Streaming potential generated by two-phase flow in a capillary

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(Received 13 September 2006; accepted 7 February 2007; published online 1 May 2007)

The streaming potential generated by pressure-driven two-phase flow in a circular capillary differs from that generated by single-phase flow. Three model problems are considered, in which the dispersed phase consists of either (i) a rigid spherical particle (possibly charged), (ii) an uncharged spherical bubble, and (iii) a long, uncharged Bretherton bubble. In all three cases, the particle or bubble is assumed to lie on the center line of the capillary tube, so that the problem is axisymmetric, and is assumed to be of almost the same diameter as the internal diameter of the capillary, so that lubrication theory can be used. The electrical potentials on the surface of the particle and on the walls of the capillary are \( \xi_p \) and \( \xi_c \), respectively, and the Debye length is assumed much smaller than the gap between the particle and the walls of the capillary. If the flow rate is held constant, the presence of the rigid particle increases the pressure drop between the ends of the capillary, and also changes the streaming potential by an amount proportional to \( \xi_c - \xi_p \). This change in potential will in general be small compared to the total streaming potential developed between the two ends of a long capillary. However, if the capillary is filled with a large number of rigid particles, not only will the changes in pressure drop and streaming potential between the two ends of the capillary be large, but there will be a significant change in the coefficient of proportionality between pressure drop and streaming potential. The presence of an uncharged spherical bubble or Bretherton bubble changes the pressure drop between the ends of the capillary (for a given flow rate) but does not change the linear relation between pressure drop and streaming potential. However, the linear relation between flow rate and streaming potential is modified for the spherical bubble, and becomes nonlinear when a Bretherton bubble is present. © 2007 American Institute of Physics. [DOI: 10.1063/1.2717847]

I. INTRODUCTION

Streaming potentials generated by the flow of a single aqueous fluid through porous rock have been widely studied and are reasonably well understood. Much less is known about the potentials generated by two-phase flow,1–3 even though two or more phases are frequently present in the rock formations of interest to the petroleum industry. Experiments are not straightforward: one set of experiments3 suggests that the injection of gas into a water-saturated rock can increase streaming potentials by several orders of magnitude, though two or more phases are not straightforward: one set of experiments3 suggests that the injection of gas into a water-saturated rock can increase streaming potentials by several orders of magnitude, though two or more phases are frequently present in the rock. The electrokinetic effects of two-phase flow can have practical applications, in particular to detect the motion of water approaching a production well.7–9

The presence of two phases is also important in electroseismics: the electric signals generated by seismic waves may be larger near a gas/liquid interface since the gas compressibility leads to enhanced motion of fluid relative to rock as the seismic wave passes by. The electrokinetic properties of permeable rock are of scientific interest in their own right, and offer information to help characterize the rock.10

Here we tackle three simple model problems, and determine the streaming potential generated as particles or bubbles are pumped along the centerline of a fluid-filled cylindrical capillary. We consider the limiting case in which the diameter \( 2R_p \) of the particle is only slightly less than the diameter \( 2R_c \) of the tube, with \( R_c - R_p = h_0 \ll R_p \). This enables us to use lubrication theory. We assume that the electrical potentials \( \xi_p \) and \( \xi_c \) at the surface of the particle and tube are fixed, and that the charge cloud thickness, characterized by the Debye length \( \kappa^{-1} \), is small, with \( \kappa^{-1} \ll h_0 \). The incompressible fluid is Newtonian, with viscosity \( \mu \), and is assumed not to slip at solid boundaries. Fluid velocities and length scales are assumed sufficiently small that inertia can be neglected. It is known11,12 that when \( R_p \ll R_c \), inertia causes spherical particles to migrate to a position \( r \approx 0.6R_c \), but when \( R_p \ll R_c \), colloidal interactions between the particle and capillary wall are likely to control stability of the axial configuration.

We first consider a rigid spherical particle on the centerline of the tube, and obtain (in Sec. II) an approximate (lubrication) solution for pressure-driven motion of fluid and particle along the capillary. We then consider the streaming potential generated by this flow acting on the double layer at the wall of the capillary (Sec. III B) and on the surface of the sphere (Sec. III C). The cumulative effect of a line of noninteracting spheres is discussed in Sec. III D, followed by analyses of the effect of surface conductivity (Sec. III E) and of streaming currents (Sec. III F). Section IV reviews previous work on electrophoresis of a sphere in a capillary and its implications for streaming potentials. Sections V and VI discuss a spherical bubble and a long Bretherton bubble,13 respectively.

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II. PRESSURE-DRIVEN FLOW PAST A CLOSE-FITTING SPHERE

The motion of a neutrally buoyant sphere in low Reynolds number Poiseuille flow is one of several problems discussed by Bungay and Brenner, who considered a sphere with arbitrary position within the tube. Here we assume that the sphere is on the axis of the tube, and it is straightforward with arbitrary position within the tube. Here we assume that the sphere is on the axis of the tube, and it is straightforward with arbitrary position within the tube. Here we assume that the sphere is on the axis of the tube, and it is straightforward with arbitrary position within the tube.

We adopt cylindrical coordinates (r, z), with the sphere center at $z = 0$ (Fig. 1). The gap width between the particle and the wall of the tube is

$$ h = h_0 + \frac{z^2}{2R_p} + \cdots = h_0 \left( 1 + \frac{z^2}{d^2} + \cdots \right), \quad (1) $$

where

$$ d = (2R_p h_0)^{1/2}. \quad (2) $$

We assume that fluid motion is due to an applied pressure gradient, unperturbed by any electric fields that are generated by the motion. We shall show in Sec. III B that this neglect of electro-osmotic flow is usually valid.

We suppose that a pressure gradient is applied, such that the particle moves with velocity $U$, and consider a frame in which the particle is at rest and the wall moves with velocity $-U$. We use $y$ as a coordinate normal to the wall of the cylinder, with $y = 0$ on the cylinder and $y = h$ on the spherical particle (Fig. 1). The cross-sectional area available for flow is

$$ A(z) = \pi[R_c^2 - (R_c - h(z))^2] $$

$$ = 2\pi R_c h, \quad h \ll R_p. \quad (3) $$

If the pressure gradient is $dp/dz = G$, the $z$ component of fluid velocity $u_p$ within the gap (in the frame of the particle) is

$$ u_p = \frac{G}{2\mu}y(y - h) + \frac{U}{h}(y - h). \quad (5) $$

Hence the flux through the gap (in the frame of the particle) is

$$ Q_p = 2\pi \int_{y=0}^{h} (R_c - y) u_p dy $$

$$ = -2\pi \left( \frac{G}{2\mu} \left( \frac{h^2 R_c}{12} - \frac{h^4}{24} \right) + \frac{U}{h} \left( \frac{R_c h}{2} - \frac{h^3}{6} \right) \right). \quad (6) $$

