

Dispersion of Solute by Electrokinetic Flow through Post Arrays and Wavy-Walled Channels

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In this work, we simulate electrokinetically driven transport of unretained solute bands in a variety of two-dimensional spatially periodic geometries (post arrays as well as sinuous/varicose channels), in the thin Debye layer limit. Potential flow fields are calculated using either an inverse method or a Schwarz–Christoffel transform, and transport is modeled using a Monte Carlo method in the transformed plane. In this way, spurious “numerical diffusion” transverse to streamlines is completely eliminated, and streamwise numerical diffusion is reduced to arbitrary precision. Late-time longitudinal dispersion coefficients are calculated for Peclet numbers from 0.1 to 3162. In most geometries, a Taylor–Aris-like scaling law for the dispersion coefficient $D_L/D_{L0} = 1 + Pe^2/\alpha$ underpredicts dispersion when $Pe \sim O(\alpha^{1/2})$ (here D_{L0} is the effective axial diffusion coefficient in the periodic geometry). A two-parameter correlation widely used in the porous media literature, $D_L/D_{L0} = 1 + Pe^n/\alpha$, agrees slightly better, but much better agreement can be obtained using a new quadratic form: $D_L/D_{L0} = 1 + Pe/\alpha_1 + Pe^2/\alpha_2$. A quasi-universal relationship for streamwise dispersion is offered that predicts 96% of the simulation data to within a factor of 2 in all geometries studied. Comparison with previous work shows that in circular post arrays, the dispersion coefficient for electrokinetic flow is a factor of 3–10 less (depending on Pe and relative post size) than for pressure-driven flow.

Post arrays are a recurring engineering motif in microscale analytical devices because they can be used as sieves, as geometric supports for very shallow channels (e.g., to prevent sagging during high-temperature bonding), or as solid supports for semisolid salt bridges or other polymer media. They are also attracting attention as engineered liquid chromatography media, due to the ease with which unprecedented geometric regularity can be achieved. He et al.¹, for example, used deep reactive ion etching to create post arrays of arbitrary geometry (Figure 1) and demonstrated that performance improvements are indeed possible when tight geometric control is exerted over the media. In all these applications, these periodic geometries always lead to some dispersion of solute passing through them.

The question “how much dispersion?” arises nowadays in discussions of the relative merits of capillary electrochromatog-

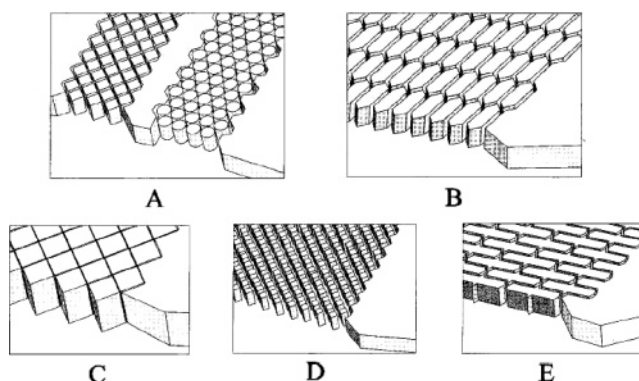


Figure 1. He et al.¹ concepts for microfabricated separations media.

raphy (CEC) versus high-performance liquid chromatography (HPLC). It is often argued that CEC has an advantage because ideal electrokinetic flow leads to reduced hydrodynamic dispersion compared with pressure-driven flow (as used in HPLC). This is certainly true in straight channels, because ideal electrokinetic flow through microchannels (uniform fluid and wall properties, dielectric walls, and vanishingly thin electric double layers (EDLs)) is purely potential^{5–7} and yields a flat velocity profile with no variation across the span of the channel. Indeed, there are data to support the assertion that the dispersion in packed columns is less for electrokinetic flow than for pressure-driven flow.⁸

On the other hand, it is also well known that U-turns, intersections, and similar channel geometries^{6,9} can create significant dispersion even with pure electrokinetic transport. Thus, one major goal of this paper is to conduct a relatively comprehensive study of the dispersion of unretained solute in pure electrokinetic flow through post arrays, to see under what conditions the dispersion is significant. We note that a comprehensive comparison of CEC and HPLC is beyond the scope of the present work, since we only consider unretained solutes. Common sources of band broadening include axial diffusion, hydrodynamic dispersion due to flow field gradients and cross-

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streamline mass transfer, and surface chemistry equilibrium, and in general, flow and chemical equilibrium are not separable as independent effects.^{2–4}

