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Simulation and theory of open-tube dispersion in short and long capillaries with slip boundaries and retention

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Abstract

Using random-walk techniques, high resolution simulations of zone shape are conducted in open capillary tubes for short and long tube conditions. Finite size solutes are used as tracers in this treatment. Slip flow boundary conditions and wall retention are utilized as needed. These simulations are able to reproduce previous work in short and long tubes. For the short tube case where dispersion does not asymptotically approach the classic Taylor-Aris and Golay solutions, the effect of slip flow boundaries in the transient region shows zone shapes with abbreviated tails where the larger slip flow values cause zone compression. The use of slip flow to lower dispersion in capillary-based, wall-coated separations is shown to favor long tube behavior. This is because slip flow is relevant for cases where slip lengths are fractions of small capillary tube diameters. Incorporating slip flow into transport in capillaries favors a very small capillary radius where the cross-sectional diffusion length is very small and sampling times are fast. The purely convective zone shape with slip flow boundaries is derived analytically. Applications for this type of separation, guided by both analytical theory and simulation, show the potential for nano-sized capillary tubes less than 1 μm in diameter and favor very fast isocratic separations. Using long tube retention theory with slip boundaries shows that the dispersion-reducing region is most important in the range $0 < k' < 1$, a relatively small retention window. Further discussion of the gradient elution technique and dispersion in packed beds suggests that the general usage of slip flow boundaries is restricted in liquid phase separation systems.

Keywords

slip flow; simulation; capillary chromatography; dispersion

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1. Introduction

The study of dispersion in open circular tubes has been the subject of numerous inquiries in basic fluid mechanics leading to insight into coupled convective and diffusive processes. The original work in this area was the theoretical development of the so-called “Taylor dispersion” mechanism whereby radial diffusion causes a broadening of the axial zone concentration profile as a function of fluid velocity [1–3]. The theory of Taylor dispersion has been the starting point for more extensive theories of both gas chromatography (GC) and liquid chromatography (LC) [4–6] and other forms of separation systems, such as field-flow fractionation [7, 8].

In all of these cases, the theories were so-called asymptotic or “long time” theories where it is assumed that the tracer probes, introduced at the head of the tube, sample the velocity field a sufficient number of times so that results are at steady state. This simplifies the mathematical treatment and is essential for many practical applications where dispersion is important and limiting, such as in chromatographic resolution. These long time theories assume that the resulting zone shapes are typically Gaussian or mildly tailed in shape.

A number of years ago, “short time” behavior of zone shape and dispersion was shown to give non-Gaussian zones, with zones forming tails and an unresolved middle-region with a large hump [9]. Essentially, the zone shape looked like multiple components were eluting when only one component was present. This work was unique because not only was this a surprising result, but it required a computer simulation to produce this. It was subsequently shown how this behavior could be reproduced mathematically for short tubes with no wall retention [10] and with retentive short tubes [11]. In both of these cases, the equations were sufficiently complicated to require computational evaluation.

In all of the cases mentioned above, the fluid flow is assumed to be that of Poiseuille flow, where the fluid at the tube wall is assumed to be part of a “no-slip” boundary. A large amount of evidence has been accumulated that suggests that fluid slippage may occur [12–14], especially for aqueous solutions near hydrophobic walls. In the original formulation of the Navier-Stokes equations which describe the motion of viscous fluids, Navier [15] allowed for wall slippage as part of the boundary condition description at the wall. Various aspects of this so-called “slip boundary” have been investigated including the correlation of the slip length [16] with fluid wetting. As applications of microfluidic devices [17] increase, the impact of the slip boundary condition becomes more important since the length scale of these devices approaches the dimensions where wall slippage becomes important. The literature in this area appears to grow substantially in an attempt to understand the mechanism, ramifications and applications where slip boundaries are important. Structured or patterned surfaces, which are known to exhibit *superhydrophobicity*, have been made with large surface slippage [18, 19]. However, in many cases, especially those with rough or patterned surfaces, the effect may be due to trapped gas and nanobubbles [20] which can exhibit a substantial slip effect.

A number of studies have been conducted in experimental LC where it has been suggested that slip flow leads to higher resolution separations of biomolecules [21–25]; small molecule

separations were not studied. These studies were observational in that it is difficult, if not impossible, to identify the details of the flow field in packed beds of very small particles that would be necessary to verify the slip flow mechanism. Neue [26] criticized early work as the reported volume fraction of the packing was thought to be in error and suggested that the particle bed was "... only partially penetrated by a marginally wetting fluid."

These experiments generated interest in the slip flow phenomena for LC and a number of theoretical and simulation papers have examined aspects of slip flow in a variety of separations with specific column geometries. One of the first studies was done by Giona and coworkers [27] who demonstrated a reduction in dispersion for non-retained zones in capillaries as the slip length was increased. These authors utilized the Taylor-Aris theory of zone dispersion with a slip flow model. In addition, the effect of slip flow with three-dimensional face-centered cubic (FCC) packed-bed geometries [28, 29] and two-dimensional pillar arrays [29] were studied. In these papers, the convection-diffusion equations are evaluated with a host of computational fluid mechanics techniques which incorporated the boundary conditions of wall slippage. In all three cases, the main feature is to explore the change in boundary conditions from a no-slip to slip condition at the fluid-solid interface. Both papers [28, 29] found that the FCC geometry gave very low plate heights, however, the presence of slip flow showed little difference at the length scales commonly found in LC.

In this paper, we study elements of zone dispersion when slip flow and wall retention are present using long and short capillary tubes. This study uses equations and random-walk simulation techniques. Very fast separations that can be implemented in short capillary tubes with a wall coating are studied. Finite tracer particle diameters are utilized and wall retention is applied with a probability-based approach. The use of a simple wall-coated capillary geometry allows the study of the consequences of slip flow boundaries in a chromatographic context for long tube behavior with a purely analytical solution that is easily checked. The results suggest that a small amount of wall slip will result in smaller dispersion for short tubes. For long tubes, dispersion theory, modified for slip flow boundaries, shows that the advantage of a slip flow boundary is most effective in the retention range of $0 < k' < 1$. For higher retention values, it is shown that slip flow boundaries offer very little advantage. The consequence of using gradient elution techniques is discussed in the context of these findings.

2. Mathematical Development

2.1. Terminology

The term "particle" is used throughout this paper in the context of random-walk (stochastic) particle simulations which employ finite-size solute tracer particles. These are mathematical structures which possess hard-sphere characteristics, i.e. these particles can only approach a surface within one radius of the particle. This simulation technique has been utilized in chromatographic mass transport studies [30–32] to mimic the process of diffusion. This term should not be confused with packed-bed particles, which are discussed in the later parts of the paper in section 5 below. These are typically larger than micron-sized particles made of

silica or organic (polymeric) materials. When packed-bed particles are discussed we will emphasize the term *packed-bed* to distinguish these from *solute particles*.

2.2. Slip Flow

On the macroscopic level, it is typically assumed that fluid located at the walls has zero velocity. With this no-slip boundary condition employed, the theoretical Hagen-Poiseuille velocity profile is parabolic [7, 33] and is described by

$$v_z(r) = \frac{r_c^2}{4\eta} \left[1 - \left(\frac{r}{r_c} \right)^2 \right] \frac{\partial P}{\partial z} \quad (1)$$

where $v_z(r)$ is the fluid velocity at a point located radially at r in the direction of flow (z), r_c is the radius of the capillary, η is the dynamic viscosity of the fluid, and P is pressure. In terms of average velocity, this velocity profile can be written as

$$v_z(r) = 2\bar{v}_z \left[1 - \left(\frac{r}{r_c} \right)^2 \right] \quad (2)$$

where $\bar{v}_z$ is the mean fluid velocity in the z direction.

The no-slip assumption has proven to be accurate for flows on the macroscopic level, but it is only an assumption that is not rooted in principle [12]. For the no-slip boundary condition to apply, attractive forces between the wall and the fluid molecules must be equal to or greater than the attractive forces between mobile phase fluid molecules [34]. This is certainly not the case when the walls of the capillary are hydrophobic and the fluid is hydrophilic. The result is a “slip” boundary with a nonzero velocity at the wall. A slip boundary can be captured using Navier’s boundary condition,

$$L_s \frac{\partial v_z(r)}{\partial r} \bigg|_{r=r_c} = -v_z(r) \big|_{r=r_c} \quad (3)$$

where L_s is defined as the slip length. When replacing the no-slip boundary condition with this new condition in the Navier-Stokes equation, the velocity profile for flow in the capillary with slip becomes

$$v_z(r) = \frac{r_c^2}{4\eta} \left[1 - \left(\frac{r}{r_c} \right)^2 + \frac{2L_s}{r_c} \right] \frac{\partial P}{\partial z} \quad (4)$$

[35]. In terms of average velocity, the velocity profile with slip is now expressed as:

$$v_z(r) = \frac{2\bar{v}_z}{1 + 2\gamma} \left[1 - \left(\frac{r}{r_c} \right)^2 + \gamma \right] \quad (5)$$

where $\gamma = 2L_s/r_c$ [27].

