Electro-hydrodynamics near Hydrophobic Surfaces

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We show that the dynamics of the electrostatic diffuse layer at the slippery hydrophobic surface depends strongly on the mobility of surface charges. For a hydrophobic surface with immobile charges the fluid transport is considerably amplified by the existence of a hydrodynamic slippage. In contrast, near the hydrophobic surface with mobile adsorbed charges it is also controlled by an additional electric force, which increases the shear stress at the slipping interface. To account for this we formulate electro-hydrodynamic boundary conditions at the slipping interface, which are applied to quantify electro-osmotic flows. Our theoretical predictions are fully supported by dissipative particle dynamics simulations with explicit charges. These results lead to a new general concept of zeta-potential of hydrophobic surfaces.

Introduction.— The electrostatic diffuse layer (EDL) is the central concept in understanding dynamic properties of charged colloidal systems since it is an origin of numerous electrokinetic effects [1]. This includes electro-osmotic (EO) flow with respect to a charged surface that provide an extremely efficient way to drive and manipulate flows in micro- and nanofluidic devices [2–4]. Most studies of EO assume no-slip hydrodynamic boundary conditions at the surface, which are typical for wettable (hydrophilic) surfaces. In this situation the outer EO velocity $u_1$ (outside of the thin EDL) due to the tangential electric field $E_1$ is given by the classical Smoluchowski formula

$$u_1 = -\frac{E_1 q_1}{\eta \kappa},$$

where $\eta$ is the viscosity of the solution, $q_1$ is the charge density at the so-called no-slip surface of shear where the fluid velocity vanishes. This can be related to the zeta-potential, $\zeta_1 = q_1 / \kappa \varepsilon$, conventionally defined at the beginning of the EDL, where EO slip is postulated to occur (but note that in some specific cases the definition could be more complex [1]). Here, $\varepsilon$ is the permittivity of the solution, and $\kappa = \lambda_D^{-1}$ is the inverse Debye screening length. Obviously, $\zeta_1$ is equal to the EDL potential.

In practice, however, non-wetting (hydrophobic) materials demonstrate hydrodynamic slip, characterized by the slip length $b$ (the distance within the solid at which the flow profile extrapolates to zero) [5]. For a charge density $q_2$ of the slipping solid interface, simple arguments show that the outer EO velocity is given by [6, 7]:

$$u_2 = -\frac{E_1 q_2}{\eta \kappa} (1 + b \kappa)$$

(2)

The apparent zeta potential was thus defined as $\zeta_2 = q_2 (1 + b \kappa) / \kappa \varepsilon$. Since at hydrophobic solids $b$ can be of the order of tens of nanometers [8–11], for typically non-metric Debye length some small enhancement of the zeta potential and EO flow was observed experimentally [12]. We remark however that Eq.(2) fails to predict a realistic $\zeta_2$ of the free interface of bubbles ($b = \infty$) or oil drops [13–15] and, in fact, of systems with large partial slip such as gas sectors of superhydrophobic surfaces [16].

Previous studies assumed that electric charge associated with slippery (hydrophobic) surface was immobile, which is not justified for bubbles or drops. This is also by no means obvious for hydrophobic solids, as the ‘gas cushion’ model of apparent hydrophobic slip relates it to the formation of a depletion layer of thickness $\delta$ at the surface [17]. This idea has received a microscopic foundation in terms of a prewetting transition [18], and was confirmed by recent simulations [19, 20]. There is a growing evidence that such an interface is charged [21]. The existence of surface charges can be caused by ion adsorption [22, 23], so that they are laterally mobile, and can respond to the external electric field by increasing shear.

FIG. 1: Sketch of the system.
stress. Indeed, recent analysis has shown that charges at the free surface could enhance the shear stress \[24\], but we are unaware of any prior work that has explored what happens at partially slipping hydrophobic solid if surface charges are mobile. Beside that, previous investigations of EO near a hydrophobic surface have not addressed the issue of the hydrophobic EO slip in a thin channel.

