Correlation effects in molecular diffusion in zeolites at infinite dilution

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Molecular diffusion in zeolites is often resumed to a random walk between specific adsorption sites within the channels and cavities of the materials. Several types of correlations between the steps of the walk come to precise this assumption: kinetic correlations due to the incomplete relaxation of the molecule in its final site, vacancy correlations arising at high loading because molecules are blocking each other, and geometrical correlations because zeolite channels and cages can boast nonsymmetric sites. The first and last correlation effects can be observed at infinite dilution. In this article we present a way of calculating an exact diffusion coefficient at infinite dilution as a function of the microscopic rate constants, taking into account both geometric and kinetic correlation effects. This is achieved by cutting the molecular motion into uncorrelated sequences of jumps, where all jumps inside one sequence are correlated to each other. This method is applied to study geometrical correlations of benzene in NaY, comparing with kinetic Monte Carlo data of Saravanan *et al.* [C. Saravanan, F. Jousse, and S. M. Auerbach, J. Chem. Phys. **108**, 2162 (1998)], and both kinetic and geometrical correlations of ethane in silicalite, comparing with molecular dynamic simulations of Kärger *et al.* [J. Kärger, P. Demontis, G. B. Suffritti, and A. Tilocca, J. Chem. Phys. **110**, 1163 (1999)]. © *2000 American Institute of Physics.* [S0021-9606(00)50502-9]

I. INTRODUCTION

According to Le Claire,[1] the first time that the assumption of random displacements in the random walk picture of diffusion was appreciated to be an oversimplification dates back to 1935, and concerned the kinetic theory of gases. Indeed, after a collision, the probability that a gas particle retains a component of its velocity along the same direction as it was moving before the collision, is larger than the probability that its velocity lies in the opposite direction. This effect was termed ''persistence of velocity,'' but for our purposes we will call it ''kinetic correlations'' since it relates to jump kinetics. Similar kinetic correlations cause double or multiple jumps in adatom diffusion.[2,3] Such a type of correlation was also considered by Jousse *et al.* for diffusion of butene isomers in theta-1 type zeolites.[4]

In 1951, Bardeen and Herring[5] noted that the vacancy mechanism of atom diffusion in solids gives rise to a similar but opposite correlation effect, since an atom has a larger probability to move backward to the hole it just vacated rather than onward. From that moment on, a large body of work was devoted to the calculation of these correlations, for different diffusion mechanisms, for a variety of lattice geometries, either theoretically or using Monte Carlo simulations.[1,6–8] These ''vacancy correlations'' arise also when studying self-diffusion of guest molecules in zeolite channels.[9,10] For very high loading, the evaluation of these correlations is similar to that of vacancy correlations in solids. We are not aware of any simple way to calculate these correlations for arbitrary loading, although relations exist for a number of specific simple geometries and particles interacting only through excluded volume interactions.[11,12] Related to these correlations is the effect giving rise to single-file diffusion, where molecules diffusing inside a unidirectional channel and unable to pass each other must diffuse all in the same direction or not at all. This effect has been extensively studied in the last few years.[13–15]

Another type of correlation effect observed in some zeolites was recognized by Kärger for the case of molecular diffusion in ZSM-5.[16] Indeed, the channel geometry of this zeolite restricts the displacements along z as compared to those along x and y, so that the diagonal elements of the diffusivity tensor should obey the correlation rule

$$\frac{a^2}{D_x}+\frac{b^2}{D_y}=\frac{c^2}{D_z}. \tag{1}$$

Since these correlation effects are caused by the geometry of

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the channel network, we will call them ''geometric correlations.'' They arise whenever the probability of jumping out of a given site is nonsymmetric.

Different types of correlation can exist at once. For example, diffusion of some guest molecule in ZSM-5 could exhibit kinetic correlations if the jumps are not completely randomized by thermalization, vacancy correlations if the fractional loading is significantly larger than zero, and geometrical correlations due to the channel geometry. Kärger *et al.*[17] introduced a ''two-step'' model of diffusion in silicalite-1 (isomorphous to ZSM-5) to account for all these correlation effects. In this model they consider that the probability of an event depends on the preceding one, so that instead of n uncoupled jumps there are $n/2$ coupled events, each corresponding to a double jump. For ethane diffusion in the zigzag channels of silicalite-1 (along the y axis), they find from molecular dynamics (MD) simulations that the probability to jump backward is larger than the probability to jump forward, so that the diffusion coefficient is decreased as compared to what would be expected from a simple random walk (RW). Below we confirm that indeed the two-step model gives results much closer to MD data than the simple RW. However, the two-step model considers that each coupled double-jump is *uncoupled* from the others, so that we expect it to underestimate the total influence of correlations. This will be shown below, where we will see that in all cases the diffusion coefficient from the two-step model along the zigzag channels is larger than the MD one.

In this article we present an alternative and generally applicable method for treating kinetic and geometrical correlation effects of molecular diffusion in zeolites. The method we describe here allows us to write an analytical expression for the self-diffusion coefficient on an *arbitrary lattice*, given the fundamental rate factor. Such an expression is particularly useful to study the relation between the rates and the global diffusivity. Rate constants can be evaluated using simple energy minimization techniques[18] or more elaborate free-energy simulations,[19] and determined experimentally using, e.g., solid-state NMR.[20] The global diffusivity, on the other hand, can be evaluated by molecular dynamics (MD) simulations or accelerated MD,[21] and measured using quasi-elastic neutron scattering (QENS)[22] or pulsed-field gradient NMR.[23] If the temperature dependence of the rate factor is known, such an analytical expression provides a simple theory for the temperature dependence of diffusion at infinite dilution. Furthermore, it allows us to study externally the influence of a change in topology or connectivity of the adsorption sites onto the guest diffusivity.

Getting such an analytical expression involves lots of probabilistic calculations, and can be cumbersome in the general case. The method we present here allows us to make these calculations somewhat simpler. To show the reader how this can be achieved, we treat exhaustively two particular examples: diffusion of benzene in NaY, and diffusion of ethane in silicalite-1. By excluding vacancy correlations, we confine ourselves in principle to diffusion at infinite dilution. However, using mean-field theory in addition to our method for treating geometrical and kinetic correlations is expected to give qualitatively reasonable trends for the loading dependence of diffusion. Note, however, that the mean-field approximation used in the applications assumes that the site-to-site rates are not affected by nearby molecules except for site blocking, and therefore are only valid for weak guest-guest interactions.

The remainder of this paper is organized as follows: Section II outlines the general method of calculation. Section III presents the example of benzene diffusion in Na-Y, which presents strong geometric correlations at low loading. In Sec. IV we treat the example of ethane diffusion in silicalite-1, comparing our model to the data of Kärger *et al.*[17] Finally, we conclude in Sec. V.

