Explorations into the Electroosmotic Flow around a Sphere

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1 Introduction

In the past, the study of colloid flows induced by electric fields has focused on the relationship between the velocity of charged particles and the electric forces acting on them. Recent work has shown that interesting (and potentially useful) flows occur even in the case of uncharged particles [2]. Perhaps the most surprising result is that at steady state, a nonuniform zeta potential is induced on the surface of conducting colloidal particles which acts to produce a flow that "sucks in fluid along the field axis and ejects it radially" but generates no net force on the particle [2].

The purpose of this paper is to explore the physical foundations of such flows and attempt to approximate the results found in Professor Bazant's work for spherical colloidal particles. We begin by examining the origins of interfacial slip velocity in electroosmosis which leads us to consider solutions of the electrodynamics problem and the Gouy-Chapman model for the charged interface. Finally, we pull all the pieces together to solve the flow problem around a stationary uncharged sphere in a uniform electric field. Throughout the analysis, vector harmonic methods will be used whenever possible.

2 Interfacial slip velocity in electroosmosis

2.1 Physical picture

The presence of a charged interface in an electrolyte solution disrupts the balance between positive and negative ions resulting in the formation of diffuse charge layers at the interface. The thickness of the diffuse charge layer is on the order of the Debye screening length, κ^{-1}, and the charge

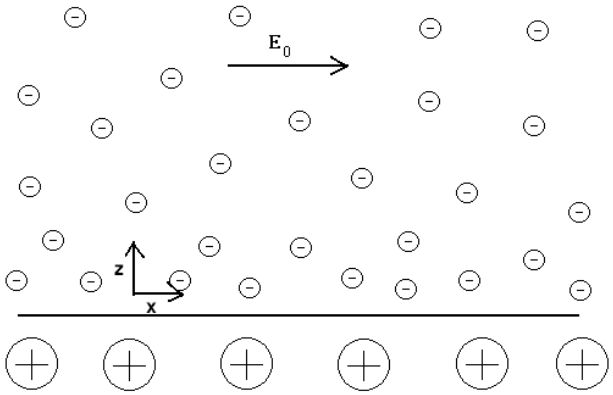

Figure 1: Diffuse layer of negative counterions (in solution) at a positively charged interface.

density within the diffuse layer, ρ_e, decays roughly exponentially in distance from the charged interface [1]. The presence of charge within the diffuse layer changes its fluid dynamics relative to the bulk and gives rise to a boundary layer at the charged interface (Figure 1).

Since the surface charge and diffuse charge layer do not form a rigid system, they move independently under the influence of external electric fields; they move in opposite directions because they have opposite signs. Furthermore, because ions drag fluid with them as they move, the net effect is an apparent slip velocity at the interface at macroscopic scales [1].

2.2 Derivation of the slip velocity

Within the boundary layer, the interface is almost flat and the electric field is approximately constant and parallel to the interface[1], so the fluid is reasonably modelled by unidirectional flow over an infinite plane of charge under the influence of an constant tangential electric field.

For this type of flow, the Navier-Stokes equations are

$$v_x \equiv v_x(y) \tag{1}$$

$$\rho\frac{\partial u}{\partial t} = -\frac{\partial P}{\partial x} + \mu\frac{\partial^2 v_x}{\partial z^2} + \rho_e(z)E_x(z), \tag{2}$$

[1] At steady state, no current can flow into the surface, so, for Ohmic materials, the normal component of the electric field must be zero.

where $\rho_e(z)$ and $E_x(z)$ are the charge density and electric field in the x-direction at a distance z from the interface. Defining the nondimensional variables

$$v_x' = \frac{v_x}{V}\ , \quad x' = \frac{x}{R}\ , \quad z' = \frac{z}{\delta}\ , \quad t' = \frac{t}{(R/V)}\ , \quad P' = \frac{P}{P_0} \tag{3}$$

where R is the length scale of the colloid particle, V is the macroscopic speed of the particle, and δ is the width of the boundary layer, the nondimensionalized form of equation (2) becomes

$$\rho \frac{V^2}{R}\frac{\partial v_x'}{\partial t'} = -\frac{P_0}{R}\frac{\partial P'}{\partial x'} + \frac{\mu V}{\delta^2}\frac{\partial^2 v_x'}{\partial z'^2} + \rho_e(z)E_x(z). \tag{4}$$

For small particles in aqueous solutions, the $Re \equiv \frac{VR}{\nu} \ll 1$, so the characteristic pressure is given by $P_0 = \frac{\mu V}{R}$. With this choice of P_0 and some rearrangement, equation (4) becomes

$$Re\frac{\delta^2}{R^2}\frac{\partial v_x'}{\partial t'} = -\frac{\delta^2}{R^2}\frac{\partial P'}{\partial x'} + \frac{\partial^2 v_x'}{\partial z'^2} + \frac{\delta^2}{\mu V}\rho_e(z)E_x(z). \tag{5}$$

