

LETTERS

Determination of Concentration Dependent Transport Diffusivity of CF₄ in Silicalite by Neutron Scattering Experiments and Molecular Dynamics

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We have used quasi-elastic neutron scattering to determine the concentration-dependent corrected and transport diffusivities for CF₄ adsorbed in silicalite at 200 and 250 K. Equilibrium molecular dynamics simulations have also been used to compute the diffusivities under the same condition. We find quantitative agreement between our simulation and experimental results, which show that the corrected diffusivity of CF₄ decreases as the molecular loading inside the zeolite is increased. Earlier simulations and experiments have examined self-diffusion of CF₄ in silicalite, so for the first time data are now available to directly compare experimental and MD results for self-diffusion and collective diffusion simultaneously. The agreement between the simulation and experimental results provide strong support for the use of atomistic simulations to quantitatively explore the diffusion of small molecules in nanoporous materials.

The ordered nanopores inside zeolites provide an ideal environment for probing the general phenomena associated with molecular diffusion in nanoporous materials. Zeolites have a host of industrial uses, and the diffusion rates of molecules inside zeolite pores are often decisive in the usefulness of zeolites in practical separations and catalysis.^{1–3} Despite the large body of work associated with molecular diffusion in zeolites,^{2,4} long standing discrepancies between experimental measurements of nominally identical systems exist.^{1,5} To resolve these discrepancies, there is a need to characterize two different diffusion coefficients, the self-diffusivity, D_s , which defines the Brownian motion of tagged molecules at equilibrium, and the transport diffusivity, D_t , which is defined by the flux generated by a macroscopic concentration gradient, $\bar{J} = -D_t \nabla c$. D_s and D_t

are both concentration dependent and are only equal in the limit $c \rightarrow 0$.^{1,2,4} Examples are known of diffusion in nanopores where the transport and self-diffusivities at finite concentrations differ enormously.^{6,7}

It can also be useful to discuss macroscopic diffusion in terms of the corrected diffusivity, D_o , which is defined in relation to D_t by^{1,4}

$$D_t(c) = D_o(c) \frac{\partial \ln f}{\partial \ln c} \quad (1)$$

where the partial derivative term involving the fugacity of the adsorbed molecules, f , is known as the thermodynamic correction factor. In systems where only a single chemical species is adsorbed, D_o is equal to the so-called Maxwell–Stefan diffusivity.^{1,4} A common approximation to the concentration dependence of D_t and D_o is to assume that D_o is independent of c .^{1,4,8,9}

The concentration dependent self- and transport diffusivities of molecules adsorbed in nanopores can be computed using

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equilibrium molecular dynamics (EMD) simulations once interatomic potentials for the host–guest system are defined^{4,7,10}. We have recently reported extensive EMD calculations of D_s , D_t , and D_o for a series of spherical molecules in silicalite at room temperature.^{9,11,12} One notable prediction of these simulations was that several species, including CF_4 and SF_6 , strongly violated the approximation mentioned above, with corrected diffusivities that decreased strongly with increasing loading.^{9,11,12} The interatomic potentials used to describe CF_4 in silicalite in these calculations were derived by Snurr et al.¹³ EMD simulations of self-diffusion at 200 and 300 K using this model for low and moderate pore loadings are in excellent agreement with experimental measurements using PFG-NMR.¹⁴

In this letter, we compare concentration dependent transport diffusivities for CF_4 in silicalite as computed with EMD simulations to experimental measurements using neutron scattering. Quasi-elastic neutron scattering (QENS) has been widely applied to measure self-diffusion of molecules in zeolites.^{5,15} QENS can also be used to determine transport diffusivities, although this type of experiment has not been widely performed. To date, transport diffusivities determined with QENS have been published only for D_2 in NaX¹⁵ and CO_2 and N_2 in silicalite.¹⁶ Our results below for CF_4 are the first example of molecular diffusion in a zeolite for which the concentration dependence of both the self- and transport diffusivities has been determined using both atomistic simulations and experiments.

Our QENS experiments were performed at the Institut Laue-Langevin, Grenoble, France, using the IN6 spectrometer. This is the same instrument that was used previously to determine the self-diffusivity and transport diffusivity of D_2 in NaX.¹⁵ The incident neutron energy was 3.12 meV, corresponding to a wavelength of 5.12 Å. The elastic energy resolution had a Gaussian line shape, whose HWHM varied from 39 μeV at small scattering angles to 47 μeV at large scattering angles. The range of momentum transfer was $0.22 < \hbar Q < 2.07 \text{ Å}^{-1}$, although a large number of detectors had to be removed, especially at large Q values, due to the Bragg peaks of silicalite.

