

Induced-Charge Electro-osmosis and Electrophoresis

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Notes and Homework Problems for Lecture 2

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1 Electro-osmosis

Consider a liquid *electrolyte*, consisting of positive and negative particles (“ions”) in solution, such as NaCl salt dissolved in water. The interface between the electrolyte and the container wall generally forms a *double layer* in equilibrium, where a nonzero surface charge (due to chemical effects) is screened by a very thin diffuse layer of excess ionic charge of width λ , the Debye screening length (typically 1-100 nm). The double layer is effectively a capacitor skin at the interface, which has a small voltage ζ across it, the *zeta potential* (typically 0.01 - 0.1 Volt), defined as the potential of the surface minus the potential just outside the double layer.

Now consider a tangential electric field E_{\parallel} applied parallel to a flat surface. The electric field acts on ions in the diffuse part of the double layer, which drag the fluid to produce an effective *slip velocity* outside the double layer, given by the Helmholtz-Smoluchowski formula,

$$u_{\parallel} = -\mu_E E_{\parallel}$$

where the constant of proportionality is

$$\mu_E = \frac{\varepsilon\zeta}{\eta}$$

in terms of the permittivity ε and viscosity η of the fluid.

An important application of electro-osmotic flow is *capillary electro-osmosis*, where an electric field is applied down a capillary tube to generate a uniform plug flow, $u = -\mu_E E$, driven by slip at the surface. Typical flow speeds of 100 $\mu\text{m}/\text{sec}$ (1 mm/min) are produced by fields of 100 Volt/cm. Electro-osmotic flows are very useful in modern microfluidic devices, since the flow speed is independent of channel radius. In contrast, pressure-driven (Poiseuille) flow down the channel produces a parabolic flow profile which decreases with miniaturization like the square of the radius due to viscous drag at the walls.

2 Electrophoresis

Reuss first observed colloidal clay particles moving in electric fields in 1806, but it was not explained until Smoluchowski’s theory of *electrophoresis* a century later, based on electro-osmotic slip generated at the surface of the colloidal particle. Smolukowski showed that particle velocity is $U = \mu_E E_b$, for a background electric field E_b , where the electrophoretic mobility, $\mu_E = \varepsilon\zeta/\eta$, is independent of particle size (for uniform surface charge, and thus uniform ζ).

(It can also be shown that the electrophoretic mobility does not depend on the shape or size of a particle with uniform ζ . This makes it impossible to separate particles by size, which might make you wonder how DNA electrophoresis works. The problem is circumvented by putting DNA fragments of different sizes in a gel, where molecular traps make larger fragments travel more slowly, thus allowing a map of the size distribution of DNA fragments, e.g. to identify a human DNA sample from a crime scene.)

This slip-driven motion is quite different from more familiar motion of particles being dragged in a viscous fluid, such as sedimentation due to gravity. An electrical analog of sedimentation is the famous Millikan Oil Drop experiment, where oil drops of radius a and charge Q are dragged through an uncharged viscous fluid (air) by an electric field. Balancing the (Stokes) drag force for a sphere, $6\pi\eta aU$, against the electrostatic force, QE_b , yields the drift velocity, $U = \mu_S E_b$, with $\mu_S = Q/6\pi\eta a$, which depends on the particle size and charge. (Millikan found that the charge always seemed to come in multiples of a certain number, which led to his Nobel Prize in 1923 for the discovery of the electron.)

Homework Problem #1: Assume that the double layer at the surface of a charged sphere in an electrolyte acts like a simple parallel plate capacitor of dielectric constant ε , width λ , voltage ζ and charge/area q . You may recall from high school physics that the capacitance/area is given by $C = \varepsilon/\lambda = q/\zeta$. Show that

$$\mu_E = \frac{3}{2} \frac{\lambda}{a} \mu_S$$

which illustrates how charge screening reduces the sphere's mobility in an electrolyte versus a non-ionic fluid, in the thin double-layer limit $\lambda \ll a$.

3 Induced-Charge Electro-osmosis

The situation changes if the surface charge (or ζ) is not fixed, but rather can change in response to an applied electric field. The electro-osmotic flow generated by an electric field acting on its own induced double-layer charge at a polarizable (e.g. metal or dielectric) surface is called *induced-charge electro-osmosis* (ICEO). Since the mobility depends on the applied field, ICEO is a nonlinear electrokinetic phenomenon, where the flow depends on the square of the field. This means the flow survives in an alternating AC field, which has many advantages in microfluidic devices (such as suppression of electrochemical reactions).

