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Statics and Dynamics of Ethane Molecules in $AlPO_4$-5: A Molecular Dynamics Simulation Study

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Abstract: From an experimental perspective, there has been disagreement among researchers on whether ethane would display single-file or normal diffusive behavior in the channels of $AlPO_4$-5. Pulsed field gradient nuclear magnetic resonance measurements implied single-file diffusion, while quasielastic neutron scattering showed normal diffusion. In this paper we present the results of extensive classical molecular dynamics simulations of the diffusion of ethane molecules adsorbed in $AlPO_4$-5. Our aim is to provide microscopic details of the static and dynamic properties of the adsorbed molecules in order to verify whether the conditions for the single-file regime can be achieved in a nondefective $AlPO_4$-5 crystal structure.

Introduction

$AlPO_4$-5 is a microporous aluminophosphate having nonintersecting and approximately cylindrical pores parallel to the *c* crystallographic axis of nominal diameter 7.3 Å (AFI structural network.)[1] The neutral framework consists of alternate tetrahedral aluminum and phosphorus atoms bridged by oxygen atoms, 6 and 12 rings of oxygen pointing inward form the walls of the pore. Diverse molecular species can be adsorbed in these relatively wide one-dimensional channels. Alkanes have been recently investigated,[2] and their heat of adsorption has mainly been attributed to van der Waals interactions as a function of the number of coordinating surface atoms increasing linearly with the chain length.[3] More interesting is the molecular transport. Experimental studies[4−7] confirmed the existence of a special diffusive regime known as *single-file diffusion*. This regime emerges in molecular sieves with a one-dimensional pore structure when the guest molecules are too large to pass each other within the channels, so mutual passages of the diffusants are excluded. This strong correlation between the movement of different particles is mirrored in the long time limit of the mean-square displacement (MSD) that will be found to be proportional to the square root of the observation time rather than to the observation time itself. It is interesting to note that Levitt[8] first described this phenomenon theoretically in 1973.

Recently, Jobic et al.[7] reported a quasi-elastic neutron scattering (QENS) study of the diffusion of ethane in $AlPO_4$-5. Whatever the loading, they observed ordinary 1D diffusion, in disagreement with previous pulsed-field gradient (PFG) NMR measurements performed by Gupta et al.[4] As remarked by Jobic, these two methods are complementary in that molecular migration is followed over a few unit cells with QENS (time scale ≈ 1 ns) and over the whole crystal with PFG NMR (time scale ≈ 1 ms). These experimental discrepancies were explained by assuming that different $AlPO_4$-5 crystal structures have been used in the measurements.

In this paper we present the results of extensive molecular dynamics simulations of the diffusion of ethane molecules adsorbed in $AlPO_4$-5. Our aim is to provide microscopic details of the static and dynamic properties of the adsorbed molecules in order to verify whether the conditions for the single-file regime can be achieved in a nondefective $AlPO_4$-5 crystal structure. We hope to offer complementary insight to interpret the experimental results.

Model, Potentials, and Simulations Parameters

The unit cell of the zeolite $AlPO_4$-5 is hexagonal with the parameters $a = b = 13.7707$ Å and $c = 8.3789$ Å[1] and contains 12 aluminum, 12 phosphorus, and 48 oxygen atoms. In Figure 1, the structure of two parallel channels, running along *c*, is shown.

Recently we proposed an effective harmonic potential for representing the structural and dynamical properties of the $AlPO_4$-5 framework.[9] We represented the interaction potentials for (Al,P)−O, Al−P, and O−O as quadratic functions of the displacement from a given equilibrium bond distance. Only nearest neighbors were considered as interacting atoms. The parameters are reported in Table 1. The simulated structural properties and the vibrational spectrum are reasonably close to the experimental ones. Moreover, the very small computational effort required to evaluate the intralattice forces makes the model particularly convenient for performing the very long simulations necessary to attain the goal of this paper. Thomson et al. recently addressed the effects of a dynamic lattice on methane self-diffusivity in $AlPO_4$-5.[10] They managed the framework oxygen degrees of freedom by exploiting the normal vibrational modes in a harmonic crystal approximation. They have shown that the flexibility of the dynamic lattice does not significantly increase methane diffusion, although it is possible that a

