Effect of correlated flights on particle mobilities during single-file diffusion

David S. Sholl* and Kristen A. Fichthorn
Departments of Chemical Engineering and Physics, The Fenske Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802
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When large adsorbates diffuse in the pores of zeolites and molecular sieves, they can undergo single-file diffusion. The mean-square displacement of particles during single-file diffusion, $\langle x^2(t)\rangle$, is proportional to $t^{1/2}$. By contrast, in the absence of other particles, an isolated adsorbate will perform normal diffusion with a tracer diffusion coefficient D_0. An important goal of theoretical treatments of single-file diffusion is to relate D_0 and the single-file mobility, $F=\langle x^2(t)\rangle/2t^{1/2}$. One physical feature that is ubiquitous in activated diffusion in periodic potentials, such as the diffusion of adsorbates in zeolites, is the appearance at sufficiently high temperatures of correlated flights that pass through multiple binding sites. We show that when isolated particles can perform multisite flights, the expression usually used to relate D_0 and F is not exact, and we investigate methods that can lead to more accurate expressions. We discuss how the existence of long flights affects equilibrium adsorbate structures and comment on the implications of our results for the interpretation of experimental measurements of single-file diffusion. [S1063-651X(97)01206-3]

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The mechanisms and rates of molecular transport through the pores of zeolites and molecular sieves are critical factors in determining the effectiveness of the wide range of technologies that utilize these microporous materials [1,2]. One important scenario for molecular transport in zeolites occurs when molecular adsorbates are sufficiently large that they cannot pass one another inside a pore. Diffusion in this strongly hindered regime is known as single-file diffusion. The best known feature of single-file diffusion is that the mean-square displacement of individual particles during single-file diffusion is proportional to the square root of time [3,4], in contrast to the linear dependence on time during diffusion when particles can pass one another [4]. Although theoretical aspects of single-file diffusion were first described many years ago [5], experimental observations of this phenomenon have only been reported recently [3,6].

The main quantitative model that has been applied to interpret experimental measurements of single-file diffusion is a hard-sphere model [3]. This model provides a direct connection between the diffusion of an isolated molecule and the mobility of particles during single-file diffusion [3]. One useful realization of this model is a lattice-gas (LG) description in which a one-dimensional zeolite pore is modeled as a series of discrete binding sites. The particles which represent adsorbed molecules are assumed to bind only in these discrete binding sites and particles are allowed to move by hopping between adjacent sites. This model has been used in a number of studies that seek to understand the interplay between single-file diffusion and the effectiveness of catalytic reactions [7,8]. If only a single particle is present in a pore, its motion is unhindered and the usual Einstein relation describes the particle's mean-squared displacement, $\langle x^2(t)\rangle=2D_0t$. Here $D_0=\nu a^2/2$, where ν is the hopping frequency and a is the lattice spacing. For convenience, we use units with $\nu=a=1$, so $D_0=1/2$. When multiple particles are present in a pore, it is assumed that only one particle can occupy any particular binding site and that any attempted hop that would move a particle into an occupied site fails. The particles then undergo single-file diffusion. At times longer than the typical interparticle collision time, the displacement of each particle satisfies

$$\langle x^2(t)\rangle=2F\sqrt{t}, \tag{1}$$

where F is known as the single-file mobility. For this model, the single-file mobility F and the isolated particle diffusion coefficient D_0 are related by [3]

$$F=\frac{(1-\theta)}{\theta}\sqrt{\frac{D_0}{\pi}}, \tag{2}$$

where θ is the fractional occupancy of the lattice. Thus, if this model is valid, D_0 can be deduced from experimental measurements of $F(\theta)$ [3]. Note that while F diverges as $\theta\rightarrow 0$, the time scale on which Eq. (1) is valid also diverges in this limit because the typical collision time becomes infinite.

The aim of this paper is to discuss the accuracy of Eq. (2) when a more realistic description of the motion of individual particles is used. The application of Eq. (2) to NMR measurements of $F(\theta)$ [3] has yielded molecular diffusivities that are very large compared to previous measurements of intercrystalline diffusion in zeolites [3]. Because these results are somewhat surprising and the model from which Eq. (2) is derived is at best a highly simplified description of the motion of molecular adsorbates in a zeolite pore, it is useful to investigate the accuracy of Eq. (2) when more accurate descriptions of the particle dynamics are used. In this paper, we focus on understanding the effects of multisite flights on the loading dependence of single-file mobilities. Our main result is that Eq. (2) is not exact when single-particle transport includes multisite flights, indicating that Eq. (2) is not as general as had previously been assumed [3].

*Permanent address: Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8017.

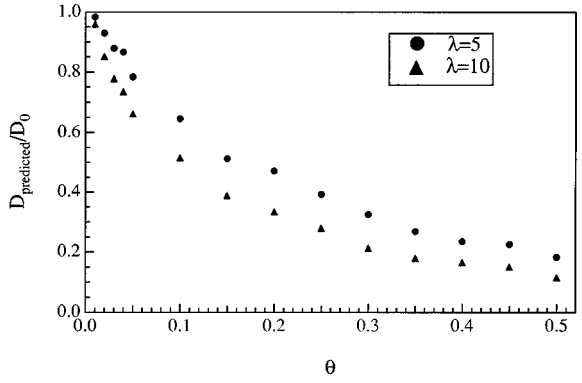

FIG. 1. Loading dependence of $D_{\text{predicted}}/D_0$ measured from MC simulations of the extended LG model. ''Ballistic'' flight distributions with $\lambda = 5$ and 10 were used.

