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## Nonlinear electrokinetics at large voltages

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**Abstract.** The classical theory of electrokinetic phenomena assumes a dilute solution of point-like ions in chemical equilibrium with a surface whose double-layer voltage is of order the thermal voltage,  $k_B T/e = 25$  mV. In nonlinear ‘induced-charge’ electrokinetic phenomena, such as ac electro-osmosis, several volts  $\approx 100k_B T/e$  are applied to the double layer, and the theory breaks down and cannot explain many observed features. We argue that, under such a large voltage, counterions ‘condense’ near the surface, even for dilute bulk solutions. Based on simple models, we predict that the double-layer capacitance decreases and the electro-osmotic mobility saturates at large voltages, due to steric repulsion and increased viscosity of the condensed layer, respectively. The former suffices to explain observed high-frequency flow reversal in ac electro-osmosis; the latter leads to a salt concentration dependence of induced-charge flows comparable to experiments, although a complete theory is still lacking.

Electrically driven flows in ionic solutions are finding many new applications in microfluidics [1]. The theory of electro-osmosis [2] was developed for slip past a surface in chemical *equilibrium*, whose double-layer voltage is typically of order  $k_B T/e = 25$  mV. However, the discovery of ac electro-osmosis (ACEO) at micro-electrodes [3, 4] has shifted attention to a new regime, where the *induced* double-layer voltage is  $\approx 100k_B T/e$ , oscillating

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at frequencies up to 100 kHz, and nonuniform at the micron scale. Related effects of induced-charge electro-osmosis (ICEO) [5, 6] also occur around colloidal particles [7] and polarizable microstructures [8] (in ac or dc fields), and asymmetric particles can move by induced-charge electrophoresis (ICEP) [5, 9].

In all of these situations, low-voltage theories fail to predict crucial experimental trends [10], such as flow decay at high salt concentration [9, 11] and flow reversal in asymmetric pumps at high voltage and high frequency [11]–[13]. In this paper, we attribute these failures to the breakdown of the dilute solution approximation at large applied voltages. Based on very simple models, we predict two general effects due to counterion crowding—decay of the double-layer capacitance and saturation of the electro-osmotic mobility—which begin to explain the experimental data. The present paper closely follows a preprint archived in March 2007 [14], which was the first to introduce these ideas; more extensive theory and literature review can be found in [15].

*Experimental puzzles*—ICEO flows are rather complex, so many simplifications have been made to arrive at an operational model [3, 4, 6, 7]. For thin double layers, the first step is to solve Laplace’s equation (Ohm’s law) for the electrostatic potential in the conducting bulk,  $\nabla^2\phi = 0$ , with a capacitance-like boundary condition to close the ‘RC’ circuit [16],

$$C_D \frac{d\Psi_D}{dt} = \sigma E_n, \quad (1)$$

where the local diffuse-layer voltage  $\Psi_D(\phi)$  responds to the normal electric field  $E_n = -\hat{n} \cdot \nabla\phi$ ; the bulk conductivity  $\sigma$  and diffuse-layer capacitance  $C_D$  are usually constants, although these assumptions can be relaxed [10]. The second step is to solve for a Stokes flow with the Helmholtz–Smoluchowski effective slip boundary condition

$$\mathbf{u}_s = -b \mathbf{E}_t = -\frac{\varepsilon_b \zeta}{\eta_b} \mathbf{E}_t, \quad (2)$$

where  $b(\Psi_D)$  is the electro-osmotic mobility,  $\mathbf{E}_t$  the tangential field,  $\zeta = \Psi_D$  is the ‘zeta potential’ at the shear plane ( $\zeta = \Psi_D$  in the simplest models), and  $\varepsilon_b$  and  $\eta_b$  are the permittivity and viscosity of the *bulk* solvent. These types of models are usually derived for a dilute solution at small applied voltages with  $\Psi_D \approx k_B T/e$  [6, 16, 17] and often manage to capture features of ICEO flows at moderate and large voltages. Nevertheless, some crucial effects are still missing.

ICEO flows have a strong sensitivity to solution chemistry, which is under-reported and unexplained. Recent experiments reveal a strong, universal decay of the mobility with bulk concentration  $c_0$ , observed in KCl for ACEO micropumps [11] and in NaCl for ICEP of colloids with partial metal coatings [9]. (For a review, see [15].) In all cases, the flow or particle motion decays above 1 mM salt concentration and becomes difficult to observe above roughly  $c_c \approx 30$  mM, which is well below the concentration of most biological fluids ( $c_0 \approx 0.3$  M). ICEO flows [15] and ac-field-induced interactions in colloids [18] are also sensitive to the particular ions, at a given concentration.