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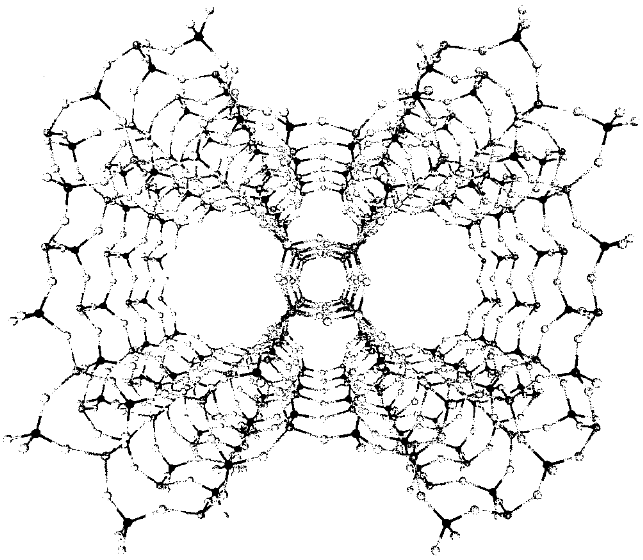

Figure 1. Pictorial view of the $AlPO_4$-5 structure. The crystallographic *a* and *b* axes lie in the plane of the figure, while the *c* axis runs along the channels, perpendicular to the plane of the figure. The 12-rings of oxygen and the alternating 6-rings are directed inward and form the walls of the pore.

Table 1. Parameters for the Effective Harmonic Potential for Aluminophosphate Molecular Sieves (Energies in kJ mol^{-1}, Distances in nm)[a]

	contact				
	Al−O	P−O	O−(Al)−O	O−(P)−O	Al−P
k (kJ mol^{-1} nm^{-2})	292 880	376 560	92 048	92 048	2 092
r_e (nm)	0.172	0.1516	0.280873[b]	0.247560[b]	0.32

[a] The functional form of the potential is $V(r) = 0.5k(r - r_e)^2$. [b] AlO_4 and PO_4 are assumed to be perfect tetrahedral structures at equilibrium, so these parameters are not independent.

flexible lattice may enhance diffusion by reducing the energy barrier for passing events.

In earlier simulations, ethane molecules were modeled as a spherical Lennard-Jones (LJ) particle in an $AlPO_4$-5 static framework.[11] We modeled ethane molecules with two oscillating interaction sites, considering the CH_3 group as a single interaction center. To preserve the possibility of a full guest−host dynamical coupling, a Morse potential describes the intramolecular bond, with parameters derived from spectroscopic data.[12] The LJ 12-6 potential is adopted to represent both the site-to-site and the site-to-framework oxygens intermolecular interactions. As in most of the simulations, we assume that the dispersion forces involving mainly oxygen atoms dictate the zeolite−ethane interactions. We adopted the site-to-site LJ parameters obtained by Jorgensen et al.[13] for liquid ethane: $\sigma = 3.775$ Å and $\epsilon = 0.867$ kJ mol^{-1}. These values have been proven suitable to describe the guest−guest interactions of ethane sorbed in the zeolite silicalite.[12] The site-to-oxygen LJ parameters are $\sigma = 3.461$ Å and $\epsilon = 1.0$ kJ mol^{-1}; the ϵ value has been increased (compared to the ethane−silicalite system) so as to reproduce quite well the extrapolated experimental heat of adsorption[3] of ethane in $AlPO_4$-5 (see below). In the simulations, the number of sorbed ethane molecule was fixed to 12, and the dimensions of the periodic box have been varied according to the loading: 1 × 1 × 12-unit cells were used at 1 molecule per unit cell, 1 × 1 × 6-unit cells were used at 2 molecules per unit cell, 1 × 1 × 4-unit cells were used at 3 molecules per unit cell, and 1 × 1 × 3-unit cells were used at 4 molecules per unit cell. In the simulations at infinite dilution, a single molecule was placed in 1 × 1 × 3-unit cells. In these boxes, the *z*-axis runs parallel to the pore direction (*c* axis of the crystal). We obtained very similar results by making comparisons between trajectories with 36 molecules in 1 × 1 × 12-unit cells and 12 molecules in 1 × 1 × 4-unit cells, so possible size effects can be excluded. All of the simulated systems were thermalized in the microcanonical ensemble by scaling the atom velocities at a running temperature of 300 K for 1 ns. Production runs of 35 ns were then carried out using a time step of 1 fs. In the simulation at infinite dilution, a very long trajectory (155 ns) was performed. The center of mass coordinates and velocities of ethane molecules were stored every 32 fs.

