

LETTERS

Direct Tests of the Darken Approximation for Molecular Diffusion in Zeolites Using Equilibrium Molecular Dynamics

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We have used equilibrium molecular dynamics and grand canonical Monte Carlo simulations to compute the transport diffusivities of CH₄ and CF₄ adsorbed in a fully atomistic model of silicalite over a wide range of temperatures and pore loadings. Our results provide a direct test of the accuracy of the Darken approximation, an expression frequently used to relate transport and self-diffusivities in zeolites. The Darken approximation is accurate for CH₄ in silicalite at 298 K, but is less accurate at higher temperatures. In contrast, CF₄ deviates strongly from the Darken approximation at all temperatures we have examined. This observation suggests that substantial deviations from the Darken approximation may be a common feature of molecular diffusion in zeolites.

Diffusion of molecules in the nanometer-scale pores of zeolites lies at the heart of many industrial applications of these crystalline microporous materials. Long-standing controversies exist regarding the relationship between molecular diffusivities measured experimentally using macroscopic techniques (e.g., chromatography or frequency response methods) and microscopic methods such as pulsed-field gradient (PFG) NMR and quasi-elastic neutron scattering (QENS). Detailed reviews of these controversies are available.^{1–4} In brief, macroscopic methods typically measure the transport diffusivity, D_t . When a single-component is adsorbed in a zeolite with concentration c , D_t is defined by the flux, \bar{J} , generated by a concentration gradient $\bar{J} = -D_t(c)\nabla c$. Because it is more thermodynamically meaningful to relate molecular fluxes to gradients in the chemical potential, μ , D_t can be written as $D_t(c) = D_c(c)(\partial \ln f / \partial \ln c)_T$, where $D_c(c)$ is called the corrected diffusivity and f is the fugacity of the adsorbed species.² Microscopic methods, in contrast, typically measure the self-diffusivity, D_s . For a zeolite with a single adsorbed component, the self-diffusivity

is defined by the mean square displacement of a single molecule via Einstein's equation: $6D_s(c)t = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$ as $t \rightarrow \infty$. Here, $\vec{r}(t)$ is the position of an adsorbed molecule at time t . As has been emphasized by previous authors, the transport, corrected, and self-diffusivities are all dependent on the concentration of the adsorbed species and are only equal in the limit of dilute concentrations.^{1–3}

The expressions above involving D_t , D_c , and D_s are all exact. To relate these three quantities in a simple way, it is frequently assumed that the corrected diffusivity, D_c , is independent of loading, that is, $D_c(c) \approx D_c(0)$. With this approximation,

$$D_t(c) = D_s(0) \left(\frac{\partial \ln f}{\partial \ln c} \right)_T \quad (1)$$

because the self- and corrected diffusivities are identical when $c = 0$. This expression is often referred to as the Darken equation. Although we will use this name in this letter, we acknowledge that it is not historically accurate. Not only was Darken not the first to derive such an equation, he also explicitly stated in his original work that D_c is not a constant with respect to composition.⁵ For a thorough historical discussion of this

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equation, see ref 4. Although it is well known that eq 1 is not exact,² it has received widespread application because of its convenience. This approximate equation has been used in many studies aiming at relating macroscopic and microscopic measurements of diffusion.⁴ In another use of eq 1, many models of permeation through zeolite membranes are based on the assumption that single-component Maxwell–Stefan diffusivities are constant.^{6–8} For single-component systems, the Maxwell–Stefan diffusivity is proportional to the corrected diffusivity, $D_c(c)$,^{8,9} so these studies implicitly use eq 1.

Despite its widespread use, surprisingly little is known about the validity or accuracy of eq 1. This issue is difficult to examine experimentally, because to do so one must ideally measure D_t and D_s under identical conditions. This has recently been accomplished by Jobic et al., who examined D_2 diffusion in NaX at 100 K using QENS.¹⁰ These experiments indicated that the corrected diffusivity of D_2 in NaX is not independent of the pore loading, rather, it increases as a function of loading up to a maximum at 4 molecules per supercage. Another avenue for investigating eq 1 is to use theoretical simulations. Numerous groups have compared self- and transport diffusivities in lattice models of 2d and 3d diffusion.³ Although these studies are instructive, it is important to note that these lattice models are rarely related in any detailed way to the known motion of molecules inside zeolite pores. Examples are known where systems that superficially appear to be good candidates for lattice models are in fact only correctly described by more detailed consideration of the underlying molecular motions.^{11–14}

