Molecular Traffic Control in a Nanoscale System

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Atomistic molecular dynamics simulations are used to elucidate a novel and exploitable transport phenomenon known as "molecular traffic control." Under some conditions a binary mixture of differently sized molecules in a structure possessing dual sized pores can exhibit a surprising effect. In the case examined, size segregation and other effects lead to physical separation of the two species through anisotropic diffusion. We have established the underlying causes of this effect in an equilibrium system and used simulations of a relaxing system to show that these causes also hold under nonequilibrium conditions.

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I. Introduction.—Diffusion of molecules in confined spaces is important in various fields, from heterogeneous catalysis to transport in living systems. As the length scale of the confinement approaches that of the molecule, unexpected effects can occur. Within the field of confined systems, one of the most fruitful areas of study has been diffusion in microporous materials such as zeolites. Zeolites are materials composed of silicon, aluminum, and oxygen that possess pores on the order of 10 Å in diameter. The wide variety of crystalline zeolite structures provide ideal, highly uniform platforms for both experimental and theoretical studies. Despite the well defined nature of the pores, the factors influencing transport in zeolites are not yet well understood [1]. Molecular simulations have been useful in understanding such systems [2,3]. Knowledge of basic effects, along with their origins, can help us understand natural phenomena in nanoporous materials, and it is likely that some such effects could be exploited in nano- and microscale devices.

This report deals with a particularly elusive and complex phenomenon termed "molecular traffic control" (MTC) by Derouane and Gabelica [4]. The idea, as originally conceived, was offered to explain why some reactions in zeolites were apparently free of counterdiffusion limitations. They proposed, on the basis of equilibrium adsorption measurements, that in some cases, reactants would enter through one type of pore and products would exit through another type as shown in Fig. 1a. This diffusional separation of the species is startling from a physical viewpoint. The MTC concept was debated in a series of letters and replies [5,6] but never convincingly established. In particular, all evidence presented so far has been indirect, involving static thermodynamic, rather than diffusional properties. This complex situation involves chemical reaction and chemical potential gradients. It is inherently nonequilibrium, and nanoscale observation and/or nanoscale experimental control of the system is needed to verify the concept.

Direct molecular simulation of a reaction system over sufficient time and length scales is not possible with current methods and computational resources. We present an alternative approach and examine an equilibrium system that has the key characteristics of the nonequilibrium MTC system. As depicted in Fig. 1b, a system that exhibits "equilibrium molecular traffic control" (eqMTC) must have one species that prefers to move in one pore direction and another species that prefers to move in a different pore direction. A more precise definition will be

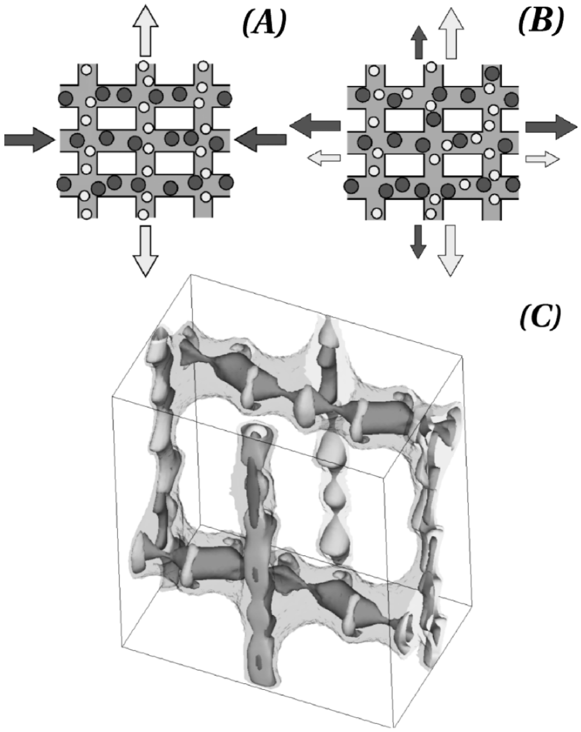

FIG. 1. Representation of the original molecular traffic control concept (A). Dark reactant molecules diffuse in through one set of channels, while lighter product molecules diffuse out unhindered. The equilibrium analog, eqMTC (B). Probability densities (C) from a simulation in the model system are shown for SF_6 (darker, large molecule), and xenon (lighter, small molecule). Each contour encloses 75% of the most probable center-of-mass position density. Pore shape shown as transparent contour.

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TABLE I. Equilibrium molecular traffic control (eqMTC) system parameters.

