Sorbate-Loading Dependence of Diffusion Mechanism in a Cubic Symmetry Zeolite of Type ZK4. A Molecular Dynamics Study

P. Demontis* and G. B. Suffritti

Dipartimento di Chimica, Università degli Studi di Sassari, Via Vienna 2, I-07100 Sassari, Italy

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In the present work we investigated how the sorbate loading controls the diffusion of spherically symmetric Lennard-Jones molecules in a cation-free zeolite of type LTA. This effect is studied by taking into account the mechanical flexibility of the framework, which allows for the energy relaxation of the sorbed molecules along with fluctuations of the window diameters. The number density of the adsorbed molecules was increased from 1 up to 15 methane molecules per cavity, which means from 8 up to 120 particles adsorbed in one unit cell. We have shown that the sorbate loading strongly alters the diffusion mechanism by inducing a transition at seven molecules per cavity from an increasing to a decreasing mobility regime.

I. Introduction

The remarkable chemical properties of zeolites[1] arise from their complex porous crystalline aluminosilicate structure. Due to the pore size comparable to molecular dimensions, they show peculiar mechanisms of diffusion where the zeolite framework plays a major role.[2] In the last decade numerical simulation procedures have been developed to the level that they are now reliable techniques for studying the sorptive behavior of guest molecules in zeolites.[3] Although problems remain, mostly concerning interatomic potentials, such studies do offer the possibility for describing the mobility of adsorbed substrates, how this mobility depends on the substrate−surface interactions, and how this mobility can control the catalytic action of the active sites on the zeolitic surface. More generally these studies provide a mechanistic base for understanding molecular motions, and this should help in clarifying details at the atomic level of the transport phenomena in restricted geometries. In the present work we report a systematic and detailed investigation on the dependence of the diffusion mechanism on the number density of the adsorbed molecules in a cubic symmetry zeolite of type LTA. The pore network consists of a cubic lattice of cavities connected by narrow windows, so that the confinement effect is enhanced by the nearly spherical shape of the pore walls which interact with the sorbed molecule.[4] A remarkable property of this class of zeolites is that the measured long range diffusivity increases when the loading is increased,[5] at least for the experimentally accessible loading range.[6] We performed a series of extensive molecular dynamics (MD)[7] simulations to study the motion from 1 up to 15 methane molecules per cavity adsorbed in all-silica zeolite ZK4. Preliminary results of MD simulations of the same system were reported previously.[8,9] The influence of the vibrations of the framework upon the long range diffusivity of methane in ZK4 was investigated in ref 8 for one and six molecules per cavity. It was ascertained that the breathing motions of the windows connecting the cavities, in the vibrating framework model, greatly favored the methane molecules (whose dimensions are close to the window diameter) in diffusing to an adjacent cavity. In ref 9 four different diffusive regimes at different time scales were evidenced: quasi-free motion, on a small time scale (up to 0.2 ps); oscillations about the preferred positions in the cavity (0.2−3 ps); intracavity diffusion (some tens of picoseconds); and long range diffusion.

Extensive MD calculations on the same system were performed also by Fritzsche *et al.*[5,10−12] using the fixed framework approximation but changing the methane-framework potential model and loading. Our aim in the present work is to provide further insights to understand how the sorbate loading will influence diffusion by altering the properties of the void space that make up the porous volume within the crystal.

II. Computational Details

A. Structure of Zeolite ZK4. In our simulations we considered zeolite ZK4 the all-silica analog of zeolite A.[13] Its structure could be schematically represented by a cubic array of nearly spherical cavities (α-cages). The diameter of each cavity is about 11.4 Å, and each one is connected to six neighboring cavities by windows of about 4.2 Å diameter. We represented its crystal structure in the $Fm\bar{3}c$ space group ($a = 24.555$ Å), the same as for the NaA zeolite.[13] One unit cell contains 8 α-cages and consists of 192 Si and 384 O atoms (it has been considered as our simulation box). We excluded the presence of aluminum in the model lattice; therefore, no extraframework cations had to be considered. We stress that due to this choice all windows are free for diffusion while with a finite Si/Al ratio the fraction of open windows is a function of the cation kind and content.[14] The presence of cations strongly alters the diffusion mechanism even in the case of neutral guest molecules and could obscure the role of sorbate loading. This is the subject of a forthcoming paper.[15]

