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Self-diffusion in single-file zeolite membranes is Fickian at long times

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We have developed a theory for self-diffusion in single-file Langmuirian zeolites of finite extent, which has been validated by open system kinetic Monte Carlo simulations. Our theory is based on a two-stage, Fickian diffusion mechanism, wherein a vacancy must traverse the entire file length to produce particle displacements of one lattice spacing. For times shorter than the vacancy diffusion time, t_c, particle transport proceeds via the nonFickian, single-file diffusion mode, with mean-square displacements increasing with the square-root of time. For times longer than t_c, however, we find that self-diffusion in single-file systems is completely described by Fick's laws. We find that the fraction of time in the single-file diffusion mode scales inversely with file length for long files, suggesting that Fickian self-diffusion dominates transport in longer single-file zeolites. Through correlations among the particle movements, the single-file self-diffusivity is sensitive to sorption limitations for short files, and scales inversely with file length for long files. Experimental verification of the theory by pulsed field gradient NMR and tracer zero-length column experiments is discussed. © *1999 American Institute of Physics.* [S0021-9606(99)51518-3]

I. INTRODUCTION

Single-file diffusion is a one-dimensional transport process involving particles that cannot pass each other.[1] The strict ordering of particles correlates motion to such an extent that Fick's laws are considered invalid for single-file systems.[2] Indeed, the absence of particle exchange leads to the well-known prediction[1] that mean-square displacements in infinite, single-file systems increase with the square-root of time, in contrast to normal diffusion where they increase linearly with time. Single-file diffusion phenomena have recently been observed experimentally in one-dimensional zeolites,[3–5] and also in biological ion channels.[6] While these experiments underscore the importance of single-file diffusion, they also remind us that actual systems are finite in extent, in contrast to the models that predict anomalous mean-square displacements. To bridge this gap, we report a new theory of single-file diffusion in finite systems, which is validated by open system kinetic Monte Carlo (KMC) simulations.[7] In this article, we examine how fundamental system parameters determine the crossover from single-file diffusion to Fickian diffusion in finite materials.

Several models of transport through finite materials have recently been proposed for elucidating fundamental aspects of permeation through biological and zeolitic channels. MacElroy and Suh developed a two-reservoir molecular dynamics (MD) algorithm for modeling permeation through uncorrugated channels, finding diffusivities that scale as $L^{-1/2}$, where L is the channel length.[8] Chou reported an analytical theory for osmotic flow through single-file pores, finding that osmosis can be sensitive to solute–solvent interactions.[9] Hahn and Kärger derived expressions for single-file diffusion in finite zeolites with various boundary conditions.[10] They found that the self-diffusion coefficient, D_S, associated with center-of-mass motion of particles within a single-file scales as L^{-1}, in contrast to the prediction of MacElroy and Suh.[8]

We have recently reported open system KMC calculations, exploring the effect of anisotropy on self-diffusion through two-dimensional lattice models of zeolite membranes.[7] Simulating transport properties with KMC facilitates modeling of systems that are controlled by rare event dynamics, by accessing time scales that are unreachable by MD. The anisotropy of the membrane in our previous study was defined by $\eta \equiv k_y/k_x$, where k_x and k_y are the elementary jump rates in the transmembrane and in-plane directions, respectively. We used steady-state tracer counterpermeation (TCP) as a method for calculating self-diffusivities in finite systems,[11] by applying Fick's first law, $J = -D_S \nabla \theta$, to the fluxes and concentration gradients extracted from TCP simulations. For membranes with $\eta = 0$, where counterpermeation is strictly single-file, we found that self-diffusivities in the bulk of the membrane exhibit normal, Fickian behavior by being independent of position. However, we also found that the anomalous character of single-file diffusion is manifested by self-diffusivities that become inversely proportional to membrane thickness for thick membranes, in agreement with the theory of Hahn and Kärger.[10]

In the present article, we investigate finite single-file systems in more detail to determine precisely under what conditions self-diffusion can be described by Fick's laws. We focus on Langmuirian host–guest systems, which involve regular lattices of identical sorption sites where particle–

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particle interactions are ignored, except for exclusion of multiple site occupancy. Such model systems exhibit Langmuir adsorption isotherms, and give single-component transport diffusivities that are independent of loading.[12] We develop a compound (two-stage) Fickian diffusion theory to explain the surprising applicability of Fick's laws, yielding an analytical formula for the L-dependence of the single-file self-diffusion coefficient. This approach is more general than Hahn and Kärger's,[10] because our model is valid for arbitrary file lengths, regardless of whether transport is sorption-limited (small L) or diffusion-limited (large L). We simulate mean-square displacements with KMC to test our single-file theory under transient conditions. We find that for short times the mean-square displacement is proportional to $t^{1/2}$, as required by theories of single-file diffusion in infinite systems. However, at times longer than a ''crossover time,''[10] the mean-square displacement becomes proportional to t, with a Fickian self-diffusivity in quantitative agreement with our compound diffusion model.

The remainder of this paper is organized as follows: in Sec. II we present our general diffusion theory, in Sec. III we describe the simulation methodology, and in Sec. IV we present our theory and simulation results in the context of single-file and Fickian diffusion. In Sec. V we discuss the experimental consequences of our results, and in Sec. VI we offer concluding remarks.

II. DIFFUSION THEORY

In this section, we will derive an expression for the Fickian counterdiffusivity of two components that have similar transport properties within single-file zeolites, as a function of file length.

