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Simulation of Diffusion and Adsorption in Zeolites

PETER H. NELSON,*,[1] ALAN B. KAISER,*,[2] AND DAVID M. BIBBY†

*Physics Department, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand and †DSIR Chemistry Division, Private Bag, Petone, New Zealand

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We show that Poisson-distributed event times are required to correctly simulate diffusion and adsorption in zeolites. The main microscopic assumptions of the diffusion model are: the zeolite is a periodic array of sites, each of which may contain only one molecule; and transport is achieved by sorbate molecules randomly "jumping" from one site to an adjacent site. Three simulation schemes for moving the molecules are compared; two of the schemes exhibit significant deviations from expected behavior, showing that seemingly reasonable schemes can introduce subtle correlations that have observable consequences. The preferred third scheme implements Poisson-distributed event times and exhibits no significant deviations from expected behavior—even for transient conditions and high occupancies. The simulation technique is then extended to independent Poisson-distributed events of more than one type. Specifically, adsorption events are added to the simulation, resulting in Langmuirian adsorption and concentration independent intralattice diffusion, in agreement with experimental results for some zeolites. The simulation correctly reflects the microscopic assumptions, thus placing this type of simulation on a sound theoretical foundation.

INTRODUCTION

Diffusion in zeolites has received much attention in the past due to zeolites finding increasing commercial applications and possessing an interesting pore structure of molecular dimensions. A simple model of the zeolite–sorbate system (*1, 2*) is that the zeolite contains a periodic array of interconnected sorption sites. Molecular migration of sorbate molecules through the array is assumed to proceed by thermally activated "jumps" from one site to an adjacent site.

Solution of this model by computer simulation has been performed (*3*) for a single molecule and extensions to more than one sorbate molecule have been presented (*4–8*). A feature of the model which does not appear to have received detailed attention is the way in which the molecular jumps are coordinated when there is more than one molecule present; this depends on the simulation scheme for moving the molecules. Simulations explicitly including events modeling adsorption from a gaseous phase have been presented (*4, 5*) but again the coordination of the two event types did not receive detailed attention. In addition, all of the previously reported simulations (with more than one molecule) exhibited unexpected deviations from mean field results.

The motivation for developing these simulation techniques for the study of diffusion and reaction in zeolites is that some processes occurring in zeolites are not easily modeled by traditional (continuum) methods but can be modeled by simulation techniques. A good example of such a process is the blocking of the channel network in the zeolite catalyst ZSM-5 by internal "coke" formed during methanol conversion to hydrocarbons. A simplified simulation of this process, using the techniques developed here, is presented elsewhere (*9, 10*).

[1] Present address: Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

[2] Address from present to August 1991: Max-Plank-Institut für Festkörperforschung, Postfach 800665, 7000 Stuttgart 80, West Germany.

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THE BASIC SIMULATION MODEL

The model assumptions, apart from the schemes for moving the molecules, are similar to those reported previously (*4, 5*). All the simulations reported here are based on an $M \times N$ two-dimensional zeolite lattice with one lattice site contained in the unit cell. Each of the lattice sites may contain one, and only one, molecule (exclusion of double occupancy). As a consequence of this last assumption the present model is more appropriate for zeolites with a pore structure than for those with a cage structure. The model is probably also applicable to numerous other systems, e.g., interstitial diffusion in a crystalline solid.

A molecule moves through the lattice by jumping from its current site to one of its (four) nearest neighbor sites. No movement occurs if the site in the direction chosen for an attempted jump is occupied. That is, there is no provision for a molecule colliding with a neighboring molecule, pushing it out of its current site and replacing it.

A fundamental physical constant in the simulations is τ, which is defined to be the average time between jumps of a single molecule in an otherwise empty lattice. With the assumptions stated above, τ is also the average time between attempted jumps of a specified molecule irrespective of the occupancy of the lattice.

For computational simplicity, the $M \times N$ lattice is surrounded with an extra layer of lattice sites, which is used to maintain the desired boundary conditions. The lateral edges of the lattice abut impermeable sites (in columns 0 and $M + 1$). The top row (1) of sites contains a fixed number C of initially randomly placed molecules, as does the row (0) above it, while the row $(N + 1)$ of sites below the bottom row contains zero molecules at all times t. At $t = 0$, all rows within the lattice except for the top row (rows 2 to N) are empty. For $t > 0$, molecules (denoted by ●'s) may jump into empty sites (+'s). With $M = 20$, $N = 20$, and $C = 10$, the lattice will typically be as shown in Fig. 1 for a lattice at steady state.