B. Potential Functions. In the present study our total energy U_{tot} consist of three terms:

$$U_{tot} = U_h + U_{gh} + U_{gg} \tag{1}$$

U_h is the total potential energy of the host framework. It is a periodic harmonic force field which takes into account only interactions between the nearest neighbor framework atoms.[16−23] Within this approach it is implicitly assumed that the oxygen atoms shield the silicon atoms so that Si−Si interactions are neglected and the initial topology of the framework bonds is an invariant during the simulation. This mechanical flexibility allows for the energy relaxation of the sorbed molecules acting as an effective heat bath.[18]

U_{gh} is the guest−host total potential energy. In order to reduce the computing time, the methane molecules were
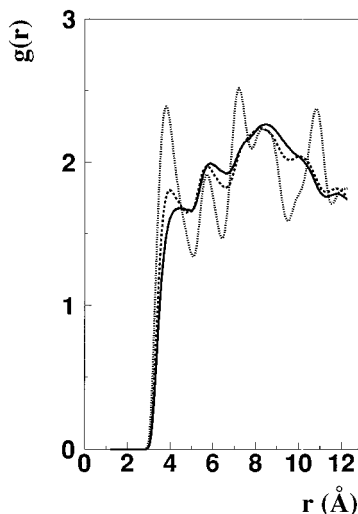

Figure 1. Methane−oxygen atoms of the framework radial distribution functions $g(r)$: continuous line, 1 molecule/cage; dashed line, 7 molecules/cage; dotted line, 15 molecules/cage.

Figure 2. Methane−methane radial distribution functions $g(r)$: continuous line, 1 molecule/cage; dashed line, 7 molecules/cage; dotted line, 15 molecules/cage.

considered as Lennard-Jones particles interacting only with the oxygen atoms of the framework. The parameter set of the potential functions was reported previously;[18,20,21] we recall only that the minimum of the pairwise potential function falls at 3.88 Å. Because solvation or cavity effects that involve physico-chemical interactions between the zeolite pore and the guest molecule are not well quantified and are still a matter of discussion, we account for forces of the van der Waals type only, which in our model control the "docking" of a molecule into the adsorption sites of the α-cage. It is our opinion that this rough estimation of the adsorbate−adsorbent and adsorbate−adsorbate interactions should be sufficient to pursue the goal of the present paper. Quantitative predictions and the very details of the physisorption phenomena will require a much more sophisticated model, though the adopted potential model yields a good estimate of the sorption heat of methane in silicalite.[18,20]

U_{gg} is the guest−guest total potential energy. It was modeled in terms of a (20-6) Lennard-Jones form where the parameters were taken from the literature.[24]

C. MD Calculations. The equations of motion were integrated by using a modified version of the Verlet algorithm,[25] with a time step of 1.0 fs. At the beginning of each simulation the initial velocities of the host and guest atoms were taken from the Maxwell−Boltzmann distribution at the run temperature 359 K. The simulations were performed in the NVE ensemble after an aging of 100 ps where the velocities of the particles were rescaled to the reference temperature. Periodic boundary conditions were used to simulate the periodicity of the crystal. The pair interactions were computed in the minimum image convention with a spherical cutoff of 12.722 Å. At each run a methane molecule was added, to reach the number of fifteen molecules per α-cage. The length of the simulations (each trajectory was about 7 ns long) ensured very good statistics for the computed properties. The fluctuations of the total energy of the system were less than 0.005%. The methane center of mass coordinates and velocities were stored for later analysis every 32 fs.