The low-voltage model also fails to describe the reversal of ICEO flow observed in some (but not all) experimental situations. Flow reversal was first reported around metal particles in water [19], where the velocity agreed with the theory [7] only for micron-sized particles and reversed for larger ones (90–400  $\mu\text{m}$ ). The transition occurred when several volts was applied across the particle and reversal was attributed to Faradaic reactions [19]. Flow reversal has also been observed at high voltage ( $> 2$  V) and high frequency (10–100 kHz) in ACEO pumping of dilute KCl [11, 12] and deionized water [13] with 10  $\mu\text{m}$  scale electrode arrays. This reversal

was first attributed to Faradaic reactions [12], but simulations with Butler–Volmer reaction kinetics have failed to predict the observed flow [10]. With non-planar three-dimensional (3D) electrodes, the low-voltage model also fails to predict the double-peaked frequency spectrum, which accompanies flow reversal in some geometries [13].

Although Faradaic reactions surely occur at large voltages, they are dominant at low frequencies in ACEO simulations [10] and experiments (when gas bubbles arise) [11]. Dilute solution theories also predict that nonlinear effects dominate at low frequencies: the differential capacitance of the diffuse layer [2],

$$C_D(\Psi_D) = \frac{\varepsilon_b}{\lambda_D} \cosh\left(\frac{ze\Psi_D}{2k_B T}\right) \quad (3)$$

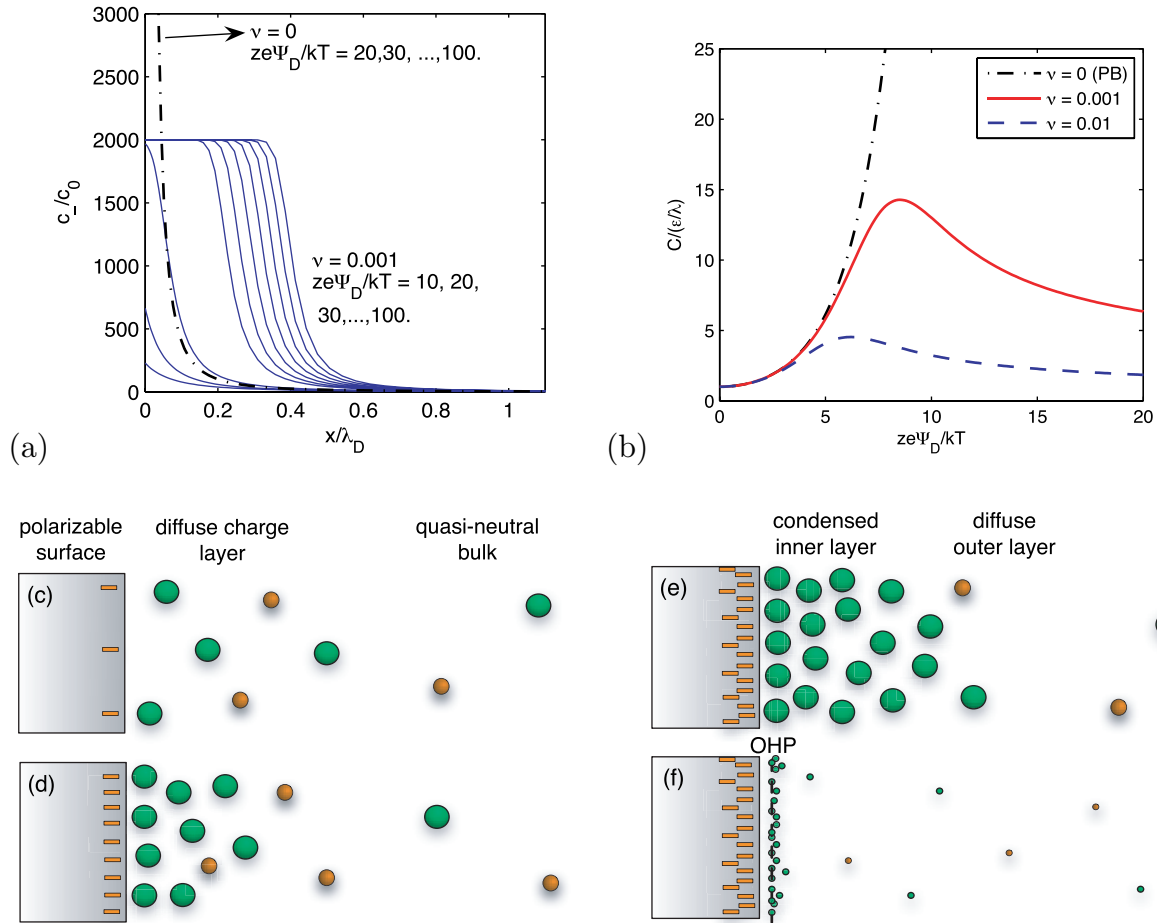
causes the RC charging time to grow exponentially with voltage [10], and salt adsorption and tangential conduction by the diffuse layer are coupled to (much slower) bulk diffusion [16]. (In equation (3),  $\lambda_D$  is the Debye screening length  $\approx 1$ –100 nm for aqueous solutions at room temperature.) Strong flow reversal is experimentally observed at much higher frequencies, and the unexplained concentration dependence seems to be independent of frequency. We conclude that dilute solution theories do not properly describe the dynamics of electrolytes at large voltages.