Xenon (4.1 Å) mass = 131 amu, SF_6 (5.1 Å) mass = 146 amu
70 kPa xenon, 31 kPa SF_6 in ideal gas phase
Adsorbed phase (13.75 molec/unit cell) is 50.5% xenon at 300 K
The sites are intersections(I)/wide pores(W)/narrow pores(N)
Site occupancy of SF_6: 7.7% I/63.7% W/28.6% N
Site occupancy of xenon: 8.7% I/24.4% W/66.9% N

provided below. However, such a system possesses the characteristics necessary to produce the nonequilibrium MTC effect. Once the origin of eqMTC is established, we relax the system using a simple nonequilibrium simulation and show that Derouane and Gabelica's MTC is quite likely to occur in similar systems. In addition, it will be shown that the same characteristics that produce the MTC effect also have interesting nanoscale separations applications.

II. Simulation methodology.—In accordance with a comparatively recent suggestion by Derouane [6] we choose a zeolite with pores of two different sizes. Boggsite has intersecting orthogonal 10-ring (5.1 Å × 5.3 Å) and 12-ring (6.9 Å) pores. It is a particularly good model pore system because the pores are relatively straight and free from large side pockets. Grand canonical Monte Carlo simulations are done to equilibrate an initial configuration for the molecular dynamics simulations. In this system, SF_6 adsorbs preferentially in the wide 12-ring pores and xenon in the narrow 10-ring pores, as shown in Table I along with other details. This segregation is due to combined enthalpic and entropic effects and has been explained previously [7].

All simulations are done at an atomistic level using simple potential models from the literature [7,8]. Lorentz-Bertholet mixing rules were used where necessary. Lattice coordinates for the siliceous form of boggsite are taken from the x-ray diffraction results of Pluth *et al.* [9] and are assumed to be rigid. Constant temperature molecular dynamics simulations using the Nosé-Hoover thermostat are used to generate trajectories of the binary mixture at 300 K. Self-diffusivities (tracer) are extracted using the Einstein equation. Activation energies were determined from simulations at six temperature points between 200 and 400 K. Long simulations, 20–50 ns, are carried out to ensure that both species cross at least a unit cell length in each direction.

III. Results.—Equilibrium MTC is defined by two *intra*pore and two *inter*pore criteria, each chosen to produce the key anisotropic diffusion characteristics of *non*equilibrium MTC. The criteria are as follows: (1) In the narrow pore, the small molecule has a higher diffusivity than the large molecule, (2) in the wide pore, the large molecule has a higher diffusivity than the small molecule, (3) the large molecule has a higher diffusivity in the wide pore than in the narrow pore, and (4) the small molecule has a higher diffusivity in the narrow pore than in the wide pore.

The physics that causes these criteria to be satisfied or not is assumed to be the same as that underlying MTC in nonequilibrium systems. For the model system investigated, all four criteria are satisfied as shown by the diffusivities in Table II. Diffusivities in the absence of sorbate-sorbate interactions (infinite dilution) are also given for comparison. We will examine each criterion in turn and describe the underlying causes.

Intrapore criteria (1) and (2) assure that each species diffuses quicker in its preferred pore than the other species. Obviously this will not happen in all systems, because usually one species will diffuse fastest in *every* type of pore. The first intrapore criterion (1) for eqMTC requires that, in the narrow pore, the small molecule have a higher diffusivity than the large molecule. Experimentally, it is common, though not universal, to observe in confined systems a decrease in diffusivity as the size and mass of the molecule increases. Numerous simulations have shown that larger molecules become trapped in wide regions of the pores, and that tight bottlenecks between these regions inhibit movement. This is expected to occur in the majority of systems and therefore explains how confinement in the narrow pore restricts the motion of the large molecule more than the small molecule.

TABLE II. Simulation results for the equilibrium molecular traffic control system and simple variations.

Self-Diffusivities (m^2 sec^{-1}):

	Infinite dilution		eqMTC mixture	
	Wide pore	Narrow pore	Wide pore	Narrow pore
SF_6	1.6×10^{-8}	3.5×10^{-10}	6.5×10^{-10}	9.2×10^{-11}
Xenon	3.2×10^{-9}	3.8×10^{-9}	2.9×10^{-10}	5.5×10^{-10}

Self-Diffusion activation energies (kJ/mol):

	Infinite dilution		eqMTC mixture		Pure components (11.6 molec/unit cell)	
	Wide pore	Narrow pore	Wide pore	Narrow pore	Wide pore	Narrow pore
SF_6	4.0 ± 0.2	6.6 ± 0.3	4.8 ± 0.5	10.8 ± 0.7	7.4 ± 0.7	10.3 ± 0.3
Xenon	11.4 ± 0.4	7.7 ± 0.2	7.1 ± 0.8	7.4 ± 0.5	4.0 ± 1.7	6.0 ± 0.4

