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Induced-charge electrokinetic phenomena

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ABSTRACT

The field of nonlinear "induced-charge" electrokinetics is rapidly advancing, motivated by potential applications in microfluidics as well as by the unique opportunities it provides for probing fundamental scientific issues in electrokinetics. Over the past few years, several surprising theoretical predictions have been observed in experiments: (i) induced-charge electrophoresis of half-metallic Janus particles, perpendicular to a uniform AC field; (ii) microfluidic mixing around metallic structures by induced-charge electro-osmosis, and (iii) fast, high-pressure AC electro-osmotic pumping by non-planar electrode arrays, and ICEK effects upon the collective behavior of polarizable particle suspensions has been studied theoretically and computationally. A new experimental system enables a clean and direct comparison between theoretical predictions and measured ICEK flows, providing a route to fundamental studies of particular surfaces and high-throughput searches for optimal ICEK systems. Systematic discrepancies between theory and experiment have engendered the search for mechanisms, including new theories that account for electrochemical surface reactions, surface contamination, roughness, and the crowding of ions at high voltage. Promising directions for further research, both fundamental and applied, are discussed.

1. Introduction

The classical subject of electrokinetics (electrically driven fluid flow and particle motion) in liquid electrolytes, originally developed in colloid science [1–3], is experiencing a renaissance in microfluidics [4–8]. Electrokinetic phenomena scale favorably with miniaturization and offer unique advantages in microfluidics, such as low hydrodynamic dispersion, no moving parts, electrical actuation and sensing, and easy integration with microelectronics. Until recently, almost all studies of electrokinetics have assumed linear response in the applied voltage, based on the hypothesis of fixed surface charge (or fixed "zeta potential" relative to the bulk solution). However, linear electrokinetic phenomena have a number of possible drawbacks: Direct current (DC) must be passed to sustain electric fields; electrophoresis cannot separate particles with fixed, uniform zeta potential by size or shape in free solution; and large voltages must be applied along centimeter or greater distances to achieve the necessary field strengths, giving little direct control over local fields and flows within microchannels.

Ten years ago, Ramos et al. [9•] discovered alternating-current electro-osmotic flow (ACEO) over microelectrodes, and Ajdari [10•] described how the effect could be exploited for low-voltage microfluidic pumping using asymmetric arrays of interdigitated electrodes. These breakthroughs, supported by the experiments of Green et al. [11,12,13••], Brown et al. [14], Studer et al. [15•] and others, focused attention on nonlinear AC electrokinetics in microfluidics [16,17••] and set the stage for the advances described in this review. This work clearly demonstrated that electrokinetic phenomena can derive from non-uniform, transient charge on an electrode surface, controlled more by the applied voltage than by chemical equilibrium.

A few years later, the present authors pointed out that the underlying physical mechanism of an electric field acting on its own induced charge near a polarizable surface is more general and coined the term "induced-charge electro-osmosis" (ICEO) to describe it [18,19••]. Through a variety of examples, such as those sketched in Fig. 1, it was argued that ICEO flows can occur around any polarizable (metal or dielectric) surface in the presence of any (DC or low-frequency AC) electric field — i.e. not exclusively over electrodes whose voltage is directly forced to oscillate at a certain frequency, as in ACEO. The fundamental physical process responsible for 'induced-charge electro-osmosis' thus unified ACEO and travelling-wave electro-osmosis (TWEO) [32,33] over micro-electrode arrays (Fig. 1d), with other seemingly unrelated phenomena, such as DC electrokinetic jets at dielectric microchannel corners [30] (Fig. 1c), AC electrohydrodynamic interactions and self-assembly of dielectric colloids on electrodes [34–37], and hydrodynamic interactions among polarizable particles [21•,22••] (Fig. 1a).

The latter effect was apparently the earliest example of "ICEO" reported in the literature, from the pioneering work of V. Murtsovkin, A. S. Dukhin and collaborators in the 1980s on polarizable colloids (reviewed in Ref. [22••]), long before analogous ICEO flows were

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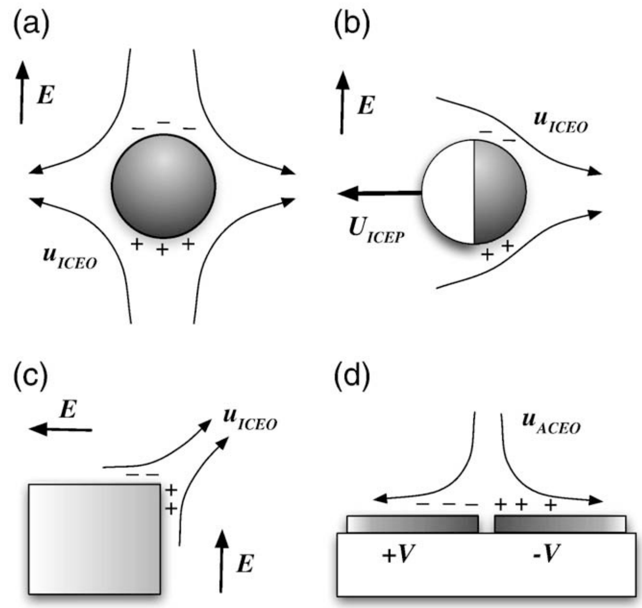

Fig. 1. Examples of nonlinear electrokinetic phenomena, driven by induced charge (+, −)in the diffuse part of the electrochemical double layer at ideally polarizable, blocking surfaces, subject to an applied electric field *E* or voltage *V*. (a) Induced-charge electro-osmosis (ICEO) around a metal post [18,19••,20•] or particle [21•,22••], (b) induced-charge electrophoresis (ICEP) of a metal/insulator Janus particle [28••,29••], (c) a nonlinear electrokinetic jet of ICEO flow at a sharp corner in a dielectric microchannel [30,31•], and (d) AC electro-osmosis (ACEO) over a symmetric pair of microelectrodes [9•,10,13••]. (Reproduced from Bazant et al. [17••]).

observed in a microfluidic device by Levitan et al. [20•]. The quadrupolar ICEO flow around an ideally polarizable sphere in a uniform electric field, and the resulting relative motion of two spheres, were first predicted by Gamayunov et al. [21•]. Murtsovkin's group proceeded to observe these flows around mercury drops [23] and metallic particles [24]. For larger particles, the flow was in the opposite direction of the theory, and this was conjectured to be due to the onset of Faradaic reactions at large induced voltages, consistent with recent experiments on millimeter scale metal objects by Barinova et al. [25]. (The Ukrainian school of Shilov [26] and Mishchuk [27] continue to make advances in nonlinear electrophoresis, e.g. involving surface conduction or convection around fixed-charge colloids, which are beyond the scope of this article.)