In this Letter, we present some general theoretical arguments and results of Dissipative Particles Dynamics (DPD) simulations, which allow us to quantify an EO flow in a channel with a partially slipping surface. This leads to a new concept of zeta-potential of hydrophobic surfaces.

**Theor~.** To illustrate our approach (and motivated by micro- and nanofluidics applications \[2 \text{–} 4\]) we consider a film of an aqueous electrolyte solution of thickness \(\kappa H \gg 1\) confined between a hydrophilic and a hydrophobic planes (Fig. 1). We keep our analysis at the mean-field level and treat ions as point-like, so that the adsorbed layers are infinitesimally thin \((d = 0)\).

The no-slip \((z = 0; \ u = 0)\) hydrophilic surface has the charge density \(q_1\), and the slipping hydrophobic surface is characterized by the density of adsorbed charge \(q_2\). To describe the local hydrodynamic slip at the hydrophobic interface allowing for mobile charges we suggest a boundary condition at the hydrophobic wall, which takes into account that the tangential stress balance represents a combination of both hydrodynamic and Maxwell stress components \[25\]

\[
\begin{align*}
  z = H : \ u = b(-\partial_z u + (1 - \mu) q_2 E_i / \eta),
\end{align*}
\]

where parameter \(\mu\) can vary from 0 for fully mobile charges to 1 in the case of fixed charges. Now we want to compute the velocity profile, which would be expected within a continuous theory when boundary condition 3 is valid.

The fluid flow satisfies Stokes’ equations with an electrostatic body force

\[
\eta \nabla^2 u = \varepsilon \nabla^2 \psi E, \quad \nabla \cdot u = 0,
\]

where electric field represents a superposition of an external and a created by surface charges fields \(E = E_i - \nabla \psi\). We assume weakly charged surfaces, so that \(\psi(z)\) satisfies the linearized Poisson-Boltzmann equation

\[
\nabla^2 \psi \simeq \kappa^2 \psi,
\]

Solving Eqs. 4 and 5 with prescribed boundary conditions we find \[25\] with (details are given in \[23\]). We use a simulation cell confined by two impermeable walls located at \(z = -\sigma\) and \(15\sigma\), where \(\sigma\) sets the length scale. The value of \(\kappa = (8\pi \ell_B c_0)^{1/2}\) with Bjerrum length \(\ell_B = e^2 / \varepsilon k_B T\) was determined by using the concentration, \(c_0\), at the electro-neutral center of the channel. This concentration was about \(5 \times 10^{-2} \sigma^{-3}\), which gives \(\kappa^{-1} = 1 - 1.2\sigma\) to provide large \(\kappa H\).

A charged hydrophilic plate, where no-slip conditions are applied, was constructed from immobile discrete charges \(\text{ions})\) aligned at \(z = -\sigma\), so that the EDL potential was located at \(z = 0\). The adsorbed ions were assigned fixed random \(x, y\)-coordinates (to avoid any periodicity-induced effects), but the distribution was always controlled to be homogeneous with surface density \(q_1 = 0.15 q_e / \sigma^2\), where \(q_e\) is the charge of an ion. We adjusted the surface charge \(4\pi \ell_B q_1 / \kappa < 1\), which insures the ‘weak charge’ behavior.

Hydrophobic walls are modeled by using a tunable slip method \[31\], which allows us to set-up slip length \(b\) up to \(\infty\) by varying \(\gamma_L\), which reflects the magnitude of particle-wall friction forces \[23\]. Fixed charges were cre-
FIG. 2: Top: LJ adsorption potential applied in simulations. Bottom: A concentration profile of adsorbed ions and the model with homogeneous charge distribution inside the adsorbed layer.

ated similarly to a hydrophilic case at $z = 15 \sigma$. The charged hydrophobic interface with mobile charges was modeled by applying an effective interfacial potential, which mimics the ion-specific adsorption. In particular, we set Lennard-Jones (LJ) potential between negative ions and the hydrophobic surface (see Fig 2), because it qualitatively reproduces the potentials of mean force (PMF) for surface active ions [31]. Uncharged hydrophobic interface could be simply made by applying repulsive potential between the wall and ions [25]. The amount of adsorbed charge, $q_2$, can be regulated by the strength of LJ potential. The ratio $q_2/q_1$ was varied from $1 \pm 0.03$ to $3 \pm 0.1$ by setting different values of $q_1$ at the no-slip (hydrophilic) surface. Being fixed in such a way, the adsorbed charge is in thermodynamic equilibrium with the bulk electrolyte solution and freely responds to $E_t$. The adsorbed charge is confined in a thin layer of a thickness $d$. In our work its value (of the order of $\sigma$ [25]) and the location of $H$ are deduced from the simulation data at the plane of the EDL potential.

