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Research Article

Loading Dependence of Self-Diffusivities of Gases in Zeolites

Experimental data on the self-diffusivities, $D_{i,self}$, of a variety of gases (CH_4, N_2, Kr, C_2H_6, and C_3H_8) in three different zeolites, LTA, FAU, and MFI, show different dependences on the molar loading, q_i. In LTA, $D_{i,self}$ appears to increase with q_i for all molecules except N_2. In FAU and in MFI the $D_{i,self}$ shows a sharp decrease with increasing q_i. In order to gain insights into the causes behind the loading dependences, molecular dynamics (MD) simulations were carried out to determine the self-diffusivities of seven gases (CH_4, N_2, Kr, C_2H_6, C_3H_8, Ar, and Ne) in six different all-silica zeolite structures (MFI, AFI, FAU, CHA, DDR, and LTA). The simulation results show that the variation of $D_{i,self}$ with q_i is determined by a variety of factors that include molecular size and shape, and degree of confinement within the zeolite. For one-dimensional channels (AFI) and intersecting channel structures (MFI), the $D_{i,self}$ invariably decreases with increasing q_i. For zeolite structures that consist of cages separated by windows (FAU, CHA, DDR, LTA), the size of the windows is an important determinant. When the windows are wide (FAU), the $D_{i,self}$ decreases with q_i for all molecules. If the windows are narrow (CHA, DDR and LTA), the $D_{i,self}$ often exhibits a sharp increase with q_i, reaches a maximum and reduces to near-zero values at saturation. The sharpness with which $D_{i,self}$ increases with q_i, is dictated by the degree of confinement at the window. Weakly confined molecules, such as Ne, do not exhibit an increase of $D_{i,self}$ with q_i.

Keywords: Self-diffusivities, Simulations, Zeolites

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1 Introduction

For the development and design of zeolite based separation and reaction processes, it is essential to have proper insights into the diffusion of molecules within zeolite structures [1]. In a recent review, Sircar [2] has underlined the need for a better understanding of the concentration, or loading, dependence of zeolite diffusivities. For example, Fig. 1 shows the experimental data of Cao et al. [3] for the self-diffusivities, $D_{i,self}$, of N_2, CH_4, and Kr in LTA-4A (small pore-size zeolite), normalized with respect to the zero-loading values. The data show that the self diffusivity of N_2 is practically constant for the range $0 < q_i < 1.5$ mol kg^{-1}. The self diffusivities of CH_4, and Kr, on the other hand, show an increasing trend with q_i. Cao et al. [3] state in their paper "No clear explanation of these behaviors

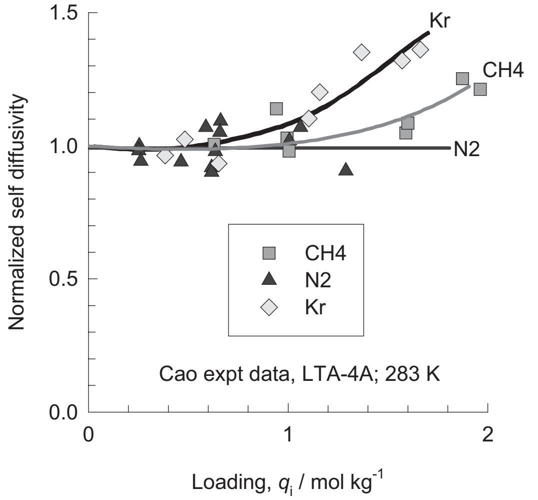

Figure 1. Experimental data of Cao et al. [3] on self-diffusivities, normalized with respect to the zero-loading values, of N_2, CH_4, and Kr in the LTA-4A zeolite at 283 K.