The fluid is incompressible. The volume flux $Q_p$ is therefore independent of position $z$, and we rewrite (6) to give the pressure gradient

$$ G = -\frac{6\mu}{R_c h^3} \left[ \frac{Q_p}{\pi} + UR_ch \left( 1 - \frac{h}{3R_c} \right) \right] \left[ 1 - \frac{h}{2R_c} \right]^{-1}. \quad (7) $$

We now use the integral form of the momentum equation on the fluid in $-R_p < z < z_2 = R_p$ (Fig. 1). At $z_1$, $z_2$, the fluid pressures are $p_1, p_2$, and the cross-sectional areas between the sphere and the outer cylindrical wall are $A_1 = A_2 = \pi R_c^2$. The shear stress acting on the cylindrical wall $y = 0$ is

$$ \sigma_{yz} = \mu \frac{\partial u_y}{\partial y} = -\frac{Gh}{2} - \frac{U\mu}{h} = \frac{4U\mu}{h} + \frac{3Q_p \mu}{\pi R_c h^3}, \quad (8) $$

and so the total force on the cylindrical wall in the $z$ direction is

$$ F_{c;2} = 2\pi R_c \int_{z_1}^{z_2} \sigma_{yz} dz = 2\pi R_c \mu \int_{z_1}^{z_2} \left[ \frac{4U}{h} + \frac{3Q_p \mu}{\pi R_c h^3} \right] dz. \quad (9) $$

By symmetry, the hydrodynamic force $F_p$ acting on the particle is parallel to the axis, and the force balance on the fluid in $z_1 < z < z_2$ gives

$$ p_1 A_1 - p_2 A_2 - F_p - F_{c;2} = 0. \quad (10) $$

But the pressure difference is
\[ p_2 - p_1 = \int_{-R_p}^{R_p} Gdz = -6 \mu \int_{-R_p}^{R_p} \left( \frac{Q_p}{\pi R_c} \left( \frac{1}{h^2} + \frac{1}{2R_c h^2} \right) \right) \]
\[ + U \left( \frac{1}{h^2} + \frac{1}{6h R_c} \right) dz, \] (11)

and hence the force balance gives
\[ F_p = 6 \mu Q_p \int_{-R_p}^{R_p} \left( \frac{R_c}{h^2} - \frac{1}{2h^2} \right) dz + U \pi \int_{-R_p}^{R_p} \left[ 6 \frac{R_c^2}{h^2} - \frac{7R_c}{h} \right] dz. \] (12)

The integrals in (12) are discussed in the Appendix, and are given by (A3) when \( h_0 \ll R_p \). If the particle is force-free (i.e., \( F_p = 0 \)), then
\[ Q_p = -\frac{4}{3} \pi R_c h_0 U \left( 1 - \frac{5h_0}{3R_c} + \cdots \right). \] (13)

The total volumetric flow rate in the frame fixed with the capillary walls is
\[ Q_c = \pi R_c^2 U + Q_p \approx \pi R_c^2 U \left( 1 - \frac{4h_0}{3R_c} + \frac{20h_0^2}{9R_c^2} + \cdots \right). \] (14)

which agrees with Eq. (7.18) of Bungay and Brenner only up to \( O(h_0/R_c) \). Bungay and Brenner worked systematically to higher order, and used a better representation of the sphere than the parabola (1) adopted here. This serves as a reminder that the analysis presented here is valid only to leading order.

The total pressure drop across the sphere is, by (11) and (13),
\[ p_1 - p_2 = \frac{4\pi \mu dU}{h_0 R_c}, \] (15)

in agreement with Eq. (7.6) of Ref. 14.

In the absence of any spherical particle, the velocity field within the capillary (in a frame in which the capillary walls are at rest) is
\[ u_c = -\frac{G}{4\mu} (R_c^2 - r^2) \] (16)

with total volumetric flow rate
\[ Q_c = \pi R_c^2 U = -\frac{G\pi R_c^4}{8\mu} \] (17)

and wall shear rate
\[ \left. \frac{d u_c}{dr} \right|_{r=R_c} = \frac{GR_c}{2\mu}. \] (18)

### III. STREAMING POTENTIALS

#### A. The electrical double layer

We assume that the \( \zeta \) potentials \( \zeta_c \) and \( \zeta_p \) are sufficiently small that the Poisson-Boltzmann equation governing the equilibrium charge clouds can be linearized, i.e., we assume \( e\zeta/kT \ll 1 \), where \( -e \) is the charge on an electron, \( k \) is the Boltzmann constant, and \( T \) is temperature. The fluid contains \( M \) ionic species, with valence \( z_i \) (\( i = 1, \ldots, M \)), mobility \( \omega_i \), and number density \( n_i^e \) in the bulk solution far from any charged surfaces, with \( \Sigma_{i=1}^{M} n_i^e = 0 \) to ensure electrical neutrality of the bulk solution. If \( \psi \) denotes the electrical potential (relative to the bulk solution), then the equilibrium number density of ions is
\[ n_i = n_i^e \exp \left( \frac{-ez_i \psi}{kT} \right) \approx n_i^e \left( 1 - \frac{ez_i \psi}{kT} + \cdots \right). \] (19)

If \( |e\psi/kT| \ll 1 \), we may neglect higher-order terms in the expansion (19), and the local charge density is therefore
\[ \rho = \sum_{i=1}^{M} e z_i n_i^e \approx -e \kappa^2 \psi, \] (20)

where \( \kappa = e_0 e_r \) is the permittivity of the suspending fluid, and
\[ \kappa^2 = \sum_{i=1}^{M} e z_i^2 n_i^e / e kT. \] (21)

Poisson’s equation then becomes
\[ \nabla^2 \psi = -\frac{\rho}{\epsilon} = \kappa^2 \psi. \] (22)

The Debye length \( \kappa^{-1} \) is typically of the order of a few nm, which we assume to be small compared to the minimum gap width \( h_0 \). As a consequence, \( \kappa^{-1} \ll R_p \) and curvature of the charge cloud can be neglected. The potential \( \psi \) at a distance \( y \) from a charged surface is therefore
\[ \psi = \zeta \exp(-\kappa y), \quad \frac{e \zeta}{kT} \ll 1, \] (23)

where \( \zeta \) is either \( \zeta_c \) or \( \zeta_p \), depending upon which surface we are considering. The permittivity of the suspending fluid is usually much higher than that of the solid wall of the capillary, and hence the surface charge density is
\[ \Sigma = -e \left. \frac{d\psi}{dy} \right|_{y=0} = e \kappa \zeta, \quad \frac{e \zeta}{kT} \ll 1. \] (24)

