight into the interfacial region. Moreover, because these effective descriptions do not correspond to the real microscopic picture, their transferability to describe all surface-charge-governed properties is not guaranteed.

MD simulations have also given new insight into the diffusion dynamics of ions in the different subsections of the EDL [125]. In their pioneering work, Lyklema et al. [126] used MD to confirm the emerging picture of a stagnant layer behaving like a gel, in which the ions can diffuse almost freely, but which does not flow globally. This picture explains the large possible differences between the surface charge one can extract from electrokinetic or surface conductivity measurements [20,27–29]. Recent MD simulations on amorphous silica [94•] found that the standard decomposition of the EDL into a Stern and a diffuse layer was inadequate. The EDL was instead decomposed into a mobile and an immobile ion population, of which the distribution overlaps. The diffusion coefficient of free ions continuously decreases close to the wall, an effect that can be described by continuum hydrodynamics [127], and can dramatically affect surface conductivity. Finally, on hydrophobic surfaces where the surface charge is carried by specifically adsorbed ions, the surface mobility of these ions can affect the electrokinetic response of the interface [13].

Even though simulations have proven valuable in the study of EDL properties, classical MD simulations are reaching their limits, because of two strong weaknesses. First, interactions between atoms are based on empirical force fields. By definition, these force fields are built to reproduce a given set of data, and their transferability to different situations is questionable. Specifically, most standard force fields are designed to reproduce equilibrium structural properties of bulk systems, and there is no guarantee that they can correctly describe the dynamical and transport properties of interfaces. A striking example concerns the effect that ions have on water diffusion and viscosity [128]. While some salts enhance water diffusion, most empirical force fields predict a systematic decrease in diffusion with increasing ion concentration [129,130••]. However, recently developed force fields have been able to qualitatively reproduce the effect of large ions [131], and to quantitatively describe the effect of small ions [132–134] on water diffusion.

The second major weakness of force field-based simulations is related to the systems described. Indeed, the atomic wall structure and charge distribution need to be constructed before the simulation can be run, often from limited information. Notably, the surface charge is usually imposed by assigning partial charges to the atoms in the substrate, conform the force field employed. These partial charges are kept constant throughout a classical simulation − rendering the bare surface charge unaffected by the rearrangement of interfacial ions or solvent molecules.

Alternatively, surface reactivity is considered by using reactive force fields [135–138] and ab initio methods [139•,140,141]. Such reactive simulations are important to investigate, for example, charge regulation [142,143], which occurs in narrow channels due to overlapping EDLs.

Ab initio molecular dynamics (AIMD) has been used to explore the structure and dynamics of water-oxide interfaces [144–159]. In particular, AIMD can be used to compute vibrational spectra and non-linear optical response [147,160–164•], and as such is a key tool to help interpret experimental observations. Recently, liquid-solid friction has been characterized with AIMD [165•,166], opening perspectives for the investigation of other transport properties with these methods.

At present, however, ab initio methods are typically based on density functional theory, and take electronic exchange and correlations into account through an approximate functional.

This limits the accuracy of ab initio methods to describe the structure and dynamics of water-solid interfaces [139•]. Most AIMD works also do not take quantum nuclear effects into account. Finally, the computational cost of reactive and ab initio simulations is very large − effectively limiting the accessible simulation time and the number of atoms. These restrictions are currently prohibitive for studying rare events, dilute electrolytes, or for simulating a sufficiently large system to accurately represent the structure and heterogeneous charge distribution of amorphous surfaces.

Size restrictions can be mitigated drastically with primitive-model simulations, in which the solvent is included implicitly [167]. For instance, such an approach was used to investigate the origin of surface charge on graphene and boron nitride [168•]. However, Lee et al. [169] found that various physical quantities that depend on the orientation of solvent molecules were not accurately predicted by the primitive model approach. Additionally, Vangara et al. [170] recently showed, by comparing explicit and implicit solvent DFT models, that both the solvent and the ions contribute to the chemical balance between surface groups and the solution.

Apart from the importance of solvent molecules and dissolved salts, various experiments have revealed intricate effects of pH on for example specific ion adsorption [171,172]. Furthermore, local enhancement of proton mobility affects the Stern conductivity [173], but may also have important consequences for surface reactivity. Simulations are, in principle, suitable for elucidating the molecular-level mechanisms responsible for such pH dependence, but current computing power does not permit explicitly accounting for near-neutral pH in molecular simulation because of the immense system size required. Interestingly, this numerical difficulty echoes the limits of experimental methods based on X-rays, which are blind to hydronium and hydroxide ions and hence unable to provide insight on the role of pH.

Explicit-pH simulations and large-scale quantum-based simulations are currently beyond the feasible. However, with the continuous improvement of computing power, ab initio simulations should progressively be able to tackle an increasingly large panel of problems. Meanwhile, the information obtained from small ab initio simulations is already transferred to classical simulations using ab initio-based force fields [174−178].

Why coupling experiments and modeling is needed, and recent attempts

Despite recent developments in experimental characterization and molecular modeling, the study of local structure and dynamics at the solid-electrolyte interface remains restricted by the inherent limitations of the respective methods. The ambiguity in what quantity is measured by each method is a considerable limitation, making it difficult to form a unified understanding of the EDL by combining data from multiple experimental techniques. Ambiguity or uncertainty of measurements can even propagate when combining techniques. For example, the charge held within the Stern layer can be estimated by combining titration experiments to determine the bare surface charge density and electrokinetic experiments to infer the charge contained in the mobile region [10••]. However, the latter relies on the assumption that the electrokinetic charge equals the charge held in the diffuse layer, i.e., the shear plane is assumed to coincide with the OHP.

Similarly, the difference between the static and electrokinetic potentials has been used to estimate the Stern layer thickness, assuming a constant permittivity across the Stern layer [179]. The calculated thickness depends linearly on the assumed Stern-layer permittivity and on the approximated potential drop between the surface potential and the electrokinetic potential, which were obtained using two different techniques and material samples. Furthermore, this approach again assumes that the shear plane marks the outside of the Stern layer. Evidently, inferred quantities, such as the Stern layer thickness and its charge, can be highly sensitive to assumptions and models.

On the other hand, simulations can help to interpret and complement experiments, without the need for assumptions or theoretical models. However, direct and quantitative comparison between experiments and simulations is often difficult for two major reasons: first, due to empirical force fields in classical MD, or approximations in ab initio methods, and second, because atomistically-detailed computations are limited to short simulation times and small systems, whereas many experiments are limited by their spatial and temporal resolution. Direct coupling between simulations and experiments thus presents a major challenge. Yet, combining these disciplines can help to leverage their complementary strengths. Specifically, experiments are essential to validate simulation results and to improve simulation force fields, while accurate simulations are helpful to interpret and explain experimental measurements.

Thus far, few studies have combined experiments and simulations to gain deep understanding of interfacial fluid properties [38,42,44•,54−57•,60•,70,85•,164•,180•,181•, 182−184•,185−190••,191,192]. For example, Předota et al. [186] performed MD simulations and titration experiments for different electrolytes near a hydroxylated (110) rutile surface. The simulations suggested that different slopes in the titration curves were caused by different adsorption mechanisms.