Table 2. Diffusion Coefficients, α Exponent, and Sorption Energies

loading (molecules/unit cell)	D (10^{-9} m^2 s^{-1})[a]	α[b]	q (kJ mol^{-1})[c]	$\langle U_{g-h} \rangle$ (kJ mol^{-1})	$\langle U_{g-g} \rangle$ (kJ mol^{-1})
0 (i.d.)	66	1	27.7	−25.2	0
1	1.8	0.66	28.9	−25.5	−0.9
2	1.6	0.96	30.3	−25.9	−1.9
3	1.6	0.95	31.2	−25.9	−2.9
4	8×10^{-4}		32.1	−25.9	−3.8

[a] Linear fit of the MSD in the range between 1000 and 2000 ps. [b] $\langle z^2(t) \rangle = At^{\alpha}$. [c] $q = -(\langle U_{g-h} \rangle + \langle U_{g-g} \rangle) + RT$.

Results and Discussion

Host−guest interactions rule static and dynamic phenomena of molecules adsorbed in zeolites. When experimental data are available, they can be considered as the starting point to find a suitable potential for simulation studies. Eder and Lercher[3] recently reported that the initial heat of sorption of alkanes in $AlPO_4$-5 (ranging from propane to isopentane) increased linearly with the chain length, with an increment of approximately 8 kJ mol^{-1} per additional CH_2 group. For alkanes, adsorption in $AlPO_4$-5 is controlled almost entirely by dispersion−repulsion force interactions, which can be adequately modeled with 12-6 LJ potentials. We adapted their results to estimate the sorption heat of ethane, and then we optimized the value of ϵ for the CH_3−oxygen LJ potential. Starting with the parameters given for ethane in silicalite[12] ($\sigma = 3.461$ Å and $\epsilon = 0.811$ kJ mol^{-1}), at a loading of 1 molecule per unit cell we obtained a heat of adsorption of 23.7 kJ mol^{-1}. After increasing ϵ to 1 kJ mol^{-1}, the sorption heat increases to 28.9 kJ mol^{-1}, close to the experimental value. The difference of 5.2 kJ mol^{-1} with respect to the nonoptimized parameters confirms that, in zeolites, small changes of the potential surface can cause dramatic changes in the sorption properties[14] as well as in the diffusion coefficients.[15] In Table 2 and Figure 2, we report the values of the heat of adsorption q at different loadings. In general, an initial sharp decrease of heat of sorption with increasing sorbate loading in the molecular sieve reveals site heterogeneity, whereas a small increase or decrease in the heat of sorption with increasing sorbate loading indicates attractive or repulsive sorbate−sorbate interaction. The adsorption sites in $AlPO_4$-5 can be considered to be energetically homogeneous. The increase in q is entirely due to stronger ethane−ethane interactions: the packing of the molecules inside the channel is more effective at higher loading. From the figure, it is also evident that the q vs l slope between 2 and 4 molecules per unit cell is lower than in the first portion of the curve: this fact suggests that when 3 or more molecules are placed in the same cell the available free volume is limited and they can no longer be arranged in order to maximize the

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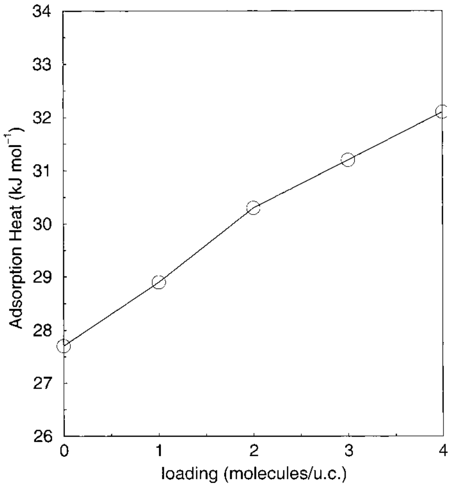

Figure 2. Heat of adsorption of ethane as a function of loading.

