Taylor dispersion in electroosmotic flows with random zeta potentials

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Abstract

Electroosmotic flows in axisymmetric capillaries with random zeta potentials were shown in [1] to exhibit axial velocity fluctuations about the mean plug flow. In this note we address the calculation of Taylor dispersion in such flows, and highlight the important differences between cross-sectional averaging (as usually used for dispersion problems) and ensemble averaging (as used in [1]).

Keywords: Electroosmotic flow, random zeta potential, microfluidics.

1 Introduction

Electroosmotic flows are extensively employed for fluid transport and sample separation in lab-on-a-chip technologies, capillary zone electrophoresis, and generally in channels and capillaries with length scales on the order of 100μm or less. Experimental flow imaging has determined the disruption of the plug flow profile as a result of inhomogeneities in the capillary wall surface [2]. These effects generally consist of parabolic flow profiles replacing the plug flow, and result in the Taylor dispersion [3] of samples being transported by the flow. It is important to quantify the levels of dispersion to optimize separation and transport technologies.

The effects of Taylor dispersion induced by a piecewise-constant zeta potential were considered in [4], and were shown to explain experimental results on zone broadening. A more realistic model for the variation in zeta potential was provided in [1], where the zeta potential is assumed to fluctuate as a Gaussian random function about its mean value. The resulting flow velocities consequently fluctuate about the mean plug profile, with the variance having an approximately parabolic form.

In this paper, we incorporate molecular diffusion effects into the random zeta potential model of [1] by following the Taylor dispersion methodology of [5]. The convection-diffusion equation for concentration of the solute is reduced to an effective one-dimensional equation for the cross-sectional average concentration. The coefficients in this equation are random function of axial position, and the possibility of ensemble-averaging (or averaging over length) is considered carefully using numerical simulations. It is shown that effective dispersion coefficients may be obtained under certain circumstances.

2 Equation for $\langle c \rangle$

We consider electroosmotic flow through a circular capillary of radius a, taking the limit of small Deybe length, see [1]. No pressure head is imposed between the ends of the capillary, so a constant plug flow profile would exist in the absence of fluctuations in the zeta potential. The equation describing the axisymmetric concentration $c(r, z, t)$ of solute in a steady flow with radial and axial velocity components $u(r, z)$ and $v(r, z)$, respectively, is

$$\frac{\partial c}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(ruc) + \frac{\partial}{\partial z}(vc) - D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) - D\frac{\partial^2 c}{\partial z^2} = 0. \tag{1}$$

We define a cross-sectional average denoted by angle brackets as:

$$\langle F \rangle = \frac{2}{a^2}\int_0^a rF dr, \tag{2}$$

and seek an equation satisfied by $\langle c \rangle$, closely following the approach of [5].

To nondimensionalize variables, we note the average axial velocity is $\langle v \rangle$, which is linearly dependent on the average $\overline{\zeta}$ of the zeta potential, see equation (15) of [1]. Using this, we define nondimensional velocities $\tilde{v}$, $\tilde{u}$ as

$$\tilde{v} = \frac{v}{\langle v \rangle}, \tag{3}$$

$$\tilde{u} = \frac{u}{\langle v \rangle}, \tag{4}$$

and use the capillary radius a and the correlation length ℓ of the zeta potential to nondimensionalize r and z respectively:

$$\tilde{r} = \frac{r}{a}, \tag{5}$$

$$\tilde{z} = \frac{z}{\ell}. \tag{6}$$

We choose to scale time as

$$\tilde{t} = \frac{\langle v \rangle}{a} t. \tag{7}$$

Only two nondimensional parameters now appear in (1); the ratio λ of the axial and longitudinal length scales

$$\lambda = \frac{\ell}{a}, \tag{8}$$

and the Peclét number

$$Pe = \frac{\langle v \rangle a}{D}. \tag{9}$$

We hereafter drop the tildes and use nondimensional quantities except where otherwise noted. The governing equation in dimensionless form is

$$\frac{\partial c}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(ruc) + \frac{1}{\lambda}\frac{\partial}{\partial z}(vc) - \frac{1}{Pe}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) - \frac{1}{Pe\lambda^2}\frac{\partial^2 c}{\partial z^2} = 0. \tag{10}$$

We begin by averaging equation (11) over the cross-section, noting that

$$\left\langle \frac{1}{r}\frac{\partial}{\partial r}(ruc) \right\rangle = 0 \tag{11}$$

since the radial velocity is zero at $r = 1$, and

$$\left\langle \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) \right\rangle = 0 \tag{12}$$

for no flux through the wall of the capillary. Moreover, we write $v = 1 + v'$ and $c = \langle c \rangle + c'$ and obtain

