Electro-osmosis on Anisotropic Superhydrophobic Surfaces

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We give a general theoretical description of electro-osmotic flow at striped superhydrophobic surfaces in a thin double layer limit, and derive a relation between the electro-osmotic mobility and hydrodynamic slip-length tensors. Our analysis demonstrates that electro-osmotic flow shows a very rich behavior controlled by slip length and charge at the gas sectors. In the case of an uncharged liquid-gas interface, the flow is the same or inhibited relative to the flow in a homogeneous channel with a zero interfacial slip. By contrast, it can be amplified by several orders of magnitude provided slip regions are uniformly charged. When gas and solid regions are oppositely charged, we predict a flow reversal, which suggests the possibility of a huge electro-osmotic slip even for electroneutral surfaces. On the basis of these observations we suggest strategies for practical microfluidic devices.

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Introduction.—Electro-osmotic (EO) ''plug'' flows are established when an electric field forces the diffuse ionic cloud adjacent to a charged surface in an electrolyte solution into motion. This classical subject of colloid science [1] is currently experiencing a renaissance in micro- and nanofluidics [2,3], which raises the fundamental question of how to pump and mix fluids at micron scales, where pressure-driven flows and inertial instabilities are suppressed by viscosity. Electro-osmosis offers unique advantages in this area of research and technologies, such as low hydrodynamic dispersion, no moving parts, electrical actuation and sensing, energy conversion and storage, and easy integration with microelectronics.

Until recently, almost all studies of EO flow have assumed uniform surface charge and no-slip hydrodynamic boundary conditions at the surface. In such a situation the *scalar* electro-osmotic mobility M_1, which relates an apparent EO ''slip'' velocity $\boldsymbol{U}_1$ (outside of the *thin* double layer) to the tangential electric field $\boldsymbol{E}_t$ is given by the classical Smoluchowski formula [4]

$$M_1 = -\frac{U_1}{E_t} = \frac{q_1}{\eta\kappa}, \tag{1}$$

where η is the viscosity of the solution, q_1 is the *constant* charge density of the no-slip surface, which can be related to the zeta potential across the diffuse (flowing) part of the double layer, $\zeta_1 = q_1/\kappa\varepsilon$, where ε is the permittivity of the solution, and $\kappa = \lambda_D^{-1}$ is the inverse Debye screening length, that characterizes the thickness of the electrical double layer (EDL).

Recent studies demonstrated the existence of a hydrodynamic slip at a hydrophobic smooth and homogeneous surface, which can be quantified by the slip length b (the distance within the solid at which the flow profile extrapolates to zero) [5,6]. The combination of the strategies of EO and hydrophobic slip, can yield enhanced EO flow.

For a charge density q_2 of the slipping interface, simple arguments show that the EO mobility is given by [7,8]:

$$M_2 = -\frac{U_2}{E_t} = \frac{q_2}{\eta\kappa}(1 + b\kappa). \tag{2}$$

Since the EO flow amplification scales as $(1 + b\kappa)$, and b can be of the order of tens of nanometers [9–12], for typically nanometric Debye length an order of magnitude enhancement might be expected.

It is now natural to assume that a massive amplification of EO flow can be reached on superhydrophobic (SH) surfaces where the effective, in general case tensorial, slip length, $\mathbf{b}_{\rm eff}$, could be of the order of several microns [13–15]. The controlled generation of such flows is by no means obvious, since both the slip length and the electric charge distribution on a SH surface are inhomogeneous and often anisotropic. Despite its fundamental and practical significance, EO flow over SH surfaces has received little attention. Recently, [16] investigated EO flow past inhomogeneously charged, flat SH surfaces in the case of thick channels ($h \gg L$), thin EDL ($\kappa L \gg 1$), and predicted

$$\mathbf{M} = M_1 \cdot \left(\mathbf{I} + \frac{q_2}{q_1}\mathbf{b}_{\rm eff}\kappa\right) \tag{3}$$

by using the Lorentz reciprocal theorem for the Stokes flow and by assuming a *perfect* slip ($b = \infty$) at gas sectors. Here $\mathbf{I}$ is the unit tensor, and we keep the notations q_1 and q_2 to characterize the surface charge density at the no-slip and slip regions, as above. This expression indicates negligible flow enhancement in case of an uncharged

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liquid-gas interface (which has been confirmed by later studies [17,18]), and shows that surface anisotropy generally leads to a *tensorial* EO response.

