Diffusion in zeolites via cage-to-cage kinetics: Modeling benzene diffusion in Na-Y

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We have performed kinetic Monte Carlo simulations of benzene diffusion in Na-Y (Si:Al=2.0) over the temperature range 200–500 K. For hopping on a tetrahedral lattice, we derive the analytical formula for D in terms of hopping lengths and times, yielding the simple-cubic relation $D = \frac{1}{6}ka^2$, even though the lattice is very different from simple cubic. We have calculated the distribution of cage residence times for benzene in Na-Y, finding single exponential decay controlled by the $S_{II} \rightarrow W$ rate coefficient, even though several processes contribute to intercage motion. Exact agreement between mean square displacement slopes and $\frac{1}{6}ka^2$ is obtained only when using kinetic intercage hopping lengths, which are found to be in excess of the static length by as much as 0.54 Å. Constructing diffusion coefficients from intercage lengths and times provides overwhelming computational speedups over calculating mean square displacements. © *1996 American Institute of Physics.* [S0021-9606(96)50833-0]

I. INTRODUCTION

The transport properties of adsorbed molecules[1] play a central role in catalytic and separation processes[2] that take place within zeolite cavities.[3] Understanding the host–guest interactions that control molecular diffusion may suggest new materials with advanced performance. We have recently calculated[4] self-diffusion coefficients for benzene at infinite dilution in Na-Y zeolite (Si:Al=2.0) over the temperature range 100–500 K.[5–11] Figure 1 shows the Na-Y supercage containing four tetrahedrally arranged Na^+ ions and four tetrahedrally arranged 12-ring windows connecting adjacent supercages. Figure 1 also shows a benzene hopping path from the S_{II} site over a Na^+ ion, to the W site in the 12-ring window. The calculated diffusion coefficients, shown in Fig. 2, are obtained from kinetic Monte Carlo[4,12–14] (KMC) simulations in which benzene executes random, uncorrelated jumps among S_{II} and W sites with frequencies determined by input rate coefficients. Although the apparent activation energy in Fig. 2 is precisely that for the $S_{II} \rightarrow W$ jump shown in Fig. 1, it is not immediately clear how to extract fundamental length and time scales from the diffusion coefficients. In the present paper, we report the use of analysis and simulation to determine which length and time scales control benzene diffusion in Na-Y.

Understanding the length and time scales which control two-dimensional surface diffusion of, e.g., atomic hydrogen on Ni(100) is more straightforward.[15,16] Figure 3 shows the square-lattice model of H diffusion on Ni(100). In the single-hop model, the diffusion coefficient satisfies $D = \frac{1}{4}ka^2$, where a is the lattice parameter (cf. Fig. 3), $1/k$ is the mean site residence time, and $k/4$ is the site-to-site hopping rate coefficient. In order to apply this formulation to benzene diffusion in Na-Y, we need to answer three questions: Does an analytical formula relate D to residence times and hopping lengths? How does the residence time relate to a site-to-site rate coefficient? Which lattice parameter determines the diffusive length?

The simplicity of the square-lattice model derives from having only one site type, while the complexity of benzene in Na-Y derives from having multiple sites. We can simplify the motion of benzene in Na-Y by imagining that—although hops really take place among S_{II} and W sites—long-range motion involves jumps from one ''cage site'' to an adjacent ''cage site.''[17–21] As such, all the S_{II} and W site structure within a cage becomes the internal structure of the cage site. A random walk through Na-Y reduces to hopping on the tetrahedral lattice of supercages, shown in Fig. 4. The diffusion coefficient would then be determined by cage residence times and cage-to-cage hopping distances. This paper is devoted to calculating these quantities and identifying their meaning, in order to construct diffusion coefficients which exactly match those from mean square displacements.

The remainder of this paper is presented as follows: Section II gives a heuristic treatment of diffusion on a tetrahedral lattice in terms of intercage lengths and times. The rigorous proof for the result of Sec. II is presented in the Appendix. Section III calculates mean cage residence times for benzene in Na-Y with KMC methods, and determines how these residence times relate to fundamental jump rates. Section IV calculates mean cage-to-cage hopping lengths with KMC, and combines these with the results of Secs. II and III to construct diffusion coefficients which exactly match those from mean square displacements.

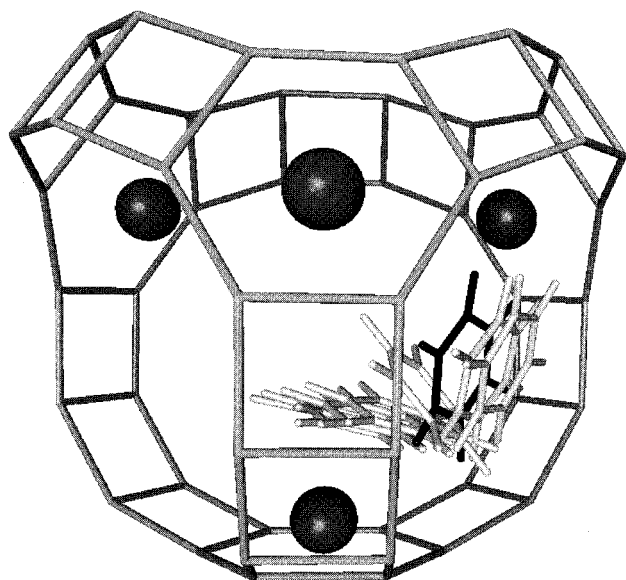[a)]Author to whom correspondence should be addressed.

FIG. 1. Supercage of Na-Y containing four tetrahedrally arranged Na^+ ions, and four tetrahedrally arranged 12-ring windows connecting adjacent supercages. The benzene closest to the left is strongly bound to a Na^+ ion 2.7 Å away, at the so-called S_{II} site. The benzene closest to the right is weakly bound in a 12-ring window, at the so-called W site. The intermediate benzenes show the minimum energy $S_{II} \rightarrow W$ hopping path, with the bold benzene at the transition state.