Since $Re \ll 1$ and $\delta/R \ll 1$, the inertial and pressure terms are negligible leaving only the viscous force to balance electric forces. Thus, the governing equation in dimensional form is

$$\mu\frac{\partial^2 v_x}{\partial z^2} + \rho_e(z)E_x(z) = 0. \tag{6}$$

To solve this equation, recall that for steady state systems, the electric field and charge density can be related to a potential function, Ψ, by

$$\mathbf{E} = -\nabla\Psi \tag{7}$$

$$\rho_e = -\frac{\epsilon}{4\pi}\nabla^2\Psi. \tag{8}$$

For this system, the potential can be written as

$$\Psi = -E_\infty x + \Psi_s, \tag{9}$$

where E_∞ is the tangential electric field felt at the outer edge of the boundary layer and Ψ_s is the potential due to the surface and diffuse charge. Note that by symmetry, $\frac{\partial\Psi_s}{\partial x} = 0 = \frac{\partial\Psi_s}{\partial y}$. Thus,

$$E_x = E_\infty \tag{10}$$

$$\rho_e = -\frac{\epsilon}{4\pi}\frac{\partial^2\Psi_s}{\partial z^2} \tag{11}$$

Substituting these results into equation (6), the governing equation becomes

$$\mu \frac{\partial^2 v_x}{\partial z^2} - \frac{\epsilon}{4\pi} E_\infty \frac{\partial^2 \Psi_s}{\partial z^2} = 0. \tag{12}$$

This equation can be integrated exactly subject to the following boundary conditions:

1. $v_x = 0$ at $y = 0$ (no-slip condition),
2. $\Psi_s(0) = \zeta$ at $y = 0$ (definition of the zeta potential),
3. $\frac{\partial v_x}{\partial z} = 0$ as $z \to \infty$ (matching between inner and outer velocity fields), and
4. $\frac{\partial \Psi_s}{\partial z} = 0$ as $z \to \infty$ ($\mathbf{E}_\perp = 0$ at outer edge of boundary layer).

to give

$$v_x = \frac{\epsilon}{4\pi\mu} \left[\Psi_s(y) - \zeta\right] E_\infty. \tag{13}$$

The slip velocity observed outside on macroscopic scales is the value of v_x at the outer edge of the boundary layer.

$$v^s = \lim_{z\to\infty} v_x = \frac{\epsilon \Psi_\Delta}{4\pi\mu} E_\infty, \tag{14}$$

where Ψ_Δ is defined to be the potential difference between the bulk solution and surface of the charged interface.

Several important observations should be made about the slip velocity. First, it is parallel to the interfacial surface. Second, it is proportional to the tangential electric field outside the boundary layer and to the difference in electric potential between the bulk solution and the interface. Thus, if the electrodynamics problem can be solved independently of the flow, equation (14) specifies the boundary conditions for the fluid flow problem. The two main issues involved in solving the electrodynamics problem,

- determining the electric field at the outer edge of the boundary layer and
- calculating the potential difference between the bulk and the interface

are discussed next.

3 The electrodynamics problem

Steady state electrodynamic problems have the convenient property that the electric field can always be related to a scalar potential function that is harmonic in regions with zero charge density. For problems with spherical or cylindrical symmetry and linear boundary conditions, this property makes it possible to easily compute the electric field using vector harmonic methods. In this section, vector harmonic methods are applied to solve electrodynamics problems that are relevant to colloidal fluid flows resulting from uniform, applied electric fields. In all cases, it is assumed that the applied electric field is $\mathbf{E}_0$, insulators are linear dielectrics ($\mathbf{D} = \epsilon\mathbf{E}$, ϵ the dielectric constant), and conductors obey Ohm's law ($\mathbf{J} = \kappa\mathbf{E}$, κ the conductivity).

For colloid flow problems, the relevant information to extract from the electrodynamics problem are the electric field at the external surface and the free surface charge. The electric field at the external surface is important because it determines the electric field at the outer edge of the fluid boundary layer; the free surface charge is important because, as will be shown in section 4, it can be directly related to the potential difference between the bulk solution and the charged interface.

3.1 Jump conditions at material interfaces

Because colloidal flow problems often involve materials with differing electrical properties, it is important to understand the jump conditions on the electric field at material interfaces.