The results of Secs. III–VI will be given in terms of the \( \zeta \) potentials at the charged surfaces, but can be easily expressed in terms of the surface charge density \( \Sigma \). If the potential \( \zeta \) is too large, (23) no longer holds. A solution of the nonlinear Poisson-Boltzmann equation is available for a symmetric electrolyte with two ionic species of equal and opposite valence. However, we shall need only the fact that curvature can be neglected in a thin double layer, and hence the Poisson equation (22) becomes
\[ \frac{d^2 \psi}{dy^2} = -\frac{\rho}{\epsilon}. \] (25)

In a dilute solution, the velocity of an ion in an electric field \( -\nabla \phi \) is \( -\omega_i e z_i \nabla \phi \), and the total current density is
\[ j = -\Sigma_{i=1}^{M} \omega_i e z_i^2 n_i \nabla \phi. \] The conductivity of the bulk solution is therefore
\[ \sigma = \sum_{i=1}^{M} \omega_i e^2 z_i^2 n_i^\infty. \]  
(26)

In the charge cloud, the perturbed ionic number densities (19) change the conductivity (26) by an amount 
\[ \sigma_1 = -\sum_{i=1}^{M} \frac{\omega_i e^2 z_i^2 n_i^\infty \psi}{kT} \]  
and the total additional conductivity is obtained by integration across the thickness of the double layer, using (23) to obtain 
\[ \int_0^\infty \sigma_1 dy = -\sum_{i=1}^{M} \frac{\omega_i e^2 z_i^2 n_i^\infty \psi}{kT} \]. 
(28)

In a typical 1-1 electrolyte, the mobilities \( \omega_1 \) of the cations and anions are usually of similar magnitude, in which case the additional conductivity (27) is small, since \( \Sigma z_i e^2 n_i^\infty = \Sigma z_i n_i^\infty = 0 \) to ensure neutrality of the bulk solution. More generally, surface conductivity due to the charge cloud plays a minor role compared to bulk conductivity if (as assumed here) \( e^2 z_i \ll kT \) and the double-layer thickness \( \kappa^{-1} \) is small compared to the typical width \( h \) of the channel. However, surface conductivity can also be created by mobility of ions within the Stern layer adsorbed on the solid surface, and it is known that surface conductivity can play an important role in real rock.\(^6\) This is particularly true if the rock permeability is low (so that pores are small, with a high surface-to-volume ratio) or if the ionic concentration is small [because the conductivity of bulk solution (26) is then small, thereby increasing the relative importance of any conductivity within the Stern layer]. Although we shall concentrate our attention on the case in which surface conductivity is negligible (since this leads to a marked simplification of the governing equations), we consider the effect of nonzero surface conductivity in Sec. III E.

**B. Streaming potential due to \( \xi_c \) on the capillary wall**

We first set \( \xi_p = 0 \) and consider streaming currents and potentials due solely to charge at the wall of the capillary. The rate at which charge within the charge cloud adjacent to the wall of the capillary is convected by the pressure-driven flow is 
\[ I_c = 2\pi R_c \int_0^\infty \mu_0 d\psi dy = -2\pi R_c \epsilon \frac{\partial \psi}{\partial y} \bigg|_{y=0} \int_0^\infty \frac{d^2 \psi}{dy^2} dy \]  
(29)

\[ = -2\pi R_c \epsilon \xi_c \frac{\partial \psi}{\partial y} \bigg|_{y=0}, \]  
(30)

where when integrating (29) we have used the fact that \( \psi \) and \( d\psi / dy \) decay to zero far from the charged surface. Note that when the double layer is sufficiently thin for (25) to hold, there is no need to appeal to the linearized solution (23) for the potential and charge density within the double layer. It is therefore tempting to suggest that the analysis given below is true for arbitrary potentials. Such a conclusion would be incorrect. At high potentials, the expansion (19) fails, and the roles of the coions and counterions are no longer symmetric. In particular, differences between the fluxes of the different ions into and out of the double layer caused by a nonuniform geometry lead to modified ionic number densities outside the double layer. Examples of this occur in analyses of electrophoresis\(^{15,16}\) and the primary electrosorptive effect\(^{17}\) for charged spherical particles, or the convection of ions along a channel of varying width.\(^{18}\) We shall be interested here solely in fields generated by steady flow, but it is known that when surface potentials are high, an oscillating applied electric field can lead to enhanced effective permittivities caused by a phase lag between the applied voltage and ionic fluxes into and out of the double layers.\(^{15,16,19}\) A full study leads to equations for the convection and diffusion of each species of ion, which will be investigated elsewhere.

If there is no return path (external to the capillary) for the electric current \( I_c \), convected by the fluid, a streaming potential \( \phi_c \) will be set up so as to generate an equal but opposite current \(-I_c\) through the capillary itself. If \( \sigma \) is the conductivity of the bulk fluid, and \( \sigma_c \) and \( \sigma_p \) are the surface conductivities of the capillary wall and particle surface, respectively, the electric field \(-\nabla \phi_c\) required to reduce the total current to zero is given by

\[ -\{A + 2\pi[R_c \sigma_c + (R_c - y) \sigma_p]\} \frac{d\phi_c}{dz} = -I_c. \]  
(31)

In the absence of any particle, the term \((R_c - y) \sigma_p\) in (31) vanishes. The wall shear rate in (30) is given by (18) so that

\[ I_c = \frac{\pi R_c^2 \epsilon \xi_c G}{\mu} = \frac{A \epsilon \xi_c G}{\mu}. \]  
(32)

Hence, by (31),

\[ \frac{d\phi_c}{dz} = \frac{A \epsilon \xi_c G}{(A + 2\pi R_c \sigma_c) \mu}. \]  
(33)

We shall consider the effect of surface conductivity in Sec. III E. For the moment, we assume that \( \sigma_c \ll A \sigma_c / R_c \), so that

\[ \frac{d\phi_c}{dz} = \frac{\epsilon \xi_c G}{\sigma_c \mu}. \]  
(34)

When the spherical particle is present, the fluid velocity in the \( z \) direction (in the rest frame of the capillary wall) is \( u_z = u_p + U \), with \( u_p \) given by (5). The rate at which charge within the charge cloud adjacent to the wall of the capillary is convected by the pressure-driven flow is, by (30) and (8),

\[ I_c(z) = -2\pi R_c \epsilon \xi_c \frac{\partial u_p}{\partial y} \bigg|_{y=0} = -2\pi R_c \epsilon \xi_c \left( \frac{4U}{h} + \frac{3Q_p}{\pi R_c h^3} \right). \]  
(35)

