Recent studies of nonlinear electrokinetic phenomena have shown that the standard theory generally overpredicts experimental observed slip velocities, often by orders of magnitude. Thin (\(O(10\text{ nm})\)) dielectric contaminant layers over the driving surface provide a natural mechanism for electrokinetic suppression. We describe experiments of induced charge electro-osmosis over gold electrodes ‘contaminated’ with silica layers of controlled thickness for nearly a thousand distinct conditions, in a system that enables direct comparisons between theoretical predictions and experimental measurements. Both the magnitude and the frequency dependence of the measured slip velocity are captured quantitatively over the entire range of experiments by accounting for both the physical capacitance of the dielectric layer and its surface chemistry. More generally, the system described here enables the quantitative EK characterization of a wide variety of surfaces, electrolytes, and experimental conditions, and will prove invaluable for the rational design and prediction of electrokinetic systems.

Electrokinetic (EK) effects involve the interaction between electric fields, electrolytic ions, fluid flows and particle motion, and have a history dating back two centuries [1]. Recent years have seen a resurgence of interest in EK effects, including protein, DNA, and particulate separations, directed assembly of colloidal particles, and transport in micro- and nanofluidic devices [2].

Despite this long history and sustained interest, the most basic elements of electrokinetics have remained largely untested. The Helmholtz-Smoluchowski (HS) equation,

\[
u_s = -\frac{\varepsilon_w \zeta_{eq} E}{\mu},
\]

relates the electro-osmotic flow (EOF) velocity, \(u_s\), to the electrostatic potential drop, \(\zeta_{eq}\), across the diffuse layer of ions that screen a charged surface. Here \(\varepsilon_w\) and \(\mu\) are the permittivity and viscosity of the electrolyte, respectively (Fig. 1a). \(\zeta_{eq}\) is generally difficult to manipulate experimentally, since it is generally set by surface chemistry [3], although some direct control has been shown in flow-FET systems [4]. While (1) is in principle predictive, its role in practice has most commonly been interpretive: given a measured \(u_s\), (1) is used to infer \(\zeta_{eq}\). The design of increasingly complex microfluidic devices, however, will require reliable predictions for EK flows under a wide range of conditions.

A variety of nonlinear EK effects have been explored and exploited in recent years, including AC [5, 6] and travelling wave electrokinetic flows [7], electrokinetic instabilities due to concentration gradients [8] and through electrochemical membranes [9], and induced charge electrokinetics (ICEK) [10–12] for transporting and mixing fluid in microchannels. All involve an applied field that perturbs the electrolyte (e.g., induces a charged double layer over a polarizable inducing surface), and then forces the perturbations into motion. An important advantage is that small AC potentials applied to closely-spaced electrodes can drive large fields without electrolysis, yet drive steady nonlinear electrokinetic flows. Furthermore, the standard Poisson-Nernst-Planck (PNP) equations for ion transport make quantitative predictions for the steady flows driven by AC fields, which can be directly compared against experimental measurements. Any discrepancies indicate physico-chemical effects that are missing from the standard model.

While measured ICEK effects generally show qualitative agreement with theoretical predictions [11, 13], both qualitative and quantitative discrepancies have been reported [12, 14]. In particular, measured nonlinear electrokinetic flows in a variety of systems are typically one to two orders of magnitude slower than the standard model predicts. Various mechanisms have been proposed, including Stern layers [15], steric interactions between double-layer ions [14] and noncontinuum effects.

Contamination of the inducing (metal) surface provides a natural mechanism for ICEK flow suppression [10]. To investigate, we deliberately and systematically contaminate ICEK inducing surfaces with silica (SiO\(_2\)) films of known thickness (\(O(10\text{ nm})\)), and compare the measured ICEO flow against theory. We measure ICEO flow profiles for 987 distinct experimental conditions, in which we vary electrolyte composition and concentration, electric field strength and frequency, and silica film thickness. In all cases, our system enables quantitative comparisons with the predictions of the PNP standard model. A naive theory (computed as though no contaminant were present) fails in a manner reminiscent of many ICEK experiments [12, 14]. Accounting for the physical capacitance of the dielectric improves the agreement, but discrepancies remain. Including the ‘buffer capacitance’ of known surface chemical reactions yields an unprecedented quantitative agreement between theory and experiment over the entire range of experiments.