II. GENERAL MODEL

In the random walk picture of diffusion, the self-diffusion coefficient along a given direction, e.g., the x-axis, is related to the second moment of the propagator by Einstein's equation

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

where $\langle x^2(t)\rangle$ is the mean-square displacement (MSD) of a given molecule moving along the x-axis and t is the observation time. If we suppose a jump diffusion mechanism, the MSD becomes

$$\langle x^2(t)\rangle=\left\langle\left(\sum_{i=1}^{N(t)} x_i\right)^2\right\rangle \tag{3}$$

$$=\sum_{i=1}^{N(t)}\langle x^2\rangle_{\text{step}}+2\sum_{i=1}^{N(t)}\sum_{j=1}^{N(t)-i}\langle x_i x_{i+j}\rangle_{\text{step}}, \tag{4}$$

where $\langle\rangle_{\text{step}}$ indicates that the average is performed over a single step, and $N(t)$ is the total number of steps in time t. When there is a single type of site and no correlations, we have that $\langle x_i x_{i+j}\rangle_{\text{step}}=0$, so that

$$\langle x^2(t)\rangle=N(t)a^2, \tag{5}$$

where a is the unit displacement along x and $N(t)$ is the average number of jumps during time t: $N(t)=t/\tau$, where τ is the average residence time in the site. The existence of correlation between jumps complicates this equation, as the cross terms no longer vanish on average. In the case where correlations are only geometric, several general ways of dealing with these cross terms exist, either with linear algebra applied to stochastic matrices[24] or through Laplace-Fourier transforms.[25,26] These methods of calculation should work for all systems presenting geometric correlations at infinite dilution. In a recent paper, Braun and Sholl[27] extended the Laplace-Fourier transform method to calculate exact self-diffusion tensors in generalized lattice-gas models with intrinsic non-Markov behavior, equivalent to what we term kinetic correlations. These methods in general involve quite heavy matrix algebra that can sometimes hide the underlying physical meaning of the parameters. We wish to present in this article another way of calculating the geometric correlations, allowing also the evaluation of kinetic correlations.

Our method is limited to a class of systems where there are uncorrelated sequences of steps. Writing the total displacement as a sum over these uncorrelated sequences rather than over single jumps, we have

$$\langle x^2(t)\rangle = N_{\mathrm{seq}}(t)\langle x^2\rangle_{\mathrm{seq}}, \tag{6}$$

where now $N_{\mathrm{seq}}(t)$ is the total number of uncorrelated sequences during t and $\langle x^2\rangle_{\mathrm{seq}}$ the average MSD during one sequence. This equation is the strict equivalent of Eq. (5), and general treatments applied to Eq. (5) such as mean-field approximations, can also be used to study Eq. (6). Although in general there is no reason why the diffusion of a guest molecule in a zeolite should present uncorrelated sequences, in practice, however, this is found to be the case for numerous systems. For example, geometric correlations disappear if the sum of all jump vectors out of a given site is zero.[1] Note that this also holds for any spatial direction independently of the others, that is, geometric correlations along a given axis x vanish if the sum of the projection of all jump vectors along this axis is zero: $\Sigma_j x_{ij}=0$ for site i. The idea to partition the correlated displacement into uncorrelated sequences is not new and has been used, e.g., by Kidson[28] or Koiwa[29] to study vacancy diffusion in solids. This method allows the development of simpler equations than the general matrix methods, and thus is easier to apply. Of course our method loses in generality what it gains in simplicity.

In this paper, we present the example of benzene diffusion within the supercages of NaY, and of ethane diffusion in the channels of silicalite-1 to show how a total displacement can be cut into uncorrelated sequences. In the latter case, we will consider the existence of kinetic correlations on top of geometrical correlations, as found by Kärger *et al.* in a recent article.[17]

III. BENZENE DIFFUSION IN NaY

The NaY framework presents a series of large cages separated by 12-membered ring (12-T) windows arranged on a tetrahedral lattice.[30] Benzene molecules diffuse on two types of sites in this lattice: S2 sites, where they face a Na(II) cation inside a supercage; and W sites, where they sit in the plane of a 12-T window[31,32]; see Fig. 1 for a schematic representation of the possible jumps of benzene in NaY. Auerbach *et al.* have extensively studied the dynamics of benzene on this lattice of sites,[9,18,33–39] by transforming the complex problem of diffusion on two heterogeneous types of sites into a simpler problem of diffusion from cage to cage. This is in the same spirit as our present work, but the exact treatment was slightly different, as they did not determine the diffusion constant explicitly from the mean-square displacement.

At infinite dilution, the problem can be solved exactly by considering the geometric correlations observed inside a cage. Indeed, in an S2 site the benzene molecule sits next to the cage wall; therefore the next jump will necessarily have a component in the direction opposite to the cage wall. If the molecule keeps jumping back and forth in the cage between S2 sites, all jumps in this sequence will be correlated to each other. On the other hand, as soon as a benzene molecule reaches a 12-T window, it has exactly the same probability to jump forward as backward, so that all correlations will be lost. Therefore we can write the total displacement as a sum over uncorrelated sequences of W→(S2→...→S2)→W, wherein the brackets represent an unbroken series of S2→S2 jumps. Since all axes are equivalent, we can write the MSD along x as

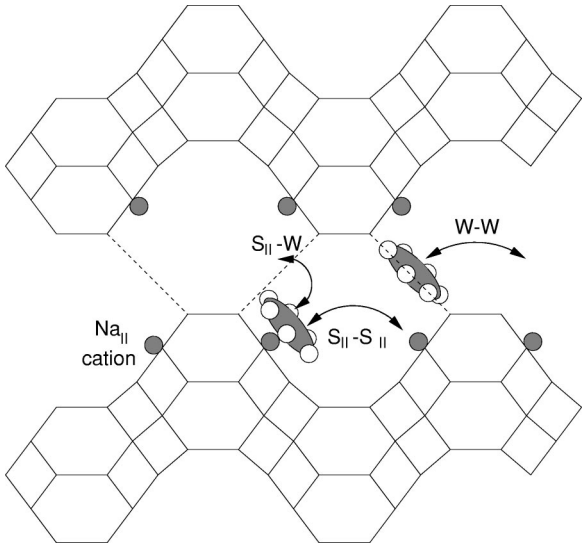

FIG. 1. Schematic view on the structure of zeolite NaY, showing the adsorption sites of benzene and the possible jumps between the sites.