II. DIFFUSION ON A TETRAHEDRAL LATTICE

We begin our treatment of diffusion on a tetrahedral lattice by first considering diffusion on a simple-cubic lattice. These two lattices are related in that they both fill three-dimensional space with only a single lattice spacing length scale. It is straightforward to show that a random walk consisting of N single jumps on a simple-cubic lattice with lattice spacing a yields the mean square displacement $\langle R^2(N) \rangle = Na^2$.[1] Assuming the average site residence time is $1/k$, such that $N=kt$ for long times, we obtain
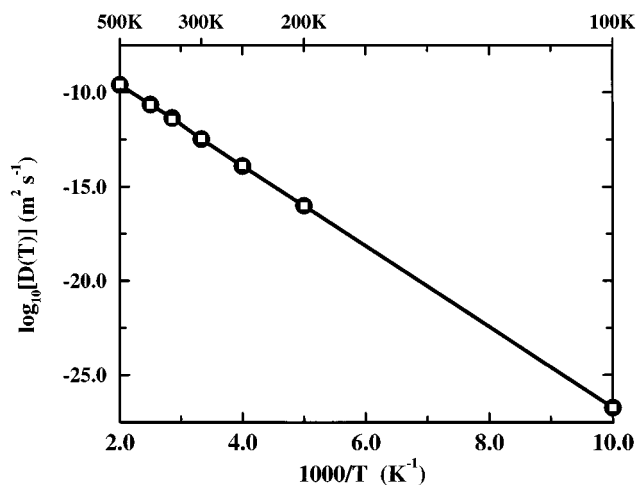

FIG. 2. Temperature dependence of calculated diffusion coefficients for benzene in Na-Y giving Arrhenius parameters $E_a = 41$ kJ mol^{-1} and $D_0 = 4.8 \times 10^{-6}$ m^2 s^{-1}.
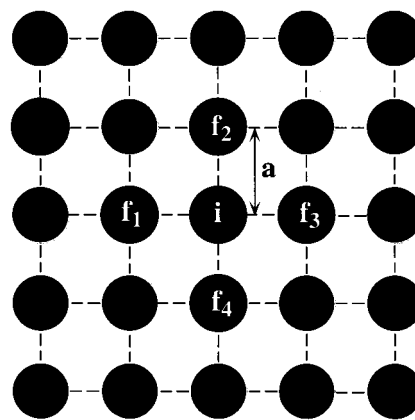

FIG. 3. Square-lattice model of two-dimensional diffusion with hopping length a, mean site residence time $1/k$, and diffusion coefficient $D = \frac{1}{4}ka^2$. The four allowed jumps $[i \rightarrow f_1, \ldots, i \rightarrow f_4]$ all have rate coefficient $k/4$.

$\langle R^2(t) \rangle = kta^2$. By equating this with the Einstein expression in three dimensions, $\langle R^2(t) \rangle = 6Dt$ where D is the diffusion coefficient, we find that $D = \frac{1}{6}ka^2$. This expression provides a simple interpretation of molecular diffusion in, e.g., Na-A zeolite which consists of cubic cages, each with six face-centered windows. In this case, a is the distance between cage centers, $1/k$ is the average residence time in a cage, and hence $\frac{1}{6}k$ is the rate to leave through one of the six face-centered windows. Applying this reasoning to diffusion in, e.g., Na-Y zeolite which consists of tetrahedrally arranged supercages, each with four windows connecting adjacent supercages, one might surmise the relation $D = \frac{1}{4}ka^2$, where a and k are analogously defined. This result is incorrect, which we demonstrate below and prove rigorously in the appendix.
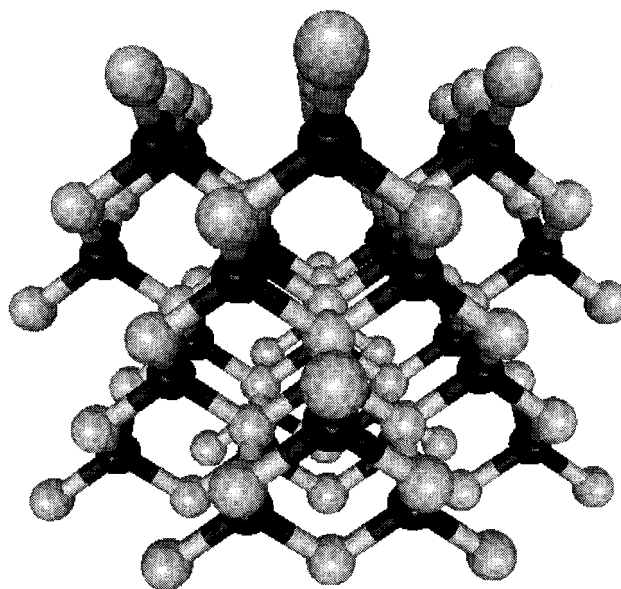

FIG. 4. Tetrahedral-lattice model of diffusion in Na-Y with hopping length a and mean site residence time $1/k$. Balls represent supercages and sticks represent 12-ring windows connecting cages. Two colors show two interpenetrating BCC sublattices. Light and dark cages each have four allowed jumps, totaling eight, each with rate coefficient $k/4$.

After N random jumps of length a on the tetrahedral lattice of Na-Y supercages, the mean square displacement is given by

$$\langle R^2(N)\rangle = \left\langle \left| \sum_{i=1}^{N} \mathbf{l}_i \right|^2 \right\rangle = \left\langle \sum_{i=1}^{N} |\mathbf{l}_i|^2 \right\rangle + \left\langle \sum_{i \neq j} \mathbf{l}_i^T \cdot \mathbf{l}_j \right\rangle$$

$$= \left\langle \sum_{i=1}^{N} a^2 \right\rangle = Na^2 = kta^2 = 6Dt. \tag{2.1}$$

The random jump vectors $\{\mathbf{l}_i\}$ are sampled from the eight possible jumps for a tetrahedral lattice (see the Appendix). The third equality results because jumps are uncorrelated, and the final equality establishes that $D = \frac{1}{6}ka^2$, identical to the expression for a simple-cubic lattice.