The silicalite sample was activated by heating to 773 K under oxygen flow. The zeolite was contained in a slab-shaped aluminum container connected to a gas inlet system. The silicalite sample was prepared and characterized as described in ref 17. Adsorption of CF_4 was performed in situ at two different temperatures, 200 and 250 K. These temperatures were selected in order to reach high CF_4 concentrations at pressures ≤ 1 bar. The loadings of CF_4 in our experiments were determined using adsorption isotherms computed with grand canonical Monte Carlo (GCMC) simulations. In these, and all the atomistic simulations discussed below, the interatomic potentials for CF_4 in silicalite derived by Heuchel et al.¹³ were used. GCMC simulations were performed as in our earlier work.^{9,11,12} The resulting adsorption isotherms are shown in Figure 1, which also shows the isotherm at 298 K from our earlier work.^{9,11,12} The thermodynamic correction factors in eq 1 were determined from the isotherms in Figure 1 after fitting our GCMC data to dual-site Langmuir isotherms.¹⁸ The GCMC-derived isotherm at 300 K is known to underestimate pore concentrations for pore loadings higher than ~ 10 molecules/unit cell,¹³ so the reported loadings from our experiments in this range of loadings may be underestimated.

Some of the experimental QENS spectra obtained at 250 K for a loading of 8 molecules per unit cell are shown in Figure 2. Despite the smaller scattering from CF_4 compared with hydrogenated molecules such as CH_4 , the statistics are quite good due to the high neutron flux available on this spectrometer.

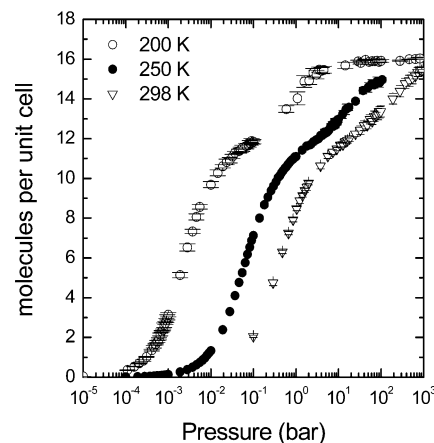


Figure 1. Adsorption isotherms for CF_4 in silicalite calculated using grand canonical Monte Carlo simulations as described in the text.

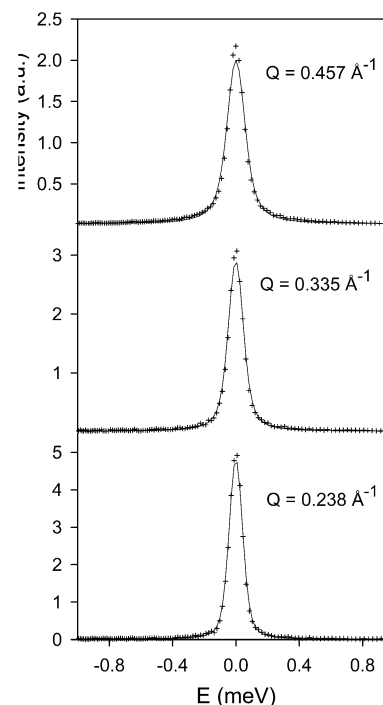


Figure 2. Comparison between experimental (+) and calculated (full lines) QENS spectra obtained for CF_4 in silicalite at different values of the momentum transfer Q ($T = 250 \text{ K}$; loading, eight molecules per unit cell).