$$\langle x^2(t)\rangle = N_W(t)\langle x^2\rangle_{\mathrm{cage}}, \tag{7}$$

where $N_W(t)$ is the number of times a molecule hops to a window during t, and $\langle x^2\rangle_{\mathrm{cage}}$ is the average MSD between two visits to a window. By definition, this displacement can only span a single cage. Consider the schematic definition of a NaY supercage presented in Fig. 2, and suppose a molecule is initially at W_1. Then its MSD during one sequence inside a cage depends on whether its next window visit will be to W_1, W_2, W_3, or W_4. More specifically, if the molecule goes to W_1 or W_3, $\langle x^2\rangle_{\mathrm{cage}}=0$, while if it visits W_2 or W_4,

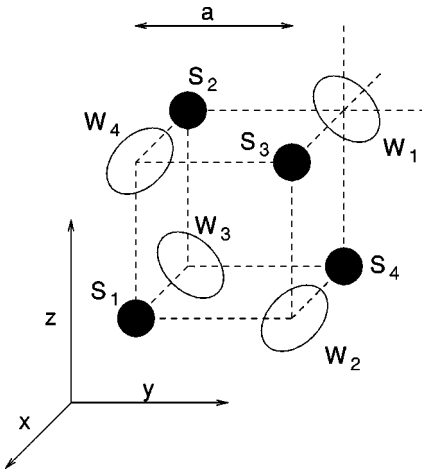

FIG. 2. Schematic view on a supercage of NaY, showing the arrangement of the window sites W_1, W_2, W_3, W_4, and of the S2 sites S_1, S_2, S_3, and S_4 as used in the text.

$\langle x^2\rangle_{\text{cage}}=a^2$. Writing $p(\mathrm{W}_i)$, the probability that a molecule goes to the site W_i either directly or after an unbroken series of S2→S2 jumps, we have that

$$\langle x^2\rangle_{\text{cage}}=2a^2[p(\mathrm{W}_2)+p(\mathrm{W}_4)], \tag{8}$$

where the factor of 2 arises because there are two symmetrical cages in which the molecule can hop. We now define p_{WW}, p_{WS}, p_{SS}, and p_{SW} as the probabilities that a molecule at a 12-T window hops to another window, to an S2 site, and that a molecule at an S2 site goes to another S2 site or to a window, respectively, and $p_n(\mathrm{W}_i)$ as the probability that the molecule is in site W_i after n jumps, so that $p(\mathrm{W}_i)=\Sigma_{n=1}^{\infty}p_n(\mathrm{W}_i)$. After the first jump, we obtain

$$p_1(\mathrm{W}_2)+p_1(\mathrm{W}_4)=\frac{p_{WW}}{3}. \tag{9}$$

After n jumps, we obtain

$$p_n(\mathrm{W}_2)+p_n(\mathrm{W}_4)=\frac{p_{SW}}{3}[2p_{n-1}(\mathrm{S}_1)+p_{n-1}(\mathrm{S}_2)+2p_{n-1}(\mathrm{S}_3)+p_{n-1}(\mathrm{S}_4)], \tag{10}$$

where $p_{n-1}(\mathrm{S}_i)$ is the probability to find the molecule at a site S_i at the end of the preceding jump. In matrix form, this can be written as

$$p_n(\mathrm{W}_2)+p_n(\mathrm{W}_4)=\frac{p_{SW}}{3}\begin{pmatrix}2\\1\\2\\1\end{pmatrix}\mathbf{P}_{n-1}^S, \tag{11}$$

where $\mathbf{P}_n^S$ is the vector containing the probabilities to be at a given site S_i at step n after an unbroken series of S2→S2 jumps. It is easy to see that

$$\mathbf{P}_n^S=\begin{pmatrix}p_n(S_1)\\p_n(S_2)\\p_n(S_3)\\p_n(S_4)\end{pmatrix}=\mathbf{M}\mathbf{P}_{n-1}^S, \tag{12}$$

with $\mathbf{M}$ the connectivity matrix between S2 sites inside a single cage, completely describing the topology of the allowed jumps of benzene in a cage,

$$\mathbf{M}=\begin{pmatrix}0&1/3&1/3&1/3\\1/3&0&1/3&1/3\\1/3&1/3&0&1/3\\1/3&1/3&1/3&0\end{pmatrix}p_{SS}. \tag{13}$$

By recurrence these relations lead to

$$\mathbf{P}_n^S=\mathbf{M}^{n-1}\mathbf{P}_1^S, \tag{14}$$

where $\mathbf{P}_1^S$ is the vector containing the probabilities to find the molecule at any given S2 site in the supercage after the first jump,

$$\mathbf{P}_1^S=\begin{pmatrix}0\\1/6\\1/6\\1/6\end{pmatrix}p_{WS}. \tag{15}$$

The total probability to find the molecule at W_2 or W_4 after any number of S2→S2 jumps in between, thus becomes

$$p(\mathrm{W}_2)+p(\mathrm{W}_4)=\frac{p_{WW}}{3}+\frac{p_{SW}}{3}\begin{pmatrix}2\\1\\2\\1\end{pmatrix}\times\left[\sum_{n=2}^{\infty}\mathbf{M}^{n-2}\right]\begin{pmatrix}0\\1\\1\\1\end{pmatrix}\frac{p_{WS}}{6}. \tag{16}$$

Using the fact that $\Sigma_{n=0}^{\infty}\mathbf{M}^n=(\mathbf{1}-\mathbf{M})^{-1}$, we finally get the mean-square displacement inside a single cage,

$$\langle x^2\rangle_{\text{cage}}=\frac{2}{3}a^2\left(p_{WW}+p_{WS}\frac{2+p_{SS}}{3+p_{SS}}\right). \tag{17}$$

For infinite dilution, we have

$$p_{WW}=\frac{k_{WW}}{k_{WW}+k_{WS}}, \tag{18}$$

$$p_{WS}=\frac{k_{WS}}{k_{WW}+k_{WS}}, \tag{19}$$

$$p_{SW}=\frac{k_{SW}}{k_{SW}+k_{SS}}, \tag{20}$$

$$p_{SS}=\frac{k_{SS}}{k_{SW}+k_{SS}}, \tag{21}$$

and,

$$N_W(t)=\frac{1}{2}\frac{k_{SW}}{k_{WS}}(6k_{WW}+6k_{WS})t, \tag{22}$$

where $k_{\alpha\beta}$ is the fundamental rate constant for a jump from site α to site β, where $\alpha,\beta=S,W$. Combining Eqs. (17) and (22) gives the complete expression for the diffusion coefficient at infinite dilution,

$$D=k_{SW}a^2\left(\frac{k_{WW}}{k_{WS}}+\frac{2k_{SW}+3k_{SS}}{3k_{SW}+4k_{SS}}\right). \tag{23}$$