III. Results and Discussion

A. Structural Properties. Radial distribution functions (rdf's) at different loadings between the sorbate and the oxygen atoms in the zeolite framework are shown in Figure 1. At the highest loading (15 molecules/cage) the first maximum is located at 3.82 Å, which corresponds to a small repulsive force exerted
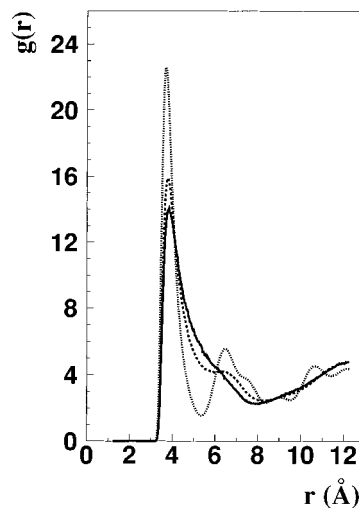
by an oxygen atom of the wall on the methane molecule. Indeed, as above mentioned, the minimum of the O_f-CH_4 potential function is found at 3.88 Å. For an intermediate loading (7 molecules/cage) the first maximum falls at about 3.96 Å in the attractive region of the O_f-CH_4 pairwise potential while the lowest loading (1 molecule/cage) shows a plateau ranging from 4.25 to 4.69 Å with a small peak at 4.48 Å. The same trend is displayed in Figure 2, where a plot of the CH_4−CH_4 rdf's is reported. The main peak is not very much affected by the loading, as it ranges between 3.70 (15 molecules/cage) and 3.84 Å (1 molecules/cage). When the loading is higher than 6 molecules/cage, a second well-defined peak begins to rise at about 6.50 Å. At first sight it seems that the number and intensity of the peaks in the rdf are well-defined functions of loading. The behavior of the rdf for increasing loading suggests ordered structures in the α-cages of ZK4. To supplement the information available from the rdf, in order to gain further details on the types of structures adopted by the sorbate molecules, we have calculated a one-body distribution function[26] by dividing the α-cage into 50 × 50 × 50 smaller cubes, counting how many configurations placed the center of a methane molecule in each cube, and averaging over the eight α-cages. In Figure 3 the contour plots in the *xy*-plane, halfway along the *z*-axis of the α-cage are reported for loading ranging from 1 to 15 molecules per α-cage. From Figure 3 it is apparent that at all loadings there are always preferential sites in front of the windows, but the probability of finding a particle in the intermediate positions decreases as the loading is increased, and with more than seven molecules/cage, it becomes negligible and finally disappears, while a preferential site in the center of the cage begins to appear. At the lower loadings the methane molecules probe almost all the available space inside the α-cage and the methane−oxygen interactions should play a significant role in orienting preferential paths in moving from one to another site near the surface. For increasing loading an increasing localization of the guest molecules occurs and a solid-like structure is obtained with 15 molecules/cage. The last picture in Figure 3 is calculated three quarters along the *z*-axis of the α-cage, and it is indistinguishable from the one calculated at one quarter. A superposition of these three distributions will show clearly that at this loading methane molecules form a distorted face-centered cube with a central atom. This finding confirms the conclusions of Steele and co-workers,[27] who expected zeolite A (and numerous others) to exhibit ordered structures for small molecules sorbed at high loadings.
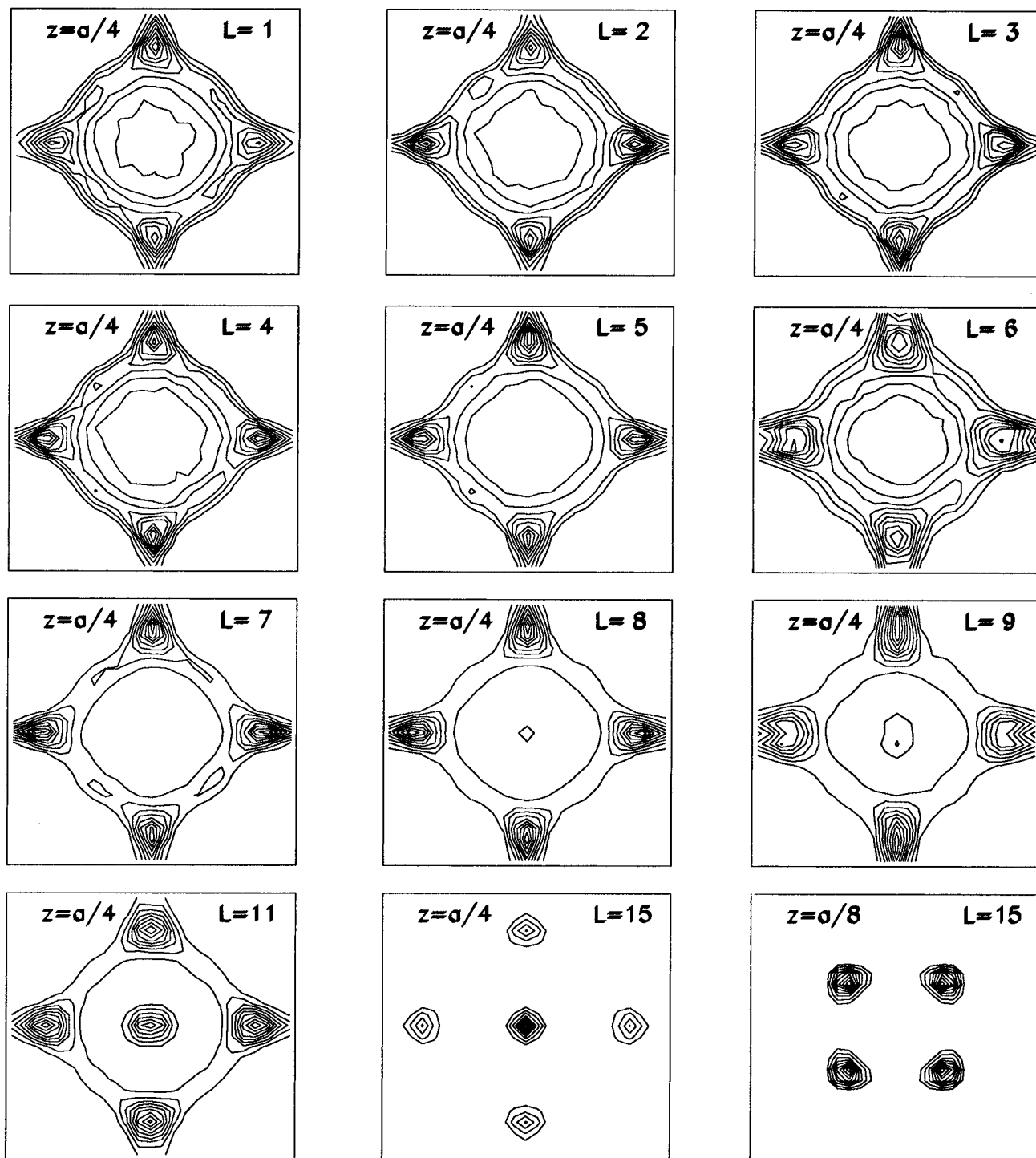
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Figure 3. One-body distribution function in the central *xy*-plane ($z = a/4$) of a cage, for methane in ZK4 zeolite at different loadings [$L = 1$, 1 molecule/cage; $L = 2$, 2 molecules/cage; ...). $z = a/8$ is calculated three quarters along the *z*-axis of the α-cage.