In this Letter, a general situation of EO flow past SH surfaces with patterns of arbitrary *partial* slip, is considered (Fig. 1). Our focus is on the canonical EO geometry of a thick parallel-plate channel with a two-component (no-slip and slip) coarse texture, varying on scales larger than the EDL thickness.

General theory.—To highlight the effect of anisotropy, we focus on an idealized, flat, periodic, charged, striped SH surface in the Cassie state, sketched in Fig. 1, where the liquid-solid interface has no slip ($b_1 = 0$) and the liquid-gas interface has a partial slip ($b_2 = b$, $0 \le b \le \infty$). As a simple estimate, lubricating gas sectors of height e with viscosity η_g much smaller than η [19] have a local slip length $b_2 \approx e(\eta/\eta_g) \approx 50e$, which can reach tens of μm. Let then ϕ_1 and $\phi_2 = \delta/L$ be the area fractions of the solid and gas phases with $\phi_1 + \phi_2 = 1$. Pressure-driven flow past such stripes has been shown to depend on the direction of the flow, and the eigenvalues of the slip-length tensor [20] read [21]

$$b_{\mathrm{eff}}^{\parallel} \simeq \frac{L}{\pi} \frac{\ln[\sec(\frac{\pi\phi_2}{2})]}{1 + \frac{L}{\pi b}\ln[\sec(\frac{\pi\phi_2}{2}) + \tan(\frac{\pi\phi_2}{2})]}, \tag{4}$$

$$b_{\mathrm{eff}}^{\perp} \simeq \frac{L}{2\pi} \frac{\ln[\sec(\frac{\pi\phi_2}{2})]}{1 + \frac{L}{2\pi b}\ln[\sec(\frac{\pi\phi_2}{2}) + \tan(\frac{\pi\phi_2}{2})]}. \tag{5}$$

These expressions depend strongly on a texture period L. When $b/L \ll 1$ they predict the area-averaged isotropic slip length, $b_{\mathrm{eff}}^{\perp,\parallel} \simeq \phi_2 b$. When $b/L \gg 1$, expressions (4) and (5) take the form

$$b_{\mathrm{eff}}^{\perp} \simeq \frac{L}{2\pi}\ln\left[\sec\left(\frac{\pi\phi_2}{2}\right)\right], \qquad b_{\mathrm{eff}}^{\parallel} \simeq 2b_{\mathrm{eff}}^{\perp}, \tag{6}$$

that coincides with results obtained for the perfect slip ($b = \infty$) stripes [22].

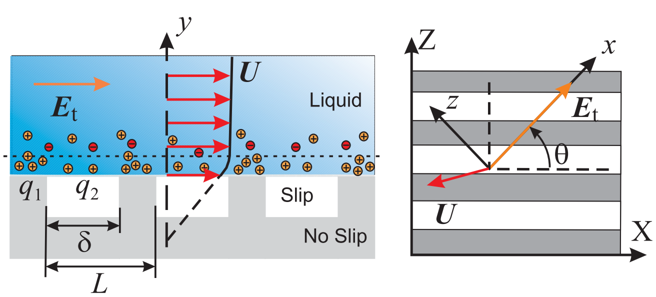

FIG. 1 (color online). (a) Sketch of the superhydrophobic effective slippage effect on the EO flow. The real situation is approximated by a periodic cell of size L, with patterns of charges and flow boundary conditions. (b) Illustration of tensorial EO response: $\theta = \pi/2$ corresponds to transverse stripes, whereas $\theta = 0$ to longitudinal stripes.

The EO mobility is represented by 2×2 matrices diagonalized by a rotation [18]. By symmetry, the eigendirections of $\mathbf{M}$ correspond to longitudinal ($\theta = 0$) and transverse ($\theta = \pi/2$) alignment with the applied electric field (Fig. 1), so we need only to compute the eigenvalues, $M^{\parallel}$ and $M^{\perp}$, for these cases.

