Electro-Osmosis on Inhomogeneously Charged Surfaces

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The electro-osmotic flow generated by an electric field $\vec{E}_{\rm ext}$ in a fluid bounded by surfaces bearing a charge varying in space is considered. Focusing on a slab geometry, I characterize the formation of steady convective rolls and describe their morphology as a function of the slab thickness. These rolls can be used to generate net currents and forces, even for zero average surface charge density. Moreover, the current (or the force) can be perpendicular to the applied field, opening the way to a variety of microscopic electromechanical devices.

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An external electric field induces motion of an electrolyte fluid in the vicinity of a charged surface. This well-known phenomenon is usually referred to as electro-osmosis or electroendosmosis. It provides a framework for relating the electrophoretic mobility of charged particles in solution to their surface or "zeta" potential [1,2]. It is also of great importance in separation technologies using electric fields as it relates overall motion of the fluid to the surface properties of the bounding walls. An especially significant case is that of capillary electrophoresis, as wall/fluid contacts are omnipresent (so as to limit dispersive convective effects resulting from Joule heating). Electro-osmosis has also been proposed as a propulsion mechanism for cells without motile apparatus but able to generate electric potential gradients [3].

In this Letter, an inhomogeneous surface charge distribution is considered. This is, in principle, of importance for at least three reasons. First, it models the effect of defects in an otherwise homogeneous system. Second, inhomogeneous systems are generic, especially in the biological world. Third, the engineering of man-made surfaces has improved considerably, and allows the design of various surface charge patterns.

To my knowledge, inhomogeneous surface charge distributions have been seldom studied [4], and then only to describe the electrophoretic mobility of colloidal particles [5]. Here I will focus on a more macroscopic slab geometry in which an electrolyte is confined between two solid, almost planar, parallel walls, and study the flow generated by an electric field applied parallel to the walls. If the surfaces are homogeneously charged, a "plug" flow is known to be generated. I will show that if the surface charge densities are modulated in a periodic way, convective hydrodynamic patterns are created. Their morphology depends on the ratio of the fluid layer thickness to the wavelength of the modulation, and changes if the modulation on the top and bottom surfaces differs in phase, amplitude, or wave vector. Furthermore, these flow patterns can be taken advantage of to generate net currents and forces even for a neutral average charge density in the liquid, and even perpendicularly to the applied field. This could help in designing electro-osmotic micropumps or micromotors.

Let us start with conventional electro-osmosis and introduce our notations. Consider two flat insulating surfaces, defined as the $z = \pm h$ planes in a (x, y, z) system of Cartesian coordinates, confining an electrolyte solution of Debye-Huckel length κ^{-1}, dielectric constant ϵ, and viscosity η. The fluid is assumed incompressible and a low Reynolds number description valid.

If the surface charge density is constant on the two surfaces $\sigma^+ = \sigma^- = \sigma_0$, the electric potential inside the solution before application of an exterior field is $\psi(z) = \zeta_0 \cosh(\kappa z)/\sinh(\kappa h)$, where $\zeta_0 = \sigma_0/\epsilon\kappa$. Indeed it satisfies the Debye-Huckel equation (valid for $e\zeta_0/kT \ll 1$) and boundary conditions

$$\Delta\psi = \kappa^2\psi, \qquad \partial_z\psi(\pm h) = \pm\sigma^{\pm}/\epsilon. \tag{1}$$

The charge density in the solution is $\rho_e = -\epsilon\Delta\psi = -\epsilon\kappa^2\psi$. If an external electric field $\vec{E}_{\rm ext}$ (or an electric current) is applied parallel to the slab, this charge density will induce a drag on the fluid, and thus a velocity field $\vec{v}$. In a linear response theory [2,6]

$$-\vec{\nabla}p + \eta\Delta\vec{v} + \rho_e\vec{E} = \vec{0}, \qquad \vec{\nabla}\cdot\vec{v} = 0, \tag{2}$$

with ρ_e the previously derived value, $\vec{E} = \vec{E}_{\rm ext} - \vec{\nabla}\psi$ the total electric field, and p the pressure. It is then useful to define $p' = p - \epsilon\kappa^2\psi^2/2$ to get a formula directly relating the velocity field to the *external* electric field:

$$-\vec{\nabla}p' + \eta\Delta\vec{v} - \epsilon\Delta\psi\vec{E}_{\rm ext} = \vec{0}, \qquad \vec{\nabla}\cdot\vec{v} = 0. \tag{3}$$