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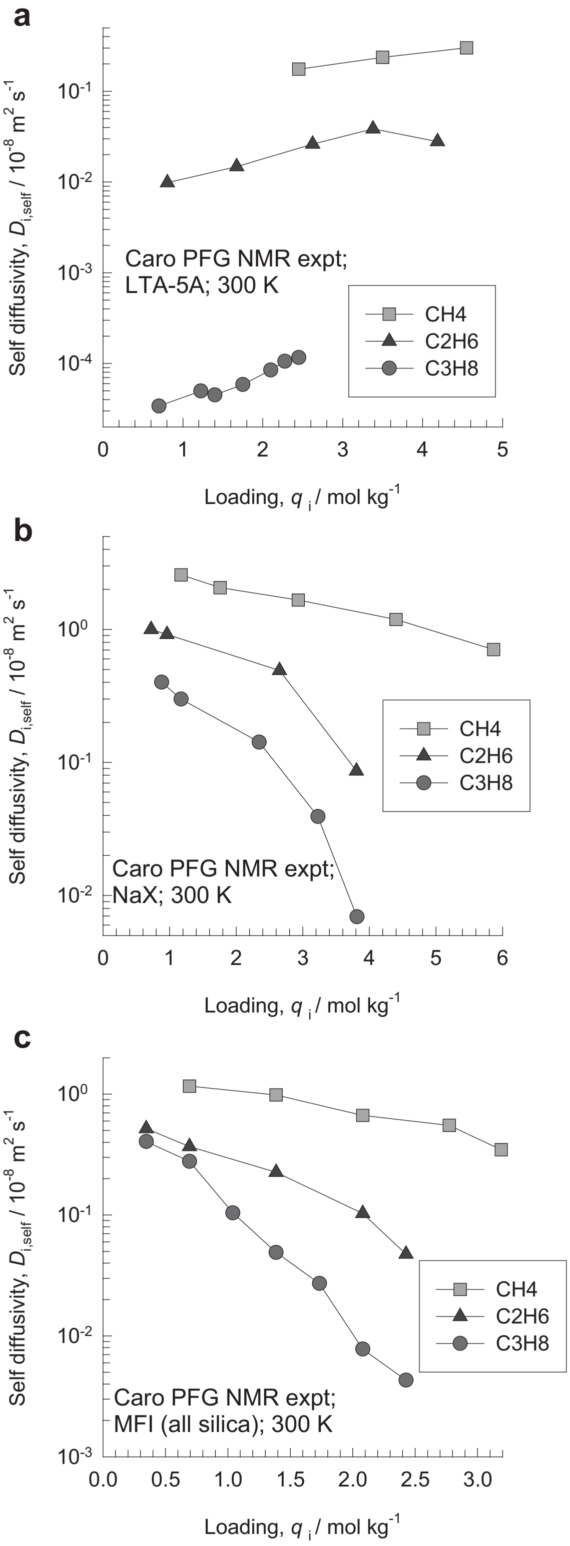

Figure 2. PFG NMR measurement data of Caro et al. [4] for the diffusion of methane, ethane and propane in: (a) LTA-5A, (b) FAU (NaX) and (c) MFI (silicalite-1) zeolites at 300 K.

can be given at this time." PFG NMR measurement data of Caro et al. [4] for diffusion of methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) also confirms the increasing trend of $D_{i,self}$ with q_i for the LTA-5A zeolite (see Fig. 2a). The loading dependences observed in Fig. 1 and Fig. 2a belong to Type V of the classification of Kärger and Pfeifer [5]. For FAU (NaX, large pore size) and MFI (silicalite-1, medium pore size) zeolites, the experimental data of Caro et al. [4] show that $D_{i,self}$ decreases with q_i (see Fig. 2b, c). This loading dependence belong to Type I of the classification of Kärger and Pfeifer [5].

The major objective of the present communication is to gain insights into the loading dependence of the self-diffusivities of molecules in zeolites. For this purpose, molecular dynamics (MD) simulations were carried out for seven different gases (CH_4, N_2, Kr, C_2H_6, C_3H_8, Ar, and Ne) in six different all-silica zeolite structures (MFI, AFI, FAU, CHA, DDR, and LTA) at a temperature of 300 K. A few simulations were also carried out to study the influence of the presence of cations in FAU and LTA zeolites. We examine the extent to which MD simulations are able to reflect the loading dependences of $D_{i,self}$ found in the experimental data of Cao et al. [3] and Caro et al. [4].

2 Molecular Simulation Methodology

The MD simulations of the self-diffusivities were carried out with the DLPOLY code [6] for a variety of molecular loadings up to saturation limits. The crystallographic data are taken from literature sources [7]. The zeolite lattices are rigid during simulations, with static atomic charges that are assigned by choosing $q_{Si} = +2.05$ and $q_O = -1.025$, following the work of Calero et al. [8] CH_4 molecules are described with a united atom model, in which each molecule is treated as a single interaction center [9]. The interaction between adsorbed molecules is described with Coulombic and Lennard-Jones terms. The parameters for CH_4 are taken from Dubbeldam et al [10]. For studying the influence of cations (Na^+, Ca^{++}) on self-diffusivities of alkanes we used the force fields described by Calero et al. [8, 11]. We use the 2LJ3CB.MSKM model for N_2 dumbbell molecules with a rigid interatomic bond of 1.098 Å [12, 13]. The partial charges of N_2 are distributed around each molecule to reproduce the experimental quadrupole moment. The Lennard-Jones parameters for CH_4-zeolite interactions are taken from Dubbeldam et al. [10]. The Lennard-Jones parameters for N_2-zeolite interactions are due to Makrodimitris et al. [13]. The force fields for Ne and Ar are those listed in Skoulidas and Sholl [14]. The force field for Kr was taken from Talu and Myers [15]. The Lennard-Jones potentials are shifted and cut at 12 Å. The number of unit cells in the simulation box was chosen such that the minimum length in each of the coordinate directions was larger than 24 Å. Periodic boundary conditions were employed.