Figure 1 illustrates the no-slip and slip velocity profiles for capillaries with equal radii and flows with equal average velocities. The slip length in the figure is equal to one-half the radius of the capillary for illustrative purposes. While the chosen slip length was arbitrarily chosen for the figure, it highlights the fact that slip length must be on the order of r_c to have an appreciable impact on the velocity profile relative to that of no-slip conditions. A slip length such that $L_s \ll r_c$ results in γ approaching zero and the velocity profile converging to no-slip conditions.

Slip lengths for various surface/liquid boundaries reported in the literature are typically on the order of tens of nanometers [14]. For this reason, the phenomenon of slip becomes significant on the nanoscale using devices such as carbon nanotubes with radii on the order of nanometers through tens of nanometers [35–37] and with sub-micron silica particles [23, 34]. It also follows that slip would be negligible for macroscopic flows resulting in the no-slip boundary condition being a valid assumption.

The contact angle between surface and fluid directly impacts slip length as contact angle is a measurement of attraction between different materials. Huang et al. developed a relationship between slip length and contact angle, θ_c , using molecular dynamics simulations stating $L_s \sim (1 + \cos \theta_c)^{-2}$, which was in accord with experimental results and supports slip lengths less than 20 nm up to a contact angle of approximately 150° [38]. Thus, larger slip lengths will require very weak interactions between surface and fluid such as water and a highly hydrophobic material.

An enhancement in flow through a capillary due to the nonzero fluid velocity at the wall is known to take place in nanoscale fluid mechanics. When a constant pressure gradient is applied, this enhancement is directly related to γ by

$$\frac{Q_{slip}}{Q_{no-slip}} = \frac{\bar{v}_{z,slip}}{\bar{v}_{z,no-slip}} = 1 + 2\gamma \quad (6)$$

[14] where Q is the volumetric flow rate through the capillary. This increase in flow rate could potentially improve the throughput and efficiency of devices used for separation [35]. At the wall, the fluid velocity is

$$v_z(r) \big|_{r=r_c} = 2\gamma \bar{v}_{z,no-slip} \quad (7)$$

For the simulations involving slip flow, γ was limited to $\gamma \leq 0.4$ or a flow enhancement of $\bar{v}_{z, slip} \leq 1.8\bar{v}_{z, no-slip}$. This limit was chosen based on studies summarized by Lauga and Stone [39] where reported slip lengths ranged from the nanometer scale to the micron scale and system size ranged from the nanometer to the millimeter scale. Despite this wide range, values of L_s/r_c differed by a factor of 40 from 0.005 to 0.2, corresponding to $0.01 \leq \gamma \leq 0.4$ [39].

Figure 2 and Table 1 summarize the above concepts by illustrating how increasing L_s will increase γ which leads to an increase in $\bar{v}_z$ and $v_z(r)|_{r=r_c}$. Figure 2 shows that the slip velocity profile is equivalent to the no-slip profile shifted up by a value equal to the slip velocity at the wall given by Eq. 7.

2.3. Plate Height Theory

Comparisons of simulation results to long tube theoretical behavior are made through the theoretical plate height. The general relationship,

$$H = \frac{L\sigma^2}{\bar{t}^2} \quad (8)$$

is used, where H is the height equivalent to a theoretical plate, L is the length of the capillary, $\bar{t}$ is the mean arrival time of solute particles at the end of the capillary, and σ is the standard deviation of the Gaussian concentration density profile in time units. The simulations provide outputs of the arrival time for each individual particle. For a given particle size, the first and second moments of the elution profiles are found so that Eq. 8 is equivalently represented as

$$H = \frac{LM_2}{M_1^2} \quad (9)$$

where M_1 is the first moment of the arrival time distribution and M_2 is the second central moment.

The theoretical mean arrival time is simply

$$\bar{t} = \frac{L}{\bar{v}_z} \quad (10)$$

To relate the second moment from simulation to theory, the theoretical plate height for open-tube systems with the slip flow boundary condition is determined using the expression,

$$H = \frac{2D_m}{\bar{v}_z} + C_m \frac{r_c^2 \bar{v}_z}{D_m} + C_s \bar{v}_z \quad (11)$$

[7, 40] where r_c is the capillary radius, and C_m and C_s are the mobile and stationary phase mass transport coefficients, respectively. D_m is the solute diffusion coefficient in the mobile phase and is calculated using the Stokes-Einstein equation,

$$D_m = \frac{k_B T}{3\pi\eta d_s} \quad (12)$$

[41] where k_B is the Boltzmann constant, T is temperature assumed to be 25°C, and d_s is the effective solute diameter. The viscosity, η , is set to 1 cP for all theory and simulations.

In the case of the open-tube system with no separation media, there is no stationary phase mass transport resistance and thus $C_s = 0$. For no-slip boundary conditions used in this ideal capillary column, it is established that [7]:

$$H = \frac{2D_m}{\bar{v}_z} + \frac{1}{24}(6R^2 - 16R + 11)\frac{r_c^2 \bar{v}_z}{D_m} \quad (13)$$

where R is the retention ratio [6] and is equal to $t_0 / \bar{t}$ where t_0 is the void time. R and the retention factor k' are related as $k' = (1/R) - 1$. The retention factor k' indicates the number of eluted column volumes minus 1; hence the void peak has $k' = 0$. For the limiting case of no wall retention, $R = 1$, and Eq. 13 reduces to the well-known relationship:

$$H = \frac{2D_m}{\bar{v}_z} + \frac{r_c^2 \bar{v}_z}{24 D_m} \quad (14)$$

For a system with input parameters of r_c , d_s , L , and $\bar{v}_z$, the approach to validate the simulation results with long tube theory is as follows: $\bar{t}$ is calculated from Eq. 10, D_m is calculated from Eq. 12, the plate height is calculated from Eq. 13, and the standard deviation of the Gaussian elution profile is calculated from Eq. 8. M_1 and M_2 from the simulation data are compared with $\bar{t}$ and σ .

A similar approach to comparing simulation results with long tube theory is employed with the slip flow boundary condition. C_m is determined via the method laid out by Martin and Guiochon [40] using the generalized dispersion theory of Aris [2]. Based on this theory,

$$C_m = I_1 - 2RI_2 + \frac{R^2}{4} \quad (15)$$

where I_1 and I_2 are defined as,

$$I_1 = \int_0^1 \frac{A^2(\rho)}{\rho} d\rho \quad (16)$$

$$I_2 = \int_0^1 \rho A(\rho) d\rho \quad (17)$$

where $\rho = r/r_c$ and

$$A(\rho) = \int_0^\rho 2\rho' \frac{v_z(\rho')}{\bar{v}_z} d\rho' \quad (18)$$

Beginning with Equation 5 in terms of ρ [27],

$$\frac{v_z(\rho)}{\bar{v}_z} = \frac{2}{1+2\gamma}(1 - \rho^2 + \gamma) \quad (19)$$

which yields

$$A(\rho) = \int_0^\rho 2\rho' \frac{2}{1+2\gamma}(1 - \rho'^2 + \gamma) d\rho' = \frac{\rho^2}{1+2\gamma}[2(1+\gamma) - \rho^2] \quad (20)$$

and performing the integrations in Eqs. 16 and 17 results in

$$I_1 = \frac{24\gamma^2 + 32\gamma + 11}{24(1+2\gamma)^2} \quad (21)$$

$$I_2 = \frac{2+3\gamma}{6(1+2\gamma)} \quad (22)$$

This leads to an expression for C_m under the conditions of slip flow by substituting I_1 and I_2 into Eq. 15:

$$C_m = \frac{24\gamma^2 + 32\gamma + 11}{24(1 + 2\gamma)^2} - 2R \left[\frac{2 + 3\gamma}{6(1 + 2\gamma)} \right] + \frac{R^2}{4} \quad (23)$$

Finding a common denominator and grouping terms with like orders of γ ,

$$C_m = \frac{24(R^2 - 2R + 1)\gamma^2 + 8(3R^2 - 7R + 4)\gamma + (6R^2 - 16R + 11)}{24(1 + 2\gamma)^2} \quad (24)$$

When $L_s = 0$, this relation simplifies to the equivalent no-slip expression for C_m in Eq. 13. For the limiting case of no wall retention, Eq. 24 simplifies to

$$C_m = \frac{1}{24(1 + 2\gamma)^2} \quad (25)$$

Using the same approach for validating the long tube simulation results with the no-slip boundary condition presented above, long tube simulation results with the slip boundary condition are compared to the theoretical Gaussian distribution moments. The only additional input required is L_s .