The electric field \(-\nabla \phi_c\) required to reduce the current to zero can be assumed to be a function only of \( z \) in the lubrication limit, and is given by (31), where \( A \) and \( I_c \) are now both functions of \( z \). Hence, assuming surface conductivity is negligible,
The electrical current generated by this shear flow is small compared to the channel dimensions so that any perturbation velocities caused by electro-osmosis are negligible. We can therefore consider the electric field \(-\nabla \phi_c\) in the absence of any particle is given by (34), and the electro-osmotic velocity created by such a field acting on the thin charge cloud at the capillary walls is

\[
\mathbf{u} = \frac{\varepsilon_c \nabla \phi_c}{\mu} = \frac{8 \varepsilon_c^2 \zeta_c^2}{\sigma \mu R_c^2} U. \tag{39}
\]

If the ionic mobilities are equal, with \(\omega_i = \omega_c\), then \(\sigma = \omega e k T \kappa^2\) [by (26) and (21)], so that

\[
\mathbf{u} = \frac{e k T}{\omega e} \frac{\varepsilon_c^2}{\kappa^2} \frac{8 U}{\mu R_c^2}. \tag{40}
\]

Taking \(\omega = 4 \times 10^{11}\) kg s\(^{-1}\), we find \(e k T / (\omega e^2 \mu) \approx 0.28\) for water. We conclude that as long as the Debye length \(\kappa^{-1}\) is small compared to the channel dimensions (either \(R_c\), or \(h_0\)), any perturbation velocities caused by electro-osmosis are small compared to the original pressure-driven velocity \(U\).

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**C. Streaming potential due to \(\zeta_c\) on the particle**

We now set \(\zeta_c = 0\) and consider streaming potentials due solely to charge on the particle.

The charged particle and its oppositely charged charge cloud are, together, electrically neutral. We can therefore move from the laboratory frame in which the capillary is at rest into a frame moving with the spherical particle without creating any electrical currents. The velocity near the surface of the particle is

\[
\mathbf{u}_p \approx (y - h) \frac{\partial \mathbf{u}_p}{\partial y} \bigg|_{y = h}, \tag{41}
\]

where the velocity gradient at the particle surface is, by (5),

\[
\frac{\partial \mathbf{u}_p}{\partial y} \bigg|_{y = h} = \frac{G h}{2 \mu} + \frac{U}{h} = -\frac{3 Q_p}{2 \pi R_c h^2} - \frac{2 U}{h}. \tag{42}
\]

The electrical current generated by this shear flow is

\[
I_p = -2 \pi R_c \varepsilon_p \frac{\partial \mathbf{u}_p}{\partial y} \bigg|_{y = h} \int_0^\infty \frac{d^2 \psi}{dx^2} ds \approx -2 \pi R_c \varepsilon_p \left( \frac{3 Q_p}{2 \pi R_c h^2} + \frac{2 U}{h} \right), \tag{43}
\]

where \(s = h - y\). The streaming potential \(\phi_p\) required to reduce the total current to zero is given by a relation of the form (31), and hence satisfies

\[
\frac{d \phi_p}{dz} = -\frac{2 \pi R_c \varepsilon_p}{A(z) \sigma} \left( \frac{3 Q_p}{2 \pi R_c h^2} + \frac{2 U}{h} \right), \tag{44}
\]

with \(\phi_p\) constant in regions of the capillary where there is no particle. The total change in potential across the particle is given by the integral (37) of \(d \phi_p / dz\) (44), which gives

\[
\phi_{p1} - \phi_{p2} = -\frac{2 \pi R_c \varepsilon_p}{A(z) \sigma} \left( \frac{3 Q_p}{2 \pi R_c h^2} + \frac{2 U}{h} \right) \int_{R_p}^{R_p} dz = -\frac{2 \pi R_c \varepsilon_p}{A(z) \sigma} \left( \frac{3 Q_p}{2 \pi R_c h^2} + \frac{2 U}{h} \right). \tag{45}
\]

If \(\zeta_p \approx \zeta_c\), the change in potential (45) is equal and opposite to that (38) due to the potential at the wall of the capillary. Thus the leading-order terms cancel. Only by working consistently to higher order in \(h / R_c\), could we estimate the next-order corrections. However, we shall see in Sec. IV that for sufficiently thin double layers (\(\kappa R_c \ll 1\)), we expect no change at all in streaming potential if \(\zeta_p \approx \zeta_c\).

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**D. The total streaming potential generated along the capillary**

Suppose we have a uniform capillary of length \(L_c\), with ends at \(z_0 = z_0 + L_c\). In the absence of any particle, the total pressure drop along the capillary is, by (17),

\[
p(z_0) - p(z_L) = -GL_c = \frac{8 \mu U L_c}{R_c^2}, \tag{46}
\]

and, by (34), the total change in streaming potential between the ends of the capillary is

\[
\phi_c(z_0) - \phi_c(z_L) = \frac{\varepsilon_c G L_c}{\sigma \mu} = \frac{8 \varepsilon_c U L_c}{\sigma R_c^2} = \frac{\varepsilon_c}{\sigma \mu} [p(z_0) - p(z_L)]. \tag{47}
\]

When the particle is present, the pressure drop may be estimated, by (15) and (46), as

\[
p(z_0) - p(z_L) \approx \frac{8 \mu U}{R_c^2} (L_c - 2 R_p) + \frac{4 \pi \mu d U}{h_0 R_c}, \tag{48}
\]

where we have neglected the small difference between the average fluid velocity in the capillary and the particle velocity \(U\), caused by fluid leakage past the particle (14). The total change in the potential \(\phi_p = \phi_c + \phi_p\) becomes, by (34), (38), and (45),
\[ \phi_{I}(z_0) - \phi_{I}(z_L) = \frac{8\varepsilon_{\infty}U}{\alpha R_c^2} (L_c - 2R_p) + \frac{\varepsilon(\zeta_c - \zeta_p) d \pi U}{2\sigma h_0^2} + O\left(\frac{\varepsilon \xi d \pi U}{\sigma h_0 R_c}\right), \]

\[ \approx \frac{\varepsilon \xi [p(z_0) - p(z_L)]}{\sigma \mu} + \frac{\varepsilon(\zeta_c - \zeta_p) d \pi U}{2\sigma h_0^2} + O\left(\frac{\varepsilon \xi d \pi U}{\sigma h_0 R_c}\right). \]  

(49)

Note that the change in the streaming potential is \(O(R_c/h_0)\) larger than the change in the pressure drop. However, this change in the streaming potential will only be large compared to the total streaming potential developed between the ends of the capillary if \(L_c/R_c^2 \ll d/h_0^2\), i.e., if

\[ L_c \ll R_c \left(\frac{R_c}{h_0}\right)^{3/2}, \]  

(50)

and unless \(h_0\) is exceedingly small this is unlikely to be true.

