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Molecular Understanding of Diffusion in Confinement

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We introduce a computational method to directly relate diffusivities to the microscopic behavior of the adsorbed molecules. We apply this method to gases in an MFI-type molecular sieve, the reference system in this field. Transitions in the number and nature of adsorption sites result in temporary local increases in the diffusion. This occurs at different loadings in each of the x, y, and z directions, giving rise to the complex loading behavior found experimentally. Our method can be applied to any adsorbent-adsorbate system, and provides a fundamental understanding of diffusion in confinement on a molecular level.

Of all nanoporous materials, zeolites are best known. Not only are they used in many industrial applications, they are also widely studied, owing to their regular crystalline shapes and wide variety of topologies [1]. Out of more than 150 zeolite topologies known to date [2], each distinguished by a three-letter code, MFI (Fig. 1) is one of the most important structures [3–7]. It is used in many commercial petrochemical and separation processes. Moreover, as large nearly perfect crystals of this material can be synthesized, it has become one of the most extensively studied materials in this field. Considering the importance of MFI for both industry and science, it is surprising that its diffusion properties are poorly understood. In particular, the loading-dependence of the diffusion has remained elusive.

Many studies have addressed the diffusion of gases in zeolites, finding a wide variety in diffusion behavior [8–11]. In many chemical engineering applications it is assumed that the corrected diffusion coefficient of particles in confinement is independent of loading [3,4,12–14]. In an elaborate study, comparing the diffusion of four gases in four zeolite topologies, Skoulidas and Sholl confirmed the validity of this assumption (the so-called Darken assumption) for *one* system only: CH_4 in MFI; in other systems it was refuted, but a general rationale for these phenomena was not discovered [5,11]. Despite the importance for many applications, conventional methods cannot explain when and why, for a given system, the diffusion will increase, decrease, or remain constant as a function of loading. A good discussion of the Darken assumption can be found in section 5.11 of Ref. [15], and in Ref. [13].

The fact that the loading dependence for even simple molecules in MFI is not yet understood points at a fundamental difficulty in interpreting diffusion coefficients in nanoporous materials. This observation motivated us to develop an alternative approach that allows for a direct molecular interpretation. Recently, we have extended dynamically corrected transition state theory to include loading effects [16]. In this Letter we will demonstrate that this method has an advantage over other methods, because it provides a direct molecular interpretation of the observed loading dependence.

In this Letter we illustrate this for two of the best-studied systems [5,9,10]: CH_4 and CF_4 in MFI-type zeolite, following the work of Skoulidas and Sholl [5]. Using molecular dynamics simulations, they showed that in MFI the Darken assumption would hold for methane, but not for CF_4. To find a molecular interpretation of the diffusion in these systems, we compute the diffusivity as a function of loading up to the maximum loading, which we, in contrast to previous studies, define as the loading where the diffusion (both self and corrected) comes to a complete halt. We show that the very irregular loading dependence that is observed in simulation is intrinsic to these types of systems and can be explained in detail, using the aforementioned method. To conclude, we discuss the consequences of our results for kinetic Monte Carlo (MC) simulations.

MFI-type zeolite is a so-called intersecting-channel type zeolite. It consists of straight 10-ring channels, running in the y direction, intersected by zigzag channels that run in the x and z directions and also consist of 10-membered ring windows (see Fig. 1). One unit cell of MFI contains two straight channels and two zigzag channels. At low loadings, there are four favorable positions per straight channel and four favorable positions per zigzag channel, making the total number of preferential adsorption sites per unit cell 16. The MFI structure was taken from Ref. [17]. To model the CH_4 molecules, we used the united atom model of Dubbeldam *et al.* [18,19], for the CF_4 molecules, the force field of Heuchel *et al.* was used [20].