B. Dynamical Properties. The *self-diffusivity* (D_s) values at various loadings obtained from the Einstein relation[28]

$$D_s = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \qquad (2)$$

are shown in Figure 4. The term in pointed brackets is the mean-squared displacement of the sorbate molecule. One finds that the cage-to-cage diffusivities of the sorbed molecules grow up as the loading grows until the intracavity mobility is effective and, at the same time, the interparticle collisions help in passing to another cage, but they grow less, with more than 7 molecules/cage, as localization sets in. It is interesting to compare this trend with the average cage residence time that we show in

Figure 5 for different loadings. As discussed in a previous paper[9] the topology of ZK4 can be considered as a three-dimensional network of connected α-cages. Each α-cage has six adsorption sites for methane located near the windows. By cage-to-cage migration we mean a complex phenomenon in which several factors can play a significant role under specific conditions. The diffusion pathway of an adsorbed methane molecule from one cage to another neighboring cage implies the crossing of an eight-membered ring window. Its radius, as stated above, is about 2.1 Å; hence, methane molecules can pass from an α-cage to another one-by-one. The cage residence time τ_c was determined from the MD trajectories by using a distance criterion to decide whether or not a molecule belonged to a specific cage. A molecule within a distance of 6.1 Å from
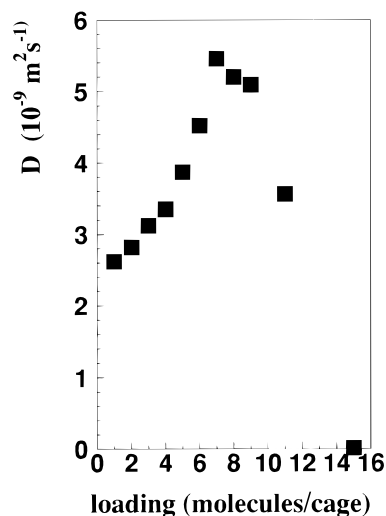
Figure 4. Diffusion coefficient, D, of a methane molecule as a function of loading (number of molecules per cage).
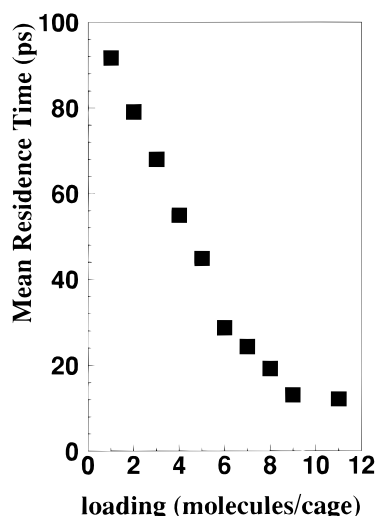

