Ising Model of Diffusion in Molecular Sieves

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We have developed a new analytical theory for activated diffusion in zeolites at finite loadings, including the effect of adsorbate-adsorbate interactions. Excellent qualitative agreement is obtained comparing our new theory to kinetic Monte Carlo simulations. We have applied this theory to benzene diffusion in faujasite, to help resolve discrepancies among different experiments. Our results are in qualitative agreement with pulsed field gradient NMR, and in qualitative disagreement with tracer zero-length column data. [S0031-9007(98)06457-6]

The transport properties of adsorbed molecules play a central role in separations and reactions that take place within zeolites and other shape-selective, microporous catalysts. Significant effort has been devoted to understanding diffusion in zeolites [1,2], revealing fascinating physical effects such as anomalous diffusion [3,4], correlated cluster dynamics [5], soft core interactions [6], and percolation [7]. Despite this recent progress, developing a predictive analytical theory for normal diffusion in zeolites has remained challenging [8], due to the coupling between infrequent event dynamics and strong adsorbate-adsorbate interactions. To address this issue, we have developed a new theory for self-diffusion in zeolites based on mean field dynamics of cage-to-cage motion. In this Letter, we show that excellent qualitative agreement is obtained comparing our new theory to kinetic Monte Carlo simulations [9].

We apply the new transport theory below to aromatic diffusion in cation-containing faujasites. These systems have received considerable attention recently because of persistent, qualitative discrepancies among different experimental probes of the coverage dependence of self-diffusion [1]. Pulsed field gradient (PFG) NMR diffusivities decrease monotonically with loading [10], while tracer zero-length column (TZLC) data *increase* monotonically with loading [11]. TZLC is a flow method that measures the desorption rate arising from tracer exchange in a zero-length chromatographic column containing zeolite particles. The TZLC data are converted to self-diffusivities through a model assuming that tracer exchange introduces no chemical potential gradient. PFG NMR differs from TZLC in that the NMR experiment directly measures the mean square displacement of magnetically labeled particles at equilibrium in a zeolite. Addressing the discrepancy between PFG NMR and TZLC with theory and simulation will provide deep understanding of the microscopic physics essential to these transport phenomena. Our new theory predicts self-diffusion coefficients in qualitative agreement with PFG NMR [10], and in qualitative disagreement with TZLC data [11].

We model self-diffusion in zeolites at finite loadings by replacing the zeolite framework with a three dimensional Ising lattice of binding sites [12]. For example, benzene has two predominant binding sites in Na-Y (Si : Al = 2.0), a synthetic version of the mineral faujasite. In the primary site, denoted as S_{II}, benzene is facially coordinated to a zeolite 6-ring, about 2.7 Å above a Na cation [13]. In the secondary site, denoted as W, benzene is centered in the 12-ring window separating adjacent cages, about 5.3 Å from the S_{II} site [13]. Figure 1 shows schematic adsorption sites and jumps for benzene in Na-Y. The lattice of benzene binding sites in Na-Y contains four tetrahedrally arranged S_{II} sites and four tetrahedrally arranged, doubly shared W sites per cage. A saturation coverage of about six molecules per cage is found for benzene in Na-Y, corresponding to occupation of all S_{II} and W sites. In what follows, the W and S_{II} sites are denoted sites 1 and 2, respectively.

We have previously shown that for self-diffusion in cage-type zeolites at finite fractional loadings, θ, the diffusion coefficient is given by $D_\theta \cong \frac{1}{6} k_\theta a_\theta^2$, where a_θ is the mean intercage jump length ($a_\theta \cong 11$ Å for Na-Y) and $1/k_\theta$ is the mean cage residence time [6]. This expression
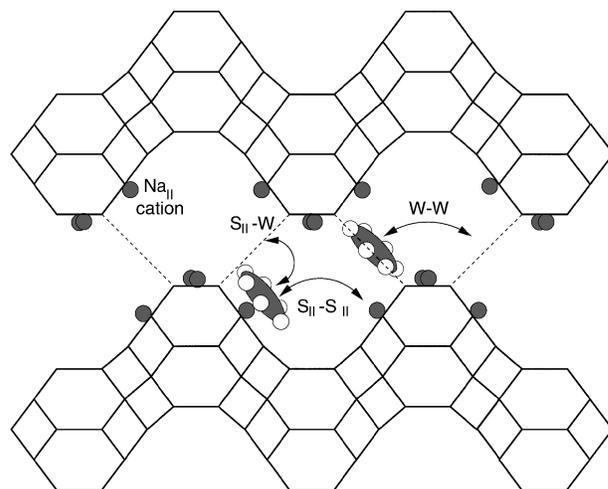
FIG. 1. Adsorption sites and jumps for benzene in Na-Y.