A. Review of two-component diffusion theory

We define the spatially and temporally varying occupancies of components A and B, coadsorbed in a Langmuirian zeolite as follows: $\theta_{A,n}(t)$ is the probability of finding an A-particle in site n of the file at time t. In the simulations described below, we consider a spatial ensemble of independent files arranged vertically (see Fig. 1). With this arrangement, $\theta_{A,n}(t)$ can also be interpreted as the number of lattice sites filled with A-particles at time t in column n, divided by the number of sites in column n; $\theta_{B,n}(t)$ is defined similarly for B-particles. $\theta_{T,n}(t)$ is the total fractional occupancy of column n at time t, defined as $\theta_{T,n}(t)=\theta_{A,n}(t)+\theta_{B,n}(t)$. In what follows, we will omit the explicit dependence on column n and time t, e.g., $\theta_{A,n}(t)\rightarrow\theta_A$, unless clarity requires otherwise.

It is well established[11,13–17] that for two-component systems, the scalar form of Fick's law should be replaced by a vector equation of the form:

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = -\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix}\begin{pmatrix} \nabla\theta_A \\ \nabla\theta_B \end{pmatrix}. \tag{1}$$

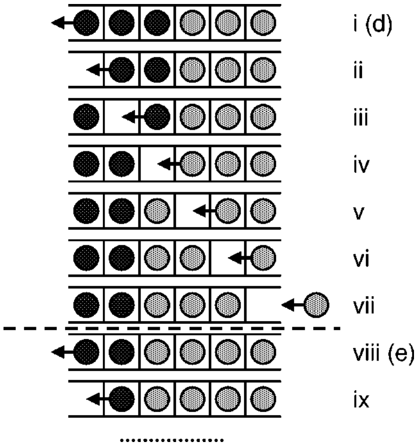

FIG. 1. Vacancy transport through an $L=6$ single-file system, with A-particles (dark) and B-particles (light). Steps (i) through (vii) represent the passage of an ''A-vacancy'' from right to left, giving particle displacement of one lattice spacing in the opposite direction.

When species A and B have *identical* diffusive properties, the matrix in Eq. (1) is asymmetric, and has two eigenvectors that correspond to the two eigenmodes of diffusion for differently labeled, identical particles. The codiffusion eigenmode involves A and B diffusing together, with driving forces proportional to their occupancies, so that the labeling of particles does not affect their transport. In this eigenmode, the flux of component A can be written in a scalar form of Fick's first law:

$$J_A=-D_A^+\nabla\theta_A, \tag{2}$$

and likewise for component B. The apparent diffusivities, D_A^+ and D_B^+, for the codiffusion eigenmode are given by:

$$D_A^+=D_B^+=D_0, \tag{3}$$

where D_0 is the single-component transport diffusivity, which is independent of loading for Langmuirian systems.[11,18] Hence, in the codiffusion eigenmode, the two components diffuse together as if the other component were not present.

The second eigenmode corresponds to equimolar counterdiffusion, where the flux of A is equal and opposite to the flux of B at constant θ_T, so that:

$$\nabla\theta_B=-\nabla\theta_A. \tag{4}$$

The apparent diffusivities for the counterdiffusion eigenmode are given by:

$$D_A^+=D_B^+=D_0(1-\theta_T)f(\theta_T)=D_S(\theta_T), \tag{5}$$

where $f(\theta_T)$ is the so-called correlation factor (*vide infra*), and $D_S(\theta_T)$ is the self-diffusion coefficient. D_0 is the single-component transport diffusivity, and is *also* the self-diffusion coefficient at infinite dilution, i.e., where all jump attempts are successful. $(1-\theta_T)$ is the fraction of jumps that are successful at finite loadings, because they are directed towards vacancies. This factor accounts for the reduction in D_S at the level of mean-field theory, which ignores correlations between successive jumps of a particle. Correlations arise because a successful jump always leaves a vacancy at the particle's original position, thereby increasing the probability that the particle will return there. Correlations are accounted for by the factor $f(\theta_T)$, which is less than one at finite loadings. Equation (5) demonstrates the correspondence between self-diffusion and equimolar counterdiffusion of identical, labelled particles, e.g., tracer counterpermeation (TCP).[7] We exploit this correspondence below, to investigate the applicability of Fick's laws to self-diffusion in single-file systems of finite extent.

B. Finite difference formulation of diffusion

The kinetic theory for sorption and diffusion in a Langmuirian host–guest system is based on a finite difference formulation (FDF) of diffusion,[7,11,18] which we briefly describe below for equimolar counterdiffusion. The FDF nodes represent adsorption sites, suggesting an FDF grid spacing equal to the distance between sites, Δx, which we chose as the fundamental distance unit in our model. For two-component diffusion in the interior of the lattice, we can write:

$$\frac{\delta\theta_{A,n}}{\delta t}=D_S(\theta_T)(\theta_{A,n-1}-\theta_{A,n})-D_S(\theta_T)\times(\theta_{A,n}-\theta_{A,n+1}). \tag{6}$$

For transport in column 1, we have:

$$\frac{\delta\theta_{A,1}}{\delta t}=\nu(1-\theta_T)-k_d\theta_{A,1}-D_S(\theta_T)(\theta_{A,1}-\theta_{A,2}), \tag{7}$$

while in column L, we obtain:

$$\frac{\delta\theta_{A,L}}{\delta t}=-k_d\theta_{A,L}-D_S(\theta_T)(\theta_{A,L}-\theta_{A,L-1}). \tag{8}$$

The counterdiffusivity, D_S, depends on the total concentration, θ_T, which is constant throughout the zeolite when focusing on the counterdiffusion eigenmode.