To put this result into perspective, we note that the formula $D = \frac{1}{6}ka^2$ is valid for diffusion in all materials—regardless of structure—provided that the length scale a is sufficiently large. To apply the formula, one imagines partitioning the material into large cubes of edge length a, and allows jumps between adjacent cubes only. If one assumes that jumps through cube edges and corners can be neglected, which is always valid in the limit $a \to \infty$ then $1/k$ becomes the average residence time in a cube. With this prescription, diffusion through any material can be viewed in terms of hopping on a simple-cubic lattice. The ''self-similar'' length scale, a_{ss}, is defined as the minimum length scale for which this simple-cubic partitioning remains valid for all longer length scales.[22] That is, once the relation $D = \frac{1}{6}k_{ss}a_{ss}^2$ is established, the relation $D = \frac{1}{6}ka^2$ must be valid for $a > a_{ss}$. The magnitude of a_{ss} depends on the structure of a given material.

For diffusion in Na-A, a_{ss} is the cage-to-cage distance (ca. 12 Å) because the cages are configured in a simple-cubic fashion. For diffusion in Na-Y, determining a_{ss} is more difficult because edge jumps contribute significantly to diffusion. Taking the Na-Y cube to be a cubic unit cell ($a \cong 25$ Å), one third of cube-to-cube jumps are edge jumps. If we arbitrarily assume that self-similarity occurs when edge jumps represent fewer than 10% of all cube-to-cube jumps, we obtain a self-similar cube consisting of 27 Na-Y unit cells, i.e., $a_{ss} \cong 75$ Å. This is much longer than for Na-A because the Na-Y structure involves tetrahedrally arranged windows at the cage-to-cage length scale (ca. 11 Å).

We thus find it intriguing that the simple-cubic formula applies to diffusion in Na-Y at a length scale *below* the self-similar length scale. That is, the formula $D = \frac{1}{6}ka^2$ holds for diffusion in Na-Y for 11 Å tetrahedral jumps and for ≥ 75 Å cubic jumps, but *not* for length scales in between. As such, by filling three dimensional space with only a single lattice spacing length scale, the tetrahedral lattice mimics the cubic lattice in its diffusion coefficient relationship.

In the remainder of this paper, we focus on calculating k for 11 Å tetrahedral jumps. At this length scale, k can be decomposed into energy and frequency scales which have important physical significance, i.e., the activation energy and attempt frequency of Na-Y cage-to-cage jumps. At the

≥ 75 Å length scale, the Arrhenius decomposition of k would not lend itself to such physically meaningful parameters.

III. KINETICS OF INTERCAGE MOTION

A. Introduction

Given the diffusion coefficient for benzene in Na-Y, and the fact that $D = \frac{1}{6}ka^2$ at the cage-to-cage length scale ($a \cong 11$ Å), we can calculate the average supercage residence time, $1/k$. For some physical systems, k determines more than just the mean site residence time. In particular, for diffusion processes among sites where each site represents a single potential minimum, k determines *all* moments of the distribution of site residence times. In this special case, k is defined by the following first-order rate equation:

$$\frac{dP_{site}(t)}{dt} = -kP_{site}(t), \tag{3.1}$$

where $P_{site}(t)$ is the distribution of site residence times, i.e., the decaying population at a site. Solving this rate equation and normalizing for a single particle, we obtain $P_{site}(t) = ke^{-kt}$. Using this distribution to calculate the average residence time

$$\langle t \rangle = \int_0^{\infty} dt \, t \, P_{site}(t), \tag{3.2}$$

we obtain $\langle t \rangle = 1/k$, as expected. The interpretation of k as a first-order kinetic rate parameter applies to many surface diffusion phenomena, such as hydrogen atom diffusion on Ni(100).[16]

For benzene diffusion in Na-Y, in which each supercage ''site'' contains several potential minima, several different fundamental hops contribute to intercage motion, each with a different microscopic rate coefficient. It is therefore not immediately obvious that the distribution of supercage residence times is determined by simple first order kinetics. To investigate this issue, we have performed kinetic Monte Carlo[4,12–14] (KMC) simulations to calculate directly the supercage residence time distribution. We do this by constructing the histogram of supercage residence times for a benzene molecule executing a KMC random walk through the Na-Y framework.

B. Kinetic simulation methods

We apply the KMC algorithm to benzene diffusion in Na-Y by replacing the zeolite framework with a three-dimensional lattice of S_{II} and W binding sites. Such a lattice model is known to accurately reproduce diffusive behavior when site residence times are much longer than travel times between sites.[13,15] This is indeed the case for benzene diffusion in cation-containing faujasites, as demonstrated by the two-dimensional NMR experiments of Wilhelm *et al.*[23] Connecting the S_{II} and W sites are four distinct hopping events, each with a characteristic rate coefficient: $k(S_{II} \to S_{II})$, $k(S_{II} \to W)$, $k(W \to S_{II})$ and $k(W \to W)$. The probability to make a particular hop is proportional to the associated rate coefficient. A hop is made every KMC step[24] and the system

TABLE I. Hopping activation energies and hypothetical Arrhenius prefactors for benzene in Na-Y. Our model predicts that leaving the W site is relatively facile.