Compared to colloids, microfluidic systems enable much greater control over experimental geometries, so this context led the present authors to shift the focus to several novel aspects of ICEO flows [18]: (i) The design of and control over local conditions for mixing and pumping of fluids in microchannels [19••], as well as direct tests of the 'standard model' of electrokinetics, and (ii) asymmetric geometries of channels and particles [28••], which give rise to some surprising phenomena from the classical colloidal standpoint. The concept of ICEO mixing by applying fields around fixed metal microstructures [18] is now beginning to be reduced to practice [38•,39,40] (see below). Motivated by Ajdari's principle of ACEO pumping [10•], various ways were also proposed to manipulate fluids and particles by exploiting *broken symmetries* in ICEO flows [18,28••]. It was predicted that an anisotropic particle subjected to a DC or AC field (below the frequency of double-layer charging) will generally translate and/or rotate by "induced-charge electrophoresis" (ICEP), while a fixed anisotropic object will pump the fluid by ICEO. These nonlinear phenomena are very different from classical electrokinetics with surfaces of constant charge and are also beginning to be observed in experiments [29••].

In this article, we review recent advances in induced-charge electrokinetics, focusing on key papers from the past several years. We begin with experimental advances in Section 2 and move on to theoretical advances in Section 3. Throughout the paper, we emphasize open questions, and in Section 4 we close with a list of suggestions to guide the next round of experimental and theoretical researches.

2. Recent experimental advances

2.1. Induced-charge electrophoresis

A classical result in electrophoresis is the prediction that a particle of uniform surface charge (or zeta potential) with thin double layers always moves parallel to an applied electric field, with an electrophoretic mobility that is independent of its shape and size [3]. With non-uniform (but fixed) surface charge, more complex motions are possible as first noted by Anderson [41], such as translation perpendicular to a DC field or continuous rotation for non-spherical shapes predicted by Long and Ajdari [42], although we are not aware of any related experimental observations. For ideally polarizable particles, the present authors [18] first predicted that any broken symmetry in ICEO flow, whether in shape, surface properties (e.g. dielectric constant), or field gradient, will generally cause a colloidal particle to move by ICEP in DC or AC fields (of sufficiently low frequency to allow double-layer relaxation).

Although homogeneous particles with irregular shapes can have rather subtle response [28••,43], perhaps the simplest example of ICEP is a spherical, metallo-dielectric Janus particle. In a free solution, the particle rotates to align the metal/dielectric plane with the applied field, while translating toward its dielectric end, ultimately translating perpendicular to the field [28••]. As shown in Fig. 1(b), the motion results from suppressing half of the ICEO quadrupolar flow for a symmetric metal sphere in Fig. 1(a) on the dielectric side, leaving the metallic side to act as an "engine".

Gangwal et al. [29••] recently reported what appears to be the first experimental observation of transverse electrophoresis (whether linear or nonlinear), using metallo-dielectric Janus particles (latex microspheres, half coated with gold). As shown in Fig. 2, the particles were observed to translate steadily in directions perpendicular to a uniform AC field. In pure water and dilute NaCl solutions, the motion had the predicted scaling $U_\infty \varepsilon E^2 R/\eta$, where E is the field amplitude, R is the particle radius, and ε and η are the permittivity and viscosity of the solution, respectively. Significant departures from the theory were observed with increasing salt concentration ($c > 1$ mM) and/or increasing voltage applied across the particles ($ER > 0.1$ V). In particular, the motion became too slow to observe above 10 mM salt concentration, as in all other experimental studies of ICEO flow (as reviewed in Ref. [17••] and discussed below).

A surprising aspect of these experiments was the strong interaction of the Janus particles and the glass walls of the microchannel. Although symmetric polarizable particles are expected to be repelled from insulating walls [45], the Janus particles were attracted to the surface and observed moving parallel to the surface, very close to it (apparently within a particle diameter). The wall attraction has been attributed to hydrodynamic torque [44], which rotates the (forward facing) dielectric end toward the wall, causing the Janus particle to swim toward it until a collision, and in some cases translate along the wall with a stable tilt angle around 45°. This example shows the rich possibilities of ICEP in confined geometries, which we believe merit further exploration.

The collective dynamics of colloids of polarizable particles in DC and low frequency AC fields have also been studied. This was the motivation for the original analysis of "ICEO" by Gamayunov, Murtsovkin and Dukhin [21•], who predicted that the quadrupolar ICEO flows around two ideally polarizable spheres cause axial attraction along the field direction and radial repulsion from the equator. Such pair interactions have recently been observed for metallic rods in simulations by Saintillan et al. [46] and experiments by Rose et al. [47,48•]. Furthermore, ICEP orientation of metallic rods

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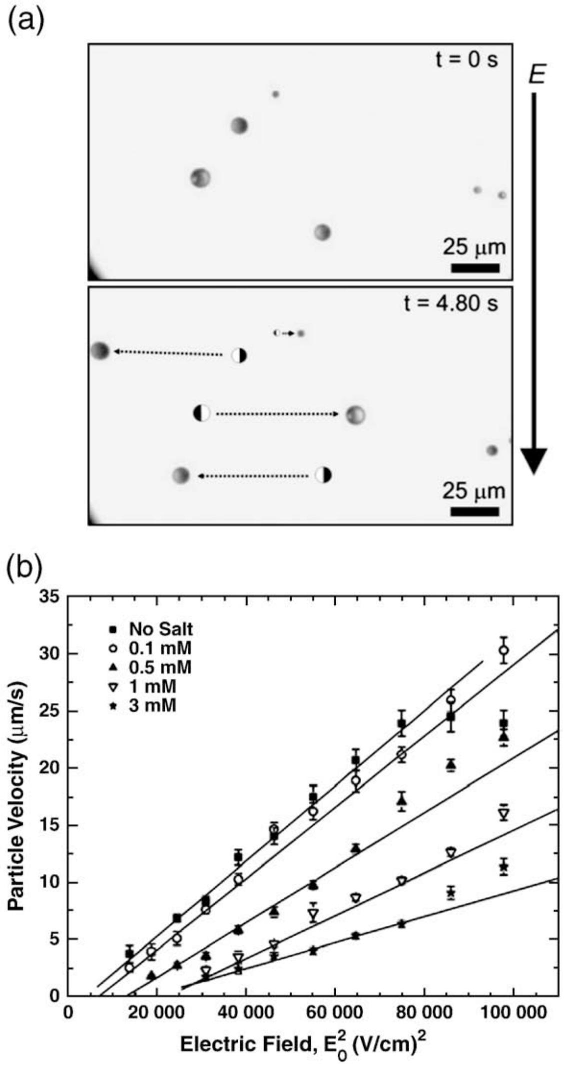

Fig. 2. Experimental observation of induced-charge electrophoresis of metallo-dielectric Janus particles (latex spheres half coated with gold) perpendicular to a uniform AC field (in either direction) by Gangwal et al. [29••], consistent with theoretical predictions [28••,44] sketched in Fig. **1**(b). (a) Snapshots of particle motion, showing that velocity increases with size (linearly up to saturation for diameters over 10 μm). (b) Velocity versus field intensity squared at 1 kHz for 5.7 μm particles at various concentrations of NaCl, showing good linear fits for small fields and low ionic strengths. (Reproduced from Gangwal et al. [29••]).

was shown to suppress a well-known sedimentation instability [49•,50]. Anisotropic polarizable particles, such as Janus spheres, would exhibit more subtle many-body correlations and new possibilities for self-assembly.