In the present article, we investigate the validity of Eqs. (6)–(8) for modeling counterdiffusion in finite, single-file systems. Equations (6)–(8), with D_S replaced by D_0, have been shown to accurately represent single-component transport diffusion in single-file systems, for all times, positions, occupancies, and concentration gradients.[18] However, since single-component transport diffusion corresponds to the codiffusion eigenmode, while self-diffusion corresponds to the counterdiffusion eigenmode, it is not obvious whether Eqs. (6)–(8) can model self-diffusion in finite, single-file systems. Our simulation results presented below show that Eqs. (6)–(8) can indeed reproduce self-diffusion in finite, single-file systems at sufficiently long times. In the remainder of Sec. II, we develop a theory for the self-diffusivity, D_S, in single-file zeolites of finite extent, finding that D_S scales inversely with L for long files.

C. Compound diffusion

In this section we explore a compound (two-stage) mechanism for diffusion in single-file systems, wherein particle displacements of one lattice spacing are produced by a vacancy traversing the entire length of the file. We begin by considering a single-file system of length $L=6$ with tracer counterpermeation boundary conditions, as shown in Fig. 1. The system is exposed to a phase of pure A on the left-hand side, and a phase of pure B on the right-hand side. We imagine that the system is at steady-state with total occupancy close to one, so that on average there will be no more than a single vacancy in the file. The starting configuration shown in Fig. 1(i) has all lattice sites filled with particles. As a result of the pure-component boundary conditions, there is a contiguous region of A-particles (dark) on the left-hand side of the file, and a contiguous region of B-particles (light) on the right-hand side. There can be no mixing of the A and B regions within the file, because each specie enters from only one side, and the single-file constraint prohibits particle exchanges. If the single-file constraint is not rigorously enforced, then the compound diffusion mechanism discussed here is not the only diffusion mode, and normal particle diffusion dominates for sufficiently large systems.[7,10]

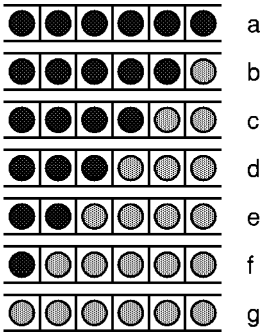

FIG. 2. Particle transport through an $L=6$ single-file system. Adjacent states (d)–(e) are separated by the vacancy moves in Fig. 1.

The arrow in Fig. 1(i) indicates that the left-most particle in the file is about to desorb from the file, with rate k_d. This desorption produces a vacancy in the lattice that moves throughout the file by exchanging with adjacent particles, as shown in Fig. 1(ii)–(vi). The sequence of configurations shown in Fig. 1(ii)–(vii) can be reached by single particle jumps in the directions indicated by the arrows, with rate k_x per jump. Although Sholl and Fichthorn have suggested the importance of correlated cluster dynamics instead of single particle jumps,[19] we are presently considering lattices with well-separated sites, i.e., Langmuirian host–guest systems, which lack the attractive guest–guest interactions modeled in Ref. 19. The transition from configuration (vii) to (viii) in Fig. 1 occurs when a B-particle from the external B-phase replaces the vacancy in Fig. 1(vii), which occurs with rate ν. We note that the reverse of the transitions shown in Fig. 1 can also occur with equal probability.

Each of the states in Fig. 1(i)–(viii) is separated by an elementary jump event. The entire sequence in Fig. 1 entails a single vacancy entering on the A-side of the file, traveling through the file and subsequently leaving on the B-side. The net effect of the vacancy transport through the file is displacement of the particles by one lattice spacing to the left. Figure 2 shows all possible configurations of the $L=6$ file without vacancies. The net effect of the sequence shown in Fig. 1 is to move the system between states (d) and (e) in Fig. 2. The other configurations in Fig. 2 are also separated by a sequence of vacancy moves similar to that shown in Fig. 1. Thus, we have shown that, in the absence of correlated cluster dynamics, a compound diffusion mechanism operates in single-file systems, which requires a vacancy to diffuse the entire file length to generate particle displacements of one lattice spacing.

We now consider a thought experiment where vacancies within the lattice are labeled by the side of the lattice on which they were created, e.g., an A-vacancy is created in the transition from steps (i) to (ii) in Fig. 1. In fact, an A-vacancy is created whenever a particle of either type desorbs into the A-phase. In Fig. 1(vii), the A-vacancy exchanges with a B-particle from the external B-phase. With this interpretation, we have a steady-state flux of A-vacancies from left to right through the lattice, and vice versa for the B-vacancies, while unlabeled vacancies have no net flux.

D. Derivation assuming local thermodynamic equilibrium

We now derive the L-dependence of D_S assuming local thermodynamic equilibrium (*vide infra*). The flux of A-vacancies is given by Fick's first law:

$$J_A^V = -D_A^V \nabla \theta_A^V, \tag{9}$$

where $\nabla \theta_A^V$ is the A-vacancy concentration gradient, and D_A^V is the apparent diffusivity of A-vacancies. At infinite vacancy dilution, D_A^V is equal to D_0, the single-component particle transport diffusivity. Hence, at steady-state there is a linear concentration gradient of A-vacancies across the system. If we assume that the edge sites are in local thermodynamic equilibrium with the external phases, then all particles and vacancies in the left-most site of the file are either A-particles or A-vacancies, since the external left-hand phase is pure A. As such, the assumption of local thermodynamic equilibrium changes the constant chemical potential boundary conditions outside the zeolite to constant concentration boundary conditions in the edge sites of the zeolite, i.e., $\theta_{A,1}^V = (1-\theta_T)$ and $\theta_{A,L}^V = 0$. Hence, applying Fick's law, Eq. (2), across the file with a linear vacancy concentration gradient, we find that:

$$J_A^V = -D_0\left(\frac{\theta_{A,L}^V - \theta_{A,1}^V}{L-1}\right) = D_0\left(\frac{1-\theta_T}{L-1}\right). \tag{10}$$