2.4. Purely convective limit with slip flow

One limit of the arrival time distribution for flow with the slip boundary condition is when diffusion is neglected, or that the movement of fluid is purely due to convective forces and particles remain on the same streamline from the beginning to the end of the capillary. Following the approach laid out by Bosworth for Poiseuille flow in cylindrical vessels [42], a similar derivation is performed for the purely convective limit with slip flow in the open-tube cylindrical capillary system. Beginning with the velocity profile given by Eq. 4, and assuming a linear pressure gradient so that $\frac{\partial P}{\partial z} = \frac{\Delta P}{L} = \phi$, the flow rate is calculated as

$$Q = \int_0^{r_c} 2\pi r v_z(r) dr = \frac{r_c^4 \pi \phi}{4\eta} \left(2\gamma + \frac{1}{2} \right) \quad (26)$$

The expected arrival time, t' , for a particle under purely convective transport located at r is given by

$$t'(r) = \frac{L}{v_z(r)} = \frac{4\eta L}{r_c^2 \phi \left[1 + \gamma - \left(\frac{r}{r_c} \right)^2 \right]} \quad (27)$$

Considering the element of a hollow cylinder of fluid with inner radius r and outer radius $r + dr$, the fraction of the total volume of fluid that enters this element in unit time is denoted as $F_r dr$ and is equivalent to

$$F_r dr = \frac{2\pi r v_z(r) dr}{Q} = \frac{2r \left[1 + \gamma - \left(\frac{r}{r_c} \right)^2 \right]}{r_c^2 \left(\gamma + \frac{1}{2} \right)} dr \quad (28)$$

Similarly, $F_{t'} dt'$ is defined as the fraction of total molecules with an arrival time between t' (r) and $t'(r) + dt'$ and is represented as

$$F_{t'} dt' = F_r \frac{1}{\frac{dr}{dt'}} dt' = \frac{r_c^2 \phi \left[1 + \gamma - \left(\frac{r}{r_c} \right)^2 \right]^3}{4\eta L \left(\gamma + \frac{1}{2} \right)} dt' = \frac{1}{t'^3} \frac{16\eta^2 L^2}{r_c^4 \phi^2 \left(\gamma + \frac{1}{2} \right)} dt' \quad (29)$$

More completely, there is some minimum theoretical arrival time corresponding to the fastest moving fluid element. This is located at $r = 0$ and is designated as t'_0 . Note that this is not the total void time, which is usually ascribed to the symbol t_0 . From Eq. 27,

$$t'_0 = \frac{4\eta L}{r_c^2 \phi (\gamma + 1)} \quad (30)$$

Substituting in t'_0 and adding a Heaviside function, $\mathcal{H}$, to Eq. 29 to more accurately capture the fact that no particles have arrival times less than t'_0 ,

$$F_{t'} = \mathcal{H}(t' - t'_0) \frac{t_0'^2 (\gamma + 1)^2}{t'^3 \left(\gamma + \frac{1}{2} \right)} \quad (31)$$

This solution reduces to the no-slip arrival time distribution when $\gamma = 0$ [42]. It is worth noting that in the no-slip case, the distribution depends only on the minimal arrival time and not any geometric parameter of the capillary. In other words, two cylinders with differing dimensions can have the same arrival time distribution if they are tuned to have the same t_0 . In the case of slip flow, the presence of γ in the distribution introduces a dependence on the slip length and capillary radius so that this geometric independence described by Bosworth no longer applies.

3. Numerical Methods

3.1. Random walk principles

The random walk technique used for these simulations is based on combining the principles of convection and diffusion to model fluid transport through the capillary. It is a common technique used in molecular and Brownian dynamics simulations [43–48].

The process consists of adding convective and diffusive contributions to the x , y , and z Cartesian coordinates with each time step. Typically, a time step, t_s , is on the order of 1×10^{-7} seconds or smaller. The new radial and z positions are calculated with each time step. If at a particular time step $Z_i = L$, where i is the i^{th} time step, the particle has reached the end of the capillary. That time is recorded as the arrival time of each particle, and combining the arrival times of all particles of a specific diameter yields the elution profile for the given solute size.

In studies of short tubes [10, 11] the “cup-mixing average” was utilized which gives an average value of concentration weighted by the velocity of the fluid where a detector of finite area is placed at the end of the column. This term is commonly utilized in chemical reactor engineering and is defined as [49] :

$$C_{ca} = \frac{\int_A C v dA}{\int_A v dA} \quad (32)$$

where C_{ca} is the cup mixing average concentration and A is the cross-sectional area of the capillary. In addition to this concentration, the “optical average” concentration, a term used in microfluidic applications, is defined as [50]

$$C_{oa} = \frac{\int_A C dA}{\int_A dA} \quad (33)$$

In this paper we assume a detector of zero volume located at the column exit (at $z = L$) which gives the instantaneous arrival times of particles across the detector cross section as given by Eq. 33. This form of concentration detection is assumed in almost all stochastic simulations of chromatographic phenomena. The cup-mixing average can be implemented in a random walk-based particle simulation if desired as the velocity of the particle is known precisely at the position of the column exit and detector cross section. The radial position of the particle, r , at the exit position, $z_i = L$, is also recorded.

3.2. Starting conditions

For each simulation, at least 20,000 particles and typically 100,000 particles are used with all particles starting at $z = 0$. Each particle is placed randomly along the front face of the capillary radial position. This is performed using random number generators to choose numbers between 0 and the boundary of the capillary accounting for the size of the solute, or

$r_c - r_s$, for both x_0 and y_0 starting coordinates. This ensures that all particles are initialized within the bounds of the capillary so that $r \leq \sqrt{x_0^2 + y_0^2}$ is satisfied; if x_0 and y_0 do not satisfy this condition, new random numbers are selected.

3.3. Convection

Convection is limited to only the z direction for the purpose of these simulations. Velocity is considered as a function of radial position alone in Hagen-Poiseuille flow. Therefore, the distance in the z direction a particle moves in a given time step due to convection is solely dependent on r_i , or the velocity streamline the particle resides on at that particular time. Mathematically,

$$z_{i+1} = z_i + v_z(r_i) \cdot t_s \quad (34)$$

The velocity profile, $v_z(r)$, is given by Eqs. 2 and 5 for no-slip and slip boundary conditions, respectively. Due to the restriction of convective flow to the z direction, there are no convective contributions to the x and y coordinates of a particle.

3.4. Diffusion

The diffusive contribution of each time step involves the addition of a randomly distributed number to each of the x , y , and z components of the location of a particle. This distribution is determined by the Einstein equation [7, 51] which describes the average distance traveled by a particle in each coordinate, $\bar{x}$, as $\bar{x} = \sqrt{2D_m t_s}$. A particle is equally likely to move in either direction for a given coordinate, so a random number is generated for each Cartesian coordinate from a normal distribution with a mean of zero and a standard deviation of $\bar{x}$. The diffusive contribution is then represented as

$$\begin{aligned} x_{i+1} &= x_i + \xi_{x,i} \\ y_{i+1} &= y_i + \xi_{y,i} \\ z_{i+1} &= z_i + \xi_{z,i} \end{aligned} \quad (35)$$

where $\xi_{x,i}$, $\xi_{y,i}$ and $\xi_{z,i}$ are normally distributed random numbers added to each coordinate at the i^{th} time step.

3.5. Stability

The Courant-Friedrichs-Lewy (CFL) condition is used as a measure of stability for the simulations [52]. This condition states that the Courant number, C_r , defined as

$$C_r = \frac{\bar{v}_z \cdot t_s}{\bar{x}} \quad (36)$$

should meet the requirement $0 < C_r < 1$ for stability. C_r is the ratio of convective and diffusive contributions with each time step, and a small enough time step must be chosen to ensure that the CFL condition is satisfied.

3.6. Retention

The probability of adsorption, P_a , controls whether a time delay should occur when a particle collides with a wall. This situation is analogous to an interfacial hopping model [53] where adsorption does not occur on every wall collision. This is implemented with a uniformly-distributed random number, ζ_i , so that if the wall collision occurs and $\zeta_i < P_a$, then the particle is considered adsorbed. When adsorbed, a Poisson (exponentially distributed) deviate is chosen with mean delay time $\langle t_d \rangle$ and this is added to the current time counter of the particle. The exponentially distributed number is obtained using the inverse transform sampling theory [54] such that $t_d = -\langle t_d \rangle \ln(\zeta_i)$.