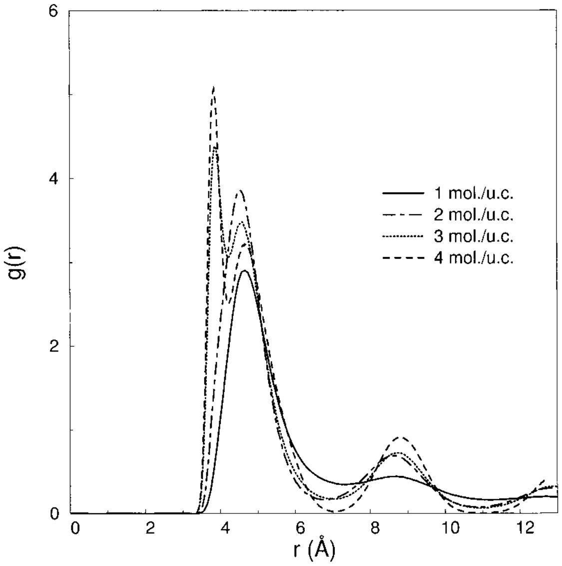

Figure 3. Ethane−ethane center-of-mass radial distribution functions $g(r)$. The main peak ranges between 4.64 and 4.5 Å. A second peak rises at about 3.82 Å.

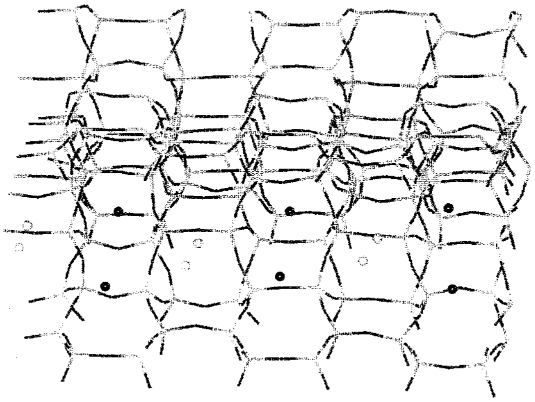

Figure 4. Snapshot of the center-of-mass location of the ethane molecules taken from a trajectory at 300 K with 4 molecules per unit cell. Black and white spheres represent the center of mass of an ethane molecule (see text for clarity), while the lines represent the zeolite structure.

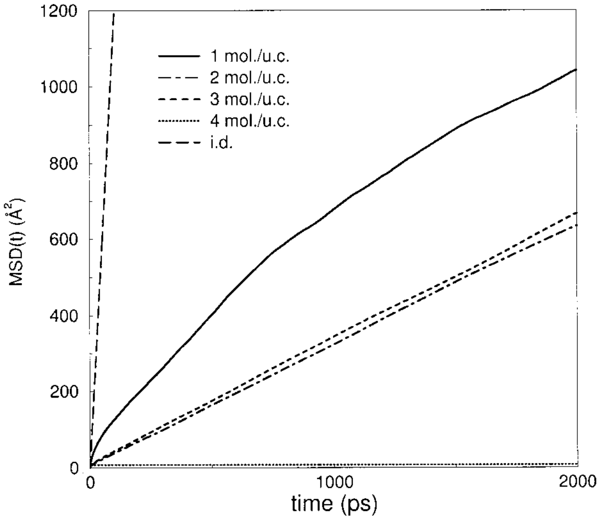

Figure 5. Ethane center-of-mass mean-square displacement as a function of loading.

favorable interactions as it was possible up to 2 molecules per unit cell. Table 2 shows a constant increase of the sorbate−sorbate contribution (~1 kJ mol^{-1}) associated with a constant value of the sorbate−zeolite contribution between 2 and 4 molecules per unit cell, suggesting that close packing of the ethane molecules occurs located at equivalent energetic sorption sites in the interior of AlPO$_4$-5.