Extensive previous work on dispersion of unretained solutes exists, but nearly all of it regards purely pressure-driven flow. Classical work by Taylor^{10,11} and Aris¹² shows that dispersion of solute in a round capillary convected by laminar pressure-driven flow behaves similarly to molecular axial diffusion, in that the band variance $\sigma^2 \propto D_L t$. Here D_L is the (longitudinal) dispersion coefficient, given by

$$D_L/D_{12} = 1 + Pe^2/\alpha \quad (1)$$

where D_{12} is the binary diffusion coefficient, the Peclet number $Pe = \bar{u}h/D_{12}$ is the ratio of convective influences to diffusive influences, $\bar{u}$ is the mean velocity, and h is the capillary diameter. For a round capillary tube, Taylor and Aris found $\alpha = 192$; for pressure-driven flow between two plates, Wooding¹³ found $\alpha = 210$ (defining h as the distance between the plates). Fried et al.¹⁴ gave extensive discussion on both longitudinal and lateral dispersions due to pressure-driven flow in porous media, and Adler¹⁵ discussed asymptotic analysis of dispersion in porous media. Brenner¹⁶ developed a moment-based description of dispersion similar to that of Aris but for the more general flows found in spatially periodic porous media. Other workers¹⁷ have employed this method for various pressure-driven flows. Edwards and others^{18,19} presented data for dispersion in packed beds, also noting $D_L \propto Pe^n$ behavior with $n < 2$ for both experimental and numerical results. Kaviany²⁰ argued that a more general flow will have $D_L \propto Pe^n$ dependence where $1 < n < 2$. Dutta and Leighton have quantified dispersion due to pressure-driven flow in wide channels of finite aspect ratio and have suggested novel channel shapes that minimize dispersion due to pressure-driven flow and gentle U-turns.^{2,3}

The problem for pure EOF and electrophoresis is simplified because electrophoretic and electroosmotic transport are potential flows if the product $\epsilon\zeta/\eta\sigma$ is uniform throughout the channel and the channel walls are an ideal dielectric material.^{5–7} In the present work, we simulate this type of electrokinetically driven geometric dispersion in several streamwise-periodic geometries using a Monte Carlo simulation for solute transport, with the benefit of a Schwartz–Christoffel transformation of the domain that makes a simpler and more accurate simulation possible. A powerful alternative would be Brenner's method¹⁶ for dispersion problems. However, this method only provides late-time behavior, and it is

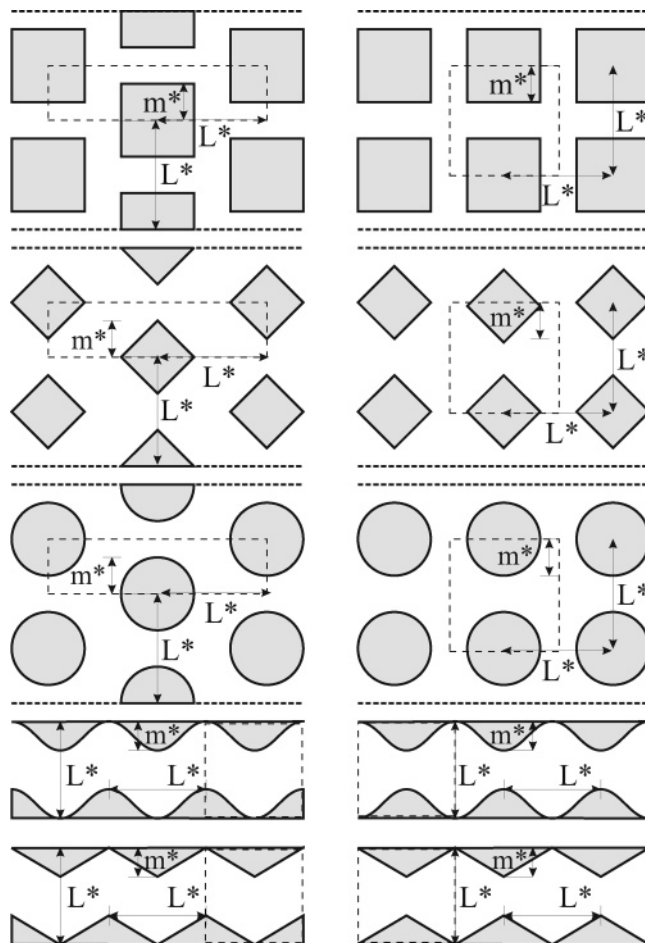


Figure 2. Geometries considered in the present work. The top three rows represent three geometries of infinitely periodic post arrays in staggered (left) and in-line (right) arrangements. The bottom two rows are the two wavy-walled channels considered in in-phase and out-of-phase geometries (phase referring to the phase of the periodic function defining the top and bottom walls). Dotted-line boxes in each case shows the periodic computational domain.

our intent to investigate early-time behavior in future work using the same code employed in the present work.

We consider a range of post array geometries typical of engineered chromatographic media: circular, diamond-shaped, and square posts at various fill ratios. We also consider wavy-walled channels, to approximate the effects of channel roughness and other lithography imperfections. We calculate effective longitudinal diffusion coefficients for a several periodic geometries over a wide range of Peclet number and correlate the results into a single “universal” dispersion function that collapses nearly all our data to within a factor of 2. It is hoped that the results can be useful as rules of thumb for the design and operation of columns incorporating post arrays, as well as a useful estimate of the effects of channel roughness on solute dispersion.