We calculated self- and corrected diffusion coefficients using conventional molecular dynamics (MD) calculations for the full loading range of CH_4 and CF_4 in MFI. In an MD calculation, Newton's equations are being solved to study particle positions as a function of time and thus obtain a mean square displacement of a tagged particle as a function of time. This mean square displacement can easily be
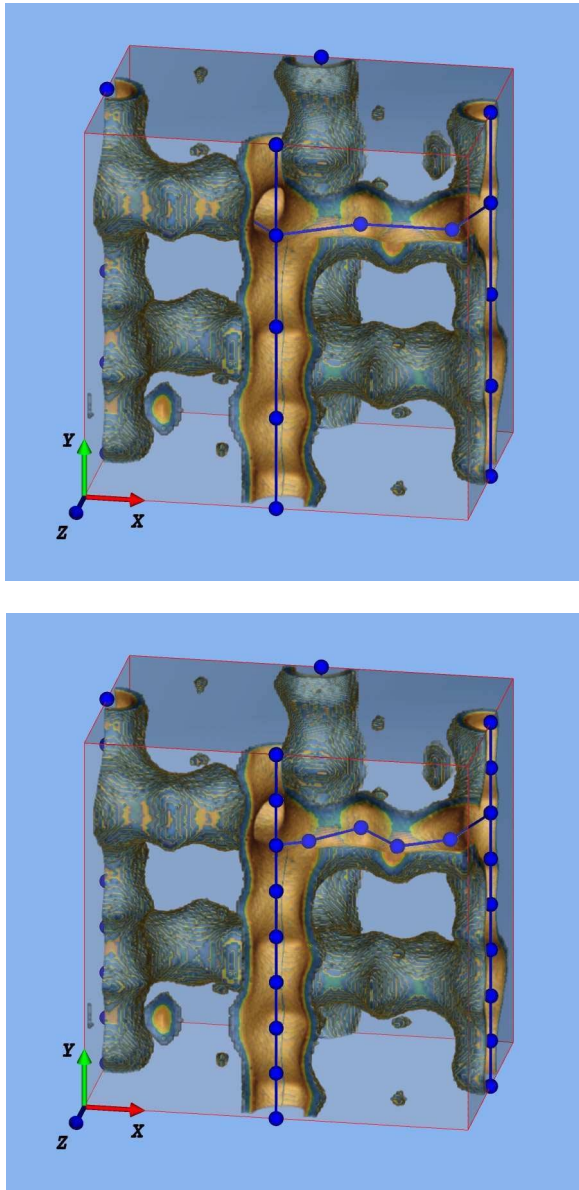
FIG. 1 (color online).   One unit cell of MFI-type zeolite at low
loading (top) and at high loading (bottom), with the lattice
spanned by the preferred adsorption sites. At low loadings, there
are four favorable positions per straight channel and four per
zigzag channel, making the total number per unit cell 16. At
higher loadings the number of preferential sites is 32. The
dimensions of the cell are $20.022 \times 19.899 \times 13.383$ Å.

converted into a self-diffusion coefficient D_S. In a similar
fashion, the corrected diffusivity D_C is related to the mean
square displacement of the center of mass. We used the
VELOCITY VERLET integration algorithm with a time step of
0.2 fs and a total simulation time of between 1.5 and
1000 ns, depending on the diffusion speed, such that the
error bars were less than 5%.

   While MD calculations are powerful and practical, the
diffusion behavior is better understood by using the dy-

namically corrected transition state theory (dcTST)
method of Beerdsen *et al.* [16]. In addition to diffusion
coefficients, this method can yield an explanation of the
diffusion behavior in terms of free energy differences.
Transition state theory regards diffusion as a hopping
process on a lattice, where the hopping from some state
A to another state B is impeded by a free energy barrier
between the two states. Together with the dynamical cor-
rection factor, free energy profiles can be used to compute
a hopping rate between state A and B, which in turn can be
converted to a self-diffusion coefficient. The free energy
profiles are computed during an *NVT*-ensemble MC or
MD simulation, in which we compute the probability to
find a particle at a particular value of the reaction coordi-
nate q. We look at a single particle, regarding all other
particles as a contribution to the external field, and implic-
itly averaging over all adsorption sites. The method relies
on the direct inclusion of all interparticle correlations in the
effective hopping rate of a particle traveling from cage A to
cage B. Further details about the method can be found in
Refs. [16,21].

   For CF_4 in siliceous MFI, up to a loading of 12 molecules
per unit cell, both the self-diffusion coefficient D_s and the
corrected diffusion coefficient D_c are a decreasing function
of loading (see Fig. 2). When the loading is further in-
creased, a striking phenomenon is observed: the diffusion
coefficient increases by 1 order of magnitude and de-
creases to zero at the maximum loading. As the x, y, and
z directions in MFI-type zeolite are crystallographically
different, we have to consider them separately. In Fig. 2 the
x, y, and z components of D_c are plotted as $D_{c,x}/3$, $D_{c,y}/3$,
and $D_{c,z}/3$, so that their sum equals D_c. The diffusion in
the y direction (the direction of the straight channels) is
highest, followed by that in the x direction, $D_{c,x}$. Figure 2
shows that both $D_{c,x}$ and $D_{c,z}$ decrease (nearly) monotoni-
cally, and above a loading of 16 molecules per unit cell the
diffusion coefficients in these directions are nearly zero.
$D_{c,y}$ has a much more complex loading behavior, with a
maximum at a loading of 17 molecules per unit cell, from
this loading onwards rapidly decreasing to reach zero at a
loading of 22 molecules per unit cell.