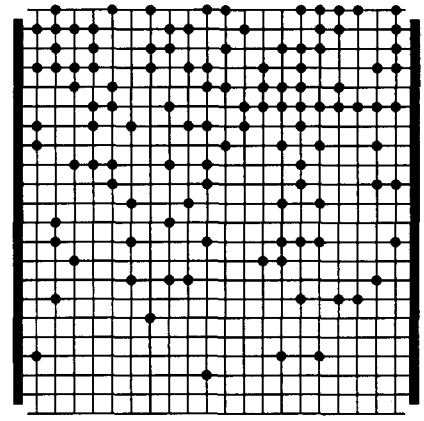

FIG. 1. A typical configuration of a 20 × 20 lattice at steady state. The extra rows at the top and bottom of the lattice are included to simplify maintenance of the constant concentration boundary conditions. The ●'s represent mobile sorbate molecules.

Attempted jumps of molecules contained within the $M \times N$ lattice are coordinated according to the different schemes discussed below. The boundary conditions for row 1 are maintained after the jump of each molecule by placing a molecule in a randomly selected vacant site or removing a randomly selected molecule as required, and similarly for the extra rows 0 and $N + 1$. As a result of this, there is only one type of independent event in the simulation—the attempted jump of a molecule. The above boundary conditions were chosen so that the simulation schemes could be implemented and compared without the complication of coordinating two types of independent events. More realistic boundary conditions are discussed later.

The Finite Difference Approximation

The finite difference approximation (FDA) is a simple approximation to the diffusion equation; for example see (*11*). The motivation for using the FDA, as opposed to a continuum formulation, is that zeolites have a periodic channel network which corresponds more closely to a finite difference

grid than to a continuum. This approach has been used previously to investigate the effective diffusivity in partially blocked zeolite lattices (*12*).

In the zero concentration limit, the FDA form of Fick's second law of diffusion can be written (*13*)

$$\delta C_n = \Gamma \delta t\{C_{n-1} + C_{n+1} - 2C_n\} \quad (1)$$

for a finite difference grid corresponding to the simulation lattice. C_n represents the average number of molecules in the n^{th} row of the lattice and δC_n is the change in the average number of molecules in row n during a short time δt. Γ is the probability per τ that a molecule jumps from one row to an adjacent row in the zero concentration limit. The diffusion constant is $D = \Gamma(\delta x)^2$, where δx is the distance between rows of lattice sites.

In our simulations the value for Γ is $\frac{1}{4}$ per τ, since when a molecule jumps it has one of four directions to move in, only one of which results in the molecule moving to a specified adjacent row.

Concentration Dependence of the FDA

The consequences of exclusion of double occupancy for a lattice not at the zero concentration limit have been considered by Slavin and Underhill (*14*) for interstitial diffusion in a crystalline solid. Adapting their analysis to the present situation results in the jump probabilities between rows depending on the number of molecules C_m in the row into which the molecule is attempting to jump. I.e., the jump probability from row n to row m is

$$\Gamma_{n,m} = \Gamma(1 - C_m/C_{\max}), \quad (2)$$

where $C_{\max}$ is the maximum number of molecules in row m. The term $C_m/C_{\max}$ is the proportion of attempted jumps from row n in the direction of row m which does not result in a molecule moving from row n to row m as a result of nearest neighbor interactions preventing a molecule jumping to an occupied site. Equation (2) means that if row m is empty the zero concentration limit is obtained; however, if row m is completely occupied then $\Gamma_{n,m}$ is zero.

Using the value for $\Gamma_{n,m}$ given in Eq. (2), the change in the concentration for row n can be written

$$\begin{aligned}\delta C_n = \Gamma\delta t\{&(1 - C_n/C_{\max})C_{n-1} \\ &+ (1 - C_n/C_{\max})C_{n+1} \\ &- (1 - C_{n-1}/C_{\max})C_n \\ &- (1 - C_{n+1}/C_{\max})C_n\} \\ &= \Gamma\delta t\{C_{n-1} + C_{n+1} - 2C_n\}\end{aligned}$$

which is identical to Eq. (1)! This perhaps surprising result means that our finite concentration model should obey Fick's second law with constant D, despite the strong concentration dependence of the individual jump probabilities between rows. This result may be rationalized by noting that the reduction in the number of molecules which jump from row $n - 1$ to row n during δt is the same as the reduction in the number of molecules which jump from row n to row $n - 1$ during δt. In general, this concentration independence can only be expected for the nearest neighbor interactions assumed here.

THREE SIMULATION SCHEMES

Scheme 1

Scheme 1 is based on a simulation scheme used previously (*4, 5*). The basic event is the *ordered* attempted jumping of all the molecules in the $M \times N$ lattice. At the beginning of the simulation the $M \times N$ lattice is empty. C molecules are then randomly inserted into row 1 with the order of insertion being recorded. C molecules are also inserted into randomly selected positions in row 0 but these molecules do not attempt to jump. The simulation then proceeds with a jump attempt for each molecule in order of decreasing age (oldest first). The basic time interval, for this scheme, is the time taken for all the molecules in the lattice (rows 1 to N) to attempt to jump and is equal to τ. We therefore use $\delta t = \tau$ in the corresponding FDA.