2.2. Induced-charge electro-osmosis

Building on the work of Soni et al.[53], Pascall et al.[51••] developed a novel automated system, capable of measuring and characterizing ICEO flows over various surfaces with various electrolytes under approximately 1000 conditions per day. In particular, they used micro-particle image velocimetry to measure the ICEO slip velocity just above an electrically floating, 50-μm-wide gold electrode, evaporatively deposited onto the floor of a microchannel (Fig. 3), which can be computed directly using the standard electrokinetic equations. To specifically test the effects of surface contamination upon ICEO flows, Pascall et al.'controllably contaminated' the electrode with an SiO_2 film of various known thicknesses, and directly compared predicted ICEO flows against measured values. Accounting for the physical dielectric effect of the contaminant, as well as the 'buffer capacitance' of ion adsorption onto reactive sites on the surface [52], gave quantitative theory/experiment agreement (within a factor of 3 for approximately 1000 experimental conditions). While their study remained within the low-ζ limit, their techniques enable high-throughput measurement and characterization of any material that can be deposited onto a conducting substrate, under a wide range of experimental conditions. Future directions will be discussed below.

The present authors proposed the use of ICEO flow around metallic microstructures (posts, surface patterns, etc.) for microfluidic mixing [18,19••], with the potential advantages of low power, programmability, and local flow control. Theoretical work has shown that ICEO-based micro-mixing can be enhanced by broken symmetries [28••], temporal modulation to achieve chaotic streamlines [54], topological shape optimization [55•], or by the introduction of sharp corners in dielectric channel side walls [31•]. The first microfluidic demonstration of ICEO flow around a metal cylinder by Levitan et al. [20•] showed steady vortices, but did not study mixing.

In 2008, two groups reported the first experimental demonstrations of microfluidic mixing by ICEO flow around metallic microstructures, effectively reducing to practice the theoretical predictions of Ref. [18]. (i) Harnett et al. [38•] integrated an array of gold-coated posts of triangular cross section in a microchannel with electrodes applying a low-frequency AC field on the side walls (Fig. 4). The post-array mixer was placed at the junction of two Y-channels, and programmable on/off mixing of two different streams of dilute electrolytes was demonstrated. Good agreement with theoretical predictions was noted, albeit with a "correction factor" of 0.25 (see below). (ii) Wu and Li [39,40] reported simulations and experiments on ICEO mixing in flow past pointed platinum "hurdles" (floating electrodes) and different geometrical designs were compared. Further design improvements could benefit from numerical optimization methods for ICEO flows [55•].

Recently, it was shown that the use of electrically floating metallic microstructures to drive ICEO flows in these kinds of microfluidic devices requires considerable care to avoid (or exploit) unexpected electrokinetic couplings. In particular, a new mechanism for ICEO flow was experimentally and theoretically demonstrated by Mansuripur et al. [56•], in which capacitive coupling between a floating electrode and the external apparatus drives asymmetric flows over what would otherwise seem to be symmetric systems. In brief, the potential drop between the applied potential ϕ_B above the floating electrode and the (ground) potential of external conductors (e.g. the microscope stage) occurs across the double layer (with total capacitance $C_{DL}A_{DL}$) and across a stray coupling capacitor C_S (e.g. through the glass slide, where $C_s \sim {}_g A_e/d$). The stray double-layer varies in phase with $\phi_B(t)$, and thus with the parallel field $E_B(t)$, giving a non-zero time-averaged flow, much like fixed-potential ICEO [19••], that is generally directed towards the grounded electrode. Mansuripur demonstrated ways to manipulate or eliminate this flow through direct control of the 'external' potential or through geometric design of the mutual capacitance C_S.

2.3. AC electro-osmosis

Since the original work of Ramos et al. [9•], a substantial theoretical and experimental literature has developed on ACEO flows over electrode pairs [9•,11,12,13••,57,58••] and interdigitated periodic arrays [10•,14,15•,59•,60–64]. This work has mostly focused on the fundamental physics of flow generation (see below), but recently, there also been rapid progress in the engineering of ACEO pumps for portable microfluidic devices. Following Ajdari's original proposal to pump fluids using asymmetric electrode arrays [10•], all experimental and theoretical work initially focused on the design of Brown et al. [14] with co-planar electrodes with unequal widths and gaps, but this