Further information on this point can be attained through the sorbate−sorbate center-of-mass radial distribution functions (rdf's) calculated at different loadings (Figure 3). The main peak is not very much affected by the loading, as it ranges between 4.64 Å (1 molecule per unit cell) and 4.50 Å (4 molecules per unit cell). When the loading is higher than 2 molecules per unit cell, a second well-defined peak rises at about 3.82 Å. The number and intensity of the peaks for increasing loading suggest ordered structures for ethane adsorbed in AlPO$_4$-5.[16] The rdf reveals a rather high density of the adsorbed phase at the maximum loading of 4 molecules per unit cell. Figure 4 shows a snapshot of the location of the center-of-mass taken from a trajectory at 300 K with 4 molecules per unit cell. The rdf peak at 3.82 Å can be attributed to a pair of molecules placed at the same height along the channel (i.e., two adjacent black or two adjacent white spheres in the figure), while the first peak above 4 Å corresponds to two molecules occupying two successive sites (a pair of neighboring spheres of different color in the figure). At high loading, the molecules are practically stuck in the symmetric solid-like configuration of Figure 4, with their centers of mass disposed in two almost perpendicular planes. Indeed, the white spheres appear to lie in roughly the same plane (torsion angles between 0 and 20°), as do the black spheres, and the angle between the two planes is between 70 and 90°. The flat center-of-mass (CM) MSD curve for 4 molecules per unit cell (Figure 5) confirms the absence of any significant translational motion of the guest species at this loading. It is interesting to observe that, while both the rdf's and the power spectra (see below) show that ordered structures begin to develop with just 3 molecules per unit cell, the ordering does not affect the diffusion at that loading. In Figure 6 are reported the power spectra obtained by Fourier transformation of the CM velocity autocorrelation function as a function of the number of molecules per unit cell. From infinite dilution to 2 molecules per unit cell, there is a low-frequency mode near 20 cm^{-1}. At higher concentrations, the main peak splits in two bands, and a structure in the high-frequency tail emerges. The shift toward higher frequencies with an increase in loading is symptomatic

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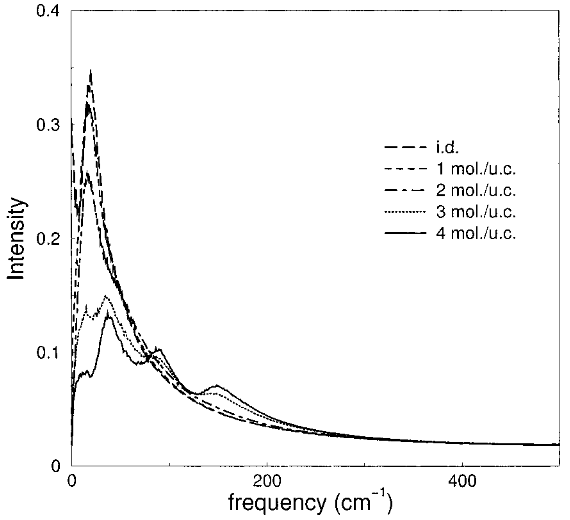

Figure 6. Power spectra as a function of loading. The spectra are obtained by Fourier transformation of the ethane center-of-mass velocity autocorrelation functions.

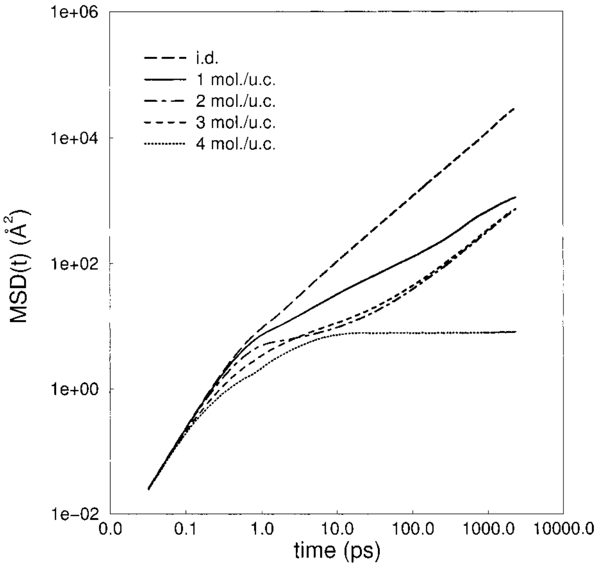

Figure 7. Log−log plot of the ethane center-of-mass mean-square displacement as a function of loading.

Table 3. Passing Events[a]

loading (molecules/ unit cell)	no. of passing attempts	no. of successful passing events
1	135	66
2	3 018	503
3	7 328	158
4	102 478	1

[a] 12 molecules in the MD simulation box; 35 ns.

of a transition from translational to vibrational motion around the sorption sites for ethane in $AlPO_4$-5.