3.7. Particle-wall algorithm

One difficulty in implementing stochastic simulations is what to do when a particle undergoing random walks moves through a boundary. This subject has been previously addressed, [55] and the three types of actions that were discussed include rejection, interruption, and specular reflection. In the rejection method, a trial trajectory is rejected when a particle moves through a boundary. New particle coordinates are chosen until the particle no longer moves through the boundary. This technique is simple to program but neglects the space nearest to the boundary. Interruption allows the particle surface to touch the wall and places the particle on the wall along the trial trajectory. The modified time step, t'_s , is calculated as $t'_s = t_s \cdot (d' / \bar{d})^2$ where d' is the distance traveled to the wall and $\bar{d}^2 = 6Dt_s$, where $\bar{d}$ is the average distance traveled in one time step. The last method, specular reflection, which is the recommended method to implement the boundary encounter [55], involves calculating the specular reflection vector component utilizing the surface normal and the dot product of the incident vector [56]. A general algorithm for this, in the context of stochastic mass transport simulations, is discussed by Maier et al. [57]. All three methods are evaluated for error and tabulated below in section 4.4.

3.8. Assumptions

Assumptions of this method and model include utilizing a fully-developed flow profile throughout the column length with no entrance effects. The solute is introduced as a perfect sheet in the column cross section. Most important, particle-particle interactions and collisions are absent; this is a zero-concentration model. The presence of both point and finite-size molecules does not perturb the bulk fluid flow. The retention of molecules on the wall surface is assumed to not affect the slip flow at the wall nor flow in the bulk inner regions of the tube. Particle-wall interactions are assumed to be that of hard spheres interacting with solid boundaries. Inertial effects leading to so-called “lift forces” [58] are not included in the model. All flow is modeled under creeping flow conditions, i.e. low Reynolds number flows where inertial effects are unimportant.

3.9. Programming tools

FORTRAN-95 was used to write all software for the simulations with parallel programming performed using the message-passing interface (MPI)[59, 60]. Analysis of arrival time data was performed in MATLAB (Mathworks, Natick, Massachusetts).

3.10. Data presentation

The widths of histogram elements used when displaying arrival time curves were based on the rule described by Freedman and Diaconis [61]. The bin width, W , was chosen as

$$W = 2(IQR)N_p^{-1/3} \quad (37)$$

where IQR is the interquartile range of the arrival time data and N_p is the number of particles used in the simulation.

4. Results

4.1. Nondimensional characterization of long and short tubes

Simulations were performed to ensure that the algorithm and assumptions used in the code produced results that were consistent with theoretical behavior. First, the well-defined behavior of Poiseuille flow with no-slip boundary conditions were examined and compared to theoretical predictions. This provided validation as well as confirmation of baseline behavior to which results with the slip flow boundary condition could be compared.

In order to differentiate between long and short tube systems, the nondimensional Graetz number, Gz , was used [62] to characterize these systems. It is the ratio of characteristic times for diffusion in the radial direction to flow in the z direction and is defined as

$$Gz = \frac{r_c^2 / D_m}{L / \bar{v}_z} = \frac{r_c^2 \bar{v}_z}{D_m L} \quad (38)$$

$Gz \ll 1$ suggests radial diffusion takes place on a much smaller characteristic time scale than axial flow. Solute particles have time to sample all radial positions within the capillary due to diffusion allowing full access to all of the Poiseuille velocity profile shown in Figure 1. Therefore, when $Gz \ll 1$, the plate height theory described in section 2.3 should allow an accurate method of determining the moments of the arrival time distribution for these long tube systems. When $Gz \approx 1$, deviations from the long tube Gaussian behavior in the form of tailing [63] typically takes place. $Gz \gg 1$ suggests solute particles flow too quickly in the axial direction to sample the entire velocity profile before reaching the end of the capillary. The result is the failure of plate height theory and arrival time distributions with non-Gaussian distorted peak shapes for these short tube systems. In addition, the more familiar Peclet number, $Pe = \bar{v}_z r_c / D_m$, is used to tabulate the ratio of convective and diffusive contributions and is included for comparison with the Graetz number.

4.2. Validation of long and short tube behavior with no-slip boundary conditions

Figure 3 presents the peak shapes for simulations run with no-slip boundary conditions and no retention ($R = 1$) at a range of Gz values. Each row corresponds to a particular Gz value. The first column only varies in d_s while holding all other system input values constant as “control inputs”: $L = 10$ cm, $\bar{v}_z = 0.1$ cm / s, and the capillary diameter, $d_c = 41.8$ μm . The second column alters one of the control input values and adjusts d_s accordingly to hold Gz constant. A visual comparison of Figures 3b with 3c, 3d with 3e, and 3f with 3g demonstrates that peak shape is indeed retained when Gz is held constant. In other words, Gz is a valid method to quantify how long or short a tube is despite size and velocity scales that may vary by orders of magnitude.

Figures 3a, 3b, and 3c are the results of long tube simulations. The first and second moments of each case are produced in Table 2 along with the theoretical prediction of the moments determined using the plate height theory for no-slip boundary conditions laid out in section 2.3. The simulation results of cases a and b show agreement with theoretical prediction for both first and second distribution moments within 1.0%.

The simulation resulting in Figure 3c shows a larger difference between simulation and theory; both the first and second moments from simulation are smaller than those predicted by theory. This can be explained by the finite size of the particles, which both the definition of Gz as well as plate height theory fail to account for. A particle that is smaller but is considerable relative to the capillary radius will result in solutes that cannot sample the entire velocity profile as the finite size prevents the center of mass from reaching $r > (r_c - r_s)$. The impact of this is a lesser velocity gradient and a larger average velocity than would be predicted by theory leading to smaller first and second moments as supported by the parameters used in making Figure 3c. To check this, the average velocity for the same velocity profile used in case c was calculated for a capillary where particles are limited to r ($r_c - r_s$) as

$$\bar{v}_z^* = \frac{\int_0^{r_c - r_s} v_z(r) \cdot 2\pi r \, dr}{\int_0^{r_c - r_s} 2\pi r \, dr} \quad (39)$$

where $\bar{v}_z^*$ is the new average velocity. For no-slip conditions, $v_z(r)$ is defined by Eq. 2 and Eq. 39 becomes

$$\bar{v}_z^* = \bar{v}_z \left[2 - \left(\frac{r_c - r_s}{r_c} \right)^2 \right] \quad (40)$$

Plugging in the values from case c yields $\bar{v}_z^* = 0.1015$ cm s⁻¹ and a new theoretical arrival time of 98.52 s. With this adjustment, the first moment of the simulation of the simulation only varied by +0.23% compared to the theoretical prediction. Therefore, the finite size of

solute particles is an aspect that needs to be considered in addition to Gz when fully describing the behavior of a system. Because particles have finite sizes, it is also a phenomenon that these simulations are able to capture while both theory and simulations that treat particles as points fail to.

The arrival time distributions of the shorter tube cases in Figures 3d-g resemble the expected behavior shown by Figure 1 in the paper of Atwood and Golay [9]. In their figure, the distributions are computed for various numbers of theoretical plates, N , which they define as

$$N = \frac{24\pi D_m L}{Q} \quad (41)$$

Since $Q = \bar{v}_z \pi r_c^2$, $N = 24/Gz$.

The plots in Figure 3 correspond to $N = 24$, $N = 2.4$, and $N = 0.24$ for $Gz = 1$, $Gz = 10$, and $Gz = 100$, respectively. Figures 3d and 3e correspond to $Gz = 1$ and exhibit the anticipated behavior marked by roughly Gaussian peak shapes but with noticeable tailing. Figures 3f and 3g correspond to $Gz = 10$ and exhibit the characteristic two-humped distributions shown in Figure 1 of the Atwood and Golay paper by the $N = 3$ curve. The two humps occur at roughly the expected average arrival time and at one-half of this value which corresponds to theory [27].

Figure 3h does not resemble the expected behavior which would be a single peak initially followed by hyperbolic decay down to zero as the purely convective limit is approached. Our simulation shows two humps still which is due to the fact that the particle diameter is one-quarter of the capillary diameter so that a large fraction of the velocity gradient is not accessed.

4.3. Long tube behavior with slip flow boundary conditions and no wall retention

Simulations were performed with the slip flow boundary condition now employed at Gz values on the order of 10^{-5} and smaller. In these simulations γ was varied between 0 and 0.4 and the moments of the arrival time distributions were compared to the theoretical moments now using Eq. 25. Note that the input for $\bar{v}_z$ was varied according to Eq. 6. In addition, Eq. 5 was substituted into Eq. 39 to account for the finite size of the particle restricting the velocity gradient near the walls. The result for slip flow is

$$\bar{v}_z^* = \frac{\bar{v}_z}{1 + 2\gamma} \left[2(1 + 2\gamma) - \left(\frac{r_c - r_s}{r_c} \right)^2 \right] \quad (42)$$

The system used was a tube of $L = 1$ cm and $r_c = 200$ nm with solute particles of $d_s = 1$ nm and $\bar{v}_{z, no-slip} = 0.1$ cm/s. This corresponds to $Gz = 9.2 \times 10^{-6}$ for no-slip conditions.