*Crowding effects*—All dilute solution theories, which describe point-like ions in a mean-field approximation, break down when the crowding of ions become significant, when steric effects and correlations potentially become important. If this can be translated into a characteristic length scale  $a$  for the distance between ions, then the validity of the Poisson–Boltzmann (PB) is limited by a cutoff concentration  $c_{\max} = a^{-3}$ , reached at a fairly small voltage,

$$\Psi_c = -\frac{k_B T}{ze} \ln(a^3 c_0) = \frac{k_B T}{ze} \ln\left(\frac{c_{\max}}{c_0}\right), \quad (4)$$

where  $z$  is the valence and  $c_0$  the bulk concentration of the counterions. In a dilute solution of small ions, this leads to cutoffs well below typical voltages for ICEO flows. For example, even if only steric effects are taken into account, with e.g.  $a = 3 \text{ \AA}$  (including a solvation shell), then  $\Psi_c \approx 0.33 \text{ V}$  for  $c_0 = 10^{-5} \text{ M}$  and  $z = 1$ . To account for the obvious excess ions in PB theory, Stern long ago postulated a static compact monolayer of solvated ions [20]. This is also invoked in some models of ICEO flows, where a constant capacitance is added to model the Stern layer and/or a dielectric coating, which carries most of the voltage when the diffuse-layer capacitance (3) diverges. It seems unlikely that a surface monolayer could withstand several volts, e.g. since dielectric breakdown occurs in most materials (including water) in fields of order  $10 \text{ MV m}^{-1} = 0.01 \text{ V nm}^{-1}$  [21], so the diffuse layer must carry a substantial voltage  $\Psi_D > \Psi_c$  in ICEO experiments. In any case, a dynamical model is required for a condensed portion of the double layer that is built and destroyed as the applied field alternates.

A variety of ‘modified PB equations’ (MPB) have been proposed to describe equilibrium ion profiles near a charged wall [22, 23]. To capture ion crowding effects across a wide range of voltages, we employ the simplest possible MPB model of Bikerman [24] and others [22, 25], which is a continuum approximation of the entropy of ions on a lattice of size  $a$ . As shown in figure 1(a), when a large voltage is applied, the counterion concentration exhibits a smooth transition from an outer PB profile to a condensed layer at  $c = c_{\max} = a^{-3}$  near the surface.