An alternative to using lattice models to describe molecular diffusion in zeolites is to use atomistic simulations of these systems. Extensive reviews of this approach are available.^{2,3} Almost all atomistic simulations of diffusion in zeolites have focused on self-diffusivities, because this can be routinely computed using the Einstein equation. Many examples have been demonstrated where good agreement is found between experimental measurements of $D_s(c)$ and the results of atomistic simulations.^{2,3} Much less work has been done to examine transport diffusivities, even though several methods are available to compute D_t using atomistic simulations. Maginn et al. used several variants of nonequilibrium molecular dynamics (NEMD) to compute the orientationally averaged transport diffusivity of CH_4 in silicalite at 300 K.¹⁵ One important result from this study was that eq 1 is an excellent approximation for this system. We return to this point below. Recently, Hoogenboom et al. reported an equilibrium MD technique based on a Green–Kubo formalism that they used to compute the transport diffusivity for Ar in $\text{AlPO}_4\text{-5}$ at a single loading and temperature.¹⁶ A more efficient EMD technique was first suggested (although not implemented) by Theodorou et al.^{2,15} In this method, EMD simulations are used to directly compute the corrected diffusivity. These data are then combined with an independent calculation of the thermodynamic correction factor, $(\partial \ln f / \partial \ln c)_T$, to define the transport diffusivity. This method has recently been applied by Sanborn and Snurr to examine the binary diffusion of CH_4 and CF_4 in faujasite.^{17,18}

In this letter, we report the transport diffusivities of CH_4 and CF_4 adsorbed as single-components in silicalite as functions of temperature and loading as computed using EMD simulations. Silicalite is a noncationic material, so the complications that can arise during diffusion in a material with long-range ionic disorder¹⁹ cannot occur. Our results allow an unambiguous examination of the validity of eq 1. This is the first set of atomistic simulations to examine the variation in zeolitic

transport diffusivities with temperature, and only the second¹⁵ to examine D_t over a full range of pore loadings.

We have adopted the atomistic models studied previously by other groups.^{2,15,20–22} Briefly, silicalite is modeled as a rigid framework in its orthorhombic form. Adsorbed molecules are represented as single-site Lennard-Jones spheres with interactions between pairs of adsorbates and between adsorbates and O atoms in the zeolite framework. We have used the potential parameters of refs 15, 20–22. This atomistic model predicts CH_4 adsorption isotherms in excellent agreement with experiment^{21,23} and CH_4 self-diffusivities in excellent agreement with PFG-NMR measurements.²⁰ Agreement between this atomistic model and experimental results for the adsorption isotherm and self-diffusivity of CF_4 is excellent for low and moderate pore loadings, although minor discrepancies between the model and experiments exist at high loadings.^{21,22}

We have computed single-component transport diffusivities using the methods first described by Theodorou et al.^{2,15} The corrected diffusivity can be written as $D_c(c) = Lk_B T/c$, where L is the Onsager transport coefficient for a single-component system. The advantage of this expression is that L can be related directly to microscopic properties of the atomistic system containing N particles by²

$$L = \frac{1}{6Vk_B T} \lim_{t \rightarrow \infty} \frac{1}{t} \langle |\sum_{i=1}^N [\vec{r}_i(t) - \vec{r}_i(0)]|^2 \rangle \quad (2)$$

Here, $\langle \dots \rangle$ represents an ensemble average over multiple independent N particle systems, in contrast to the situation for self-diffusion, where an average can be taken over a single large system. This expression can also be formulated in terms of microscopic fluxes² and can easily be extended to multicomponent systems.^{2,17,18} We have computed L , and as a result, $D_c(c)$, by using EMD simulations of the atomistic models defined above. We used NVT-MD with the Nosé–Hoover thermostat with trajectories lasting 10.3 ns for CH_4 and 24.7 ns for CF_4 . We checked that using NVE-MD gave virtually identical results. For each loading, eq 2 was averaged over 20 independent trajectories. Before each trajectory, NVT-MC and then NVT-MD were used for equilibration. Our simulations used a volume defined by two unit cells in each direction, except when we had less than 3 molecules per unit cell, in which case we used a $3 \times 3 \times 3$ simulation volume.

To complete our calculation of D_t , we computed the adsorption isotherms for our atomistic models using grand canonical Monte Carlo (GCMC) simulations.^{15,21} Examples of our results are shown in Figure 1 for CH_4 adsorbed in silicalite. In these calculations we determined the fugacity of the bulk gas phase using a fourth-order virial expansion.²⁴ To determine the required thermodynamic correction factor from our isotherms, we fit the isotherms at 200 and 298 K using

$$c(P) = \frac{c_1 P}{c_2 + P} + \frac{c_3 P}{c_4 + P} + c_5 P \quad (3)$$

and differentiated this function. At 373 and 473 K we fitted the isotherms using $c(P) = c_1 P / (1 + c_2 P)$.