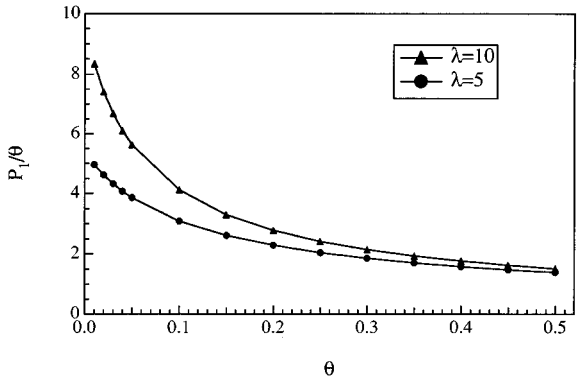

FIG. 2. Loading dependence of P_1/θ measured from the same MC simulations as in Fig. 1.

The LG model defined above assumes that particle transport only occurs by particles hopping between adjacent binding sites. While this is certainly an accurate description of molecular diffusion in zeolite pores at sufficiently low temperatures [4,9], at temperatures where thermal energies are comparable to or larger than the energy barrier to hopping, particles can frequently traverse multiple binding sites in a correlated fashion before they become localized in a binding site. This type of behavior has been observed in a wide variety of physical systems, including diffusion in zeolites [9,10] and atomic and molecular diffusion on crystal surfaces [11–13]. To examine the implications of multisite flights for single-file diffusion in a general manner, we consider an extended LG model in which in each unit of time each particle attempts a flight covering n sites where the flight length is chosen randomly from a normalized flight distribution f_n. We assume that a flight terminates if the moving particle encounters an occupied site. This extended model reduces to the original LG model if $f_1=1$ and $f_i=0$ for $i>1$. For the extended model, the single-particle diffusion coefficient for an isolated particle is [13]

$$D_0=\frac{1}{2}\sum_n n^2 f_n . \tag{3}$$

We have measured the loading-dependent, single-file mobilities of the extended LG model by performing Monte Carlo (MC) simulations of the model and defining

$$F_{\text{MC}}=\lim_{t\to\infty}\frac{\langle x^2(t)\rangle}{2\sqrt{t}}. \tag{4}$$

The results presented below are typically calculated by averaging over 300 independent runs, each containing 300 particles with periodic boundary conditions. In each case, we began the simulations with random distributions of particles and equilibrated the system for 125 units of time before beginning the measurement of $\langle x^2(t)\rangle$. We have verified that our results are insensitive to these numerical details. If Eq. (2) is exact, we can rearrange it to predict the single-particle diffusion coefficient from our measurements of F_{MC}:

$$D_{\text{predicted}}=\pi\frac{\theta^2 F_{\text{MC}}^2}{(1-\theta)^2}. \tag{5}$$

We have verified that $D_{\text{predicted}}=1/2$ if only nearest-neighbor hops are allowed. We can assess the general validity of Eq. (2) by comparing the results obtained using Eqs. (3) and (5).

Some measured values of $D_{\text{predicted}}/D_0$ for versions of the extended LG model that included long flights are shown in Fig. 1. In this figure, the flight distribution was taken to be the ''ballistic'' distribution [13] $f_n=A\exp(-n/\lambda)$, where A is a normalization constant defined by truncating the distribution at $n=50$ and λ is a mean free path. It is clear from Fig. 1 that Eq. (2) is not exact. At all nonzero loadings, the predicted diffusion coefficient based on Eq. (2) is less than the actual isolated particle diffusion coefficient. These results suggest that the task of accurately inferring D_0 from measurements of $F(\theta)$ may be more complicated than was previously assumed [3]. Figure 1 shows that $D_{\text{predicted}}$ does approach the correct value for D_0 as $\theta\to 0$. However, this limit is very difficult to examine experimentally [3] because F is a very rapidly varying function of θ in this regime, so small errors in the measurement of θ can lead to significant errors in the estimation of D_0.