We consider a semi-infinite electrolyte in the region $y > 0$ above a patterned surface at $y = 0$ subject to an electric field, $\boldsymbol{E}_t = E_t\hat{\boldsymbol{x}}$, in the x direction. For nanoscale patterns ($L < 1$ μm), we can neglect convection ($Pe \ll 1$ for a typical ionic diffusivity D), so that $\psi(x, y, z)$ is independent of the fluid flow [23]. We also assume a weak field ($|E_t|L \ll |\psi|$) and a weakly charged surface ($|\psi| \ll k_BT/(ze) = 25/z$ mV) for a z:z electrolyte, so that ψ satisfies the Debye-Hückel equation with a boundary condition of prescribed surface charge,

$$\nabla^2\psi = \kappa^2\psi, \qquad \varepsilon\partial_y\psi = -q(x, 0, z). \tag{7}$$

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

$$\eta\nabla^2\boldsymbol{u} = \nabla p + \varepsilon\kappa^2\psi E_t\hat{\boldsymbol{x}}, \qquad \nabla\cdot\boldsymbol{u} = 0, \tag{8}$$

with the boundary conditions at $y = 0$

$$\boldsymbol{u}_t = b(x, z)\partial_y\boldsymbol{u}_t, \qquad \hat{\boldsymbol{y}}\cdot\boldsymbol{u} = 0, \tag{9}$$

where $\boldsymbol{u}_t = u\hat{\boldsymbol{x}} + w\hat{\boldsymbol{z}}$ is the lateral, and $v = \hat{\boldsymbol{y}}\cdot\boldsymbol{u}$ is normal to the surface velocities. We also neglect surface conduction (which tends to reduce EO flow) compared to bulk conduction ($Du \ll 1$) [23]. Far from the surface, $y \to \infty$, $\boldsymbol{u}$ approaches the EO slip velocity $\boldsymbol{E} = -\mathbf{M}\cdot\boldsymbol{E}_t$ and

$$\psi \to 0, \qquad \partial_y\boldsymbol{u} \to 0. \tag{10}$$

For a longitudinal configuration only the velocity component parallel to $\boldsymbol{E}_t = E_t\hat{\boldsymbol{x}}$ remains. In case of transverse to applied field stripes, normal velocity $v\cdot\hat{\boldsymbol{y}}$ does not vanish due to mass conservation condition in (8), which can significantly modify the EO flow. Rigorous calculations [23] allow one to find exact solutions for $U^{\parallel,\perp}$, and thus obtain the eigenvalues of the EO mobility tensor:

$$M^{\parallel,\perp} = M_1\left(b_{\mathrm{eff}}^{\parallel,\perp}\frac{q_2 - q_1 + q_2\kappa b}{q_1 b} + 1\right), \tag{11}$$

where the effective slip lengths are given by Eqs. (4) and (5). The flow is thus anisotropic and there is a simple relationship between the EO mobility and hydrodynamic slip-length tensors [24]

$$\mathbf{M} = M_1\cdot\left[\mathbf{I} + \frac{\mathbf{b}_{\mathrm{eff}}}{b}\left(\frac{q_2}{q_1}(1 + \kappa b) - 1\right)\right]. \tag{12}$$

In the limit of $b/L \gg 1$ the general expression transforms to Eq. (3). When $b/L \ll 1$ we get isotropic EO flow

$$M = \phi_1 M_1 + \phi_2 M_2. \tag{13}$$

Discussion.—To demonstrate examples of very rich and unusual fluid behavior at the SH surface it is instructive to consider some limiting cases of Eq. (12) with different values of q_1 and q_2. The results (shown in Fig. 2) are somewhat remarkable. We see, in particular, that if the gas area is uncharged, the EO flow related then only to the charge q_1 on the solid-liquid interface is generally *inhibited* as compared with a homogeneous, solid no-slip surface with uniform charge density [see Fig. 2(a)]

$$\mathbf{M} = M_1 \cdot \left[\mathbf{I} - \frac{\mathbf{b}_{\rm eff}}{b}\right]. \tag{14}$$