Such impressive agreement validates our experimental system and the theory developed for this parameter regime. Our system can easily be adapted to drive strongly nonlinear induced double layers, enabling direct and systematic measurements of the breakdown of the standard model. Furthermore, our system enables the EK characterization of any material.
that can be deposited as a planar film atop a metal surface, under a variety electrolytes and driving conditions, enabling the rational optimization of surface materials for EK applications.

We begin with the standard description of ICEO, in which an applied field induces a charged screening cloud around a polarizable surface, and then drives that induced cloud into electrokinetic motion. A suddenly applied electric field initially intersects normal to an (equipotential) metal strip (Fig. 1b), driving ions in solution toward the metal surface. In the absence of electrochemical (Faradaic) reactions, positive ions accumulate near the field source, and negative ions near the field sink, to form a dipolar induced double layer (IDL) at steady state leaving a purely tangential bulk electric field that drives the IDL to flow analogous to that in (a).

In the quasi-steady limit \( \omega \ll \tau_c^{-1} \), an applied field \( E(t) = E_o \cos(\omega t) \) induces a quasi-steady double layer with \( \zeta_i = E(t)x \). Assuming \( \zeta_i \) to superpose with the native \( \zeta_{eq} \), the time-averaged slip velocity is given by (1) to be

\[
\langle u_x \rangle = -\frac{\varepsilon_w E_o \omega (\zeta_{eq} + E_o x \cos \omega t)}{\mu} = -\frac{\varepsilon_w E_o^2 x}{2\mu}.
\]

Notably, \( \zeta_{eq} \) does not survive the time-average, and the quantitative prediction in (2) depends solely on variables that can be directly controlled in experiments.

Transit double-layer charging becomes important when \( \omega \gtrsim \tau_c^{-1} \). In this system, as with ACEO over coplanar electrodes, the charging timescale depends upon the distance from the electrode’s centerline. Adapting the charging model in [5] leads to a time-averaged slip velocity that depends on both position and frequency:

\[
\langle u_x \rangle = -\frac{\varepsilon_w E_o^2 x}{2\mu (1 + \tau_c^2 \omega^2)},
\]

where \( \tau_c = \varepsilon_w \pi |x| / \sigma \lambda_D \). Explicit numerical calculations (COMSOL AB) are in excellent agreement with (3).

We now describe our experiments (Figure 2a). We coated molecularly smooth fused silica plates (University Wafer) with a silane-thiol monolayer (as in [16], but with 575 mTorr \( \text{O}_2 \) plasma exposure) to make an adhesion/wetting layer. We then patterned 50 x 900 \( \mu \text{m} \) gate electrodes using standard photolithographic methods, evaporating 200 \( \AA \) of gold at 0.5 \( \AA / \text{s} \) via electron beam evaporation with subsequent lift off of the photoresist. Using an additional electron-beam evaporation step, we deposited silica films of various thickness (33, 66, or 100 nm). Both evaporation steps were performed on the same day to prevent fouling of the electrode surface.

Using soft lithography [17], we microfabricated PDMS channels of length 1 cm, height 100 \( \mu \text{m} \), and width 300 \( \mu \text{m} \), which we ozone-bonded to the substrate so that the microelectrode was located at the midpoint of the microchannel and oriented perpendicular to it (Fig. 2a). We designed the electrode to minimize stray asymmetric flows due to capacitive cou-
pling with the microscope [18]. Fluid ports were punctured at the channel ends with 26 gauge Luer stubs (McMaster-Carr). Stainless steel pins (New England Small Tube, 23 gauge) were inserted to act as fluidic vias and driving electrodes.

Electrolytes of concentration 10, 1, 0.1, and 0.01 mM KCl or NaCl were made by diluting a stock electrolyte consisting of Milli-Q water with 10 mM added electrolyte. 520 nm fluorescent microspheres (Bangs Laboratories, FS03F/5069) were added to each electrolyte (0.02 wt%) to serve as flow tracers for micro-particle image velocimetry (μPIV).