Equations (1) and (3) constitute the basis for our description. In the homogeneous problem, the simple solution is $p' = $ const and $\vec{v} = (\epsilon/\eta)[\psi(z) - \psi(0)]\vec{E}_{\rm ext}$. Away from the wall Debye layers, the velocity is thus almost uniform $\vec{v} \simeq \mu_0 \coth(\kappa h)\vec{E}_{\rm ext}$ with $\mu_0 = -\epsilon\zeta_0/\eta = -\sigma_0/\eta\kappa$. The minus sign is easily understood: If σ_0 is positive, negative charges are in excess close to the surface, and the fluid there is driven in a direction opposite to that of $\vec{E}_{\rm ext}$.

Now consider surface charge densities modulated along x: $\sigma^+ = \sigma_0^+ \cos(q^+x + \gamma^+)$, $\sigma^- = \sigma_0^- \cos(q^-x + \gamma^-)$, and the field applied along the same axis $\vec{E}_{\rm ext}^{\parallel} = E_{\parallel}\vec{x}$. Then the electro-osmotic drag on the fluid close to the

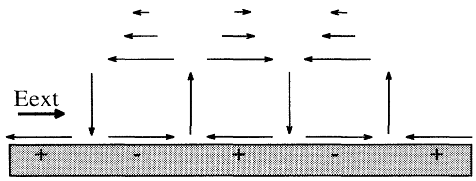

FIG. 1. On a charge-modulated surface, the fluid close to the wall is pulled periodically in opposite directions. As a result, recirculation rolls develop on a scale proportional to the modulation wave length.

surfaces alternates in direction. Incompressibility imposes recirculation in the slab, and convective rolls appear (Fig. 1).

Thanks to the linearity of the equations, solving the problem with arbitrary surface charge densities on the surfaces reduces to the analysis of two geometries, which we choose to provide even and odd solutions in z. In the first one the surfaces are charged in a symmetric way: $\sigma_1^+(x) = \sigma_1^-(x) = \sigma_0 \cos(qx)$. In the second one, the sign of the potential of the lower plate is reversed (or its phase shifted by π): $\sigma_2^+(x) = -\sigma_2^-(x) = \sigma_0 \cos(qx)$. Equation (1) gives the corresponding electrostatic potentials:

$$\psi_1(x,z) = (\sigma_0/Q\epsilon)\cos(qx)\frac{\cosh(Qz)}{\sinh(Qh)}, \quad (4)$$

$$\psi_2(x,z) = (\sigma_0/Q\epsilon)\cos(qx)\frac{\sinh(Qz)}{\cosh(Qh)}, \quad (5)$$

with $Q^2 = q^2 + \kappa^2$. The incompressibility condition in (3) allows us to introduce a stream function $\phi(x,z)$ such that $\partial_z\phi = v_x$ and $\partial_x\phi = -v_z$. Then

$$\phi_i(x,z) = \mu_0 E_\parallel \cos(qx) g_i(z), \qquad i = 1,2. \quad (6)$$

The functions $g_i(z)$ can be obtained generally [7], but their expressions get much simpler in the usual limit of very thin Debye layers $\kappa \gg q, h^{-1}$, where $Q \simeq \kappa$:

$$g_1(z) \simeq \frac{h\cosh(qh)\sinh(qz) - z\sinh(qh)\cosh(qz)}{hq - \sinh(qh)\cosh(qh)}, \quad (7)$$

$$g_2(z) \simeq \frac{z\cosh(qh)\sinh(qz) - h\sinh(qh)\cosh(qz)}{hq + \sinh(qh)\cosh(qh)}. \quad (8)$$

This approximation amounts to replacing Eqs. (1) and (3) by a simple Stokes problem, changing the electrostatic boundary conditions $\sigma = \sigma_0 f(x)$ into hydrodynamic "slip" boundary conditions $\vec{v} = \mu_0 f(x)\vec{E}_{\text{ext}}$.