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{1}{\lambda}\frac{\partial \langle c \rangle}{\partial z} + \frac{1}{\lambda}\frac{\partial}{\partial z}\langle v'c' \rangle - \frac{1}{Pe\lambda^2}\frac{\partial^2 \langle c \rangle}{\partial z^2} = 0. \tag{13}$$

Closing this equation requires an expression for $\langle v'c' \rangle$ in terms of $\langle c \rangle$. Returning to equation (11), writing $u = \langle u \rangle + u'$ (where $\langle u \rangle$ may depend on z), and using incompressibility leads to

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{\partial c'}{\partial t} + (\langle u \rangle + u')\frac{\partial c'}{\partial r} + (1+v')\frac{1}{\lambda}\frac{\partial \langle c \rangle}{\partial z} + (1+v')\frac{1}{\lambda}\frac{\partial c'}{\partial z} - \frac{1}{Pe}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c'}{\partial r}\right) - \frac{1}{Pe\lambda^2}\frac{\partial^2}{\partial z^2}(\langle c \rangle + c') = 0. \tag{14}$$

Subtracting equation (13) from equation (14) and rearranging terms, we have

$$\frac{\partial c'}{\partial t} + (\langle u \rangle + u')\frac{\partial c'}{\partial r} - \frac{1}{\lambda}\frac{\partial}{\partial z}\langle v'c' \rangle + \frac{1}{\lambda}\frac{\partial c'}{\partial z} + \frac{v'}{\lambda}\frac{\partial c'}{\partial z} + \frac{v'}{\lambda}\frac{\partial \langle c \rangle}{\partial z} = \frac{1}{Pe}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c'}{\partial r}\right) + \frac{1}{Pe\lambda^2}\frac{\partial^2 c'}{\partial z^2}. \tag{15}$$

This is the analogue of equation (6) of [5], the only difference being the presence here of radial convective terms. We now invoke similar arguments to those used in [5], [3]—let $v' = O(1)$ while $c' \ll \langle c \rangle$, and take the quasi-steady limit of long times—to claim that the dominant balance in (15) is between the final term on the left-hand side and the first term on the right-hand side:

$$\frac{v'}{\lambda}\frac{\partial \langle c \rangle}{\partial z} \approx \frac{1}{Pe}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c'}{\partial r}\right). \tag{16}$$

Integrating twice, and satisfying $\partial c'/\partial r = 0$ at the wall leads to

$$c'(r,z,t) = -\frac{Pe}{\lambda}F(r,z)\frac{\partial \langle c \rangle}{\partial z} + c'(0,z,t), \tag{17}$$

where we define F by

$$F(r,z) = \int_0^r dr_1 \frac{1}{r_1}\int_{r_1}^1 dr_2\, r_2\, v'(r_2,z). \tag{18}$$

We can now write $\langle v'c' \rangle$ in terms of $\langle c \rangle$ as required to close equation (13):

$$\frac{\partial}{\partial z}\langle v'c' \rangle = -\frac{Pe}{\lambda}\langle v'(r,z)F(r,z) \rangle \frac{\partial^2 \langle c \rangle}{\partial z^2} - \frac{Pe}{\lambda}\frac{\partial \langle c \rangle}{\partial z}\frac{\partial}{\partial z}\langle v'(r,z)F(r,z) \rangle. \tag{19}$$

The first term on the right-hand side of this equation gives z-dependent dispersion, as expected. Rather more surprising is the second term, which acts as a z-dependent drift term. We show in section 4 that the ensemble average (equivalent to averaging along the length of the capillary) of this random drift term is zero, but its effect may nevertheless be non-negligible in experiments. For completeness, we record here the one-dimensional convection-diffusion equation we have derived for the cross-section averaged concentration $\langle c \rangle$:

$$\frac{\partial \langle c \rangle}{\partial t} + \left[\frac{1}{\lambda} - \frac{Pe}{\lambda^2}\frac{\partial}{\partial z}\langle v'(r,z)F(r,z) \rangle\right]\frac{\partial \langle c \rangle}{\partial z} - \left[\frac{1}{Pe\lambda^2} + \frac{Pe}{\lambda^2}\langle v'(r,z)F(r,z) \rangle\right]\frac{\partial^2 \langle c \rangle}{\partial z^2} = 0 \tag{20}$$

3 Numerical simulations

The one-dimensional convection-diffusion equation (20) has z-dependent drift and diffusion coefficients. It is interesting to see how these coefficients vary, given a zeta potential with random fluctuations along the length of the capillary. As in section 7 of [1], realizations of the zeta potential are created using N Fourier modes:

$$\zeta(z) = 1 + \frac{\sigma}{\bar{\zeta}\sqrt{N}}\sum_{n=1}^{N} A_n \cos(k_n z) + B_n \sin(k_n z), \tag{21}$$

where k_n, A_n and B_n are chosen randomly from independent Gaussian distributions with unit variances, and the zeta potential has been normalized by its mean $\bar{\zeta}$.