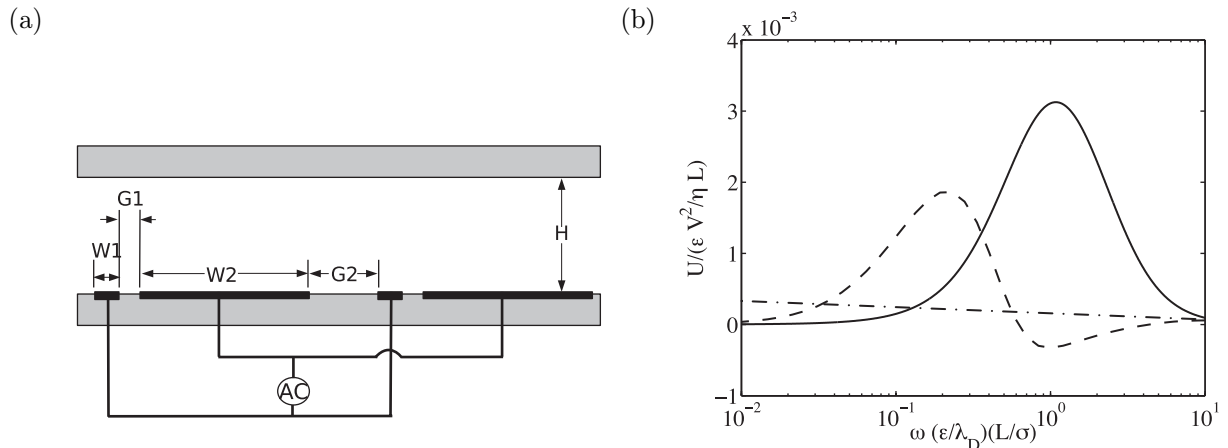


**Figure 1.** (a) The equilibrium distribution of counterions near a surface in PB and a modified (MPB) theory taking into account a minimum ion spacing  $a$  for large applied voltages  $ze\Psi_D/k_B T = 7, 10, 20, \dots, 100$ . (b) The voltage dependence of the differential capacitance  $C_D$  of the diffuse layer from (3) and (5), where  $\nu = 2a^3 c_0$  is the bulk volume fraction of ions. (c)–(f) Physical picture: in a dilute solution, counterions move closer to the surface with increasing voltage from (c) to (d); at larger voltages, with finite-sized ions (d), the counterions inevitably become crowded and form an expanding condensed layer, whereas in classical PB Stern model, (e) point-like ions arbitrarily pile up at the outer Helmholtz plane (OHP).

Equation (3) of the dilute-solution theory predicts that  $C_D$  diverges with  $\Psi_D$ , but with this model, following Freise [26], we predict the opposite dependence [22],

$$C_D^v = \frac{(\epsilon/\lambda_D) \sinh(ze\Psi_D/k_B T)}{[1 + 2\nu \sinh^2(ze\Psi_D/2k_B T)]\sqrt{(2/\nu)[1 + 2\nu \sinh^2(ze\Psi_D/2k_B T)]}}, \quad (5)$$

where  $\nu = 2a^3 c_0$  is the bulk volume fraction of ions. As shown in figure 1(b), the capacitance reaches a maximum near the critical voltage  $\Psi_c$  and then *decreases* at larger voltages because the effective capacitor width grows due to steric effects.



**Figure 2.** (a) Sketch of two periods of a planar electrode-array ACEO pump [4, 27], and (b) the (dimensionless) flow rate versus frequency for the most experimentally studied geometry with period  $L = W1 + W2 + G1 + G2$ , where  $W1 = 4.2 \mu\text{m}$ ,  $W2 = 25.7 \mu\text{m}$ ,  $G1 = 4.5 \mu\text{m}$  and  $G2 = 15.6 \mu\text{m}$  [11, 13, 27] from simulations with different models discussed in the text. In the low-voltage limit  $V \ll k_B T/e = 25 \text{ mV}$ , all models predict a single peak (solid line). For a typical experimental voltage,  $V = 100 k_B T/e = 2.5 \text{ V}$ , PB theory breaks down and its diverging capacitance (3) shifts the flow to very low frequency (dot-dashed line), but accounting for steric effects (5) with a finite bulk volume fraction of ions  $\nu = 0.001$  (dashed line) suppresses this shift and predicts high-frequency flow reversal, similar to experiments [11, 28].

This decrease of diffuse-layer capacitance at large voltages is robust to variations in the model and has major consequences for nonlinear electrokinetics. For example, it provides a simple explanation for the flow reversal seen in ACEO experiments, without invoking Faradaic reactions. As shown in figure 2, numerical simulations of a well-studied planar pump geometry [11, 27] with the standard linear model [3, 4] predict a single peak in flow rate versus frequency at all voltages. If the nonlinear PB capacitance (3) is used in (1) [10], then the peak is reduced and shifts to much lower frequency (contrary to experiments), due to slower charging dynamics at large voltage [16]. The MPB capacitance with steric effects (5) reduces the peak shift and introduces flow reversal similar to experiments, albeit with a large value of  $a = 0.0005 c_0^{-1}$ , perhaps due to the underprediction of liquid steric effects by the lattice approximation [23]. In comparing this model to the experimental data of [11], we find an ion size of approximately 4.4 nm is required, an order of magnitude larger than expected, although hard-sphere models can reduce this discrepancy with ion sizes as small as 1 nm. (See [28] for more details.)