In Ref. 35, Auerbach *et al.* show that the diffusion coefficient for benzene diffusion in NaY at infinite dilution can be written

$$D=\frac{1}{6}\frac{b^2(T)}{\tau_c}, \tag{24}$$

where τ_c is the average residence time in a cage,

$$\tau_c=\frac{1+2k_{WS}/k_{SW}}{3(k_{WW}+k_{WS})}, \tag{25}$$

and $b(T)$ a temperature-dependent kinetic length describing the average cage-to-cage jump distance. Comparison with our expression of the diffusion coefficient shows that this kinetic length can be written as

$$b(T)=\sqrt{2}a\left(\frac{k_{WW}}{k_{WS}}+\frac{2k_{SW}+3k_{SS}}{3k_{SW}+4k_{SS}}\right)^{1/2}\cdot\left(\frac{k_{SW}+2k_{WS}}{k_{WW}+k_{WS}}\right)^{1/2}. \tag{26}$$

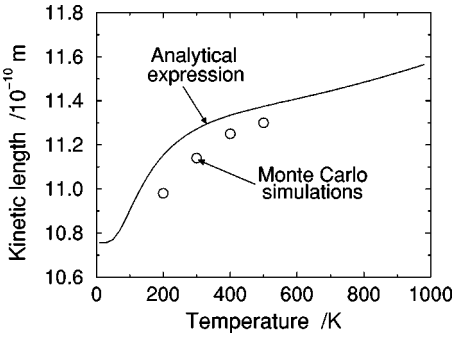

FIG. 3. Kinetic length for the cage-to-cage jumps of benzene in NaY, calculated from Eq. (26) using temperature-dependent rates from Ref. 34, and determined by direct Monte Carlo simulations in Ref. 34.

Figure 3 compares the kinetic length from Eq. (26) with the results of the Monte Carlo simulation reported in Ref. 34, using the temperature-dependent rates given in the same reference. There is a very good agreement between the analytical expression of the kinetic length and the MC data. We see that it is an increasing function of temperature, starting from $\sqrt{3}a = 10.76$ Å at 0 K and increasing to ≈ 11.6 Å at 1000 K.

The expressions derived above are *a priori* valid only for infinite dilution. To extend its use to finite loading, we consider a simple mean-field expression with site-blocking, i.e., allowing at most single occupancy at each site. Then Eqs. (18) to (22) become

$$p_{WW} = \frac{k_{WW}\left(1-\frac{n_W}{N_W}\right)}{k_{WW}\left(1-\frac{n_W}{N_W}\right)+k_{WS}\left(1-\frac{n_S}{N_S}\right)}, \tag{27}$$

$$p_{WS} = \frac{k_{WS}\left(1-\frac{n_S}{N_S}\right)}{k_{WW}\left(1-\frac{n_W}{N_W}\right)+k_{WS}\left(1-\frac{n_S}{N_S}\right)}, \tag{28}$$

$$p_{SW} = \frac{k_{SW}\left(1-\frac{n_W}{N_W}\right)}{k_{SW}\left(1-\frac{n_W}{N_W}\right)+k_{SS}\left(1-\frac{n_S}{N_S}\right)}, \tag{29}$$

$$p_{SS} = \frac{k_{SS}\left(1-\frac{n_S}{N_S}\right)}{k_{SW}\left(1-\frac{n_W}{N_W}\right)+k_{SS}\left(1-\frac{n_S}{N_S}\right)}, \tag{30}$$

and

$$N_W(t) = \frac{n_W}{n}\left[6k_{WW}\left(1-\frac{n_W}{N_W}\right)+6k_{WS}\left(1-\frac{n_S}{N_S}\right)\right]t. \tag{31}$$

In these equations n_W and n_S are the average number of molecules in window and S2 sites, respectively, for a given loading of n molecules, and N_W and N_S are the total number of available sites. n_W and n_S are given by the mean-field master equations,

$$n = n_W + n_S, \tag{32}$$

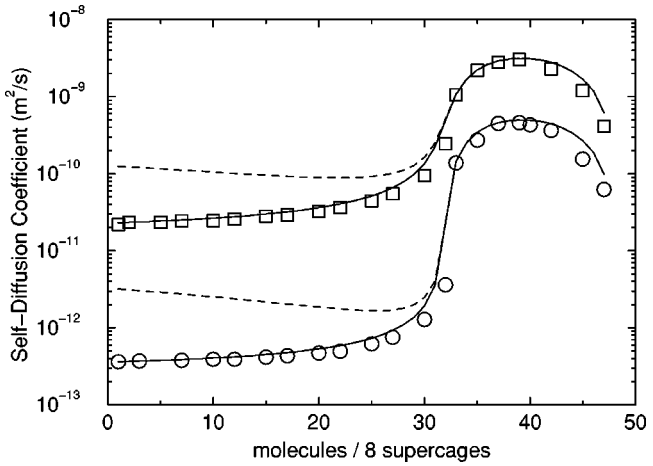

FIG. 4. Diffusion coefficient for benzene in NaY using a site blocking model with single occupancy of the sites. Solid line: present analytical treatment; dashed line: same analytical treatment, without considering geometric correlations; points: results of a kinetic Monte Carlo simulation of Saravanan *et al.* (Ref. 9).

$$\frac{dn_W}{dt} = 0 = -6n_W k_{WS}\left(1-\frac{n_S}{N_S}\right)+3n_S k_{SW}\left(1-\frac{n_W}{N_W}\right). \tag{33}$$

Figure 4 presents a comparison between the analytical results derived here and the kinetic Monte Carlo (KMC) simulation at 300 and 400 K of Saravanan *et al.*[9] The agreement is exact at infinite dilution, and remains very good at nonzero loading. An apparent step around 32 molecules/8 supercages is an artifact due to the small size of the system used in the KMC simulations.[36] The other differences between analytical formulas and simulated points stem from vacancy correlations, which are ignored by the mean-field results presented here. For comparison we also show in dashed lines the theoretical curves obtained without including geometrical correlations. Above 32 molecules/8 supercages, the overwhelming majority of all displacements comes from window-to-window jumps. Since these jumps do not present geometric correlations, the computation with and without correlations gives the same result. Below 32 molecules in 8 supercages, however, the influence of geometrical correlations is important since it reaches more than one order of magnitude at 300 K and infinite dilution.

In the case of benzene in NaY, the existence of only two types of sites, only one of which presents geometrical correlations, simplifies the treatment and allows us to get easily the expression of the self-diffusion coefficient. It is clear that when there are more types of sites, the derivation of an analytical expression becomes more complicated. Nonetheless, the present approach is very general and can be applied, at least in principle, to the calculation of any self-diffusion coefficient exhibiting geometrical correlations. We will see in the next section how the same method can be used to account also for kinetic correlations.