The flux of B-particles though the interior of the file can be obtained from Fick's first law, giving:

$$J_B = -D_B^+ \nabla \theta_B, \tag{11}$$

where $\nabla \theta_B$ is the local B-particle concentration gradient, and D_B^+ is the local apparent diffusivity. D_B^+ determines the rate at which the single-file system can move between adjacent states in Fig. 2. At steady-state, the flux of B-particles is uniform throughout the file, and is related to the flux of A-vacancies by the following ansatz:

$$J_B = -\frac{J_A^V}{L-1}. \tag{12}$$

The factor of $(L-1)^{-1}$ arises because an A-vacancy must traverse the length of the file, as shown in Fig. 1, to complete the transition between any of the adjacent states in Fig. 2. Equations (11) and (12) can be combined to obtain the flux of B-particles, giving:

$$D_B^+ = \frac{J_A^V}{(L-1)\nabla \theta_B}, \tag{13}$$

where J_A^V is given by Eq. (10). If we assume again that the edge sites are in local thermodynamic equilibrium with the external phases, then the concentrations of B-particles in the left-most and right-most sites of the file are equal to $\theta_{B,1} = 0$ and $\theta_{B,L} = \theta_T$, respectively. Furthermore, if we assume that the apparent B-particle diffusivity is constant throughout the system,[7] then the steady-state particle concentration profiles will be linear, giving $\nabla \theta_B = \theta_T/(L-1)$. Combining this with Eqs. (10) and (13), we find that:

$$D_B^+ = \frac{D_0(1-\theta_T)}{(L-1)\theta_T}. \tag{14}$$

When $(L-1)$ is replaced with L, Eq. (14) becomes the expression recently obtained by Hahn and Kärger, for the self-diffusion coefficient associated with center-of-mass motion of particles within the file.[10] Hahn and Kärger obtained their expression by analyzing the Gaussian statistics of several correlated random walkers in a single-file system. Our derivation of Eq. (14) shows that Hahn and Kärger's result is consistent with assuming local thermodynamic equilibrium at the file boundaries, which becomes valid in the long-file limit as we show below.

E. General derivation

A more general expression can be obtained by relaxing the assumption that the file edges are in local thermodynamic equilibrium with the external phases. Instead, we analyze the fluxes produced by the constant chemical potentials of the external phases. The flux of A-vacancies entering the left-hand edge of the file from the external phase is given by:

$$J_A^V = k_d \theta_{T,1} - \nu \theta_{A,1}^V. \tag{15}$$

The first term on the right is the rate of A-vacancy creation in column 1, while the second term is the rate of A-vacancy destruction, due to A-particle insertion into column 1 from the external phase. At the right-hand edge, the flux of A-vacancies is given by:

$$J_A^V = \nu \theta_{A,L}^V, \tag{16}$$

which is the rate at which A-vacancies leave the right-hand edge by exchanging with B-particles from the B-phase. The flux of A-vacancies throughout the interior of the file is given by Fick's first law:

$$J_A^V = -D_0\left(\frac{\theta_{A,L}^V - \theta_{A,1}^V}{L-1}\right). \tag{17}$$

At steady-state, these three fluxes in Eqs. (15)–(17) must be equal, giving the result:

$$J_A^V = \frac{D_0 \theta_T k_d}{\nu(L-1) + 2D_0}. \tag{18}$$

This expression for the A-vacancy flux holds regardless of the presence of local thermodynamic equilibrium at the file edges. Equation (18) has two limiting forms, depending upon whether A-vacancy transport through the system is sorption-

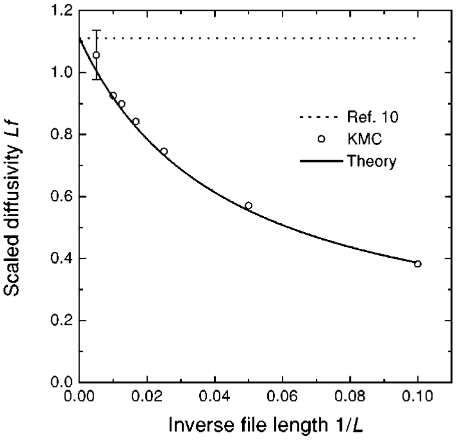

FIG. 3. File length dependence of the scaled diffusivity, from simulation (open circles), present theory (solid line), and theory in Ref. 10 (dashed line).

limited or diffusion-limited. In the limit that $\nu(L-1) \gg D_0$, A-vacancy transport is diffusion-limited, Eq. (18) reduces to Eq. (10), and the assumption of local thermodynamic equilibrium at the edge sites becomes valid. Alternatively, when $\nu(L-1) \ll D_0$, A-vacancy transport is sorption-limited, and Eq. (18) reduces to $J_A^V = \theta_T k_d/2$.