Figure 6. Mean jump length of a methane molecule as a function of loading (number of molecules per cage).

Figure 5. Mean residence time of a methane molecule in a cavity as a function of loading (number of molecules per cage).

Figure 7. Methane velocity autocorrelation function, VAF: dashed−dotted line, 1 molecule/cage; dotted line, 7 molecules/cage; dashed line, 11 molecules/cage; continuous line, 15 molecules/cage.

a cage center is assigned to the cage in question. The ensemble average of individual residence times yields the values of τ_c shown in Figure 5. We note a decreasing function of loading up to 11 molecules/cage, and then it increases to a value two orders of magnitude larger for 15 molecules/cage. We would like to interpret these results by applying the Einstein−Smoluchowski relation for the 3-dimensional diffusion in a cubic lattice:[29]

$$D_s = l^2/6\tau_c \qquad (3)$$

We consider l as the mean jump length in the time scale for which diffusion occurs, so it will be a function of the cage residence time τ_c and the self-diffusivity D_s. We remark that eq 3 is only correct in the absence of correlation effects, so that τ_c can only be considered as an "effective" residence time. The calculated values of l are reported in Figure 6. The variation of the jump length as a function of loading could be tentatively explained by the following considerations. The long-range motion results from the migration between adsorption sites from one cage to a neighboring cage. At lower concentrations the predominant mode of diffusion is likely to be surface-mediated diffusion: the population of the adsorbate is larger near the inner surface of the cage and smaller or negligible toward the cage center. In this mode the sorbate slides along the surface of the zeolite cage and therefore is expected to be distant from the
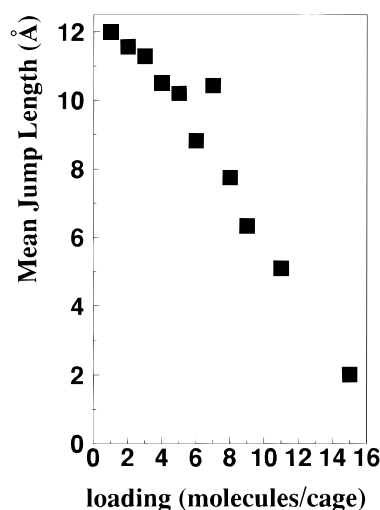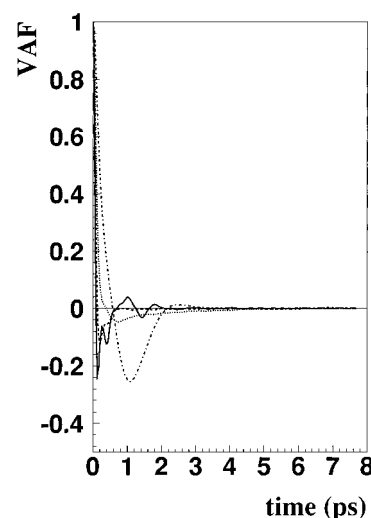
center of the cage. When loading is higher the adsorbate can visit a larger portion of the inner void space of the α-cage and the diffusion process can be considered as in a fluid. At very high concentrations the adsorbed molecules are very much localized and the cage residence time rapidly increases, indicating the presence of a loading-induced sorbate structural transition. Therefore the jump length l will be very sensitive to the number of empty adsorption sites in front of the windows inside an α-cage. When the six adsorption sites are satured, we get a maximum in the diffusion coefficients at a loading of 7 molecules/cage. In order to better understand the physical information provided by these simulations, we consider in Figure 7 the normalized velocity autocorrelation functions:

$$\psi(t) = \frac{\langle \mathbf{v}(t)\, \mathbf{v}(0)\rangle}{\langle \mathbf{v}(0)\, \mathbf{v}(0)\rangle}$$