Scheme 2

In scheme 2, the basic event is the attempted jump of one molecule. The molecule is selected, at random, from all those contained in the $M \times N$ lattice before the attempted jump. The physical unit of time (δt), corresponding to the time interval between attempted jumps, is taken to be the average time interval between an attempted jump of any one of the molecules in the lattice and the next attempted jump of any one of the molecules in the lattice, which, assuming the rate of attempted jumps of each molecule is independent of the others, is (*10*)

$$\delta t(S) = \tau/S, \tag{3}$$

where $S = S(t)$ is the number of molecules in the $M \times N$ lattice before the molecule attempts to jump. We therefore let δt be a function of S according to Eq. (3) in the corresponding FDA.

Scheme 3

The previous schemes were based on a deterministic time interval between basic events. In scheme 3, which is similar to scheme 2, the molecules are moved in the same manner but $\delta t(S)$ is now a continuous stochastic variable, with an expected probability distribution as derived below. This means that the configuration of the lattice, according to schemes 2 and 3, is the same after n similar steps but the time associated with the configuration will, in general, be different.

Let us consider a lattice containing a fixed number of molecules, S. Further let $\mu = \mu(S)$ be the average rate of attempted jumps for all the molecules in the lattice. Now, if the Poisson assumptions are made that all molecules are identical and independent with respect to their rate of attempted jumps, and the probability of an attempted jump for any molecule in equal time intervals is a constant, then the expected probability distribution for the number of attempted jumps, per unit time, is given by the Poisson distribution. The expected distribution for the inter-attempted jump time $P_{\text{int}}(t)$ is therefore

$$P_{\text{int}}(t) = \mu e^{-\mu t}, \tag{4}$$

where the average time interval between attempted jumps is $1/\mu$.

Representative time intervals, for the expected distribution (4), can be generated (*10*) from a uniformly random integer r in the range 0 to 32767 inclusive (i.e., 0 to $2^{15} - 1$) by assigning to each random integer r, a representative time interval $t_{\text{ave}}(r)$ which is given by

$$t_{\text{ave}}(r) = \frac{-2^{15}}{\mu}\left[r_2 \ln(r_2) - r_1 \ln(r_1) - \frac{1}{2^{15}}\right], \tag{5}$$

where

$$r_1 = 1 - \frac{r+1}{2^{15}} \quad \text{and} \quad r_2 = 1 - \frac{r}{2^{15}}.$$

The value of 2^{15} can, of course, be replaced by the appropriate power of two for any random number generator.

In the simulation a real valued variable is associated with time; this variable is incremented by $\delta t(S) = t_{\text{ave}}(r)$ to determine the time of occurrence of the next attempted jump. The molecule which will attempt to jump is selected, at random, from those contained within the lattice. If the selected molecule leaves the lattice, or if a new molecule enters the lattice (as a result of the boundary conditions), then the value for μ changes for the next value of $t_{\text{ave}}(r)$.

We compare this scheme to the FDA with a very small value of δt, e.g., $\delta t = \tau/10000$. Using this value for δt there is no significant difference between the FDA values and values from a continuum time formulation at the FDA grid points.

Results for the Three Schemes

Simulations using the schemes set out above were conducted on 1×3 and 20×20 lattices. A large number (see below) of simulation runs were averaged to reduce the

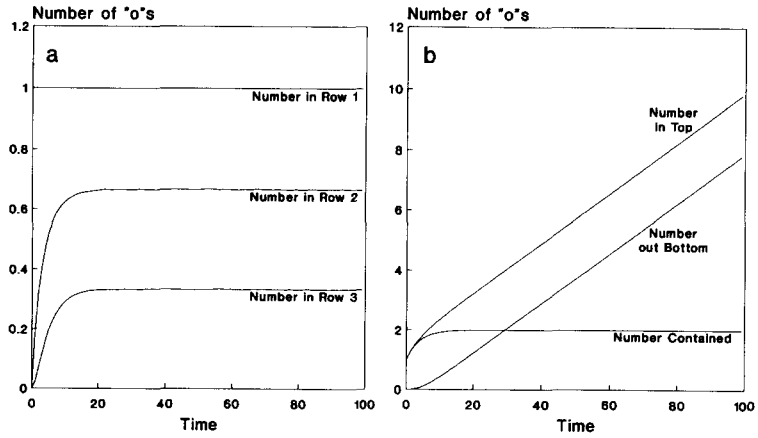

FIG. 2. Averaged output from $n = 500{,}000$ simulation runs of a 1×3 zeolite lattice for the preferred scheme 3 employing Poisson-distributed event times. Time is given in units of τ (see text). (a) molecules contained in each row. (b) molecules contained, entering and exiting.