For linear materials, the Maxwell equations for the electric field at steady state are

$$\nabla \bullet \mathbf{D} = \epsilon \nabla \bullet \mathbf{E} = 4\pi\rho_e \tag{15}$$

$$\nabla \times \mathbf{E} = 0, \tag{16}$$

where $\mathbf{E}$ and $\mathbf{D}$ are the electric field and displacement. The integral forms of these equations lead to the jump conditions

$$(\mathbf{D} - \hat{\mathbf{D}}) \bullet \mathbf{n} = \epsilon(\mathbf{E} - \hat{\mathbf{E}}) \bullet \mathbf{n} = 4\pi\sigma \tag{17}$$

$$(\mathbf{E} - \hat{\mathbf{E}}) \bullet \mathbf{t} = 0, \tag{18}$$

across material interfaces, where $\mathbf{n}$ is the unit normal and $\mathbf{t}$ is any unit tangent to the surface defined by the material interface and σ is the surface density of free charge. For moving interfaces, the second equation becomes

$$(\mathbf{E} - \hat{\mathbf{E}}) \bullet \mathbf{t} = -(\mathbf{n} \bullet \beta)[\mathbf{n} \times (\mathbf{B} - \hat{\mathbf{B}})] \bullet \mathbf{t} \tag{19}$$

where $\mathbf{v} = c\beta$ is the velocity of the interface and $\mathbf{B}$ is the magnetic field [7]. Fortunately, for Stokes flow problems, $\mathbf{v}$ is very small compared to the speed of light, so the tangential jump condition for the electric field is well approximated by equation (18).

An important feature of steady state problems is that the current density must be divergence free, $\nabla \bullet \mathbf{J} = 0$. In integral form, this condition on the current density implies that there can be no jump in the normal component of the current density across any surface. That is if a surface, S, has normal vector, $\mathbf{n}$,

$$(\mathbf{J} - \hat{\mathbf{J}}) \bullet \mathbf{n} = 0. \tag{20}$$

For conducting materials that obey Ohm's law, this jump condition for the current density translates directly into a jump condition on the electric field:

$$(\kappa\mathbf{E} - \hat{\kappa}\hat{\mathbf{E}}) \bullet \mathbf{n} = 0. \tag{21}$$

where $\mathbf{n}$ is defined as for equations (17) and (18).

At first glance, equations (17) and (21) seem to be independent normal jump conditions for the electric field. Fortunately, they are consistent due to the presence of free surface charge. Since equation (21) is self contained, it is easier to use in solving the electrodynamics problem. The electric displacement jump condition can then be used to find the amount of free surface charge present at material interfaces.

3.2 Conducting material containing a spherical conductivity anomaly

Suppose that a sphere of radius a with conductivity $\hat{\kappa}$ is embedded within a conducting material with conductivity κ (Figure 2).

To determine the electric field, we proceed by seeking a potential function, Ψ, that is a linear combination of $\mathbf{E}_0$ and the vector harmonics. The appropriate boundary conditions for this problem are

1. $\mathbf{E} \to \mathbf{E}_0$ as $r \to \infty$,
2. $(\mathbf{E} - \hat{\mathbf{E}}) \bullet \mathbf{t} = 0$ at $r = a$, and
3. $(\mathbf{J} - \hat{\mathbf{J}}) \bullet \mathbf{n} = (\kappa\mathbf{E} - \hat{\kappa}\hat{\mathbf{E}}) \bullet \mathbf{n} = 0$ at $r = a$.

In the region outside the conductivity anomaly, we use the exterior vector harmonics to obtain

$$\Psi = -\mathbf{E}_0 \bullet \mathbf{x} + \alpha \frac{\mathbf{E}_0 \bullet \mathbf{x}}{r^3}. \tag{22}$$

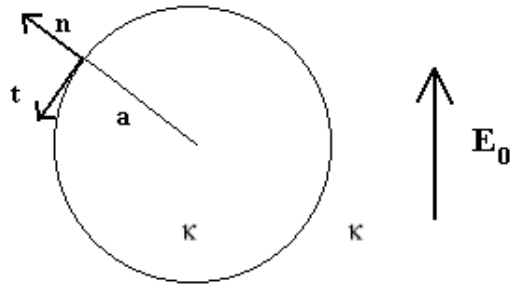

Figure 2: Spherical conductivity anomaly with conductivity $\hat{\kappa}$ embedded within a conducting material with conductivity κ.

Similarly, we obtain

$$\hat{\Psi} = \hat{\alpha}\mathbf{E}_0 \bullet \mathbf{x} \tag{23}$$

for the potential within the conductivity anomaly. Thus, the corresponding electric fields are

$$\mathbf{E} = \mathbf{E}_0 - \alpha\frac{\mathbf{E}_0}{r^3} + 3\alpha\frac{(\mathbf{E}_0 \bullet \mathbf{x})\mathbf{x}}{r^5} \tag{24}$$

$$\hat{\mathbf{E}} = -\hat{\alpha}\mathbf{E}_0. \tag{25}$$

Applying the boundary conditions, we find that

1. is automatically satisfied by the choice of Ψ,
2. $1 - \frac{\alpha}{a^3} = -\hat{\alpha}$, and
3. $\kappa\left(1 + 2\frac{\alpha}{a^3}\right) = -\hat{\kappa}\hat{\alpha}$.