Regardless of the model, the physical mechanism for flow reversal is robust and simple: at low voltage, the pumping direction is set by the larger electrode, but at large voltages, since the more highly charged smaller electrode has its ‘RC’ charging time reduced by steric effects, it ‘wins’ in pumping against the larger electrode at higher frequency. Perhaps a similar effect is responsible for the double-peaked structure at high voltage with some non-planar stepped electrodes [13].

*Induced viscosity increase*—The strong decay of ICEO flow with increasing concentration suggests a dramatic increase in the viscosity of a highly charged diffuse layer. Classical continuum theory provides a general formula for the electro-osmotic mobility [2],

$$b = \int_0^{\Psi_D} \frac{\varepsilon}{\eta} d\Psi = \frac{\varepsilon_b \bar{\zeta}}{\eta_b}, \quad (6)$$

as an integral over the potential difference  $\Psi$  entering the diffuse layer from the bulk. At large voltages, the effective zeta potential  $\bar{\zeta}$  (a measure of flow generated) should be smaller than  $\Psi_D$  as  $\varepsilon$  decreases (due to alignment of water dipoles) and  $\eta$  increases (due to viscoelectric effects) within the diffuse layer.

Focusing on the viscoelectric effect in water, Lyklema and Overbeek [29, 30] first derived a modified slip formula by assuming  $\eta \propto E^2$  in PB theory and predicted that  $b(\Psi_D)$  saturates at a constant value, which decays with increasing  $c_0$ . The saturation, however, relies on the unphysical divergence of the counterion concentration (and thus  $E$ ) in PB theory. Even with a physical cutoff from MPB theory, it seems unrealistic to attribute the solution viscosity solely to the solvent at such large counterion densities.

Instead, we postulate a charge-induced thickening of the electrolyte, where the solution viscosity increases with charge density. In a very crude attempt, we adopt the MPB theory above and postulate that  $\varepsilon/\eta$  diverges as the counterion density (equivalent to the charge density  $\rho$ ) approaches the steric limit as

$$\frac{\varepsilon}{\eta} = \frac{\varepsilon_b}{\eta_b} \left( 1 - \frac{a^3 |\rho|}{ze} \right). \quad (7)$$

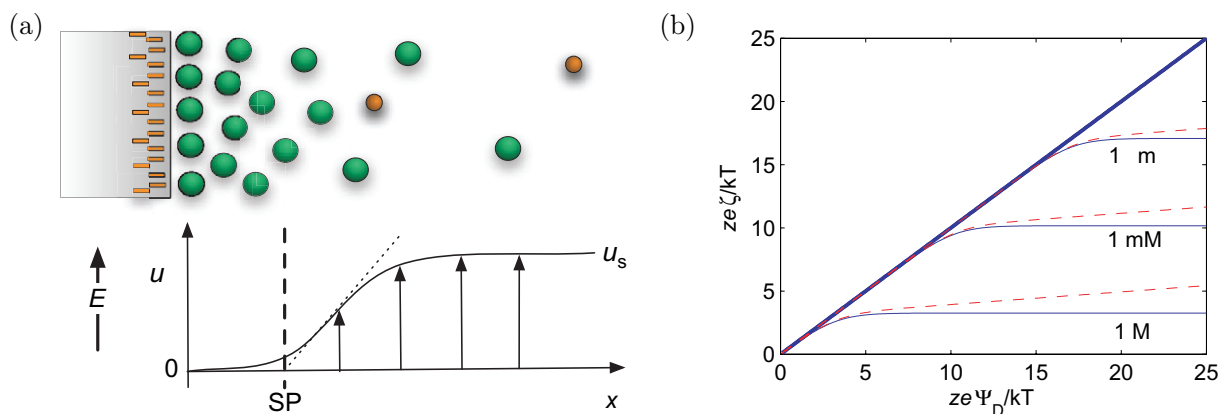
This (arbitrary) choice leads to a simple formula for the effective zeta potential

$$\bar{\zeta} = \Psi_D - \text{sgn}(\Psi_D) \frac{k_B T}{ze} \log \left[ 1 + 4a^3 c_0 \sinh^2 \left( \frac{ze\Psi_D}{k_B T} \right) \right], \quad (8)$$