If the capillary contains \(N \ll L_c/R_c\) particles, sufficiently well separated that they do not interact, we might expect the total pressure drop to be

\[ p(z_0) - p(z_L) \approx \frac{8\mu U}{R_c^2} (L_c - 2NR_p) + \frac{4N\pi \mu d U}{h_0 R_c}, \]  

(51)

and the total change in potential becomes

\[ \phi_{I}(z_0) - \phi_{I}(z_L) = \frac{8\varepsilon_{\infty}U}{\alpha R_c^2} (L_c - 2NR_p) + \frac{Ne(\zeta_c - \zeta_p) d \pi U}{2\sigma h_0^2} + O\left(\frac{Ne \xi d \pi U}{\sigma h_0 R_c}\right), \]

\[ = \frac{\varepsilon \xi [p(z_0) - p(z_L)]}{\sigma \mu} + \frac{Ne(\zeta_c - \zeta_p) d \pi U}{2\sigma h_0^2} + O\left(\frac{Ne \xi d \pi U}{\sigma h_0 R_c}\right). \]  

(52)

Since we can have \(N = O(L_c/R_c)\), the total change in the coefficient of proportionality could be by a factor of order

\[ 1 + \frac{\xi - \xi_p}{8\xi_c} \left(\frac{R_c}{h_0}\right)^4. \]  

(53)

The particle considered here is rigid, so that the geometry is independent of flow rate. The streaming potential is therefore proportional to both the applied pressure gradient and to the imposed flow rate.

E. Surface conductivity

We now examine how the above analysis is modified by surface conductivity. As in Sec. III B, we first assume that the spherical particle is uncharged (\(\zeta_p = 0\)). The surface conductivities of the capillary wall and the particle are \(\sigma_c\) and \(\sigma_p\) respectively.

The current generated by fluid motion at the wall of the capillary is still given by (35), but the electric field \(-\nabla \phi_c\) required to reduce the current to zero is now

\[ \frac{d\phi_c}{dz} = -\frac{2\pi R_c \varepsilon_{\infty}}{A\sigma + 2\pi[R_c \sigma_c + (R_c - h) \sigma_p]} \left(\frac{4U}{h} + \frac{3Q_p}{\pi R_c h^2}\right), \]

(54)

rather than (36). We use the approximation (4) for \(A(z) = 2\pi R_c h/\alpha\) and the parabolic approximation (1) for \(h\), so that

\[ A\sigma + 2\pi[R_c \sigma_c + (R_c - h) \sigma_p] \approx 2\pi R_c \sigma h_c. \]

(55)

where

\[ h_c = h_1 (1 + \xi^2/d_1^2), \]  

(56a)

\[ h_1 = h_0 + \frac{\sigma_c + \sigma_p (1 - h_0 R_c)}{\sigma} > h_0, \]  

(56b)

\[ d_1^2 = \frac{h_0^2}{h_0^2 - h_0(h_0(\sigma R_c))} = \frac{2R_ch_1}{1 - (\sigma R_c)} > d^2. \]  

(56c)

If surface conductivity is sufficiently large, the resistance of the gap between the particle and capillary wall is not dominated by the neighborhood of the narrowest gap \(h_0\). We exclude this case by requiring \(\sigma_c + \sigma_p \ll \sigma R_c\) so that \(d_1 \ll R_c\) and therefore integrals of inverse powers of \(h_c\) can be approximated as in the Appendix (A5). Integrating the potential gradient (54), we find that Eq. (38) for the change in electric potential across the particle becomes

\[ \phi_{x1} - \phi_{x2} = \frac{\varepsilon_{\infty}U}{\sigma} \int_{-R_p}^{R_p} \left(\frac{4U}{h} + \frac{3Q_p}{\pi R_c h^2}\right) dz \]

\[ \approx \frac{\varepsilon_{\infty}U}{h_0 h_1} \left(\frac{4U}{d_1 + d} + \frac{3Q_p(d_1 + 2d)}{2\pi R_c h_0 (d_1 + d)^2}\right) \]

\[ \approx \frac{2\varepsilon_{\infty}U}{\sigma h_0 h_1 (d_1 + d)^2}. \]  

(57)
since $Q_p$ is given by (13). If the surface conductivity terms in (56) are small,

$$d_i = d\left(1 + \frac{\sigma_c + \sigma_p}{2\sigma h_0} + \ldots\right)$$  \hspace{1cm} (58)

and

$$\phi_{c,1} - \phi_{c,2} \approx \frac{\xi \epsilon dU}{2\sigma h_0} \left(1 - \frac{\sigma_c + \sigma_p}{2\sigma h_0}\right).$$  \hspace{1cm} (59)

Surface conductivity has reduced the streaming potential.

As in Sec. III C, we now set $\zeta = 0$ and consider streaming potentials due solely to charge on the particle. The electrical current generated by flow past the surface of the particle is still given by (43), but the field gradient required to reduce the total current to zero is now

$$\frac{d\phi_p}{dz} = -\frac{\xi \epsilon}{h_0 \sigma} \left(\frac{3Q_p}{\pi R_h^2} + \frac{2U}{h}\right),$$  \hspace{1cm} (60)

rather than (44). The total change in potential across the particle is now

$$\phi_{p,1} - \phi_{p,2} = \frac{\xi \epsilon}{\sigma} \int_{-R_p}^{R_p} \left(\frac{2U}{h_{hc}} + \frac{3Q_p}{\pi R_h^2 h_{hc}}\right) dz$$

$$\approx \frac{\xi \epsilon d_1}{h_0 \sigma} \left(\frac{2U}{d_1 + d} + \frac{3Q_p (d_1 + 2d)}{2\pi R_h h_0 (d_1 + d)^2}\right)$$

$$\approx -\frac{2\xi \epsilon d_1^2 d_1}{\sigma h_0 h_1 (d_1 + d)^2}.$$

If $\zeta = \zeta_c$ and surface conductivities are nonzero, the change in potential (61) is no longer equal and opposite to that (57) due to the potential at the wall of the capillary. In the limit of small surface conductivities, (61) becomes

$$\phi_{p,1} - \phi_{p,2} \approx -\frac{\xi \epsilon dU}{2\sigma h_0^2} \left(1 - \frac{\sigma_c + \sigma_p}{\sigma h_0}\right).$$  \hspace{1cm} (62)

### F. The streaming potential

The streaming potential builds up when there is no external path for current, so that the charge convected by fluid motion has to return via conduction through the capillary itself. If the ends of the capillary at $z_0$ and $z_L$ are shorted by an external electrical path of zero resistance, the potential difference between the two ends of the capillary will be zero, and a streaming current $I_s$ will flow through the external circuit. Since charge cannot accumulate at any point, the current within the capillary is also $I_s$, and hence the local potential gradient adjusts so that

$$-\{\sigma A(z) + 2\pi[R_c \sigma_c + (R_c - y) \sigma_p]\} \frac{d\phi}{dz} + I_c + I_p = I_s.$$  \hspace{1cm} (63)