From Fig. 6(b) of Ref. 7, we note that the local apparent diffusivity of B-particles, $D_B^+ = D_S$, is constant throughout the interior of the file. Hence, we can approximate the B-particle flux through the interior of the system as:

$$J_B = -D_S\left(\frac{\theta_{B,L} - \theta_{B,1}}{L-1}\right), \tag{19}$$

where $D_B^+ = D_S(\theta_T, L)$ is the self-diffusivity of the B-particles in a file of length L at total concentration θ_T. At the left-hand edge of the system, the flux is given by:

$$J_B = -k_d \theta_{B,1}, \tag{20}$$

while the right-hand edge flux is given by:

$$J_B = k_d \theta_{B,L} - \nu(1-\theta_{T,L}). \tag{21}$$

We can eliminate the edge concentrations from Eqs. (19)–(21) by equating them at steady-state, giving:

$$J_B = -\frac{D_S(1-\theta_T)\nu}{k_d(L-1)+2D_S}. \tag{22}$$

Combining the expressions for the flux of B-particles, Eqs. (12), (18), and (22), we obtain:

$$D_S = \frac{D_0 \theta_T k_d^2 (L-1)}{(1-\theta_T)(L-1)\nu[\nu(L-1)+2D_0] - 2D_0\theta_T k_d}. \tag{23}$$

Equation (23) is the main theoretical result of this article, and will be compared with simulation under various counterdiffusion conditions below. In the limit that $L \to \infty$, Eq. (23) reduces to Eq. (14), since vacancy transport becomes diffusion-limited. Equation (23) is more general than Hahn and Kärger's expression,[10] because Eq. (23) is valid for arbitrary file lengths, i.e., regardless of whether vacancy transport is sorption-limited (small L) or diffusion-limited (large L).

III. SIMULATION METHODOLOGY

We will now briefly summarize the lattice model parametrization and simulation methodology. We refer the reader to our previous article[7] for a complete description of the model zeolite system and simulation techniques used. Figure 1 shows a number of single-file systems containing either A-particles (dark) or B-particles (light). Each adsorption site is indicated by a square, which can contain either an A-particle, a B-particle, or be vacant. Double occupancy of adsorption sites is prohibited, and adjacent particles do not interact with each other in our model, except for exclusion of multiple occupancy. Apart from the labeling, the A- and B-particles are identical with respect to their adsorptive and diffusive properties. At equilibrium, the zeolite is filled with particles up to a fractional occupancy, θ_{eq}, given by the Langmuir isotherm:

$$\theta_{\mathrm{eq}} = \frac{1}{1+k_d/\nu}, \tag{24}$$

where ν is the insertion rate of particles from external phases at either edge of the zeolite, as shown by the arrow in Fig. 1(vii), and k_d is the desorption rate of particles from edge sites, as shown in Fig. 1(i).

For consistency with our previous two-dimensional study,[7] the fundamental time scale in our present model is $\tau = 1/4k_x$, which is half the average residence time of an isolated particle in the one-dimensional system considered here. The desorption rate is chosen to be $k_d = k_x/100$, to reflect the fact that heats of adsorption exceed diffusion activation energies. Since site-to-site hopping and particle desorption are both thermally activated processes in our model, governed by Arrhenius temperature dependencies, this choice of k_x/k_d corresponds to experimental data for cyclohexane in silicalite,[20] at a temperature of $T = 656$ K, and with a time scale of $\tau = 2 \times 10^{-7}$ s. In all the simulations reported below, the steady-state combined occupancy was chosen to be $\theta_{\mathrm{eq}} = 0.9$, by selecting the appropriate insertion frequency, ν.[7]

IV. SIMULATION RESULTS

In this section, we will present simulation results that test the usefulness of Fick's first and second laws applied to single-file, counterdiffusion problems. We have considered a variety of initial and boundary conditions, including steady-state tracer counterpermeation (TCP), transient TCP, tracer exchange boundary conditions that model tracer zero-length column (TZLC) experiments, as well as mean-square displacement (MSD) calculations for counterdiffusing tagged particles. We have found that all these single-file systems give results consistent with Fick's laws at long times compared with the characteristic time for vacancy diffusion. Below we detail only the steady-state TCP simulations and MSD calculations.

A. Steady-state simulations

Figure 3 shows TCP diffusivities plotted as the scaled correlation factor, $Lf = LD_S/D_0(1-\theta_T)$, obtained from KMC simulations (circles) for single-file systems with L

$=10$ to 200. The dashed line in Fig. 3 is obtained by evaluating Eq. (14),[10] while the solid line is obtained from Eq. (23). The diffusion correlation factor, f, is scaled by L to remove the inverse length dependence of the expression obtained by Hahn and Kärger,[10] so that their expression is represented by the horizontal dashed line. We plot Lf against inverse file length, $1/L$, so that the limiting form as $L\rightarrow\infty$ appears as the intercept at $1/L=0$.

The $L=10$ to 100 simulations were obtained from 2500 to 16 000 statistically independent files, depending on the simulation times required. The error bars for these data points are smaller than, or comparable to, the size of the symbols. The equilibration time of these systems is proportional to L^3, so that the time scale of the $L=200$ simulation is approximately an order of magnitude longer than that for the $L=100$ simulations. As a result, a relatively small number (100) of statistically independent files were averaged for $L=200$, resulting in the relatively large error bar in Fig. 3.

Figure 3 shows that our single-file theory, Eq. (23), quantitatively predicts the apparent single-file diffusivities calculated by KMC. Figure 3 also shows that the theory of Hahn and Kärger[10] over-estimates the diffusivity in finite systems, because it neglects sorption limitations in the transport of vacancies. From Eq. (18), we see that the ratio $\nu L/D_0$ determines whether vacancy transport is limited by sorption or diffusion. For the simulations shown in Fig. 3, $\nu L/D_0$ ranges from 0.9 for $L=10$ to 18 for $L=200$. When $\nu L/D_0\approx 1$, the system is neither sorption-limited nor diffusion-limited, and Eq. (23) should be used to predict the compound diffusivity. However, when $\nu L/D_0 \gg 1$, vacancy transport becomes diffusion-limited, the assumption of local thermodynamic equilibrium becomes valid at the edges, and Eq. (14) becomes a useful approximation.