Results and discussion.— Fluid velocity profiles $u(z)$ were first simulated for the channel with $q_2/q_1 = 1$, $\kappa H = 12$, and $b/H = 1.2$, by setting mobile ($\mu = 1$) and immobile ($\mu = 0$) charges at the slipping wall. The results are shown in Fig. 3(a). Also included are the data obtained for a channel with two hydrophilic walls ($b = 0$). A general conclusion from this plot is that the simulation results are in excellent agreement with predictions of Eq.(6), confirming the validity of a continuum description and electro-hydrodynamic boundary condition, Eq. (3). For a hydrophilic channel we observe a classical behavior, where the inner fluid velocity in the EDL increases from zero on the surfaces with high gradients to form an outer ‘plug’ EO flow in the electro-neutral center. A hydrophobic slippage strongly amplifies the velocity if surface charges are immobile with an outer ‘shear’ flow, perfectly described by Eq.(7). The slipping surface with mobile charges generates a ‘plug’ profile in the center, and neither outer nor inner EO velocities show a manifestation of the hydrodynamic slip. Simulation data show that this is however accompanied by some negative ‘flow’ of the adsorbed layer. We finally note that simulated ion density profiles are superimposed in all cases as seen in Fig. 3(b). This clarifies the definition of $H$ in simulations and confirms that the EO slip near hydrophobic surfaces no longer reflect the sole EDL potential.

To explore flow behavior near a hydrophobic surface with mobile charges in more details, we continue with varying the ratio $q_2/q_1$ from 0 to 3 at fixed $b/H = 1.2$. The simulation results and predictions of Eq.(6) are given in Fig. 4 and are again in a good agreement (since the
‘flow’ in the adsorbed layer is qualitatively the same as in Fig. 3(a) we do not show it here and below). We see that an apparent EO slip at the wall, $u_2$, increases with $q_2/q_1$, but a variety of physically different situations occurs depending on the value of this ratio. Uncharged hydrophobic surface induces an EO slip at the wall, and we see a manifestation of an outer ‘shear’ flow. As discussed above, in the case of symmetric charges, $q_2/q_1 = 2$, and $\mu = 0$ (symbols). From top to bottom $b/H = 0, 1.2, \infty$. Solid curves show predictions of Eq. (6), dotted lines - of Eq. (7).

\[
\zeta_2 = \frac{q_2(1 + \mu \kappa b)}{\kappa \varepsilon}
\]

and zeta-potential becomes a characteristic of a hydrophobic surface solely. Eq. (9) is relevant for the understanding of highly debated zeta-potential measurements on free interfaces of (not confined) bubbles and oil drops \[1,2,13\], and justifies the use of the Smoluchowsky equation when $\mu = 0$.

Conclusion.– We have formulated an electro-hydrodynamic slip boundary condition, providing an explicit expression for the EO velocity in the channel with a hydrophobic wall, and have demonstrated that both confinement and mobility of surface charges has a dramatic effect on the dynamic properties of the EDL and EO flow. Simple analytical formulae for the apparent EO slip and zeta-potential at the hydrophobic surface have been suggested, which resolve a number of paradoxes and confusions in the literature. Our results may be immediately extended to describe an EO between two hydrophobic interfaces, which is relevant for free soap and foam films that are currently a subject of active research \[32, 33\], and/or for the challenging case of $\kappa H = O(1)$ and smaller $b/H$, where the outer EO is absent. Another fruitful direction could be to apply them to revisit calculations of an EO flow past superhydrophobic surfaces \[34, 35\].

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