Using the linearity of the problem, Eqs. (6)–(8) allow us to determine the influence of each plate. For example, if only the upper plate is charged $\sigma^+ = \sigma_0\cos(qx)$, the resulting stream function is $\phi_+ = (\phi_1 + \phi_2)/2$. More generally, for arbitrary charge modulations, the contributions of the different wave vectors (6) can be summed to obtain the stream function.

Let us recall at this point that the iso-ϕ lines are the streamlines of the flow. Thus a contour plot of ϕ illustrates the convection pattern induced by $\vec{E}_{\text{ext}}^{\parallel}$. The velocity field is obtained as $v_x = \mu_0 E_\parallel \cos(qx) g'(z)$ and $v_z = \mu_0 E_\parallel \sin(qx) q g(z)$, where g is the linear combination of g_1 and g_2 appropriate to fit the given electrostatic boundary conditions.

If $\vec{E}_{\text{ext}}$ is applied perpendicular to the charge modulation $\vec{E}_{\text{ext}}^{\perp} = E_\perp \vec{y}$, only $v_y(x,z)$ is nonzero. Equation (3) leads to the requirement that $v_y + \mu_0 E_\perp \psi/\zeta_0$ be a harmonic function. In the limit $\kappa \gg q, h^{-1}$, the even and odd charge distributions (4) and (5) lead to the velocity fields

$$\vec{v}_1 \simeq \mu_0 \cos(qx)\left[\frac{\cosh(qz)}{\cosh(qh)}\right]\vec{E}_{\text{ext}}^{\perp}, \quad (9)$$

$$\vec{v}_2 \simeq \mu_0 \cos(qx)\left[\frac{\sinh(qz)}{\sinh(qh)}\right]\vec{E}_{\text{ext}}^{\perp}. \quad (10)$$

The electric field drives the fluid along y in alternating directions as one goes along x. This surface effect vanishes (and the velocity reaches its average value zero) over a distance $\simeq q^{-1}$ in the z direction. The flow created by an arbitrary field $\vec{E}_{\text{ext}} = E_\parallel\vec{x} + E_\perp\vec{y}$ is obtained by a linear combination of (6), (9), and (10).

Let us return to the more interesting recirculating patterns obtained for a "parallel" field $\vec{E}_{\text{ext}}^{\parallel} = E_\parallel \vec{x}$.

What if the plates are far from each other? Consider the lower plate charged $\sigma^- = \sigma_0\cos(qx)$ and a gap width much larger than the modulation wavelength $2\pi/q$ (and than κ^{-1}). Focusing on the vicinity of the lower plate $z_> = z + h \ll h$, (7) leads to $g(z) \simeq z_> e^{-qz_>}$, and thus the velocity field

$$v_x = \mu_0 E_\parallel \cos(qx)(1 - qz_>)e^{-qz_>}, \qquad v_z = \mu_0 E_\parallel \sin(qx) q z_> e^{-qz_>}. \quad (11)$$

This characterizes the pattern of convective rolls, of transverse size $\simeq q^{-1}$, created by the application of $\vec{E}_{\text{ext}}^{\parallel}$ on a single surface (Fig. 1). For distances larger than q^{-1} the flow along x is in the direction opposite to what is close to the surface. The velocity decays exponentially at large distances.

What happens if we narrow the gap in the even "face-to-face" electrical geometry described by Eq. (4) (Fig. 2)? When the two surfaces are far apart they develop almost noninteracting patterns, the exponential tails in the stream function melting in a cosh shape. A plot of $v_x(z)$ thus displays two symmetric extrema characterizing recirculation. If the plates are brought closer, however, the two patterns tend to compress each other, and the z size of the rolls eventually becomes h (Fig. 2). The recirculating flows of the two surfaces merge so that $v_x(z)$ now only has a single extremum at $z = 0$. The transition occurs for $\tanh(qh) = qh/3$. In the limit $\kappa \gg h^{-1} \gg q$, the flow is locally (at a given x)

