Static and Dynamic Properties of the Electrical Double Layer Near Amorphous Silica: Relevance for Device Design

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ABSTRACT

To explain why dynamical properties of an aqueous electrolyte near a charged surface seem to be governed by a surface charge less than the actual one, the canonical Stern model supposes an interfacial layer of ions and immobile fluid. However, large ion mobilities within the Stern layer are needed to reconcile the Stern model with surface conduction measurements. Modeling the aqueous electrolyte/amorphous silica interface at typical charge densities, a prototypical double layer system, the flow velocity does not vanish until right at the surface, yet electroosmotic flow far from the walls is in accord with the Stern model. The Stern model is a good *effective* model away from the surface, but cannot be taken literally near the surface. Indeed, simulations show no ion mobility where water is immobile, nor is such mobility necessary since the surface conductivity in the simulations is comparable to experimental values.

Keywords: electrical double layer, nanofluidics, molecular dynamics

1 INTRODUCTION

Near a charged surface, an imbalance of cations and anions is maintained in an electrolyte, producing a net charge in the fluid that compensates the surface charge. This is the celebrated electric double layer [1, 2]. An electric field applied to an electrolyte solution induces electrophoretic motion of cations in the direction of the field and anions opposite to the field. When the field is applied parallel to a charged surface, the net charge in the fluid, or even charge segregation near a surface, will induce a net body force on the fluid causing fluid motion known as electroosmotic flow. The static and dynamic properties of the electrical double layer is a classic problem in physical chemistry, biology and colloid science. It is also of great current relevance. For example, electroosmotic flow provides a method to generate controlled fluid transport in nanoscale devices [3], and a microscopic understanding of electrokinetic transport is essential for predicting device characteristics.

It has long been known that observed electroosmotic flow is less than the amount expected based on the measured surface charge. This led Stern in 1924 to propose that an immobile layer of fluid and counter-ions lies next to the surface [4]. Separation of the ion atmosphere into the immobile Stern layer and a diffuse outer layer, the Gouy-Chapman-Stern model, has become a canonical part of the double layer literature, although certainly more elaborate models have been proposed [5]. In this work we will investigate the foundation of the Stern model in a system to which it has often been applied, the surface of amorphous silica.

When applied to electrokinetic phenomena, the Stern model dictates that the surface where hydrodynamic stick (no-slip) boundary conditions are enforced should reside near the boundary between the Stern layer and the diffuse layer. While the Stern model successfully rationalizes a vast body of experimental data, certain conceptual problems have arisen. A completely static Stern layer model does not account for surface conduction, the contribution to ionic current arising from the altered charge density near the surface [6,7]. Surface conduction becomes increasingly important with smaller channel size and also with lower salt concentration, as the bulk region contributes less to the total current relative to the counterion atmosphere of the charged surface. Under these conditions, the Stern layer contains a significant fraction of the total counter-ion population, and the remaining counter-ion population cannot account for observed surface conduction. Most of the experimental evidence for oxides is based on the fact that conductance measurements indicate a substantially higher surface charge than electrophoretic mobilities [8, 9]. Retaining the Stern layer concept, it is required to postulate that ions within the immobile layer have mobilities near bulk values, a model known as the dynamic Stern layer [6,7,10–13], to describe the measured surface conduction. In the following we will see that the notion of a sharp boundary (or even somewhat rounded as, for example, Lyklema and Overbeek [14] have suggested) between mobile and immobile electrolyte near a surface is in need of revision. Furthermore, a more complex picture of the surface region can account for surface conduction without invoking the passage of ions through immobile solvent.

2 MODEL

We have previously developed a tractable model for the water/amorphous silica interface [15], and recently extended it to treat dissociation of the silanol groups [16], $\cdots$Si-O-H $\rightarrow \cdots$Si-O$^-$ + H$^+$, which gives the surface a negative charge. Our model was developed to describe the water-amorphous silica interface. The bulk water and amorphous silica regions are described by the SPC/E [17] and BKS [18] potentials, respectively. The complex hydroxylated amorphous silica surface depends on preparation history, and has not been precisely characterized, either experimentally or theoretically [19]. However, we believe that our model captures enough features correctly to qualitatively describe electrokinetic phenomena near this important interface. The calculated heat of immersion agrees with experiment [15]. Benchmarks against more accurate *ab initio* simulations are only feasible for smaller system sizes and run times, and would have to be repeated over many realizations of the disordered surface before quantitative comparison with larger analytical model simulations. The benchmarks that we have performed [15, 16, 20] indicate that our interaction model captures at least one important feature of the water/amorphous silica interface, the relative hydrophobicity of siloxane ($\cdots$Si-O-Si$\cdots$) compared to silanol ($\cdots$Si-O-H) groups.

