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Guest-specific diffusion anisotropy in nanoporous materials: Molecular dynamics and dynamic Monte Carlo simulations

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Abstract For anisotropic nanoporous materials, guest diffusion is often reflected by a diffusion tensor rather than a scalar diffusion coefficient. Moreover, the resulting diffusion anisotropy may notably differ for different guest molecules. As a particular class of such systems, we consider an array of two types of channels, mutually intersecting each other, where the rates of diffusion in the different directions depend on the nature of the guest molecules. The simultaneous adsorption of two types of guest molecules is considered, as in technical applications of porous materials such as catalysis. A case study is presented in which atomistic molecular dynamics (MD) and coarse-grained dynamic Monte Carlo (DMC) simulations are compared and shown to yield qualitatively similar results for non-steady-state diffusion. The two techniques are complementary. MD simulations are able to predict the details of molecular propagation over distances of a few unit cells, whereas the evolution of sorption profiles over distances comparable with entire crystallites can be studied with DMC simulations. Consideration of these longer length and time scales is necessary for applications of such systems in chemical separations and heterogeneous catalysis.

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1 Introduction

Host-guest systems consisting of molecules constrained within nanostructured porous materials have found wide-spread use in chemical separations (Ruthven, 1984) and shape-selective catalysis (Chen et al., 1994). Crystalline nanoporous materials are also ideal hosts for gaining a better understanding of the dynamics of strongly confined molecules. With the continuing discovery of new types of porous materials and the seemingly unlimited possibilities to tailor them for particular applications (Snurr et al., 2004), numerous investigations have appeared in recent years on both the fundamentals of molecular transport in such systems and related practical issues (Kärger and Ruthven, 1992; Kärger et al., 2005; Conner and Fraissard, 2006).

For materials having two types of intersecting pores, the rates of molecular diffusion in the different directions may be different, especially if the molecules fit very tightly in the pores. As an example, such diffusion anisotropy has been demonstrated by both PFG NMR measurements (Hong et al., 1991) and molecular dynamics (MD) simulations (June et al., 1990) for methane in the zeolite silicalite, which has intersecting straight and zig-zag channels; methane diffuses faster in the straight channels than in the zig-zag channels. For simultaneous adsorption of two types of guest species, one can imagine that one species A might diffuse preferentially in one set of channels (call them the α channels) and the other species B might diffuse preferentially in the other set of channels (call them the β channels). For a simple catalytic reaction A → B, this could lead to reduced counterdiffusion limitations, as reactants A enter through the α channels and products B exit through the β channels. This idea was proposed in 1980 by Derouane and Gabelica (1980) and termed "molecular traffic control" (MTC). Recent modelling, by both dynamic Monte Carlo (DMC) simulations (Bräuer et al., 2003) and analytical arguments (Brzank et al., 2004), has confirmed the expected enhancement in the overall production rate of B compared to a reference system not exhibiting MTC—if the required diffusion anisotropy in the MTC system is assumed.

Derouane and Gabelica had no experimental evidence for such diffusion anisotropy. Instead they indirectly supported their idea with results from equilibrium adsorption measurements and arguments about preferential siting of different species in different channel types. The first dynamical evidence for this special type of diffusion anisotropy was provided by MD simulations of xenon and SF_6 guest molecules in boggsite zeolites (Clark et al., 2000), which have intersecting 10-ring and 12-ring channels (5.1 Å × 5.3 Å and 6.9 Å diameters, respectively). In these studies, Clark et al. noted that 4 conditions must be satisfied if one species is to diffuse preferentially in one pore direction and the other species is to diffuse preferentially in the other pore direction. These 4 conditions are as follows: (i) in the α channels, species A diffuses faster than species B, (ii) in the β channels, species B diffuses faster than species A, (iii) species A has a higher diffusivity in the α channels than in the β channels, and (iv) species B has a higher diffusivity in the β channels than in the α channels. The DMC simulations of MTC to date have invoked a stronger assumption, where the A molecules cannot enter the β channels at all and similarly the B molecules cannot enter the α channels (Neugebauer et al., 2000; Kärger et al., 2000; Bräuer et al., 2001, 2002). This so-called "hard" MTC condition can be considered a limiting case of the diffusion anisotropy described by Clark et al. In hard MTC the diffusivity for species A in the β channels is zero and the diffusivity for species B in the α channels is also zero, thus satisfying all 4 conditions.