   To explain this behavior we analyze the free energy
profiles. The diffusion can be fully accounted for by the
loading dependence of the free energy profiles, i.e., the
dynamical correction is a monotonously decreasing func-
tion of loading. As the interesting behavior is observed in
the x, y direction, we focus on the profiles along these axes
(Fig. 3). The diffusion coefficients calculated from these
profiles are consistent with MD results. The minima in the
profiles are entropic traps: at the intersections the particles
can enter a channel perpendicular to the present reaction
coordinate. At low loadings one can observe two local
minima located inside the y channels, corresponding to
the energetically most favorable adsorption sites. Because
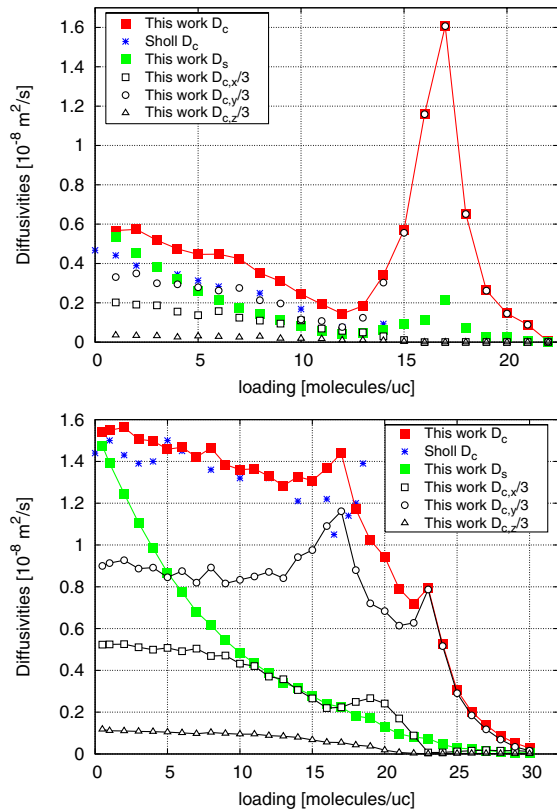of the size of CF_4, only one of these sites can be occupied.

FIG. 2 (color online). Diffusion of CF$_4$ (top) and CH$_4$ (bottom) in MFI-type zeolite at 300 K, as a function of loading, from MD simulations, and D_c as calculated by Skoulidas and Sholl [5]. The x, y, and z components of D_c are plotted as $D_{c,x}/3$, $D_{c,y}/3$, and $D_{c,z}/3$, so that their sum equals D_c. The fastest diffusion occurs in the y direction, the slowest in the z direction, since a particle diffusing in this direction has to pass both an x and a z channel, the x channel being longer.

In the x direction there is one adsorption site in each channel.

At low loadings, the particles in the zigzag channels increase the barrier at the entry of the straight channel. From 12 molecules per unit cell onward, the molecules in the zigzag channels start to pack more tightly. Since a packing of 2 molecules per zig or zag channel is commensurate with the structure of this channel, they form a tight ordering with very large barriers for diffusion. As a consequence, the diffusion in both the x and z directions halts. Because the zigzag channels are blocked, particles coming from the straight channel cannot enter. The result is a very flat free energy profile and a remarkable increase in the diffusion coefficient. At a loading of 16 molecules per unit cell, all favorable positions inside the zeolite (4 per straight channel and 4 per zigzag channel) are occupied. In order to accommodate more molecules, new adsorption positions have to be created. A reordering takes place, changing the adsorption lattice from Fig. 1 (top) to Fig. 1 (bottom). From these loadings onwards, the diffusion becomes evermore slow, until it comes to a complete halt at the maximum
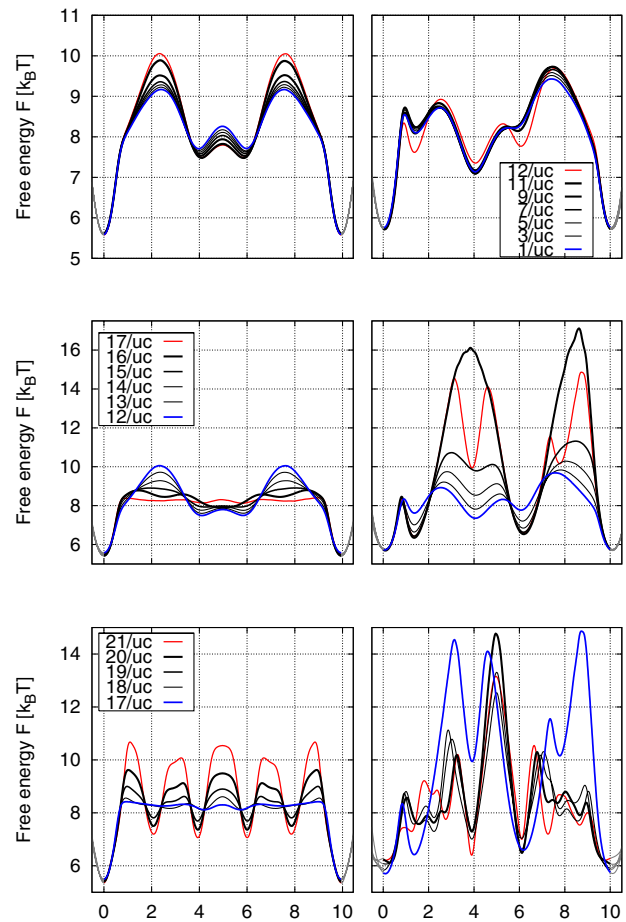