3 NON-EQUILIBRIUM MOLECULAR DYNAMICS OF ELECTROOSMOTIC FLOW

To explore the static and dynamic properties of a partially dissociated silica surface, an electric field was introduced and temperature in the non-equilibrium molecular dynamics simulation maintained with a Nosé-Hoover thermostat [21, 22]. The field is much larger than typical experimental fields, and is used to enhance signal-to-noise from simulations. Velocity profiles, such as those shown in Fig. 1, are 5 times smaller when the field is reduced by a factor of 5, confirming that the simulations are within the linear response regime. Hence, any velocity profiles we calculate simply scale linearly with electric field.

Fig. 1 shows the density of water, Na$^+$ ions and the O$^-$ atoms of dissociated silanol groups near a silica slab. The conditions of this study are appropriate for low salt concentrations, perhaps in the millimolar range, where Cl$^-$ co-ions would be scarce. As can be seen in Fig.1, the Na$^+$ counterions accumulate near the surface. However they are not immobile. One measure of their mobility is their residence time, the average time that a Na$^+$ ion will linger near one of the O$^-$ atoms on the silica surface [23, 24]. The residence time ranges from an upper limit of ~600ps to a lower limit of ~10ps. Many of the counter-ions actively hop from site to site on the surface, and are not fixed.

A better measure of ion and water mobility is the velocity distribution as a function of distance from the surface, shown in Fig. 1. Comparing Figs. 1b and 1c, the velocity profile is
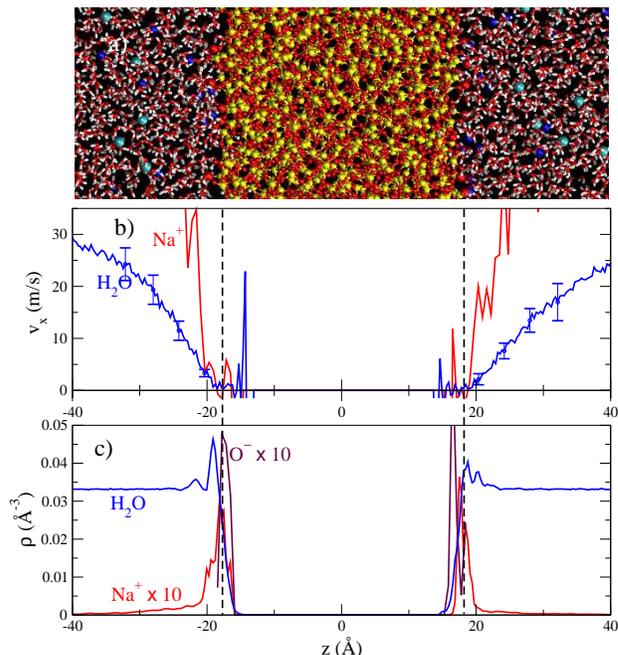

Figure 1: (a) Configuration taken from a typical non-equilibrium molecular dynamics simulation used to generate data in Figs. 1-3. The O$^-$ atoms of dissociated silanol groups are the large red spheres of the (centered) silica slab. Na$^+$ and Cl$^-$ ions are visible in solution. (b) Average velocities of Na$^+$ ions and water with a surface charge density of $12.7\mu C\ cm^{-2}$ = $0.795e\ nm^{-2}$, no ions except the Na$^+$ ions needed to neutralize the silica, and an applied electric field of $7 \times 10^8 V\ m^{-1}$. Meaningless velocity spikes appear inside the silica slab where fluid rarely penetrates, and sampling is insufficient to average normal thermal motion ($\sim 400\frac{m}{s}$) to zero. (c) Densities of water, Na$^+$ions and O$^-$ groups of dissociated silanols. The vertical dashed lines are guides for the eye to facilitate comparison of the velocity and density profiles.

seen to approach zero at roughly 20Å from the center of the silica slab, right at the silica surface, and not 5-10Å from the surface as the Stern layer model would imply. Similar results are seen for larger salt concentrations (Fig. 2).

