Taylor dispersion for coupled electroosmotic and pressure-driven flows in all time regimes

Supplementary Material

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CONTENTS

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A. Analytical reduction of our quasi-steady solution to Griffiths & Nilson's (1999) solution for electroosmotic flow only

We here demonstrate how our solution for the quasi-steady dispersion coefficient reduces to that of Griffiths & Nilson (1999) for the case of pure electroosmotic flow (EOF; $\beta = 0$). We begin with our expression for the dimensionless dispersion coefficient, (3.20) from the main paper:

$$D_{\text{eff}}^{*} = 1 + Pe^{2}\left(\beta^{2}\gamma_{p} + \beta(1-\beta)\gamma_{pe} + (1-\beta)^{2}\gamma_{e}\right). \tag{S1}$$

Substituting $\beta = 0$ and re-arranging, we can rewrite (S1) as follows:

$$Pe^{-2}\left(D_{\text{eff}}^{*} - 1\right) = \gamma_{e} = \left(\frac{\eta}{1-\eta}\right)^{2}\left(\frac{3}{8} + \frac{2}{\phi^{2}} - \frac{1}{\eta\phi^{2}} - \frac{1}{\eta^{2}\phi^{2}}\right), \tag{S2}$$

where the value of γ_{e} is given by (3.15) of the main paper. First, we consider the term $\eta^{2}/(1-\eta)^{2}$. We may express the latter as

$$\left(\frac{\eta}{1-\eta}\right)^{2}\cdot\frac{I_{0}(\phi)^{2}}{I_{0}(\phi)^{2}} = \frac{4I_{1}(\phi)^{2}}{\phi^{2}}\cdot\left(\frac{4I_{1}(\phi)^{2}}{\phi^{2}} - \frac{4I_{0}(\phi)I_{1}(\phi)}{\phi} + I_{0}(\phi)^{2}\right)^{-1} = 8I_{1}(\phi)^{2}\left(2\phi^{2}\left(2\phi^{-1}I_{1}(\phi) - I_{0}(\phi)\right)^{2}\right)^{-1}. \tag{S3}$$

Substituting (S3) into (S2),

$$Pe^{-2}\left(D_{\text{eff}}^{*} - 1\right) = \gamma_{e} = \left(2\phi^{2}\left(2\phi^{-1}I_{1}(\phi) - I_{0}(\phi)\right)^{2}\right)^{-1} 8I_{1}(\phi)^{2}\left(\frac{3}{8} + \frac{2}{\phi^{2}} - \frac{1}{\eta\phi^{2}} - \frac{1}{\eta^{2}\phi^{2}}\right). \tag{S4}$$

Next, expanding the term $8I_{1}(\phi)^{2}\left(\frac{3}{8} + \frac{2}{\phi^{2}} - \frac{1}{\eta\phi^{2}} - \frac{1}{\eta^{2}\phi^{2}}\right)$,

$$8I_{1}(\phi)^{2}\left(\frac{3}{8} + \frac{2}{\phi^{2}} - \frac{1}{\eta\phi^{2}} - \frac{1}{\eta^{2}\phi^{2}}\right) = 3I_{1}(\phi)^{2} + 16\phi^{-2}I_{1}(\phi)^{2} - 8I_{1}(\phi)^{2}\left(\frac{I_{0}(\phi)}{2\phi I_{1}(\phi)} + \frac{I_{0}(\phi)^{2}}{4I_{1}(\phi)^{2}}\right) = \left(3 + 16\phi^{-2}\right)I_{1}(\phi)^{2} - 4\phi^{-1}I_{0}(\phi)I_{1}(\phi) - 2I_{0}(\phi)^{2}. \tag{S5}$$

Lastly, substituting (S5) into (S4) and multiplying by ϕ^2,

$$\phi^2 Pe^{-2}\left(D_{\text{eff}}^{*}-1\right)=\left(2\left(2\phi^{-1}I_1(\phi)-I_0(\phi)\right)^2\right)^{-1}\left(\left(3+16\phi^{-2}\right)I_1(\phi)^2-4\phi^{-1}I_0(\phi)I_1(\phi)-2I_0(\phi)^2\right). \quad \text{(S6)}$$