We remark and stress that in contrast to common expectations, the situation described by Eq. (14) corresponds to $M^{\parallel} \leq M^{\perp}$; i.e., the maximal directional mobility is attained in a transverse, and minimal—in the longitudinal direction [26]. When $b/L \ll 1$ we simply get $M = \phi_1 M_1$. In other words, the (isotropic) EO mobility shows no manifestation of the slip, being equal to the surface averaged velocity generated by no-slip regions. This result coincides with what is expected for hydrophilic uncharged sectors. In the limit of $b/L \gg 1$ this inhibition becomes negligibly small, and we obtain the simple results of [16,18], where EO mobility becomes equal to M_1 regardless of the orientation or area fraction of the slipping stripes. These results suggest that although the absence of the screening cloud near the gas region tends to inhibit the effective EO slip, the hydrodynamic slip acts to suppress this inhibition.

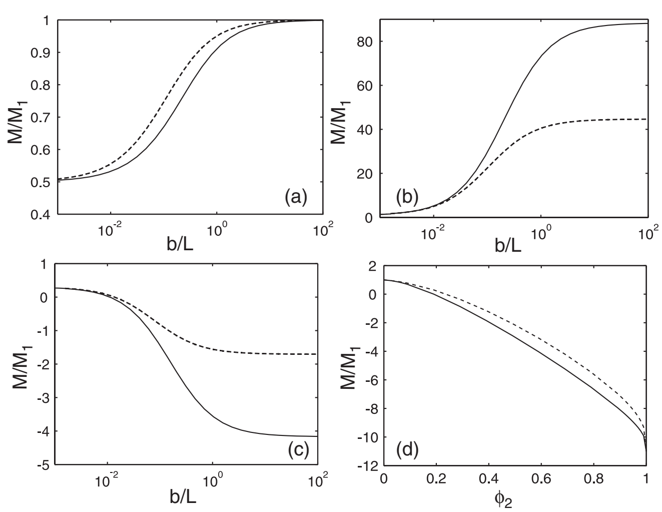

FIG. 2. Eigenvalues of normalized EO mobility. Solid curves represent longitudinal, and dashed—transverse alignment of stripes with electric field. $M^{\parallel,\perp}/M_1$ vs amplitude of the local slip b/L for (a) uncharged slip areas ($q_2 = 0$, $\phi_2 = 0.5$, $\kappa L = 10^2$), (b) uniform charge distribution ($q_2 = q_1$; $\phi_2 = 0.45$, $\kappa L = 10^3$) and (c) oppositely charged slip and no-slip areas ($q_2 = -q_1$. $\phi_2 = 0.35$, $\kappa L = 10^2$). $M^{\parallel,\perp}/M_1$ plotted against (d) the fraction of gas sectors ($b/L = 0.1$, $q_2 = -q_1$, $\kappa L = 10^2$).

The situation is very different if the slipping interface carries some net charge, which is not an unreasonable assumption [27]. To gain some insight into the possible EO flow *enhancement*, we consider first the case of uniform surface charge $q_1 = q_2$, where Eq. (12) gives

$$\mathbf{M} = M_1 \cdot [\mathbf{I} + \kappa \mathbf{b}_{\rm eff}], \tag{15}$$

which might be seen as a natural tensorial analog of Eq. (2). Figure 2(b) includes theoretical results calculated with Eq. (15) for a geometry of stripes, and is intended to demonstrate that the flow is truly anisotropic and can exhibit a large enhancement from effective hydrodynamic slip, possibly by several orders of magnitude. We stress that such an enhancement is possible even at a relatively low gas fraction, i.e., when $\mathbf{b}_{\rm eff}$ is relatively small [but the amplification factor, $(\mathbf{I} + \kappa \mathbf{b}_{\rm eff})$, might be huge]. Also note that in this situation $M^{\parallel} \geq M^{\perp}$; i.e., the fastest (slowest) direction can correspond only to longitudinal (transverse) stripes.