A canonical example of interest for microfluidics is the ICEO flow around uncharged metal cylinder of radius a in a uniform background field E_b . It is convenient to solve for the electrostatic potential $\phi(x, y)$ in the (x, y) plane, whose (negative) gradient is the electric field,

$$\vec{E} = E_x \hat{x} + E_y \hat{y} = -\vec{\nabla} \phi = - \left(\hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} \right) \phi$$

If the field is not strong enough to perturb the bulk concentration of ions, then the potential satisfies Laplace's equation from electrostatics,

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0$$

Homework Problem #2: Show that

$$\phi(x, y) = -E_b x \left(1 + \frac{pa^2}{x^2 + y^2} \right)$$

satisfies Laplace's equation outside the cylinder with the boundary condition, $\phi \sim -E_b x$ as $x, y \rightarrow \infty$, where p is the *electric dipole moment* of the charge distribution.

In polar coordinates, (r, θ) defined by $x = r \cos \theta, y = r \sin \theta$, the potential takes the form,

$$\phi(r, \theta) = -E_b r \cos \theta \left(1 + \frac{pa^2}{r^2} \right)$$

When the field is first turned on, the boundary condition on the cylinder is that of a conductor, $\phi = 0$, which implies $p = -1$, but this situation is unsteady since the nonzero normal electric field drives ions into the double layer. After a very short charging time, the induced double-layer charge expels the electric field, which must wrap around the cylinder with $p = 1$ in steady state.

We are now ready to calculate the steady ICEO flow around the cylinder. The (non-uniform) induced zeta potential, maximal along the field direction, is

$$\zeta(\theta) = \phi_s - \phi(r = a, \theta) = -2E_b a \cos \theta$$

where we set the cylinder potential to zero, $\phi_s = 0$ by symmetry. The tangential electric field, maximal perpendicular to the field direction, is

$$E_{\parallel}(r = a, \theta) = -\frac{1}{a} \frac{\partial \phi}{\partial \theta} = -2E_b \sin \theta$$

The Helmholtz-Smoluchowski formula then gives the fluid slip distribution on the surface,

$$u_{\parallel}(\theta) = -\frac{\varepsilon \zeta(\theta) E_{\theta}(\theta)}{\eta} = 2 \frac{\varepsilon a E_b^2}{\eta} \sin(2\theta) = 2U_{ICEO} \sin(2\theta)$$

The slip is maximal at 45° to the field direction and causes the fluid to be sucked in toward the cylinder along the field axis and expelled perpendicular to the field axis. Note that the fluid velocity is proportional to E_b^2 ("nonlinear"), so it does not depend on the sign of E_b and thus has a nonzero time average with AC forcing. In contrast, classical (linear) electro-osmosis time-averages to zero in an AC field.

4 Induced-Charge Electrophoresis

Consider an uncharged metal sphere at the origin with half its surface, the lower hemisphere ($y < 0$), coated by an insulator, placed in a background electric field, $E_b \hat{x}$ as above. By similar calculations the fluid slip can be shown to be

$$u_{\parallel}(\theta) = \frac{9}{8} U_{ICEO} \sin(2\theta)$$

but only on the upper hemisphere ($y > 0$), and zero below. The broken symmetry of the coating causes the metal sphere to move by *induced-charge electrophoresis* (ICEP), even though it is uncharged!

Homework Problem #3: Explain why the sphere will move by ICEP in the direction of its coating ($-\hat{y}$ direction); draw a sketch of the flow to support your argument. Then use the Stone-Samuels formula,

$$\vec{U} = -\frac{1}{4\pi a^2} \oint \vec{u}_{\parallel} dA$$

to calculate the velocity of the sphere, \vec{U} , as minus the surface average of the slip velocity, $\vec{u}_{\parallel} = u_{\parallel}(\theta)\hat{\theta}$. [Hint: In case you have not taken 18.02, this can be reduced to the following formula involving elementary integrals from 18.01:

$$U_y = -\frac{9U_{ICEO}}{32\pi} \left(\int_0^{\pi} \sin \phi d\phi \right) \left(\int_{-\pi}^{\pi} \sin(2\theta) \cos \theta \sin \theta d\theta \right)$$

since $\hat{y} \cdot \hat{\theta} = \cos \theta \sin \phi$, where (θ, ϕ) are the angles in spherical coordinates.]

This example illustrates how complicated translational (and rotational) ICEP motion can result in metal colloids of asymmetric shapes or surface properties.

For further reading: <http://math.mit.edu/~bazant/ICEO>.