Although the value of capillary radius chosen here appears very small, this is in the range of values where the slip length is a significant fraction of the capillary radius. It is in this range

that slip lengths are particularly viable and effective. Larger slip lengths may be obtainable, but as mentioned in the introduction, these are probably due to trapped gas and this situation would make for a very irreproducible system.

Capillary inner diameters as small as 200 nm are commercially available such as capillaries offered by the Polymicro Technologies division of the Molex Corp. (Lisle, IL, USA). This scale is also conducive to chip-based microfluidic separation systems. Alternatively, the technique of electrospinning could be utilized to produce hollow nanofibers that would function as capillary systems on this size scale. This method uses a high voltage electrical driving force which forces a polymer melt or solution through a spinneret and is capable of producing fibers ranging from several nanometers to several microns [64]. A wide range of polymers and ceramics can be used which allows the ability to tailor aspects such as fiber diameter and surface properties [65, 66].

Figure 4 displays M_1 and M_2 for a range of γ values along with the theoretical expectations from Eq. 42. The simulation data closely traces the long tube theory over the entire range of γ values: M_1 and M_2 vary from theory at most by 0.0078% and 0.77%, respectively. M_1 and M_2 are reduced to 55.7% and 17.4% of the no-slip values, respectively, when γ reaches 0.4. The potential benefits of slip flow are highlighted by the decrease in both moments as shorter arrival times result in higher throughput and smaller variance results in sharper elution peaks.

4.4. Comparison of particle-wall algorithms

The same system in section 4.3 was used to compare the three wall collision methods detailed in section 3.7. Table 3 summarizes the percent differences between simulation and theory with each of the three methods for a range of γ values. In addition, Table 3 compares how each collision method compares to theory both when the finite size of the particle is accounted for (velocity profile given by Eq. 42) and when it is not (velocity profile given by Eq. 5).

The rejection method resulted in M_1 and M_2 consistently lower than the theoretical prediction. Both the interruption and specular reflection methods resulted in moments that were closer to theory, and specular reflection was slightly closer to theory than the interruption method when the particle size was accounted for. For all three values of γ using specular reflection and particle size accounted for, M_1 varied from theory in magnitude by only 0.01% and M_2 varied from theory at a maximum of 0.77%. Therefore, the simulations in section 4.3 and all subsequent sections utilize the specular reflection method for handling particle-wall collisions.

4.5. Long tube behavior with slip flow boundary conditions and wall retention

Having verified that the simulation and theory are in agreement for long tube behavior with slip flow boundary conditions, we can use the theory developed in section 2.3 and specifically Eq. 24 to evaluate the effect of slip flow with retention in the long tube limit. The results are shown in Figure 5 at different values of the retention factor k' .

A number of features are highlighted from this figure. At zero retention conditions, i.e. $k' = 0$, the reduction in C_m , the mobile phase mass transport coefficient, as a function of γ , is significant compared to C_m with no-slip conditions, showing an $\approx 30\%$ reduction when $\gamma = 0.1$. However, in terms of the overall plate height, as described by Eq. 11, there is a reduction but it is slight. At the same slip length, more retained zones show a much smaller effect. For example, for $k' = 10$, the reduction in C_m is $< 10\%$ and this is about the same reduction as that found for $k' = 5$. These results suggest that the main reduction in plate height by utilizing slip flow takes place in the region where retention is in the range $0 < k' < 1$. This suggests that utilizing slip flow for chromatographic separations is not routinely applicable to all regions of the chromatogram. Furthermore, we have examined the zone widths predicted by Eq. 11 using C_m given by Eq. 24 and for most practical choices of input values the dominant term appears to be the diffusive term $2D_m / \bar{v}_z$. This is in essential agreement with Desmet *et al.* [29] who used fluid mechanics simulations and found that slip flow boundaries had little effect on plate heights with the parameter sets they chose.

4.6. Short tube behavior with slip flow boundary conditions and no wall retention

Short tube conditions were simulated for the same $r_c = 200$ nm as in section 4.3. In order to reach $Gz > 10$, parameters of $L = 1$ μm , $d_s = 20$ nm and $\bar{v}_{z, \text{no-slip}} = 1$ cm/s were chosen.

Note that the length of the capillary here is ultra-short and would be expected from a thin membrane, micro- or nano-channel, or even a pore in a chromatographic particle. Further aspects of this will be presented in the discussion section below. These parameter values correspond to Gz ranging from 18.3 for no-slip conditions to 33.0 for $\gamma = 0.4$. The elution profiles varying γ while holding all parameters constant are displayed in Figure 6. As expected, the velocity enhancement provided by the increase in γ leads to the distribution shifting towards shorter elution times and becoming narrower in shape. The second hump of the profile becomes more pronounced as γ increases.

The dashed lines in Figure 6 correspond to no-slip boundary conditions but with the same enhancement in $\bar{v}_z$ as if there was slip occurring. For small values of γ , slip and enhanced no-slip curves nearly overlap, meaning that any shift in the profile is due to the velocity enhancement opposed to the conditions at the wall. As shown throughout Figure 6, as γ gets larger, these two curves diverge, and the slip conditions result in narrower profiles at earlier times with a more pronounced second hump. Therefore, the presence of a finite wall velocity impacts zone shape under short tube conditions, in addition to the overall velocity enhancement that results from slip flow. This is reminiscent of the reduced dispersion in capillary electrophoresis with electroosmotic flow [67, 68] where the velocity distribution of fluid is essentially flat across the capillary as electroosmosis moves the fluid at constant velocity.

A comparison of the decrease in M_1 and M_2 is provided in Figure 7. Similar to long tube conditions, M_2 decreases more than M_1 relative to the corresponding no-slip values. M_1 drops to 53.2% of its no-slip value when $\gamma = 0.4$ while M_2 drops to 10.5% of its no-slip value. These are comparable to the drops seen under long tube conditions.

Figure 7 also illustrates the difference between the enhanced no-slip flow and flow with slip boundary condition. The difference in M_1 between the two cases is small across the entire range of γ . Conversely, the difference in M_2 becomes large as γ increases. The effect of slip at the wall (opposed to just increased velocity) is therefore larger for M_2 compared to M_1 under short tube conditions.

4.6.1. Purely convective limit—To test the derivation performed in section 2.4, short tube conditions must be achieved so that convection dominates diffusion. Small tube radii where slip flow applies is not conducive to these conditions as it allows for fast sampling of the entire velocity field. This means that diffusion will always be a factor unless velocity is increased greatly to increase $Gz \gg 1$. In addition, $L \gg \bar{x}$ for the theory to apply. At these velocities and capillary lengths, the Reynolds number becomes greater than 100 where these simulations using laminar flow no longer apply.

Figure 8 illustrates the theoretical impact of slip flow on the purely convective limit if these short tube conditions could be met. In practice, these conditions cannot be met because, as stated previously, the capillary diameters where slip flow is a significant part of the velocity profile are small and this promotes long tube behavior even with short-length tubes. This is reflected in the r_c^2 dependency of the Graetz number where the radius of the capillary is the controlling parameter as contrasted to all other parameters in Eq. 38 which have a linear dependence. In attempts to compare simulation and the pure convective theory with slip flow, it was found that for small-length capillaries, axial diffusion was significant enough to render the comparison poor even if the radial Taylor dispersion was not included. From the viewpoint of practical separations which could use slip flow to reduce dispersion, the length scales involved favor long tube behavior and this can be a positive driving force for using slip flow; i.e. very short tubes can give fast and efficient separations without the zone development experienced with short tubes.

4.7. Short tube behavior with slip flow boundary conditions and wall retention

As mentioned previously, it is difficult to find conditions where slip flow and short tube behavior are possible. This is due to the dueling requirements of a small capillary radius to accommodate slip flow and a large enough capillary to promote the short tube behavior. From an experimental viewpoint this is an advantageous situation since short tube zone profiles are undesirable from a high resolution analytical sense. However, there are examples where a binary separation is desirable and zone shape is important. We used the same set of conditions from section 4.6 here to illustrate what happens in the case of an extremely short, extremely fast set of conditions with and without slip flow for illustration purposes and these are shown in Figures 9 ($P_a = 0.1$) and 10 ($P_a = 1.0$).

In all cases shown in Figures 9 and 10, slip flow is helpful in compressing the tails of these types of zones. This is due to the limited amount of low velocities which the solute molecules sample. Short tube behavior emphasizes both low and high velocity regions because molecules cannot diffuse out of these regions fast enough. However, slip flow limits the extent of available low velocity regions.