IV. CORRELATED DIFFUSION OF ETHANE IN SILICALITE-1

The channel network of the all-siliceous analog of ZSM-5, silicalite-1, is presented in Fig. 5. There are two

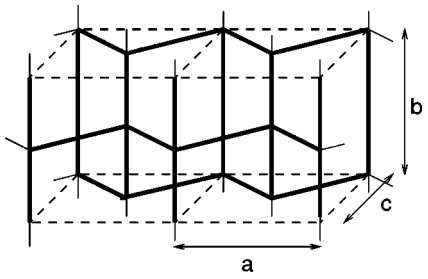

FIG. 5. Schematic view on the channel network of silicalite-1.

types of channels, a straight channel along y and a sinusoidal or zigzag channel in the xz plane, running along x. Sufficiently large adsorbed molecules diffuse through this network *via* a jump diffusion mechanism between the channel intersections.[16,17,40,41]

Kärger *et al.*[17] have shown using molecular dynamics simulations that diffusion of ethane in silicalite-1 presents correlated motions, even at infinite dilution. In particular, the probability to jump twice in the same direction in a sinusoidal channel is much smaller than the probability to jump backward. Although these correlations are most likely kinetic correlations, there are also geometrical correlations due to the confinement of the channel along the z direction.[16] Let us first consider kinetic correlations.

At infinite dilution, all correlations with any preceding jump will be lost as soon as the guest molecule turns from a straight into a sinusoidal channel, or from a sinusoidal channel into a straight channel, since a $\pi/2$ turn on the right has exactly the same probability as a $\pi/2$ turn on the left. Therefore, we can cut the molecule's displacement into N_{seq} sequences of jumps, where each sequence is composed only of jumps occurring inside the same straight or sinusoidal channel. Following our previous reasoning, the displacement in each sequence is uncorrelated with the preceding ones, so that we can write

$$\langle x^2(t)\rangle = N_{\mathrm{seq}}(t) \times \langle x^2\rangle_{\mathrm{seq}}, \tag{34}$$

where $N_{\mathrm{seq}}(t)$ is the total number of sequences of jumps during t, and $\langle x^2\rangle_{\mathrm{seq}}$ the average mean-square displacement during one sequence. In fact, the geometry of silicalite allows us to write for x and y,

$$\langle x^2(t)\rangle = N^{zc}(t)\langle x^2\rangle_{zc}, \tag{35}$$

$$\langle y^2(t)\rangle = N^{sc}(t)\langle y^2\rangle_{sc}, \tag{36}$$

where N^{zc} and N^{sc} are the number of sequences in zigzag and straight channels, respectively, the displacements $\langle x^2\rangle_{zc}$ and $\langle z^2\rangle_{zc}$ are counted in zigzag channels only, and $\langle y^2\rangle_{sc}$ in straight channels only. Since all sequences are alternate by definition, we have that $N^{zc}=N^{sc}=N_{\mathrm{seq}}/2$. For the z-axis, the existence of correlations between sequences implies

$$\langle z^2(t)\rangle = N^{zc}(t)\langle z^2\rangle_{zc} + 2\sum_{i=1}^{N^{zc}} \sum_{j=1}^{N^{zc}-i} \langle z_i z_{i+j}\rangle_{zc}. \tag{37}$$

These correlations between sequences along z stem from the geometry of the channel network, and are therefore geometrical correlations akin to what has been computed for the diffusion of benzene in NaY. These correlations have been recognized by Kärger and used to develop the correlation rule for random walk diffusion in silicalite-1.[16] Their evaluation will be discussed later.

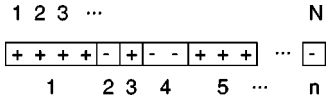

FIG. 6. A sequence of N jumps arranged in n series going in the same direction.

We define six different probabilities representing the correlations: (i) p_{sc}^{f} is the probability that, the preceding jump being in a straight channel, the next jump occurs in the same forward direction; (ii) p_{sc}^{b}, the probability that, the preceding jump being in a straight channel, the next jump occurs in the opposite backward direction; (iii) p_{sc}^{zc}, the probability that, the preceding jump being in a straight channel, the next jump occurs in a zigzag channel; (iv) p_{zc}^{f}, the probability that, the preceding jump being in a zigzag channel, the next jump occurs in the same forward direction; (v) p_{zc}^{b}, the probability that, the preceding jump being in a zigzag channel, the next jump occurs in the opposite backward direction; and (vi) p_{zc}^{sc}, the probability that, the preceding jump being in a zigzag channel, the next jump occurs in a straight channel. Of course $p_{sc}^{f}+p_{sc}^{b}+p_{sc}^{zc}=1$ and $p_{zc}^{f}+p_{zc}^{b}+p_{zc}^{sc}=1$. Consider a series of exactly N jumps in a single straight channel; the probability of such a series of events is $p(N)=A\tilde{p}(N)$, where A is a normalization constant and

$$\tilde{p}(N) = p(zc) \times p_{zc}^{sc}(p_{sc}^{f}+p_{sc}^{b})^{N} p_{sc}^{zc}, \tag{38}$$

where $p(zc)$ is the probability to be inside a zigzag channel before the series, p_{zc}^{sc}, the probability to jump into a straight channel, and p_{sc}^{zc}, the probability to jump to a zigzag channel at the end of a sequence. Since there are no series of 0 jumps, the normalization constant is $A=[\Sigma_{N=1}^{\infty}\tilde{p}(N)]^{-1} = [p(zc)p_{zc}^{sc}(p_{sc}^{f}+p_{sc}^{b})]^{-1}$, so that the average number of jumps in one sequence along a straight channel becomes

$$\langle N\rangle_{sc} = \sum_{N=1}^{\infty} Np(N) = (p_{sc}^{zc})^{-1}. \tag{39}$$

The total time a guest molecule has spent in the zeolite can be written as

$$t = \frac{N_{\mathrm{seq}}}{2}(\langle N\rangle_{sc}\Delta t_{sc} + \langle N\rangle_{zc}\Delta t_{zc}), \tag{40}$$

thus allowing us to write explicitly N_{seq} as a function of time. Note that we have supposed here for generality that $\Delta t_{sc} \neq \Delta t_{zc}$, although we consider only one type of site in the system.

We are left with the calculation of $\langle x^2\rangle_{zc}$ and other similar terms. Let us first examine what happens along a straight channel. Consider a series of N jumps occurring inside the same straight channel, such as the one presented in Fig. 6. Such a series can be cut into n smaller fragments during which the molecule always goes in the same direction, either $y+$ or $y-$. The probability for such a series is

$$p = p_{zc}^{sc}(p_{sc}^{f})^{N-n}(p_{sc}^{b})^{n-1}p_{sc}^{zc}, \tag{41}$$

wherein $n-1$ appears because the first term of each fragment is a backward jump (except for the first term of the first fragment which is a zigzag→straight jump) and all others are forward jumps. Note that no series can have 0 fragment or 0 jump.