which reduces to (2) ( $\bar{\zeta} \sim \Psi_D$ ) for  $\Psi_D \ll \Psi_c$  but saturates  $\bar{\zeta} \sim \Psi_c$  for  $\Psi_D \gg \Psi_c$ . From (4), we recover the experimentally observed scaling with concentration in the large voltage limit,  $u \propto \log(c_c/c_0)$ , with  $c_c = c_{\max} = a^{-3}$ . The mobility  $b = \varepsilon_b \bar{\zeta} / \eta_b$  from (8) is also sensitive to the solution chemistry, through  $a$ ,  $z$  and  $c_0$ , unlike the classical formula (2) valid at low voltages. The saturation of  $\bar{\zeta}$  also implies that the scaling of ICEO flows changes from quadratic,  $u \propto E^2$  or  $V^2$ , to linear,  $u \propto |E|$  or  $|V|$  for large dc voltages, and nonlinearity in relaxation times further alters the scaling for ac voltages.

These predictions make the theory more realistic, but the experimentally observed  $c_c = 10$  mM implies a mean ion spacing of  $a = 4.4$  nm (roughly 40 atomic diameters) for the divergence of  $\varepsilon/\eta$ . Even if we view ‘ $a$ ’ in (8) as another cutoff  $a^*$  independent of the steric  $a$  in (5), how could we explain such a large value? Perhaps at large voltages, counterions condense into a sort of Wigner crystal, which resists shear due to strong electrostatic correlations (in addition to viscoelectric effects in the solvent). Indeed, the mean-field approximation breaks down when ion spacings approach the Bjerrum length,  $l_B = (ze)^2 / 4\pi\epsilon k_B T$ , which is 7 Å for bulk water and monovalent ions ( $z = 1$ ). If  $\varepsilon \approx 0.1\varepsilon_b$  (as electrochemists infer for the Stern layer [20]), then  $a \approx l_B$  is possible, so correlation effects on electro-osmotic flow (which to our knowledge have never been studied) could be very significant at large voltages, even in dilute bulk solutions. For a discussion of additional physical effects, see [15].

In conclusion, we have argued that (at least) two new phenomena arise in electro-osmosis at large induced voltages: (i) crowding effects decrease the differential capacitance (figure 1),



**Figure 3.** (a) Sketch of finite-sized hydrated ions near a highly charged surface as in figure 1(e), showing the solution velocity  $u$  profile in response to a tangential electric field; the crowding of hydrated ions increases the viscosity of the condensed layer, and the apparent slip plane ‘SP’ (dashed line) moves away from the surface with increasing voltage. (b) MHS slip formula (8) using Bikerman’s model with ion size  $a = 4 \text{ \AA}$  and charge-induced thickening (7) at different bulk concentrations,  $c_0 = 1 \mu\text{M}$ ,  $1 \text{ mM}$  and  $1 \text{ M}$ . The viscosity is postulated to diverge either at a mean ion spacing  $a_j = a$  (solid curves), so the condensed layer in figure 1(a) is effectively rigid, or at  $a_j = 0.9a$  (dashed curves), so it flows with a large, but finite viscosity.

which can explain high-frequency flow reversal in ACEO pumps (figure 2); (ii) viscosity increase upon ion crowding saturates the mobility (figure 3), which implies dependence on solution chemistry and flow decay with increasing concentration. Although we believe these predictions are robust we have not managed to combine our simplest models (5) and (8) into a complete theory. For example, choosing  $a \approx 1\text{--}4 \text{ nm}$  in (8) to fit the critical concentration  $c_c \approx 0.01\text{--}0.05 \text{ M}$  tends to eliminate flow reversal in figure 2(b) since the reduced mobility of small electrode in figure 2(a) offsets its faster charging. Choosing a ‘steric’ value  $a \approx 1\text{--}4 \text{ \AA}$  in (5) shifts the flow to too low frequency in dilute solutions (as in PB theory [10]) and overestimates the concentration scale for ICEO flow suppression in (8). More realistic MPB models, which predict stronger steric effects [23], may improve the fit, but correlation effects on ICEO flow may also need to be described.

Of course, our models are over-simplified, but remember that the challenge is to describe ICEO flow over more than three decades of diffuse-layer voltage from  $k_B T/e = 25 \text{ mV}$  to  $\approx 10 \text{ V}$ . The upper limit corresponds to a new regime for the theory of electro-osmosis, where counterions are condensed near a highly charged surface. Nanoscale experiments and atomic-level simulations will be crucial to further develop the theory.

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