When comparing Figures 9a and 9d with Figures 9b and 9e, it is seen that a small amount of retention with a limited probability of adsorption will extend the tail, and slip flow counteracts this tail extension. This may be helpful where a fast affinity separation is to be utilized at trace concentration levels and under extreme speed conditions. It must be realized that this is extremely difficult to implement because it is assumed that the zone is introduced as a perfect plug of infinitely thin axial extent; any variation in sample introduction would cause spillover to the column outlet. At longer retention conditions, shown in Figures 9c and 9f, the same effect is shown; zone compression by slip flow boundaries yield zone shapes that do not include as large a tail. However, when the probability of adsorption is increased to 1.0 in Figure 10, a more extreme tailing is shown, especially at the longest average adsorption time. Under these conditions, slip flow is ineffective at preventing long tails that resemble column bleed. This is a very similar situation to adsorption in capillary electrophoresis where even small amounts of adsorption severely degrades resolution [63].

5. Discussion

We have surveyed a theoretical and simulation approach towards understanding the zone shape and dispersion in capillaries where slip flow boundary conditions are imposed. A number of important points were determined from these calculations and simulations, and these will be discussed here.

As is now accepted and demonstrated in a number of cases in this paper, the use of slip flow boundaries to reduce chromatographic dispersion is limited to very small tube diameters. Very small particles have been recommended for packed-bed LC incorporating slip flow [69]. It is impossible in these cases to isolate out the source of fluid-surface interaction from surface roughness, which is also known to be a source of fluid boundary slippage [12–14, 18, 19]. However, capillaries with surface modification by hydrophobic coatings used for the preparation of reversed-phase LC particles may facilitate slip flow. In this regard, long tube behavior is facilitated by slip flow boundaries, and this favors the use of short capillaries for high speed, high plate count separations.

A number of other effects come out in the analysis. In Figure 5, where the reduction in dispersion is shown as a function of the nondimensional slip length γ and the retention factor k' , moderate reduction in dispersion is limited to the early part of the chromatogram where $k' \approx 1$. The larger is γ , the larger is the reduction in plate height compared to no-slip boundaries. The liquid phase typically would be pure water to maximize γ . However, gradient elution chromatography, the mainstay of high resolution LC, will lessen γ as organic solvents are introduced into an aqueous mobile phase resulting in surface wetting [70, 71] and a decrease in the advantage of slip flow.

This brings into question the general use of slip flow boundaries being restricted to a narrow range of solvents and fundamentally incompatible with gradient elution. Even with isocratic operation, the curves in Figure 5 suggest a limited elution range in improving the dispersion and lowering plate heights for general usage. Nonetheless, the use of slip flow for very fast, high resolution separations of a limited number of components with small retention values may be a feasible method for implementing fast capillary-based separations.

Porous layer open tube (PLOT) columns [72–74] have many advantages over packed-bed chromatography. For example, it was recently shown [75] that extremely high resolution separations in very small i.d. capillaries ($\approx 2 \mu\text{m}$) are possible by etching the capillary surface and applying a hydrophobic bonded phase. In both [75] and the model used herein, retention is implemented with a molecularly-thin retentive layer bound directly to the capillary wall without a porous layer. This configuration promotes a negligible mass transport resistance in the stationary phase resulting in very high performance columns. However, as smaller capillary i.d.'s are implemented, smaller amounts of analyte will be required to prevent overloading and this can create detection problems [75].

Although this study utilized a wall-coated capillary for study, statements can be made for packed-bed LC with nonporous, fully porous, or superficially porous packed-bed particles. Note that for the rest of the discussion, the term *particle* is assumed to be that of a *packed-bed particle*. These particle configurations have a much more complicated zone broadening theory due to the random packing structure and the contributions from eddy dispersion and flow field extrema which liquid phase mass transport theory must include [6, 7]. As found in previous computational studies of slip flow in ordered media [28, 29] the ordered media caused the majority of the reduction in zone dispersion, not the presence of slip flow. For capillaries we reiterate that the diffusive term $2D_m / \bar{v}_z$ tends to dominate over that due to the resistance to mass transport term in the mobile phase.

If the particle is nonporous, the particle hull is the effective boundary and slip flow would be similar to that of a random bed of capillaries with some effective capillary diameter and with a finite radial flow. If the particle surface is porous, the slip flow surface is mostly on the inside of the particle where the flow is effectively zero except for large-pore materials [76]. However, the hull region, which typically encompasses the first sol particle depth in the outer region of a porous particle [76], would influence the interstitial boundary and would probably cause some limited form of slip flow at the fluid-particle boundary.

Since the liquid phase mass transport dispersion in one capillary (as opposed to bundles of capillaries [77]) will be less than the dispersion found in a packed bed of particles, the values computed for a capillary represent the optimal case free of eddy dispersion, flow field variations, and other zone broadening mechanisms characteristic of random packed beds. Behavior similar to that of Figure 5 is expected with the implication of restricted dispersion improvement outside the range $0 < k' < 1$.

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References

- [1]. Taylor GI, Dispersion of soluble matter in solvent flowing slowly through a tube, Proceedings of the Royal Society A 219 (1953) 186–203.

- [2]. Aris R, On the dispersion of a solute in a fluid flowing through a tube, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences 235(1200) (1956) 67–77.
- [3]. Frankel I, Brenner H, On the foundations of generalized Taylor dispersion theory, J. Fluid Mech 204 (1989) 97–119.
- [4]. Lapidus L, Amundson NR, Mathematics of adsorption in beds vi. the effect of longitudinal diffusion in ion exchange and chromatographic columns, J. Phys. Chem 56 (1952) 984–988.
- [5]. Golay MJE, Theory of chromatography in open and coated tubular columns with round and rectangular cross-sections in Gas Chromatography 1958, Desty DH, editor, Academic Press, New York, 1958.
- [6]. Giddings JC, Dynamics of Chromatography, Marcel Dekker, New York, 1965.
- [7]. Giddings JC, Unified Separation Science, John Wiley and Sons, Inc., New York, 1991.
- [8]. Lightfoot EN, Chiang AS, Noble PT, Field-flow fractionation (polarization chromatography), Ann. Rev. Fluid Mech 13 (1981) 351–378.
- [9]. Atwood J, Golay M, Dispersion of peaks by short straight open tubes in liquid chromatography systems, J. Chrom 218 (1981) 97–122.
- [10]. Shankar A, Lenhoff A, Dispersion in laminar flow in short tubes, AIChE 35 (1989) 2048–2052.
- [11]. Shankar A, Lenhoff A, Dispersion and partitioning in short coated tubes, Ind. Eng. Chem. Res 30 (1991) 828–835.
- [12]. Tretheway D, Meinhardt C, Apparent fluid slip at hydrophobic microchannel walls, Phys. of Fluids 14 (2002) L9.
- [13]. Neto C, Evans DR, Bonaccorso E, Butt H-J, Craig VSJ, Boundary slip in newtonian liquids: a review of experimental studies, Rep. Progr. Phys 68 (2005) 28592897.
- [14]. Lauga E, Brenner M, Stone H, Microfluidics: The no-slip boundary condition, in: Foss J, Tropea C, Yarin A (Eds.), Handbook of Experimental Fluid Dynamics, Springer, New York, 2005, Ch. 15, pp. 1–27.
- [15]. Navier CLMH, Mémoire sur les lois du mouvement des fluides, Mem. Acad. R. Sci. Paris 6 (1823) 389–416.
- [16]. Voronov R, Papavassiliou D, Lee L, Boundary slip and wetting properties of interfaces: Correlation of the contact angle with the slip length, J. Chem. Phys 124 (2006) 204701. [PubMed: 16774358]
- [17]. Squires T, Quake S, Microfluidics: Fluid physics at the nanoliter scale, Rev. Mod. Phys 77 (2005) 977–1026.
- [18]. Lee C, Choi C-H, J. K. C, Structured surfaces for a giant liquid slip, Phys. Rev. Lett 101 (2008) 064501. [PubMed: 18764458]
- [19]. Rothstein JP, Slip on superhydrophobic surfaces, Ann. Rev. Fluid Mech 42 (2010) 89109.
- [20]. Maali A, Bhushan B, Nanobubbles and their role in slip and drag, Journal of Physics: Condensed Matter 25 (18) (2013) 184003. [PubMed: 23598711]
- [21]. Malkin DS, Wei B, Fogiel AJ, Staats SL, Wirth MJ, Submicrometer plate heights for capillaries packed with silica colloidal crystals, Anal. Chem 82 (2010) 2175–2177. [PubMed: 20158216]
- [22]. Wei B, Rogers B, Wirth M, Slip flow in colloidal crystals for ultraefficient chromatography, J. Am. Chem. Soc 134 (2012) 10780–10782. [PubMed: 22708746]
- [23]. Rogers B, Wei B, Wirth M, Ultra high efficiency protein separations with submicrometer silica using slip flow, LC GC N. Am 30(10) (2012) 890–897. [PubMed: 25267924]
- [24]. Wu Z, Rogers B, Wei B, Zhang X, Wirth M, Insights from theory and experiments on slip flow in chromatography, J. Sep. Sci 36(12) (2013) 1871–1876. [PubMed: 23686940]
- [25]. Wu Z, Wei B, Zhang X, Wirth M, Efficient separations of intact proteins using slip-flow with nanoliquid chromatography-mass spectrometry, Anal. Chem 86 (2014) 1592–1598. [PubMed: 24383398]
- [26]. Neue UD, Comment on “submicrometer plate heights for capillaries packed with silica colloidal crystals”, Anal. Chem 83 (2011) 460–461. [PubMed: 20923143]
- [27]. Adrover A, Cerbelli S, Garofalo F, Giona M, Convection-dominated dispersion regime in wide-bore chromatography: A transport-based approach to assess the occurrence of slip flows in microchannels, Anal. Chem 81 (2009) 8009–9014. [PubMed: 19739656]