Experimental data were acquired as follows: Syringes were connected to the stainless steel pins via tygon tubing and an electrolyte of given ionic strength and composition (starting with the lowest ionic strength) was flowed into the channel. Syringes were then removed, and the ends of the tubing were placed in an electrolyte reservoir to avoid stray capillary pressure gradients. Electric leads were attached to the stainless steel pins and driven with a sinusoidal potential (Agilent 33220A function generator, amplified by a Trek PZD350 M/S). For each electrode/electrolyte combination, an automated system (Labview, National Instruments) applied AC potentials from 50 - 150 V to the stainless steel pins at frequencies from 100 Hz - 30 kHz. Between runs, the channel was flushed with at least 1 mL of the next electrolyte. Fluorescence video microscopy (Andor iXon 885, Nikon TE2000-U with 20X ELWD, 0.45 NA objective) was used to record microsphere positions and μPIV algorithms were used to determine velocity profiles[19] (Fig. 2c), which were corrected for the finite depth of focus of the optics [20]. A detailed description of similar experimental protocols is given in [18].

Since we expect (and observe) no flow perpendicular to the applied field, we average the data in the perpendicular direction to obtain the mean velocity profile across the field of view (Fig. 2d). The slope, \( u' \), of this profile over the central 20 \( \mu \text{m} \) of the gate electrode was compared to the theoretically predicted slope, \( u'_o = -\varepsilon_w \varepsilon_r^2 / 2\mu \). 987 combinations of the trials had an observed velocity above the error threshold (set so that Brownian motion of the tracer particles accounts for no more than 20% of the observed velocity [21]).

Figure 3a shows measured slip velocities \( u' \), scaled by \( u'_o \), from the naïve ICEO theory (as if the metal were clean), plotted versus frequency (scaled by \( \tau_c = \varepsilon_w (\pi |x_c|) / \sigma \lambda_D \), with \(|x_c| = 10 \mu \text{m} \) at the edge of the region of interest). At frequencies in which the double layer fully charges (\( \tau_c \omega \ll 1 \)), the experimental velocities are consistently 10-1000 times slower than predicted by theory, consistent with other ICEO and ACEO experiments[14]. Additionally, the frequency dependence is poorly captured by the theory.

Of course, the naïve theory presented above omits the silica contaminant, which adds a capacitance in series with the double layer [10] and splits the total potential drop, \( \Delta V = E\tau_c \), between the double-layer \( \zeta_i = E\tau_c / (1 + \delta) \), which contributes to ICEK flow, and the dielectric \( \Delta V_D = \delta E\tau_c / (1 + \delta) \), which does not. Here \( \delta = \varepsilon_w d / \varepsilon_d \lambda_D \) represents the capacitance ratio between the linearized double layer and the dielectric layer, where \( \varepsilon_d = 4.6\) [22] and \( d \) are the permittivity and thickness of the silica layer. In these experiments, \( \delta \) ranged from 0.18-566. The dielectric capacitor reduces both \( u_s \) and \( \tau_c \):

\[
u'_o = u'_o (1 + \delta)^{-1} , \tau_{phys} = \tau_c (1 + \delta)^{-1} .
\]

Scaling the measured velocities to account for the physical effect of the dielectric improves the agreement with theory significantly (Fig. 3b), yet significant scatter remains even between experiments with the same silica thickness. Accounting for the nonlinear double layer capacitance, \( C_{DL} = \varepsilon_w / \lambda_D \cosh(\varepsilon \zeta / 2 k_B T) \), leads to at most 20% changes, which is insufficient to account for the discrepancies. A missing

FIG. 3: (Color online) Normalized slip velocity vs. dimensionless frequency. Data points are coded by silica film thickness: (●) 33 nm, (■) 66 nm, (♦) 100 nm. Solid lines represent theoretical predictions. (a) \( u' \) scaled by the naïve ICEO theory, ignoring the dielectric. Inset: Neglecting the dielectric layer, all of the potential difference \( \Delta V \) between the electrode and the bulk electrolyte occurs over the double layer. (b) \( u' \) scaled assuming the dielectric acts only as a physical capacitor, in series with the double layer. Inset: The physical capacitance of the dielectric layer reduces \( \zeta_i \) by \( (1 + \delta)^{-1} \), where \( \delta = C_{DL} / C_d \). (c) \( u' \) scaled accounting for both surface chemistry (via buffer capacitance \( C_{buff} \)) and the physical capacitance. Inset: Surface chemistry immobilizes some ions that would otherwise contribute to EK flows, further reducing \( \zeta_i = \Delta V / (1 + \delta + \beta) \), where \( \beta = C_{buff} / C_d \). 99% of all measurements (representing 987 distinct conditions) lie within a factor of 3 of this theory.
mechanism for the observed discrepancy thus remains.