In a recent study, Bourg et al. combined X-ray reflectivity, MD simulation, and complexation theory to provide detailed insight into the interfacial structure of 0.1 M alkali chloride solutions on a muscovite mica surface [190••]. The authors showed that the structure of the first molecular layer of water was determined predominantly by interactions with the surface, whereas the structure of the second layer depended also on interactions with adsorbed interfacial ions. Water beyond the first two monolayers exhibited density layering, but showed no evidence of sensitivity to short-range interactions with either the surface or adsorbed ions. With the exception of Li^+, the experimentally and computationally measured ion exchange energies were in close agreement.

The trend in the exchange energy of different ions suggested that not only the hydration free energy was important, but also the match between the surface structure and the hydration structure of the ions.

Combined experiments and simulations were also used to understand the mechanisms underlying charge inversion [90]. Labbez and coworkers combined surface titration measurements, electrophoretic experiments, and implicit-solvent grand canonical Monte Carlo simulations to study the charging behavior of calcium silicate hydrate [181•,183]. The authors found that the apparent charge inversion observed for concentrated divalent solutions decreased, or even disappeared, upon the addition of monovalent electrolytes to the electrolyte mixture. This contrasts the idea that charge inversion increases with ion concentration. Using MD simulations and electrophoresis experiments, Calero et al. observed charge inversion for large organic monovalent ions near a hydrophobic colloid, but not near a hydrophilic surface [85•]. This demonstrated that charge inversion can occur also when ion-ion correlations are negligible. Semenov et al. [185] calculated the electrokinetic mobility of a single latex colloid in a trivalent electrolyte solution from implicit-solvent MD simulations combined with hydrodynamic theory. Electrostatic and specific adsorption were both essential to predict the mobility reversal observed in their optical tweezer experiments.

The insights obtained in the studies described above could not be obtained solely using experiments, due to the need for non-invasive measurements with a sub-nanometer resolution, or detailed insight into the interactions between individual atoms. On the other hand, only modeling the problem would also be unsatisfactory, as the validity of the results is not guaranteed.

Conclusions and outlook

A complete understanding of the dynamics and structure of ions repartition near surfaces requires first a full experimental investigation. Most of the techniques nowadays rely on determining charge transport properties (probing electrokinetics mainly) *or* static properties such as surface potential or ion repartition structure. However, most recent advances show that both are intimately coupled; transport can indeed change the ion repartition and vice versa. Only a full characterization of the liquid structure near the interface while electrokinetic transport takes place, under a range of conditions, would allow giving realistic inputs in this subject. Another direction that needs to be tackled is the identification of specific solid systems. Indeed, most oxide surfaces, especially silica, are complex: their properties depend a lot on the preparation and despite huge efforts in developing methodology in the experimental community, results are poorly reproducible from one group to the other. Identifying robust model materials would be a real asset.

Molecular simulations can be a valuable tool in the quest for identifying suitable model materials and the coupling between static and transport properties. Leveraging the strengths of AIMD, and combining this with computationally cheaper tools, may hold much promise for the future of computational molecular research. In fact, AIMD has adopted an increasingly important role in the study of molecular fluids and fluid-solid interfaces in recent years. The main drawback of this technique has thus far been its large computational cost, which strongly limits the accessible simulation time and system sizes. Although the accessible time scale in AIMD is insufficient to directly probe transport properties, AIMD could instead be used to explore free energy profiles [193,194]. Alternatively, the limitation of accessible time scales can be mitigated using machine learning, e.g., to predict infrared spectra [195]. Machine learning was also key to mitigate high computational costs to calculate free energy differences in a classical MD system [196]. Machine learning, combined either with classical or quantum simulation, can be a powerful tool in the development of more versatile and transferable simulation force fields, which require optimization against a large set of conditions and variables. Particularly, fingerprint algorithms, an aspect of machine learning, were recently suggested as a '*useful building block for constructing data-driven next generation force fields*' [197]. In addition to the potential speedup to be achieved with machine learning, the arrival of quantum computing may hold promise for drastically accelerating molecular simulations. Finally, advanced techniques capable of taking quantum nuclear effects into account are increasingly accessible [184•,198–200] and could help improving the description of water-based systems.

In conclusion, both experimental characterization and numerical modeling of charged interfaces have vastly progressed over the past years, and current developments give hope for a bright future. MD does not only help to understand the microscopic phenomena; it also helps to extend the validity of the experimental measurements. Indeed, numerous macroscopic parameters that are necessary to interpret the measurements (adsorption constant, slip length, etc.) can be calculated from MD, so that the treatment of experimental data is facilitated. Furthermore, very often, simulations and experiments can be directly compared without requiring the use of ill-defined concepts such as ζ-potential or effective surface charges. This does not mean that such macroscopic parameters are not useful anymore. Any macroscopic theory needs such average quantities. It means that thanks to this direct comparison between experiments and simulations, one can decide which effective quantity is relevant for a given system.

New, more efficient models have been developed in recent years, but there is still room for improvement. For instance, future models could go beyond traditional assumptions of distinct layers separated by sharp interfaces. In particular, the complex 3D structure and dynamics of the EDL due to surface roughness and chemical heterogeneities could be taken explicitly into account. Such 3D models could indeed provide more insight into the discrepancy between static and dynamic surface charge, and identify parameters controlling this discrepancy. Coupling experiments and atomistic

modeling is the best method to assess the value of recent and future models.

We hope we have convinced the reader that major advances in the understanding and detailed characterization of surface charge(s) will come from the coupling between state-of-the-art experiments and molecular simulations.

Conflict of interest statement

Nothing declared

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References^{·,··}

[1] Andelman D. Electrostatic properties of membranes: the Poisson-Boltzmann theory. Handbook of Biological Physics, vol. 1B. ; 1995. p. 603–42.

[2] Israelachvili JN. Intermolecular and Surface Forces. Academic Press; 2011.

[3] Hunter RJ. Foundations of Colloid Science. Oxford University Press; 2001.

[4] Lyklema J. Fundamentals of interface and colloid science. Solid-Liquid Interfaces, vol. 2. ; 1995.

[5] Anderson J. Colloid transport by interfacial forces. Annu Rev Fluid Mech 1989;21:61–99.

[6] Siria A, Poncharal P, Biance A-L, Fulcrand R, Blase X, Purcell ST, Bocquet L. Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube. Nature 2013; 494:455–8.

[7] Feng J, Graf M, Liu K, Ovchinnikov D, Dumcenco D, Heiranian M, Nandigana V, Aluru NR, Kis A, Radenovic A. Single-layer MoS2 nanopores as nanopower generators. Nature 2016;536:197–200.

[8] Siria A, Bocquet M-L, Bocquet L. New avenues for the large-scale harvesting of blue energy. Nat Rev Chem 2017;1:0091.

[9] Delgado A, González-Caballero F, Hunter R, Koopal L, Lyklema J. Measurement and interpretation of electrokinetic phenomena. J Colloid Interface Sci 2007;309:194–224. Review on electrokinetic transport measurements, discussing the models used for their interpretation.