- [28]. Yan X, Wang Q, Numerical investigation into the effects of ordered particle packing and slip flow on the performance of chromatography, *J. Sep. Sci* 36 (2013) 1524–1529. [PubMed: 23436781]
- [29]. Smits W, Deridder S, Desmet G, Theoretical study on the impact of slip flow on chromatographic performance, *J. Chromatogr. A* 1366 (2014) 120125.
- [30]. Schure MR, Particle simulation methods in separation science, in: Brown PR, Grushka E (Eds.), *Adv. Chromatography*, Vol. 39, Marcel Dekker Publishing, New York, 1998, Ch. 2, pp. 139–200.
- [31]. Daneyko A, Hlushkou D, Khirevich S, Tallarek U, From random sphere packings to regular pillar arrays: Analysis of transverse diffusion, *J. Chromatogr. A* 1257 (2012) 98–115. [PubMed: 22921359]
- [32]. Schure MR, Maier RS, Ellipsoidal particles for liquid chromatography: fluid mechanics, efficiency and wall effects, *J. Chromatogr. A* 1580 (2018) 30–48. [PubMed: 30429084]
- [33]. White FM, *Viscous fluid flow*, 2nd Edition, McGraw-Hill, New York, 1991.
- [34]. Rogers B, Wu Z, Wei B, Zhang X, Cao X, Alabi O, Wirth M, Submicrometer particles and slip flow in liquid chromatography, *Anal. Chem* 87 (2015) 2520–2526. [PubMed: 25646567]
- [35]. Thomas J, McGaughey A, Reassessing fast water transport through carbon nanotubes, *Nano Letters* 8(9) (2008) 2788–2793. [PubMed: 18665654]
- [36]. Kannam S, Todd B, Hansen J, Davis P, How fast does water flow in carbon nanotubes?, *J. Chem. Phys* 138 (2013) 094701. [PubMed: 23485316]
- [37]. Mattia D, Calabró F, Explaining high flow rate of water in carbon nanotubes via solid-liquid molecular interactions, *Microfluid Nanofluid* 13 (2012) 125–130.
- [38]. Huang D, Sendner C, Horinek D, Netz R, Bocquet L, Water slippage versus contact angle: A quasiuniversal relationship, *Phys. Rev. Lett* 101 (2008) 226101. [PubMed: 19113490]
- [39]. Lauga E, Stone H, Effective slip in pressure-driven stokes flow, *J. Fluid Mech* 489 (2003) 55–77.
- [40]. Martin M, Guiochon G, Axial dispersion in open-tubular capillary liquid chromatography with electroosmotic flow, *Anal. Chem* 56 (1984) 614–620.
- [41]. Russel W, Saville D, Schowalter W, *Colloidal Dispersions*, 1st Edition, Cambridge University Press, Cambridge, 1989.
- [42]. Bosworth R, Distribution of reaction times for laminar flow in cylindrical reactors, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 39 (1948) 847–862.
- [43]. Tildesley DJ, Allen MP, *Computer simulation of liquids*, Oxford University Press, Oxford, England, 1987.
- [44]. Berg HC, *Random Walks in Biology*, Princeton University Press, Princeton, N. J., 1993.
- [45]. Weiss GH, *Aspects and applications of the random walk*, North-Holland Publishing, New York, 1994.
- [46]. Maier RS, Kroll DM, Kutsovsky YE, Davis HT, Bernard RS, Simulation of flow through bead packs using the lattice Boltzmann method, *Phys. Fl* 10 (1) (1998) 60–74.
- [47]. Schure MR, Maier RS, Kroll DM, Davis HT, Simulation of packed-bed chromatography utilizing high resolution flow fields: Comparison with models, *Anal. Chem* 74 (2002) 6006–6012. [PubMed: 12498196]
- [48]. Schuss Z, *Brownian Dynamics at Boundaries and Interfaces*, Springer, New York, 2013.
- [49]. Deen WM, *Analysis of transport phenomena*, 1st Edition, Oxford University Press, New York, 1998.
- [50]. Finlayson BA, Mixing of liquids in microfluidic devices, http://faculty.washington.edu/finlayso/che499/Mixing_Summary.pdf (2008).
- [51]. Einstein A, *Investigations on the theory of the Brownian movement*, Dover Publications, Inc., New York, 1956.
- [52]. Courant R, Friedrichs K, Lewy H, On the partial difference equations of mathematical physics, *IBM Journal of Research and Development* 11 (1967) 215–234.
- [53]. Wang D, Wu H, Schwartz DK, Three-dimensional tracking of interfacial hopping diffusion, *Phys. Rev. Lett* 119 (2017) 268001. [PubMed: 29328686]
- [54]. Hamming RW, *Numerical methods for scientists and engineers*, 2nd Edition, Dover Publications, New York, 1987.

- [55]. Szymczak P, Ladd AJC, Boundary conditions for stochastic solutions of the convection-diffusion equation, *Phys. Rev. E* 68 (2003) 036704.
- [56]. Shirley P, Realistic Ray Tracing, 1st Edition, A. K. Peters, Natick, MA, 2000.
- [57]. Maier RS, Schure MR, Transport properties and size exclusion effects in wide-pore superficially porous particles, *Chem. Eng. Sci* 185 (2018) 243–255. [PubMed: 30613108]
- [58]. Cevheri N, Yoda M, Lift forces on colloidal particles in combined electroosmotic and poiseuille flow, *Langmuir* 30 (2014) 1377113780.
- [59]. Gropp W, Lusk E, Skjellum A, Using MPI: Portable parallel programming with the message-passing interface, 2nd Edition, The MIT Press, Cambridge, 1999.
- [60]. MPI Forum, MPI: A Message-Passing Interface Standard, Version 3.1, June 4, 2015, <http://mpi-forum.org/docs/mpi-3.1/mpi31-report.pdf> (11 2016) (2016).
- [61]. Freedman D, Diaconis P, On the histogram as a density estimator: L_2 theory, *Z. Wahrscheinlichkeitstheorie verw. Gebiete* 57 (1981) 453–476.
- [62]. Nellis G, Klein S, Heat Transfer, 1st Edition, Cambridge University Press, New York, 2009.
- [63]. Schure MR, Lenhoff AM, Consequences of wall adsorption in capillary electrophoresis: Theory and simulation, *Anal. Chem* 65 (1993) 3024–3037.
- [64]. Bhardwaj N, Kundu S, Electrospinning: A fascinating fiber fabrication technique, *Biotechnology Advances* 28 (2010) 325–347. [PubMed: 20100560]
- [65]. Homaeigohar S, Davoudpour Y, Habibi Y, Elbahri M, The electrospun ceramic hollow nanofibers, *Nanomaterials* 7 (2017) 383.
- [66]. Khajavi R, Abbasipour M, Electrospinning as a versatile method for fabricating coreshell, hollow and porous nanofibers, *Scientia Iranica F* 19 (2012) 2029–2034.
- [67]. Rice CL, Whitehead R, Electrokinetic flow in a narrow cylindrical capillary, *J. Phys. Chem* 69 (1965) 4017–4024.
- [68]. Khaledi MG, High-Performance Capillary Electrophoresis: Theory, Techniques, and Application, Wiley, New York, 1998.
- [69]. Rogers B, Wirth M, Slip flow through colloidal crystals of varying particle diameter, *ACS Nano* 7 (2013) 725–731. [PubMed: 23237590]
- [70]. Zhang L, Sun L, Siepmann JI, Schure MR, Molecular simulation study of the bonded-phase structure in reversed-phase liquid chromatography with neat aqueous solvent, *J. Chromatogr. A* 1079 (2005) 127135.
- [71]. Walter TH, Iraneta P, Capparella M, Mechanism of retention loss when c8 and c18 hplc columns are used with highly aqueous mobile phases, *J. Chromatogr. A* 1075 (2005) 177–183. [PubMed: 15974131]
- [72]. Collins DA, Nesterenko EP, Paul B, Porous layer open tubular columns in capillary liquid chromatography, *Analyst* 139 (2014) 1292–1302. [PubMed: 24358459]
- [73]. Knob R, Kulsing C, Boysen RI, Macka M, Hearn MTW, Surface-area expansion with monolithic open tubular columns, *Trends Anal. Chem* 67 (2015) 16–25.
- [74]. Li R-N, Wang Y-N, Peng M-H, Wang X-Y, Guo G-S, Preparation and application of porous layer open tubular capillary columns with narrow bore in liquid chromatography, *Chin. Jour. Anal. Chem* 45 (2017) 18651873.
- [75]. Yang Y, Chen H, Beckner MA, Xiang P, Lu JJ, Cao C, Liu S, Narrow, open, tubular column for ultrahigh-efficiency liquid-chromatographic separation under elution pressure of less than 50 bar, *Anal. Chem* 90 (2018) 10676–10680. [PubMed: 30139252]
- [76]. Schure MR, Maier RS, Shields TJ, Wunder CM, Wagner BM, Intraparticle and interstitial flow in wide-pore superficially porous and fully porous particles, *Chemical Engineering Science* 174 (2017) 445–458.
- [77]. Schisla D, Ding H, Carr P, Cussler E, Polydisperse tube diameters compromise multiple open tubular chromatography, *AIChE. J* 39 (1993) 946–953.