Solving this system of equations for α and $\hat{\alpha}$ gives $\alpha = a^3\left(\frac{\epsilon-1}{\epsilon+2}\right)$ and $\hat{\alpha} = \left(\frac{-3}{\epsilon+2}\right)$ where $\gamma = \hat{\kappa}/\kappa$. So, the interior and exterior potentials are

$$\Psi = -\left(1 - \left(\frac{a}{r}\right)^3\left(\frac{\gamma-1}{\gamma+2}\right)\right)\mathbf{E}_0 \bullet \mathbf{x} \tag{26}$$

$$\hat{\Psi} = \left(\frac{-3}{\gamma+2}\right)\mathbf{E}_0 \bullet \mathbf{x}. \tag{27}$$

The corresponding electric fields are

$$\mathbf{E} = \left(1 - \left(\frac{a}{r}\right)^3 \left(\frac{\gamma - 1}{\gamma + 2}\right)\right) \mathbf{E}_0 + 3 \left(\frac{a}{r}\right)^3 \left(\frac{\gamma - 1}{\gamma + 2}\right) (\mathbf{E}_0 \bullet \mathbf{n})\, \mathbf{n} \tag{28}$$

$$\hat{\mathbf{E}} = \left(\frac{3}{\gamma + 2}\right) \mathbf{E}_0. \tag{29}$$

As a side note, it is interesting to observe that these potentials and fields are the same as those for a spherical dielectric material with dielectric constant γ in a vacuum under the influence of a uniform applied electric field $\mathbf{E}_0$.

The important information to extract from these potentials are the electric field immediately outside of the sphere and the surface charge on the sphere. For this problem, these are

$$\mathbf{E} = \left(\frac{3}{\gamma + 2}\right) \mathbf{E}_0 + 3 \left(\frac{\gamma - 1}{\gamma + 2}\right) (\mathbf{E}_0 \bullet \mathbf{n})\, \mathbf{n} \tag{30}$$

$$\sigma = \frac{1}{4\pi} \left(\mathbf{E} - \hat{\mathbf{E}}\right) \bullet \mathbf{n} = \frac{3}{4\pi} \left(\frac{\gamma - 1}{\gamma + 2}\right) (\mathbf{E}_0 \bullet \mathbf{n}) \tag{31}$$

because $\epsilon = 1$ for conductors[2].

3.3 Insulating sphere embedded in a conductor

Suppose that an insulating sphere of radius a with dielectric constant ϵ is embedded within a conducting material with conductivity κ (Figure 3).

As in the previous case, we seek a potential function, Ψ, that is a linear combination of $\mathbf{E}_0$ and the vector harmonics. For this problem, the appropriate boundary conditions are

1. $\mathbf{E} \to \mathbf{E}_0$ as $r \to \infty$,
2. $(\mathbf{E} - \hat{\mathbf{E}}) \bullet \mathbf{t} = 0$ at $r = a$, and
3. $\mathbf{J} \bullet \mathbf{n} = \kappa \mathbf{E} \bullet \mathbf{n} = 0$ at $r = a$.

The last boundary condition arises because no current can flow through the insulating sphere. Because the only difference between this and the previous problem are the boundary conditions, the same potential functions can be used:

$$\Psi = -\mathbf{E}_0 \bullet \mathbf{x} + \alpha \frac{\mathbf{E}_0 \bullet \mathbf{x}}{r^3} \tag{32}$$

$$\hat{\Psi} = \hat{\alpha} \mathbf{E}_0 \bullet \mathbf{x}. \tag{33}$$

[2]Actually, for "physical" conductors that are finite in extent, ϵ may effectively differ from 1 due to the finite accumulation of charge at the conductor boundaries.

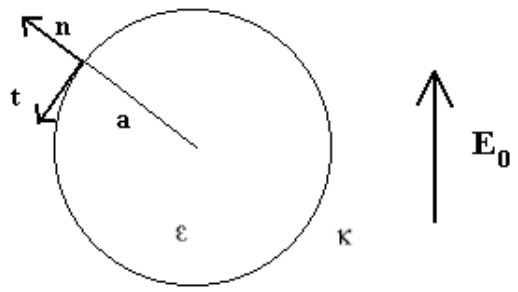

Figure 3: Insulating sphere with dielectric constant $\hat{\epsilon}$ embedded within a conducting material with conductivity κ.

Applying the boundary conditions, we find that

1. is automatically satisfied by the choice of Ψ,
2. $1 - \frac{\alpha}{a^3} = -\hat{\alpha}$, and
3. $\kappa\left(1 + 2\frac{\alpha}{a^3}\right) = 0$.