statistical uncertainty in the data. $\Sigma S(t)$ and $\Sigma S(t)^2$ were extracted from the simulations at predefined points in time. These values were used to calculate the mean values of $S(t)$ and the standard error of the mean values for $S(t)$. The sample standard deviations, $s(t)$, for $S(t)$ were calculated using

$$s(t)^2 = \frac{n\Sigma S(t)^2 - (\Sigma S(t))^2}{n(n-1)}, \qquad (6)$$

where n is the number of simulation runs averaged. $\sigma_\mu(t)$, the standard errors of the mean values for $S(t)$, were estimated using

$$\sigma_\mu(t)^2 = s(t)^2/n, \qquad (7)$$

where $s(t)^2$ is given by Eq. (6).

The mean values and standard errors of the mean values for the number of molecules in each row and for the accumulated fluxes into and out of the lattice were determined similarly (*10*).

1 × 3 Lattice

In these simulations $M = 1, N = 3, C = 1$, and $n = 500{,}000$. M and C were chosen to investigate any possible concentration dependence of diffusion in a narrow channel. Narrow channels may be formed in ZSM-5, for example, during methanol conversion as a result of site blocking deactivation processes. For each scheme the results are compared with the FDA. δt in the FDA was chosen, where possible, to correspond to δt in the simulation, as discussed above.

Figure 2a shows the average number of molecules in each of the three rows as a function time, in units of τ, for scheme 3. Steady-state values are reached at about $t = 30\tau$ and are $\frac{2}{3}$ and $\frac{1}{3}$ for C_2 and C_3, respectively. These values correspond to a linear decrease from row 1 to row 4, rows 1 and 4 being fixed at 1 and 0 molecules, respectively.

Figure 2b shows: $S(t)$, (number contained); $I_{top}(t)$, the average accumulated number of molecules that have entered the top edge of the lattice (number in top); and $E_{bot}(t)$, the average accumulated number of molecules that have exited the bottom edge of the lattice (number out bottom). At steady state $S(t)$ is constant at 2. The initial value of $S(t)$ is 1 as the boundary conditions require that there be one molecule in row 1 at time $t = 0$. At steady state, the slopes of $I_{top}(t)$ and $E_{bot}(t)$ are constant and equal to the same value, the flux into the lattice being equal to the flux out of the lattice. The value of the steady-state slope for $I_{top}(t)$ and $E_{bot}(t)$ is $\frac{1}{12}$, which is equal to DC/N.

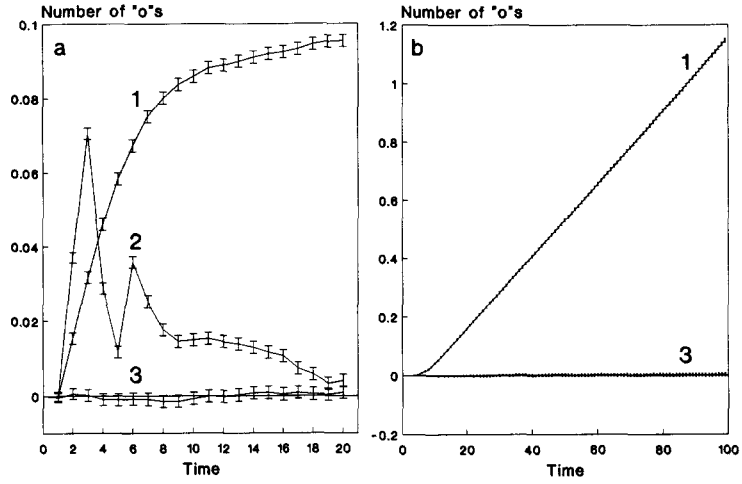

FIG. 3. Deviation between the average of $n = 500{,}000$ simulation runs and corresponding FDA values for a 1×3 lattice. Error bars correspond to two standard errors of the mean value. (1) scheme 1. (2) scheme 2. (3) scheme 3—Poisson-distributed event times. (a) $S(t)$—number contained (c.f. Fig. 2a). (b) $E_{bot}(t)$—number exiting (c.f. Fig. 2b).

Figure 3a shows the difference between the simulation and corresponding FDA values of $S(t)$ (simulation data minus FDA value) for the three schemes. The error bars correspond to plus or minus two standard errors of the mean as estimated by Eq. (7) and hence correspond to the 95% confidence interval for the population mean. For scheme 1, the deviation from the FDA increases with time, approaching a constant deviation of about 5% at steady state. The deviation of the simulation from the FDA for scheme 2 is large for transient conditions ($t < 20\tau$) but approaches zero in the steady state ($t \rightarrow \infty$). For scheme 3, there are no significant deviations from the values expected from the FDA for transient conditions as shown in Fig. 4. In addition, the steady-state behavior of scheme 3 exhibited no significant deviations from the FDA.

