Electroosmotic Flow and Zone Broadening in Microfluidic Channels of Variable Cross-Section and Wall Charge

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ABSTRACT

Electroosmotic flow is often the method of choice for generating fluid flows in microfluidic devices. The resulting flow has a characteristic flat profile which has the advantage of very low axial dispersion. This is only the case, however, if the wall zeta potential is constant. In many applications, the wall zeta potential is variable, either through accident (wall adsorption of analytes) or design (patterned charges). An analytical solution is developed for electroosmotic and pressure driven flows in straight microfluidic channels of arbitrary cross-sectional shape and distribution of zeta-potential, in the asymptotic limit where variations in the axial direction take place on long length scales compared to a characteristic diameter. A method is provided for computing “effective fluidic impedances” for such inhomogeneous microfluidic channels. The theoretical results are used to explain certain experimental data on CZE in a straight microcapillary.

Keywords: Electroosmosis, electrophoresis, zeta-potential, zone-broadening, dispersion

1 Introduction

Electroosmotic flow (EOF) is a convenient mechanism for transporting fluid in microfluidic devices. One advantage of such flows over classical pressure driven flows is that, the flow profile is uniform over the cross-section of the channel, except for the very thin Debye layer at the walls within which the flow velocity decreases to zero in order to satisfy the ‘no slip’ boundary conditions. However, the uniformity of the flow profile and the resulting low Taylor dispersion are characteristic of microfluidic channels with a uniform wall charge. In the presence of inhomogeneities in the wall charge, induced pressure gradients are created that distort the uniformity of the flow profile [1]. Such nonuniformities could arise from various sources. A common cause of nonuniformity of the wall charge is the adsorption of analytes that alter the wall ζ-potential [2]. Nonuniformities could also arise from imperfections in the fabrication process. A patterned charge on the wall may also be deliberately engineered to built novel fluidic properties (such as chaotic mixing) into the microfluidic channel.

The problem of EOF in the presence of variable ζ-potential have been studied by Anderson & Idol [3], Herr et al. [1], Ajdari [4],[5], and Stroock et al. [6]. The analysis presented here differs from the earlier ones in that straight channels of arbitrary cross-sectional geometry and wall charge are considered, subject only to the restriction that such properties be “slowly varying” in the axial direction.

2 Lubrication Theory

On account of the narrowness of microfluidic channels, axial nonuniformities in wall charge could typically be expected to occur over a characteristic length that is very much larger than a characteristic channel width. This is true, for example, in situations where the variation of wall charge is due to the adsorption of analytes from the flow stream. Under such conditions an asymptotic solution in the small parameter ε (the ratio of characteristic channel diameter to length scale for axial inhomogeneities) to the full electrohydrodynamic problem is possible. The solution allows a reduced description of the fluid flow problem in all situations where this so called “lubrication approximation” can be justified.

The complete mathematical description in the limit of thin Debye layers is provided by the following equations:

\[
\rho_0 (\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \mu \nabla^2 \mathbf{u},
\]

\[
\nabla \cdot \mathbf{u} = 0
\]

\[
\nabla^2 \phi = 0
\]

where the fluid velocity \( \mathbf{u} \), and pressure \( p \), are defined in the region \( \Omega \) representing the interior of the channel, and \( \phi \) is the electric potential. \( \rho_0 \) and \( \mu \) are the fluid density and viscosity. In the limit of thin Debye layers, the electrical and hydrodynamic problems are coupled through the Helmholtz-Smoluchowski slip boundary conditions [7]

\[
\left[ \mathbf{u} + \frac{\kappa \mathbf{E}}{4\pi \mu} \right]_{\partial \Omega} = 0,
\]

on the solid-fluid interface \( \partial \Omega \), where \( \kappa \) is the dielectric constant, \( \zeta = \zeta(x,y,z) \) is the wall ζ-potential and
\( \mathbf{E} = -\nabla \phi \) is the electric field. Neglecting the electrical conductivity of the substrate we also have

\[
[\mathbf{n} \cdot \nabla \phi]_{\partial \Omega} = 0, \tag{5}
\]

where \( \mathbf{n} \) is the outward directed unit normal on \( \partial \Omega \).