MD simulations performed under equilibrium conditions showed that xenon and SF_6 in boggsite satisfy the 4 conditions listed above, based on the self-diffusion coefficients of the 2 species in the different channel directions (Clark et al., 2000). This held true both at infinite dilution (where, of course, the 2 species do not sense one another) and at finite loadings of molecules. In addition, Clark et al. (2000) demonstrated the effect of guest-specific diffusion anisotropy under non-steady-state conditions. They equilibrated an equimolar mixture of xenon and SF_6 in boggsite at a loading close to saturation using an MD simulation with normal periodic boundary conditions. Then they removed the periodic boundary conditions and let the system relax for 1.0 ns, allowing the molecules to diffuse into the surrounding (initially) empty zeolite. Highly anisotropic diffusion was observed. The larger SF_6 molecules diffused almost exclusively in the wide pore direction, while the smaller xenon molecules diffused predominantly in the narrow pore direction. Hence, the MD simulations led to the patterns of guest-specific diffusion anisotropy expected for anisotropic materials in both the particle distributions at finite loadings and their diffusivities at infinite dilution.

In this paper we show that the non-steady-state situation modelled by MD can also be treated with a simple DMC simulation yielding qualitatively similar results. We pay particular attention to the question of what is the simplest coarse-grained DMC model one can use and still capture the essential physics of the detailed MD model. Previous DMC simulations have modelled only steady-state situations. In addition, they have invoked the hard MTC conditions. By switching to a so-called soft MTC condition, we find that the previous DMC model may be further simplified by completely eliminating the lattice sites for the channel segments between the intersections. The model used in this paper includes only the channel intersections, and the probabilities to hop in various directions are chosen to match the ratio of self-diffusivities obtained in infinite-dilution MD simulations under equilibrium conditions.

In Section 2, we briefly review the MD simulations of xenon and SF_6 in boggsite, which we take as a model system. In Section 3, the model used in the DMC simulations is presented. Section 4 compares the results provided by both techniques and provides a short discussion of the complementary nature of the techniques and how the essential physics is preserved in the more coarse-grained model.

Table 1 Self-diffusivities in m^2/s for infinite dilution in boggsite at 300 K from MD simulations

Molecule	Narrow pores = αchannels	Wide pores = βchannels
A = xenon	3.8×10^{-9}	3.2×10^{-9}
B = SF_6	3.5×10^{-10}	1.6×10^{-8}

We dedicate this paper to John Sherman, in thankful commemoration of many stimulating discussions and his ability to condense complicated situations to the few decisive key points (Sherman, 1999). In some way, by simplifying our MD simulations to dynamic MC simulations we try to follow this strategy.

2 MD simulations

Equilibrium molecular dynamics simulations of xenon and SF_6 in the zeolite boggsite were carried out as described before (Clark et al., 2000). Briefly, both xenon and SF_6 were treated as simple Lennard-Jones spheres. Oxygen atoms of the zeolite were also represented by Lennard-Jones sites, placed at the positions determined from crystallography. Grand canonical Monte Carlo simulations were used to generate equilibrated initial configurations for the MD simulations. Simulations were carried out at 300 K using the Nosé-Hoover thermostat and normal periodic boundary conditions. Results from MD simulations performed at infinite dilution are presented in Table 1 for the self-diffusivities of the two components in the two channel directions. The table also includes the nomenclature used for the channels and molecules in the DMC simulations.

In addition, non-equilibrium MD simulations were performed as follows. First, 2085 molecules were equilibrated as described above. Then the periodic boundary conditions were removed, and the molecules were allowed to expand into the surrounding, infinite, initially-empty zeolite lattice by performing molecular dynamics simulations for 5 ns without periodic boundary conditions.