Jump	Activation energy (kJ mol^{-1})	Arrhenius prefactor (s^{-1})
$S_{II} \rightarrow S_{II}$	35	10^{13}
$S_{II} \rightarrow W$	41	10^{13}
$W \rightarrow S_{II}$	16	10^{13}
$W \rightarrow W$	18	10^{13}

FIG. 5. Linear-bin histogram of cage residence times for benzene in Na-Y at $T = 300$ K, calculated by kinetic Monte Carlo random walk.

clock is updated accordingly. This is in contrast to the standard thermal Monte Carlo procedure which has no obvious clock. The mean time elapsed before each hop is the inverse of the *total* rate coefficient to leave the originating site.[24] For example, if benzene hops from an S_{II} site, the time elapsed is

$$\Delta t(S_{II}) = \frac{1}{3[k(S_{II} \rightarrow S_{II}) + k(S_{II} \rightarrow W)]}, \qquad (3.3)$$

where the factor of three counts available target sites in the Na-Y supercage structure. Since the rate coefficients for leaving the S_{II} site are typically much smaller than those for leaving the W site, the elapsed S_{II} time is much larger than the elapsed W time. Thus the KMC random walk algorithm efficiently models both sluggish and rapid motions in the Na-Y–benzene system.

In Ref. 4 and in the present study, we estimate rate coefficients using the Arrhenius formula, in which $k \cong \nu e^{-\beta E_a}$, where ν and E_a are temperature independent. We assume that the Arrhenius prefactors $\{\nu\}$ resemble typical vibrational frequencies, of order 10^{13} s^{-1}. We believe these rate coefficients are sufficiently accurate for the purpose of drawing qualitative conclusions. Our calculated hopping activation energies and hypothetical Arrhenius prefactors, first reported in Ref. 4, are summarized in Table I. We note that leaving the W site is much more facile than leaving the S_{II} site in our model. Indeed, the predicted 300 K residence time at the S_{II} site is more than 5000 times longer than at the W site. Reference 4 discusses the detailed hopping mechanisms, in addition to the reasonable agreement between our activation energies and those measured experimentally.

Care must be taken in defining a cage-to-cage hop, and hence the time elapsed prior to such a hop, because W sites are shared by adjacent supercages. Although one solution to this difficulty is to assign W sites to particular supercages (two W sites per cage), we avoided this approach because the assignment is arbitrary and breaks Na-Y symmetry. Instead, we used the following approach: If the nth KMC step is a W site, we calculate the distance between benzene center of mass positions for KMC steps $n-1$ and $n+1$. If this distance is nonzero and different from the four characteristic intracage distances[6] [$d(S_{II}, S_{II}) = 5.48$ Å, $d(S_{II}, W) = 5.31$ Å, $d(S_{II}, W') = 8.74$ Å, and $d(W, W) = 8.79$ Å], then a cage-to-cage jump is registered with t_{n+1} stored as the arrival time in the new cage. The residence time is the difference between t_{n+1} and the previously stored arrival time.

For a given KMC run we calculate two histograms, based on distinct binning procedures. The first histogram is
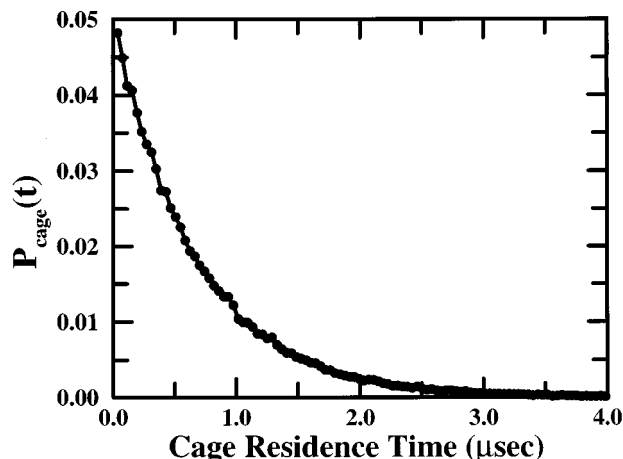
based on linear bins, in which we calculate the difference between the longest and shortest supercage residence times, and divide that difference into several hundred bins. We then run through all residence times to accumulate bin occupancies, normalizing the distribution once occupancies are determined. The use of linear bins focuses the histogram toward longer time scales. Indeed, if supercage residence times spanning 10^{-15}–10^{-5} s are assigned to 100 linear bins, the first bin accumulates supercage residence times ranging over 10^{-15}–10^{-7} s. Below we find that linear-bin histograms give results consistent with kinetic rate theory by focusing on those time scales for which kinetic rate theory is intended.

The second histogram is based on logarithmic bins, in which we calculate the difference between the logarithms of the longest and shortest supercage residence times, dividing that difference into several hundred bins. We then run through all the logarithms of residence times to accumulate occupancies of logarithmic bins, also normalizing once occupancies are determined. As opposed to linear binning, the logarithmic-bin histogram reveals both short and long time scales. Indeed, if supercage residence times spanning 10^{-15}–10^{-5} s are assigned to 100 logarithmic bins, the first bin accumulates supercage residence times ranging over 10^{-15}–$10^{-14.9}$ s. These simulations are sufficiently well converged ($N_{KMC} = 3 \times 10^6$) that placing rapid cage-to-cage events into short time logarithmic bins does not deteriorate long time statistics. Below we find that the short time phenomena revealed by logarithmic binning do not significantly affect benzene diffusion in Na-Y. Nevertheless, the logarithmic-bin histogram captures the many dynamical time scales which determine our KMC simulation, and hence illustrates how kinetic theories subsume many dynamical time scales into a single rate coefficient.