COMPUTATIONAL MODEL AND VALIDATION

Geometries. Figure 2 shows the three geometries of periodic post arrays (diamonds, circles, squares) and two geometries of wavy-walled channels (sinusoidal, sawtooth) in both arrangements (in-line, staggered) that are considered in the present work. The total of 10 different geometries are each parametrized by the

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relative post size or wave amplitude m^* , which is the half-width of the square, radius of the circle, or half-diagonal of the diamond. The post spacing in the vertical and horizontal directions is L^* ; as shown in the figure, this is used to normalize m^* into a dimensionless parameter m defined as $m = m^*/L^*$. In this study, m was varied from 0.141 to 0.424 for diamonds, 0.150–0.395 for circles, and 0.1–0.35 for squares. For wavy channels, m was varied from 0.03 to 0.12. Note that, for in-line geometries, $m = 0.5$ corresponds to complete channel blockage.

Flow Solution. In the thin Debye layer limit, the velocity of the i th species is $\mathbf{u}_i = (\mu_{EP,i} + \mu_{EO})\mathbf{E}$, where $\mu_{EP,i}$ and μ_{EO} are the electrophoretic and electroosmotic mobilities and $\mathbf{E}$ is the electric field.^{5,21} Thus, the velocity field can be expressed as the gradient of a scalar potential, and the continuity and irrotationality of the field require that $\nabla_{xy}^2\phi(x, y) = 0$ and that $\nabla_{xy}^2\psi(x, y) = 0$, where the velocity potential ϕ and stream function ψ have impermeable wall boundary conditions at the channel walls. We normalize $\phi = 0$ at $x = 0$ and $\phi = \Delta\phi$ at $x = 1$; ψ along the lower streamline is taken as zero, but ψ along the top streamline must be computed since it is equal to the flow rate through the system, which is not known a priori with a fixed potential gradient.

The most common way to solve for $\phi(x, y)$ and $\psi(x, y)$ numerically is to approximate these equations by gridding the domain into finite differences or elements, but this requires higher-order methods or grid refinement to be accurate near sharp corners. An alternative approach is an inverse method (a special case of boundary-fitted coordinates), in which the problem is posed in (ϕ, ψ) -space, as described in previous references^{6,7,22,23} and in the Supporting Information. The domain is then a simple square, and boundary conditions and gridding become very easy to apply. This also has significant advantages in the scalar transport simulations, as will be evident momentarily. In this formulation the governing equations are

$$\nabla_{\phi\psi}^2 x(\phi, \psi) = \nabla_{\phi\psi}^2 y(\phi, \psi) = 0 \quad (2)$$

where the subscript $\phi\psi$ denotes derivatives in (ϕ, ψ) -space. These equations can be solved, using appropriate compatibility conditions, using second-order finite differences or by conformal mapping via the Schwarz–Christoffel transformation.^{24–30} Both were employed and compared, and although the methods agreed to within 1%, in general the latter proved to be much more robust. Since the Schwarz–Christoffel transformation is defined only for polygonal geometries, circles and sine waves were approximated by polygons made of 64 equal line segments, but squares and diamonds were defined exactly. Values of the x - and y -fields for a

regular grid of ϕ - and ψ -values were thus found $x + iy = f(\phi + i\psi)$ on a 601×601 grid. Solutions were validated by testing the orthogonality of x - and y -fields ($\nabla_{\phi\psi}x \cdot \nabla_{\phi\psi}y = 0$), which show relative error $O[10^{-3}]$, with most of the error occurring near regions where the boundary changes rapidly. Details are given in the Supporting Information available online.

Solute Transport. Finite element methods are particularly ill-suited to simulating scalar transport at high Peclet numbers. The natural formation of scalar gradients over very short length scales creates a computationally stiff problem subject to spurious “numerical diffusion”³¹ competing with the dispersive phenomena of interest. Since “apparent” diffusivity is the quantity we wish to compute, even modest numerical diffusion would be intolerable for this study. Therefore, the computational cost for typical finite differences/elements approaches would be quite high to achieve the needed accuracy. Using published rules of thumb for accurate simulation of convection–diffusion problems³² and Taylor’s criterion¹¹ for when dispersion reaches late-time behavior, the anticipated computational cost is $O[10Pe^{3.5}]$, which becomes very expensive at high Pe .

For these reasons we employ a Monte Carlo method,^{31–35} wherein the solute is represented by an ensemble of particles that undergo deterministic and random steps in space at each time step. This approach greatly diminishes many of the aforementioned problems and has the advantage of lower computational cost $O[NPe^2]$, where N is the number of particles used to represent the solute. Additional advantages are obtained by following Griffiths and Nilson^{6,7} and conducting the simulation in (ϕ, ψ) -space. Each particle takes a deterministic step along a constant ψ -line corresponding to convection and a random step corresponding to diffusion. That is, defining our Peclet number as $Pe = (\Delta\phi/L^*)(L^*/D_{12})$ and setting $D_{12} = 1$ (without loss of generality), each particle takes a deterministic step proportional to $Pe\Delta t$ and a random step proportional to $(\Delta t)^{1/2}$. The random step’s length is also proportional to a normally distributed random number, and a split time stepping scheme is used for higher accuracy. More details of the time stepping and random step calculation methods, as well as code validation, are given in the Supporting Information.