B. Transient simulations

While the agreement between Eq. (23) and the steady-state simulations shown in Fig. 3 is impressive, the question now arises as to whether our compound diffusion theory, Eqs. (6)–(8) and (23), can reproduce *transient* diffusion phenomena. To investigate this, we simulated transient TCP, tracer exchange as occurs in TZLC experiments, and MSDs of tagged particles as functions of time. All of these systems showed good agreement with the FDF at sufficiently long times. For brevity, we discuss only the MSD calculations below.

An $L=60$ single-file system was initially filled with particles up to an average occupancy of $\theta_T=0.9$ throughout. Particles in column 30 were labeled as B-particles, while the remainder were labeled as A-particles. At $t=0$, both edges of the system were exposed to a phase of A-particles with an insertion rate that maintained the equilibrium A-occupancy at $\theta_A=0.9$. The external phases are assumed to be well stirred and of infinite extent, so that when B-particles leave the file, they cannot return. With these initial and boundary conditions, the diffusion solution for the B-particles in the zeolite is entirely within the counterdiffusion eigenmode. As such, the matrix diffusion equation, Eq. (1), can be replaced by a scalar FDF given by Eqs. (6)–(8), with D_S given by Eq. (23).

Figure 4 shows B-particle concentration profiles at three times separated by $30\,000\tau$. The symbols represent average KMC simulation data at the specified times, while the lines indicate the FDF solution using the diffusivity predicted by Eq. (23). The initial concentration spike develops into a Gaussian peak that spreads with time according to Fick's second law. The excellent fit between theory and simulation in Fig. 4 indicates that the spreading of B-particles is governed by Fick's second law on these time scales, with the diffusivity predicted by Eq. (23). Hence, except for the fact that the diffusivity in Eq. (23) depends on file length, self-diffusion in single-file systems is Fickian in the sense that Fick's first and second laws are obeyed for a file of given length.

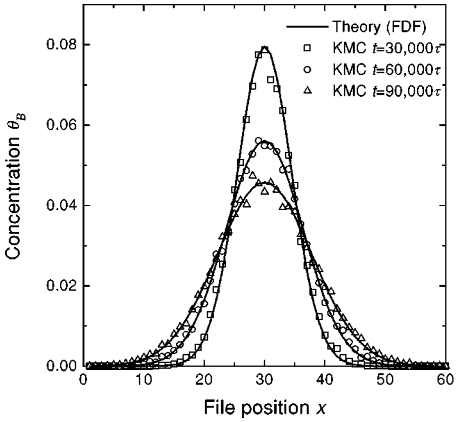

FIG. 4. Concentration profiles during self-diffusion in an $L=60$ single-file system, from simulation (symbols) and the diffusion equation (solid lines).

It is well known[1,2,10] that the MSD of particles in single-file systems of infinite extent evolves as $t^{1/2}$. The excellent agreement in Fig. 4 between simulation and Fick's laws suggests, however, that the MSD in our finite single-file systems may evolve *linearly* with time at long times, consistent with normal Fickian diffusion. In order to investigate this, we have calculated the time dependence of the MSD for all simulation times, as shown in Fig. 5. Figure 5 shows that except for very short times (see inset), the MSD is linear in

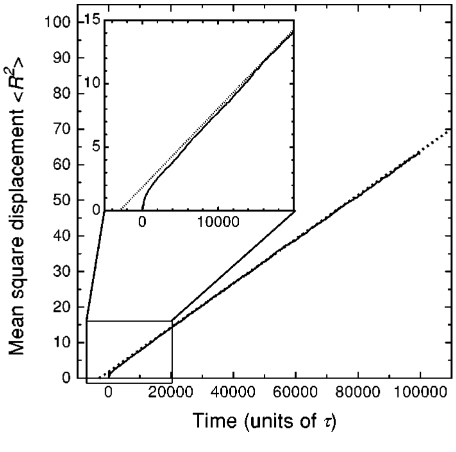

FIG. 5. Mean-square displacements of B particles in an $L=60$ single-file system, from simulation (solid line) and linear fit at long times (dashed line). Inset is enlargement at short times.

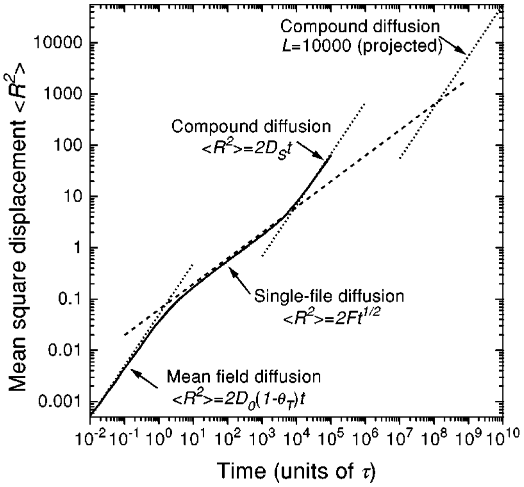

FIG. 6. Log-log plot of mean-square displacements of B particles in an $L=60$ single-file system, from simulation (solid line), mean-field diffusion theory giving slope of 1 (left-most dotted line), single-file diffusion theory giving slope of $\frac{1}{2}$ (dashed line), and compound diffusion theory giving slope of 1 (middle and right-most dotted lines).

time. The dashed line is a least-squares linear fit to the data between $t=30\,000\tau$ and $t=60\,000\tau$, consistent with Einstein's equation:

$$\langle R^2(t)\rangle = 2D_S t, \tag{25}$$

where $\langle R^2(t)\rangle$ is the MSD for a one-dimensional system.