Figure 3b shows the difference between the simulation and FDA values for $E_{bot}(t)$, the accumulated flux out of the bottom of the lattice, for schemes 1 and 3. The corresponding values for scheme 2 are not shown in this figure, for clarity. The deviation for scheme 1 is more pronounced in this figure, the incremental errors being cumulative. The steady-state flux for scheme 1 is about 15% greater than expected from the FDA. In contrast to scheme 1, scheme 3 exhibits no significant deviations from the corresponding FDA.

20 × 20 Lattice

To investigate any dependence of the deviations on the size of the lattice or on concentration, two simulations using each of schemes 1 and 3 were conducted on a 20×20 lattice. In the first, C was fixed at 20 molecules and in the second, C was fixed at one molecule. In the $C = 20$ simulations, the top row was always completely occupied as it was in the 1×3 simulations. As can be seen in Fig. 4a, increasing the size of the lattice does not reduce the steady-state deviation in the flux through the lattice for scheme 1. The deviation in the flux is in fact slightly larger being 18% at steady state. However, increasing the size of the lattice does not have any adverse effect on $E_{bot}(t)$ for scheme 3.

For the $C = 1$ simulations, Fig. 4b, scheme 3 again shows no significant deviations from the corresponding FDA. However, for scheme 1, the positive discrepancy

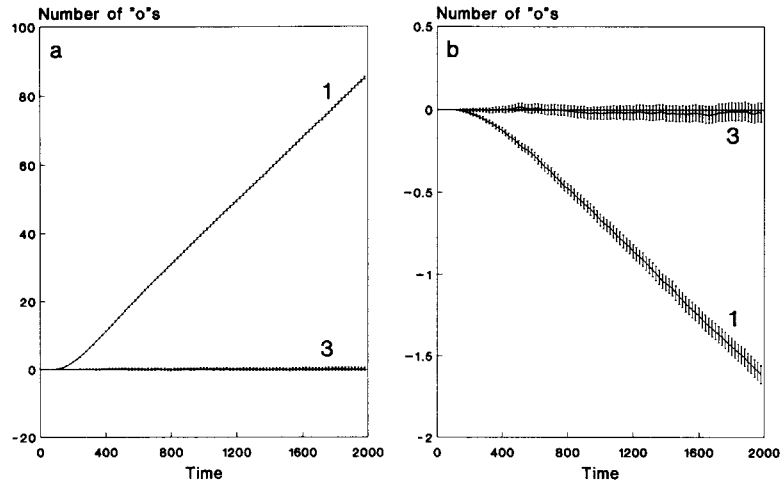

FIG. 4. Deviation between simulation and FDA values for $E_{bol}(t)$ for a 20 × 20 lattice at (a) high occupancy (C = 20 at top edge) and (b) low occupancy (C = 1 at top edge).

for the steady-state flux disappeared, and was replaced by a small (8%) negative deviation that is an artifact of the constant concentration boundary condition in conjunction with the sequential scheme for moving the molecules (*10*).

Discussion of the Three Schemes

Scheme 3 implements Poisson-distributed event times and behaves as expected from the FDA. Scheme 2 does not utilize Poisson-distributed event times, as the time interval between attempted jumps of molecules is set at the average value. During this fixed time interval no molecules, other than the one selected, may attempt to jump, which means that the molecules are not independent with respect to their instantaneous rate of attempted jumping and the rate of attempted jumps for any molecule is not constant as required. As scheme 2 does not behave as predicted by the FDA and scheme 3 does, we can conclude that Poisson-distributed event times are required for concentration independent diffusion. Scheme 2 indirectly results in Poisson-distributed event times when the number of molecules in the lattice becomes large, $S \rightarrow \infty$.

Scheme 1 does not utilize Poisson-distributed event times as the molecules are not identical, since each has a unique "age"; nor are the molecules independent, since all attempt to jump once each δt. For scheme 1, the ordering of the movement of the molecules will mean that the molecules in the 1 × 3 lattice will be spatially arranged in order of increasing age from the top to the bottom of the lattice. This means that the lowest molecule will attempt to jump first. If this molecule jumps downward, then a molecule above it will be able to jump downward and take its place within the same τ. This results in unexpected "group migrations" as in Ref. (*4*) which can occur even for large lattices. We can therefore conclude that care must be taken to ensure that the Poisson assumptions are met. For more detailed discussion of the causes of the deviations exhibited by the simulations and for a more detailed explanation of why scheme 3 reproduces concentration independent diffusion see (*10*).