Solving for α and $\hat{\alpha}$, we obtain $\alpha = -\frac{a^3}{2}$ and $\hat{\alpha} = -\frac{3}{2}$. With these values of α and $\hat{\alpha}$, the potential functions are

$$\Psi = -\left(1 + \frac{1}{2}\left(\frac{a}{r}\right)^3\right)(\mathbf{E}_0 \bullet \mathbf{x}) \tag{34}$$

$$\hat{\Psi} = -\frac{3}{2}\mathbf{E}_0 \bullet \mathbf{x}. \tag{35}$$

Thus, the electric field is given by

$$\mathbf{E} = \left(1 + \frac{1}{2}\left(\frac{a}{r}\right)^3\right)\mathbf{E}_0 - \frac{3}{2}\left(\frac{a}{r}\right)^3(\mathbf{E}_0 \bullet \mathbf{n})\,\mathbf{n} \tag{36}$$

$$\hat{\mathbf{E}} = \frac{3}{2}\mathbf{E}_0. \tag{37}$$

For this problem, the electric field immediately outside of the sphere is

$$\mathbf{E} = \frac{3}{2}\mathbf{E}_0 - \frac{3}{2}(\mathbf{E}_0 \bullet \mathbf{n})\,\mathbf{n} \tag{38}$$

and the surface charge is

$$\sigma = \frac{1}{4\pi}\left(\mathbf{E} - \epsilon\hat{\mathbf{E}}\right) \bullet \mathbf{n} = -\frac{3\epsilon}{8\pi}(\mathbf{E}_0 \bullet \mathbf{n}). \tag{39}$$

As would be expected, the solution for this problem agrees with the results of the previous section in the limit that $\gamma = \hat{\kappa}/\kappa \to 0$.

A few observations should be made about equations (38) and (39). First, the exterior electric field at the sphere's surface is purely tangential because the surface charge that accumulates during pre-steady state current flow acts to keep external electric field lines from entering the sphere. Second, a greater polarizability of the material in the sphere results in a larger surface charge build up. This effect arises because a highly polarizable material will respond to the electric field by placing a large amount of bound charge at the poles of the sphere. To balance the bound charge, a correspondingly high amount free surface charge is required at the poles.

Finally, it is important note that the results of this problem are applicable regardless what the charge carriers are in the conductor. That the carriers cannot flow between the conductor and the material in the sphere is the significant feature of the system. Therefore, analysis of this type of problem is directly applicable to the situation of a metal sphere placed in an non-reacting electrolyte solution because the metal sphere is impenetrable to ions in solution. In this case, the finite bounds of the metal sphere and the fact that the solution is an electron insulator gives the metal an effective dielectric constant greater than 1 due to charge build up at the surface. For colloidal fluid flows, it is this interpretation of an insulator embedded within a conductor that is relevant.

4 The charged interface model

Having solved the electrodynamics problem, it remains to calculate the potential difference, Ψ_Δ, between the bulk solution and the charged interface. It turns out that Ψ_Δ can be related to the surface density of free charge using a model for the charged interface.

There are many models of the charge distribution that arises at charged interfaces. For historical reasons, these are known as *double layer* models [3]. The simplest model that gives a relation between the free surface charge is the Gouy-Chapman model that was developed in the early 1900's. In this model, the ions in solution form a diffuse layer at the interface (Figure 4). In the Gouy-Chapman model, the charged interface is assumed to be in

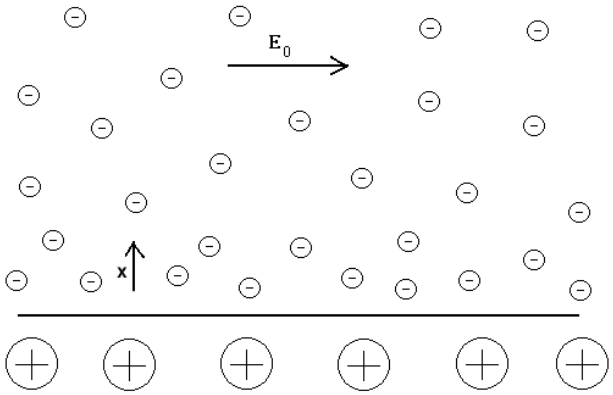

Figure 4: Diffuse layer of negative counterions (in solution) at a positively charged interface. (The only difference between this figure and Figure 1 is the coordinate system.)

thermal equilibrium[3]. So, the concentration of ions obeys Boltzmann's law

$$n_i(x) = n_i^0 \exp\left(\frac{-z_i e \Psi_\delta}{kT}\right) \tag{40}$$

where $n_i(z)$ is the concentration of the i-th species at a distance z from the interface, n_i^0 is the bulk concentration of the i-th species, z_i is the valency of the i-th species, $\Psi_\delta \equiv \Psi(x) - \Psi(\infty)$ is the potential at x relative to the bulk potential, e is charge of an electron, k is Boltzmann's constant, and T is the absolute temperature. Thus, the charge density at a distance x from the interface is

$$\rho_e(x) = \sum_i n_i z_i e = \sum_i n_i^0 z_i e \exp\left(\frac{-z_i e \Psi_\delta}{kT}\right) \tag{41}$$

Substituting this expression for the charge density into Poisson's equation, we obtain the differential equation

$$\frac{\partial^2 \Psi_\delta}{\partial x^2} = -\frac{4\pi \rho_e(x)}{\epsilon} = -\frac{4\pi}{\epsilon} \sum_i e n_i^0 z_i \exp\left(\frac{-z_i e \Psi_\delta}{kT}\right) \tag{42}$$