The latter simplified equation is equivalent to equation (38) of Griffiths & Nilson (1999). Thus, in the restrictive case of EOF only, our solution for the coefficient of effective dispersion in the long-time regime reduces to Griffiths & Nilson's solution of the coefficient of effective dispersion

B. Benchmark comparisons of quasi-steady solution and Brownian dynamics simulations for $Pe=20$ and $Pe=1000$

We here present additional comparisons between our analytical solution for the two-dimensional concentration field and Brownian dynamics simulations for the cases of $Pe=20$ and 1000. Figure 4 presents a similar comparison for $Pe=100$. Figure 5 presents a similar comparison for $Pe_e=100$ and $Pe_p=-100$. The figures provided here are therefore complementary to figures 4 and 5 of the main paper. As in the main paper, figures S1 and S2 each show solute distributions for three dimensionless times (in blue, orange and green). The top half of each channel is an example Brownian dynamics simulation, while the bottom half shows the analytical solution (from (3.40) of the main paper). Figure S1 and S2 respectively show cases with Pe of 20 and 1000. The values of β and ϕ are indicated along the right of the figures.

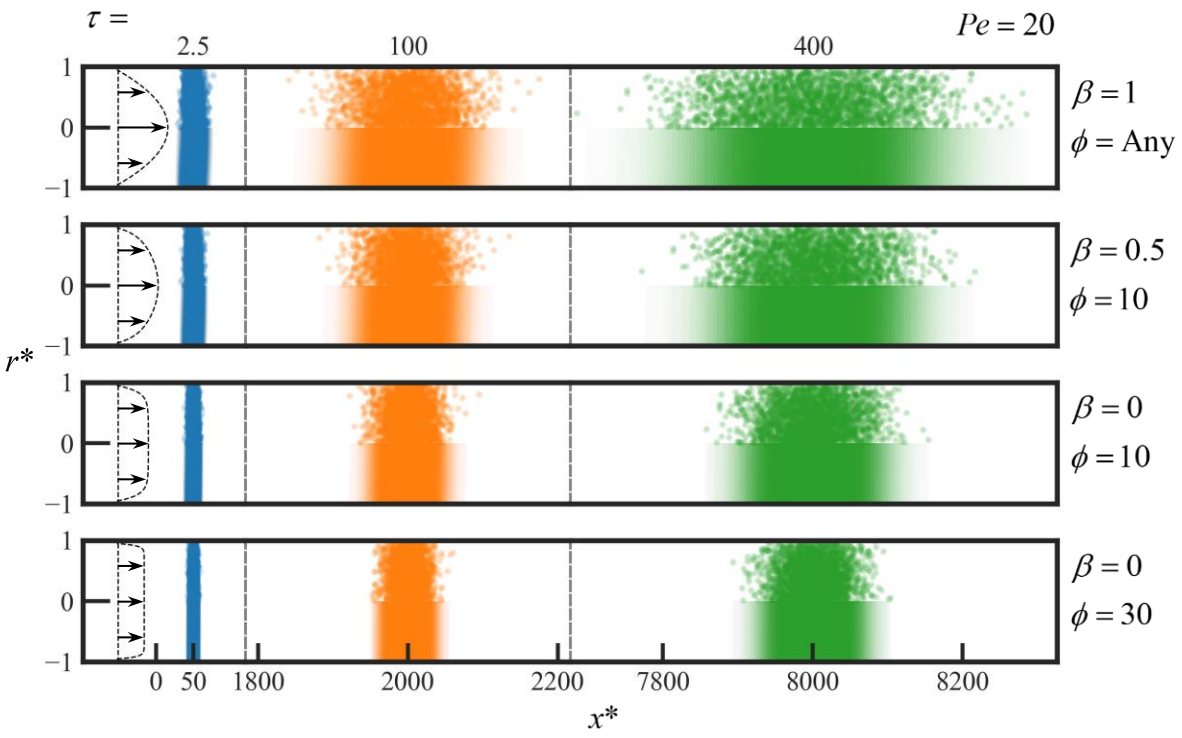

Figure S1. Benchmark comparisons between Brownian dynamics simulations and the analytical solution of the quasi-steady solute concentration field at three values of dimensionless time, $\tau = tD/a^2$. This is the equivalent of figures 4 and S2 but created for $Pe = 20$. The plot shows dimensionless radius, r^*, on the ordinate and dimensionless axial position, x^*, on the abscissa. The top half of each subplot shows individual particles from the Brownian dynamics simulations and the bottom half of each subplot shows the concentration field predicted by the analytical solution in (3.40). Subplots show four combinations of the fraction of bulk velocity caused by pressure, β , and the tube radius scaled by Debye length, ϕ . The far left of the subplots shows the flow profile used to generate the data for each row.