All the QENS spectra could be fitted with only one Lorentzian function, corresponding to diffusion, convoluted with the instrumental resolution. Convolution with isotropic rotational motion, which has to be taken into account in the case of an incoherent scatterer such as CH_4 , can be neglected here. This is due to the fact that the quantities $a^2(Q)$, which govern the intensities of the Lorentzian functions corresponding to rotational diffusion, depend on the geometry of the molecule following¹⁹

$$a_l^2(Q) = \sum_{m,m'=1}^n a_{\text{coh}}^m a_{\text{coh}}^{m'} j_l(Qr_m) j_l(Qr_{m'}) P_l(\cos \Theta_{mm'}) \quad (2)$$

where a_{coh}^m is the average bound coherent scattering length for nucleus type m in a molecule with n atoms, j_l is a spherical Bessel function, \mathbf{r}_m and $\mathbf{r}_{m'}$ denote the positions relative to the center of mass of two nuclei within the same molecule, P_l is a Legendre polynomial, and $\Theta_{mm'}$ is the angle between \mathbf{r}_m and $\mathbf{r}_{m'}$. Because of high symmetry of CF_4 , the terms with j_1 and j_2 are zero and the term in j_3 is negligible for $Q < 1 \text{ Å}^{-1}$.

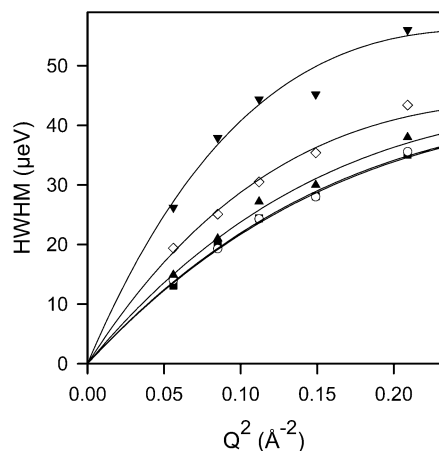


Figure 3. Broadenings derived for CF₄ in silicalite at 250 K, at five different loadings per unit cell: (■) 2 molecules, (○) 4 molecules, (▲) 5.5 molecules, (◇) 8 molecules, and (▼) 11.1 molecules. The different points correspond to individual fits of the spectra and the solid lines to simultaneous fits with a jump diffusion model.

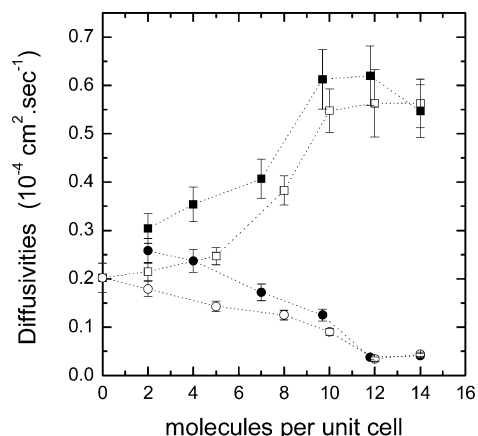


Figure 4. Transport diffusivities (squares) and corrected diffusivities (circles) as determined from QENS experiments (filled symbols) and atomistic simulations (open symbols) for CF₄ in silicalite at 200 K.

Figure 3 shows the HWHMs observed experimentally for several CF₄ loadings at 250 K. The individual points shown in Figure 3 correspond to the HWHMs obtained from the individual fits. The broadening behavior evident in Figure 3 is typical of a jump-like diffusion mechanism. The transport diffusivities have to be determined at small Q values, corresponding to large distances. In the case of Fickian diffusion, one has a linear variation of the broadening as a function of Q^2 . To take into account the deviation from the linear behavior at smaller distances, a jump diffusion model with a fixed jump length²⁰ was used to fit several spectra (Figure 3). At a given loading, only the first five spectra were fitted simultaneously because a narrowing of the HWHM is expected at larger Q values, near the maximum of the structure factor $S(Q)$.¹⁵ The structure factor, which could be extracted from the QENS spectra in the case of D₂ in NaX,¹⁵ could not be obtained for CF₄ in silicalite, because of severe overlap of Bragg reflections above 1 Å⁻¹.

The experimental transport diffusivities at 200 and 250 K derived from the data analysis described above are shown in Figures 4 and 5 as filled squares. The experimental corrected diffusivities, also shown in the same figures as filled circles, were obtained using eq 1 with the transport diffusivities determined experimentally and thermodynamic correction factors calculated from the isotherms in Figure 1.

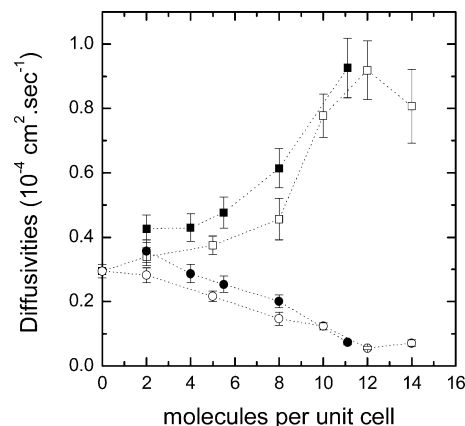


Figure 5. Same plot as Figure 4 but at 250 K.