A simulation has been reported very recently (*8*) which has boundary conditions similar to those used in this paper. The net flux through one of the boundaries was used for comparison with Fick's first law that the net flux (at steady state) is proportional to

the diffusion coefficient for a fixed-size lattice. The results for the diffusion coefficient, from simulations with assumptions equivalent to those used here (Fig. 5 of (*8*)), show relatively large reproducible fluctuations (up to 20%) from the constant value of $\frac{1}{4}$ predicted by the FDA that were not the result of low statistical significance. However, using their method to estimate D for our scheme 3 simulations results in $D = 0.25000 \pm 0.00007$ for the 1×3 lattice, and $D = 0.2498 \pm 0.0005$ and $D = 0.2502 \pm 0.0002$ for the 20×20 lattice with $C = 1$ and 20, respectively.

These results reinforce our conclusion that care must be taken when selecting a scheme for moving the molecules if the simulation is to behave as expected.

EXTENSION TO GASEOUS BOUNDARY CONDITIONS

The preferred simulation model is now extended to independent events of more than one type. In particular, attempted insertions (adsorption) of molecules into the edge of the lattice from a gaseous phase are added to the simulation. We will ensure that these events are Poisson distributed, and that the jump attempts remain Poisson distributed. The technique presented can easily be modified for any simulation in which there are one or more types of events which occur independently of each other.

The motivation for modifying the boundary conditions is that those used above (a fixed number of molecules *always* present at the edge of the lattice) are not particularly realistic.

Gaseous Boundary Conditions

For computational simplicity the edges of the lattice are surrounded by a layer of fictitious "external sites" which are used to implement the desired boundary conditions. For an edge site exposed to the gaseous phase at a pressure, given by a pressure parameter β, β insertion attempts from the gas are made, on average, into the edge site per τ. These insertion attempts correspond to collisions of gaseous molecules with an entrance to the edge site. If the site is not occupied then a molecule is inserted into the site. Otherwise, if the site is occupied, no molecule is inserted (exclusion of double occupancy). The corresponding external site contains zero molecules at all times. This means that if a molecule in an edge site attempts to jump out of the lattice, then it will always leave.

FDA with Gaseous Boundary Conditions

The incremental change δC_1 in the top edge row which is exposed to a constant pressure $P = M\beta$ can be obtained (*10*) by considering the average number of molecules that move into or out of row 1 during δt:

$$\delta C_1 = r\{B_0 + C_2 - 2C_1\}, \qquad (8)$$

where

$$B_0 = (P/\Gamma)(1 - C_1/C_{\max}).$$

B_0 may be thought of as the effective number of molecules in row 0 for the FDA. It should be noted that B_0 is not a constant and, in general, decreases with time for the boundary conditions considered here. Analysis for the bottom row is similar and is not set out. The fluxes into and out of the lattice can also be easily determined (*10*).

In the continuum limit $N \to \infty$, and the length of the crystal, L, is much larger than the distance between rows. In addition, the time taken for the concentration at the top edge to reach equilibrium with the gas is short, compared with the characteristic time for the diffusion problem (L^2/D). Hence, for $t > 0$, the concentration c_0 at the edge of the lattice, in the continuum limit is given by (*10*)

$$c_0 = \beta/(\Gamma + \beta) \quad \text{for } t > 0, \qquad (9)$$

which is a Langmuir isotherm (*15*).

Coordination of Different Event Types

There are two types of independent events which can occur in a simulation with gaseous boundary conditions: (a) an at-

tempted jump of a molecule and (b) an insertion attempt of a molecule from the gaseous phase. It can be shown (*10*) that if there are k types of *independent* events with corresponding average rates μ_i for $i = 1$ to $i = k$, all of which are governed by a different Poisson distribution, with $\mu_i t$ events of type i occurring in a time t (on average), then the expected distribution of the inter-event time, $P_{\text{int}}(t)$ irrespective of the type of event that occurs next is given by Eq. (4), where $\mu = \Sigma\mu_i$. The probability that an event selected at random is of type i is $P_i = \mu_i/\mu$.

Applying this to the simulation of diffusion through a membrane, there is an average instantaneous rate of $S(t)$ attempted jumps per τ and an average rate of P insertion attempts per τ into the top edge. These events are assumed to be independent of each other at any given instant in time. The expected distribution of the inter-event time, irrespective of the type of event, is therefore given by Eq. (4), where μ is equal to $S + P$. The probability that an event chosen at random is an attempted jump is given by

$$P_J = S/(P + S). \tag{10}$$

The probability that an event chosen at random is an insertion attempt is thus $1 - P_J$.

In the simulation, time intervals between events are again generated from a random integer r using Eq. (5). The type of event which occurs next is determined from Eq. (10). This can be done as we have assumed that the different types of events are independent of each other.