The fact that the MSD is linear for long times in Fig. 5 is further evidence that the system studied here diffuses in accordance with Einstein's and Fick's laws. As can be seen in the inset to Fig. 5, the increase in the mean-square displacement is more rapid at short times, but approaches the linear regime at longer times. During the time shown in Fig. 5, essentially none of the tagged particles has left the file (cf. Fig. 4). Once several particles leave the ensemble of files, Einstein's equation becomes less useful in describing the system. However, the FDF of the diffusion problem remains valid at all times, and can be used in a straightforward manner to determine the net fluxes throughout the file and at the file edges.

In order to examine the short-time behavior in more detail, we have replotted the MSD of Fig. 5 as the solid line on the log-log plot in Fig. 6. The dotted lines have slope equal to 1 on the log-log plot, indicating that the MSD is proportional to t, whereas the dashed line has a slope of $\frac{1}{2}$, indicating that the MSD is proportional to $t^{1/2}$. The short-time behavior is consistent with mean-field theory, where the dotted line is given by Einstein's equation with $D_S = D_0(1-\theta_T)$. This is because at very short times ($t<\tau$), the tagged particles have made at most one jump attempt, so that the diffusivity is determined by the fraction of initial jump attempts that are successful, which is given by the mean-field factor $(1-\theta_T)$. At long times, the MSD in Fig. 6 (middle dotted line) is again given by Einstein's equation with D_S given by Eq. (23), giving transport that is dominated by compound diffusion. At intermediate times, transport is achieved by a single-file mode that operates as if the file were of infinite extent, with an MSD given by:

$$\langle R^2(t)\rangle = 2Ft^{1/2}, \tag{26}$$

where F is the single-file mobility given by:[10,16]

$$F = \frac{1-\theta_T}{\theta_T}\sqrt{\frac{D_0}{\pi}}. \tag{27}$$

The crossover time between single-file diffusion and compound diffusion is given by the intersection of the dashed and dotted lines in Fig. 6, which can be obtained by equating Eqs. (25) and (26). For long files, we can use Eq. (14) for the self-diffusivity, giving the following crossover time:

$$t_c = \frac{(L-1)^2}{\pi D_0}. \tag{28}$$

If we replace $(L-1)$ with L, this expression is the same as that obtained by Hahn and Kärger,[10] and is proportional to the characteristic time for vacancy diffusion through the system.[21] For shorter files, where vacancy transport is also influenced by sorption limitations, Eqs. (23) and (26) should be used to determine t_c. t_c defines what we mean by ''long times'' in the title and throughout this article, indicating when diffusion in single-file systems becomes Fickian. For large systems, where Eq. (14) is valid, the MSD at the crossover time is given by:

$$\langle R^2(t_c)\rangle = \frac{2}{\pi}\left(\frac{1-\theta_T}{\theta_T}\right)L. \tag{29}$$

The root MSD at the crossover time, $R_c \equiv \sqrt{\langle R^2(t_c)\rangle} \propto L^{1/2}$, specifies the average distance when diffusion becomes Fickian.

We can also calculate the crossover time from mean-field diffusion to single-file diffusion, which is given by $t_c = 1/\pi D_0 \theta_T^2$. For our system this quantity is of order unity, indicting that the crossover between mean-field and single-file diffusion occurs at $t_c \cong \tau$, which is the average time it takes a particle to attempt a jump within the lattice. These two crossover times separate the MSD into three time regimes, determined by the extent of correlations in the motion of particles. For short times, motion is uncorrelated and is given by the mean-field diffusivity. At intermediate times, correlations in the particle motion spread out as if the file were of infinite extent. In this regime, Einstein's equation must be replaced with Eq. (26) because the MSD is proportional to $t^{1/2}$. However, once the extent of correlations is comparable to the file length, a global compound diffusion mechanism dominates, and the MSD is once again governed by Einstein's equation, with a diffusivity that is greatly diminished by correlations according to Eq. (23).

The long-range correlations in compound diffusion arise because moving all the particles by only one lattice spacing requires a vacancy to traverse the entire file length. In this process, a particle is adsorbed at one edge, and a particle desorbs at the other edge. Hence, the motion of any particle is influenced by the file edges, forcing the boundary conditions to influence the diffusivity of B-particles *long before* they reach the file edges.

Figure 6 also includes a line for a zeolite of the size typically used in diffusion experiments, i.e., $L=10\,000$, corresponding to a ZSM-5 crystallite of about 10 μm in the file direction. The crossover from single-file to compound diffusion occurs at a time that is well approximated by Eq. (28). Thus, as the file length increases, the observation window for single-file diffusion also increases. In the next section, we discuss the experimental implications of these findings.

V. DISCUSSION

In this article we make two different predictions about single-file transport. The first is embodied in Eq. (23), that the counterdiffusivity scales as $1/L$ for sufficiently large systems. Second, the MSD makes a transition from being proportional to $t^{1/2}$, to being proportional to t, in the time it takes a vacancy to traverse a zeolite particle. This crossover time, t_c, determines the beginning of the long-time regime when diffusion in single-file systems is Fickian, and hence determines the maximum time regime when single-file diffusion can be observed in finite systems.