In this paper, the main question of interest is whether ethane molecules will find the conditions for the single-file regime in a nondefective $AlPO_4$-5 crystal structure. We focus on long time diffusion processes at different sorbate loading. We remember that, in contrast to ordinary diffusion, the time dependence of the MSD in the single-file regime is proportional to the square root of the observation time. In a general form,

$$\langle z^2(t)\rangle = 2Ft^{\alpha} \tag{1}$$

where F denotes the *single-file mobility factor*[17] when $\alpha = 0.5$, while in the case of normal or unidirectional diffusion $\alpha = 1$ and F coincides with the diffusion coefficient D. The direct calculation of the MSD from molecular dynamics simulations and evaluation of the parameter α deserves some care.[18] Time regimes and system size effects can significantly influence the results if they are not properly handled. In the present study, the relatively short simulations (35 ns) and the size of systems considered are sufficient to exclude a transition to a single-file regime in our observation time. Indeed, the frequency of particle passing increases on going from 1 to 3 molecules per unit cell. At 1 molecule per unit cell, the exponent α reported in Table 2 is significantly less than 1. Nevertheless, the value of 0.66 that is actually found shows a departure from rigorous single-file behavior. This is strong evidence of an infrequent particle passing that already affects the diffusion at short correlation time. Upon increasing the loading, the values of α become roughly 1, since particle crossing is sufficiently frequent that normal diffusion occurs. The CM MSD curves reported in Figure 5 and in logarithmic scale in Figure 7 clearly show the prevalence of normal diffusion in this short time limit. At the maximum loading of 4 molecules per unit cell, molecular diffusion is no longer detectable on the time scale of our simulation. According to Thomson et al.,[10] a significant quantity to characterize diffusion is the number of passing events or the passing attempts that succeed. We counted a passing event when any two centers of mass of the appropriate molecules passed each other for a time longer than 1 ps. Thus, in a given simulation we would exclude the possible rapid oscillations between centers of mass that could overestimate the number of passing events. The values reported in Table 3 show that the number of passing attempts increases as the loading increases, while the effective passing events are much more sensitive to the crowding of the unit cell. A crowded unit cell means a reduced void space and an increased number of collisions between neighboring molecules with an increased probability to restore the former setting in the pore after some time. At 1 molecule per unit cell, the number of successful passing events is relatively small, and this finding is in agreement with the observed value of α. At 4 molecules per unit cell, the large number of passing attempts in comparison to the passing events is clear evidence of the oscillations of the center of mass around the sorption site. At 2 and 3 molecules per unit cell, the passing events are sufficiently frequent to induce the observed normal diffusion ($\alpha \approx 1$) regime. This confirms that our relatively short observation time (35 ns) is, in this case, adequate to sample enough passing attempts to make unidimensional diffusion evident.

At this point, it is interesting to consider whether a transition from normal to single-file diffusion can be plausible over observation times longer than those of the present simulations. We start from the following conjecture: after a sufficiently long activation time, the interacting ethane molecules form stable clusters which diffuse in the single-file regime consistent with the PFG NMR experimental observation window (ca. 1−100 ms).[4] It is evident that molecular dynamics simulations cannot cover such a large time interval, so we disregarded the process of cluster formation while focusing on the mean lifetime and stability of previously formed clusters. Sholl and Fichthorn first reported concerted diffusion of molecular clusters in AlPO4−