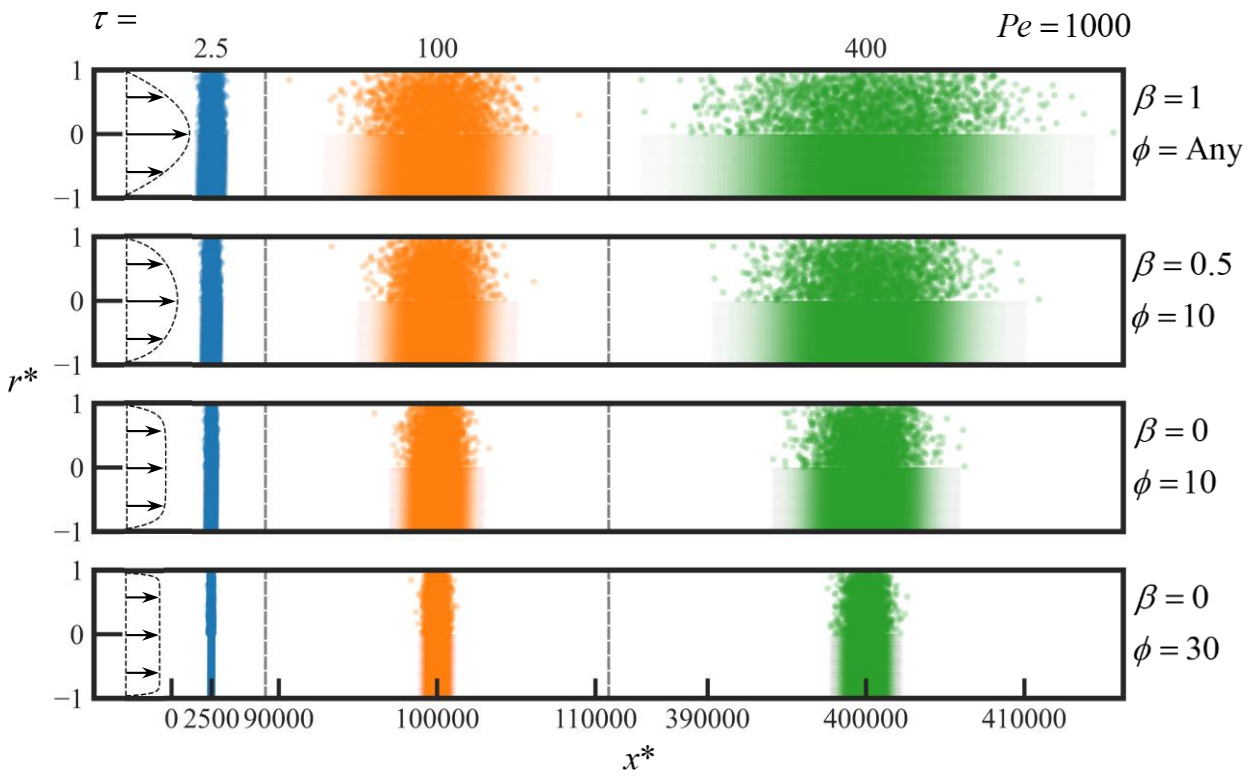

Figure S2. Benchmark comparisons between Brownian dynamics simulations and the analytical solution of the quasi-steady solute concentration field at three values of dimensionless time, $\tau = tD/a^2$. This is the equivalent of figures 4 and S1 but created for $Pe = 1000$. The plot shows dimensionless radius, r^* , on the ordinate and dimensionless axial position, x^*, on the abscissa. The top half of each subplot shows individual particles from the Brownian dynamics simulations and the bottom half of each subplot shows the concentration field predicted by the analytical solution in (3.40). Subplots show four combinations of the fraction of bulk velocity caused by pressure, β , and the tube radius scaled by Debye length, ϕ . The far left of the subplots shows the flow profile used to generate the data for each row.

As in figures 4 and 5 of the main paper, the analytical solution and Brownian dynamics simulations show excellent agreement for all combinations of parameters.

C. Nomenclature

We here provide a comprehensive list of the nomenclature used in the main paper.

Operators

$\langle(.)\rangle = \int_0^1 2r^*(.)\mathrm{d}r^* =$ cross-sectional area average

$(.)' = (.) - \langle(.)\rangle =$ deviation from cross-sectional area average

$(.)^* =$ dimensionless variable

$(.)^{\mathrm{tms}} =$ variable associated with transient solution (from method of moments)

$(.)^c =$ evaluated at the axial centreline of the channel

$(.)^{\mathrm{res}} =$ evaluated in an electroneutral reservoir

$\overline{(.)} = (.)/\langle u\rangle =$ normalization by bulk velocity

Dimensional

$a =$ inner radius of tube

$\boldsymbol{a} =$ positional vector at the slipping plane