[10] Lyklema J. Surface charges and electrokinetic charges: distinctions and juxtapositionings. Colloids Surf A Physicochem Eng Asp 2011;376:2–8. This article presents a critical discussion of the difference between bare surface properties and electrokinetic quantities among other things.

[11] Lyklema J. Surface conduction. J Phys Condens Matter 2001; 13:5027–34.

[12] Björneholm O, Hansen MH, Hodgson A, Liu L-M, Limmer DT, Michaelides A, Pedevilla P, Rossmeisl J, Shen H, Tocci G, Tyrode E, Walz M-M, Werner J, Bluhm H. Water at interfaces. Chem Rev 2016;116:7698–726. Review on latest advances in understanding the structure and dynamics of water at various interfaces.

[13] Maduar SR, Belyaev AV, Lobaskin V, Vinogradova OI. Electrohydrodynamics near hydrophobic surfaces. Phys Rev Lett 2015;114:118301.

[14] Stern O. Zur Theorie der Elektrolytischen Doppelschicht. Z Elektrochem 1924;30:508–16.

[15] Grahame DC. The electrical double layer and the theory of electrocapillarity. Chem Rev 1947;41:441–501.

[16] Bockris JO, Devanathan MAV, Muller K. On the structure of charged interfaces. Proceedings of the Royal Society A: Mathematical, 274. Phys Eng Sci; 1963. p. 55–79.

[17] Bikerman JJ. Ionentheorie der Elektrosmose, der Strömungsströme und der Oberflächenleitfähigkeit. Z Phys Chem 1933;163A:378–94.

[18] Zukoski IV C, Saville D. The interpretation of electrokinetic measurements using a dynamic model of the stern layer: I. The dynamic model. J Colloid Interface Sci 1986;114:32–44.

[19] Zukoski IV C, Saville D. The interpretation of electrokinetic measurements using a dynamic model of the stern layer: II. Comparisons between theory and experiment. J Colloid Interface Sci 1986;114:45–53.

[20] Rosen LA, Baygents JC, Saville DA. The interpretation of dielectric response measurements on colloidal dispersions using the dynamic stern layer model. J Chem Phys 1993;98:4183–94.

[21] Netz RR. Electrofriction and dynamic stern layers at planar charged surfaces. Phys Rev Lett 2003;91:138101.

[22] Huang X, Gordon MJ, Zare RN. Current-monitoring method for measuring the electroosmotic flow rate in capillary zone electrophoresis. Anal Chem 1988;60:1837–8.

[23] Santiago JG, Wereley ST, Meinhart CD, Beebe DJ, Adrian RJ. A particle image velocimetry system for microfluidics. Exp Fluids 1998;25:316–9.

[24] van der Heyden FHJ, Stein D, Dekker C. Streaming currents in a single nanofluidic channel. Phys Rev Lett 2005;95:116104. This work compared the streaming current using various channels and ion concentrations.

[25] Stein D, Kruithof M, Dekker C. Surface-charge-governed ion transport in nanofluidic channels. Phys Rev Lett 2004;93: 035901.

[26] Li S, Leroy P, Heberling F, Devau N, Jougnot D, Chiaberge C. Influence of surface conductivity on the apparent zeta potential of calcite. J Colloid Interface Sci 2016;468:262–75.

[27] Kijlstra J, van Leeuwen HP, Lyklema J. Low-frequency dielectric relaxation of hematite and silica sols. Langmuir 1993;9:1625–33.

[28] Rowlands WN, O'Brien RW. The dynamic mobility and dielectric response of kaolinite particles. J Colloid Interface Sci 1995;175: 190–200.

[29] Rasmusson M, Rowlands W, O'Brien RW, Hunter RJ. The dynamic mobility and dielectric response of sodium bentonite. J Colloid Interface Sci 1997;189:92–100.

[30] Ducker WA, Senden TJ, Pashley RM. Direct measurement of colloidal forces using an atomic force microscope. Nature 1991;353:239–41.

[31] Atkins DT, Pashley RM. Surface forces between zinc sulfide and mica in aqueous electrolytes. Langmuir 1993;9:2232–6.

[32] Larson I, Drummond CJ, Chan DYC, Grieser F. Direct force measurements between titanium dioxide surfaces. J Am Chem Soc 1993;115:11885–90.

[33] Li YQ, Tao NJ, Pan J, Garcia AA, Lindsay SM. Direct measurement of interaction forces between colloidal particles using the scanning force microscope. Langmuir 1993;9: 637–41.

[34] Biggs S, Mulvaney P, Zukoski CF, Grieser F. Study of anion adsorption at the gold-aqueous solution interface by atomic force microscopy. J Am Chem Soc 1994;116:9150–7.

[·] of special interest.
^{··} of outstanding interest.

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[35] Lützenkirchen J, Preočanin T, Kovačević D, Tomišić V, Lövgren L, Kallay N. Potentiometric titrations as a tool for surface charge determination. Croat Chem Acta 2012;85:391–417.

[36] Atkins PW, Atkins PW. The Elements of Physical Chemistry. , vol. 496Oxford United Kingdom: Oxford University Press; 1992.

[37] Lu JR, Thomas RK. Neutron reflection from wet interfaces. J Chem Soc Faraday Trans 1998;94:995–1018.

[38] Wang H-W, DelloStritto MJ, Kumar N, Kolesnikov AI, Kent PRC, Kubicki JD, Wesolowski DJ, Sofo JO. Vibrational density of states of strongly H-bonded interfacial water: insights from inelastic neutron scattering and theory. J Phys Chem C 2014;118:10805–13.

[39] Audry M-C, Piednoir A, Joseph P, Charlaix E. Amplification of electro-osmotic flows by wall slippage: direct measurements on OTS-surfaces. Faraday Discuss 2010;146:113. Comparison between AFM and electrokinetic measurements, showing the amplification of electrokinetic mobility by liquid-solid slip.

[40] Attard Ph, Antelmi D, Larson I. Comparison of the zeta potential with the diffuse layer potential from charge titration. Langmuir 2000;16:1542.

[41] Perera GS, Nettles CB, Zhou Y, Zou S, Hollis TK, Zhang D. Direct observation of ion pairing at the liquid/solid interfaces by surface enhanced Raman spectroscopy. Langmuir 2015;31:8998–9005.

[42] Steinrück H-G, Cao C, Tsao Y, Takacs CJ, Konovalov O, Vatamanu J, Borodin O, Toney MF. The nanoscale structure of the electrolyte-metal oxide interface. Energ Environ Sci 2018;4:1166–9.

[43] Lee SS, Fenter P, Nagy KL, Sturchio NC. Changes in adsorption free energy and speciation during competitive adsorption between monovalent cations at the muscovite (001)-water interface. Geochim Cosmochim Acta 2013;123:416–26.

[44] Bellucci F, Lee SS, Kubicki JD, Bandura A, Zhang Z, Wesolowski DJ, Fenter P. Rb + adsorption at the quartz(101) aqueous interface: comparison of resonant anomalous X-ray reflectivity with ab initio calculations. J Phys Chem C 2015;119:4778–88. X-ray reflectivity and ab initio simulations are used to explore cation adsorption at the water-quartz interface.