C. Kinetic simulation results

In Fig. 5 we show the linear-bin histogram of benzene cage-to-cage hopping times for Na-Y at $T = 300$ K. The semilog plot of $P_{cage}(t)$ shown in Fig. 6 demonstrates that
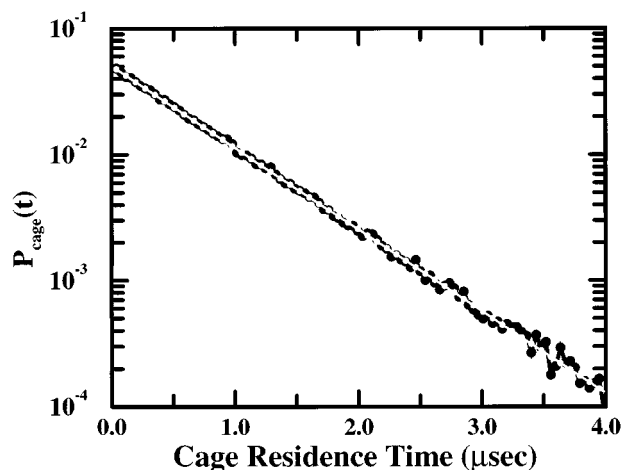
FIG. 6. Semilog plot of Fig. 5, which demonstrates simple exponential decay of cage residence time distribution. Decay rate is 1.7 μs^{-1}, which fits well to $\frac{1}{2} \times 4 \times k(S_{II} \rightarrow W)$.

FIG. 7. Temperature dependence of $\frac{1}{2} \times 4 \times k(S_{II} \rightarrow W)$ (open circles), which agrees with cage-to-cage rate coefficient from kinetic Monte Carlo (thick line). The $S_{II} \rightarrow W$ jump controls rate of interchange motion, and hence determines diffusion coefficient.

$P_{cage}(t)$ obeys simple exponential decay for cage-to-cage hopping. This result indicates that although many different microscopic processes contribute to cage-to-cage migration, the contribution from one of them is particularly important. The mean cage residence time extracted from Fig. 6 is 0.67 μs, indicating that in our model intercage motion is extremely infrequent compared to typical molecular dynamics time scales.[7] The cage-to-cage rate coefficient, k, is very nearly equal to $\frac{1}{2} \times 4 \times k(S_{II} \rightarrow W)$, a result which has the following interpretation. Most benzene jumps originate *from* an S_{II} site because of its energetic stability. An intercage jump can take place only when benzene hops *to* a W site, because the windows connect adjacent supercages. The factor of 0.50 accounts for randomizing in the W site which halves the probability to leave the cage. The factor of 4 accounts for the four ways to leave the supercage through one of the four windows. These conclusions remain valid irrespective of the relative values of $E_a(S_{II} \rightarrow S_{II})$ and $E_a(S_{II} \rightarrow W)$, since the $S_{II} \rightarrow S_{II}$ jump does not contribute to diffusion.[4]

The temperature dependence of the cage-to-cage rate coefficient, obtained from our KMC calculations, is plotted in Fig. 7 (thick line) along with $\frac{1}{2} \times 4 \times k(S_{II} \rightarrow W)$ (open dots). An Arrhenius fit to the latter rate coefficients yields ($E_a = 41$ kJ mol^{-1}, $\nu = 2 \times 10^{13}$ s^{-1}), while a fit to the KMC calculated intercage rate coefficients yields ($E_a = 41$ kJ mol^{-1}, $\nu = 2.6 \times 10^{13}$ s^{-1}). The discrepancy is mostly due to Monte Carlo error from the low temperature calculation. Figure 7 demonstrates that our interpretation of the factors which control the mean cage residence time remains valid over a wide temperature range.

Given the cage-to-cage rate coefficient for benzene in Na-Y, and the fact that $D = \frac{1}{6} k a^2$ at the cage-to-cage length scale ($a \cong 11$ Å), we can construct D and compare it to the results of a KMC simulation of the mean square displacement.[4] We analyze this comparison in detail in the next section. Before doing so, we pause to ask the following question. Although we have shown that only one fundamental rate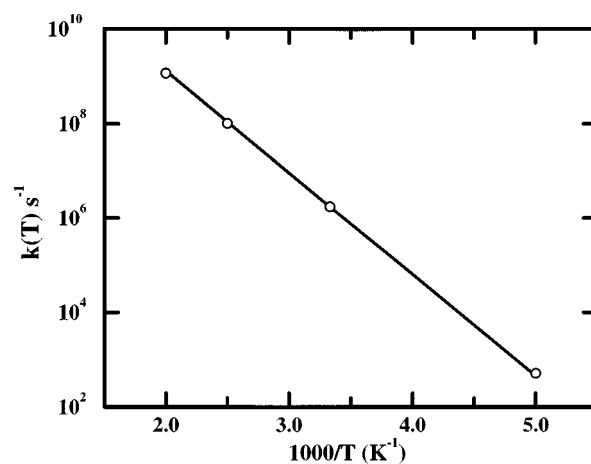 coefficient controls intercage benzene motion, is it possible to construct a histogram of cage residence times which resolves the *many* fundamental time scales used by our KMC calculation? This would demonstrate how kinetic theories of infrequent events subsume many dynamical time scales into a single rate coefficient. Such a histogram, obtained with the logarithmic binning procedure outlined above, is shown in Fig. 8 for benzene intercage motion at $T = 300$ K.