At this point, the data seems to suggest that the Stern layer concept has limited validity. However, an immobile layer was originally proposed to explain the experimental fact that the driving force for electroosmotic flow was typically less than what one would expect based on the measured wall charge. Charge within an immobile Stern layer behind the surface where stick boundary conditions are enforced cannot drive fluid flow, and hence was thought to explain observed phenomena. Actually, something different from the traditional Stern layer picture happens, but it still explains why the driving force for electroosmotic flow is less than predicted by the full wall charge. In Fig. 2 the velocity profile for three salt concentrations from molecular dynamics calculations are compared with predictions of the
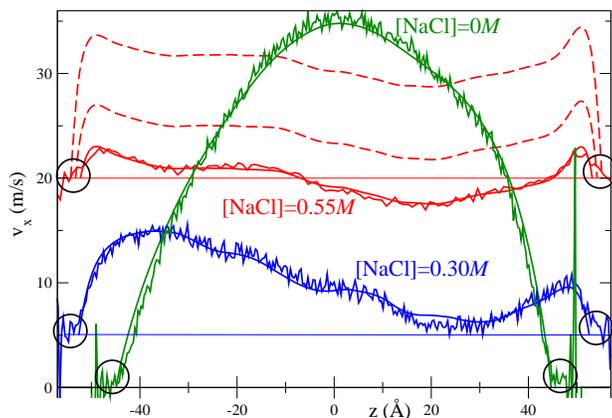
Figure 2: Comparison of velocity profiles from simulations with solutions to the Navier-Stokes equation (solid smooth curves). Stick boundary conditions are enforced at points that generated the best agreement with the molecular dynamics velocity profile across the channel. The velocity profiles are for a surface charge of $12.7 \frac{\mu C}{cm^2} = 0.795 \frac{e}{nm^2}$, and three different NaCl concentrations. The curves for $0.30M$ and $0.55M$ NaCl are shifted up by 5 and $20m\ s^{-1}$, respectively. The two extra continuum hydrodynamics curves for $0.55M$ salt (dashed curves) were calculated by enforcing stick boundary conditions at successive points 1Å closer to the point where the actual molecular dynamics velocity profile approached zero.

Navier-Stokes equation of continuum hydrodynamics. [25] The charge density from the simulations was used as input in the solution of the Navier-Stokes equation. This charge density reflects the statistical variations in the placement of charge groups in the simulation and is not symmetric across the channel, as reflected in the velocity profiles of Fig. 2. The charge density from Poisson-Boltzmann theory, although not that far off, would not be adequate because the velocity profile, as shown in Fig. 2, is very sensitive to the charge density near the walls.

The close agreement between molecular dynamics and Navier-Stokes results in Fig.3 was achieved by adjusting the point where stick boundary conditions are enforced. Moving those points by even 1Å drastically degrades the agreement between continuum hydrodynamics and molecular dynamics simulations, as illustrated by the dashed curves in Fig. 2. Focusing on the region near the walls, the circled regions in Fig. 2, one sees most clearly when salt is present (red and blue curves) that near the silica surface the velocity decreases at a slower rate as the surface is approached compared to the Navier-Stokes predictions. To obtain agreement with the actual velocity profile from simulations, stick boundary conditions for the Navier-Stokes equation must be enforced at a point ~3Å into the fluid from where the actual velocity profile goes to zero. The effect of moving the shear plane in continuum theory either 1 or 2 Å closer to the point where the velocity actually goes to zero in MD simulations is shown in Fig. 2, confirming there is little room for adjusting the effec-

tive no-slip point.