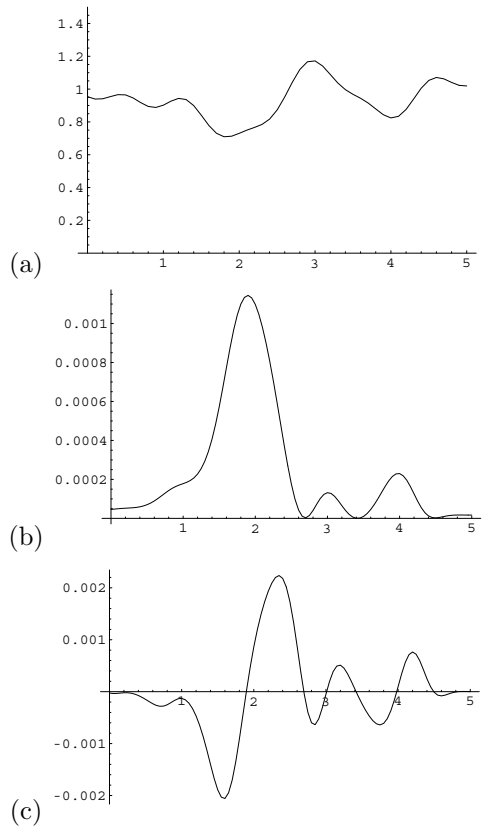

Figure 1: A single realization of: (a) zeta potential, with corresponding (b) Taylor dispersion coefficient $\langle v'F\rangle$, and (c) Taylor drift coefficient $-\frac{\partial}{\partial z}\langle v'F\rangle$ as functions of z. The random zeta potential has $\overline{\zeta}=1$, standard deviation $\sigma=0.15$, and correlation length $\lambda=0.5$.

The standard deviation σ measures the extent of fluctuations of the zeta potential about the mean; the appropriate nondimensional parameter is defined hereafter as

$$\epsilon=\sigma/\overline{\zeta} \tag{22}$$

In Figure 1(a) we plot a particular realization of a random zeta potential (21), with standard deviation $\epsilon=0.15$, and correlation length $\ell=0.5a$, using $N=50$ random modes (similar to Figure 1(b) of [1]). The induced z-dependent Taylor dispersion coefficient for (20) is (up to a factor of Pe/λ^2) $\langle v'(r,z)F(r,z)\rangle$. This is plotted in Figure 1(b). The drift coefficient in (20) depends on the z-derivative of $\langle v'F\rangle$ and is plotted in Figure 1(c). The mean plug velocity is normalized to unity, so the $O(\epsilon^2)$ fluctuations are small, but may nevertheless be significant if the Peclét number is large.

4 Ensemble averages

In the previous sections we have considered averages over cross-section (denoted by angle brackets), and so reduced to a one-dimensional convection-diffusion problem, with z-dependent coefficients. It is natural to consider the motion of solute down a long capillary with homogeneous fluctuations in the zeta potential, and to ask if a single effective diffusion coefficient can be found to measure the spread of the solute plug at the end of the capillary. In this section we calculate the ensemble average of the Taylor coefficients defined in (20), and argue (see section 5) that they answer the above question.

Our goal here is the calculation of

$$\overline{\langle v'(r,z)F(r,z)\rangle}, \tag{23}$$

where the overbar indicates averaging over an ensemble of realizations of the zeta potential. As in section 3 of [1] we choose a simple (dimensional) correlation function for the homogeneous zeta potential

$$\begin{aligned} R(z) &= \frac{1}{\sigma^2}\overline{\left[\zeta(z)-\overline{\zeta}\right]\left[\zeta(0)-\overline{\zeta}\right]} \\ &= \exp\left(-\frac{z^2}{2\ell^2}\right), \end{aligned} \tag{24}$$

with correlation length $\ell=\lambda a$. The axial velocity is given in terms of the zeta potential by equation (8) of [1], and the calculation then proceeds along similar lines to that yielding equation (16) of [1]. The result reduces to a single nondimensional integral:

$$\overline{\langle v'(r,z)F(r,z)\rangle}=\epsilon^2\int_{-\infty}^{\infty}\Gamma(k,k)\hat{R}(k)dk, \tag{25}$$

where ϵ is defined as in (22), and $\hat{R}$ is the Fourier transform of the correlation function as in equation (14) of [1]. The function Γ is defined as:

$$\begin{aligned} \Gamma(k',k) &= \left\langle \hat{G}(r,k')\int_0^r dr_1\frac{1}{r_1}\int_{r_1}^1 dr_2\, r_2\,\hat{G}(r_2,k)\right\rangle \\ &= 2\int_0^1 dr\, r\,\hat{G}(r,k')\int_0^r dr_1\frac{1}{r_1}\int_{r_1}^1 dr_2\, r_2\,\hat{G}(r_2,k), \end{aligned} \tag{26}$$