Corrected diffusivities for CF₄ in silicalite at 200 and 250 K were also obtained from EMD simulations using the interatomic potentials described above. These simulations involve performing 20–30 independent EMD simulations of length ~4 ns at each loading. Each configuration was equilibrated prior to recording data by a combination of canonical Monte Carlo and MD. Temperature control in the EMD simulations was achieved with a Nosé–Hoover thermostat. Details of the simulation techniques used to obtain D_0 from EMD are given in our earlier work.^{9,11,12} Transport diffusivities from our atomically detailed model were obtained via eq 1, with thermodynamic correction factors calculated from the GCMC isotherms shown in Figure 1. The resulting corrected and transport diffusivities are shown in Figures 4 and 5 as open symbols.

The overall agreement between our QENS experiments and our atomistic simulations is good. The atomistic model underestimates the magnitude of the observed corrected and transport diffusivities at all loadings, with the largest relative differences occurring at low loadings. Using the experimental data with 2 molecules/unit cell at 200 and 250 K to estimate the activation energy associated with the transport diffusivity yields an activation energy of 2.8 kJ/mol. Treating our MD data at infinite dilution, where the most accurate data can be obtained, in the same way gives an activation energy of 3.25 kJ/mol. EMD data from higher temperatures (298–473 K) yield a slightly higher activation energy of 4.4 kJ/mol at infinite dilution.¹¹ The prediction from the simulations that the corrected diffusivity decreases strongly with increasing pore loading at both temperatures is confirmed by the experimental data. Both the experiments and the simulations indicate that the corrected diffusivity increases slightly at the highest pore loadings examined at 200 K. This trend is also evident in the simulation data at 250 K, but our experiments were not able to probe loadings higher than 11 molecules per unit cell at this temperature. As reported previously by Snurr and Kärger, the self-diffusivities computed using this atomistic model are in essentially exact agreement with PFG-NMR measurements at 200 K for loadings of 4 and 8 molecules/unit cell.¹⁴ For example, at 8 molecules/unit cell, PFG NMR¹⁴ yielded a self-diffusivity of $0.61 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, while EMD gives $0.55 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The consistency of these NMR experiments and our QENS experiments can be examined by extrapolating the diffusivities from both experiments at 200 K to zero loading, where the self- and transport diffusivities are equal. This extrapolation suggests that the NMR diffusivities are slightly smaller than those observed from QENS.

Our results and the earlier results of Snurr and Kärger¹⁴ demonstrate that atomistic simulations capture the concentration

dependence of the self, corrected, and transport diffusivities of CF_4 in silicalite with quantitative accuracy. Snurr and Kärger also found good agreement between EMD simulations and PFG NMR measurements of self-diffusion of CF_4/CH_4 mixtures in silicalite.¹⁴ We have previously found satisfactory agreement between calculations based on EMD simulations of binary transport diffusivities and CF_4/CH_4 mixture permeance through polycrystalline silicalite membranes.²¹ These observations lend considerable credence to the use of atomistic simulations as a means to explore diffusive phenomena in zeolite pores.

Our experiments confirm that the approximation of a concentration independent corrected diffusivity is inaccurate for CF_4 in silicalite. The behavior of CF_4 in silicalite is more accurately described by the so-called “strong confinement” scenario, where the corrected diffusivity decreases linearly with pore concentration.¹⁸ We note that there are other adsorbates for which the corrected diffusivity in silicalite is approximately concentration independent.^{9,11,12} Recent work has also compared the corrected diffusivities observed using QENS and computed using MD for N_2 and CO_2 in silicalite.¹⁶ Both of these systems show much weaker dependence of the corrected diffusivity on loading than we have observed for CF_4 in the same material. It is important to note that the approximation of concentration-independent corrected diffusivities and the “strong confinement” scenario are not based on fundamental descriptions of host–guest interactions; rather, they are both merely convenient mathematical approximations. The availability of extensive EMD simulations of corrected diffusion coefficients will be extremely useful in future efforts to determine predictive theories for describing the concentration dependence of diffusion coefficients in nanopores.

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