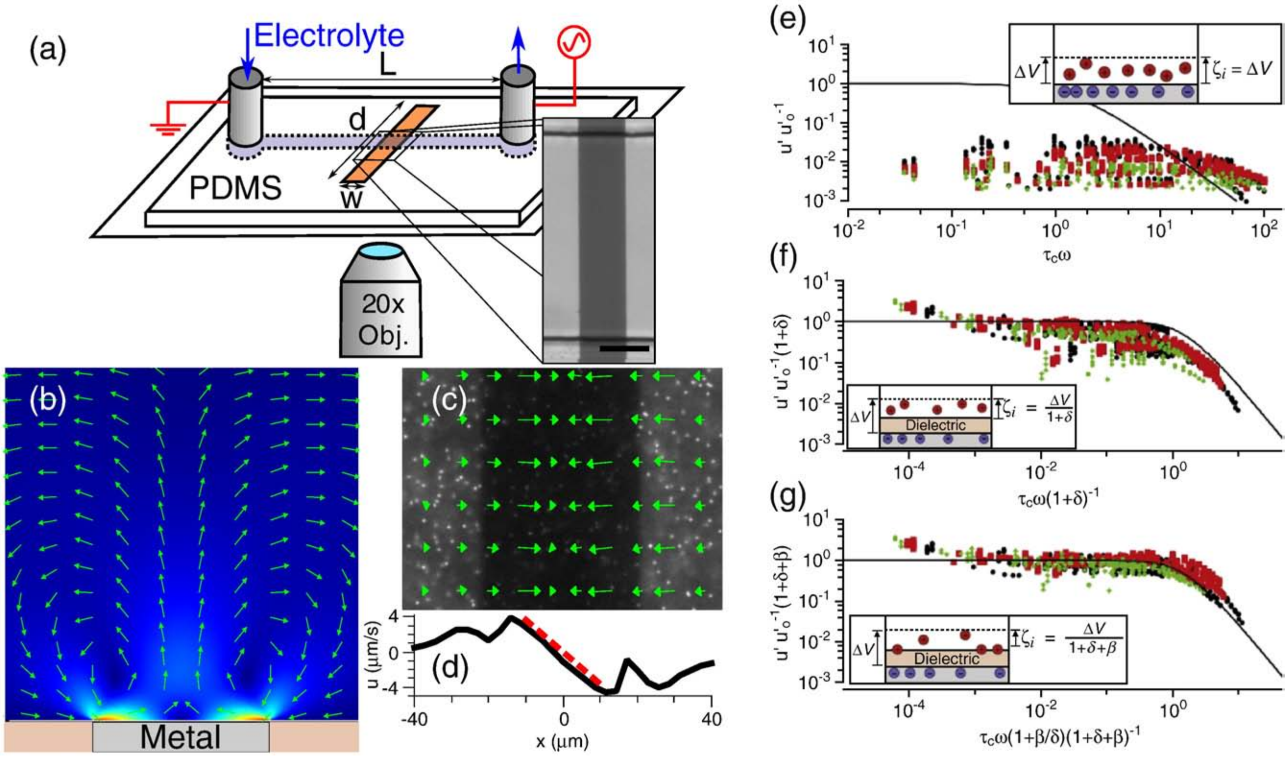

Fig. 3. The experimental system of Pascall and Squires [51••] enables the systematic comparison of theory and experiment, under about 1000 distinct conditions per day, in a relatively simple system, enabling ICEK studies for general thin film materials that can be deposited on metal electrodes. A planar gold strip (50 μm) sits perpendicular to a PDMS microchannel, along which an AC field is applied, driving two counter-rotating ICEK rolls (b). Micro-PIV measurements just above the metal strip (c–d) recover an ICEK slip velocity that varies linearly with distance from the strip center. Measurements over strips 'controllably contaminated' with SiO_2 films of varying thickness (33–100 nm) show poor agreement with a theory that ignores the SiO_2 (e), improved agreement when the physical dielectric property of the contaminant is included (f), and remarkable collapse when the surface chemistry of the SiO_2 layer is included. Both the frequency dependence and magnitude are quantitatively captured for 987 distinct experimental conditions using a single unknown parameter (buffer capacitance [52]). Figure adapted from [51••].

design is inherently inefficient and prone of flow reversals due to the competition of opposing slip velocities. Bazant and Ben predicted theoretically that much faster and more robust flows can be generated by three-dimensional (3D) electrode shapes, which raise the forward slip velocities on steps and recess the reverse slip velocities in counter-rotating vortices, resulting in a "fluid conveyor belt" [59•]. Pumping by 3D ACEO arrays was then investigated in experiments [60,61] and simulations [63].

Huang et al. recently reported the state-of-the-art in 3D ACEO micropumps and demonstrated the first integration of ACEO (or ICEO) flow control in a portable biomedical lab-on-a-chip device [65••]. (See Fig. 5.) Their design is based on (i) theoretically optimal electrode shapes to achieve ultrafast flows [63] and (ii) long, serpentine microchannels to dramatically boost the head pressure, by an order of magnitude over previous devices. With 1.06 V (rms) applied at 1–10 kHz, the pump achieved pressures over 0.01 atm and mean velocities over

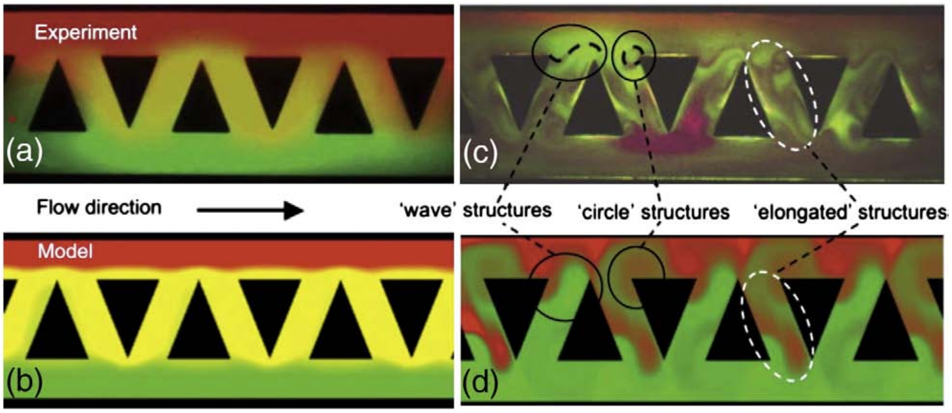

Fig. 4. Experimental observation of induced-charge electro-osmotic mixing by Harnett et al. [38•], consistent with the theoretical predictions [18,19••,28••] sketched in Fig. 1(a). Two colored fluid streams of 0.1 mM KCl flowing at 0.1 μl/min from left to right undergo convective mixing by an array of asymmetric metal posts in a transverse AC field (6 Vpp, 100 Hz applied by electrodes above and below, separated by the channel width 200 μm). Images from experiments (a,c) and simulations of advection–diffusion in ICEO flow in the same geometry (b,d) show the distribution of red and green fluorescent beads after loading (a,b) and during mixing (c,d). (Reproduced from Harnett et al. [38•]).

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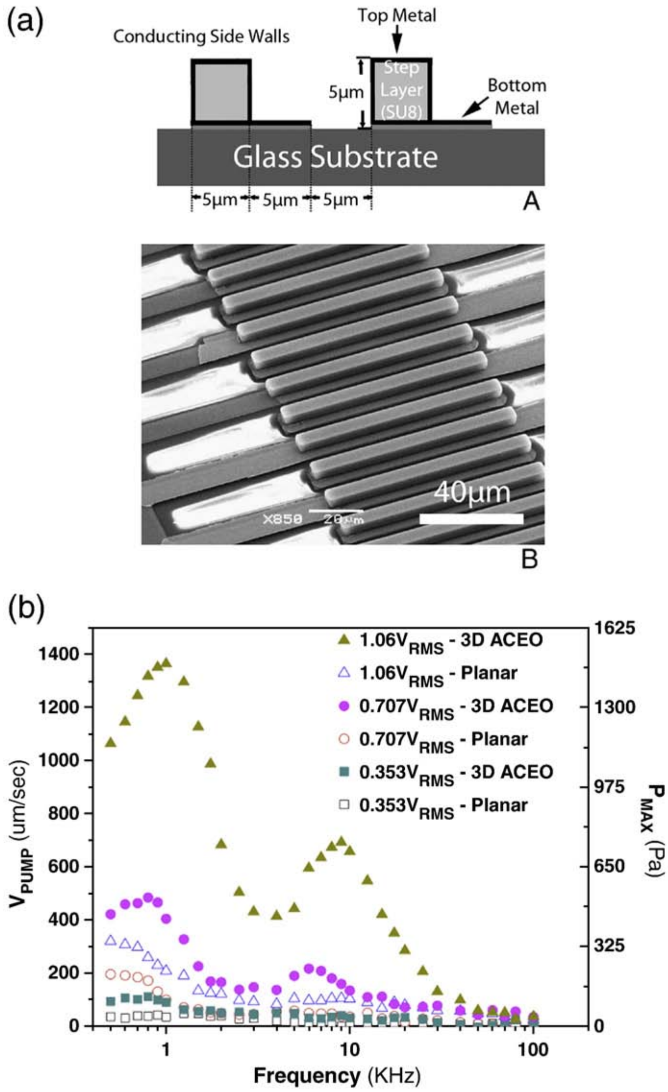

Fig. 5. State-of-the-art ACEO micropumps by Huang et al. [65••], using theoretical predicted optimal electrode shapes to create a "fluid conveyor belt" [59•,63]. (a) Fabrication schematic and SEM image of a 3D stepped electrode array, close to the predicted optimal geometry. (b) Experimental demonstration of ultrafast (>1 mm/s) mean velocity over the pump for water in a microfluidic loop with 1.06 Vrms (3 Vpp), outperforming the standard planar pump [14,15•] shown below in Fig. 6(b). The head pressure (>1% atm) is increased by an order of magnitude using long serpentine channels to hinder reverse pressure-driven flow. (Reproduced from Huang et al. [65••]).