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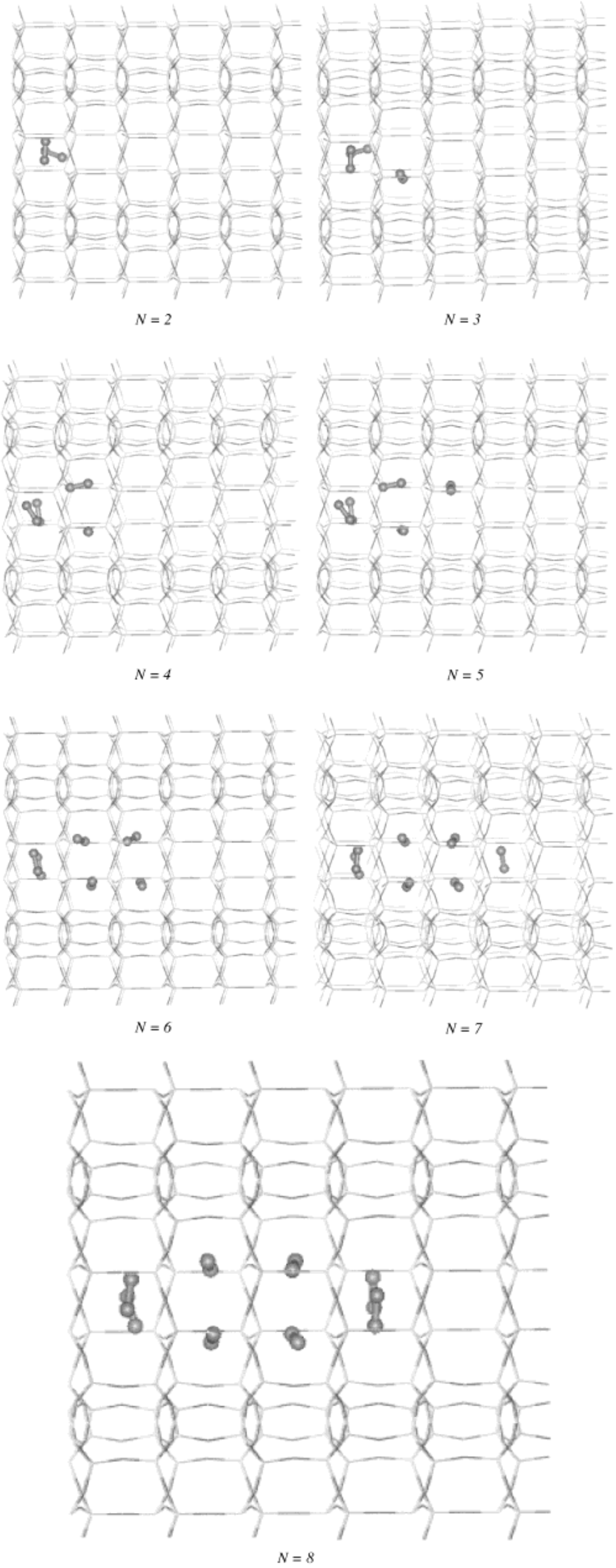

Figure 8. Minimized structures of the ethane clusters in the interior of AlPO$_4$-5. The number N of ethane molecules per cluster was varied between 2 and 8. The lines represent the zeolite structure.

5.[19] In this study, they examined several adsorbates that, because of their dimensions, are naturally unable to pass each other. The mismatch between the lattice spacing of the pore and the adsorbate–adsorbate spacing that minimizes the interadsorbate interaction energy gives rise to a concerted diffusion mechanism. Here we are considering molecules that can pass each other in the pores, so we are looking for a stable cluster structure that, once formed, moves in the channels like a single molecule. In our conjecture, the framework might play the fundamental role of stabilizing the structures for sufficiently long time. Our initial goal was to perform MD simulations to identify the relevant parameters of the diffusion process of such stable structures and then to develop a coarse-grained model to simulate a system of interacting clusters on a microsecond time scale.[20] We proceeded as follows to generate an initial condition for simulating a cluster containing N molecules. We minimized the energy of each cluster of N molecules in the interior of AlPO$_4$-5. To obtain good statistics, 20 such minimized, *non*interacting clusters were randomly distributed in a system of 1 × 1 × 12-unit cells. To better detail the possible stabilizing effect of the framework, we initially excluded any vibrational–translational and vibrational–vibrational energy transfer by freezing the framework degrees of freedom. Such a large number of clusters simultaneously moving within the channels would determine an excessive distortion of the host lattice, which in turn could affect the properties of the clusters themselves. These indirect (and artificial) interactions between different clusters are avoided by keeping the AlPO$_4$-5 lattice rigid. At this point, the dynamics of each cluster can be studied independently of the others. After a further energy minimization, each cluster was equilibrated at 300 K for 10 ps, and then we measured its mean lifetime. We used a distance criterion to detect cluster dissociation. We defined a cluster to have dissociated whenever any neighbor molecules became separated by more than 12.7 Å. We found this apparently large value following the empirical approach proposed by Sholl.[21] We examined the sorbate–sorbate CM rdf (Figure 3). The main peaks located between 3.82 and 4.64 Å imply an average distance of about 4.2 Å between sorbed molecules. Three times this average value is, in our opinion, a careful criterion to mark cluster dissociation. Whenever a cluster dissociated, its lifetime was recorded, and the cluster was replaced by another one randomly positioned in the channel by repeating the above-described procedure. Consequently, 20 noninteracting clusters were always placed in the channel. The number N of ethane molecules per cluster was varied between 2 and 8, and the MD trajectories were followed for 3 ns for each value of N. In Figure 8, we report the minimized structures of the ethane clusters which were used as the starting point of our simulations. The probability of finding a cluster of N molecules after a time t_0 is given by