This histogram demonstrates two predominant time scales, corresponding to a fast intercage process $(W)_{cage\ 1} \rightarrow W \rightarrow (S_{II}$ or $W)_{cage\ 2}$ and a slow intercage process $(S_{II})_{cage\ 1} \rightarrow W \rightarrow (S_{II}$ or $W)_{cage\ 2}$. At relatively short times this histogram is far from being a single exponential function.[25] At sufficiently long times, for which kinetic rate theories are intended, the single exponential reappears.[25] The rapid intercage process is unimportant for diffusion because the prob-
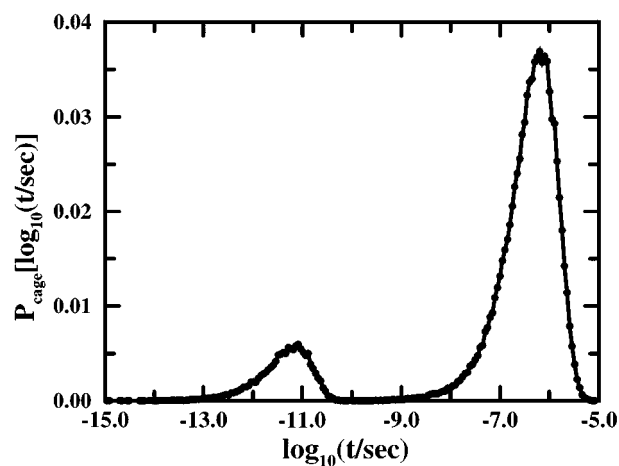

FIG. 8. Logarithmic-bin histogram of cage residence times for benzene in Na-Y at $T = 300$ K, which shows nonexponential dependence at short times and exponential decay at longer times. The rate determining $S_{II} \rightarrow W$ time scale is ca. 1 μs, while the 10 ps $W \rightarrow W$ intercage process has an exponentially damped probability due to the high W site energy.

TABLE II. Comparison between ''exact'' diffusion coefficients ($m^2\,s^{-1}$) calculated from mean square displacements, and ''static'' ones constructed from intercage hopping times and the static intercage distance, $a = 10.76$ Å. The errors suggest that a kinetic hopping length is required for exact agreement.

Temp (K)	D_{exact}	D_{static}	% Error
200	9.45×10^{-17}	8.58×10^{-17}	-9.2
300	3.29×10^{-13}	3.06×10^{-13}	-7.0
400	2.07×10^{-11}	1.90×10^{-11}	-8.3
500	3.03×10^{-10}	2.59×10^{-10}	-14.5

TABLE III. Comparison between ''exact'' diffusion coefficients ($m^2\,s^{-1}$) calculated from mean square displacements, and ''kinetic'' ones constructed from intercage hopping times and kinetic intercage distances, which increase with temperature because of $W \rightarrow W$ jumps. The agreement is essentially exact, except for small Monte Carlo errors.

Temp (K)	D_{exact}	$D_{kinetic}$	% Error	Kinetic length (Å)
200	9.45×10^{-17}	9.21×10^{-17}	-2.5	10.98
300	3.29×10^{-13}	3.43×10^{-13}	4.2	11.14
400	2.07×10^{-11}	2.01×10^{-11}	-2.7	11.25
500	3.03×10^{-10}	2.90×10^{-10}	-4.3	11.30

ability of a $(W)_{cage\ 1} \rightarrow W \rightarrow (S_{II}$ or $W)_{cage\ 2}$ jump is exponentially damped by the Boltzmann factor, due to the relative instability of the W site. The logarithmic-bin histogram shape is consistent with $P_{cage}(t)$ being a Boltzmann weighted sum of two decaying exponentials, corresponding to the two predominant time scales. The linear-bin histogram subsumes cage residence times over many orders of magnitude into its first time bin, averaging different types of dynamical motions to yield a single rate coefficient.

IV. LENGTH SCALES OF INTERCAGE MOTION

Given a set of fundamental hopping processes and rates, ''exact'' diffusion coefficients can be obtained from a KMC calculation of the mean square displacement. These can be compared to diffusion coefficients constructed from the relation $D = \frac{1}{6}ka^2$, the cage-to-cage rate coefficients calculated above, and the crystallographically measured cage-to-cage distance, $a = 10.76$ Å.[6] We perform this comparison, shown in Table II, over the temperature range 200–500 K. The second column contains exact diffusion coefficients, the third column contains constructed ones, and the fourth column shows percent error from exact results. The errors are small, indicating that this is a useful procedure for determining diffusion coefficients in faujasite type zeolites. However, the pattern of error is not typical of Monte Carlo statistics; i.e., the error appears to be systematic. We show below that assuming the static intercage distance $a = 10.76$ Å, calculated between the centers of adjacent supercages, is incorrect for a large pore zeolite where sites are located on the inner surface of the supercage, and not in the center of the cage.

In the previous section we calculated the distribution of intercage hopping time scales to determine k. It follows that we must also calculate a distribution of intercage hopping length scales to determine a. Although this fact is usually ignored because a varies weakly with temperature, calculating a kinetic length is the only way to obtain essentially exact agreement between the KMC mean square displacement and $D = \frac{1}{6}ka^2$. The kinetic intercage length, $a(T)$, is the root mean square of the distribution of cage-to-cage hopping lengths. This is obtained along side the calculation of intercage hopping times, and adds no computational expense or difficulty.

The comparison between exact diffusion coefficients and those constructed from $D = \frac{1}{6}ka^2(T)$ is shown in Table III, along with the kinetic intercage lengths. As Table III demonstrates, $a(T)$ increases weakly with temperature, and is systematically larger than the static intercage length. Increasing temperature populates W sites, from which the longer $(W)_{cage\ 1} \rightarrow W \rightarrow (S_{II}$ or $W)_{cage\ 2}$ hop can occur. The comparison between diffusion coefficients shows much closer agreement than in Table II, essentially exact within Monte Carlo error. In addition, the pattern of error is more typical of Monte Carlo statistics. As such, the diffusion coefficient for benzene in Na-Y can be written *exactly* as $D = \frac{1}{6}ka^2(T)$, and to good accuracy as $\frac{1}{3}k(S_{II} \rightarrow W)a^2$.