1 mm/s in water, sufficient to drive flows for an on-chip DNA micro-array assay. The current (mA) and power consumption (mW) are easily provided by a small Li–ion battery, so this work opens new possibilities for portable or implantable microfluidic systems. As with other ICEO phenomena, however, ACEO pumps require dilute electrolytes, which may be a fundamental limitation [17••].

Other recent experimental advances pertain to the role of Faradaic reactions in ACEO micropumps. Lian and Wu [66•] demonstrated ultrafast mean flow over a planar electrode array using AC forcing with a large DC bias (2.5 mm/s at 5.4 Vrms), which requires electrolysis or other Faradaic reactions to sustain the direct current. This work builds on previous experimental studies [67,68], although the mechanism of flow control by DC bias has not yet been well understood or predicted by a mathematical model. A promising step in this direction was taken by Garcia-Sanchez et al. [69••] in the different situations of travelling-wave electro-osmosis, where fast, reverse pumping at high voltage was associated with electrolysis, bulk pH gradients, and electro-convection (see below).

3. Recent theoretical advances

3.1. Background

The current theoretical understanding of induced-charge electrokinetics is based on the "Standard Model" [1,2] — namely, the Poisson–Nernst–Planck (PNP) equations of ion transport, coupled to the Navier–Stokes (NS) equations of viscous fluid flow, in the limit of double layers that are thin compared to geometrical length scales in the system. The standard model has had many successes in predicting new phenomena, yet fails to provide robust quantitative predictions [17••]. The crucial assumption is that of "weakly nonlinear" charging dynamics [70•,71], which requires that the applied voltage be small enough not to significantly perturb the bulk salt concentration, whether by double-layer salt adsorption, surface currents, or Faradaic reactions. In this regime, the problem is greatly simplified, and the electrokinetic problem decouples into one of electrical relaxation and another of viscous flow. The electrical problem involves solving Laplace's equation with a time-dependent "RC" boundary condition for capacitive charging of the double layers. The tangential electric field then acts on the induced charge in the diffuse part of the double layer to drive electro-osmotic slip. The flow problem involves creeping (Stokes) flow, driven by the induced-charge electro-osmotic slip.

Although this model can be rigorously justified only for very small voltages, $\Psi_D \ll kT/e$, in a dilute solution [12•,19••,70•,71], it manages to describe many features of ICEO flows at much larger voltages. The Standard Model has been widely used to model nonlinear electrokinetic phenomena in microfluidic devices, such as ACEO flows around electrode pairs [9•,11,12,13••] and arrays [10•,14,59•,61–63], TWEO flows [32,33,72], ICEO flow around metal structures [18,19••,20•,39,40, 54,55•,73] and dielectric corners [30,31•] and particles [19••,74,75], fixed-potential ICEO around electrodes with a DC bias [19••,51••], ICEP motion of polarizable asymmetric particles [18,19••,28••,43], collections of interacting particles [46,47,49•,76], particles near walls [44,45], and particles in field gradients [28••].

In spite of many successes, the Standard Model, and its underlying basis in the PNP/NS equations, has serious shortcomings, recently reviewed and analyzed in Ref. [17••]. In all cases, it over-estimates observed fluid velocities, sometimes by orders of magnitude. (See Table 1 of Ref. [17••]). The reasons for these discrepancies are not yet understood. As noted above, it also fails to capture key experimental trends, such as the decay of ICEO flow with increasing salt concentration, flow reversals at high voltage and/or high frequency, and ion-specificities.

In the remainder of this section, we discuss recent theoretical advances, which extend the Standard Model in several ways: (i) thin-double-layer approximations for large induced voltages based on the classical PNP/NS equations, (ii) thick-double-layer approximations at low voltages, (iii) modified boundary conditions for electrochemical processes, and (iv) modified PNP/NS equations for large voltages and/or concentrated solutions.

3.2. Nonlinear charging dynamics of thin double layers

Starting from a given transport model, thin-double-layer approximations can be systematically derived by the method of matched asymptotic expansions (where the double layer acts as a mathematical boundary layer of non-zero diffuse charge at leading order). As reviewed in Ref. [70•], this approach has been extensively applied to the classical PNP/NS equations for dilute solutions in the contexts of electrokinetics and electrochemical systems, although mostly for steady-state problems and weakly charged surfaces (small double-layer voltages). In this regime, asymptotic analysis has been used to derive the Standard Model for ACEO flow at electrodes [12•] or more general cases of ICEO flow at ideally polarizable [19••] or dielectric [31•] surfaces. (In the different situations of large normal current, e.g.

at electrodialysis membranes [77] or Faradaic electrodes [78], there has also been extensive analysis of the breakdown of the quasi-equilibrium double-layer approximation and associated hydrodynamic instability [79].)

Nonlinear extensions of the Standard Model are beginning to be developed for electrochemical relaxation and ICEO flow in response to large, time-dependent voltages. Bazant, Thornton and Ajdari [70•] considered ideally polarizable parallel-plate electrodes and first showed that linear "RC" response to a large applied voltage is followed by a slower diffusive relaxation, as highly charged double layers begin to adsorb a significant amount of neutral salt from the bulk solution. They also distinguished "weakly nonlinear" and "strongly nonlinear" dynamical regimes, by the intensity of salt concentration perturbations. In the weakly nonlinear regime, Suh and Kang [80] showed that oscillating diffusion layers form in response to AC forcing, similar to Warburg impedance [81], but with twice the applied frequency, since salt adsorption by the double layers does not depend on the polarity of the voltage. They applied this model to ACEO flow over an electrode pair, and found improved agreement with experiment (also due to modified boundary conditions — see below). In the strongly nonlinear regime, Olesen et al. [82] recently reported the analysis of strongly nonlinear response to large AC voltages, which significantly deplete the bulk solution and can even drive the double layers significantly out of equilibrium.

Another surface phenomenon in electrolytes, which becomes important at the same time as double-layer salt adsorption [70•], is tangential conduction through the double layer [71,83,84]. Building on the early work of Bikerman [85], Dukhin developed the theory of surface conduction and concentration polarization in linear electrokinetics [86]. In nonlinear electrokinetics, Murtsovkin [22••] first estimated the effects of surface conduction (non-zero Dukhin–Bikerman number) in what we call "ICEO flow" around highly charged polarizable particles in small electric fields. Surface conduction tends to "short circuit" double layer polarization and thus typically reduces ICEO flow. Even in the absence of flow, the analysis of surface transport phenomena is rather complicated for large applied fields, since salt adsorption is nonlinearly coupled to surface transport and bulk diffusion [71]. The combination of nonlinear electrochemical relaxation with electrokinetics at large induced voltages is a very challenging theoretical problem, which to our knowledge only been tackled in the Ph.D. thesis of Olesen [87•].