Silicas contain silanol groups which can react with hydronium ($H_3O^+$) ions in the double layer via

$$\text{SiOH} + H_2O \rightarrow \text{SiO}^- + H_3O^+, \quad (5)$$

which we assume to be in quasi-equilibrium with the hydronium ion concentration in the double layer. An increase (decrease) in $\zeta_i$ lowers (raises) $[H_3O^+]$ in the double layer, which shifts the equilibrium in (5) to the left (right). The surface thus acts to “buffer” changes in the double layer $[H_3O^+]$ [23], introducing a buffer capacitance in parallel with the double layer [24]:

$$C_{\text{buff}} = \frac{\varepsilon^2 N_s}{k_BT} \left( \frac{K_a a_H \exp(-e\zeta/k_BT)}{K_a + a_H \exp(-e\zeta/k_BT)} \right), \quad (6)$$

where $N_s$ is the silanol site density, $K_a \sim 10^{-6}$ is the equilibrium constant for (5) [23, 25], and $a_H$ is the activity of $H_3O^+$ in the bulk electrolyte.

Accounting for both buffer and physical capacitance yields an induced zeta potential $\zeta_i = E\zeta/(1 + \delta + \beta)$, where $\beta = C_{\text{buff}}/C_d$, which reduces the theoretical slip velocity and changes the double layer dynamics by

$$u_{\text{BP}}' = \frac{u_o'}{1 + \delta + \beta}, \quad \tau_{\text{BP}} = \frac{1 + \beta/\delta}{1 + \delta + \beta} \tau_{\text{c}}. \quad (7)$$

Here $N_s, a_H$ and $\zeta_{eq}$ are specific to the experimental system and are required to calculate $C_{\text{buff}}$. Reasonable upper bounds are known: $N_s \leq 7.8 \text{ nm}^{-2}$ [25] and $-50 \leq \zeta_{eq} \leq -25 \text{ mV}$ [3]. The in-channel pH of the electrolyte was determined to be $\leq 4$ via fluorescent indicators.

Since $\zeta_i$ is generally low in our experiments (0.2-10.3 mV), and $N_s$ and $\zeta_{eq}$ do not vary significantly between experiments, a single value for $C_{\text{buff}}$ is expected for all experiments. Indeed, setting $C_{\text{buff}} = 24 \text{ mF m}^{-2}$ yields remarkable agreement, capturing both the magnitude and frequency dependence of the theory for 987 experiments (Fig. 3c). 99% of our data lie within a factor of three of theory. Additionally, the parameter bounds presented above yield a consistent magnitude for $C_{\text{buff}}$. By contrast, poor fits are obtained using a linear Stern layer capacitance (in series with the double layer and dielectric) instead of $C_{\text{buff}}$.

To summarize, we have demonstrated an unprecedented agreement between theoretical predictions and experimental measurements of ICEO flow over controllably contaminated surfaces. Values from 987 distinct experiments, representing a wide range of conditions, collapse onto a single theoretical curve. Both the magnitude and frequency dependence of the observed velocities are in excellent agreement with a theory that accounts for the additional capacitance introduced by the physical dielectric contaminant and its surface chemistry. In principle, all of the parameters that determine $C_{\text{buff}}$ for a given surface chemistry could be experimentally measured, yielding an ICEO theory with no free parameters.

Our results represent a crucial first step towards the quantitative prediction of EK systems. The system described here is remarkably general, and enables the EK characterization of any material that can be deposited as a thin film atop a planar electrode, under a range of conditions and electrolytes. Here, controllable contamination yielded induced double layers with relatively small $\zeta_i < k_BT/e$. An important future direction will be to perform analogous tests with strongly nonlinear induced double layers.

References