also applies to diffusion in, e.g., ZSM-5 zeolite [1], where channel intersections play the role of cages. Furthermore, we have determined that $k_\theta = \kappa k_1 P_1$, where $P_1 = [1 + K_{eq}(1 \rightarrow 2)]^{-1}$ is the probability of occupying a W site, $\langle \tau_1 \rangle = 1/k_1$ is the mean W site residence time, and κ is the transmission coefficient for cage-to-cage motion [6]. Our theory thus provides a picture of cage-to-cage motion involving transition state theory ($k_1 P_1$) with dynamical corrections (κ). Such a picture also applies to diffusion in ZSM-5, where channels play the role of W sites. This finding is significant since it shows that kinetics needs to be considered only for jumps originating at threshold sites between cages. It is reasonable to expect that $\kappa \cong \frac{1}{2}$ for all but the highest loadings. We also expect that P_1 will increase with loading, and that k_1 will decrease with loading. Below we determine the loading dependencies of κ, k_1, and P_1 using mean field theory [12] and kinetic Monte Carlo simulations. Our results elucidate how the balance between k_1 and P_1 controls the resulting concentration dependence of the self-diffusion coefficient.

The loading dependence of P_1, the probability of occupying a W site, is influenced by blocking stable S_{II} sites and by adsorbate-adsorbate interactions that modify the relative stabilities of adsorption sites. We determined the loading dependence of P_1 with the Ising model, limiting the range of adsorbate-adsorbate interactions to nearest neighbors. The Ising Hamiltonian for a lattice with M sites takes the form:

$$H(\vec{n}) = \sum_{i=1}^{M} n_i \tilde{\varepsilon}_i + \frac{1}{2} \sum_{i,j=1}^{M} n_i \tilde{J}_{ij} n_j, \quad (1)$$

where $\vec{n} = (n_1, n_2, \ldots, n_M)$ are site occupation numbers listing a configuration of the system, and $\tilde{\varepsilon}_i$ is the energy for binding in site i. In Eq. (1), $\tilde{J}_{ij}$ is the nearest neighbor interaction between sites i and j; i.e., $\tilde{J}_{ij} = 0$ if sites i and j are not nearest neighbors. In the Na-Y lattice, with twice as many S_{II} sites as W sites, P_1 is given by $1/(1 + 2\theta_2/\theta_1)$, where θ_1 and θ_2 are the fractional coverages on W and S_{II} sites, respectively. The total fractional coverage is $\theta = (\theta_1 + 2\theta_2)/3$. Determining θ_1 and θ_2 thus provides the loading dependence of P_1.

We apply mean field theory in the grand canonical ensemble to average over local fluctuations in the instantaneous field on each adsorption site. Mean field theory is qualitatively valid at the temperatures studied herein, because strong zeolite-guest binding reduces the critical temperatures of these systems to very low values. To implement this approach for benzene in Na-Y, it is convenient to distinguish explicitly S_{II} and W site occupation numbers. For a lattice with M_1 W sites and $M_2 = 2M_1 = M - M_1$ S_{II} sites, the Ising Hamiltonian takes the form:

$$H(\vec{s}, \vec{\sigma}) = \sum_{i=1}^{M_1} s_i \varepsilon_1 + \frac{1}{2} \sum_{i,j=1}^{M_1} s_i J_{ij}^{11} s_j + \sum_{i=1}^{M_1} \sum_{j=1}^{M_2} s_i J_{ij}^{12} \sigma_j$$
$$+ \frac{1}{2} \sum_{i,j=1}^{M_2} \sigma_i J_{ij}^{22} \sigma_j + \sum_{i=1}^{M_2} \sigma_i \varepsilon_2, \quad (2)$$

where $\vec{s}$ and $\vec{\sigma}$ are site occupation numbers for W and S_{II} sites, respectively, and ε_1 and ε_2 are their respective site energies. In Eq. (2), J_{ij}^{11}, J_{ij}^{12}, and J_{ij}^{22} are the nearest neighbor W-W, W-S_{II}, and S_{II}-S_{II} interactions, respectively; i.e., $J_{ij}^{11} = J_{11}$ for nearest neighbor W sites and zero otherwise, and so on for J_{ij}^{12} and J_{ij}^{22}. The fractional loadings, θ_1 and θ_2, are evaluated within mean field theory according to $\theta_1 = \langle s_i \rangle_{MF}$ and $\theta_2 = \langle \sigma_i \rangle_{MF}$.