Because the convection step is along constant ψ (a streamline), the method introduces no spurious transverse numerical diffusion even at infinite Pe . In addition to improved accuracy, the method reduces computational expense because we take full advantage of the periodicity of the domain by simply keeping track of which integer period each particle is in, and the use of the inverse domain also simplifies application of reflective boundary conditions for the particles, since the boundaries are square. The calculations are performed taking $\Delta\phi = 1$ and using varying values of D_{12} , but they could be performed equally well taking $D_{12} = 1$ and varying $\Delta\phi$, since it is only the dimensionless parameter Pe that matters.

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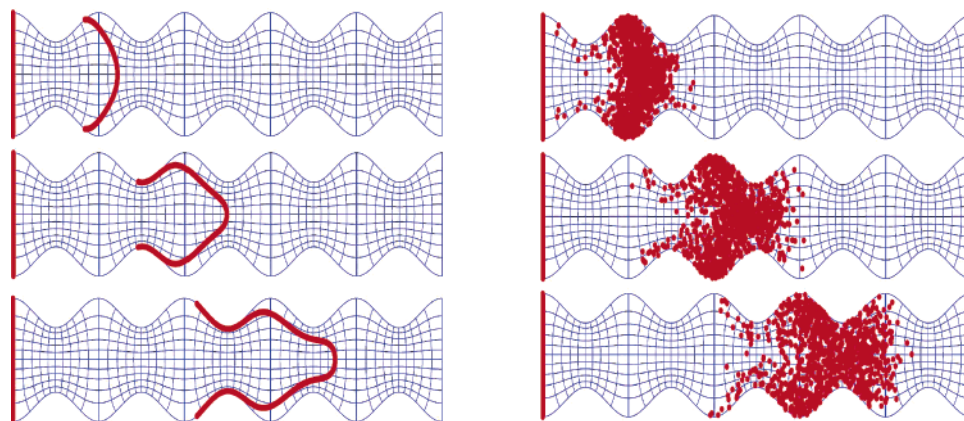


Figure 3. Early time series of Monte Carlo simulation of solute transport in sinusoidal wavy-walled channels ($m = 0.12$). Grid lines are streamlines and isopotential lines, and dots represent solute “particles”. The line at left in each frame shows the initial location of the particles at the start of the simulation. Left: three snapshots in time at $Pe = \infty$. The inverse/Monte Carlo simulation method tracks the solute band faithfully even at infinite Peclet number without spurious numerical diffusion; this would be virtually impossible using a finite differences/elements approach. Right: Early time series for the same geometry at $Pe = 100$.

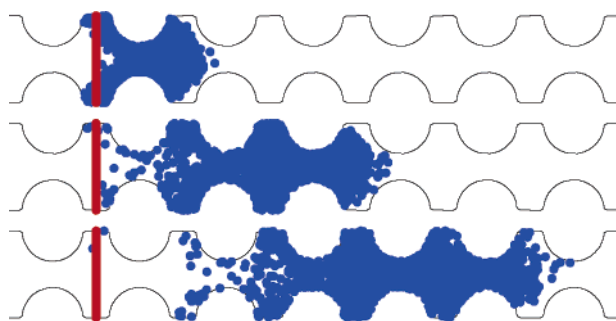


Figure 4. Time series of solute transport in an in-line circle post array ($m = 0.35$, $Pe = 100$, $N = 2000$). The lines on the left of each figure show the initial positions of the particles. The frames correspond to $t = 0.1, 0.3$, and 0.5 .

This method was validated against theory for pressure-driven flow between flat plates¹³ using various values of N . Excellent agreement, achieving goodness of fit of $\chi^2 = 0.19$ was obtained nearly independently of the choice for $N > 5000$. For the simulations presented here, $N = 50\,000$ just to keep statistical error as low as reasonable. This approach still has a much lower computational cost than finite differences or elements when $Pe > (N/10)^{2/3} = 300$. We wish to perform high Pe simulations to reveal asymptotic behavior, so this approach offers significant savings.

Figure 3 shows the flow field solution (potential lines and streamlines) as well as early time evolution of the scalar field. The figure shows the transport of particles with diffusion completely turned off ($Pe = \infty$) as well as $Pe = 100$ cases for a sinusoidal wavy channel. Figure 4 shows similar results for a periodic array of circular posts. For each individual geometry, simulations were performed at values of Pe from 10^{-1} to $10^{3.5}$ at half-decade intervals in order to obtain information in practical ranges of Pe as well as to gain insight into asymptotic behavior at large Pe .

The simulations are run for a much longer time than is shown in Figures 3 and 4. They are typically run so that the solute band runs at least $Pe/2$ channel widths downstream or until the bandwidth σ is at least 10 channel widths in axial extent. We also

require convergence to “late time” behavior. This is determined by monitoring the variance (σ^2) of the particle locations in the axial direction, and the error on the variance³⁵ $\sigma_{\sigma^2} = \sigma^2(2/N)^{1/2}$, at every time step of the simulation. Convergence in the slope of $\sigma^2(t)$ is judged to be achieved when the slopes change by less than 0.5% when the number of time steps is doubled. Dispersion coefficient is then calculated as $D_L = \sigma^2/2t$; estimated error on this quantity based on the convergence criterion is 1%.