Fig. 3 shows snapshots of the location of N_2 molecules, for example, within the one-dimensional (1D) channel structure of AFI, intersecting channels of MFI, cages separated by large windows of FAU, and cages separated by narrow windows of LTA, CHA, and DDR. These snapshots were obtained from Monte Carlo simulations in the grand canonical ensemble.

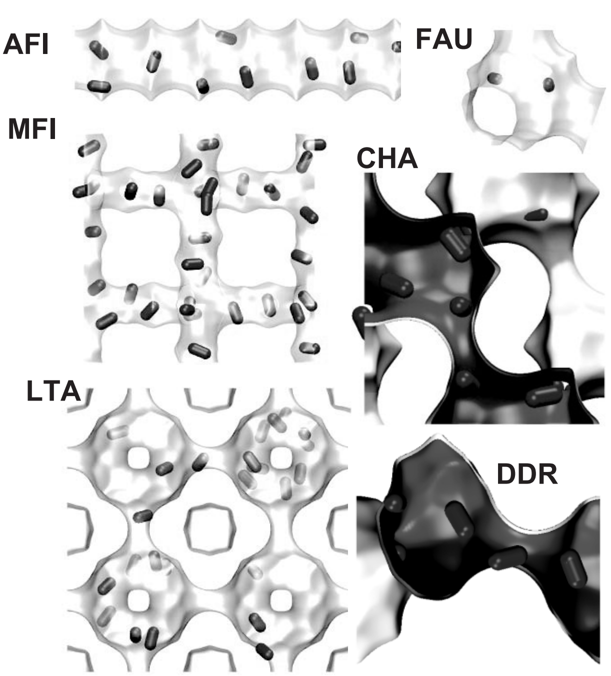

Figure 3. Snapshots of the locations of N_2 molecules within the one-dimensional channel structure of AFI, intersecting channels of MFI, cages separated by large windows of FAU, and cages separated by narrow windows of LTA, CHA, and DDR. Note that the zeolites are not all drawn to the same scale.

The self-diffusivities, $D_{\mathrm{i,self}}$, were computed by analyzing the mean square displacement of each component:

$$D_{\mathrm{i,self}} = \frac{1}{2N_{\mathrm{i}}} \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \left\langle \left(\sum_{l=1}^{N_{\mathrm{i}}} \left(r_{l,\mathrm{i}}(t+\Delta t) - r_{l,\mathrm{i}}(t) \right)^2 \right) \right\rangle \qquad (1)$$

In this expression N_{i} represents the number of molecules of species *i*, and $\mathbf{r}_{l,i}(t)$ is the position of molecule *l* of species *i* at any time *t*. For the 1D channel structures of AFI, the reported diffusivities are along the *z*-direction. For DDR, the reported diffusivities are the averages of the *x*- and *y*-directions. For all other cases (MFI, FAU, LTA, CHA), the average values in the three coordinate directions are presented. In all cases reported here, the MSD values were linear in *t* for $t > 10$ ps (used in data regression analysis to determine the diffusivities) and we found no evidence of single file diffusion characteristics. Additionally, the self-diffusivities were determined in the pure fluids using the methodology described earlier [16].

3 Loading Dependence of the Self Diffusivity in All-Silica Zeolites

First, let us consider the loading dependence of $D_{\mathrm{i,self}}$ of molecules in large and medium pore-size zeolites: (a) AFI (12-ring 1D channels of 7.3 Å size), (b) FAU (12-ring window of 7.4 Å size), and (c) MFI (10-ring intersecting channels of 5.1–5.6 Å size); see Figs. 4a, b, c. In all cases $D_{\mathrm{i,self}}$ decreases with the molar loading per mass of the zeolite framework, q_{i}. For any zeolite, the hierarchy of diffusivity values is dictated by molecular size, which increases roughly in the sequence Ne, Ar, N_2, Kr, CH_4, C_2H_6, C_3H_8. Let us define the degree of confinement as the size of the molecule with respect to typical pore dimension. We note that the stronger the degree of confinement, the sharper is the decrease of $D_{\mathrm{i,self}}$ with q_{i}. All diffusivities tend to approach vanishingly small values at saturation loadings.