$A =$ cross-sectional area of tube

$c(r,x,t) =$ concentration of solute

$c_o =$ scaling parameter for cross-sectionally averaged concentration field

$c_o' =$ scaling parameter for deviation from cross-sectionally averaged concentration field

$\boldsymbol{c} =$ positional vector at the axial centreline of the channel

$D =$ molecular diffusivity

$D_{\mathrm{eff}} =$ coefficient of effective dispersion

$D_{\mathrm{eff}}^{\mathrm{trns}} = D_{\mathrm{eff}}^{\mathrm{trns}}(\tau) =$ coefficient of effective dispersion associated with transient solution

$e =$ elementary charge

$E =$ electric field

$k_{\mathrm{B}} =$ Boltzmann constant

$L =$ a specific axial distance of interest

$L_0 =$ initial width of a "top hat" solute zone

$n_i(\boldsymbol{r}) =$ ionic density function of the i^{th} species

$N =$ moles of solute in tube

$\boldsymbol{r} =$ three-dimensional position vector

$T =$ absolute temperature

$u_e(r) =$ flow profile of the electroosmotic flow component

$u_p(r) =$ flow profile of the pressure-driven flow component

$u(r) = u_p(r) + u_e(r) =$ flow profile

$\langle u_e \rangle =$ bulk velocity from electroosmotic flow

$\langle u_p \rangle =$ bulk velocity from pressure-driven flow

$\langle u \rangle = \langle u_p \rangle + \langle u_e \rangle =$ net bulk velocity

$u_{\mathrm{HS}} = -\varepsilon_e E\zeta/\mu =$ Helmholtz-Smoluchowski velocity scale

$\boldsymbol{w} =$ positional vector within an electroneutral reservoir

$x' = x - \langle u \rangle t =$ axial position in a moving frame at the net bulk velocity

$\boldsymbol{x} =$ path between channel centreline and an electroneutral reservoir at constant electrochemical potential