RESULTS

Dispersion Coefficients. The key results of this paper are the normalized dispersion coefficients D_1/D_{12} for the post arrays (Figure 5) and wavy channel geometries (Figure 6). In each plot, the dispersion for pressure-driven flow through a uniform 2D channel¹³ is also plotted for comparison. Not surprisingly, significantly higher dispersion is found at larger m . At large Pe , we note that the effective diffusivity appears in all cases to be asymptotically approaching proportionality to Pe^2 . For a given post size m , we also observe that diamond shapes confer the smallest dispersion of the three geometries, and squares confer the most dispersion. Interestingly, the plot for square posts shows that, at high fill factors, electrokinetic flow through square post arrays can create even more dispersion than pressure-driven flow through straight channels. Of course, this is not entirely a fair comparison from a chromatographic sense, since the surface area in the latter case is much higher. But it does suggest that the design in Figure 1E, for example, may be a particularly bad choice from a good chromatographic resolution standpoint, while the diamond shapes in A–D would probably perform quite well (indeed, our results suggest that He et al.¹ intuitively chose a very good geometry for their experimental device). For wavy channels, we observe the somewhat surprising result that sinusoidal walls actually confer slightly more dispersion than sawtooth-shaped walls. At low Pe , all of these partially obstructed geometries actually lead to less axial diffusion than would be obtained from a straight tube.

Surprisingly, out-of-phase channels result in only somewhat higher dispersion compared to in-phase capillary geometries. In contrast, Eidsath et al.¹⁹ found for pressure-driven flow that in-line arrays are the highest dispersion geometrical configuration for a given interstitial volume when compared to both staggered

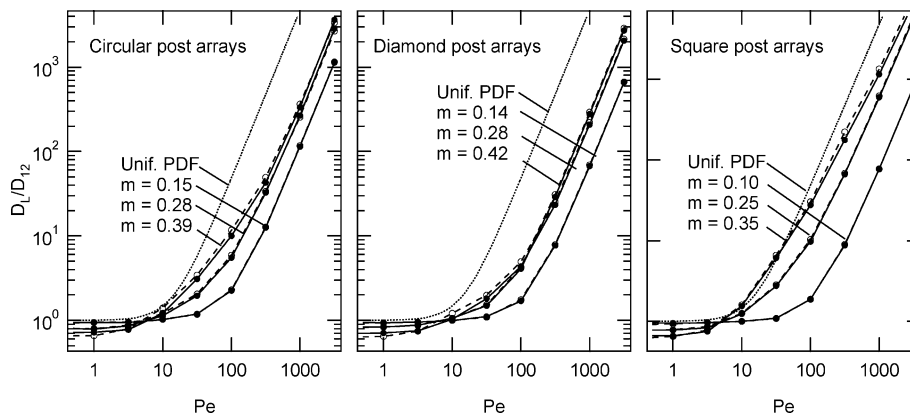


Figure 5. Effective longitudinal diffusion coefficient for post arrays of various geometries (from left to right: circles, diamonds, and squares) and amplitude denoted within each plot. In-line geometries are shown with dashed lines, staggered geometries are shown with solid lines. The fine dotted line shows effective diffusivity for pressure-driven flow through a uniform 2D channel without posts,¹³ $D_L/D_{12} = 1 + Pe^2/210$.

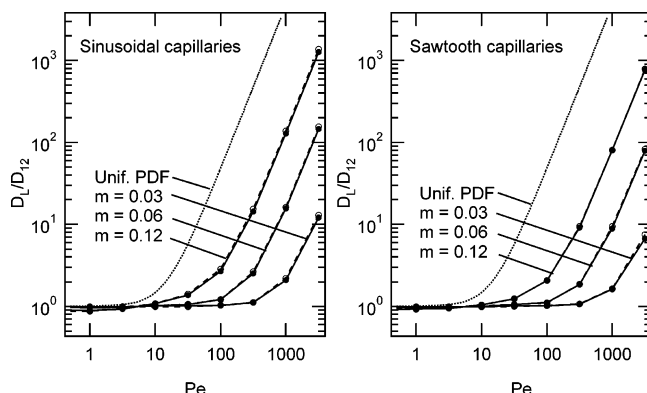


Figure 6. Effective longitudinal diffusion coefficient for wavy channels with sinusoidal (left) and sawtooth (right) wall shapes. Amplitude is denoted within each plot. In-phase walls are shown with solid lines, and out-of-phase walls are shown with dashed lines. The fine dotted line shows effective diffusivity for pressure-driven flow through a uniform 2D channel,¹³ $D_L/D_{12} = 1 + Pe^2/210$.

and random arrays. However, in pressure-driven flows, cavity flows with closed streamlines can form that are most pronounced in in-line geometries, and these contribute substantial dispersion. For potential flow resulting from ideal electrokinetic transport, smooth streamlines are guaranteed, and we would suggest that this character explains why the in-line and staggered arrays are not substantially different. Another reason may be our definition of Pe based on $\Delta\phi/L^*$ rather than on average flow speed. While it makes sense to base Pe on $\Delta\phi/L^*$ for an electrically driven system, the flow rate for in-line geometries is often lower than for staggered geometries at the same $\Delta\phi/L^*$. Were Pe based on average flow speed, the in-line curves would be shifted slightly to the left in these plots.