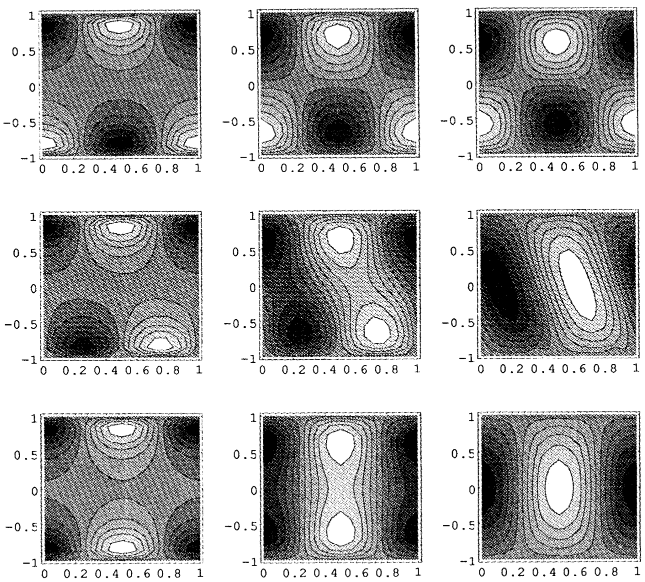

FIG. 2. Streamlines (iso-ϕ lines) plotted on a reduced scale: $(xq/2\pi; z/h)$. The fluid rotates in opposite directions in bright and dark areas. From left to right the gap is reduced, $hq = 6; 3; 0.5$. From top to bottom the shift is increased, $\gamma^- - \gamma^+ = 0; \pi/2; \pi$.

the sum of a pluglike electro-osmotic flow corresponding to the local value $\sigma(x)$ and a recirculation Poiseuille flow:

$$v_x \simeq -\mu_0 E_\parallel \cos(qx)\left[1 - \frac{3}{2}\frac{(h^2 - z^2)}{h^2}\right]. \quad (12)$$

An even clearer transition is obtained (Fig. 2) when the charge modulations of the two surfaces are opposite [or shifted by π, Eq. (5)]. Again, when $h \gg q^{-1}$, the two surfaces develop almost independent convective patterns. But upon narrowing of the gap, these merge so as to reduce the dissipation due to shear: recirculation now brings the fluid directly from one surface to the other (Fig. 2). Correspondingly, $v_x(z)$ becomes monotonic for qh smaller than a critical value given by $\coth(qh) = qh/2$.

For phase shifts of the modulations $\gamma^- - \gamma^+$ intermediate between 0 and π, the streamline patterns are bent with respect to the z axis, but tend to straighten as h is reduced (Fig. 2). Using linear combinations of (7) and (8), one can analyze generic situations where the modulations on the two plates are of different wave vector, amplitude, or phase [7].

Let us now consider the possibility of generating a net fluid current. In the geometries considered above [(6), (9), and (10)] only the $q = 0$ components of the surface charge density modulations were able to induce an average flow. This is due the symmetry between positive and negative charge densities in this linear problem. To obtain a net current one thus needs to break this symmetry.

There are simple ways to do so, even for a symmetric charge density modulation of zero mean value. Take, for example, the case where only the bottom plate is charged, $\sigma^+ = 0$, $\sigma^- = \sigma_0 \cos(qx)$. Then $\vec{E}_{\rm ext}^{\parallel} = E_\parallel \vec{x}$ tends to push fluid upwards for $qx = -\pi/2 \,(\mathrm{mod}\, 2\pi)$, and pull it downwards for $qx = \pi/2 \,(\mathrm{mod}\, 2\pi)$. By placing on top an undulated surface $z^+ = h[1 + \alpha\cos(qx)]$, with $\alpha > 0$ (Fig. 3), the upward stream is "bent" *to* the right (direction of $\vec{E}_{\rm ext}^{\parallel}$), whereas the downward stream pumps liquid *from* the left. It is thus natural to expect an average current to the right.