$$f(t_0) = 1 - \int_0^{t_0} \mathrm{d}t\, \tau(t) \qquad (2)$$

where $\tau(t)$ is the normalized mean lifetime distribution of the clusters. The $f(t_0)$ curves are reported in Figure 9 and show an increasing stabilization when the cluster size increases from 2 to 6 molecules. The turning point is from 7 to 8, where the dissociation prevails over stabilization effects. We found that the maximum lifetime is around 500 ps for clusters formed by 5–6 ethane molecules in a *rigid* lattice environment. This time is still too short to support our conjecture, and so we draw the conclusion that for ethane molecules a transition to the single-file regime is not allowed in a defect-free AlPO$_4$-5 crystal structure. At this point, the last thing to do was to compare the rigid lattice results with a dynamical framework simulation. Following the same procedure, we inserted a single cluster of

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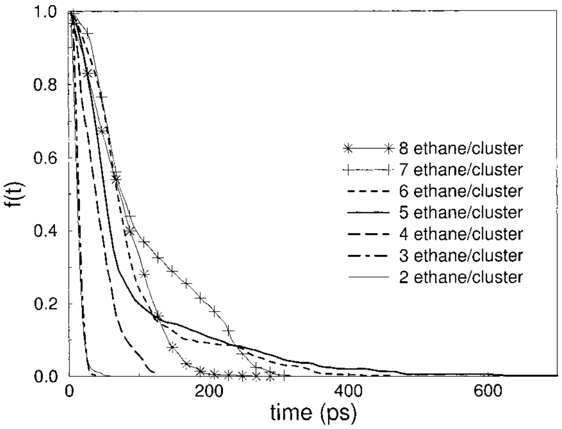

Figure 9. Probability of finding a cluster of *N* molecules after a time t_0 as a function of loading.

6 molecules in our model of vibrating framework. Several trials were carried out by selecting the more stable structures from the rigid lattice simulations, i.e., those with the larger lifetimes. We detected a very short lifetime, generally 1 order of magnitude less than the one observed in the rigid lattice simulations, further substantiating the previous conclusion. This last observation also indicates that the framework dynamics is an important factor in determining the nature of the molecular motion in microporous media. The continuous interaction of the sorbed molecule with the walls of the substrate, including its thermal excitations, results in a strong coupling with comparable characteristic relaxation time of energy and momentum.[12] Kantola et al.[22] recently discussed the effects of the dynamic cage on a tightly confined system such as Xe in $AlPO_4$-11. They found that the effective activation energy of jumps between neighboring cells was significantly lower than what was calculated for a rigid system. In a less confining system such as methane in $AlPO_4$-5, Thomson et al.[10] showed that a dynamic lattice did not significantly increase diffusion when passing events are frequent. In our opinion, this shows that it is essential to take into account the cage motion in microporous solids when the size of the cavities is comparable with the size of the adsorbates.

Concluding Remarks

We have carried out extensive molecular dynamics simulations of the diffusion of ethane molecules adsorbed in $AlPO_4$-5, offering a microscopic description of the relevant static and dynamic properties. The objective of the present paper is to supplement the information available from experiment and, when possible, to compare with earlier simulations. To make the calculations more realistic, we represented ethane as two connected spheres. This internal structure and flexibility, as opposed to the spherical structureless LJ center used in a previous[11] model, are probably the main sources of the observed differences. The complex behavior of the adsorbed molecules as a function of loading can be interpreted using a standard analysis of the MD trajectories. When the diffusion of molecules which can pass each other is considered, the single-file regime could be attained only through the formation of stable cluster structures which move in a concerted way for very long times. We investigated this possibility by directly studying the lifetime of ethane clusters and their stability inside the $AlPO_4$-5 channels. We have shown that the static lattice model yields cluster lifetimes 1 order of magnitude greater than the one observed with a fully dynamic lattice. It is evident that the flexibility of the framework significantly modifies the mechanism of energy exchange, destabilizing ethane clusters in the interior of $AlPO_4$-5. Thus, one should be careful when excluding the cage motion in microporous solids with cavities of size similar to the size of the adsorbates.

In conclusion, our simulations did not provide evidence for concerted ethane cluster diffusion, and we confirm, as observed experimentally, that for ethane molecules a transition to the single-file regime is not allowed in a defect-free $AlPO_4$-5 crystal structure.

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