3 DMC simulations

The DMC simulations were performed using a procedure similar to that described previously (Bräuer et al., 2006) with the main difference that now all sites between the crossing points are omitted, i.e., all lattice points are crossing points. We consider a square lattice of $n \times n$ sites having lattice spacing λ, with $n = 30$ and $\lambda = 2.03$ nm in the x-direction and 1.19 nm in the y-direction. Note that this is a finite lattice without periodic boundary conditions. Prior to the simulation runs, molecules of type A (xenon) and B (SF_6) are randomly distributed over the lattice to achieve the desired initial loadings. During the time unit τ of the simulations ($\tau = 1$ "time step"), n^2 sites of the lattice are randomly addressed in turn. If the selected site is occupied by a particle, one of the four possible directions towards adjacent sites is randomly selected with uniform probability $\frac{1}{4}$ for a jump attempt. Jump attempts into occupied sites are immediately rejected. If the destination site is unoccupied, jump attempts of the B molecules (SF_6) in the direction of the β channels (wide pores) are accepted with probability $P_{B,\beta} = 1$, whereas jump attempts of the B molecules in the direction of the α channels (narrow pores) are only accepted with probability $P_{B,\alpha} = 0.022$. Jump attempts of the A molecules (xenon) in the direction of the α channels are accepted with probability $P_{A,\alpha} = 0.238$ and in the direction of the β channels with $P_{A,\beta} = 0.200$. The set of probabilities P_{ij} with $i = A, B$ and $j = \alpha, \beta$ is chosen to satisfy the requirement

$$P_{ij} = D_{ij}/D_{B,\beta} \tag{1}$$

and thus to ensure proportionality between the single-particle diffusivities at infinite dilution in the MD and DMC simulations.

Jump attempts from the edge sites into the gas phase are performed with the same probabilities as from the internal sites, with the self-evident understanding that jump attempts out of the lattice are not affected by neighboring particles. No particles are allowed to jump back into the crystal from the gas phase, corresponding, for example, to the use of a sweep gas.

To mimic the expansion simulation performed with non-equilibrium MD, the initial conditions of the DMC simulation are obtained by distributing molecules uniformly over only a central part of the lattice ($m \times m$ sites, representing one ninth of the lattice), keeping the remaining eight ninths (i.e. eight squares of equal size surrounding the central one) initially empty.

Mimicking the conditions of the MD simulations, the initial loading in this central part corresponds to an average site occupancy of $\Theta = 1$, with equal numbers of A and B molecules, i.e. $\Theta_A = \Theta_B = 0.5$. All DMC simulations were performed 1000 times, using different sets of random numbers (Marsaglia et al., 1990), and the results were averaged together to obtain better statistics. A software package (Surfer, 1997) was used to produce smoothed presentations of the concentration profiles during molecular desorption.

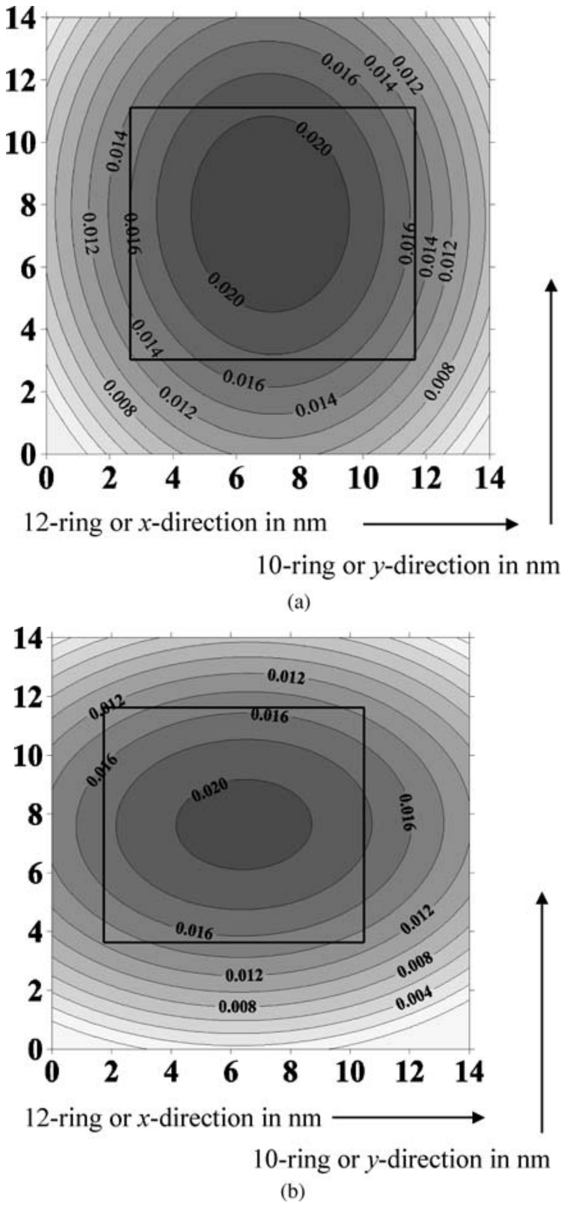
4 Following guest expansion by MD and DMC simulations