[45] ben Jabrallah S, Malloggi F, Belloni L, Girard L, Novikov D, Mocuta C, Thiaudière D, Daillant J. Electrolytes at interfaces: accessing the first nanometers using X-ray standing waves. Phys Chem Chem Phys 2017;19:167–74. X-ray standing waves are used to explore ion distribution at the water-silica interface.

[46] Brown MA, Abbas Z, Kleibert A, Green RG, Goel A, May S, Squires TM. Determination of surface potential and electrical double-layer structure at the aqueous electrolyte-nanoparticle interface. Phys Rev X 2016;6:011007. This work introduces X-ray photoelectron spectroscopy from a liquid microjet, which provides insight into the potential drop across the Stern layer.

[47] Gmür TA, Goel A, Brown MA. Quantifying specific ion effects on the surface potential and charge density at silica nanoparticle-aqueous electrolyte interfaces. J Phys Chem C 2016;120:16617–25.

[48] Jubb AM, Allen HC. Sulfate adsorption at the buried fluorite solution interface revealed by vibrational sum frequency generation spectroscopy. J Phys Chem C 2012;116:9085–91.

[49] Lovering KA, Bertram AK, Chou KC. New information on the ion-identity-dependent structure of stern layer revealed by sum frequency vibrational spectroscopy. J Phys Chem C 2016;120:18099–104.

[50] Schaefer J, Gonella G, Bonn M, Backus EHG. Surface-specific vibrational spectroscopy of the water/silica interface: screening and interference. Phys Chem Chem Phys 2017;19:16875–80.

[51] Lütgebaucks C, Gonella G, Roke S. Optical label-free and model-free probe of the surface potential of nanoscale and microscopic objects in aqueous solution. Phys Rev B 2016;94:195410.

[52] Tarasov A, Wipf M, Stoop RL, Bedner K, Fu W, Guzenko VA, Knopfmacher O, Calame M, Schönenberger C. Understanding the electrolyte background for biochemical sensing with ion-sensitive field-effect transistors. ACS Nano 2012;6:9291–8.

[53] Parizi KB, Xu X, Pal A, Hu X, Wong HSP. ISFET pH sensitivity: counter-ions play a key role. Sci Rep 2017;7:41305.

[54] Sivakumarasamy R, Hartkamp R, Siboulet B, Dufrêche J-F, Nishiguchi K, Fujiwara A, Clément N. Selective layer-free blood serum ionogram based on ion-specific interactions with a nanotransistor. Nat Mater 2018;17:464–70.

[55] Fitts JP, Machesky ML, Wesolowski DJ, Shang X, Kubicki JD, Flynn GW, Heinz TF, Eisenthal KB. Second-harmonic generation and theoretical studies of protonation at the water/α-TiO2 (110) interface. Chem Phys Lett 2005;411:399–403.

[56] Hosseinpour S, Tang F, Wang F, Livingstone RA, Schlegel SJ, Ohto T, Bonn M, Nagata Y, Backus EH. Chemisorbed and physisorbed water at the TiO2/water interface. J Phys Chem Lett 2017;8:2195–9.

[57] Siretanu I, Ebeling D, Andersson MP, Stipp SLS, Philipse A, Stuart MC, van den Ende D, Mugele F. Direct observation of ionic structure at solid-liquid interfaces: a deep look into the stern layer. Sci Rep 2014;4:4956. The authors combine AFM experiments with DFT simulations to measure and explain how different electrolytes and concentrations affect the effective surface charge.

[58] Zhao C, Ebeling D, Siretanu I, van den Ende D, Mugele F. Extracting local surface charges and charge regulation behavior from atomic force microscopy measurements at heterogeneous solid-electrolyte interfaces. Nanoscale 2015;7:16298–311.

[59] Liu F, Klaassen A, Zhao C, Mugele F, van den Ende D. Electroviscous dissipation in aqueous electrolyte films with overlapping electric double layers. J Phys Chem B 2018;122:933–46.

[60] Ricci M, Spijker P, Stellacci F, Molinari J-F, Voïtchovsky K. Direct visualization of single ions in the stern layer of calcite. Langmuir 2013;29:2207–16. This study succeeded in probing adsorbed ions with high-resolution AFM experiments, supported by MD simulation.

[61] Ricci M, Trewby W, Cafolla C, Voïtchovsky K. Direct observation of the dynamics of single metal ions at the interface with solids in aqueous solutions. Sci Rep 2017;7:43234.

[62] Abécassis B, Cottin-Bizonne C, Ybert C, Ajdari A, Bocquet L. Boosting migration of large particles by solute contrasts. Nat Mater 2008;7:785.

[63] Shi N, Nery-Azevedo R, Abdel-Fattah AI, Squires TM. Diffusiophoretic focusing of suspended colloids. Phys Rev Lett 2016;117:258001.

[64] Lee C, Cottin-Bizonne C, Biance A-L, Joseph P, Bocquet L, Ybert C. Osmotic flow through fully permeable nanochannels. Phys Rev Lett 2014;112:244501.

[65] Burelbach J, Zupkauskas M, Lamboll R, Lan Y, Eiser E. Colloidal motion under the action of a thermophoretic force. J Chem Phys 2017;147:094906.

[66] Scheu R, Chen Y, Subinya M, Roke S. Stern layer formation induced by hydrophobic interactions: a molecular level study. J Am Chem Soc 2013;135:19330–5.

[67] Jalil AH, Pyell U. Quantification of zeta-potential and electrokinetic surface charge density for colloidal silica nanoparticles dependent on type and concentration of the counterion:

probing the outer Helmholtz plane. J Phys Chem C 2018;122: 4437−53.

[68] Lis D, Backus EHG, Hunger J, Parekh SH, Bonn M. Liquid flow along a solid surface reversibly alters interfacial chemistry. Science 2014;344:1138−42. SFG experiments showed that surface charge can be reversibly affected by a flow, suggesting a strong coupling between chemistry and transport.

[69] Blanc B, Bonhomme O, Brevet P-F, Benichou E, Ybert C, Biance A-L. Electroosmosis near surfactant laden liquidair interfaces. Soft Matter 2018;14:2604−9.

[70] Lützenkirchen J, Scharnweber T, Ho T, Striolo A, Sulpizi M, Abdelmonem A. A set-up for simultaneous measurement of second harmonic generation and streaming potential and some test applications. J Colloid Interface Sci 2018;529:294−305.

[71] Knecht V, Risselada HJ, Mark AE, Marrink SJ. Electrophoretic mobility does not always reflect the charge on an oil droplet. J Colloid Interface Sci 2008;318:477−86.

[72] Pagonabarraga I, Rotenberg B, Frenkel D. Recent advances in the modelling and simulation of electrokinetic effects: bridging the gap between atomistic and macroscopic descriptions. Phys Chem Chem Phys 2010;12:9566.

[73] Lyklema J. Molecular interpretation of electrokinetic potentials. Curr Opin Colloid Interface Sci 2010;15:125−30.

[74] Rotenberg B, Pagonabarraga I. Electrokinetics: insights from simulation on the microscopic scale. Mol Phys 2013;111:827−42.