$z_i =$ valence number of the i^{th} species

$\varepsilon_e =$ permittivity of fluid

$\zeta =$ zeta potential

$\lambda_D =$ Debye length

$\mu =$ dynamic viscosity of fluid

$\overline{\mu}_i =$ electrochemical potential of the i^{th} species

$\rho(\boldsymbol{r})$ = electric charge density function

σ_x = characteristic width of solute zone

$\psi(r)$ = electric potential

Dimensionless

$c^*(r^*, x^*, \tau) = \pi a^3 c(r^*, x^*, \tau)/N$ = dimensionless concentration of solute

$c_n^*(r^*, \tau) = \int_{-\infty}^{\infty} (x^*)^n \, c^*(r^*, x^*, \tau) \mathrm{d}x^*$ n^{th} moment of the concentration field integrated along the x-axis

$D_{\text{eff}}^* = D_{\text{eff}}/D$ = dimensionless coefficient of effective dispersion

$D_{\text{eff}}^{*\text{trns}} = D_{\text{eff}}^{\text{trns}}/D =$ dimensionless coefficient of effective dispersion associated with transient solution

$f_i(r)$ = eigenfunction associated with transient solution

$G(x', t \mid x_i)$ = Green's function

$L^* = L/a$ = dimensionless distance of tube for optimization of Pe

$M_n(\tau) =$ n^{th} moment of the concentration field

$Pe = a\langle u \rangle / D$ = Péclet number based on net bulk velocity

$Pe_e = a\langle u_e \rangle / D = (1-\beta) Pe$ = Péclet number based on electroosmotic flow bulk velocity

$Pe_p = a\langle u_p \rangle / D = \beta Pe$ = Péclet number based on pressure-driven flow bulk velocity

$r^* = r/a$ = dimensionless radial coordinate

$\nu_n(\tau) =$ n^{th} moment about the axial mean of the concentration field

x_i = Green's function variable for axial dimension

$x^* = x/a$ = dimensionless x-position (for method of moments solution)

$x_\sigma^* = x/\sigma_x =$ x-position scaled by solute zone width (for quasi-steady state solution)

$\alpha_i =$ i^{th} root of $J_1(z)$

$\beta = \langle u_p \rangle / \langle u \rangle =$ ratio of pressure-driven flow bulk velocity to net bulk flow velocity

$\gamma_e =$ coefficient that quantifies the contribution of electroosmotic flow to the dispersion

$\gamma_p =$ coefficient that quantifies the contribution of pressure-driven flow to the dispersion

$\gamma_{pe} =$ coefficient that quantifies the contribution to dispersion associated with the coupling of pressure-driven flow and electroosmotic flow

$\eta = 1 - \langle u_e \rangle / u_{\mathrm{HS}} =$ function relating Helmholtz-Smoluchowski velocity to electroosmotic bulk velocity

$\mu_i =$ eigenvalue associated with transient solution

$\varepsilon = a/\sigma_x =$ smallness parameter defined as the ratio between tube inner radius and solute zone width (used in quasi-steady state solution)

$\tau = tD/a^2 =$ dimensionless time

$\tau_o =$ characteristic dimensionless time of interest

$\phi = a/\lambda_D =$ tube radius scaled by Debye length

$\chi(r^*) = \dfrac{a}{D} u(r^*) =$ Péclet number in terms of the (radially varying) velocity profile

Optima

$Pe_o =$ optimum value of Pe to minimize variance for transporting solute (over an arbitrary axial distance)

$Pe_o^{\mathrm{trns}} =$ optimum value of Pe to minimize variance for transporting solute (over a fixed axial distance)

$\beta_o =$ optimum value of β to minimize rate of increase of variance (for quasi-steady state solution)

$\beta_o^{\mathrm{trns}}(\tau_o) =$ optimum value of β to minimize variance obtained from transient solution

$u_o(r) =$ specific flow profile associated with $\beta = \beta_o$

REFERENCES

Griffiths, S. K. & Nilson, R. H. 1999. Hydrodynamic dispersion of a neutral nonreacting solute in electroosmotic flow. *Analytical Chemistry*, **71** (24).