FIG. 3 (color online). Free energy profiles for CF$_4$ in MFI-type zeolite along the y (left) and x (right) directions, for 1–12 molecules per unit cell (top), 12–17 molecules per unit cell (middle), and 17–21 molecules per unit cell (bottom). The global minima at 0 Å and 10 Å correspond to the intersections of the straight channels with the zigzag channels (in the x-z plane).

loading of about 24 molecules per unit cell. Not all 32 adsorption sites are being filled. Because CF$_4$ molecules are rather large, once adsorbed they have a large energetic influence on close-by neighboring sites, preventing all 32 sites from being filled simultaneously. Note that the reordering at 12 molecules per unit cell, which causes a peak in the diffusion graph, is also reflected in the adsorption isotherm, as found earlier by Krishna *et al.* [6], confirming that events on a molecular scale affect both adsorption and diffusion.

A more complex diffusion behavior is found for CH$_4$ in MFI. CH$_4$ is a slightly smaller molecule (see Fig. 2) than CF$_4$. Again, we observe an increase in the $D_{c,y}$, caused by the "freezing" of particles in the zigzag channels that "smoothens" the straight channels, and a transition to a different adsorption lattice beyond a loading of 16 molecules per unit cell. However, in the case of CH$_4$, the peak is smaller and is counterbalanced by the general decreasing

trend in $D_{c,x}$ and $D_{c,z}$. We do not observe a maximum in D_c, but there is a distinct "kink" at a loading of about 16 molecules per unit cell. As in the case of CF_4 the high-loading lattice has 32 adsorption sites, and since CH_4 molecules are smaller than CF_4, all of them can be filled simultaneously, making the maximum loading 32 molecules per unit cell.

The simulations have been run sufficiently long for the error bar to be smaller than twice the symbol size. Therefore the irregular behavior of the diffusion coefficient is not the result of poor statistics, but an intrinsic phenomenon in these systems. It has some very characteristic features that could easily be dismissed as "noise," if the free energy profiles are not examined. Detailed inspection of the components of the diffusion coefficients shows that these humps can be related to events in one of the components. It is possible to attribute each hump to a reordering of the adsorbed molecules, often being a transition in the number of adsorption sites. For example, the small maximum in $D_{c,x}$ is caused by a transition in the zigzag channel from 4 adsorption sites (2 per zig and 2 per zag channel) to 8 adsorption sites. As the transition takes place, the system is temporarily incommensurate with both 4 and 8 adsorption sites. This causes a lowering of the free energy barrier and hence an increase in the diffusion coefficient. In addition, an increase in the number of adsorption sites raises the number of vacancies, which often results in an increase in the mobility. Based on free energy profiles, we are able to explain diffusion behavior on a molecular level.

While our data are in good agreement with those of Skoulidas and Sholl, we do not support their conclusion that the Darken approximation holds for CH_4 in MFI-type zeolite. While it seems safe to use the Darken approximation to estimate the CH_4 diffusion at experimentally accessible pressures (1×10^6 kPa is required at 300 K for 16 molecules per unit cell of CH_4, 100 kPa for 18 molecules per unit cell of CH_4), the diffusion is not constant over the entire loading range.

Our results have considerable consequences for kinetic Monte Carlo simulations on these systems. In these simulations, diffusion is considered as a hopping process on a loading-independent lattice of adsorption sites. Previous studies have shown that in three-dimensional systems, such as MFI, geometric correlations are present that are difficult to capture in a lattice model [11,22,23]. Here we have shown that, on top of these problems, as the effective topology changes as a function of loading, these correlations change too, making lattice model simulations highly impractical.

We note that the presented method is by no means limited to simple molecules in zeolites, but can be extended to more complex molecules, including mixtures, in arbitrary geometries. We have focused on simple gases in MFI as this is considered to be the reference system in this field.

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