[3]Because the boundary layer in the flow problem is very thin, it is not unreasonable to assume that the charged interface reaches thermal equilibrium on a time scale that is very short compared to the time scale of fluid motion.

where ϵ is the dielectric constant of the solution. While this equation can be solved exactly [5, 3], it is simpler and more illuminating to use the Debye-Hückel approximation under conditions where the electrical energy is small compared to the thermal energy. Expanding the exponential and keeping only the first two terms, we obtain

$$\frac{\partial^2 \Psi_\delta}{\partial x^2} == -\frac{4\pi}{\epsilon}\left(\sum_i e n_i^0 z_i - \sum_i \frac{e^2 n_i^0 z_i^2 \Psi_\delta}{kT}\right). \tag{43}$$

Since, the first sum must be zero in electrically neutral solutions, we are left with the linear equation

$$\begin{aligned}\frac{\partial^2 \Psi_\delta}{\partial x^2} &= \frac{4\pi}{\epsilon}\left(\sum_i \frac{e^2 n_i^0 z_i^2}{kT}\right)\Psi_\delta \\ &= \kappa^2 \Psi_\delta\end{aligned} \tag{44}$$

where

$$\kappa = \left(\frac{4\pi e^2 \sum n_i^0 z_i^2}{\epsilon kT}\right)^{1/2}. \tag{45}$$

With the boundary conditions,

1. $\Psi_\delta = \zeta - \Psi(\infty) = -\Psi_\Delta$ at $x = 0$,
2. $\Psi_\delta \to 0$ as $x \to \infty$, and
3. $\frac{\partial \Psi_\delta}{\partial x} \to 0$ as $x \to \infty$,

equation (44) can be integrated to give

$$\Psi_\delta = -\Psi_\Delta \exp(-x/\kappa^{-1}) \tag{46}$$

where κ^{-1} is the Debye screening length.

The surface charge density observed at macroscopic scales can be obtained by integrating the diffuse charge density, ρ_e, from the interface surface to infinity to give

$$\begin{aligned}\sigma = \int_0^\infty \rho_e dx &= -\frac{\epsilon}{4\pi}\int_0^\infty \frac{\partial^2 \Psi_\delta}{\partial x^2} dx \\ &= -\frac{\epsilon}{4\pi}\left.\frac{\partial \Psi_\delta}{\partial x}\right|_{x=0}^{x=\infty} = \frac{\epsilon\kappa}{4\pi}\Psi_\Delta\end{aligned} \tag{47}$$

This equations allows us to compute the potential difference between the surface and the bulk solution, Ψ_Δ, from the surface charge density found by solving the electrodynamics problem. With this relationship in place, we now have all the pieces necessary to define the slip boundary conditions for flow past a colloid particle.

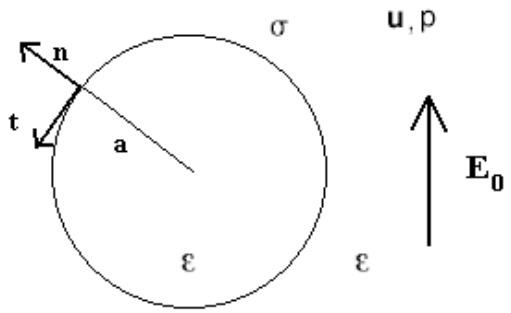

Figure 5: Spherical colloid particle with dielectric constant ϵ_s in an electrolyte solution with dielectric constant ϵ in an uniform applied electric field.

5 Flow around a stationary uncharged sphere in a uniform electric field

Having solved the slip velocity, electrodynamics, and charged interface problems, we are now in a position to solve the Stokes flow problem

$$\mu \nabla^2 \mathbf{u} = \nabla p \ , \ \nabla \bullet u = 0. \tag{48}$$

for the situation of an uncharged sphere in a uniform applied electric field (Figure 5).

Combining equations (14), (38), (39), and (47), the slip velocity on the surface of the sphere is

$$v^s = -\frac{9\epsilon_s \kappa^{-1}}{16\pi}(\mathbf{E}_0 \bullet \mathbf{n})(\mathbf{E}_0 \bullet \mathbf{t}) \tag{49}$$

where $\mathbf{n}$ and $\mathbf{t}$ are the unit normal and unit tangent to the surface of the sphere, κ^{-1} is the Debye screening length, and ϵ_s is the dielectric constant for the material composing the sphere[4]. Defining $\lambda = \frac{9\epsilon_s \kappa^{-1}}{16\pi}$, the boundary conditions for this problem are specified by

1. $\mathbf{u} \bullet \mathbf{n} = 0$ and
2. $\mathbf{u} \bullet \mathbf{t} = v^s = -\lambda(\mathbf{E}_0 \bullet \mathbf{n})(\mathbf{E}_0 \bullet \mathbf{t})$

[4]In the case of a conducting sphere, recall that for real conducting spheres, there is still an effective dielectric constant due to its finite polarizability.

at $r = a$.