Membrane and Uptake Simulations

Simulations having gaseous boundary conditions and employing Poisson-distributed event times were conducted (*10*) for diffusion through 1×3 and 20×20 membranes. Both high- and low-occupancy situations were investigated as above. In addition, high- and low-pressure uptake diffusion into a 20×20 lattice was simulated (*10*) with the top and bottom edges exposed to a gas at constant pressure. The number of sorbate–sorbate "collisions" was also stored in the uptake diffusion simulations. A collision was defined to occur in the simulation when a molecule attempted to jump into an already occupied site. The collision rate in the FDA can be determined (*10*) by considering the proportion of attempted jumps (or insertion attempts) into a given site which are prevented by a molecule being at that site.

A comparison, similar to that discussed above, showed (*10*) that the simulation results for all the variables stored exhibited no significant deviations from the corresponding FDA values. These null results confirm the FDA theory by simulation both for diffusion through a membrane and uptake diffusion. In addition, the null results show that independent Poisson-distributed events, of more than one type, result in a simulation that behaves as expected.

Equilibrium Occupancy

For uptake diffusion with the boundary conditions used here the equilibrium occupancy of the lattice, θ, is given (*10*) by

$$\theta = \beta/(\Gamma + \beta), \tag{11}$$

which is a Langmuir isotherm and is equivalent to Eq. (9). This result is independent of the size of the lattice and can easily be derived from Eq. (8) since $\delta C_1 = 0$, $C_1 = C_2$, and $\theta = C_1/C_{\max}$ for uptake diffusion at equilibrium.

The two 20×20 uptake simulations (with $\beta = 0.005$ and 0.5) agreed with Eq. (11). To confirm that the simulation behaves as expected for a wider range of pressures, simulations with pressures ranging over six orders of magnitude were conducted. The duration of each of the simulations was chosen so that the lattice was essentially at equilibrium. As shown in Table 1, all the observed values agree (within statistical uncertainty) with the values predicted by the FDA in Eq. (11). The time taken for the lattice to reach equilibrium varies because the rate at which the edges reach equilibrium

TABLE 1

Expected (FDA) and Observed (Simulation) Values of Equilibrium Occupancy (θ)

β (Pressure)	θ^a FDA	θ^b Simulation	T^c Simulation
249.75	0.999	0.9989 ± 0.0001	0.07
24.75	0.99	0.9897 ± 0.0003	0.7
2.25	0.9	0.8997 ± 0.0009	7.0
0.25	0.5	0.500 ± 0.002	40.0
0.027778	0.1	0.100 ± 0.001	60.0
0.0025253	0.01	0.0101 ± 0.0003	70.0
0.0002503	0.001	0.0010 ± 0.0001	70.0

[a] Langmuir isotherm, Eq. (11).

[b] Average occupancy from 100,000 2 × 2 lattice simulations at time T.

[c] Approximate time for the lattice to reach equilibrium

with the gas is dependent on the pressure. This delay is correctly predicted by the FDA and is most prominent for small lattices (*10*).

Comparison with Previous Simulations

Theodorou and Wei (*4, 5*) performed simulations to investigate the effect of occupancy and pore blocking on a simple isomerization reaction under equilibrium conditions. As the diffusivities of the two species were identical, the results should be the same as for a single species (for combined occupancy at steady state). The results for these simulations showed deviations from expected behavior which were attributed to the "finiteness" of the crystal (11 × 11 sites). For example, the maximum occupancy (for infinite pressure) was found to fluctuate between 0.90 and 0.97 as opposed to full occupancy as expected.

Another effect, noted by Theodorou (*5*), was a reduction in equilibrium occupancy of a border blocked lattice with $\beta = \frac{1}{8}$ per unblocked border site. From Eq. (11) one would expect that at equilibrium each of the accessible *unblocked* sites would have an occupancy of $\theta = \frac{1}{3}$. The value obtained by Theodorou was 0.1263 ± 0.0009. Simulation of diffusion in an 11 × 11 lattice with only one unblocked edge site was conducted using Poisson-distributed event times as discussed above. The equilibrium occupancy was measured at 5000τ, and 2000 runs were averaged. The value obtained in this way was 0.332 ± 0.002, which is as predicted by the FDA (within statistical uncertainty).

We can therefore conclude that the two previously reported deviations discussed above were due to the simulation scheme not employing Poisson-distributed event times. There is a "finiteness" effect in the present simulation but this relates to the time required for the exposed edges to reach equilibrium with the gas. This effect is accounted for by the FDA and becomes less important as the size of the lattice is increased (*10*).

Comparison with Experiment

Membrane experiments having boundary conditions similar to those used here have been reported by Hayhurst and Paravar (*16–18*). The outflow, $E_{bot}(t)$, was determined by measuring the increase in pressure on the "vacuum" side of the crystal. The crystal used in the experiments (*16–18*) was large ($N \approx 10^5$) so that a continuum solution for $E_{bot}(t)$ can be used. This solution is given (*11*) by an infinite series solution which becomes linear at long times. The intercept of the line on the time axis is $L^2/6D$, the so-called time lag, which is independent of the concentration (pressure) in the top row.