But the electric currents $I_c$ and $I_p$ due to convection of the charge cloud can be expressed in terms of the streaming potential contributions $\phi_p$ and $\phi_c$ by means of (31). Hence

$$\int_{z_0}^{z_L} \frac{d\phi}{dz} dz = \int_{z_0}^{z_L} \left(\frac{d\phi_p}{dz} + \frac{d\phi_c}{dz}\right) dz + I_s Z,$$  \hspace{1cm} (64)

where

$$Z = \int_{z_0}^{z_L} \left\{\sigma A(z) + 2\pi[R_c \sigma_c + (R_c - y) \sigma_p]\right\}^{-1} dz.$$  \hspace{1cm} (65)

is the resistance of the capillary (partially blocked by the particle). The two ends of the capillary are at the same potential, so the left-hand side of (64) is zero, and hence

$$I_s = (\phi_c(z_0) - \phi_c(z_L)) / Z.$$  \hspace{1cm} (66)

where $\phi_c = \phi_c + \phi_p$. The electrical conductance around the particle can be approximated by (55), so that lubrication analysis gives the resistance of the portion of the pipe containing the particle as

$$\int_{-R_p}^{R_p} \frac{dz}{2\pi R_c h_{hc}} \approx \frac{d_1}{2\sigma R_c h_1}$$

$$\approx \frac{1}{\sigma (2R_h h_0)^{1/2}} \left(1 + \frac{\sigma_c + \sigma_p}{\sigma h_0}\right)^{-1/2},$$  \hspace{1cm} (67)

where $d_1$ and $h_1$ are defined by (56) and the integral is approximated by (AA3a). To this must be added the resistance of the length $L_c - 2R_p$ of the capillary containing only liquid, so that the total resistance of the capillary is

$$Z = \frac{1}{\sigma} \left\{\frac{L_c - 2R_p}{(2R_h h_0)^{1/2}} \left(1 + \frac{\sigma_c + \sigma_p}{\sigma h_0}\right)^{-1/2}\right\}.$$  \hspace{1cm} (68)

### IV. COMPARISON WITH STUDIES OF ELECTROPHORESIS

We have considered the electrical streaming potential generated by a pressure-driven flow, and the results are thought to be new. However, there have been several previous studies of the related phenomenon of electrophoresis of a spherical particle in a cylindrical tube. We restrict our attention to classical steady electrophoresis of a charged particle, with velocities proportional to the applied electric field, rather than to more recent work in which the charge on the body is induced by the applied electric field.\(^{20,21}\)

Electrophoresis of a charged sphere in an uncharged tube has been studied in the limit of thin double layers $\kappa R_p \gg 1$.\(^{22-25}\) The case of spherical particles small compared to the radius of the cylinder ($R_p \ll R_c$), and constrained to lie on the axis of the cylinder, was discussed by Keh and Anderson,\(^{22}\) with numerical results given by Keh and Chiu.\(^{23}\) Spheres not constrained to lie on the centerline were studied by Yariv and Brenner, either for a sphere of radius small compared to that of the cylinder,\(^{24}\) or for a tight-fitting sphere.\(^{25}\)

When the sphere lies on the axis of the cylinder, and the gap between sphere and cylinder is small, the electrophoretic velocity of the sphere is one-half that of the sphere in unbounded fluid.\(^{25}\) Although the hydrodynamic resistance to
motion of the sphere is increased by the walls of the cylinder, the field strength is larger within the narrow gap than it is far from the sphere. Thus the driving force acting on the sphere is also larger when the surrounding fluid is unbounded. A similar phenomenon has been predicted for broadside electrophoretic motion of a thin circular disk in unbounded fluid. The electric field is singular at the sharp edge of the disk, and this strong electric field produces a larger than expected electrophoretic velocity.26

The case in which both the particle and capillary wall are charged has been considered by Ennis and Anderson27 for spherical particles on the axis of the cylinder, with arbitrary double-layer thickness. Long cylindrical particles, either on or off the axis, were investigated by Liu et al.28 In both cases, if the double layer is thin, the particle does not move if \( \xi_p = \xi_c \). If the electric field is \( -\nabla \phi \), the fluid velocity is \( \mathbf{u} = \varepsilon \xi \nabla \phi / \mu \), with a thin boundary layer at the solid walls to satisfy the no-slip condition, and with hydrodynamic pressure \( p = 0 \). In the absence of surface conductivity, the electric field strength is proportional to the cross-sectional area available for flow, so the fluid velocity is such as to maintain a constant volumetric flow rate as the cross-sectional area changes. The electric current density is

\[
\mathbf{i} = -\sigma \nabla \phi = -\frac{\sigma \mu}{\varepsilon_0} \mathbf{u}. \tag{69}
\]

We can express the fluid volumetric flow \( Q \), the electrical current \( I \), and the particle velocity \( U_p \) in terms of the pressure difference \( \Delta p \), the potential difference \( \Delta \phi \), and the external force \( F_p \) on the particle by linear relations of the form

\[
\begin{pmatrix} Q \\ I \\ U_p \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{pmatrix} \begin{pmatrix} \Delta p \\ \Delta \phi \\ F_p \end{pmatrix}. \tag{70}
\]

The insertion of a particle changes the coefficients \( L_{ij} \) from those describing flow in a capillary containing only liquid. However, if \( \xi_p = \xi_c \), the particle moves if the double layer is not sufficiently thin. In this case, the streaming potential will also be modified by the presence of the particle.

V. THE SPHERICAL BUBBLE

We now repeat the above analysis for a spherical bubble with a stress-free interface. It is natural to assume that at a stress-free boundary, any charge at the bubble surface is counteracted by the flowing fluid at the same velocity as the adjacent charge cloud, leading to no net electric current and hence no streaming potential. If the bubble surface is charged due to the presence of ionic surfactants, these are likely to modify the stress-free boundary,29,30 making it closer to the rigid surface considered in Sec. III. Here we simply assume an uncharged, stress-free bubble surface. The effect of charged surfactants at the interface merits more attention.