The $D_{\mathrm{i,self}}$–q_{i} dependence of molecules in LTA, CHA, and DDR that consists of cage structures separated by *narrow* windows (smaller than 5 Å) is different primarily because the degree of confinement is much stronger in this case (see Figs. 4d, e, f). Also, the $D_{\mathrm{i,self}}$ of any molecule, at low q_{i} values, is significantly lower than those in AFI, FAU and MFI. The self-diffusivity of Ne in LTA (8-ring window of 5 Å size) shows only a mild decrease with loading for the range of q_{i} values considered (see Fig. 4d). This is because the saturation loading is very high, and the loadings considered are considerably lower than the saturation loading. The $D_{\mathrm{i,self}}$ of Ar and N_2 in LTA is practically constant for $q_{\mathrm{i}} < 3$ mol kg^{-1}; only for higher loadings is there an inevitable decrease to near-zero values as saturation is approached. For more strongly confined molecules, Kr, CH_4, C_2H_6, and C_3H_8, the diffusivities in LTA increase with q_{i} until a maximum is reached and thereafter reduce to near-zero values as saturation loading is approached. The stronger the degree of confinement (that increases roughly in the sequence: Kr, CH_4, C_2H_6, C_3H_8) the sharper is the increase in the $D_{\mathrm{i,self}}$ with q_{i}.

An explanation for the increase in the diffusivity has been put forward by Beerdsen et al. [17, 18] in terms of the reduction in the energy barrier for inter-cage hopping with increased loading. The maximum loadings reached in the experiments of Cao et al. [3] were lower than 2 mol kg^{-1}. This is the reason that Cao et al. [3] conclude that the self-diffusivity of N_2 is independent of loading. If higher loadings were to have been employed, the diffusivity of N_2 would have decreased. The MD simulations for Kr and CH_4 in LTA-4A are in qualitative agreement with the measurements of Cao et al. [3], who found a sharp increase in $D_{\mathrm{i,self}}$ for q_{i} values up to 2 mol kg^{-1}. However the measurements were not carried out to high enough loadings to detect the maximum found in the MD simulations. The measurements of Caro et al. [4] for the diffusivity of CH_4, C_2H_6, and C_3H_8 in LTA-5A show an increase in $D_{\mathrm{i,self}}$ with q_{i} up to loadings reaching 5, 4 and 2.5 mol kg^{-1}, respectively. This trend is in agreement with those presented in Fig. 4d.

The window sizes for CHA (8-ring window of 3.8 Å size) and DDR (8-ring window of 3.6–4.4 Å size) are smaller than that of LTA and, consequently, the confinement is stronger, causing even Ar and N_2 to exhibit a maximum in $D_{\mathrm{i,self}}$ (see Figs. 4e, f). For Kr and CH_4, which are much more strongly confined within the windows than Ar and N_2, the maximum in the $D_{\mathrm{i,self}}$–q_{i} trend is sharp. We may also conclude from the MD simulation results that structures such as CHA and DDR are particularly suited for kinetic separations that rely on differences based on molecular size. This is because small differences in molecular size lead to significantly larger differences in diffusivities. Consequently, CHA and DDR are prime candidates for zeolite membrane separations of CO_2 and CH_4 [19–21]. CO_2 is a more slender molecule than the "rounded" CH_4