Collapsing Results for All Geometries. These figures show in nearly all cases that $D_L \propto Pe^2$ as $Pe \rightarrow \infty$. This suggested to us that there might be some hope of developing a quasi-“universal” correlation for D_L that could collapse the data from all geometries. To this end, we first normalize the dispersion coefficient D_L by its value at $Pe = 0$, which we call D_{L0} . Note that this is different from the molecular diffusion coefficient D_{12} , because of the geometric obstructions to diffusion presented by the solid boundaries. We call this the “effective axial diffusion coefficient”.

Leaving aside for the moment the question of how to predict D_{L0} , we then considered what form of analytical fitting function is appropriate for D_L/D_{12} . Three fitting functions were considered. The first of these is suggested by Aris' result for a unidirectional flow:

$$D_L/D_{L0} = 1 + Pe^2/\alpha_1 \quad (3)$$

As discussed previously, this form was derived by Aris presuming the flow is purely axial. However, as will be shown shortly, as m increases and flow becomes less unidirectional, the relative error in such fits becomes quite large.

A second fit function has been suggested by the porous media community to deal with highly nonunidirectional flows:^{18,19,36,20}

$$D_L/D_{L0} = 1 + Pe^{n_2}/\alpha_2 \quad (4)$$

Data in the porous media literature suggest that $n_2 \approx 2$ but falls as the flow becomes more tortuous. Since this approach has two free parameters, whereas the first fit function has only one, better matching with experimental/numerical data is expected. However, the present data in Figures 5 and 6 clearly show $D_L \propto Pe^2$ at large Pe . For this reason we considered a third correlation form, which to our knowledge has not appeared in the literature previously:

$$D_L/D_{L0} = 1 + Pe/\alpha_{3,1} + Pe^2/\alpha_{3,2} \quad (5)$$

This form was inspired by Adler's¹⁵ suggestion that $D_L/D_{L0} \propto Pe$ when dispersion is dominated by velocity variations, plus our data clearly showing that $D_L \propto Pe^2$ as $Pe \rightarrow \infty$ in Figure 7. In other words, we considered that Adler's suggestion might apply to an intermediate range of Pe . We note that, like the second fitting function (eq 4), this form has two fitting parameters; however, it has the obvious advantage that it behaves correctly at high Pe .

To compare these various fitting approaches, for each geometry (fixed shape and m), the numerical data for D_L/D_{L0} versus Pe were fit by these three functions, using the method of

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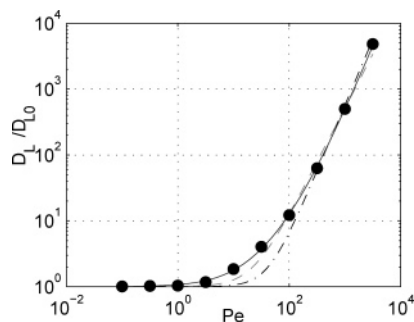


Figure 7. Best-fit curves for in-line circle post array dispersion results at $m = 0.35$. Values for free parameters can be found in Table 1. The first, second, and third fit functions are denoted by the dash-dot, dash, and solid curves, respectively.

Table 1. Fit Parameters and Length Scales for In-Line Circles

m	D_{L0}	$\alpha_1^{1/2}$	χ^2_1	$\sqrt[3]{\alpha_2}$	n_2	χ^2_2	$\alpha_{3,1}$	$\alpha_{3,2}^{1/2}$	χ^2_3
0.150	0.922	88	21	84	1.955	16	286	91	6
0.169	0.906	75	32	71	1.947	24	191	78	8
0.200	0.883	62	52	56	1.928	37	112	65	9
0.226	0.862	55	76	49	1.912	53	78	58	11
0.250	0.843	50	118	43	1.892	83	54	54	16
0.282	0.794	45	213	36	1.847	144	32	49	26
0.300	0.774	44	266	33	1.808	163	26	48	22
0.339	0.726	42	458	25	1.692	229	16	48	18
0.350	0.703	42	527	22	1.640	227	14	48	13
0.357	0.690	42	586	21	1.606	244	12	49	12
0.395	0.657	44	865	14	1.454	178	9	52	25

maximum likelihood³⁷ (minimum χ^2 , where χ^2 is the goodness of fit). Each different geometry had a different set of fit coefficients, but correlating the results with the parabolic function (eq 5) consistently achieved much smaller χ^2 than the other fitting functions. Figure 7 shows an example of this for the circular post data at $m = 0.35$. Previously suggested correlation functions have significant error near Pe 10–100. Only the parabolic form (eq 5), suggestive of an asymptotic series, performs well at all Pe and large feature amplitude m .

This is shown in more detail in tabular form for all circular post geometries in Table 1: curve fit coefficients as well as χ^2 goodness-of-fit parameters χ^2_1 , χ^2_2 , and χ^2_3 (corresponding to the three curve fits, eqs 3–5, respectively) are given for the case of circular posts. Additional data for other geometries are reported in Supporting Information. As clearly shown in the tables, the χ^2 values for the new correlation function (last column of Table 1) are dramatically lower at high values of m .