- Capillaries with slip boundaries are simulated using random-walk techniques
- Taylor-Aris dispersion theory is presented for slip boundaries including retention
- The limited retention range advantage of slip boundaries is discussed
- Short tube transient response is reduced by a slip boundary

Figure 1:

Velocity profiles for both no-slip and slip conditions with equal average fluid velocity. Left: Hagen-Poiseuille pressure-driven flow with zero velocity at the capillary walls. Right: Slip flow with nonzero velocity at walls. A slip length of $L_s = 0.5r_c$ is used for visualization.

Figure 2:

Velocity profiles for varying slip lengths relative to capillary radius. $\bar{v}_z$ is enhanced when slip flow occurs relative to no-slip conditions. The profiles with slip are equivalent to shifting the no-slip profile to the right by the velocity at the wall given by Eq. 7.

Figure 3:

Arrival time distributions for long tube and short tube systems. Each row corresponds to a constant value of Gz . The simulations of the first column have constant inputs of $L=10$ cm, $\bar{v}_z = 0.1$ cm/s, $d_c = 41.8$ μm , and $N_p = 20000$, with varying values of d_s . Pe values for each case are a) 4.78×10^1 ; b) 4.78×10^2 ; c) 1.51×10^3 ; d, e, g) 4.78×10^3 ; f) 4.78×10^4 ; h) 4.78×10^5 . The dependent variable in these graphs is in units of concentration.

Figure 4:

First (a) and second (b) moments of simulation results for long tube system with slip boundary condition and comparison to theory. Simulation parameters: $L=1$ cm, $\bar{v}_{z, no-slip} = 0.1$ cm/s, $r_c = 200$ nm, $d_s = 1$ nm, and $N_p = 100,000$. This corresponds $Gz = 9.2 \times 10^{-6}$ and $Pe = 0.46$ for no-slip conditions.

Figure 5:
The mobile phase mass transport coefficient normalized to $\gamma = 0$ for retention at differing k' values.

Figure 6:

Zone shapes for varying slip lengths under short tube conditions without retention. Solid lines: slip boundary condition. Dashed lines: no-slip boundary condition but with the same velocity enhancement as the corresponding γ value. Simulation parameters: $L = 1 \mu\text{m}$, $\bar{v}_{z, no-slip} = 1 \text{ cm/s}$, $r_c = 200 \text{ nm}$, $d_s = 20 \text{ nm}$, and $N_p = 100,000$. Gz and Pe range from 18.3 and 91.6 for $\gamma = 0$ to 33.0 and 165 for $\gamma = 0.4$. The dependent variable in these graphs is in units of concentration.

Figure 7:

First (squares) and second (circles) moments for varying slip lengths under short tube conditions without retention. Black: slip boundary conditions. Blue: no-slip boundary condition but with the same velocity enhancement as the corresponding γ value. Simulation parameters: $L = 1 \mu\text{m}$, $\bar{v}_{z,no-slip} = 1 \text{ cm/s}$, $r_c = 200 \text{ nm}$, $d_s = 20 \text{ nm}$, and $N_p = 100,000$. Gz and Pe range from 18.3 and 91.6 for $\gamma = 0$ to 33.0 and 165 for $\gamma = 0.4$.

Figure 8:

Theoretical impact of slip flow on pure convective limit. The derivation for this limit is produced in section 2.4. A no-slip t_0 value of 1 time unit is used for these curves. The dependent variable is in units of concentration.

Figure 9:

Simulation results for slip flow with retention for $P_a = 0.1$ and multiple $\langle t_d \rangle$ values. The $\langle t_d \rangle$ values correspond to 2.5% and 7.5% of M_1 from Figure 9a (no-slip and no retention).

Simulation parameters: $L = 1 \mu\text{m}$, $\bar{v}_{z, no-slip} = 1 \text{ cm/s}$, $r_c = 200 \text{ nm}$, $d_s = 20 \text{ nm}$, and $N_p = 100,000$. $\gamma = 0$: $Gz = 18.3$ and $Pe = 91.6$; $\gamma = 0.2$: $Gz = 25.6$ and $Pe = 128$. The dependent variable in these graphs is in units of concentration.

Figure 10:

Simulation results for slip flow with retention for $P_a = 1.0$ and multiple $\langle t_d \rangle$ values. The $\langle t_d \rangle$ values correspond to 2.5% and 7.5% of M_I from Figure 10a (no-slip and no retention).

Simulation parameters: $L = 1 \mu m$, $\bar{v}_{z, no-slip} = 1 \text{ cm/s}$, $r_c = 200 \text{ nm}$, $d_s = 20 \text{ nm}$, and $N_p = 100,000$. $\gamma = 0$: $Gz = 18.3$ and $Pe = 91.6$; $\gamma = 0.2$: $Gz = 25.6$ and $Pe = 128$. The dependent variable in these graphs is in units of concentration.

Table 1:

Average velocity with slip flow and velocity at capillary wall for varying slip lengths as a fraction of average velocity in the axial direction under no-slip conditions.

L_s	γ	$\frac{\bar{v}_z}{\bar{v}_{z, no-slip}}$	$\frac{v_z(r) _{r=r_c}}{\bar{v}_{z, no-slip}}$
0	0	1	0
$0.05r_c$	0.1	1.2	0.2
$0.1r_c$	0.2	1.4	0.4
$0.2r_c$	0.4	1.8	0.8

Table 2:

Long tube simulations with no-slip boundary condition and comparison to theoretical distribution. Simulation parameters: $L = 10$ cm, $\bar{v}_z = 0.1$ cm/s, and $N_p = 20000$ for all cases. The “Figure” column corresponds to the label of the elution profile in Figure 3.

Figure	Inputs			Results		Theory			Percent Difference	
	Gz	d_c (μm)	d_s (nm)	M_1 (s)	M_2 (s ²)	$\bar{t}$ (s)	H (μm)	σ^2 (s ²)	In Arrival Time (%)	In Variance (%)
a	0.01	41.8	1	99.99	4.21	100	42.5	4.25	−0.01	−1.02
b	0.1	41.8	10	100.18	41.30	100	416.8	41.68	0.18	−0.89
c	0.1	13.2	100	98.74	38.68	100	416.7	41.67	−1.26	−7.18

Table 3:

Results of wall collision method testing for long tube capillaries with no-slip and slip conditions. The simulations are compared to theoretical moments for both the case of accounting for finite size and not accounting for it. For all trials, $L = 1$ cm, $\bar{v}_{z, no-slip} = 0.1$ cm/s, $r_c = 200$ nm, $d_s = 1$ nm, and $N_p = 100,000$.

This corresponds to $Gz = 9.2 \times 10^{-6}$ and $Pe = 0.46$ for $\gamma = 0$, $Gz = 1.2 \times 10^{-5}$ and $Pe = 0.60$ for $\gamma = 0.16$, and $Gz = 1.7 \times 10^{-5}$ and $Pe = 0.82$ for $\gamma = 0.40$. All values reported are the percent differences in moments between simulation and theory.

Collision Method	Size Accounted?	$\gamma = 0$		$\gamma = 0.16$		$\gamma = 0.40$	
		M_1	M_2	M_1	M_2	M_1	M_2
Rejection	No	-3.78	-11.1	-2.89	-8.43	-2.14	-5.59
	Yes	-3.30	-9.72	-2.52	-7.39	-1.87	-4.81
Interruption	No	-0.01	-0.53	0.00	-0.23	0.00	0.02
	Yes	0.49	0.96	0.37	0.91	0.27	0.85
Reflection	No	-0.50	-1.60	-0.38	-0.86	-0.28	-0.06
	Yes	-0.01	-0.12	-0.01	0.27	-0.01	0.77