The second of the intrapore criteria (2) requires that, in the wide pore, the large species have a higher diffusivity than the small species. Note that this criterion requires essentially the opposite explanation as the first; i.e., there must exist a regime in which the diffusivity *increases* as the size of the molecule approaches that of the pore. In this situation, there is only an insignificant difference in sorption energy between the open and the bottleneck regions of the pores. One can see how this is more likely in the wide pore from looking at the transparent pore shape in Fig. 1c. The wide pore has smaller corrugations relative to its diameter than does the narrow pore. Thus, as the size of the molecule is increased, the confinement effects serve to restrict the motion of the molecule to a linear path, rather than to a volume between bottlenecks. Derouane *et al.* [10] anticipated this and called it the "floating molecule" effect. It was later substantiated by Bandyopadhyay and Yashonath [11] using simulations in the silicalite (MFI) and VPI-5 (VFI) zeolites. They show, as predicted, that the mean absolute value of the force in the axial pore direction decreases as the molecule size approaches the pore size. Martin *et al.* [12] observe this effect experimentally in the one-dimensional pores of $AlPO_4$-5, where neopentane has a higher diffusivity than methane.

The presence of this floating molecule effect in our eqMTC system can be easily checked by performing simulations where the size (σ) of the molecule is varied. Varying σ shifts the Lennard-Jones potential curve without shifting the potential well depth. Figure 2 shows the results of such simulations on the single components in the absence of sorbate-sorbate interactions (infinite dilution). It can be seen that SF_6 (Fig. 2a) at its "real" size is at a diffusivity maximum in the 12-ring (wide) pore direction. Thus, the SF_6 molecule can be said to "float" since this maximum is near the pore size. Conversely, the real size of xenon (Fig. 2b) is near a minimum that is probably due to the good fit of the molecule in the wide pore corrugations (see Fig. 1c). Note also that the floating effect is nearly absent and the diffusivity dropoff is much faster in the narrow pore, as one would expect in a pore that has larger relative corrugations.

Other possible explanations for the second of the intrapore criteria involve effects from intermolecular interactions. The idea that the large molecule is pushing the small molecule into corrugations in the wide pore can be ruled out by comparing the probability density maps (Fig. 1c) with and without sorbate-sorbate interactions. They are nearly identical (not shown); therefore the large molecule does not significantly affect the positioning of the small molecule in the wide pore. However, it is possible that the presence of other xenon molecules in the wide pore affects the xenon diffusivity. The data in Table II indicate that as the concentration of xenon in the wide pore increases, the activation energy *decreases*. This decrease is substantial, and opposite the SF_6 trend; the activation energy drops from 11.4 ± 0.4 kJ/mol at infinite dilution to 4.0 ± 1.7 kJ/mol at a loading of 11.6 molecules/unit cell. The presence of the SF_6 decreases the percent of xenon in the wide pores. Xenon, therefore, is driven into a lower concentration, higher activation energy (7.1 ± 0.8 kJ/mol) regime.

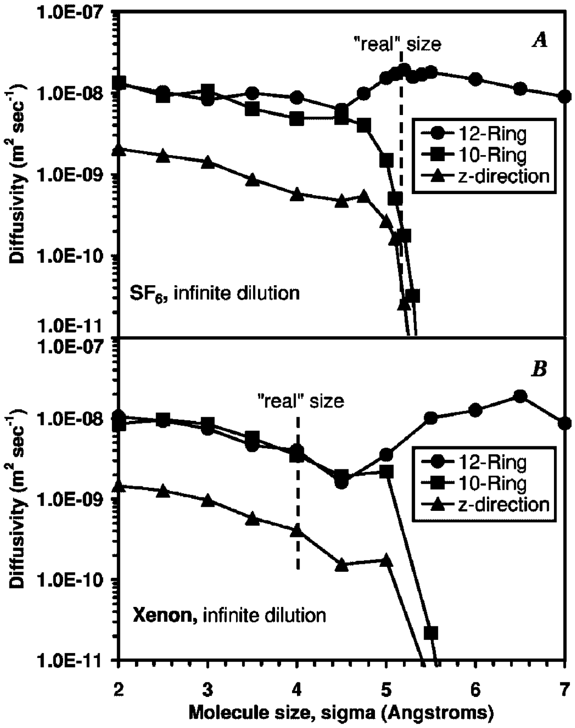

FIG. 2. Presence of the floating molecule effect in the eqMTC system. A peak in the SF_6 diffusivity as the sorbate size approaches the wide pore size indicates that the SF_6 used in the eqMTC simulations "floats."