Now having identified eq 5 as the best form for fitting the data, the task remains to find a “universal” means for predicting the correlation coefficients α for different geometries and various m . To account for the fact that diamonds and circles, for example, have different dispersion coefficients at the same m , we turn to Johnson et al.,^{38,39} who suggested an effective pore size Λ^* for porous media to serve as a means for normalizing Darcy permeabilities of different pore geometries:

$$\Lambda^* \equiv \frac{2 \int_A |\mathbf{u}|^2 dA}{\int_p |\mathbf{u}|^2 dp} \quad (6)$$

where p is the wetted perimeter per unit length of the periodic domain, $\mathbf{u}$ is the velocity (assuming potential flow), and A is the cross-sectional area. In the case of straight tubes of arbitrary cross-section geometry, this is equivalent to half the hydraulic diameter $d_h = 4A/p$ since the velocity is uniform for straight tubes in potential flow. In keeping with other length scale normalizations throughout this paper, we normalize $\Lambda = \Lambda^*/L^*$. As an aside, the Johnson et al. formulation also has a parameter they called the “formation factor”, F , which relates to the effective open area of the medium. The length scale Λ and $1/F$ are similar to the tortuosity and porosity (respectively) more often used to describe porous media. For axially varying geometries, the value of Λ must be calculated using a potential flow solver in general. We tabulate Λ for each geometry and m in the Supporting Information, but it can also be easily estimated for slowly varying geometries in the lubrication theory limit. That is, if $A(x)$ does not vary too quickly, one can assume that $\mathbf{u}$ is nearly uniform across the cross section, and from continuity $u(x) \approx Q/A(x)$. Given an axial profile $A(x)$, the above integral can be evaluated directly. The simplified form on the right-hand side comes from using relations developed above and the definition of the Jacobian to scale differential volumes between variable spaces ($dx dy = J d\phi d\psi$).

This normalized effective pore size $\Lambda = \Lambda^*/L^*$ collapses much of the numerical data we have obtained to a nearly “universal” dispersion law for the geometries studied. For starters, in the case of pure diffusion ($Pe = 0$), all data from all geometries studied are reasonably well correlated by $D_{L0}/D_{12} = \Lambda^{0.32}$ as shown in Figure 8. We have also found a minimum χ^2 correlation for all available numerical data as follows:

$$\frac{D_L}{D_{12}} = \Lambda^{0.32} \left[1 + \frac{Pe}{7.01(1 - \Lambda)^{-3.04}} + \frac{Pe^2}{343.3(1 - \Lambda)^{-3.02}} \right] \quad (7)$$

which predicts all simulated effective longitudinal diffusivities within a factor of ~ 2 for $\sim 95\%$ of the cases simulated, and within a factor of 3 for all cases simulated. For increased accuracy, however, one might prefer to use the geometry-specific correlations given in Table 2. Geometry-specific correlations predict longitudinal effective diffusion coefficients to within a factor of 2.2 of all numerical data at all Pe .

We note that free best-fit parameters found in eq 7 seem close to round numbers, suggesting a power-series expansion. That is, that the expression could have been written almost to within three significant digits of accuracy as

$$\frac{D_L}{D_{12}} = \Lambda^{1/3} \left[1 + \frac{Pe}{7(1 - \Lambda)^{-3}} + \frac{Pe^2}{7^3(1 - \Lambda)^{-3}} \right] \quad (8)$$

While this is an interesting note, we believe this to be purely fortuitous, although the simplified dependencies on Λ that can be derived may be easier to remember as rules of thumb.

Comparison with Pure Diffusion and Pressure-Driven Flow. We take a moment to compare the dispersion from pure

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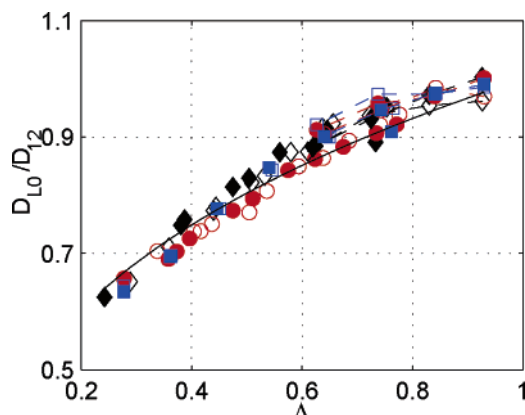


Figure 8. Apparent axial diffusion coefficient at $Pe = 0$ (pure diffusion). Post arrays are represented by points *not* connected by dashed lines, and each marker symbol (diamonds, circles, squares) correspond to the post shape. Points representing in-line and in-phase geometries are filled in. Sinusoidal channels are represented by diamonds. Parameters for capillary geometries are connected by dashed lines to guide the eye in distinguishing them from post array cases. The solid line shows $D_{L0}/D_{12} = \Lambda^{0.32}$.