As a first effect of the loading we observe a shortening of the crossover time (the time at which the correlation function first becomes negative) with values from 0.56 ps (1 molecule/cage) up to 0.08 ps (15 molecules/cage). This is the average time required for a guest molecule to be backscattered, and they are displayed in Figure 8 for all simulated loadings. At these short times momentum is transferred from a guest molecule to its first neighbors, whose average number depends on loading. We
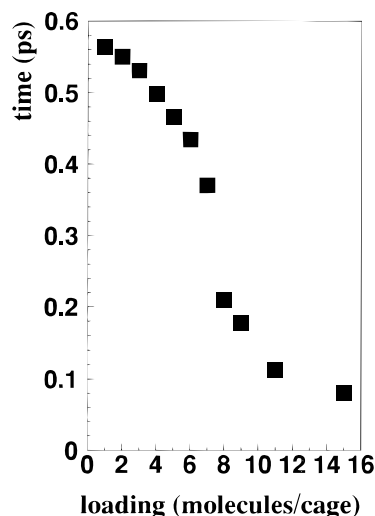
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Figure 8. Crossover time as a function of loading (number of molecules per cage).

note an abrupt change in the slope of the curve between 7 and 8 molecules/cage. A convenient indicator of how crowded a cage is may be found in the one-body distribution functions of Figure 3. It is evident that in going from 7 to 8 molecules/cage the center of the cavity begins to be permanently populated, and this alters the correlation of molecular collisions. This is reflected in the shortening of the crossover time. Therefore, at this loading molecules which are present at the center of the cavity rule the momentum transfer. However, another important piece of information is directly evident in the extension of the negative region, which is essential for establishing the value of the self-diffusivity D_s. The negative velocity correlations have generally been attributed to molecules reflected in a backward direction during the characteristic time for molecular collisions. Increasing loading decreases the extension of the negative region, and we get a maximum in the diffusion coefficient for 7 molecules/cage; so the reduction of the negative velocity correlation produces a substantial rise in the diffusivity. As we pass from 7 to 8 molecules/cage, oscillations in the negative region are observed. This is indicative of much more correlated backscattering events which could be interpreted in terms of a much more effective clustering of sorbed molecules. A similar conclusion was drawn by Berry and Li in a recent paper.[30] They investigated by Nosè isothermal MD simulations how the sodium cations and the Xe−Xe interactions influence aspects of the adsorption and dynamics of Xe clusters inside a single NaA zeolite α-cage at various temperatures. They estimated for clusters larger than Xe_6 an increased mobility of the Xe atoms, arguing that the frequency of Xe−Xe collisions at small impact parameters is the probable cause of the observed large change in chemical shifts from Xe_6 to Xe_7 clusters.

IV. Conclusions

We have shown that the sorbate loading controls the diffusion of spherically symmetric Lennard-Jones molecules in a cation-free zeolite of type LTA. The lowering of the available void space in the α-cage favors the appearance of ordered structures which are made stable by the confinement of the walls at temperatures much higher than the melting point of the sorbate, as pointed out by Steele *et al.*[27] At the same time we observe a transition from an increasing (from 1 to 7 molecules/cage) to a decreasing (from 8 to 15 molecules/cage) mobility regime, which is shown by the calculated self-diffusion coefficient. By direct inspection of the trajectories we find that the decreasing mobility regime increases the probability that a molecule could visit the same cage many times despite a reduced value of the

cage residence time τ_c. For low loadings the interactions between the sorbate molecules are less important and the energetic barriers for inter- and intracavity migration are roughly the same. Increasing the loading causes a reduction of the available adsorption sites, and the collisions between sorbed molecules become much more frequent. This is mirrored in the shortening of the crossover time, as computed from the velocity autocorrelation functions. When a loading higher than 15 molecules per cage is reached, the diffusive process becomes very slow, going beyond the time scale of our simulation.

In conclusion, the elucidation of these mechanisms, beyond the speculative and, possibly, practical interest of the presence of solid-like structures formed by molecules in ordered microporous materials, is important to understand the diffusive processes in zeolites of different topology and to cast light into the catalytic properties and the other applications of these materials.

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