We have demonstrated how the diffusion coefficient for benzene in Na-Y zeolite can be decomposed into fundamental energy, length and time scales, yielding insight into the microscopic processes that control diffusion in zeolites. Conversely, we have demonstrated a reliable procedure for constructing the diffusion coefficient from these basic quantities. This has an important consequence regarding computation time. The CPU time required by a KMC mean square displacement calculation scales as N^2, where N is the number of KMC steps. Alternatively, the intercage hopping length and time calculations scale linearly with N. In practice, a well converged mean square displacement calculation may require hours to days, whereas the intercage length and time calculations always complete in minutes. This may facilitate KMC calculations on more complex diffusive systems.

V. CONCLUSIONS

We have performed kinetic Monte Carlo (KMC) simulations of benzene diffusion in Na-Y (Si:Al=2.0), a tetrahedrally structured zeolite, over the temperature range 200–500 K. We decompose the resulting diffusion coefficients into hopping lengths and cage residence times, in analogy to two-dimensional surface diffusion. For hopping on a tetrahedral lattice, we derive the analytical formula for D in terms of hopping lengths and times. The result turns out to be the simple-cubic relation, $D = \frac{1}{6}ka^2$, even though the simple-cubic partitioning of Na-Y is invalid at the cage-to-cage length scale.

We have performed additional KMC simulations to calculate the distribution of cage residence times for benzene in Na-Y, to determine which fundamental jumps control intercage motion. The cage residence time distributions exhibit single exponential decay, with decay rates equal to twice the fundamental $k(S_{II} \rightarrow W)$ hopping rate coefficient. This jump controls the rate of intercage motion, and hence determines

the diffusion coefficient. Logarithmic-bin histograms resolve a more rapid intercage process involving $W \to W$ jumps, whose importance is damped by an exponentially small Boltzmann factor.

We compare diffusion coefficients calculated from mean square displacements to those constructed from intercage lengths and times. Exact agreement is obtained only when kinetic intercage hopping lengths are calculated, in analogy with kinetic intercage hopping times. These lengths are greater than the static cage-to-cage length by as much as 0.54 Å at $T = 500$ K.

We have demonstrated a reliable procedure for constructing the diffusion coefficient from fundamental energy, length and time scales. This has an important consequence regarding computation time. A well-converged mean square displacement calculation may require hours to days, whereas the intercage length and time calculations always complete in minutes. This may facilitate KMC calculations on more complex diffusive systems.

Our procedure for constructing the diffusion coefficient from fundamental energy, length and time scales can be applied to other host–guest systems as well. For example, methanol diffusion in K-L zeolite would be treated with a one-dimensional diffusion relation, $D = \frac{1}{2}ka^2$, where a is the lattice parameter along the channel, and k is the rate for hopping between adjacent unit cells along the channel. Treating diffusion through more complex host systems with our lattice model can also be contemplated. The general procedure involves first constructing a lattice of *effective* sites with mean residence time $1/k$ and hopping distance a. An analytical derivation analogous to that shown in the appendix would then be carried out to determine how the diffusion coefficient depends upon k and a. Finally, a KMC simulation would be performed to calculate k given a set of underlying rate coefficients for hopping on a lattice of *actual* sites.

We plan to extend these calculations to model the diffusion of benzene at finite loadings in Na-Y. Two approaches are currently being tested, both based on the relationship $D = \frac{1}{6}k(c)a^2$ (see the appendix), where $k(c)$ is the concentration dependent intercage hopping rate coefficient. In the simpler model, a many-benzene KMC simulation is performed using site energies and hopping activation energies calculated for benzene in Na-Y at infinite dilution. The more accurate model corrects these energies for the particular loading in question, giving the formally exact diffusion coefficient. The difference between the two methods measures the importance of medium range (ca. 5 Å) guest–guest interactions. Results from these calculations will be reported in a forthcoming publication.[26]

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APPENDIX: RIGOROUS TREATMENT OF TETRAHEDRAL HOPPING

We begin our derivation of the mean square displacement for a random walk on a tetrahedral lattice by defining the probability distribution used to calculate statistical averages. This is based on the multinomial expansion[27]

$$\left(\sum_{i=1}^{M} x_i \right)^N = \sum_{n_1,\ldots,n_M}{}' \frac{N!}{n_1! \cdots n_M!} x_1^{n_1} \cdots x_M^{n_M}, \quad \text{(A1)}$$

where the primed summation on the right-hand side of Eq. (A1) implies that $\Sigma_{i=1}^{M} n_i = N$. When each x_i is non-negative and $\Sigma_{i=1}^{M} x_i = 1$, we interpret x_i as the probability for the ith jump, giving rise to the normalized Bernoulli distribution[1]

$$1 = \sum_{n_1,\ldots,n_M}{}' P(n_1,\ldots,n_M;N)$$

$$= \sum_{n_1,\ldots,n_M}{}' \frac{N!}{n_1! \cdots n_M!} p_1^{n_1} \cdots p_M^{n_M}. \quad \text{(A2)}$$

The Bernoulli distribution function can be interpreted as the normalized probability that, given a random walk with N steps, the walker executes n_1 jumps of type 1, n_2 jumps of type 2,…,n_M jumps of type M. The combinatorial factor counts the number of particular jump sequences consistent with $(n_1,\ldots,n_M)$, while the $p_i^{n_i}$ factors determine probabilities of repeated, fundamental jumps. For example, a one-dimensional random walker can execute two distinct jumps, i.e., $M = 2$. In the isotropic case $p_1 = p_2 = \frac{1}{2}$, and the mean square displacement after N jumps on a lattice with spacing a is given by

$$\langle R^2(N) \rangle = a^2 \langle (n_1 - n_2)^2 \rangle = 2a^2 (2\langle n_1^2 \rangle - N\langle n_1 \rangle) = Na^2. \quad \text{(A3)}$$

The averages in Eq. (A3) are calculated using the relation

$$\langle n_i^k \rangle = \left(p_i \frac{\partial}{\partial p_i} \right)^k \sum_{n_1,\ldots,n_M}{}' \frac{N!}{n_1! \cdots n_M!} p_1^{n_1} \cdots p_M^{n_M}$$

$$= \left(p_i \frac{\partial}{\partial p_i} \right)^k \left(\sum_{j=1}^{M} p_j \right)^N. \quad \text{(A4)}$$