The probability $p(n_+,n_-)$ that a molecule makes n_+ jumps toward $y+$ and n_- jumps toward $y-$ in this series has already been calculated by Jousse *et al.*[4] to represent the correlated diffusion of butene in theta-1, and can be written,

$$p(n_+,n_-)=\frac{p^b}{p^f}(p^f)^N\Bigg\{2\sum_{k=0}^{s}\binom{m}{k}\binom{s}{k}\left(\frac{p^b}{p^f}\right)^{2k}+\sum_{k=0}^{s}\binom{m}{k+1}\binom{s}{k}\left(\frac{p^b}{p^f}\right)^{2k+1}+\sum_{k=0}^{s-1}\binom{m}{k}\times\binom{s}{k+1}\left(\frac{p^b}{p^f}\right)^{2k+1}\Bigg\}; \tag{42}$$

$$p(n_+,0)=p(0,n_-)=(p^f)^N. \tag{43}$$

Here, $N=n_++n_-$, $m=n_+-1$, $s=n_--1$, and we assume here that $m\geqslant s$ (a symmetric expression is found when $m<s$). Since this expression is valid for any type of sequence, we only write the forward and backward probability p^f and p^b without indication of a specific channel. The total probabilities $p(n_+,n_-)$ in Eqs. (42) and (43) are not normalized. In contrast with the treatment in Ref. 4, we have kept the term $(p^f)^N$ that proves important in the present case. Indeed, in theta-1 the diffusion is unidirectional so that correlation is never lost and we can put $N\to\infty$ in Eqs. (42) and (43), resulting in huge simplifications. However, in the present case, correlations are lost after only a few N and it is necessary to keep the full expression. The MSD is calculated from Eqs. (42) and (43) by evaluating

$$\langle y^2\rangle_{sc}=\langle n^2\rangle_{\text{seq}}\left(\frac{b}{2}\right)^2. \tag{44}$$

$\langle n^2\rangle_{\text{seq}}$ represents the average MSD during one sequence, in terms of jumps,

$$\langle n^2\rangle_{\text{seq}}=\frac{\Sigma_{n_-=0}^{\infty}\Sigma_{n_+=0}^{\infty}(n_+-n_-)^2p(n_+,n_-)}{\Sigma_{n_-=0}^{\infty}\Sigma_{n_+=0}^{\infty}p(n_+,n_-)-1}, \tag{45}$$

where the 1 in the denominator accounts for the fact that the term $n_+=n_-=0$ has to be excluded from the sum, since no series can have 0 jump. Calculating these series requires some effort. We need to recognize that the different sums can be rearranged, so that,

$$\sum_{m=0}^{\infty}\sum_{s=m}^{\infty}\sum_{k=0}^{s}+\sum_{s=0}^{\infty}\sum_{m=s+1}^{\infty}\sum_{k=0}^{m}=\sum_{k=0}^{\infty}\sum_{m=k}^{\infty}\sum_{s=k}^{\infty}. \tag{46}$$

Using the fact that, for $|x|<1$,[42]

$$\sum_{n=0}^{\infty}\binom{n+k}{n}x^n=\frac{1}{(1-x)^{k+1}}, \tag{47}$$

we finally get

$$\langle n^2\rangle_{\text{seq}}=\frac{1+p\chi}{1-p\chi}\frac{1}{1-p}. \tag{48}$$

In this expression, $p=p^f+p^b$ is the total probability that the molecule's next jump will be in the same channel, irrespective of the direction. We call it the ''channel probability.'' $\chi=(p^f-p^b)/(p^b+p^f)$ is the correlation coefficient: $\chi=-1.0$ indicates that the molecule always jumps backward, $\chi=0.0$ is the normal uncorrelated random walk, and $\chi=+1.0$ indicates that the molecule always jumps forward. We can verify that in the case $\chi=0$, Eq. (44) gives the simple result: $\langle n^2\rangle_{sc}(\chi=1)=(p_{sc}^{zc})^{-1}$. If there are no correlations, necessarily $\Delta t_{sc}=\Delta t_{zc}$ so that using Eqs. (34), (39), and (40) gives

$$D_y=\frac{1}{2}\frac{\langle y^2(t)\rangle}{t}=\frac{1}{2}kp_{zc}^{sc}\left(\frac{b}{2}\right)^2, \tag{49}$$

where $k=N/t$ is the total rate constant for a jump so that $(1/2)kp_{zc}^{sc}$ represents the rate for a jump through a straight channel, which is the usual uncorrelated result.

We can write the same equation as (44) for the MSD $\langle x^2\rangle_{zc}$ by replacing b with a in Eq. (44), and using the same expression of $\langle n^2\rangle_{\text{seq}}$. The case of $\langle z^2\rangle_{zc}$ is slightly different, and in fact much simpler. Indeed there is no important difference with the calculation in the case of normal random walk treated by Kärger.[16] Each sequence of jumps in a zigzag channel will result in a displacement of $+c/2$, $-c/2$, or 0: 0 if the sequence has an even number of jumps, $\pm c/2$ if it has an odd number of jumps, depending on the channel it is in; indeed, some intersections can only give $+c/2$ displacements and other $-c/2$ displacements. The first term of Eq. (37) is simply the probability that there is an odd number of jumps in the sequence along the zigzag channel. Writing this probability ζ_o, we have

$$\langle z_i^2\rangle_{zc}=\left(\frac{c}{2}\right)^2\zeta_o. \tag{50}$$

We need to recognize, as does Kärger, that if a molecule starts at a given type of intersection, it will be found in the same type of intersection if there has been an even number of jumps in between and at the other type if there has been an odd number of jumps. Suppose a first sequence in a zigzag channel results in a displacement of $+c/2$; then a jth sequence afterward will also present a displacement of $+c/2$ (provided it has an odd number of jumps) if the total number of jumps in the $j-1$ sequences along the straight channel and the $j-1$ sequences along the zigzag channel in between is even; a displacement of $-c/2$ in the opposite case. Introducing ζ_o ($\zeta_e=1-\zeta_o$, respectively), the probability that a sequence in a zigzag channel is made of an odd number of jumps (even, respectively), and σ_o ($\sigma_e=1-\sigma_o$, respectively), the probability that a sequence along a straight channel is made of an odd number of jumps (even, respectively), we see that

$$\langle z_iz_{i+j}\rangle_{zc}=\left(\frac{c}{2}\right)^2\zeta_o\times(\sigma_o\zeta_o-\sigma_o\zeta_e-\sigma_e\zeta_o+\sigma_e\zeta_e)^{j-1}\times(\sigma_o-\zeta_o)\zeta_o, \tag{51}$$

where the first ζ_o indicates that only those jumps with a nonzero displacement are correlated with subsequent jumps, the term in brackets represents the probability to have an