To make a direct comparison of the 3-dimensional MD studies and the 2-dimensional DMC studies, the results of the MD simulation were projected into the plane formed by the α-channels (10 ring channels in y-direction) and β-channels (12 ring channels in x-direction), i.e. the narrow-pore and wide-pore directions of boggsite. Subsequently, the resulting map of particle positions was smoothed (Surfer, 1997) and converted into an iso-line representation. Figures 1(a) and (b) show the resulting concentration profiles for xenon and SF_6 5 ns after the onset of expansion out of an initial area of $\Delta A = x \times y = 8.0944$ nm $\times$ 9.5192 nm $= 77.05$ nm^2.

These profiles can be compared with those resulting from the DMC simulations, where the details of the molecular trajectories are neglected and molecular propagation is simply considered as a hopping process with different hopping rates for different molecular species and directions. As noted above, the ratios of these rates were taken from equilibrium MD simulations performed in the limit of negligible concentrations.

Figures 1 and 2 provide a comparison of the iso-line presentations of the distribution of the A molecules (Xe) and B molecules (SF_6) after release from their initial, rectangular array into the surroundings. In fact, both types of simulations agree nicely in their main feature, viz. a pronounced anisotropy in the SF_6 distribution with fast propagation in the direction of the 12-ring channels, notably exceeding that of xenon.

Not unexpectedly, the two sets of results do not totally coincide. The reasons leading to these differences include the following items:



(a)

(b)

Fig. 1 Iso-lines of the relative concentration profiles of xenon (Fig. 1(a)) and SF_6 (Fig. 1(b)) projected onto the y-x-plane from atomistic MD simulations (Clark et al., 2000) after an expansion time of 5 ns. 12-ring channels are in x direction and hence correspond to the β-channels in Fig. 2. Correspondingly, 10 ring channels are in y direction, representing the α-channels in Fig. 2. The rectangle indicates the initially occupied region

(i) The MD simulations have been performed within the real, three-dimensional pore-space, while for the DMC model we confined ourselves to considering diffusion in two dimensions. The comparison becomes possible by simply projecting