The fluid velocity \( u_p \) within the gap (in the frame of the bubble) is

\[
u_p = \frac{G}{2\mu} y(y - 2h) - U, \tag{72}
\]

rather than as given by (5). Hence the flux through the gap (in the frame of the bubble) is

\[
\begin{align*}
Q_p &= 2\pi \int_{y=0}^{h} (R_c - y) u_p \, dy \\
&= 2\pi \left[ \frac{G}{\mu} \left( \frac{5h^3}{24} - \frac{h^3 R_c}{3} \right) + U \left( \frac{h^2}{2} - R_c h \right) \right], \tag{73}
\end{align*}
\]

and so

\[
G = -\frac{3\mu}{R_c h^3} \left[ \frac{Q_p}{2\pi} \left( 1 + \frac{5h^3}{8R_c h} \right) + UR_c h \left( 1 + \frac{h}{8R_c h} \right) \right]. \tag{74}
\]

We again use the integral form of the momentum equation on the fluid in \( z_1 = -R_c < z < z_2 = R_p \) (Fig. 1). The shear stress acting on the cylindrical wall \( y = 0 \) is

\[
\sigma_{yz} = \mu \frac{\partial u_p}{\partial y} \bigg|_{y=0} = -G h = \frac{3Q_p \mu}{2\pi R_c h^2} + \frac{3U \mu}{h} \tag{75}
\]

and so the total force on the wall in the \( z \) direction is

\[
F_{z12} = 2\pi R_c \int_{z_1}^{z_2} \sigma_{yz} \, dz = 2\pi \mu \int_{z_1}^{z_2} \left[ \frac{3UR_c}{h} + \frac{3Q_p}{2\pi h^2} \right] \, dz. \tag{76}
\]

The pressure difference is

\[
p_2 - p_1 = \int_{-R_c}^{R_p} G dz = -3\mu \int_{-R_c}^{R_p} \left[ \frac{Q_p}{2\pi R_c} \left( 1 + \frac{5h}{8R_c h} \right) \\
+ U \left( \frac{1}{h^2} + \frac{1}{8R_c h} \right) \right] \, dz, \tag{77}
\]

The force balance on the fluid in \( z_1 < z < z_2 \) gives

\[
p_1 A_1 - p_2 A_2 - F_p - F_{z12} = 0, \tag{78}
\]

where \( F_p \) is the total force on the bubble, and hence

\[
\begin{align*}
F_p &= 3Q_p \int_{-R_c}^{R_p} \left( \frac{R_c}{2h^3} - \frac{11h^3}{16R_c} \right) \, dz \\
&+ 3U \pi \int_{-R_c}^{R_p} \left[ \frac{R_c^2}{h^2} - \frac{15R_c}{8h} \right] \, dz. \tag{79}
\end{align*}
\]

Since the particle is force-free, \( F_p = 0 \), and hence...
The streaming potential generated by two-phase flow Phys. Fluids

The streaming current generated by convection is given by

\[ I_c = -2\pi R_c \varepsilon \zeta \frac{\partial u}{\partial y} \bigg|_{y=0} = \frac{\pi R_c \varepsilon \zeta G}{\mu} = \frac{A \varepsilon \zeta G}{\mu}, \]

since (if \( h \ll R_c \)) the cross-sectional area \( A = 2\pi R_c h \). This current is canceled by a streaming potential

\[ \frac{d\phi_e}{dz} = \frac{\varepsilon \zeta G}{\sigma \mu}. \]

More generally, even if \( h \) is comparable to \( R_c \), in the absence of shear stress over the surface of the bubble, the pressure gradient is directly related to the wall shear stress \( \sigma_{\text{wall}} \), with

\[ A \frac{d\sigma}{dz} = -2\pi R_c \varepsilon \zeta \frac{\partial u}{\partial y} \bigg|_{y=0} = -2\pi R_c \mu \frac{\partial u}{\partial y} \bigg|_{y=0}. \]

The streaming current is then

\[ I_c = -2\pi R_c \varepsilon \zeta \frac{du}{dy} \bigg|_{y=0} = \frac{A \varepsilon \zeta \frac{dp}{dz}}{\mu}. \]

Hence (84) holds even if \( h \) is comparable to \( R_c \), and the change in electrical potential \( \Delta \phi_e \) is proportional to the pressure drop \( \Delta p \). The total pressure drop across the bubble is given by (81), and hence the total change in streaming potential across the bubble is

\[ \phi_e(-R_p) - \phi_e(R_p) = \left( \frac{\varepsilon \zeta}{\sigma} \right) \frac{2\pi dU}{h_0 R_c}. \]

This is smaller than the equivalent result (37) for a rigid particle, by a factor \( 4h_0/R_c \).

The local relation between pressure gradient and streaming potential for the stress-free interface (84) is the same as that for a fluid-filled pipe (34), for which the centerline is a line of zero shear stress. The introduction of a bubble therefore changes the streaming potential as a function of flow rate, but does not change the linear relation between pressure gradient and flow rate.

The spherical bubble is assumed not to conduct electricity. The electrical resistance \( Z \) of the capillary containing a bubble is therefore identical to that (68) for a capillary containing a rigid spherical particle.

VI. A BRETHERTON BUBBLE

We now turn to Bretherton’s analysis\(^{13}\) of a long bubble in a capillary, in order to determine the streaming potential. We follow Bretherton and assume (as in Sec. V) that the surface of the bubble is stress-free. All surface potentials are taken to be sufficiently small that the electrical double layers can be described by linearized Debye-Huckel theory, with surface conductivity negligibly small. Thus the analysis is somewhat simpler than that of Tikhistanov et al.,\(^{30}\) who considered bubble motion generated electro-osmotically by an applied electric field.

The bubble, depicted in Fig. 2, has length \( L \) and for most of its length it is a cylinder of radius approximately \( R_p = R_c - h_0 \). The uniform gas pressure within the bubble differs from the hydrodynamic pressure outside by the Laplace pressure difference due to interfacial tension with coefficient \( \gamma \). This leads to an equation governing the bubble shape that has to be integrated numerically. By matching this numerical solution to the hemispherical form of the end caps, Bretherton determined the gap width

\[ h_0 = 0.643 \left( \frac{3\mu U}{\gamma^2} \right)^{2/3}, \]

where

\[ \frac{dU}{dz} = \frac{h_0}{R_c}. \]
Ca = \frac{3\mu U}{\gamma} \ll 1 \quad (89)

is a capillary number that measures the ratio of viscous stresses to those due to interfacial tension. The velocity $U$ of the bubble differs from the average speed $U_i$ of liquid in the tube, with

$$U_i = \left[1 - 1.29 \left(\frac{3\mu U}{\gamma}\right)^{2/3}\right]. \quad (90)$$

To leading order, the two ends of the bubble take the form of hemispherical caps of radius $R_p$, and hence, to leading order there is no difference between the pressures external to the two ends of the bubble. However, by matching the two (slightly different) spherical caps onto the solution of the lubrication equation for the bubble shape, Bretherton obtained the pressure difference

$$\Delta p_b = p(z_1) - p(z_2) = 4.81 \frac{\gamma}{R} \left(\frac{3\mu U}{\gamma}\right)^{2/3}, \quad (91)$$

where the coefficient 4.81 (see, e.g., Ref. 31) differs slightly from the value 4.52 originally given by Bretherton. This pressure difference depends nonlinearly upon the bubble velocity $U$, unlike the linear relation (81) found for a spherical bubble. In the absence of any liquid motion, the Bretherton bubble expands to fill the entire diameter of the capillary; more generally, the gap width $h_0$ (88) varies with $U$.