[75] Yoshida H, Mizuno H, Kinjo T, Washizu H, Barrat J-L. Molecular dynamics simulation of electrokinetic flow of an aqueous electrolyte solution in nanochannels. J Chem Phys 2014;140:214701.

[76] Dewan S, Carnevale V, Bankura A, Eftekhari-Bafrooei A, Fiorin G, Klein ML, Borguet E. Structure of water at charged interfaces: a molecular dynamics study. Langmuir 2014;30:8056−65.

[77] Lowe B, Skylaris C-K, Green N, Shibuta Y, Sakata T. Calculation of surface potentials at the silica-water interface using molecular dynamics: challenges and opportunities. Jpn J Appl Phys 2018;57 [04FM02].

[78] Uematsu Y, Netz RR, Bonthuis DJ. Analytical interfacial layer model for the capacitance and electrokinetics of charged aqueous interfaces. Langmuir 2018;34:9097−113 [acs. langmuir.7b04171].

[79] Nagata Y, Ohto T, Backus EHG, Bonn M. Molecular modeling of water interfaces: from molecular spectroscopy to thermodynamics. J Phys Chem B 2016;120:3785−96.

[80] Dufrêche J-F, Marry V, Bernard O, Turq P. Models for electrokinetic phenomena in montmorillonite. Colloids Surf, A 2001;195:171−80.

[81] Horinek D, Netz RR. Specific ion adsorption at hydrophobic solid surfaces. Phys Rev Lett 2007;99:226104.

[82] Huang D, Cottin-Bizonne C, Ybert C, Bocquet L. Ion-specific anomalous electrokinetic effects in hydrophobic nanochannels. Phys Rev Lett 2007;98:177801. MD work showing anomalous electroosmosis due to ionic specificity, resulting for instance in a nonzero zeta potential for a neutral surface.

[83] Huang DM, Cottin-Bizonne C, Ybert C, Bocquet L. Aqueous electrolytes near hydrophobic surfaces: dynamic effects of ion specificity and hydrodynamic slip. Langmuir 2008;24: 1442−50.

[84] Ben-Yaakov D, Andelman D, Podgornik R, Harries D. Ion-specific hydration effects: extending the Poisson-Boltzmann theory. Curr Opin Colloid Interface Sci 2011;16:542−50.

[85] Calero C, Faraudo J, Bastos-González D. Interaction of monovalent ions with hydrophobic and hydrophilic colloids: charge inversion and ionic specificity. J Am Chem Soc 2011;

133:15025−35. This study combines MD simulation and electrophoresis experiments to demonstrate that solvation free energy can cause or prevent charge inversion, depending on the colloid surface hydrophobicity.

[86] Cazade P-A, Hartkamp R, Coasne B. Structure and dynamics of an electrolyte confined in charged Nanopores. J Phys Chem C 2014;118:5061−72.

[87] Hartkamp R, Siboulet B, Dufrêche J-F, Coasne B. Ion-specific adsorption and electroosmosis in charged amorphous porous silica. Phys Chem Chem Phys 2015;17:24683−95.

[88] Hocine S, Hartkamp R, Siboulet B, Duvail M, Coasne B, Turq P, Dufrêche J-F. How ion condensation occurs at a charged surface: a molecular dynamics investigation of the stern layer for water? Silica interfaces. J Phys Chem C 2016;120:963−73.

[89] Uematsu Y, Netz RR, Bonthuis DJ. The effects of ion adsorption on the potential of zero charge and the differential capacitance of charged aqueous interfaces. J Phys Condens Matter 2018;30: 064002.

[90] Grosberg A, Nguyen T, Shklovskii B. Colloquium: the physics of charge inversion in chemical and biological systems. Rev Mod Phys 2002;74:329.

[91] Lorenz CD, Travesset A. Charge inversion of divalent ionic solutions in silica channels. Phys Rev E 2007;75:061202.

[92] Lorenz CD, Crozier PS, Anderson JA, Travesset A. Molecular dynamics of ionic transport and electrokinetic effects in realistic silica channels. J Phys Chem C 2008;112:10222−32.

[93] Jardat M, Dufrêche J-F, Marry V, Rotenberg B, Turq P. Salt exclusion in charged porous media: a coarse-graining strategy in the case of montmorillonite clays. Phys Chem Chem Phys 2009;11:2023.

[94] Siboulet B, Hocine S, Hartkamp R, Dufrêche J-F. Scrutinizing electro-osmosis and surface conductivity with molecular dynamics. J Phys Chem C 2017;121:6756−69. This computational study reveals interesting insights by deviating from the traditional way of looking at the electrical double layer.

[95] Bonthuis D, Gekle S, Netz R. Dielectric profile of interfacial water and its effect on double-layer capacitance. Phys Rev Lett 2011;107:1−5.

[96] Zhu H, Ghoufi A, Szymczyk A, Balannec B, Morineau D. Anomalous dielectric behavior of nanoconfined electrolytic solutions. Phys Rev Lett 2012;109:107801.

[97] Bonthuis DJ, Netz RR. Beyond the continuum: how molecular solvent structure affects electrostatics and hydrodynamics at solid-electrolyte interfaces. J Phys Chem B 2013;117:11397−413. MD work showing that both viscosity and dielectric permittivity are affected by solvent structure close to interfaces.

[98] Zhang C, Gygi F, Galli G. Strongly anisotropic dielectric relaxation of water at the nanoscale. J Phys Chem Lett 2013;4:2477−81.

[99] Parez S, Předota M, Machesky M. Dielectric properties of water at rutile and graphite surfaces: effect of molecular structure. J Phys Chem C 2014;118:4818−34.

[100] De Luca S, Kannam SK, Todd BD, Frascoli F, Hansen JS, Daivis PJ. Effects of confinement on the dielectric response of water extends up to mesoscale dimensions. Langmuir 2016; 32:4765−73.

[101] Bocquet L, Charlaix E. Nanofluidics, from bulk to interfaces. Chem Soc Rev 2010;39:1073−95. Very complete review on both experimental and theoretical aspects on coupled electrokinetic transport near solid interfaces.

[102] Hansen JS, Dyre JC, Daivis P, Todd BD, Bruus H. Continuum Nanofluidics. Langmuir 2015;31:13275−89.

[103] Bocquet L, Barrat J-L. Flow boundary conditions from nano- to micro-scales. Soft Matter 2007;3:685−93.

[104] Marry V, Dufrêche J-F, Jardat M, Turq P. Equilibrium and electrokinetic phenomena in charged porous media from microscopic and mesoscopic models: electro-osmosis in montmorillonite. Mol Phys 2003;101:3111.

[105] Joly L, Ybert C, Trizac E, Bocquet L. Hydrodynamics within the electric double layer on slipping surfaces. Phys Rev Lett 2004;93:257805. MD work showing that the zeta potential depends critically on hydrodynamic boundary condition, and can be amplified by liquid-solid slip.

[106] Dufrêche J-F, Marry V, Malikova N, Turq P. Molecular hydrodynamics for electro-osmosis in clays: from kubo to smoluchowski. J Mol Liq 2005;118:145.