At lowest order in the small parameter \( \epsilon \), the solution to the problem formulated above may be summarized as follows [8]. The velocity is in the axial \( \mathbf{x} \) direction at leading order, \( \mathbf{u} \sim \hat{\mathbf{u}}(x, y, z) + O(\epsilon) \), and so is the applied electric field, \( \mathbf{E} = -\nabla \phi \sim \hat{\mathbf{E}}(x) + O(\epsilon) \). Pressure gradients in the cross-channel direction may be neglected, \( p = p(x) \). The axial velocity is given by

\[
u = -\frac{u_p}{\mu} \frac{dp}{dx} + \frac{k \psi E(x)}{4 \pi \mu}, \tag{6}\]

The functions \( u_p \) and \( \psi \) are defined by

\[
\frac{\partial u_p}{\partial y^2} + \frac{\partial u_p}{\partial z^2} = -1, \quad u_p|_{\partial D(x)} = 0, \tag{7}\]

and

\[
\frac{\partial \psi}{\partial y^2} + \frac{\partial \psi}{\partial z^2} = 0, \quad \psi|_{\partial D(x)} = -\zeta. \tag{8}\]

Both of these functions \( u_p \) and \( \psi \) may be evaluated by quadrature from a knowledge of the Green’s function, \( G \), of the Laplace operator with zero boundary condition corresponding to the 2D domain \( D(x) \), that corresponds to the channel cross-section at axial location \( x \) with boundary \( \partial D(x) \):

\[
u_p = \frac{1}{4\pi} \int_{D(x)} G(x; y, z, y_*, z_*) dy_*, dz_*, \tag{9}\]

\[
\psi = \frac{1}{4\pi} \int_{\partial D(x)} \zeta(x, y, z_*) \hat{\mathbf{n}} \cdot \nabla_* G ds_*, \tag{10}\]

where \( \hat{\mathbf{n}} = \mathbf{n} - (\mathbf{n} \cdot \hat{\mathbf{i}}) \hat{\mathbf{i}} \), and \( \nabla_* \) denotes the two dimensional gradient \( (\partial_{y_*}, \partial_{z_*}) \).

The remaining unknown functions \( E(x) \) and \( p(x) \) are determined using solvability conditions on the electrohydrodynamic problem at the next order in the expansion in \( \epsilon \). Physically, these conditions are nothing but the requirements of the conservation of volume flux of fluid and electric flux:

\[
Q = -\frac{\hat{a}_p}{\mu} A(x) \frac{dp}{dx} + \frac{k F \psi}{4 \pi \mu}, \tag{11}\]

\[
E(x) A(x) = F. \tag{12}\]

Here \( F \) is a constant representing the electric flux through any cross-section, \( A(x) \) is the cross-sectional area and the overbar indicates average over the cross-section, \( \bar{f} = A^{-1} \int f \, dy dz \).

One consequence of equations (11) and (12) may be easily seen by solving (11) for \( dp/dx \), and, integrating both sides over the entire length of the channel. This gives the result that the volume flux \( Q \) through such an inhomogeneous channel is exactly equal to the flux through an “equivalent” uniform cylindrical capillary of radius \( a_* \) and \( \zeta \)-potential \( \zeta_* \):

\[
Q = \frac{p_p - p_b}{8 \mu L} \pi a_*^4 - \frac{k \zeta_*}{4 \pi \mu} a_*^2 V_s - V_b, \tag{13}\]

where

\[
a_* = \left[ \frac{8}{\pi (a_p^{-1} A^{-1})} \right]^{1/4}, \quad \zeta_* = -\langle \bar{\psi} a_p^{-1} A^{-1} \rangle / 8 \pi (A^{-1})(a_p^{-1} A^{-1})^{1/2}, \tag{14}\]

and \( \langle \ldots \rangle \) denotes average axial over the length of the channel. The concept of the effective radius and effective \( \zeta \)-potential could be quite useful in the analysis of microfluidic circuit components, the coefficients of \( p_p - p_b \) and \( V_s - V_b \) in (13) may be thought of as “fluidic impedances” in analogy with electric circuit theory.

In problems of electroosmotic flow through porous media (such as the electrophoretic pump) a useful model consists of approximating the porous media as a series of parallel channels with undulating walls and possibly variable \( \zeta \)-potential. Equation (14) could then be useful for calculating the effective resistance to fluid flow through such a media. Since the lubrication solution requires only the evaluation of an integral once the Green’s function is known, it could be used as an efficient algorithm for numerical solution of flow problems through slowly varying channels. This is specially true in cases where the Green’s function, or equivalently, \( u_p \) and \( \psi \) are known analytically. The linear problems (7) and (8) represent respectively the deformation field in a curvilinear cylinder subjected to a small twist [9], and, the distribution of electric potential in a closed 2D domain when the potential distribution on the wall is known. These are well studied problems in applied mathematics, and, analytical solutions are available for a variety of cross-sectional geometries.

The lubrication approximation is independent of the thin Debye layer approximation, and, the development outlined above may also be carried out in the presence of finite Debye layers [10].

### 3 Experiments

As an example of the usefulness of the results presented above, we will now apply them to certain experiments on the effects of protein adsorption on capillary walls reported by Towns & Regnier (henceforth TR) [2] in the context of CZE.