In order to develop viable theory and simulation strategies for modeling k_1, the total rate of leaving a W site, we need to account for the blocking of target sites and adsorbate-adsorbate interactions that modify jump activation energies. There would thus be a multitude of fundamental rate coefficients contributing to k_1, depending upon specific configurations of the system. A mean field expression summarizing these effects is given by $k_1 \cong 6(1 - \theta_1)\langle k_{1\rightarrow1} \rangle + 6(1 - \theta_2)\langle k_{1\rightarrow2} \rangle$, where $6(1 - \theta_j)$ counts available target sites, and $\langle k_{1\rightarrow j} \rangle$ averages over fluctuating rate coefficients for jumps leaving W sites. In order to account for such effects, we have generalized a model that relates binding energies to transition state energies used previously by Hood et al. [14], and also used by us for predicting mobilities in zeolites [15]. We assume that the minimum energy hopping path connecting adjacent sorption sites is characterized by intersecting parabolas, shown in Fig. 2, with the site-to-site transition state located at the intersection point. For a jump from site i to site j, with $i, j = 1, \ldots, M$, the hopping activation energy including adsorbate-adsorbate interactions is given by

$$E_a(i,j) = E_a^{(0)}(i,j) + \Delta E_{ij}\left(\frac{1}{2} + \frac{\delta E_{ij}^{(0)}}{k_{ij} a_{ij}^2} \right)$$
$$+ \Delta E_{ij}^2 \left(\frac{1}{2 k_{ij} a_{ij}^2} \right), \quad (3)$$

where $E_a^{(0)}(i,j)$ is the activation energy without guest-guest interactions, i.e., the infinite dilution activation energy, and a_{ij} is the jump distance. ΔE_{ij} is the *shift* in the energy difference between sites i and j resulting from guest-guest interactions, and is given by $\Delta E_{ij} = \delta E_{ij} - \delta E_{ij}^{(0)} = (E_j - E_i) - (\tilde{\varepsilon}_j - \tilde{\varepsilon}_i)$, where $E_k = \tilde{\varepsilon}_k + \sum_{l=1}^{M} \tilde{J}_{kl} n_l$ for a particular lattice configuration $\vec{n}$. This method allows the rapid estimation of configuration dependent barriers during a kinetic Monte Carlo simulation, knowing only infinite dilution barriers and the nearest neighbor Ising interactions defined above. The parabolic jump model is most accurate when the spatial paths of jumping molecules are not drastically changed by adsorbate-adsorbate interactions, although the energies can change as shown in Fig. 2. We have performed several many-body reactive-flux correlation function calculations [12] that give barriers in qualitative agreement with the parabolic jump model. A more detailed test of this method will be reported in a forthcoming publication [16].

The parabolic jump model is also amenable to mean field theory. Assuming that fluctuations in the
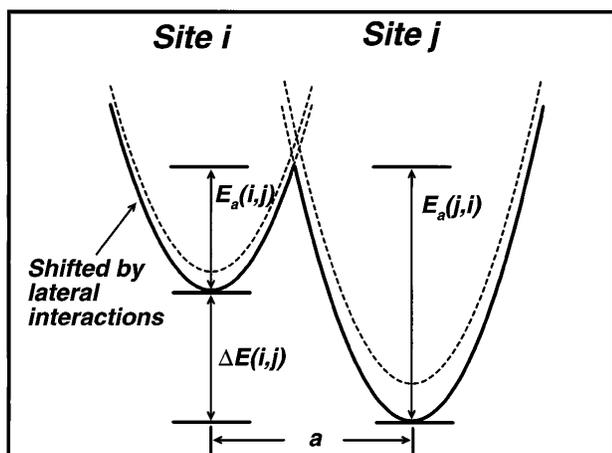
FIG. 2.   Model relating altered binding energies to modified transition state energies.