[107] Joly L, Ybert C, Trizac E, Bocquet L. Liquid friction on charged surfaces: from hydrodynamic slippage to electrokinetics. J Chem Phys 2006;125:204716.

[108] Botan A, Marry V, Rotenberg B, Turq P, Noetinger B. How electrostatics influences hydrodynamic boundary conditions: Poiseuille and electro-osmostic flows in clay nanopores. J Phys Chem C 2013;117:978–85.

[109] Jing D, Bhushan B. The coupling of surface charge and boundary slip at the solidliquid interface and their combined effect on fluid drag: a review. J Colloid Interface Sci 2015; 454:152–79.

[110] Muller VM, Sergeeva IP, Sobolev VD, Churaev NV. Boundary effects in the theory of electrokinetic phenomena. Colloid J USSR 1986;48:606–14.

[111] Stone HA, Stroock AD, Ajdari A. Engineering flows in small devices: microfluidics toward a lab-on-a-chip. Annu Rev Fluid Mech 2004;36:381–411.

[112] Bouzigues CI, Tabeling P, Bocquet L. Nanofluidics in the Debye layer at hydrophilic and hydrophobic surfaces. Phys Rev Lett 2008;101:114503.

[113] Joly L, Detcheverry F, Biance A-L. Anomalous ζ potential in foam films. Phys Rev Lett 2014;113:088301.

[114] Barbosa De Lima A, Joly L. Electro-osmosis at surfactant-laden liquid gas interfaces: beyond standard models. Soft Matter 2017;13:3341–51.

[115] Ajdari A, Bocquet L. Giant amplification of interfacially driven transport by hydrodynamic slip: diffusio-osmosis and beyond. Phys Rev Lett 2006;96:186102.

[116] Morthomas J, Würger A. Thermophoresis at a charged surface: the role of hydrodynamic slip. J Phys Condens Matter 2009;21: 035103.

[117] Fu L, Merabia S, Joly L. What controls thermo-osmosis? Molecular simulations show the critical role of interfacial hydrodynamics. Phys Rev Lett 2017;119:214501.

[118] Lee C, Cottin-Bizonne C, Fulcrand R, Joly L, Ybert C. Nanoscale dynamics versus surface interactions: what dictates osmotic transport? J Phys Chem Lett 2017;8:478–83.

[119] Zhang H, Hassanali Aa, Shin YK, Knight C, Singer SJ. The water-amorphous silica interface: analysis of the stern layer and surface conduction. J Chem Phys 2011; 134:024705.

[120] Předota M, Machesky ML, Wesolowski DJ. Molecular origins of the zeta potential. Langmuir 2016;32:10189–98. This study uses MD simulation to provide deep understanding of the origin of the macroscopically measured zeta potential.

[121] Předota M, Cummings PT, Wesolowski DJ. Electric double layer at the rutile (110) surface. 3. Inhomogeneous viscosity and diffusivity measurement by computer simulations. J Phys Chem C 2007;111:3071–9.

[122] Knecht V, Klasczyk B, Dimova R. Macro- versus microscopic view on the electrokinetics of a water-membrane interface. Langmuir 2013;29:7939–48. MD work discussing the limits of traditional models of electoosmosis in the context of lipid membranes.

[123] Uematsu Y, Netz RR, Bonthuis DJ. Power-law electrokinetic behavior as a direct probe of effective surface viscosity. Chem Phys Lett 2017;670:11–5.

[124] Todd BD, Hansen JS, Daivis PJ. Nonlocal shear stress for homogeneous fluids. Phys Rev Lett 2008;100:195901.

[125] Bouhadja M, Skelton AA. Dynamical properties of water and ions at the quartz (101)-water interface at a range of solution conditions: a classical molecular dynamics study. J Phys Chem C 2018;122:1535–46.

[126] Lyklema J, Rovillard S, De Coninck J. Electrokinetics: the properties of the stagnant layer unraveled. Langmuir 1998; 14:5659–63.

[127] Happel J, Brenner H. Low Reynolds Number Hydrodynamics: With Special Applications to Particulate Media. , Vol. 1Springer Science & Business Media; 2012.

[128] Marcus Y. Effect of ions on the structure of water: structure making and breaking effect of ions on the structure of water: structure making and breaking. Chem Rev 2009;109: 1346–70.

[129] Kim JS, Wu Z, Morrow AR, Yethiraj A, Yethiraj A. Self-diffusion and viscosity in electrolyte solutions. J Phys Chem B 2012;116:12007–13.

[130] Ding Y, Hassanali AA, Parrinello M. Anomalous water diffusion in salt solutions. Proc Natl Acad Sci U S A 2014;111:3310–5. An article illustrating the power of ab initio methods, which can describe the effects of salts on water diffusion, in contrast with force field-based simulations.

[131] Kann ZR, Skinner JL. A scaled-ionic-charge simulation model that reproduces enhanced and suppressed water diffusion in aqueous salt solutions. J Chem Phys 2014;141:104507.

[132] Yao Y, Kanai Y, Berkowitz ML. Role of charge transfer in water diffusivity in aqueous ionic solutions. J Phys Chem Lett 2014; 5:2711–6.

[133] Yao Y, Berkowitz ML, Kanai Y. Communication: modeling of concentration dependent water diffusivity in ionic solutions: role of intermolecular charge transfer. J Chem Phys 2015;143: 241101.

[134] Li J, Wang F. Pairwise-additive force fields for selected aqueous monovalent ions from adaptive force matching. J Chem Phys 2015;143:194505.

[135] van Duin ACT, Dasgupta S, Lorant F, Goddard WA. ReaxFF: a reactive force field for hydrocarbons. J Phys Chem A 2001; 105:9396–409.

[136] Raymand D, van Duin AC, Goddard WA, Hermansson K, Spångberg D. Hydroxylation structure and proton transfer reactivity at the zinc oxide water interface. J Phys Chem C 2011;115:8573–9.

[137] Kim S-Y, Kumar N, Persson P, Sofo J, van Duin ACT, Kubicki JD. Development of a ReaxFF reactive force field for titanium dioxide/water systems. Langmuir 2013;29: 7838–46.

[138] Senftle TP, Hong S, Islam MM, Kylasa SB, Zheng Y, Shin YK, Junkermeier C, Engel-Herbert R, Janik MJ, Aktulga HM, Verstraelen T, Grama A, van Duin ACT. The ReaxFF reactive force-field: development, applications and future directions. npj Comput Mater 2016;2:15011.

[139] Gillan MJ, Alfè D, Michaelides A. Perspective: how good is DFT for water? J Chem Phys 2016;144:130901. A review discussing the interest and shortcomings of ab initio methods to describe aqueous systems.

[140] Nagata Y, Ohto T, Bonn M, Kühne TD. Surface tension of ab initio liquid water at the water-air interface. J Chem Phys 2016;144:204705.

[141] Chen M, Ko H-Y, Remsing RC, Calegari Andrade MF, Santra B, Sun Z, Selloni A, Car R, Klein ML, Perdew JP, Wu X. Ab initio theory and modeling of water. Proc Natl Acad Sci 2017;114: 10846−51.