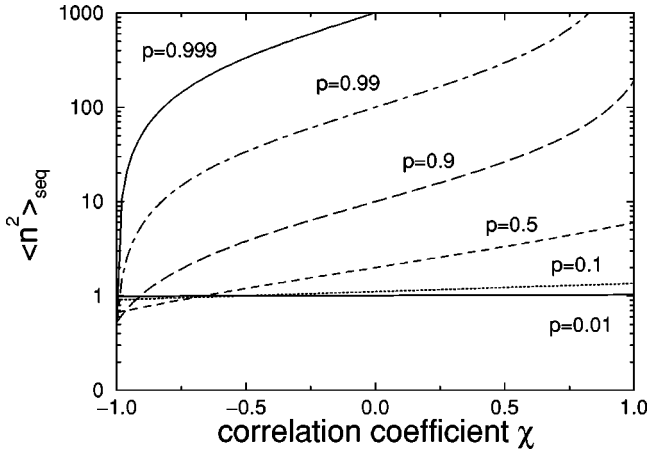

FIG. 7. Plot of $\langle n^2\rangle_{\mathrm{seq}}$ as a function of the correlation coefficient $\chi=(p^f-p^b)/(p^f+p^b)$, for different fixed values of the channel probability $p=p^f+p^b$.

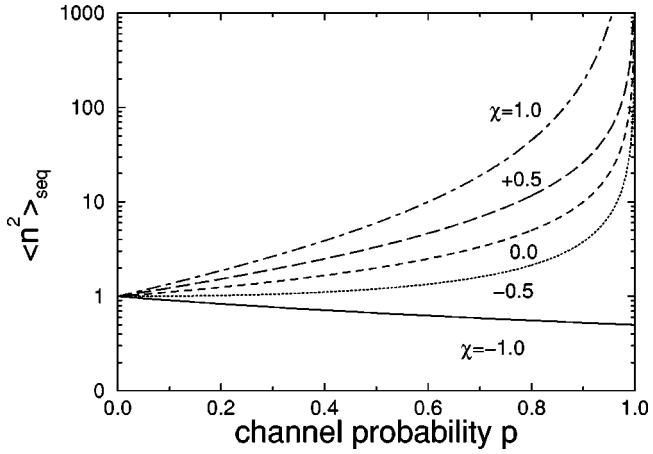

FIG. 8. Plot of $\langle n^2\rangle_{\mathrm{seq}}$ as a function of the channel probability $p=p^f+p^b$ for different fixed values of the correlation coefficient $\chi=(p^f-p^b)/(p^f+p^b)$.

even or odd number of jumps in between, and the last term the probability that the jth displacement is nonzero. Putting back Eqs. (50) and (51) into (37) gives

$$\langle z^2\rangle = N^z\left(\frac{c}{2}\right)^2 \frac{\zeta_o\sigma_o}{\zeta_o\sigma_e+\zeta_e\sigma_o}. \tag{52}$$

The probability that a series contains an odd or an even number of jumps is easily calculated from Eq. (38), where in contrast with Ref. 16 no series of zero jumps is allowed,

$$\zeta_o=\frac{1}{2-p_{zc}^{sc}}, \quad \zeta_e=1-\zeta_o, \tag{53}$$

with the same equations for σ_o and σ_e where p_{zc}^{sc} is replaced by p_{sc}^{zc}. This leads to the particularly simple expression,

$$\langle z^2\rangle = N^{zc}(t)\left(\frac{c}{2}\right)^2 \frac{1}{2-(p_{sc}^{zc}+p_{zc}^{sc})}. \tag{54}$$

When there are no correlations, we have that $p_{sc}^{zc}+p_{zc}^{sc}=1$ by definition, so that with Eqs. (39) and (40), Eq. (54) transforms into

$$D_z=\frac{1}{2}\left(\frac{c}{2}\right)^2 k p_{sc}^{zc}p_{zc}^{sc}, \tag{55}$$

that is, the normal random walk result consistent with Kärger's correlation rule.[16]

Figure 7 presents a plot of $\langle n^2\rangle_{\mathrm{seq}}$ as a function of the correlation coefficient χ for different values of the channel probability $p=p_{sc}^f+p_{sc}^b$, as calculated from Eq. (48). Figure 8 presents a plot of $\langle n^2\rangle_{\mathrm{seq}}$ as a function of the channel probability p for different values of the correlation coefficient χ, also from Eq. (48). The uncorrelated case corresponds to $\chi=0.0$, while $\chi<1$ indicates a larger probability to go backward and $\chi>1$ a larger probability to go forward. The channel probability p indicates the probability that the next jump will be in the same channel, irrespective of the direction. When $p\ll 1$, the molecule only jumps once in the channel before going to another channel, so that $\langle n^2\rangle_{\mathrm{seq}}\to 1$, whatever the correlation coefficient; when $p\approx 1$ the sequence of jumps inside one channel becomes larger and larger, so that $\langle n^2\rangle_{\mathrm{seq}}$ also increases, with the exception of the case $\chi=-1.0$. In this case indeed, the molecule *always* jumps backward, so that the maximum displacement is 1. The largest effect of the correlation is observed for $p\approx 1$, that is, for quasi-unidirectional motion in a channel. The case $p=1$ is treated in Ref. 4. Note that Eq. (48) is a very general result, and can be used for any sequence of jumps.

While we have already said that the present approach applies strictly speaking only to infinite dilution, it is nevertheless worthwhile to look at the agreement between theory and simulations as a function of loading. We therefore performed kinetic Monte Carlo simulations on the model of ethane diffusion in silicalite, using the jump diffusion model with correlations presented in Ref. 4, considering only excluded volume interactions between molecules. The special case $p_{sc}=p_{zc}=1/2$ and $k=1$ ps is presented here. With only excluded volume interactions, $\langle N\rangle_{sc}$, $\langle N\rangle_{zc}$, and $\langle n^2\rangle_{\mathrm{seq}}$ are independent of loading, so that the only loading-dependent quantity is N_{seq}, which takes the following simple form:

$$N_{\mathrm{seq}}(c)=N_{\mathrm{seq}}(0)(1-c), \tag{56}$$

where c is the fractional concentration of guest molecules. Figure 9 shows the agreement between theory and kinetic Monte Carlo simulations, for concentrations of 0, 0.4, 0.8, and 0.95. Points are KMC simulation results for the self-diffusion coefficient along x, as a function of the correlation coefficient, while the lines are the corresponding theoretical curves. The agreement is exact at infinite dilution, but a slight discrepancy appears with increasing loading. This discrepancy is a measure of the vacancy correlation factor, since kinetic correlations are already taken into account. Figure 10 presents the corresponding vacancy correlation factor as a function of loading, defined as the ratio of the diffusion coefficient from simulation and from mean-field theory: $f=D_x/D_x^{\mathrm{MF}}$. For small to medium concentration, f is nearly independent of the kinetic correlation coefficient. Only for high loading do we observe an influence of χ, as positive kinetic correlations tend to decrease the f while negative correlations increase f.