We do not need to repeat Bretherton’s analysis. In Sec. V, we showed that if the bubble interface is stress-free, the relation between pressure gradient and gradient of streaming potential is given by (84). In a capillary of length $L_c$, the total pressure drop is given by the sum of the pressure drop across the bubble and that in the fluid-filled portion of the pipe, with

$$p(z_0) - p(z_L) = 4.81 \frac{\gamma}{R} \left(\frac{3\mu U}{\gamma}\right)^{2/3} + (L_c - L) \frac{8\mu U}{R^2} + O\left(\frac{\mu U}{R}\right), \quad (92)$$

where the error term in (92) is the next term in an expansion in terms of the small capillary number $Ca = 3\mu U / \gamma$.

Takhistov et al. estimated the electrical resistance of the capillary when a bubble is present by approximating the bubble as a spherocylinder of total length $L$, with two hemispherical end caps of radius $R_c = h_0$. This gives a total resistance

$$Z = \frac{L_c - L}{\pi R_c^2} + \frac{L - 2R_c}{2\pi h_0 R_c} + \frac{1}{(2R_c h_0)^{1/2}} \quad \Rightarrow \quad \frac{1}{\sigma} \left[\frac{L_c - L}{\pi R_c^2} + \frac{L - 2R_c}{2\pi h_0 R_c} + \frac{0.88}{R_c} \left(\frac{\gamma}{3\mu U}\right)^{1/3}\right]. \quad (93)$$

A full numerical computation, using Bretherton’s equation for the bubble shape, gives a coefficient 0.87, rather than 0.88, in the final term on the right-hand side of (93). Thus (93) is a good approximation, though as pointed out by Takhistov et al., if $U$ is sufficiently small, the gap width $h_0$ may become so small that surface conduction (in either the charge cloud or the Stern layer) is no longer negligible compared to conduction in the bulk fluid.

VII. CONCLUDING REMARKS

We have presented results for the streaming potential generated first by a single particle in a capillary, and then by a line of particles in the same capillary. The next step will be to consider a two-dimensional network of capillaries. Such networks have already proved to be successful models for the single-phase electro-osmotic properties of porous media.

The diameters of the capillaries in such networks are usually chosen such that they represent the distribution of throat and pore diameters found in a real porous medium. They are therefore not all identical, and a solid sphere that fits tightly in one capillary would either be too large for the next capillary, or would fit so loosely that the analysis presented here does not hold. This problem does not occur with a Bretherton bubble, which can adjust its shape as it passes from one capillary to the next. Manga has investigated models for gas-liquid flow in rock, based upon networks of capillaries containing Bretherton bubbles. The flow rate in such a network is a nonlinear function of the applied pressure drop, which Manga assumed sufficiently small compared to ambient pressure for compressibility to be negligible. We have shown here that for a Bretherton bubble, the streaming potential is proportional to the pressure (after a suitable choice for the reference potential and pressure), and the coefficient of proportionality is unaffected by the presence or absence of the bubble. Manga’s network computations of pressure drop as a function of flow rate can therefore predict streaming potentials if the zeta potential $\zeta_c$ is the same in all capillaries.

If Bretherton’s gas bubble is replaced by a long droplet of viscous fluid, the coefficient of proportionality between the gradients of the streaming potential and pressure will be modified by the presence of the droplet. The streaming potential predicted by a network model will no longer be a constant multiple of the predicted pressure drop. This merits further investigation.

The analysis presented here assumes that the continuous liquid phase within the capillary is an aqueous electrolyte. If the continuous liquid phase is oil, Debye lengths will be larger, and electrical effects may not be totally absent (e.g., Refs. 38 and 39). Much less is known about streaming potentials caused by fluid adjacent to oil-wet surfaces.

ACKNOWLEDGMENTS

I thank an anonymous referee for drawing my attention to various papers in the geophysics literature, and for suggesting that the effect of surface conductivities should be investigated.

APPENDIX: INTEGRALS

In the absence of surface conductivity, we require the following integrals of inverse powers of $h = h_0(1 + z^2 / d^2)$:
\[ \int_{z_1}^{z_2} \frac{dz}{h} = \frac{d}{h_0} \left[ \tan^{-1} \left( \frac{z_2}{d} \right) - \tan^{-1} \left( \frac{z_1}{d} \right) \right], \quad (A1a) \]

\[ \int_{z_1}^{z_2} \frac{dz}{h^2} = \frac{d}{2h_0} \left[ \frac{s}{1 + s^2} + \tan^{-1} \left( \frac{z_1}{d} \right) \right] \quad (A1b) \]

\[ \int_{z_1}^{z_2} \frac{dz}{h^3} = \frac{d}{8h_0} \left[ \frac{3s^2 + 5s}{(1 + s^2)^2} + 3\tan^{-1} \left( \frac{z_1}{d} \right) \right] \quad (A1c) \]

If \( z_2 = z_1 = R_p \gg d, \)

\[ \tan^{-1} \left( \frac{R_p}{d} \right) = \frac{\pi - d}{2} + \frac{d^3}{3R_p^3} + \cdots, \quad (A2) \]

and hence

\[ \int_{-R_p}^{R_p} \frac{dz}{h} = \frac{d}{h_0} \left( \pi - \frac{2d}{R_p} + O(d/R_p^3) \right)^3, \quad (A3a) \]

\[ \int_{-R_p}^{R_p} \frac{dz}{h^2} = \frac{d}{2h_0} \left[ \pi + O(d/R_p^3) \right], \quad (A3b) \]

\[ \int_{-R_p}^{R_p} \frac{dz}{h^3} = \frac{d}{8h_0} \left[ 3\pi + O(d/R_p^3) \right]. \quad (A3c) \]

When surface conductivity is present, and \( h_{sc} = h_1(1 + z^2/d^2), \)

\[ \frac{1}{h_{sc}} = \frac{1}{h_1 h_1(d_1^2 - d^2)} \left[ \frac{d_1^2}{1 + z^2/d^2} - \frac{d^2}{1 + z^2/d_1^2} \right], \quad (A4a) \]

\[ \frac{1}{h^2 h_{sc}} = \frac{d_1^2}{h_1 h_1(d_1^2 - d^2)(1 + z^2/d^2)^2} + \frac{1}{h_1 h_1(d_1^2 - d^2)^2} \left[ \frac{d^4}{1 + z^2/d_1^2} - \frac{d_1^2}{1 + z^2/d^2} \right] \quad (A4b) \]

Consequently, since we have assumed \( R_p \gg d, \) the integrals \((A3)\) give

\[ \int_{-R_p}^{R_p} \frac{dz}{h_{sc}} = \frac{\pi d_1 d}{h_1 h_1(d_1 + d)}. \quad (A5a) \]

\[ \int_{-R_p}^{R_p} \frac{dz}{h^2_{sc}} = \frac{d_1 d_R d(d_1 + 2d)}{2h_1 h_1(d_1 + d)^2}. \quad (A5b) \]