The first experiment (TR) consisted of applying a known voltage drop to a cylindrical capillary of fixed length containing a buffer of known pH. A small amount of protein mixed with a neutral marker (Mesityl Oxide)
of this coupled problem is difficult. A useful simplification is to use an ad hoc form for the function \( Z(x) \) 
\[ Z(x) = \gamma_0 + (\gamma_1 - \gamma_0) \exp(-\alpha x) \]
where \( \alpha \) is a positive parameter of dimension inverse length that determines the strength of the adsorption. Let the altered \( \zeta \)-potential at the capillary entrance, which is different from the unaltered \( \zeta \)-potential, \( \gamma_0 \), be denoted by \( \gamma_1 \). The exponential model is not entirely unreasonable as it may be shown very easily that a simple linear model for protein adsorption, \( \dot{\gamma} = -\alpha \gamma \) where \( \gamma \) is the amount of protein in the plug and \( \alpha \) is a constant, would, for example, lead to such an exponential distribution if the alteration of the electroosmotic flow is neglected. On using this assumed form of \( Z(x) \) in (15) we get a differential equation for determining \( X \) which may be readily solved in closed form giving the following expression for the elution time \( t_e \) for a station located at a distance \( X \) from the injection end:

\[
t_e = \frac{L}{u_e} \frac{1}{p - f} \ln \left[ \frac{f}{p} + \left( 1 - \frac{f}{p} \right) \exp \left( \frac{pX}{L} \right) \right]
\]

where \( L \) is the total length of the capillary, \( u_e \) is the electroosmotic flow speed in the absence of protein adsorption, \( p = \alpha L \) and \( f = 1 - \gamma_1/\gamma_0 \) are dimensionless parameters. Equation (17) is fitted to the experimental data of TR in figure 1 using \( f \) and \( p \) as adjustable parameters in the case of each protein.

In the second experiment (TR) the \( \zeta \)-potential distribution was fixed (did not evolve with the flow). A plug containing only a neutral (nonadsorbing) marker, Mesityl Oxide was used in a capillary, a section of which was coated with 20-kDa poly(ethylenimine) or PEI 200, a polymer that masks the silanol groups on the surface of the fused silica capillary giving it a net positive charge. The ratio of coated to uncoated section was altered by successively cutting off and removing 3 cm sections of the capillary from the inlet end, and simultaneously adjusting the applied voltage to keep the electric field strength constant. The \( \zeta \)-potential is then a step function, and \( \dot{\gamma} \) may be easily calculated from (16), which allows the calculation of the elution time. In figure 2, this theoretical calculation of the elution time is compared with the experimental measurement choosing the unknown parameter \( f \) to get the best fit (\( f = 1.326 \)).

In the case of cylindrical geometry, \( u_\psi \) and \( \psi \) are known, so that the velocity profile in the case of a partially coated capillary may be explicitly calculated. This allows us to determine the effective axial diffusion coefficient given by the sum of the molecular diffusion, \( D \), and the Taylor-Aris dispersion\[12,\] \[13\] 
\[ D_* = D + \frac{(v_0^2 u_m^2)}{(192D)} \]
where \( u_m \) is the maximum magnitude of the parabolic part of the velocity profile. Since the bulk velocity is known, the travel times through each section, \( t \) may be calculated and hence the variance acquired by the plug in traveling through this section, \( 2D_* t \) is determined. The total variance \( \sigma^2 \) is then the

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**Figure 1: Comparison of experiment (symbols, from Figure 4 of TR) with (17) (lines) for elution times in an adsorbing capillary**

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### Notes

- \( \zeta(x,t) = \left\{ \begin{array}{ll}
Z(x) & \text{if } x < X(t) \\
\gamma_0 & \text{if } x > X(t)
\end{array} \right. \)  \hspace{1cm} (15)

- since for a cylindrical capillary, \( \zeta_* = \langle \zeta \rangle \) \[8\], a result also established by Anderson & Idol from their exact solution for cylindrical capillaries \[3\]. The right hand side would in general be a function of \( X \). In order to explicitly evaluate it, we need to know the distribution \( Z(x) \). This distribution however is determined by the complex nonlinear physics of the interaction of the analyte with the wall, and, a full analytical solution...
sum of the initial variance $\sigma_0^2$ and the contributions to the variance from each of the two capillary sections (of total length $X'$). The number of theoretical plates $N = \frac{X}{X'}$ may then be calculated [14], and this is compared in Figure 3 with the experimental data. The initial variance ($\sigma_0^2 = 0.0252 \text{ cm}^2$) and diffusion coefficient ($D = 6.991 \times 10^{-6} \text{ cm}^2/\text{s}$) are chosen in order to provide the best fit.

REFERENCES