An interesting scenario is expected for oppositely charged solid and gas sectors. If $q_1 = -q_2$, then Eq. (12) transforms to

$$\mathbf{M} = M_1 \cdot \left[\mathbf{I} - 2\frac{\mathbf{b}_{\rm eff}}{b} - \kappa \mathbf{b}_{\rm eff}\right], \tag{16}$$

which for $b/L \ll 1$ simply gives $M = M_1[\phi_1 - \phi_2(1 + \kappa b)]$. The calculation results for this situation are presented in Fig. 2(c), and suggest a very rich fluid behavior. We see, in particular, that inhomogeneous surface charge can induce EO flow along or opposite to the field, depending on the fraction of the gas area as shown in Fig. 2(d). Already a very small fraction of the gas sectors would be enough to reverse the effective EO flow. Another striking result is that an electro-neutral surface ($\phi_1 q_1 + \phi_2 q_2 = 0$) can generate an extremely large EO slip. With our numerical example this corresponds to $\phi_2 = 0.5$. In other words, a superhydrophobic surface of average positive charge or even zero charge can induce an EO flow (different for longitudinal and transverse to applied field stripes) in the direction of the applied field as if it is uniformly and

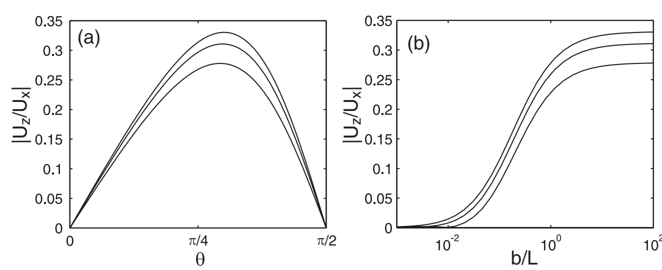

FIG. 3. The ratio of EO velocity components, $|U_z/U_x|$, (at $\phi_2 = 0.5$, $\kappa L = 10^2$) as a function of (a) angle θ at $b/L = 10^2$ and (b) local slip length at the optimal angle θ. From top to bottom $q_2/q_1 = 2$, 1, 0.5.

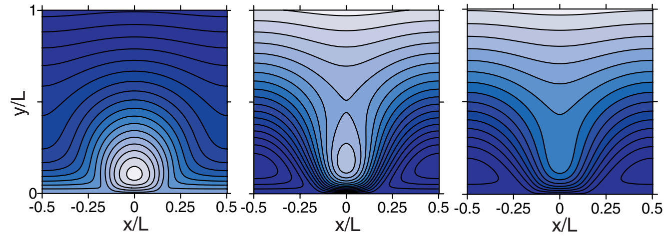

FIG. 4 (color online). Streamlines of the EO flow computed at $\phi_2 = 0.35$ and $\kappa L = 10^2$ for $q_2/q_1 = -0.43$ and $\theta = \pi/2$. The origin of coordinates coincides with the center of the gas region. From left to right the local slip length is $b/L = 0.1$, 0.5, and 10^2.

negatively charged. These findings are similar to those of [4,28] that the electrokinetic mobility depends on the charge distribution on the object, and not solely on its total charge. However, in our case the flow is dramatically amplified due to hydrodynamic effective slip.

These results may guide the design of SH surfaces for transverse electrokinetic flows in microfluidic devices [28]. As we have shown above, effective EO mobility of anisotropic striped surfaces is generally tensorial, due to secondary flow transverse to the direction of the applied electric field. Anisotropy ($|U_z/U_x|$) is maximized in the direction of $\theta_{\max}$ [as it is seen in Fig. 3(a)] and requires that q_2/q_1 and κb are as large as possible. In a thick SH channel a transverse plug EO flow seems to be a very fruitful direction compared to transverse hydrodynamic phenomena, where flow is "twisted" only near the wall [29].

Another mixing mechanism is related to the formation of patterns of steady convective rolls on the scale proportional to the texture period (Fig. 4). This can happen in the situation of oppositely charged and transverse to applied field stripes. Figure 4 illustrates the effect of the local slip on the morphology of the steady rolls formation. We see, in particular, that increase of b leads first to the appearance of additional convective patterns near no-slip areas, and then to a transition to a flow morphology, where recirculation of a fluid is observed only at the no-slip regions. This, in turn, induces the flow reversal [as in Fig. 2(d)].