Our results for the transport diffusivity of CH_4 in silicalite at 200, 298, 373, and 473 K are summarized in Figure 2. At each temperature, the results of our EMD simulations are compared to the predictions of eq 1. Molecular diffusion in silicalite is anisotropic.²⁰ Figure 2 shows the orientationally averaged results for CH_4 . We return to the anisotropy of these systems below. Our EMD results at 298 K are in excellent agreement with the

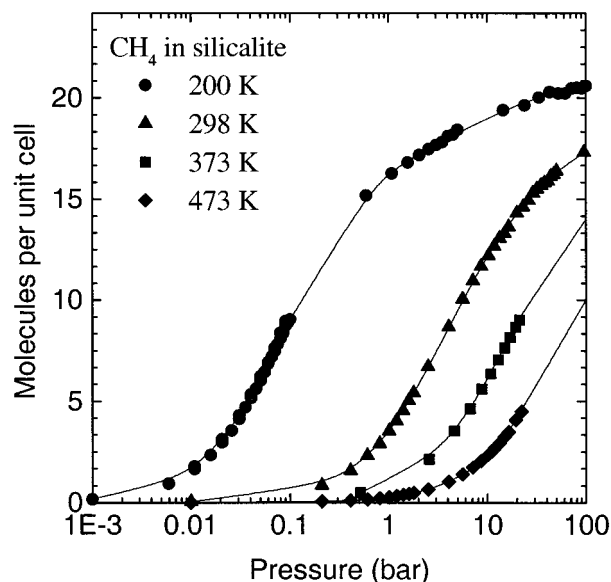


Figure 1. Adsorption isotherms for CH_4 in silicalite at $T = 200, 298, 373,$ and 473 K. The symbols are results from GCMC simulations and the curves are the fitted isotherms described in the text.

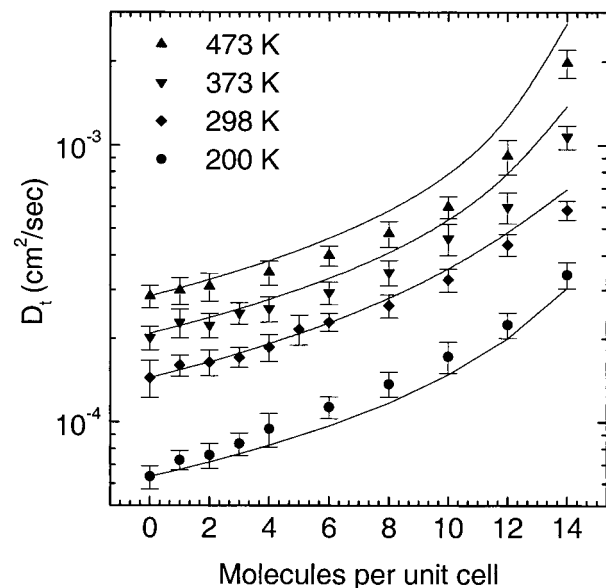


Figure 2. Orientationally averaged transport diffusivities for CH_4 in silicalite at $T = 200, 298, 373,$ and 473 K. The symbols are the results of EMD simulations and the curves are the predictions of eq 1.

NEMD results of Maginn et al.¹⁵ at 300 K, as should be expected. At all of the temperatures we examined, the transport diffusivity increases monotonically with pore loading. The most intriguing feature of Figure 2 is that whereas eq 1 is quite accurate at 298 K, it is less accurate at all of the other temperatures we have examined. At 373 and 473 K, eq 1 overestimates D_t for pore loadings exceeding 6 molecules per cell. At 200 K, on the other hand, eq 1 underestimates D_t appreciably. These data lead to the interesting conclusion that the excellent agreement between eq 1 and D_t observed by Maginn et al.¹⁵ in their NEMD study of CH_4 at 300 K was largely due to a fortuitous choice of temperature.

Applying the same methods to examine the diffusion of CF_4 in silicalite yields the results summarized in Figure 3. CF_4 is a larger molecule than CH_4 and adsorbs more strongly in silicalite.²¹ The most important feature of Figure 3 is that strong deviations from the predictions of eq 1 are observed for all pore

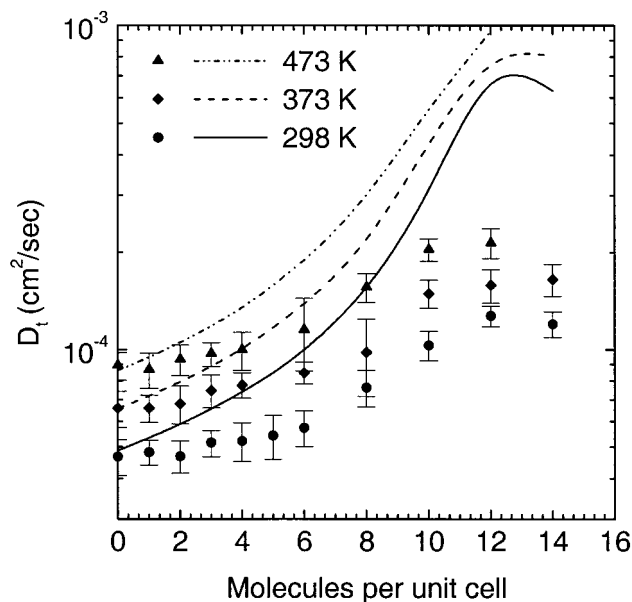


Figure 3. Orientationally averaged transport diffusivities for CF_4 in silicalite at $T = 298, 373,$ and 473 K. The symbols are the results of EMD simulations and the curves are the predictions of eq 1.