with the function $\hat{G}(r,k)$ as given in equation (9) of [1]. For $k'=k$, the integration may be performed completely in closed form, using a generalized hypergeometric function [6]:

$$\begin{aligned} \Gamma(k,k)=\gamma(k)^2\Bigg[&k^2I_0(k)^2-k^2\frac{I_0(k)^4}{I_1(k)^2}+2k\frac{I_0(k)^3}{I_1(k)} \\ &-2I_1(k)^2-\frac{1}{12}k^4\ {}_1F_2\left(\frac{3}{2};(2,4);k^2\right)\Bigg], \end{aligned} \tag{27}$$

with $\gamma(k)$ defined in equation (43) of [7].

Using this, we calculate the integral in (25) for different values of λ, see Figure 2. In the limit $\lambda\to\infty$, $\hat{R}$ becomes a delta function and the integral is

$$\Gamma(0,0)=\frac{1}{48}, \tag{28}$$

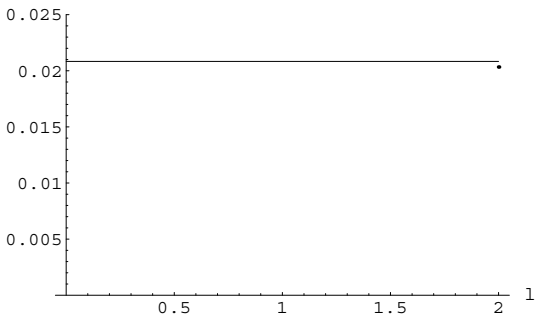

Figure 2: Ensemble-averaged Taylor dispersion coefficient at values of λ (ratio of correlation length l to radius a) from 0 to 2. The solid line is the Poiseuille flow limit of 1/48.

yielding the familiar Poiseuille flow Taylor dispersion coefficient. Moreover, note that the ensemble averaging eliminates all z-dependence in (25), so the average value of the additional drift term in (20) is zero.

5 Limits of validity

We have made two sets of approximations; the first is justified using the standard Taylor dispersion arguments, leading from the full convection-diffusion equation (11) to the one-dimensional equation (20) for $\langle c \rangle$:

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{1}{\lambda}\frac{\partial \langle c \rangle}{\partial z} - \frac{1}{Pe\lambda^2}\frac{\partial}{\partial z}\left[\left(1 + Pe^2 \langle v'F \rangle\right)\frac{\partial \langle c \rangle}{\partial z}\right] = 0. \tag{29}$$

The second approximation is the replacement of the the z-dependent term $\langle v'F \rangle$ by its ensemble- (or length-) average, which simplifies equation (29) to a constant-coefficient convection-diffusion equation:

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{1}{\lambda}\frac{\partial \langle c \rangle}{\partial z} - \frac{1}{Pe\lambda^2}\left(1 + Pe^2\overline{\langle v'F \rangle}\right)\frac{\partial^2 \langle c \rangle}{\partial z^2} = 0. \tag{30}$$

Following the usual arguments to estimate the range of Peclét numbers where these approximations are valid (see, e.g., Probstein [8]), we require convective effects to dominate (Taylor) dispersion:

$$\frac{1}{\lambda} \gg \frac{Pe\overline{\langle v'F \rangle}}{\lambda^2}, \tag{31}$$

while Taylor dispersion should dominate molecular diffusion:

$$Pe^2\overline{\langle v'F \rangle} \gg 1. \tag{32}$$

If we take the large-λ limit of $\overline{\langle v'F \rangle}$ from (25) for simplicity, the above constraints can be written as

$$\frac{48\lambda}{\epsilon^2} \gg Pe \gg \frac{\sqrt{48}}{\epsilon}. \tag{33}$$

Implicit in the above discussion is the assumption that the replacement of the z-dependent dispersion coefficient $\langle v'F \rangle$ by its length-average is valid, provided that convection is strong enough to provide an efficient sampling of the fluctuations.

6 Discussion

For a zeta potential that varies in the axial direction along a capillary, we have derived the convection-diffusion equation (20) for the cross-section average concentration. The coefficients of (20) depend on axial position. In section 4 we calculated the ensemble average of the coefficients, in particular showing that the ensemble-averaged drift term vanishes, and that the diffusion coefficient limits to its Poiseuille flow value as the correlation length approaches infinity.

In section 5 we claim that the replacement of the z-dependent Taylor dispersion coefficient by its ensemble average is likely to be valid for those Peclét numbers where Taylor's approximations are good. Note this implies that the ensemble average can be used whenever Taylor dispersion appears. Further work is required to formalize the limits of validity of the approximations, and compare with numerical simulations.

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