The gradual decrease in mobility near the surface may be attributed to increased viscosity near the walls, surface roughness, chemical heterogeniety of the surface, or a combination of these effects. Since increased viscosity and surface roughness have many similar signatures, we may be able to eliminate or confirm certain mechanisms, but ultimately it may prove meaningless to distinguish between increased viscosity and roughness, e.g. roughness may be understood as an increased effective viscosity. The viscoelectric theory proposed by Lyklema and Overbeek [14] explains several trends. For example, careful comparison of the best fit of continuum theory to molecular dynamics in the limit of no salt (green curves in Fig. 2) shows that the simulation fluid velocity start to dip below the Navier-Stokes solution rather far from the surface, as one would expect from the viscoelectric theory [14] in the presence of a weakly screened electric field emanating from the surface. Also, increasing the surface charge to extremely high values (Fig. 3) greatly decreases the fluid velocity near the surface, as would be expected from a viscoelectric effect. However, even with the appearance of an immobile fluid layer at extremely large surface charge, there is no evidence that ions are mobile within immobile solvent. In Fig. 3, the difference in Na^+ and water flow velocities, i.e. the total ion current minus its convective component, for the highly charged surface is proportional to the local ion mobility. The ion mobility does not maintain its bulk value or even level off at a reduced value, but instead vanishes where the solvent is not mobile. Simulations for more typical surfaces charges (Figs. 1,2) also do not show evidence of anomalous ion mobility near the surface. Nevertheless, the surface conductivity calculated from the data is in qualitative agreement with experiment. The clearest comparison can be made with no added salt, as in Fig. 1, where the entire ion current is the result of surface conduction and the surface conductivity can be calculated from $2K^\sigma = \frac{e}{E} \int dz \rho_{Na^+}(z) v_{Na^+}(z)$, where the factor of 2 is included because there are two surfaces driving ion transport in the simulations. The surface conductivity of Na^+ near silica in the limit of vanishing salt concentration calculated in this manner is $K^\sigma = 2.5 nS$ (nanoSiemens). Establishing a precise experimental value for comparison is difficult, although the existence of the effect is clear under conditions where bulk conduction is suppressed. One of the earliest measurements by Rutgers placed K^σ in the limit of vanishing KCl concentration in the range of $10 nS$ [26]. Jednacak-Biscan et al.'s measurements of K^σ ranged from 1.78 to $4.63 nS$ for water, and $6.46 nS$ for $10^{-5}M$ NaCl in contact with fused silica [27]. Most recently, Erickson, Li and Werner reported K^σ to be $1.31 nS$ for vanishing KCl concentration near silica [28]. Without invoking anomalous surface conduction, our calculated value of K^σ is comparable to these experimental values. More has to be done to establish model-free comparisons of K^σ.
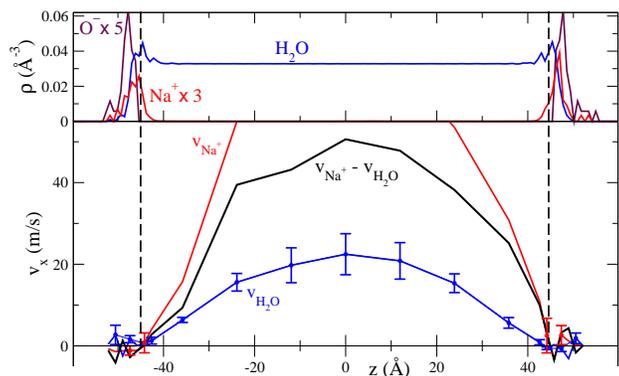
Figure 3: Densities (top) and flow velocities (bottom) near an almost completely dissociated silica surface with a large surface charge of $58.7 \frac{\mu C}{cm^2} = 3.67 \frac{e}{nm^2}$ in the limit of low salt concentration. Because of the extremely large surface charge, the fluid is less mobile near the surface, which is apparent comparing the location of the dotted lines in this figure and Fig. 1. The local ion mobility of sodium ions is proportional to $(v_{Na^+} - v_{H_2O})$.

4   CONCLUSION

In conclusion, we see that the solvent adjacent to the charged surface in the electrical double layer is not immobile. Except for extremely large surface charge density, it is a region of gradually reduced mobility. The classical Stern model is successful as an "effective" model that reproduces some experimental features. However, conceptual problems arise when it is taken literally. Molecular simulations show no evidence that ions have enhanced mobility relative to solvent near a charged surface. Nevertheless, the simulations exhibit a surface conductivity similar to experiment, indicating that effects previously attributed to anomalously large surface conductivity can be explained by a unified model without anomalous transport near the surface. We note recent efforts to reconcile measurements of the ζ-potential by different methods without the assumptions of the dynamic Stern layer model [29]. Our analysis should provide guidance for the formulation of a unified model. With regard to device design, this research confirms that continuum hydrodynamics performs remarkably well away from channel walls, but must be combined with a molecular perspective within a few Angstroms of the surface.

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