To quantify this statement I consider more generally an undulation $z^+ = h[1 + \alpha\cos(qx + \Phi)]$, always in the limit of a very thin Debye layer. The corresponding Stokes problem, with boundary conditions $\vec{v}(x, -h) = \mu_0 \cos(qx)\vec{E}_{\rm ext}(x, -h)$ on the lower plate and $\vec{v}(z^+) = \vec{0}$ on the upper one, can be solved perturbatively for small values of α. For a field parallel to both the undulation and charge modulation, the average current $\vec{J}_\parallel$ in the slab is to first order in α [7]:

$$\vec{J}_\parallel = -\frac{\mu_0 h}{2} f_\parallel(qh)\alpha\cos(\Phi)\vec{E}_{\rm ext}^{\parallel}, \quad (13)$$

with

$$f_\parallel(u) = u\frac{\cosh(2u)[2u - \tanh(2u)]}{2[\sinh^2(u)\cosh^2(u) - u^2]} + \frac{u}{\sinh(2u)}, \quad (14)$$

which is positive. Thus for $\sigma_0 > 0$, $\alpha > 0$, $\Phi = 0$, $\vec{J}_\parallel$ is in the same direction as $\vec{E}_{\rm ext}^{\parallel}$ (recall that μ_0 is then negative), in agreement with the qualitative picture sketched above (Fig. 3). It is also wise to verify that changing the sign of α is identical to shifting Φ by π. The current (13) logically increases with α and is significant when the shape and charge effects, both of range q^{-1}, interact: $qh < 1$ [$f_\parallel(qh) \simeq 8(qh)^2\exp(-2qh)$ for $qh \gg 1$ and $f_\parallel(qh) \simeq 3/2$ for $qh \ll 1$]. Using, for example, biologically sound values of a charge per nm^2, a field of 0.1 mV/μm, $\kappa^{-1} \simeq 1$ nm, and $\eta \simeq 10^{-2}\ \mathrm{g\,cm^{-1}\,s^{-1}}$, velocities of order 1 μm/s can be obtained for $\alpha \simeq 10^{-1}$.

The flow also generates an average stress $\vec{\tau}_\parallel$ on the upper plate, which to first order in α is [7]

$$\vec{\tau}_\parallel = \frac{\eta\mu_0}{4h} k_\parallel(qh)\alpha\cos(\Phi)\vec{E}_{\rm ext}^{\parallel}, \quad (15)$$

where $k_\parallel(u) = f_\parallel(u) - 2u/\sinh(2u)$ is positive [$k_\parallel(u) \simeq 1/2$ for small u]. So if the upper plate is allowed

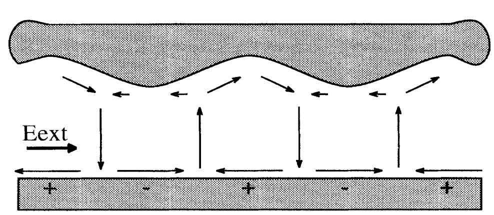

FIG. 3. If an undulated surface is adequately placed on top of a charge-modulated surface, the symmetric flow is biased, and a net current is generated.

to move along x, its two equilibrium positions $\Phi = \pm\pi/2$ correspond to no current situations, the sign of $E_{\parallel}$ dictating which one is stable ($\Phi = -\pi/2$ for $E_{\parallel}, \alpha, \sigma_0 > 0$).

If an electric field perpendicular to the modulation $\vec{E}_{\rm ext}^{\perp} = E_{\perp}\vec{y}$ is applied, the hydrodynamic problem is easily solved as $\vec{v} = v_y(x,z)\vec{y}$. To first order in α a net shear flow is generated with an average current

$$\vec{J}_{\perp} = -\frac{\mu_0 h}{2} f_{\perp}(qh)\alpha\cos(\Phi)\vec{E}_{\rm ext}^{\perp}, \qquad (16)$$

with $f_{\perp}(u) = -u/\sinh(2u) < 0$. The sign can be checked through the following argument, valid for small qh. Take $\zeta_0 > 0$, $\alpha > 0$, and $\Phi = 0$. Then the slab is narrower in the regions where the charge density in the solution is positive. The local current is the average velocity times the local thickness of the slab. The average velocity is roughly half of the one imposed by the Debye layer, and has thus the same absolute value in negative and positive charge regions. The local current is thus stronger in the wider regions of negative charge densities, which leads to an overall current in the direction opposite to $\vec{E}_{\rm ext}^{\perp}$, in agreement with (16) as $\mu_0 < 0$. A formula similar to (15) holds upon replacing $\parallel$ by $\perp$, with $k_{\perp} = f_{\perp}$.