To solve the problem, we can apply vector harmonic methods. Since the boundary conditions are quadratic in the applied electric field, we seek a potential functions that are linear in the vector harmonics but quadratic in the electric field. This method should work because changing the functional dependence of the solution on the physical parameters has no effect on the harmonicity of the solution. Unfortunately, the number of combinations to consider is increased as a result of the quadratic nature of the boundary conditions. While this increases the amount of algebra, the fundamental approach is unchanged. Note that because we do not know what the flow will be as $r \to \infty$, the potential functions need to include both exterior and interior harmonics.

For this problem, the potential functions are

$$\phi = \alpha\left[\frac{\mathbf{E}_0 \bullet \mathbf{E}_0}{r^3} - 3\frac{(\mathbf{E}_0 \bullet \mathbf{x})^2}{r^5}\right] + \beta\left[r^2(\mathbf{E}_0 \bullet \mathbf{E}_0) - 3(\mathbf{E}_0 \bullet \mathbf{x})^2\right] + \gamma\left[\frac{\mathbf{E}_0 \bullet \mathbf{E}_0}{r}\right] + \delta\left[\mathbf{E}_0 \bullet \mathbf{E}_0\right] \quad (50)$$

$$\psi = 0 \quad (51)$$

$$\mathbf{A} = \xi\left[15\frac{(\mathbf{E}_0 \bullet \mathbf{x})^2}{r^7}\mathbf{x} - 3\frac{(\mathbf{E}_0 \bullet \mathbf{x})}{r^5}\mathbf{E}_0\right] + \omega\left[3r^2(\mathbf{E}_0 \bullet \mathbf{x})\mathbf{E}_0 - 15(\mathbf{E}_0 \bullet \mathbf{x})^2\mathbf{x}\right] + \theta\left[\frac{\mathbf{E}_0 \bullet \mathbf{x}}{r^3}\mathbf{E}_0\right] + \tau\left[(\mathbf{E}_0 \bullet \mathbf{E}_0)\mathbf{x}\right] + \chi\left[(\mathbf{E}_0 \bullet \mathbf{x})\mathbf{E}_0\right] + \varrho\left[\frac{\mathbf{E}_0 \bullet \mathbf{E}_0}{r^3}\mathbf{x}\right]. \quad (52)$$

Because $[\mathbf{E}_0 \bullet \mathbf{E}_0]$ has zero gradient and $\left[\frac{\mathbf{E}_0 \bullet \mathbf{E}_0}{r^3}\mathbf{x}\right]$ is divergence free, they do not contribute to $\mathbf{u}$ or p. Thus, we can immediately set δ and ϱ to zero. Using the "Hinch method," the velocity field is found to be

$$\mathbf{u} = \mathbf{x}\left[\left(-\tfrac{3\alpha}{r^5} + 2\beta - \tfrac{\gamma}{r^3}\right)(\mathbf{E}_0 \bullet \mathbf{E}_0) + \left(\tfrac{15\alpha}{r^7} - \tfrac{90\xi}{r^7} - \tfrac{3\theta}{r^5} + 6\omega\right)(\mathbf{E}_0 \bullet \mathbf{x})^2\right] + \mathbf{E}_0\left[\left(-\tfrac{6\alpha}{r^5} - 6\beta + \tfrac{30\xi}{r^5} - 30\omega r^2\right)(\mathbf{E}_0 \bullet \mathbf{x})\right]. \quad (53)$$

Notice that the $\tau\left[(\mathbf{E}_0 \bullet \mathbf{E}_0)\mathbf{x}\right]$ and $\chi\left[(\mathbf{E}_0 \bullet \mathbf{x})\mathbf{E}_0\right]$ terms do not contribute to the velocity field, so we can set $\tau = 0 = \chi$. Applying the boundary conditions to equation (53), we find that

$$0 = \left(-\frac{3\alpha}{a^4} + 2\beta a - \frac{\gamma}{a^2}\right)(\mathbf{E}_0 \bullet \mathbf{E}_0) + \left(\tfrac{9\alpha}{a^4} - 6\beta a - \tfrac{60\xi}{a^4} - \tfrac{3\theta}{a^2} - 24\omega a^3\right)(\mathbf{E}_0 \bullet \mathbf{n})^2 \quad (54)$$

$$-\lambda(\mathbf{E}_0 \bullet \mathbf{n})(\mathbf{E}_0 \bullet \mathbf{t}) = \left(-\tfrac{6\alpha}{a^4} - 6\beta a + \tfrac{30\xi}{a^4} - 30\omega a^3\right)(\mathbf{E}_0 \bullet \mathbf{n})(\mathbf{E}_0 \bullet \mathbf{t}). \tag{55}$$

Equating the coefficients of $(\mathbf{E}_0 \bullet \mathbf{E}_0)$, $(\mathbf{E}_0 \bullet \mathbf{n})$, and $(\mathbf{E}_0 \bullet \mathbf{t})$ gives the three equations

$$-\frac{3\alpha}{a^4} + 2\beta a - \frac{\gamma}{a^2} = 0 \tag{56}$$

$$\frac{3\alpha}{a^4} - 2\beta a - \frac{20\xi}{a^4} - \frac{\theta}{a^2} - 8\omega a^3 = 0 \tag{57}$$

$$-\frac{6\alpha}{a^4} - 6\beta a + \frac{30\xi}{a^4} - 30\omega a^3 = -\lambda. \tag{58}$$

We need three more equations to determine unique solution. These can be found by using $\nabla \bullet \mathbf{u} = 0$.