Concluding remarks.—We have described EO flow on inhomogeneously charged and slipping anisotropic surfaces. Our analysis provided the necessary tools to describe a significant modification of EO phenomena on SH surfaces: to quantify the inhibition and enhancement of flow, the transition from its anisotropy to isotropy, onsets of convective rolls formation and a relevant flow reversal, which can generate a huge EO slip even in the situation of a zero mean charge. Our results may find numerous applications in microfluidic lab-on-a-chip devices.

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[1] J. Lyklema, *Fundamentals of Interface and Colloid Science. Volume II: Solid-Liquid Interfaces* (Academic Press Limited, San Diego, CA, 1995).

[2] H. A. Stone, A. D. Stroock, and A. Ajdari, Annu. Rev. Fluid Mech. **36**, 381 (2004).

[3] J. C. T. Eijkel and A. van den Berg, Microfluid Nanofluid **1**, 249 (2005).

[4] J. L. Anderson, Annu. Rev. Fluid Mech. **21**, 61 (1989).

[5] O. I. Vinogradova, Int. J. Miner. Process. **56**, 31 (1999).

[6] E. Lauga, M. P. Brenner, and H. A. Stone, in *Handbook of Experimental Fluid Dynamics* edited by C. Tropea, A. Yarin, and J. F. Foss (Springer, NY, 2007), Chap. 19, pp. 1219–1240.

[7] V. M. Muller, I. P. Sergeeva, V. D. Sobolev and N. V. Churaev, Colloid J. USSR **48**, 606 (1986).

[8] L. Joly, C. Ybert, E. Trizac, and L. Bocquet, Phys. Rev. Lett. **93**, 257805 (2004).

[9] O. I. Vinogradova and G. E. Yakubov, Langmuir **19**, 1227 (2003).

[10] C. Cottin-Bizonne, B. Cross, A. Steinberger, and E. Charlaix, Phys. Rev. Lett. **94**, 056102 (2005).

[11] L. Joly, C. Ybert, and L. Bocquet, Phys. Rev. Lett. **96**, 046101 (2006).

[12] O. I. Vinogradova, K. Koynov, A. Best, and F. Feuillebois, Phys. Rev. Lett. **102**, 118302 (2009).

[13] J. Ou and J. P. Rothstein, Phys. Fluids **17**, 103606 (2005).

[14] P. Joseph, C. Cottin-Bizonne, J. M. Benoǐt, C. Ybert, C. Journet, P. Tabeling, and L. Bocquet, Phys. Rev. Lett. **97**, 156104 (2006).

[15] P. Tsai, A. M. Peters, C. Pirat, M. Wessling, R. G. H. Lammerting, and D. Lohse, Phys. Fluids **21**, 112002 (2009).

[16] T. M. Squires, Phys. Fluids **20**, 092105 (2008).

[17] D. M. Huang, C. Cottin-Bizzone, C. Ybert, and L. Bocquet, Phys. Rev. Lett. **101**, 064503 (2008).

[18] S. S. Bahga, O. I. Vinogradova, and M. Z. Bazant, J. Fluid Mech. **644**, 245 (2010).

[19] O. I. Vinogradova, J. Colloid Interface Sci. **169**, 306 (1995).

[20] M. Z. Bazant and O. I. Vinogradova, J. Fluid Mech. **613**, 125–134 (2008).

[21] A. V. Belyaev and O. I. Vinogradova, J. Fluid Mech. **652**, 489 (2010).

[22] E. Lauga and H. A. Stone, J. Fluid Mech. **489**, 55 (2003).

[23] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.107.098301 for details of the analysis.

[24] Note some similarity with [25], where a thermophoretic mobility was found to depend on κb and b/R.

[25] J. Morthomas and A. Würger, J. Phys. Condens. Matter **21**, 035103 (2009).

[26] This surprising observation likely reflects the fact, that the reduction of the interfacial stress (and the mobility) due to slip in the absence of the diffuse layer should be smaller for transverse stripes since it is partly compensated by the local pressure drop.

[27] V. Tandon, S. K. Bhagavatula, W. C. Nelson, and B. J. Kirby, Electrophoresis **29**, 1092 (2008).

[28] A. Ajdari, Phys. Rev. E **65**, 016301 (2001).

[29] O. I. Vinogradova and A. V. Belyaev, J. Phys. Condens. Matter **23**, 184104 (2011).