I have thus shown that for commensurate surface undulation and (zero-average) surface charge modulation, an external field indeed creates a current and a drag on the plates. To reverse the direction of the current one can simply reverse the sign of the field, or move the upper plate by π/q to reverse the role of positive and negative charges. Moreover, the parallel and perpendicular "susceptibilities" are of opposite sign (and thus different). So, for a generic field $\vec{E}_{\rm ext} = E_{\parallel}\vec{x} + E_{\perp}\vec{y}$, the generated average current and average force will have components perpendicular to $\vec{E}_{\rm ext}$. The current (or the force) can even be strictly perpendicular to $\vec{E}_{\rm ext}$ for a precise orientation of the latter. All these effects are of first order in the undulation amplitude and quantified by Eqs. (13)–(16). In contrast, for a homogeneously charged surface and an undulated one, the transverse current is $O(\alpha^2)$ and the parallel one is $O(\alpha^0)$ and always nonzero [7].

A variety of geometries where the plus or minus charge symmetry is broken [7,8] give rise to similar effects. In particular, it is much easier and robust to engineer simultaneously the undulation and the charge modulation on the same plate, for example, by erasure along periodic strips of a thick deposit. This furthermore grants interaction of shape and charge effects even if the gap is larger than the modulation wavelength.

In summary, I have described electro-osmosis on inhomogeneously charged surfaces. To address the problem I have used standard linearizations. First, the electrostatics in the electrolyte have been described by the Debye-Huckel approximation (1). Second, I have focused on the linear response to the applied field $\vec{E}_{\rm ext}$ and thus neglected the deformation of the counterion cloud (2). Eventually Eq. (2) is the linearized version of the Navier-Stokes equation valid at low Reynolds number.

However, this linear analysis proved sufficient to exhibit and quantify the onset of a pattern of convective rolls, the possibility of generating average currents and forces even in situations of zero mean charge density, and the fact that these may have components perpendicular to the applied electric field. These calculations provide the necessary tools to quantify the influence of surface defects in usual electro-osmosis. They are also meant to suggest experimental studies of roll patterns in man-made geometries designed by lithography [9,10]. Eventually, electromechanical couplings are essential for the design of micropumps and micromotors, a current field of interest to both physicists and biologists [3,8–11].

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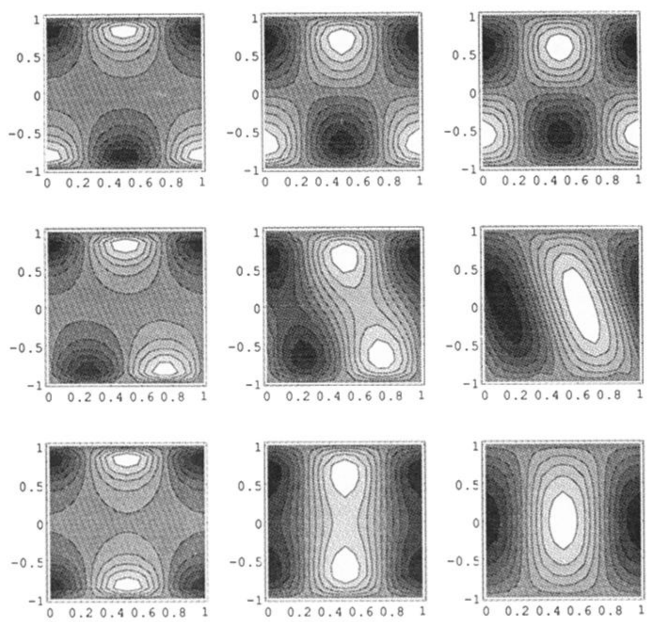

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