By the diverence theorem, we know that

$$\int_S \mathbf{u} \bullet \mathbf{n} dS = 0 \tag{59}$$

over any surface, S, containing the entire sphere $r = a$. Note that we can ignore the contibution of the surface of the sphere $r = a$ to the a "total" surface integral because $\mathbf{u} \bullet \mathbf{n} = 0$ on the sphere. Taking S to be a sphere of radius $r > a$,

$$0 = \int_S \left(-\tfrac{3\alpha}{r^4} + 2\beta r - \tfrac{\gamma}{r^2}\right)(\mathbf{E}_0 \bullet \mathbf{E}_0) dS + \int_S \left(\tfrac{9\alpha}{r^4} - 6\beta r - \tfrac{60\xi}{r^4} - \tfrac{3\theta}{r^2} - 24\omega r^3\right)(\mathbf{E}_0 \bullet \mathbf{n})^2 dS. \tag{60}$$

Recognizing that $\int_S dS = 4\pi r^2$ and $\int_S (\hat{\mathbf{z}} \bullet \mathbf{n}) dS = 4\pi r^2$ and rearranging, we see that

$$0 = 4\pi r^2 (\mathbf{E}_0 \bullet \mathbf{E}_0)\left(-\frac{\gamma + \theta}{r^2} - \frac{20\xi}{r^4} - 8\omega r^3\right). \tag{61}$$

Since this must hold for any r, we require that $\gamma = -\theta$ and $\xi = 0 = \omega$. Using these results, the system of equations (56) - (58) simplifies to

$$\frac{3\alpha}{a^4} - 2\beta a - \frac{\theta}{a^2} = 0 \tag{62}$$

$$\frac{6\alpha}{a^4} + 6\beta a = \lambda. \tag{63}$$

Unfortunately, there is still one degree of freedom. To eliminate this degree of freedom, we make the assumption that the pressure field around the sphere is constant because colloidal particles are so small[5]. Thus, $\theta = 0$ so that

$$\alpha = \frac{\lambda a^4}{15} \tag{64}$$

$$\beta = \frac{\lambda}{10a}. \tag{65}$$

Plugging the values for all the constants into equation (53), we find that[6]

$$\mathbf{u} = \lambda \mathbf{n} \left[\frac{1}{5} \left(1 - \left(\frac{a}{r} \right)^4 \right) (\mathbf{E}_0 \bullet \mathbf{E}_0) + \left(\frac{a}{r} \right)^4 (\mathbf{E}_0 \bullet \mathbf{n})^2 \right] - \frac{1}{5} \lambda \mathbf{E}_0 \left(3 + 2 \left(\frac{a}{r} \right)^4 \right) (\mathbf{E}_0 \bullet \mathbf{n}). \tag{66}$$

Notice that the flow field is proportional to λ. Thus, a greater flow rate is achieved by increasing the polarizability of the sphere or the thickness of the boundary layer. It is also interesting to observe that this velocity field has the "qualitative" features of Bazant's theory. Along the axis of the electric field, fluid is sucked in because the fluid velocity in the axial direction is

$$\mathbf{u} = -\frac{2\lambda |\mathbf{E}_0|^2}{5} \left[1 + \left(\frac{a}{r} \right)^4 \right] \mathbf{n}. \tag{67}$$

In directions perpendicular to the electric field, fluid flows away from the sphere because for $\mathbf{n}$ perpendicular to $\mathbf{E}_0$

$$\mathbf{u} = \frac{\lambda |\mathbf{E}_0|^2}{5} \left[1 - \left(\frac{a}{r} \right)^4 \right] \mathbf{n} \tag{68}$$

and $1 - (a/r)^4 > 0$ when $r > a$.

6 Conclusion

In this paper, we have discussed the major theoretical components required to compute the flow field around a spherical, colloidal particle in an electrolyte solution. To take advantage of the spherical symmetry in the problem, vector harmonic methods were used whereever possible. It was shown

[5] This is a MAJOR handwave and probably bogus, but I couldn't think of anything else before the project deadline.

[6] It would have been nice to plot the velocity field, but I didn't have the time.

that vector harmonic methods give reasonable results even for problems where the boundary conditions are not linear in the physical parameters of the problem. Further investigation of the solution found in section 5 is necessary to verify this hypothsis. In particular, a more rigorous way close the system of equations (62) and (63) needs to be found and the resulting flow fields should be compared with results derived using other analytic methods.

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