Heuristically, the inexactness of Eq. (2) for the extended LG model arises because flights of differing lengths are not equally affected by particle collisions. To quantitatively understand the loading-dependent mobilities observed in the extended LG model, it is important to describe what types of flights actually take place. The distribution of successful flights is determined by the equilibrium distribution of par-

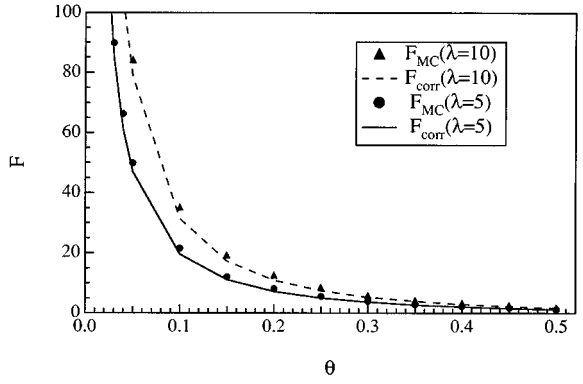

FIG. 3. Single-file mobilities measured from the same MC simulations as in Fig. 1 (filled symbols) and the single-file mobilities calculated from Eq. (8) (curves).

ticle spacings on the lattice. If only nearest-neighbor hops are allowed, there are no spatial correlations between particles when the system is at equilibrium [14]. For example, the conditional probability that a site adjacent to an occupied site is also occupied, P_1, is simply θ. However, if multisite hops can take place, the equilibrium configuration is more complicated. This fact is illustrated in Fig. 2, which shows the measured values of P_1/θ from the simulations described above. As indicated by Fig. 2, the presence of multisite hops increases the probability of finding particles close to one another relative to uncorrelated systems. These correlations appear because all flights that terminate due to the presence of another particle result in the creation of a pair of particles on adjacent sites and they are particularly marked at low loadings. More generally, multisite hops increase the probability of observing clusters of particles. This type of phenomenon has also been observed in simple models of hard-disk gases in which particles are allowed to collide inelastically [15–17]. The equilibrium distribution of particles in LG models is in general the steady-state solution of an infinite hierarchy of rate equations [14,18], which can only be found analytically in exceptional circumstances (such as a LG model with only nearest-neighbor hops [14]). It appears that the equilibrium state of the LG model with multisite hops can only be found from simulations such as those we have described above.

Despite the complicated equilibrium structures that are caused by multisite flights, if the actual flight distribution that occurs at a given loading is known, it is possible to predict the single-file mobility quite accurately using a generalization of Eq. (2). We define g_n to be the normalized flight-length distribution of hops that move particles at least one site. It is important to realize that g_n is a complicated function of the loading-dependent equilibrium structure and the free-particle flight distribution f_n. For example, if P_n is the probability that the closest occupied site to a particle in its direction of motion is n sites away,

$$g_1 = f_1 + \frac{P_2}{1-P_1} \sum_{n>1} f_n . \tag{6}$$

We can directly measure g_n from our MC simulations. We now define an effective diffusion coefficient D_{eff}, which is the single-particle diffusion coefficient of an isolated particle with flight distribution g_n [cf. Eq. (3)],

$$D_{\mathrm{eff}} = \frac{1}{2} \sum_n n^2 g_n , \tag{7}$$

and use this quantity in an expression analogous to Eq. (2),

$$F_{\mathrm{eff}} = \frac{(1-\theta)}{\theta} \sqrt{\frac{D_{\mathrm{eff}}}{\pi}}. \tag{8}$$

The results of this expression are compared with our direct measurements of $F_{\mathrm{MC}}(\theta)$ in Fig. 3. It can be seen from Fig. 3 that while Eq. (8) is not exact, it yields an accurate estimate of the single-file mobility at all loadings. In the examples we have examined, Eq. (8) typically underestimates F by 5–10 %. By contrast, if F is predicted by using Eqs. (2) and (3), the mobility is overestimated by as much as a factor of 3 at the highest coverages shown in Fig. 3. This type of overestimation has also been observed in MD simulations of single-file diffusion in $AlPO_4$-5 at temperatures where long flights are likely to occur [4]. Unfortunately, Eq. (8) can only be used predictively if the observed flight distribution g_n is known. While it is straightforward to calculate g_n if the particles are randomly distributed, the nonrandom distribution of particles in the presence of multisite hops causes the true g_n to deviate significantly from that expected for a random adsorbate distribution.

The extended LG model we have examined includes only a very simplistic description of the role of multisite hops in single-file diffusion. For example, it ignores any effects due to momentum transfer between particles as flights are terminated. Nevertheless, the model clearly demonstrates that the usual expression that has been used to relate $F(\theta)$ and D_0 [3] is not exact. Our results indicate two possible methods that could be used to exclude the effects of multisite flights and allow a direct quantitative connection to be made between experimental measurements of $F(\theta)$ [3,6] and the diffusivity of an isolated adsorbate: (i) measure F in the regime where $\theta \to 0$ or (ii) measure F at temperatures where the existence of multisite hops can be ruled out. Unfortunately, both of these suggestions lead to other significant difficulties. As mentioned above, the sensitivity of F to θ at low loadings makes accurate measurements very difficult as $\theta \to 0$, so suggestion (i) seems impractical. The difficulty associated with suggestion (ii) is perhaps even more important: at low temperatures the effect of attractive interactions between adsorbates, which is entirely ignored in the LG models discussed above, must be accounted for. We have recently studied the diffusion mechanisms of clusters of adsorbates in several systems exhibiting single-file diffusion and have found that in many cases attractive adsorbate interactions play a dominant role at low temperatures [19]. Until quantitative theories that account for the roles of adsorbate interactions and multisite hops are developed, the task of accurately extracting the diffusivity of isolated particles from experimental measurements of single-file mobilities should be approached with caution.

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