preexponentials can be ignored and that activation energies are Gaussian distributed, we have that $\langle k_{i \to j} \rangle \cong \nu_{i \to j} \langle e^{-\beta E_a(i,j)} \rangle = \nu_{i \to j} e^{-\beta \langle E_a(i,j) \rangle} e^{-\beta^2 \sigma_a^2(i,j)/2}$, where $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, and $\sigma_a^2(i,j)$ is the variance of the Gaussian distribution of activation energies, i.e., $\sigma_a^2(i,j) = \langle [E_a(i,j) - \langle E_a(i,j) \rangle]^2 \rangle = \langle [E_a(i,j)]^2 \rangle - \langle E_a(i,j) \rangle^2$. We see from Eq. (3) that applying mean field theory requires averages of ΔE_{ij}^k up to $k = 4$. We only consider terms up to second order, since higher order terms will typically be small. Using the notation that 1 and 2 denote nearest neighbor W and S_{II} sites, respectively, we obtain for benzene in Na-Y

$$\langle \Delta E_{11} \rangle = 0 \,,$$

$$\langle \Delta E_{12} \rangle = (3J_{12} - 6J_{11})\theta_1 + (3J_{22} - 6J_{12})\theta_2 \,, \qquad (4)$$

$$\langle \Delta E_{11}^2 \rangle = 8J_{11}^2 \theta_1 (1 - \theta_1) + 8J_{12}^2 \theta_2 (1 - \theta_2) \,,$$

$$\langle \Delta E_{12}^2 \rangle = \alpha_1 \theta_1 + \alpha_2 \theta_2 + \gamma_1 \theta_1^2 + \gamma_2 \theta_2^2 + \eta_{12}\theta_1\theta_2 \,,$$

where

$$\alpha_i = 3J_{i2}^2 + 6J_{1i}^2 - 4J_{1i}J_{i2} \,,$$

$$\gamma_i = 6J_{i2}^2 + 30J_{1i}^2 - 32J_{1i}J_{i2} \,, \qquad (5)$$

$$\eta_{12} = 18J_{12}J_{22} + 72J_{11}J_{12} - 36(J_{11}J_{22} + J_{12}^2) \,.$$

Here we have *not* used the summation convention for adjacent indices. The numerical prefactors in Eqs. (5) arise from the site connectivity of benzene in Na-Y, and are straightforwardly calculable for other host-guest systems. The second order terms in Eqs. (4) are typically small, suggesting that the different connectivity of S_{II} and W sites contributing to $\langle \Delta E_{12} \rangle$ is largely responsible for activation energy fluctuations in this system.

To determine the accuracy of our mean field treatment, we perform kinetic Monte Carlo (KMC) simulations on benzene in Na-Y in the canonical ensemble, using the parabolic jump model described above. For a given configuration of N random walkers, $\vec{n}$, a process list is compiled containing all available jumps for all molecules. Site-to-site rate coefficients are calculated for each jump

in the process list according to $k_{i \to j} = \nu_{i \to j} e^{-\beta E_a(i,j)}$, where the activation energy accounts for the local configuration of adsorbates according to Eq. (3). A single-molecule hop is made every KMC step, and the system clock is updated with variable time steps [17]. The mean time elapsed before each hop is the inverse of the *total* rate coefficient, $k_{\text{tot}}(\vec{n})$, determined by summing over all rate coefficients in the process list. The actual KMC time step for a given configuration, $\Delta t(\vec{n})$, is a random time chosen from a Poisson distribution with first moment equal to $1/k_{\text{tot}}(\vec{n})$, i.e., $\Delta t(\vec{n}) = -\ln(1 - x)/k_{\text{tot}}(\vec{n})$, where $x \in [0, 1)$ is a uniform random number. The probability to make a particular jump is proportional to the associated rate coefficient. After making a jump, the process list and relevant ensemble averages are updated. We use time averages to calculate equilibrium values of θ_1, θ_2, κ, P_1, k_1, k_θ, a_θ, and D_θ. Below we focus on comparing theory and simulation for k_θ, the cage-to-cage rate coefficient.