loadings and all temperatures that we examined. At each temperature shown in Figure 3, eq 1 overestimates the true transport diffusivity. We reiterate that our simulation results give the exact transport diffusivity for our atomistic model, so the differences between these results and those from eq 1 stem from the inaccurate assumption in eq 1 that $D_c(c)$ is independent of c for these systems.

It is important to note that there is nothing particularly unusual about CF_4 adsorbed in silicalite that would suggest the results in Figure 3 are anomalous compared to other adsorbate/zeolite systems. The adsorption isotherm of CF_4 in silicalite is a simple monotonic function.²¹ D_s decreases with loading,²² as it does for many adsorbed species in zeolites. Adsorbed CF_4 molecules are distributed relatively uniformly throughout silicalite pores.²¹ On this basis, it seems reasonable to conclude that the strong discrepancies between eq 1 and the actual transport diffusivities shown in Figure 3 may be a common feature of many adsorbed species in zeolites.

We conclude by briefly discussing the anisotropy of transport diffusivities in silicalite. It is straightforward to extract the $x, y,$ and z components of D_t from the simulations described above. One use of these data is to examine the accuracy of eq 1 for each component individually. An example of this analysis is shown in Figure 4, where we plot $D_{t,i}(c)/[D_{t,i}(0)\partial \ln f/\partial \ln c]$ for $i = x, y,$ and z for CH_4 and CF_4 in silicalite at 298 K. For both species, $D_y > D_x > D_z$ at zero loading.²⁰ Note that the normalized diffusivity shown in Figure 4 can also be interpreted as the corrected diffusivity normalized by its zero loading value, so if eq 1 is correct the normalized diffusivity is equal to 1 at all loadings. The corrected diffusivity of CH_4 at 298 K is roughly constant up to about 10 molecules per unit cell. At higher loadings, the x and z components of the transport diffusivity deviate noticeably from eq 1, whereas the y component exhibits only very minor deviations. For CF_4 the situation is somewhat different. The fastest component of the diffusivity, the y component, shows the strongest deviations from eq 1 at all loadings higher than 1 molecule per unit cell. Perhaps the most important point illustrated by Figure 4, however, is that qualitatively the deviations from eq 1 are similar for all three components of the anisotropic diffusion of CH_4 and CF_4 in silicalite.

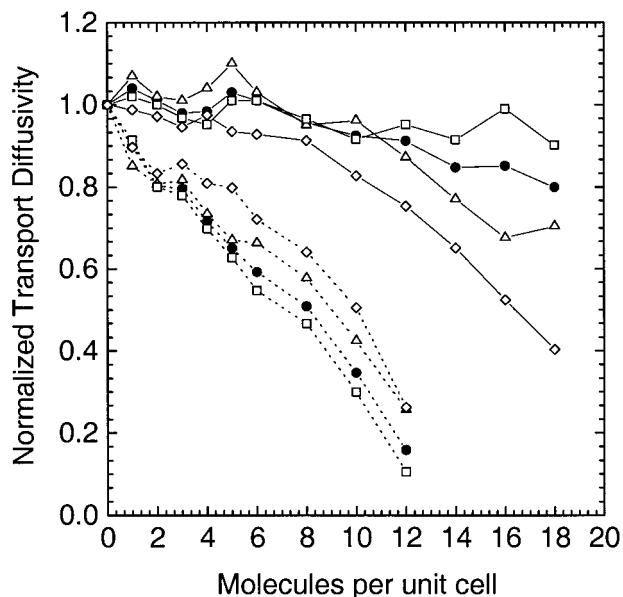


Figure 4. Components of the transport diffusivity for CH_4 (solid lines) and CF_4 (dashed lines) in silicalite at $T = 298$ K normalized by the prediction of eq 1 for each component. For each species, the x (open triangles), y (open squares), z (open diamonds), and orientationally averaged (filled circles) results are shown.

In this letter we have shown that equilibrium MD can be used to directly compute anisotropic transport diffusivities for atomistic models of molecules diffusing in zeolites. Our results are the first to systematically document deviations from the so-called Darken approximation over a wide range of loadings and temperatures. The fact that these deviations appear in a relatively simple system, CF_4 diffusing in silicalite, suggests that these deviations might occur in many related systems.

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