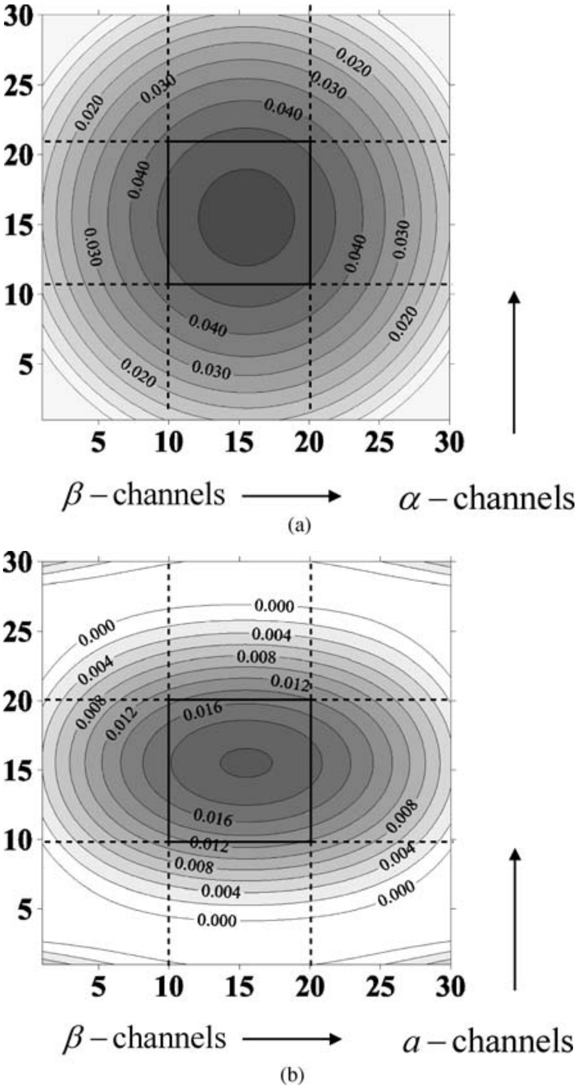


Fig. 2 Iso-lines of the relative concentration profiles of xenon (A molecules, Fig. 2(a)) and SF_6 (B molecules, Fig. 2(b)) from DMC simulations after an expansion time $\tau = 1000$ from the initial lattice with $n_\alpha \times n_\beta = 100$ sites into the eight empty lattice areas of $m_\alpha \times m_\beta = 100$ sites each, surrounding the initial lattice. The site occupancy of the initial lattice is $\Theta = 1$, with mole fraction $x_B = 0.5$. The hopping probabilities for the A and B particles in the direction of the α and β channels are, respectively, $P_{A,\alpha} = 0.238$, $P_{A,\beta} = 0.200$, $P_{B,\alpha} = 0.022$ and $P_{B,\beta} = 1$

the results of the MD simulations into the plane spanned by the 12- and 10-ring channels. As a consequence, in the two-dimensional simulations the mutual hindrance of the diffusing particles has to be much more pronounced.

(ii) The particle densities considered in our simulations are not high enough to ensure accurate iso-line presentations within the chosen smoothing procedure. This appears in particular in the fact that the centres of the iso-lines are found to deviate from the centre of the region from which the particles have been released.

(iii) The DMC simulations are performed with a finite network of sites in contrast to the infinite lattice considered in the MD simulation.

(iv) The molecules in the DMC simulations interact only through a hard-core repulsion, which does not necessarily reflect the concentration dependence of molecular propagation in the same way as the MD simulations.

(v) The channel segments are neglected in the DMC simulations and their effect is included only through the jump probabilities in the different directions.

Paschek and Krishna (2001) have also analyzed the ability of DMC simulations to match MD results (Snurr and Kärger, 1997), but under equilibrium conditions. Jump probabilities were chosen to match pure-component MD self-diffusivities at infinite dilution, and the DMC simulations were able to reproduce some, but not all, of the basic features for self-diffusion of methane and CF_4 mixtures in silicalite.

Given the rather drastic differences in the MD and DMC models, it is encouraging that the two techniques yield the same qualitative results. Atomistic MD simulations can only access time scales of nanoseconds and thus diffusion lengths of hundreds of Angstroms. The more efficient DMC simulations, on the other hand, can be used to simulate processes covering length scales of entire zeolite crystals and the longer time scales necessary for consideration of combined diffusion and chemical reaction. The use of hopping probabilities from infinite-dilution equilibrium MD results is particularly attractive for building a coarse-grained DMC model because such MD simulations can be performed rather quickly with standard software, whereas non-equilibrium MD at finite loadings requires special software and much longer computing times.

5 Conclusions

Differences in the diffusion anisotropy of two different species of guest molecules have been shown to lead to a novel type of dynamic separation in porous materials, viz., that the two molecular species may diffuse into different regions of the pore space surrounding their original location, rather than diffusing out uniformly. This phenomenon has been demonstrated by both MD and DMC simulations. While the diffusion distances that may be covered in MD simulations are limited to a few unit cells, DMC simulations can access length scales commensurate with entire crystals. The equivalence of the essential results from MD and DMC shown here may be of use in future investigation of molecular traffic control and related phenomena in porous materials, as the relevant time and length scales are often beyond those accessible to MD. This work also emphasizes that guest-specific diffusional anisotropy can lead to molecular traffic control, whereas previous work has focused on the role of segregation of different molecules in the different channels. This is clearly seen in the DMC simulations in this work, which focus exclusively on molecules in the channel intersections and do not include channel segment sites.

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