For a given temperature and loading, the following parameters are required by our new model to calculate the self-diffusion coefficient: $E_a^{(0)}(i,j)$, $\nu_{i \to j}$, a_{ij}, and J_{ij} for $i, j = 1, 2$. These are the infinite dilution jump activation energies and preexponential factors, jump lengths, and Ising nearest neighbor interactions for each site pair. The jump lengths can be deduced from structural data [13], and fall in the range of about $5-9$ Å. The Ising coupling can be obtained from the second virial coefficient of the heat of adsorption [18], yielding about -3 kJ mol^{-1}. We have calculated the preexponential factors for benzene in Na-Y using transition state theory with dynamical corrections [19,20], giving results in reasonable agreement with NMR relaxation dynamics [15]. We have also calculated the infinite dilution activation energies for benzene in Na-X and Na-Y [15,19]. However, since the diffusivity is especially sensitive to activation energies, we must recognize that our calculated barriers may not be the most accurate of all available data. We first regard these barriers as flexible parameters, to determine in the most general sense what loading dependencies are consistent with our model.

Figure 3 shows that three "diffusion isotherm" types emerge. We see in Fig. 3 excellent qualitative agreement between theory (lines) and simulation (dots). Theory consistently overestimates simulated diffusivities because mean field theory neglects correlation effects that make $\kappa < \frac{1}{2}$ for finite loadings. These diffusion isotherm types differ in the coverage that gives the maximum diffusivity: $\theta_{\max} = 0$ is defined as type I, $\theta_{\max} \in (0, 0.5]$ is type II, and $\theta_{\max} \in (0.5, 1]$ is type III. Defining the parameter $\chi \equiv \beta[E_a^{(0)}(2,1) - E_a^{(0)}(1,2)]$, we find that type I typically arises from $\chi < 1$, type II from $\chi \sim 1$, and type III from $\chi > 1$. This suggests that when the S_{II} and W sites are nearly degenerate, i.e., $\chi \lesssim 1$, the coverage dependence of P_1 is weak, and hence k_θ and D_θ are dominated by the decreasing coverage dependence of
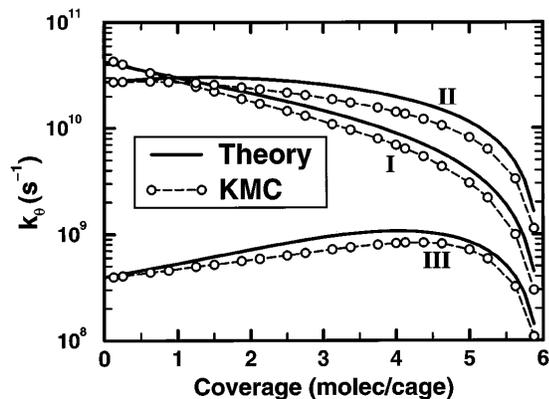
FIG. 3. Comparison between theory and simulation for three diffusion isotherm types.

k_1. Alternatively, when $\chi \gtrsim 1$, the enhancement of P_1 at higher loadings dominates the diffusivity until $\theta_1 \sim \theta_2$, at which point the decreasing k_1 begins to dominate. We also obtain excellent qualitative agreement between theory and simulation for the temperature dependence of diffusion for all cases studied.

Barriers consistent with energetic data for benzene in Na-X [15] are $E_a(2 \rightarrow 1) \cong 25$ kJ mol^{-1} and $E_a(1 \rightarrow 2) \cong 10$ kJ mol^{-1}. Figure 4 shows the resulting theoretical diffusion isotherms for $T = 393$ and 468 K, compared to PFG NMR data [10] at the same temperatures (uniformly scaled by a factor of 5), and TZLC diffusivities [11] at $T = 468$ K (uniformly scaled by a factor of 100). The experimental data were scaled to facilitate comparison with the loading dependence predicted by theory, which itself was *not* fitted to either experimental result. Figure 4 shows that our model is in excellent qualitative agreement with the PFG NMR results, and in qualitative disagreement with TZLC. Our model overestimates PFG NMR diffusivities at high loadings, because the lattice model allows 6 molecules per cage while the observed saturation coverage is 5.4 molecules per cage [10].

In conclusion, we have described an analytical theory of activated self-diffusion in zeolites with adsorbate-adsorbate interactions. Our new theory, which is based on mean field dynamics of cage-to-cage motion, gives excellent qualitative agreement with kinetic Monte Carlo simulations for a wide variety of system parameters. Moreover, our theory provides understanding of the microscopic physics essential to these transport phenomena. Our new theory predicts self-diffusion coefficients in qualitative agreement with pulsed field gradient NMR, and in qualitative disagreement with tracer zero-length column data. We anticipate that this theoretical approach can be used to complement experimental data for a wide variety of other host-guest transport systems.

FIG. 4. Loading dependence of self-diffusion for benzene in Na-X.

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