It is interesting to consider whether PFG NMR measurements of the MSD in single-file systems can detect the crossover from single-file to compound diffusion. This should be possible for files that are short enough to bring the crossover time into the experimental observation window, which is ca. 1–100 ms.[2] Performing PFG NMR measurements in the compound diffusion regime may be complicated by interferences from zeolite particle boundaries, and from spin-lattice relaxation.

Although the duration of single-file diffusion increases with file length, the relative importance of single-file motion decreases with file length. This becomes clear by analyzing the fraction of time that particles spend single-file diffusing while adsorbed in a zeolite crystallite. This fraction is given by t_c/τ_{intra}, where t_c is the crossover time and τ_{intra} is the intracrystalline residence time,[2] which scales as L^2/D_S. Since $t_c \propto L^2$ while $D_S \propto 1/L$ for long files, we see that the fraction of time in single-file diffusion mode scales as $1/L$ for long files. Ironically, while single-file diffusion is more easily measured in longer files, compound diffusion becomes the dominant transport process in larger zeolite particles.

The most direct way of testing the theoretical predictions for the compound diffusivity as given by Eq. (23), is to measure the long-time counter-diffusivity of guest molecules in zeolite single crystals of varying file lengths, using macroscopic techniques such as TZLC or TCP, or using a technique that measures the MSD such as PFG NMR. The results of Hahn and Kärger,[10] as well as ours, predict that the diffusivity will become inversely proportional to thickness for large systems. This experiment is challenging because it requires defect-free, single crystals of various sizes. Another, more practical method would be to compare the codiffusivity and counterdiffusivity for a given host–guest system in defect-free single crystal(s) of one size. The codiffusivity could be measured by uptake or ZLC, while the counterdiffusivity could be measured by TZLC or PFG NMR. Our theory predicts that the codiffusivity will be many orders of magnitude larger than the counterdiffusivity. For example, in the Langmuirian single-file zeolite considered here, assuming $\theta_T = 0.9$ and $L = 10\,000$, corresponding to a 10 μm ZSM-5 crystallite, the single-component transport diffusivity is five orders of magnitude greater than the compound diffusivity. To achieve this differential between the co- and counterdiffusivities, events contrary to single-filing, such as particle jumps between files or particle exchanges within a file, must be rare on a time scale comparable with the crossover time between single-file diffusion and compound diffusion. If such events are frequent on this time scale, then the counterdiffusivity will become ''normal'' in the sense that the diffusivity will become independent of file length for sufficiently large crystals.[7,10]

VI. CONCLUDING REMARKS

We have presented a theory for self-diffusion in single-file zeolites of finite extent, which has been validated by extensive open system kinetic Monte Carlo (KMC) simulations. We have focused on modeling zeolite host–guest systems exhibiting Langmuir isotherms. Our theory is based on a compound (two-stage) diffusion mechanism, wherein a vacancy must traverse the entire file length to produce particle displacements of one lattice spacing. In the first stage, vacancy transport through the lattice is governed by Fick's first law with constant diffusivity, D_0. In the second stage, particle transport within the counterdiffusion mode is also governed by Fick's first law, with a diffusivity that is much less than D_0. Through correlations in the movement of all particles in the compound diffusion mode, a particle jump of one lattice spacing feels the edges of the file, so that boundary resistances can modify the counterdiffusivity if vacancy transport is sorption-limited.

The theory, which was derived from an analysis of steady-state tracer counter-permeation (TCP), is shown to apply to a more general class of systems, including transient counterdiffusion problems at long times. Examples explored by KMC simulations include mean-square displacements (MSDs) of tagged particles as measured by PFG-NMR experiments, and tracer exchange as occurs in tracer zero-length column (TZLC) experiments. In general, we find that self-diffusion in finite, single-file systems is completely described by Fick's laws at times that are well below intracrystalline residence times, with diffusivities that depend upon file length.

In order to test our single-file diffusion theory, we have simulated diffusion over eight orders of magnitude in time, to investigate the short-, medium-, and long-time behavior in single-file systems of finite extent. At short times, the MSD increases linearly with time, according to Einstein's equation, with a slope given by the mean-field self-diffusivity. At intermediate times, the MSD is proportional to the square-root of time, with a slope determined by the single-file mobility. At longer times, the MSD is once again proportional to time according to Einstein's equation, with a greatly reduced diffusivity predicted by our compound diffusion theory. For long files, where vacancy transport is diffusion-limited, this diffusivity becomes inversely proportional to file length, in agreement with the previously published theory of Hahn and Kärger.[10] This dependence on file length makes counterdiffusion many orders of magnitude slower than codiffusion in single-file zeolites of practical size. For short files, however, vacancy transport can also be influenced by sorption limitations. Our theory provides a generalization of Hahn and Kärger's treatment,[10] since our expression is valid for arbitrary file lengths, i.e., regardless of whether vacancy transport is sorption-limited (small L) or diffusion-limited (large L).

We have identified a crossover time that separates the single-file and compound diffusion modes. This time is proportional to the square of the system size, showing that the experimental window for observing single-file diffusion increases with systems size. However, the fraction of time that particles spend in the single-file mode, while adsorbed in a zeolite crystallite, scales inversely with file length for long files. Thus, while single-file diffusion is more easily measured in longer files, compound diffusion becomes the dominant transport process in larger zeolite particles.

The theory and simulations presented here relate to high occupancy, defect-free files with open ends. In future work, we plan to investigate the applicability of the theory to systems with lower equilibrium occupancy. Furthermore, since the compound diffusion mechanism discussed here is sensitive to any resistance that alters vacancy fluxes, we plan to study the effects of various kinds of disorder on transport through strongly anisotropic zeolites.

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