3.3. Linear response for thick double layers

A number of theoretical studies have allowed for arbitrary DL thickness in a dilute solution while solving the linearized equations of ion transport and fluid flow in the regime of low voltages. This modeling approach has been applied to ACEO [12•] and TWEO [88] flows over electrode arrays and ICEK flows around metal spheres in uniform [89] and non-uniform [90] fields. Gregersen et al. [73] examined ICEO flows over thick planar electrodes, and directly compared results from finite-element solutions of the full PNP and NS equations against those obtained using a thin-DL 'slip' approximation, in both the linear and the weakly nonlinear regime. They found surprisingly large discrepancies: even modest (5%) agreement with full numerical calculations required exceedingly thin double layers ($\lambda_D/\text{height} < 10^{-3}$), and 40% discrepancies were found around metal cylinders of radius a even for $\lambda_D/a = 10^{-2}$. By contrast, the analytic solution of Yariv and Miloh [89] for ICEO around a metallic sphere with finite λ_D/a reveals the relative deviation to be $3\lambda_D/a$, implying a much less surprising 3% discrepancy for $\lambda_D/a \sim 10^{-2}$. The source of the strong discrepancies in [73] is not clear. The thin-DL approach in [73] includes surface conduction, but neglects bulk concentration polarization (CP), which generally retards ICEO flows as ζ increases. Nonetheless, Gregersen et al. found significant discrepancies even for small ζ, where CP is negligible. If the thin-DL 'slip velocity' approximation does indeed err so dramatically, it will be important to determine the reason for the error and patch it, as thin-DL 'slip' models are much easier to implement in investigating systems of any real complexity.

3.4. Electrochemical kinetics

The specific adsorption of ions on an electrode surface is a crucial aspect of double-layer modeling in electrochemistry [91], which is beginning to be included in models of nonlinear electrokinetics. For example, surface adsorption of hydronium ions onto the acid sites of silica surfaces contributes an additional capacitor (called the 'buffer capacitance' by van Hal et al. [52]) which reduces the charge stored in the diffuse part of the double layer. From a physical standpoint, some ions in the 'induced' double-layer chemically adsorb onto reactive sites on the surface, and as such do not contribute to ICEO flow. This reduces the magnitude of the field-effect flow control, wherein an auxillary electrode is used to directly change the surface potential [92]. Varying both auxillary and bulk fields at the same frequency leads to a non-zero, time-averaged, AC flow-FET whose magnitude is well-described using surface adsorption of hydronium ions [93]. Recently, Suh and Kang [58••] used a Langmuir isotherm for (non-specific) surface adsorption of ions in a model of ACEO flow over an electrode pair and demonstrated improved fitting of the original experimental data of Green et al. [13••].

Another important electrochemical effect at large voltages is the onset of Faradaic charge–transfer reactions, such as electrolysis of water, as clearly evidenced by bubble formation in low-frequency ACEO experiments [15•]. Ajdari [10•] first predicted that Faradaic reactions can lead to weak flow reversal of planar ACEO pumps at low frequency, and this effect has recently been observed in experiments by Gregersen et al. [94]. Olesen et al. [95•] also included Faradaic reactions in low-voltage models of planar ACEO pumps using linearized Butler–Volmer equation but were unable to predict the experimentally observed strong flow reversal at high frequency (see below). However, it is clear from this work that Faradaic reactions can "short circuit" capacitive charging of the double layers, and thus generally reduce ICEO flows.

Recent advances in modeling TWEO have begun to reveal more clearly the role of Faradaic reactions. Linearized models of low-voltage TWEO have been developed by Ramos et al. [72,88], which also allow for effects of electro-convection *outside* the double layers, due to concentration polarization and differences in ion mobilities. Strong flow reversal has been observed at high voltage (and all frequencies) in TWEO by García-Sanchez et al. [69••,96•] and correlated with evidence of Faradaic reactions, including pH gradients, slow diffusive relaxation, and bulk electro-convection. This work shows that induced charges in the quasi-neutral bulk region may be responsible for large-voltage flow reversal of TWEO and suggests that Faradaic reactions and bulk electro-convection should be included in models of other induced-charge electrokinetic phenomena.

An interesting direction may be to focus on fixed-potential ICEO flow around a flat floating metal electrode in a microchannel, as in the experiments of Pascall et al. [51••] discussed above, only without the dielectric coating layer. At low frequency and high voltage, electrochemical reactions become important, and the metal acts as a "bipolar electrode" with one end polarized as a cathode and the other as an anode, in response to applied field. (The system then resembles two electrochemical cells in series.) Under direct current conditions, Duval et al. [97•,98,99,100] have shown that Faradaic reactions with a known redox couple can alter the electrokinetic response of the metal surface, and the groups of Crooks and Tallerek [101,102,103•] have shown how water and buffer reactions can lead to electric field gradient focusing of charged analytes, due to the spatially dependent electrophoretic velocity near the bipolar electrode. It would be interesting to extend the models in these papers to include diffuse-

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layer effects on reaction rates (the generalized Frumkin correction to the Butler–Volmer equation [104,105]) and apply them to AC forcing of the bipolar electrode with a DC bias, or other examples of ICEO phenomena described above.

3.5. Modified electrokinetic equations

Given the systematic discrepancies between theory and experiment in ICEO flows at large induced voltages, another possible explanation is the breakdown of the underlying PNP/NS equations, which are strictly only valid for dilute solutions at low voltages [17••,106]. Indeed, certain experimentally observed effects, such as the high-frequency flow reversal and strong concentration dependence of planar ACEO pumps [15•,60], have not yet been understood using the classical electrokinetic equations, even with the various nonlinear effects discussed above [87•,95•]. Possible modifications of the electrokinetic equations are reviewed and analyzed in Ref. [17••], so here we only discuss some key points.

Various non-local generalizations of the PNP equations are available, e.g. based on density functional theory [107], weighted density approximations [108] or self-consistent correlation functions [109], which involve systems of nonlinear integro-partial differential equations. These approaches can accurately reproduce the behavior of simple statistical models, such as charged hard spheres in a dielectric continuum, although at considerable computational expense. Non-local modified PNP have begun to be applied to linear electrokinetics in nanochannels by Liu et al. [110], but here we focus on simpler continuum models making the local density approximation, following Cervera et al. [111], which are easier to apply to time-dependent, nonlinear problems in induced-charge electrokinetics.