[142] Markovich T, Andelman D, Podgornik R. Charge regulation: a generalized boundary condition? EPL 2016;113:1−6.

[143] Trefalt G, Behrens SH, Borkovec M. Charge regulation in the electrical double layer: ion adsorption and surface interactions. Langmuir 2016;32:380−400.

[144] Masini P, Bernasconi M. Ab initio simulations of hydroxylation and dehydroxylation reactions at surfaces: amorphous silica and brucite. J Phys Condens Matter 2002;14:4133−44.

[145] Criscenti LJ, Kubicki JD, Brantley SL. Silicate glass and mineral dissolution: calculated reaction paths and activation energies for hydrolysis of a Q 3 Si by H 3O + using ab initio methods. J Phys Chem A 2006;110:198−206.

[146] Tielens F, Gervais C, Lambert JF, Mauri F, Costa D. Ab initio study of the hydroxylated surface of amorphous silica: a representative model. Chem Mater 2008;20:3336−44.

[147] Kumar N, Neogi S, Kent PRC, Bandura AV, Kubicki JD, Wesolowski DJ, Cole D, Sofo JO. Hydrogen bonds and vibrations of water on (110) rutile. J Phys Chem C 2009;113:13732−40.

[148] Liu C, Li Z. Molecular dynamics simulation of composite nanochannels as nanopumps driven by symmetric temperature gradients. Phys Rev Lett 2010;105:1−4.

[149] Cimas A, Tielens F, Sulpizi M, Gaigeot M-P, Costa D. The amorphous silica liquid water interface studied by ab initio molecular dynamics (AIMD): local organization in global disorder. J Phys Condens Matter 2014;26:244106.

[150] Gaigeot M-P, Sprik M, Sulpizi M. Oxide/water interfaces: how the surface chemistry modifies interfacial water properties. J Phys Condens Matter 2012;24:124106.

[151] Sulpizi M, Gaigeot M-P, Sprik M. The SilicaWater Interface: how the silanols determine the surface acidity and modulate the water properties. J Chem Theory Comput 2012;8: 1037−47.

[152] Tazi S, Rotenberg B, Salanne M, Sprik M, Sulpizi M. Absolute acidity of clay edge sites from ab-initio simulations. Geochim Cosmochim Acta 2012;94:1−11.

[153] Wesolowski DJ, Sofo JO, Bandura AV, Zhang Z, Mamontov E, Předota M, Kumar N, Kubicki JD, Kent PRC, Vlcek L, Machesky ML, Fenter PA, Cummings PT, Anovitz LM, Skelton AA, Rosenqvist J. Comment on "structure and dynamics of liquid water on rutile TiO2 (110)". Phys Rev B 2012;85:167401.

[154] Tocci G, Michaelides A. Solvent-induced proton hopping at a WaterOxide Interface. J Phys Chem Lett 2014;5:474−80.

[155] Laporte S, Finocchi F, Paulatto L, Blanchard M, Balan E, Guyot F, Saitta AM. Strong electric fields at a prototypical oxide/water interface probed by ab initio molecular dynamics: MgO(001). Phys Chem Chem Phys 2015;17:20382−90.

[156] Pfeiffer-Laplaud M, Gaigeot M-P. Adsorption of singly charged ions at the hydroxylated (0001) α-quartz/water interface. J Phys Chem C 2016;120:4866−80.

[157] Pfeiffer-Laplaud M, Gaigeot M-P. Electrolytes at the hydroxylated (0001) α-quartz/water interface: location and structural effects on interfacial silanols by DFT-based MD. J Phys Chem C 2016;120:14034−47.

[158] DelloStritto MJ, Kubicki JD, Sofo JO. Effect of ions on H-bond structure and dynamics at the quartz(101)-water interface. Langmuir 2016;32:11353−65.

[159] Réocreux R, Jiang T, Iannuzzi M, Michel C, Sautet P. Structuration and dynamics of interfacial liquid water at hydrated γ-alumina determined by ab initio molecular simulations: implications for nanoparticle stability. ACS Appl Nano Mater 2018;1:191−9.

[160] Zhang C, Wu J, Galli G, Gygi F. Structural and vibrational properties of liquid water from van der Waals density functionals. J Chem Theory Comput 2011;7:3054−61.

[161] Wan Q, Spanu L, Galli GA, Gygi F. Raman spectra of liquid water from ab initio molecular dynamics: vibrational signatures of charge fluctuations in the hydrogen bond network. J Chem Theory Comput 2013;9:4124−30.

[162] Thomas M, Brehm M, Fligg R, Vöhringer P, Kirchner B. Computing vibrational spectra from ab initio molecular dynamics. Phys Chem Chem Phys 2013;15:6608.

[163] Sulpizi M, Salanne M, Sprik M, Gaigeot M-P. Vibrational sum frequency generation spectroscopy of the water LiquidVapor Interface from density functional theory-based molecular dynamics simulations. J Phys Chem Lett 2013;4:83−7.

[164] Khatib R, Backus EHG, Bonn M, Perez-Haro M-J, Gaigeot M-P, Sulpizi M. Water orientation and hydrogen-bond structure at the fluorite/water interface. Sci Rep 2016;6:24287. A recent work showing how coupling SFG and ab initio simulations can help to understand water-mineral interfaces at the molecular level.

[165] Tocci G, Joly L, Michaelides A. Friction of water on graphene and hexagonal boron nitride from ab initio methods: very different slippage despite very similar interface structures. Nano Lett 2014;14:6872−7. AIMD was used to show that liquid-solid friction can depend crucially on specific electronic structure effects.

[166] Joly L, Tocci G, Merabia S, Michaelides A. Strong coupling between nanofluidic transport and interfacial chemistry: how defect reactivity controls LiquidSolid friction through hydrogen bonding. J Phys Chem Lett 2016;7:1381−6.

[167] Heyes DM. Molecular dynamics simulations of restricted primitive model 1:1 electrolytes. Chem Phys 1982;69:155−63.

[168] Grosjean B, Pean C, Siria A, Bocquet L, Vuilleumier R, Bocquet M-L. Chemisorption of hydroxide on 2D materials from DFT calculations: graphene versus hexagonal boron nitride. J Phys Chem Lett 2016;7:4695−700. DFT calculations were used to explore the origin of surface charge on graphene and boron nitride.

[169] Lee JW, Templeton JA, Mandadapu KK, Zimmerman JA. Comparison of molecular and primitive solvent models for electrical double layers in nanochannels. J Chem Theory Comput 2013;9:3051−61.

[170] Vangara R, Brown D, van Swol F, Petsev D. Electrolyte solution structure and its effect on the properties of electric double layers with surface charge regulation. J Colloid Interface Sci 2017;488:180−9.

[171] Darlington AM, Jarisz TA, DeWalt-Kerian EL, Roy S, Kim S, Azam MS, Hore DK, Gibbs JM. Separating the pH-dependent behavior of water in the stern and diffuse layers with varying salt concentration. J Phys Chem C 2017;121:20229−41.