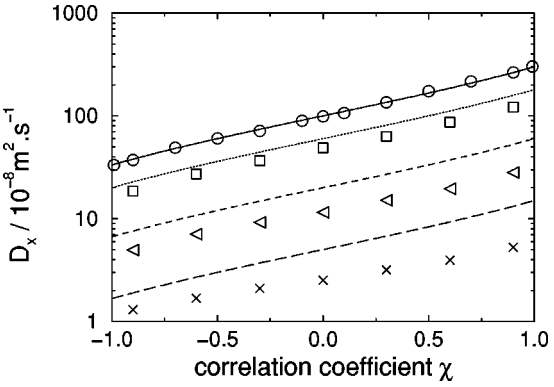

FIG. 9. Plot of the self-diffusion constant D as a function of the correlation coefficient χ in the zig-zag channel x for the model diffusion of ethane in silicalite described in the text, for several loading with excluded volume interactions. The following values of the parameter were used: $p_s = p_z = 1/2$; $k = 1.0$ ps. Points are results of a kinetic Monte Carlo simulation, lines are the theoretical curves within the mean-field approximation. Circles and straight line: infinite dilution $c = 0.0$; squares and dotted line: $c = 0.4$; triangles and dashed line: $c = 0.8$; cross and long-dashed line: $c = 0.95$.

Table I presents a comparison of the diffusion coefficients of ethane in silicalite-1, as computed with the current model using a probability set calculated from molecular dynamics (MD) simulations in Ref. 17, with the diffusion coefficients computed in Ref. 17 from MD, from a simple random walk model (RW), and from the two-step random walk model (two-step). In almost all cases the current model improves the agreement with the MD diffusion coefficient, for all D_x, D_y, and D_z. This is particularly true for D_x, which exhibits strong negative kinetic correlations in the MD calculations (corresponding to $\chi \approx -0.5$ to -0.7, depending on loading and temperature), making a forward jump much less probable than a backward jump in the zigzag channels. This shows that our model handles in a much more accurate way these strong kinetic correlations. The agreement remains fair over the range of loadings presented, although we have explicitly stated that our model is only approximate in these cases: indeed, vacancy correlations show up both inside a sequence of jumps and between sequences. Vacancy correlations, however, remain small,[1] so that this agreement is plausible.

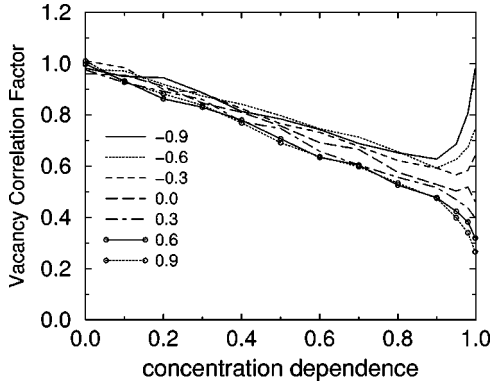

FIG. 10. Plot of the vacancy correlation factor $f = D_x / D_x^{MF}$ as a function of loading, for several values of the correlation coefficient χ.

TABLE I. Calculated diffusion coefficients using data from Ref. 17. (1) 300 K, 1 mol./uc; (2) 300 K, 2 mol./uc; (3) 300 K, 4 mol./uc; (4) 300 K, 6 mol./uc; (5) 400 K, 4 mol./uc; (6) 500 K, 4 mol./uc.

$D/10^{-9}$ m^2/s^2	MD[a]	RW[b]	Two-step[c]	Current model[d]
$D_x^{(1)}$	5.7	13.4	8.6	6.4
$D_y^{(1)}$	13.1	12.4	12.2	12.6
$D_z^{(1)}$	1.8	2.9	2.1	1.6
$D_x^{(2)}$	5.7	14.3	8.2	5.7
$D_y^{(2)}$	8.3	13.8	12.6	12.6
$D_z^{(2)}$	2.0	3.2	2.0	1.5
$D_x^{(3)}$	5.5	12.4	7.6	5.5
$D_y^{(3)}$	9.1	11.0	10.7	10.8
$D_z^{(3)}$	1.2	2.7	1.6	1.2
$D_x^{(4)}$	2.9	10.0	5.1	3.4
$D_y^{(4)}$	5.3	9.4	7.9	7.3
$D_z^{(4)}$	0.7	2.2	1.3	0.9
$D_x^{(5)}$	7.7	16.7	11.2	8.6
$D_y^{(5)}$	14.7	15.7	15.1	14.4
$D_z^{(5)}$	1.5	3.7	2.5	1.9
$D_x^{(6)}$	8.1	19.9	13.8	10.3
$D_y^{(6)}$	22.5	21.7	19.1	17.5
$D_z^{(6)}$	2.3	4.8	3.4	2.8

[a]From molecular dynamics simulations, values of Ref. 17.
[b]From a simple random walk model, data from Ref. 17.
[c]From a two-step random walk model, data from Ref. 17.
[d]From the model presented in this paper.

V. CONCLUSION

We have shown how to partition the correlated displacement of one molecule in a zeolite represented by a lattice of sites into uncorrelated sequences of jumps, in order to allow an easy calculation of the diffusion coefficient at infinite dilution. This approach can be used to analyze both geometric correlations due to the nonsymmetric nature of some adsorption sites in zeolite pores, and kinetic correlations due to an insufficient thermalization of the molecule in its final site. These correlations can have an important effect on the diffusion coefficient, resulting in a difference that can range over several orders of magnitude for very strong correlations. We have applied this method to two model systems, that is, benzene in NaY and ethane in silicalite. In both cases the analytical expressions derived from the model capture the behavior of the self-diffusion coefficient, as compared with kinetic Monte Carlo simulations as well as molecular dynamics simulations. Although the exact analytical expression of the self-diffusion coefficient as a function of the basic rate constants is necessarily system-specific, the two examples presented here provide the reader with a number of methods and some results allowing one to study generally diffusion of small adsorbates in cage or channel zeolites. In particular, Eq. (48) is completely general and applies to any sequence of kinetically correlated jumps, whatever the system.

This approach can be used to determine the self-diffusion coefficient as a function of the fundamental rate constants for any type of guest on a zeolite lattice. Thus it allows us to study in a simple way the influence of the lattice geometry and connectivity on the diffusion coefficient. This type of relation is particularly interesting to link the results of experimental techniques such as pulsed-field gradient NMR or quasielastic neutron scattering, which probe directly

the guests' mean-square displacement, to other techniques such as solid-state NMR, which probe the residence-time distributions and orientational correlation times, and hence the fundamental rate constants.

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