It should be noted that the values for the time lag are *not* independent (*10*) of the inflow pressure for finite N in the FDA and simulations with gaseous boundary conditions. However, as the depth of the lattice (N) is increased, the values of the time lag tend to the same value for different pressures (*10*) and the continuum limit is approached as N is increased. This trend can be understood in terms of the finiteness effect discussed above.

For each species tested by Hayhurst and Paravar (*16–18*), the time lag was found to be independent of the (constant) inflow pressure. A relatively wide range of occupancies were investigated. They concluded that the diffusion coefficient for each species was

independent of the diffusant concentration. The diffusion coefficient determined (*17*) by measuring the slope of the steady-state portion of the outflow curve was identical with the value obtained from the time lag method (within experimental error), as was the diffusion coefficient determined by gravimetric sorption uptake experiment. Thus, the results and conclusions of Hayhurst and Paravar (*16–18*) are consistent with the simple model simulated here.

Equilibrium sorption isotherms for *n*-butane and *iso*-butane reported in (*17*) were fitted (*10*) to Eq. (11). The resulting fitted isotherms were quite good for pressures resulting in fitted occupancies of less than 90%, i.e., for pressures over nearly two orders of magnitude. The region of good fit includes the inflow pressures used in the membrane experiments (*16–18*).

Sorption (uptake experiments) into zeolite ZSM-5 with an Si/Al ratio of 23 was investigated by Prinz and Riekert (*19*), as opposed to sorption into silicalite. They reported that "sorption of benzene in the same sample follows exactly and reproducibly the solution of the diffusion equation for a plane sheet with constant diffusivity." This is in complete agreement with the model presented here. It therefore appears that benzene is a "good" sorbant in ZSM-5. This is supported by the finding (*7*) that benzene resides at the channel intersections at low occupancies. It should be noted, however, that the experimental results (*19*) for more elongate sorbate molecules showed results which deviated from concentration independent (Fickian) diffusion at long times.

The simulation model presented here therefore appears to be a reasonable first-order approximation for adsorption and diffusion in some zeolites. For a more complete discussion see (*10*).

CONCLUSIONS

In all of the simulations discussed here, only those implementing Poisson-distributed event times behaved as expected from the corresponding numerical model. Previously reported simulations, and those presented here which did not implement Poisson-distributed event times, all exhibited deviations from expected behavior.

It appears that for a simulation to behave as expected it must meet the Poisson assumptions that: all events of a given type are identical and independent with respect to their rate of occurrence; and the probability of any possible event of a given type in equal time intervals is a constant. When formulating simulations care must be taken to ensure that these conditions are met (when appropriate). We recommend that any new simulation developed be verified (if possible) by simulating a system for which a numerical (FDA) solution is available to ensure that no unwanted correlations are present.

We have confirmed by simulation that diffusion with nearest neighbor interactions preventing double occupancy is concentration independent, even for large concentrations of diffusing molecules, so long as Poisson-distributed event times are used. This justifies the use of an FDA-like approach (*12*) in the determination of the diffusivity in zeolites with partially blocked pores, not only in the zero concentration limit, as stated in (*12*), but for all concentrations (if the present diffusion model is appropriate).

Techniques for simulating two or more types of independent Poisson-distributed events have been presented. In particular, adsorption events were introduced into the simulation resulting in a Langmuir equilibrium adsorption isotherm for simulated crystals with uptake boundary conditions. Intra-lattice diffusion remained concentration independent as before. This is in agreement with experimental results for some zeolite/sorbate systems, for which a Langmuir isotherm is also a reasonable first-order approximation.

The simulation scheme for producing Poisson-distributed event times is extendible to any simulation having independently occurring discrete events. For example, generalization to a three-dimensional system with a cubic lattice is relatively straightforward. Each site will then have six nearest

neighbors so that Γ will be $\frac{1}{6}$ for jumps from one plane to another. In light of the results presented here, we expect deviations due to unphysical correlations unless Poisson-distributed event times are used. Other types of simulations may also benefit from employing Poisson-distributed event times. For example, the 2D Ising model (e.g., (*20*)) has five types of independent events determined by the number of nearest neighbor sites with the same spin.

The simulations presented here employing Poisson-distributed event times are entirely self-consistent, and agree with numerical predictions (within statistical uncertainty), thereby providing a sound theoretical foundation, into which further microscopic features such as reactions and coking can be added (e.g., (*9, 10*)); one can then have confidence that the simulation implements the conceptual model correctly. It is hoped that the techniques presented here will stimulate further investigation of heterogeneous catalysis.

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