[172] Dewalt-Kerian EL, Kim S, Azam MS, Zeng H, Liu Q, Gibbs JM. pH-dependent inversion of Hofmeister trends in the water structure of the electrical double layer. J Phys Chem Lett 2017;8:2855−61.

[173] Chinen H, Mawatari K, Pihosh Y, Morikawa K, Kazoe Y, Tsukahara T, Kitamori T. Enhancement of proton mobility in extended-nanospace channels. Angew Chem Int Ed 2012;51:3573−7.

[174] Předota M, Bandura AV, Cummings PT, Kubicki JD, Wesolowski DJ, Chialvo AA, Machesky ML. Electric double layer at the

rutile (110) surface. 1. Structure of surfaces and interfacial water from molecular dynamics by use of ab initio potentials. J Phys Chem B 2004;108:12049−60.

[175] Masia M. Ab initio based polarizable force field parametrization. J Chem Phys 2008;128:184107.

[176] Machesky ML, Predota M, Wesolowski DJ, Vlcek L, Cummings PT, Rosenqvist J, Ridley MK, Kubicki JD, Bandura AV, Kumar N, Sofo JO. Surface protonation at the rutile (110) Interface: explicit incorporation of solvation structure within the refined MUSIC model framework. Langmuir 2008;24:12331−9.

[177] Tazi S, Molina JJ, Rotenberg B, Turq P, Vuilleumier R, Salanne M. A transferable ab initio based force field for aqueous ions. J Chem Phys 2012;136:114507.

[178] Butenuth A, Moras G, Schneider J, Koleini M, Köppen S, Meißner R, Wright LB, Walsh TR, Ciacchi LC. Ab initio derived force-field parameters for molecular dynamics simulations of deprotonated amorphous-SiO 2/water interfaces. Phys Status Solidi Basic Res 2012;249:292−305.

[179] Brown MA, Goel A, Abbas Z. Effect of electrolyte concentration on the stern layer thickness at a charged interface. Angew Chem Int Ed 2016;55:3790−4.

[180] Předota M, Zhang Z, Fenter P, Wesolowski DJ, Cummings PT. Electric double layer at the rutile (110) surface. 2. Adsorption of ions from molecular dynamics and X-ray experiments. J Phys Chem B 2004;108:12061−72. A combined MD and X-ray study of ion adsorption at the water-rutile interface

[181] Labbez C, Jonsson B, Pochard I, Nonat A, Cabane B. Surface charge density and electrokinetic potential of highly charged minerals: experiments and Monte Carlo simulations on calcium silicate hydrate. J Phys Chem B 2006;110: 9219−30. This study combined simulations with potentiometric titration and electrophoresis experiments, as well as theory, to study the effect of pH and ion concentration of surface charging.

[182] Labbez C, Nonat A, Pochard I, Jönsson B. Experimental and theoretical evidence of overcharging of calcium silicate hydrate. J Colloid Interface Sci 2007;309:303−7.

[183] Labbez C, Pochard I, Jönsson B, Nonat A. C-S-H/solution interface: experimental and Monte Carlo studies. Cem Concr Res 2011;41:161−8.

[184] Nagata Y, Pool RE, Backus EH, Bonn M. Nuclear quantum effects affect bond orientation of water at the water-vapor interface. Phys Rev Lett 2012;109:1−5. A combination of SFG spectroscopy and path integral MD simulations showed that the molecular structure of water-vapor interfaces is affected by nuclear quantum effects.

[185] Semenov I, Raafatnia S, Sega M, Lobaskin V, Holm C, Kremer F. Electrophoretic mobility and charge inversion of a colloidal particle studied by single-colloid electrophoresis and molecular dynamics simulations. Phys Rev E Stat Nonlinear Soft Matter Phys 2013;87:1−7.

[186] Predota M, Machesky ML, Wesolowski DJ, Cummings PT. Electric double layer at the rutile (110) surface. 4. Effect of temperature and ph on the adsorption and dynamics of ions. J Phys Chem C 2013;117:22852−66.

[187] Page AJ, Elbourne A, Stefanovic R, Addicoat MA, Warr GG, Voïtchovsky K, Atkin R. 3-dimensional atomic scale structure of the ionic liquid graphite interface elucidated by AM-AFM and quantum chemical simulations. Nanoscale 2014;6:8100−6.

[188] Brkljača Z, Klimczak M, Miličević Z, Weisser M, Taccardi N, Wasserscheid P, Smith DM, Magerl A, Smith AS. Complementary molecular dynamics and x-ray reflectivity study of an imidazolium-based ionic liquid at a neutral sapphire interface. J Phys Chem Lett 2015;6:549−55.

[189] Hussain H, Tocci G, Woolcot T, Torrelles X, Pang CL, Humphrey DS, Yim CM, Grinter DC, Cabailh G, Bikondoa O, Lindsay R, Zegenhagen J, Michaelides A, Thornton G. Structure of a model TiO2photocatalytic interface. Nat Mater 2016;16:461−6.

[190] Bourg IC, Lee SS, Fenter P, Tournassat C. Stern layer structure and energetics at mica-water interfaces. J Phys Chem C 2017; 121:9402−12. The consistent views provided by the experiments and simulations in this study contribute to a better understanding of the Stern layer.

[191] Perrine KA, Parry KM, Stern AC, Van Spyk MHC, Makowski MJ, Freites JA, Winter B, Tobias DJ, Hemminger JC. Specific cation effects at aqueous solution vapor interfaces: surfactant-like behavior of Li+ revealed by experiments and simulations. Proc Natl Acad Sci 2017;114:13363−8.

[192] Ge Z, Wang Y. Estimation of nanodiamond surface charge density from zeta potential and molecular dynamics simulations. J Phys Chem B 2017;121:3394−402.

[193] Baer MD, Mundy CJ. Toward an understanding of the specific ion effect using density functional theory. J Phys Chem Lett 2011;2:1088−93.

[194] Yao Y, Kanai Y. Free energy profile of NaCl in water: first-principles molecular dynamics with SCAN and ωB97X-V exchange correlation functionals. J Chem Theory Comput 2018;14:884−93.

[195] Gastegger M, Behler J, Marquetand P. Machine learning molecular dynamics for the simulation of infrared spectra. Chem Sci 2017;8:6924−35.

[196] Riniker S. Molecular dynamics fingerprints (MDFP): machine learning from MD data to predict free-energy differences. J Chem Inf Model 2017;57:726−41.

[197] Tang Y-H, Zhang D, Karniadakis GE. An atomistic fingerprint algorithm for learning ab initio molecular force fields. J Chem Phys 2018;148:034101.

[198] Cisneros GA, Wikfeldt KT, Ojamäe L, Lu J, Xu Y, Torabifard H, Bartók AP, Csányi G, Molinero V, Paesani F. Modeling molecular interactions in water: from pairwise to many-body potential energy functions. Chem Rev 2016;116:7501−28.

[199] Markland TE, Ceriotti M. Nuclear quantum effects enter the mainstream. Nat Rev Chem 2018;2:0109.

[200] Litman Y, Donadio D, Ceriotti M, Rossi M. Decisive role of nuclear quantum effects on surface mediated water dissociation at finite temperature. J Chem Phys 2018;148:102320.