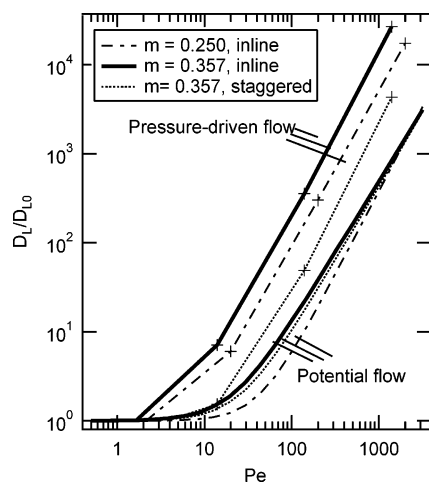


Figure 9. Dispersion coefficient at various Pe due to pressure-driven flow, compared with pure electrokinetic flow through circular post arrays. Computational results for pressure-driven flow are from Edwards et al.,¹⁸ shown as lines connecting their data points (+ symbols) to guide the eye.

Table 2: Correlations Used To Predict Dispersion According to Eq 5

geometry	D_{L0}/D_{12}	$\alpha_{3,1}$	$\alpha_{3,2}^{1/2}$
diamonds	$\Lambda^{0.30}$	$8.17(1 - \Lambda)^{-3.21}$	$38.21(1 - \Lambda)^{-0.71}$
circles	$\Lambda^{0.34}$	$3.98(1 - \Lambda)^{-2.97}$	$36.50(1 - \Lambda)^{-0.55}$
squares	$\Lambda^{0.33}$	$2.23(1 - \Lambda)^{-3.82}$	$19.61(1 - \Lambda)^{-1.16}$
sinusoidal	$\Lambda^{0.24}$	$6.97(1 - \Lambda)^{-2.90}$	$19.53(1 - \Lambda)^{-1.50}$
sawtooth (BT)	$\Lambda^{0.19}$	$8.66(1 - \Lambda)^{-3.09}$	$24.57(1 - \Lambda)^{-1.47}$
sawtooth (SC)	$\Lambda^{0.18}$	$14.02(1 - \Lambda)^{-2.77}$	$24.58(1 - \Lambda)^{-1.49}$

electrokinetic flow with previous work on pressure-driven flow in similar geometries. Edwards et al.¹⁸ gave values for longitudinal dispersion in the limit of pure diffusion ($Pe = 0$) for two in-line circular post arrays and staggered circular post arrays. The current results are in agreement to within 4% of their results.

Edwards et al. also calculated values for longitudinal dispersion due to pressure-driven flow at various values of Pe . Noting that they defined Pe slightly differently, selected data for three

representative cases from Edwards et al.¹⁸ are compared with fits to our electrokinetically driven circular post cases in Figure 9. Dispersion is significantly higher in the pressure-driven flow case—as much as an order of magnitude higher depending on the case and the Peclet number. Interestingly enough, for pressure-driven flow, the staggered array ($m = 0.357$) is far less dispersive than either of the in-line cases. The effect of staggered versus inline is not nearly so pronounced for electrokinetic flow.

We also note that Blom et al.⁴⁰ performed simulations and experiments to measure dispersion in a variety of square post array and sawtooth capillary geometries under electrokinetic flow. Values of Λ calculated from the velocity field and used to calculate α_1 according to correlations similar to those in Table 2. Observations indicate that results for the square post array agree within a factor of 2.

CONCLUSIONS

This paper presents computations of effective longitudinal diffusion due to geometric dispersion in pure electrophoretic (potential) flow around post arrays and wavy-walled channels. It is hoped that these results provide useful engineering rules for column designs in electrokinetically driven chromatography systems, as well as systems with mixed electrokinetic and pressure-driven flow, by using previously reported results.¹⁸ Thus, the data are presented in a practical format in Figures 5 and 6. Additionally, a quasi-“universal” correlation for (eq 7) should predict D_L to within a factor of 3 (and therefore predict bandwidths to within a factor of $3^{1/2}$) for geometries similar to those studied here. In general, at high Pe the results show that $D_L \propto Pe^2$ for all geometries as $Pe \rightarrow \infty$.

Dispersion from square posts is the highest for the geometries studied and from diamonds the least. In the case of relatively large in-line squares, the dispersion in electrophoresis is nearly as high as in pressure-driven flow, owing to the large path length differences from streamline to streamline in the domain. At relatively high Peclet numbers (say 100) and for relatively large diameter posts, the square posts give effective an effective diffusivity D_L/D_{12} that is ~ 3 times that for circular posts (keeping diameter of circular post equal to the side length of the square post). Diamond posts give effective diffusivities that are still another factor of 2 lower than for circular posts. Keeping Peclet number below 30 and using diamond-shaped posts should ensure that geometric band broadening is never more than 40% more than broadening due to binary diffusion in a straight channel. The results for wavy-walled channels show that if the roughness is less than $\sim 5\%$ of the total width of the channel, the additional dispersion can be kept to less than 40% of that due to binary diffusion as long as $Pe < 200$.

The numerical results presented in this paper only describe the fully developed late-time dispersion. In future work, we plan to analyze early-time behavior as well in order to characterize the performance of relatively short columns.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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