For motion on a tetrahedral lattice, the situation is slightly more complex. This lattice is composed of two interpenetrating BCC lattices (cf. Fig. 4), denoted here as sublattices A and B. As can be seen from Fig. 4, a random walker *must* alternate between sublattices at each jump, i.e. all jumps in Fig. 4 connect light cages to dark, or dark cages to light. As such, during N jumps, $N/2$ jumps visit each sublattice. Each cage in sublattice A has four allowed jumps, labeled by $(1+,2+,3+,4+)$. Similarly, each cage in sublattice B has four allowed jumps, labeled by $(1-,2-,3-,4-)$, which are obtained by reversing the A jump directions. The

alternation between sublattices causes the Bernoulli distribution for a tetrahedral lattice to factor into an A distribution and a B distribution, according to

$$1 = 1_A 1_B = \sum_{n_{1+},\ldots,n_{4+}}' \frac{(N/2)!}{n_{1+}!\cdots n_{4+}!} p_{1+}^{n_{1+}}\cdots p_{4+}^{n_{4+}}$$

$$\times \sum_{n_{1-},\ldots,n_{4-}}' \frac{(N/2)!}{n_{1-}!\cdots n_{4-}!} p_{1-}^{n_{1-}}\cdots p_{4-}^{n_{4-}}, \quad (A5)$$

where $p_{i+} = p_{i-} = \frac{1}{4}$ for $i = 1,\ldots,4$ and the primed summations imply that $\Sigma_{i=1}^{4} n_{i+} = \Sigma_{i=1}^{4} n_{i-} = N/2$. Because of the factorization, averages such as $\langle n_{1+} n_{1-} \rangle$ separate into $\langle n_{1+} \rangle \langle n_{1-} \rangle$, whereas $\langle n_{1+} n_{2+} \rangle$ is nonseparable.

The mean square displacement for a random walk of N steps on a tetrahedral lattice with spacing a is given by $\langle R^2(N) \rangle = \langle \delta x^2(N) \rangle + \langle \delta y^2(N) \rangle + \langle \delta z^2(N) \rangle$, where

$$\delta x/a = \Delta n_1 f_{1x} + \Delta n_2 f_{2x} + \Delta n_3 f_{3x} + \Delta n_4 f_{4x},$$

$$\delta y/a = \Delta n_1 f_{1y} + \Delta n_2 f_{2y} + \Delta n_3 f_{3y} + \Delta n_4 f_{4y}, \quad (A6)$$

$$\delta z/a = \Delta n_1 f_{1z} + \Delta n_2 f_{2z} + \Delta n_3 f_{3z} + \Delta n_4 f_{4z}.$$

In Eq. (A6), $\Delta n_i = n_{i+} - n_{i-}$ and the coefficients $\{f_{i\alpha}\}_{\alpha=x,y,z}$ resolve the spatial components of each jump. These are necessary for the calculation because cross terms such as $\langle \Delta n_1 \Delta n_2 \rangle$ are nonvanishing. Otherwise, the jump components enter in through the sum $\Sigma_\alpha f_{i\alpha}^2$, which equals unity for $i = 1,\ldots,4$. With a judicious choice of coordinate system, four of the jump components vanish, e.g., $f_{3x} = f_{4x} = f_{1z} = f_{2z} = 0$. The others are given by $f_{1x} = f_{3z} = -f_{2x} = -f_{4z} = \sqrt{2/3}$ and $f_{1y} = f_{2y} = -f_{3y} = -f_{4y} = \sqrt{1/3}$.

The remainder of the calculation requires averages of the form $\langle \Delta n_i \Delta n_j \rangle$. The diagonal terms, where $i = j$, are given by $2[\langle n_{i+}^2 \rangle - \langle n_{i+} \rangle^2] = 3N/16$. The off-diagonal terms, where $i \neq j$, are computed as $2[\langle n_{i+} n_{j+} \rangle - \langle n_{i+} \rangle \langle n_{j+} \rangle] = -N/16$. Substituting these results and the jump components into Eq. (A6), we find that $\langle \delta x^2(N) \rangle = \langle \delta y^2(N) \rangle = \langle \delta z^2(N) \rangle = Na^2/3$, which implies that $\langle R^2(N) \rangle = Na^2$, as advertised in Eq. (2.1). This result is valid for all lattices—regardless of dimension—as long as they fill space with a single hopping length scale.

A similar expression applies to *any* lattice, even those with multiple hopping length scales, such as benzene in Na-Y zeolite.[1] This is obtained by replacing a^2 with its average value $\langle a^2 \rangle$ in Eq. (2.1). Such a definition is particularly useful when $\sqrt{\langle a^2 \rangle}$ resembles a fundamental hopping length, as we discuss in Sec. IV.

One can utilize the above formulation to compute cross correlation terms of the form $\langle \delta x \delta y \rangle$. One can show that they all identically vanish for a single random walker on the tetrahedral lattice. It would be interesting to repeat the above derivation with many random walkers on a tetrahedral lattice, in order to simulate concentration effects in diffusion, which will introduce nonvanishing cross correlations and configuration-dependent hopping probabilities. This means that the four Monte Carlo probabilities, for benzene to execute an intercage jump through one of the four windows, will not necessarily be equal all the time. Although this seems to imply that the tetrahedral lattice includes nonidentical cages, a long KMC simulation should average away differences among cages, since they are all fundamentally equivalent. Thus, for finite loadings the relation $D = \frac{1}{6} k(c) a^2$ should hold, where $k(c)$ is the concentration dependent intercage hopping rate coefficient. Further study on this point will be reported in a forthcoming publication.[26]

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