It has long been understood that the Gouy–Chapman/Poisson–Boltzmann theory of the double layer makes unphysical predictions at large voltages, significantly exceeding the thermal voltage. Not only is the dilute-solution approximation violated, but also point-like ions can become compressed into a region much thinner than a single molecule. To avoid this situation, Stern introduced the notion of a monolayer of solvent molecules separating the continuum region, or diffuse part of the double layer, from the inner, or compact part, which carries most of any large voltage drop. The Stern layer is essentially a first approximation of the effects of finite molecular size and short-range many-body interactions near a highly charged surface, which is widely used to fit electrochemical measurements [91]. For ICEO flows, however, one must have a dynamical model for transient charging and flow generation in the compact layer, with correlation effects

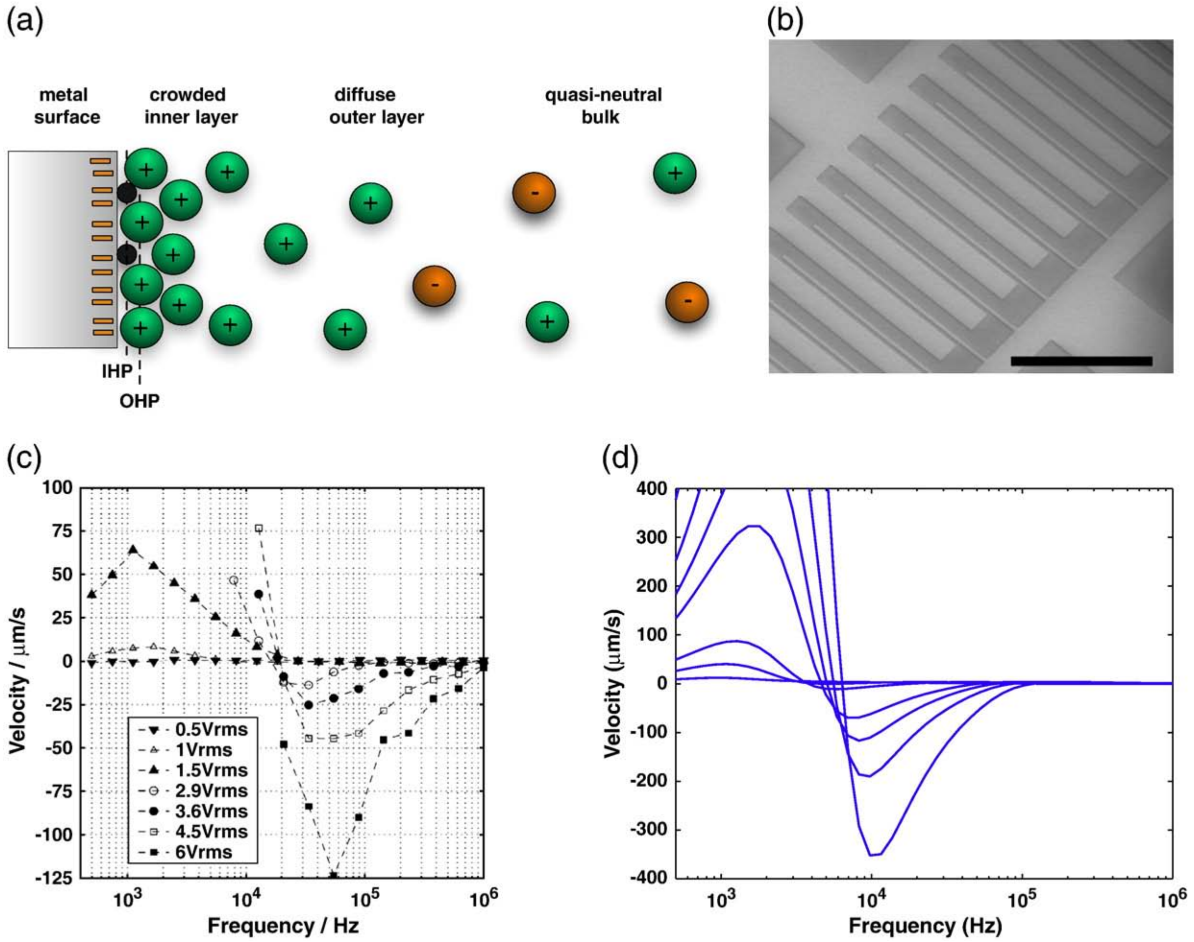

Fig. 6. Crowding of finite-sized ions and high-frequency flow reversal of planar ACEO pumps [17••,64,106]. (a) Sketch of the double layer near a blocking electrode at high voltage; solvated counter-ions (green) are crowded in the inner region and smoothly transition across the outer diffuse region to a dilute solution with solvated anions (orange); an ion can break free from its solvation shell and adsorb on the surface (black), thus moving from the outer Helmholtz plane (OHP) to the inner Helmholtz plane (IHP); solvent molecules outside the solvation shell are not shown (reproduced from Bazant et al. [17••,106]). (b) SEM image of the standard ACEO pump design of Brown et al. [14] consisting of interdigitated planar electrodes of widths 4.2 μm and 25.7 μm and gaps 4.5 μm and 15.6 μm; scale bar indicates 100 μm (reproduced from Urbanski et al. [60]). (c) Experimentally observed velocity pumping of 0.1 mM KCl by the ACEO pump in (b) around a microfluidic loop versus AC frequency at different peak-to-peak voltages (reproduced from Studer et al. [15•]). (d) Simulations by Storey et al. [64] of the same flow using a modified electrokinetic equations with an effective hydrated ion size $a = 4.4$ nm for a lattice gas in the mean-field local-density approximation; similar results are obtained using a solvated ion diameter $a \approx 1$ nm for hard spheres with dielectric saturation in water (reproduced from Ref. [64]).

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extending smoothly into the diffuse layer. This may seem unnecessary in typical situations with dilute bulk solutions, but the application of a large voltage inevitably leads to the crowding of (solvated) ions near the surface [106,112•].

The very existence of a finite-size cutoff has important implications for charging dynamics at a blocking surface. Dilute-solution theory predicts a diverging differential capacitance with increasing double-layer voltage, but concentrated solution theories predict the opposite: Once counter-ions become crowded, the double layer must expand, causing a decrease in differential capacitance [112•]. This effect alone suffices to predict high-frequency flow reversal of ACEO pumps using the Standard Model in good agreement with experiments [64], as shown in Fig. 6, although with an artificially large effective ion size, depending on the model.

As counter-ions become crowded in the inner part of the double layer, it is clear that they contribute less and less to electro-osmotic flow. As noted above, some counter-ions can be prevented from driving flow by chemical adsorption (trapping ions on the surface) or Faradaic reactions (altering their charge) at large induced voltages. Even at an ideally polarizable, blocking surface, however, there can also be a decrease in electro-osmotic mobility at large voltages, due to an increase in the local solution viscosity. A field-dependent viscoelectric effect in the solvent was considered long ago by Lyklema [113]. Recently, Bazant et al. [17••] proposed a charge-induced thickening of the solution, where the viscosity increases due to short-range and electrostatic correlations and diverges near the maximum volume fraction of solvated counter-ions. This hypothesis helps to explain the strong decay of ICEO flows with increasing salt concentration, but a complete quantitative theory is still lacking, which can simultaneously describe the dependence of ICEO flows on voltage, frequency, ionic strength, and interfacial chemistry.

4. Future directions

Despite the impressive advances in ICEK phenomena, many challenges remain, both theoretical and experimental, fundamental and practical. In particular, many discrepancies persist between theory and experiment, ranging from the quantitative (measured ICEO flows are persistently lower than theoretical predictions, at times by orders of magnitude [17••]) to even qualitative (ICEK effects decrease with increasing electrolyte concentration, and high-frequency flow reversal in ACEO). These discrepancies reflect gaps in our fundamental understanding of induced-charge electrokinetic phenomena. An understanding of their origin may point the way to their alleviation, which will be key to the utilization of ICEO in practical systems. Here we discuss promising future directions for research, both experimental and theoretical, in ICEK.