In contrast to the intrapore criteria, the *inter*pore criteria (3) and (4) for eqMTC serve to guarantee that the large and small molecules diffuse more quickly in their preferred pores than they do in the other pore. In analogy to the intrapore criteria, the attainment of the two interpore criteria can be attributed to the bottleneck effect and a more unexpected effect. Criterion 3 is satisfied because the large molecule is more confined in the narrow pore. Satisfaction of criterion 4 is due to segregation of the large, pore blocking SF_6 out of the narrow pore, thereby allowing xenon to move more freely.

We have seen that the two pairs of intra- and interpore criteria are satisfied for our chosen system due to a variety of root causes including the bottleneck pore diffusion effect, the floating molecule effect, intermolecular interaction effects, and the segregation effect. These same effects should also be present in a nonequilibrium MTC system as it was originally conceived. To substantiate this claim we perform a simple nonequilibrium simulation. A large eqMTC system (2085 molecules) is equilibrated using the molecular dynamics (MD) technique then allowed to relax for 1.0 ns after the periodic boundary conditions are removed. The initial and final configurations are shown in

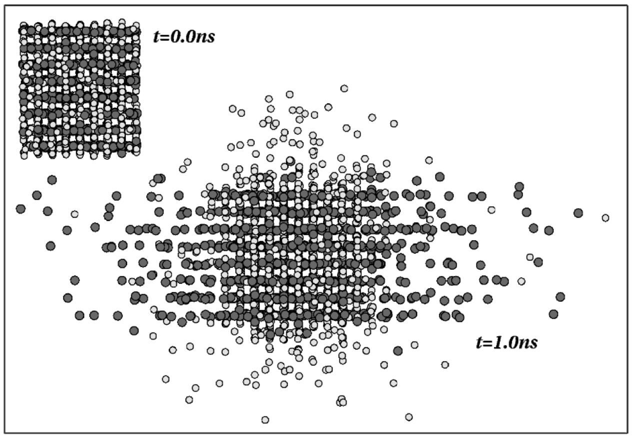

FIG. 3. Relaxation of the eqMTC system to establish that the underlying features of eqMTC hold under nonequilibrium conditions. Lightly shaded spheres are xenon, darker spheres are SF_6. The infinite, periodic 3D zeolite lattice is not shown for clarity.

Fig. 3. It can be seen that in the presence of concentration gradients this formerly equilibrium MTC system shows highly anisotropic diffusion. The large SF_6 molecules diffuse almost exclusively in the wide pore direction (horizontal), while the small xenon molecules diffuse predominantly in the narrow pore direction (vertical). Since reaction is unlikely to change this behavior, it appears that Derouane's original MTC effect can indeed occur. This transient situation may also provide an avenue for experimental verification, albeit a challenging one.

IV. Conclusions.—As originally conceived, MTC was thought to be caused by segregation of species within a zeolite pore system. While segregation is certainly important, it is not sufficient because anything less than perfect segregation does not preclude at least one of the species from diffusing in both pores. We have shown that in a model system with a dual pore size zeolite and two, differently sized sorbates, equilibrium molecular traffic control can be observed. The underlying causes behind this curious effect persist under nonequilibrium conditions.

It is not yet clear how prevalent this effect is in real systems. However, some conditions, beyond the presence of the cited effects, can be hypothesized. The sizes of the molecules are important. For example, if the size of SF_6 is decreased to 5.0 Å from 5.1 Å the eqMTC effect disappears, though the segregation is not significantly different. The topology of the pores is also important. Without the small, xenon-trapping pockets along the side of the 12-ring pore, xenon behavior might be very different. For example, we performed MD simulations in zeolite CIT-1 (CON) [13], which also has 10- and 12-ring pores; the simulations do not exhibit the eqMTC effect using the molecules, or small perturbations thereof, that were used in this work. Finally, the relative mass of the two sorbates is important, since $\mathcal{D} \propto M^{-\frac{1}{2}}$ [1].

There are at least two other factors that could further increase the importance of MTC. If *shape* rather than size differences in the pores and/or molecules could produce the characteristics seen in this model system, the effect could be quite common in practical systems. For example, branched/unbranched alkanes could show MTC in silicalite. Even though silicalite has two pores of nearly the same size, though not shape, sizable segregation effects have been seen in simulations [14–16]. Second, if the root causes scale appropriately with system size, this effect could be used to separate biomolecules or other larger molecules. If it is applicable in the micrometer length scale, standard etching techniques could be used to make channels to perform separations like that shown in Fig. 3. Further studies could reveal a wealth of applications.

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