4.1. Experiment

Experiments have established that ICEK flows are generally slower than one would expect from theory, by an amount that varies from system to system and from material to material [17••]. From the standpoint of fundamental science, systematic and reproducible experiments will be necessary to establish the root causes of these discrepancies. Additionally, systematic and high-throughput experiments will be required to address the materials science challenge: to determine electrode/electrolyte combinations that give rise to strong ICEO flows. A robust, generally-applicable ICEK system would ideally work in an arbitrary solution; this will require the discovery of suitable materials or coatings for the 'inducing surfaces'.

The system of Pascall et al.[51••] is well-suited for such studies, as it enables direct ICEO slip velocity measurements for potentially any liquid electrolyte, over any material that can be deposited (e.g. sputtered, evaporated, or chemically adsorbed) onto a metal substrate, and enables approximately ~10^3 measurements per day. Furthermore, combining measurements of the differential capacitance of a particular electrode–electrolyte system using conventional techniques from electrochemistry with direct ICEK measurements would give indispensible complementary information about electrochemical double-layer processes that influence the observed electrokinetic flows, and may help deconvolve potential sources of theory–experiment discrepancy.

4.1.1. Electrolyte materials

A promising direction for both fundamental and applied electrokinetics, involves systematic studies of different electrolytes. Given the importance of surface ion adsorption in reducing ICEK flows, it would be interesting to systematically vary the liquid electrolyte itself, in an attempt to systematically connect interfacial electrochemistry with ACEO flow and to determine the range of applicability of ACEK effects. Examples include:

- The systematic study of effects of electrochemical reactions, through the use of electrode/electrolyte combinations that involve a known redox couple [97•] or water and buffer reactions [103•], coupled to measurements of impedance [94,96•] and pH [69••];
- The study of ion crowding effects, through the use of non-adsorbing ions (e.g. KPF_6 or NaF on silver or gold surfaces) [17••];
- The use of organic solvents, which typically have much lower ionic conductivity and mobility [114], but can still exhibit significant electrokinetic response (e.g. as in DC electro-osmotic pumps for direct methanol fuel cells [115]) without electrochemical reactions;
- Ionic liquids – electrolytes, such as molten salts, that consist entirely of ions without any solvent – have been explored extensively for electrochemical energy storage, can enable higher applied potentials (~4 V) without Faradaic reactions, and represent the 'fully crowded' limit of electrolytes [17••,116]. Disadvantages – and opportunities – include significantly higher viscosity, relative unfamiliarity to the electrokinetics community, and some uncertainty as to how to model them effectively.

4.1.2. New surfaces

Along with different electrolytes, another promising direction is to explore inducing surfaces beyond the noble metals used thus far. Varying the physical and chemical properties of inducing surfaces in a systematic and controlled way may lead to the discovery of systems that exhibit stronger, more reproducible and more robust flows. Furthermore, systematic studies may shed light on the qualitative and quantitative discrepancies between theory and experiment for ICEK systems. Potentially interesting options for ICEK surfaces include:

- *Electrochemically inert coatings*. Both Faradaic reactions and surface adsorption of ions or proteins may occur on bare metal electrodes, which might be prevented by passivation with a coating that is thick enough to block reactions, yet thin enough for the induced ζ to remain appreciable. For example, poly(ethylene glycol) is often used to passivate surfaces against non-specific adsorption of proteins, and self-assembled monolayers (generally thiol-terminated alkane chains) are routinely used to control the surface chemical properties of gold surfaces.
- *Coatings with well-defined chemistry*. Alkane–thiol SAMS can be synthesized or purchased with a variety of chain lengths and terminal chemical groups. Additionally, a variety of materials can be sputtered or evaporated to 'controllably contaminate' the surface [51••].
- *Controlled surface roughness*. Messinger and Squires [117] have demonstrated theoretically that even nanoscale roughness can lead to suppressed electrokinetic flows with strongly charged surfaces, due to the strong gradients in surface conduction (i.e. moderate to high Dukhin numbers). A systematic experimental study of the effects of surface roughness would likewise be interesting.

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- *High-slip polarizable surfaces*. Hydrodynamic slip has been predicted [118,119] to enhance flow, and indeed such enhancements have been observed [120•]. It would be interesting to experimentally work with conducting, but hydrophobic, surfaces over which slip would be expected. Examples include graphene (slip length $b \approx 30\ \text{nm} \gg \lambda_S$), carbon nanotubes, or ultra-smooth gold electrodes passivated by a hydrophobic alkane–thiol SAM. Micro-engineered superhydrophobic 'Cassie' surfaces (e.g. metallized grooves passivated by a hydrophobic alkane–thiol SAM) may be even more effective due to their much larger effective slip, but subtleties for the electrokinetic problem [121,122•,123]may preclude significant amplifications.

4.2. Theory

We have already described various opportunities to develop improved theoretical models for ICEO flows, and an extensive discussion can also be found in Ref. [17••]. Therefore, we close by briefly listing what we think could be the most promising directions:

- *Include electrochemistry*. Current models focus on the physics of electrostatics, ion transport, and fluid flow, but mostly neglect the chemistry of interfacial and bulk reactions. This may be appropriate at low voltage, but certainly at high voltage, as in most experiments, electrochemical effects must be included in the models. These include surface phenomena, such as Faradaic reactions and specific adsorption of ions, which enter as boundary conditions, and bulk phenomena, such as water splitting reactions, which enter as volumetric source/sink terms in the transport equations.
- *Include concentration polarization*. The Standard Model assumes a constant bulk salt concentration, but there are several possible mechanisms for concentration polarization. In addition to electrochemical reactions, (physical) salt adsorption and tangential transport in the diffuse part of the double layer can also lead to concentration gradients, which in turn drive surface flows (diffusio-osmosis) and bulk flows (electro-convection). The latter effect is enhanced for asymmetric electrolytes with different ionic diffusivities.
- *Go beyond dilute-solution theory*. The edifice of electrokinetic theory is built on the mean-field and local density approximations for an ideal, dilute solution of ions. Out of the many possibilities for new physics in concentrated solutions and/or large applied voltages, we must find ways to unambiguously test from experiments or simulations which ones are most important, and what level of mathematical description is required.
- *Compare to molecular simulations*. In this effort, it could be crucial to connect continuum models with molecular dynamics simulations, since experiments cannot as easily probe dynamical phenomena in electrolytes at the nanoscale. However, a challenge for simulations will be to reproduce experimental conditions of large transient voltages and various electrochemical processes at interfaces.

Regardless of the next theoretical developments, the goal should remain to make only those changes required to fit experiments, with as few adjustable parameters as possible. Unlike 'classical' electrokinetics, ICEK provides a natural way to externally 'tune' the zeta potential, to use a given theoretical model to make a falsifiable prediction, and then to perform the appropriate experiment to test this prediction. In particular, we hold out hope that the Standard Model, which has allowed extensive analytical predictions and basic understanding of ICEO phenomena, may be modified in relatively simple ways to improve its predictive power. Our hope is that this may be accomplished most easily by developing better effective boundary conditions for the quasi-neutral bulk equations, taking into account only the most important microscopic effects in the near a highly charged polarizable surface.

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