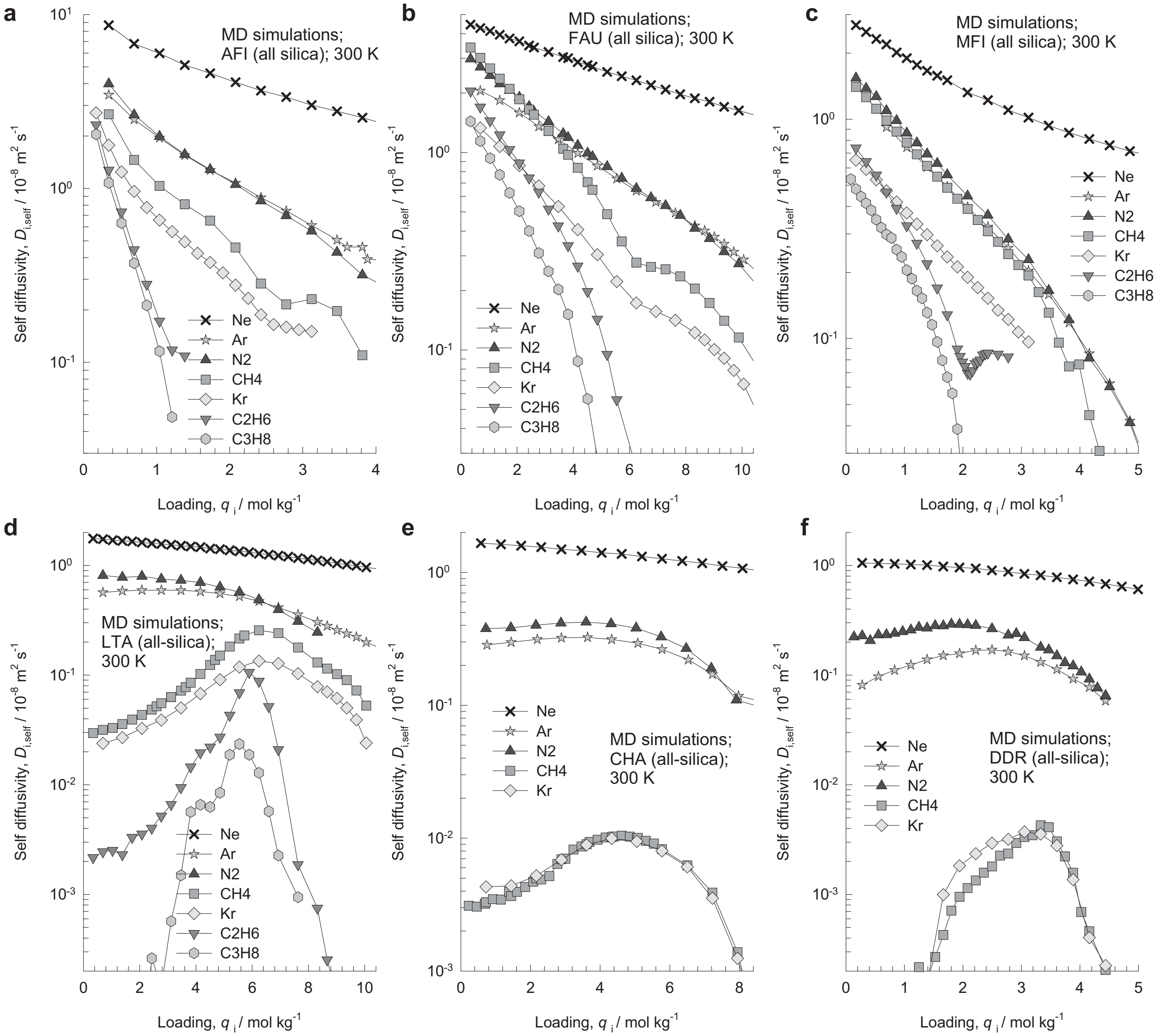

Figure 4. MD simulations of the self-diffusivities $D_{i,self}$, as a function of the molar loading q_i, of seven molecules (CH_4, N_2, Kr, C_2H_6, C_3H_8, Ar, and Ne) in: (a) AFI, (b) FAU, (c) MFI, (d) LTA, (e) CHA, and (f) DDR.

and has a significantly higher diffusivity in CHA and DDR [22].

For each molecule we now compare the loading dependence of $D_{i,self}$ in the six different zeolites. For a fairer comparison of different zeolites we plot $D_{i,self}$ against c_i, defined as:

$$c_i = q_i / V_p \qquad (2)$$

The pore volumes, V_p, of the different zeolites are estimated as 9.21, 22.7, 8.3, 20.3, 14.9, and $6.99 \cdot 10^{-5}$ m^3 kg^{-1}, respectively, for AFI, FAU, MFI, LTA, CHA, and DDR. Fig. 5 compares the $D_{i,self}$–c_i dependences of (a) Ne, (b) Ar, (c) N_2, (d) Kr, (e) CH_4, and (f) C_2H_6 in the six zeolites. Also included are the MD simulated $D_{i,self}$ values for pure fluids. The first point to note is that even for pure fluids $D_{i,self}$ decreases with c_i and therefore there is no reason to expect $D_{i,self}$ within zeolites to be independent of loading. A further point to note is that at the highest loadings, the diffusivities of any molecule in all zeolites approach one another. The diffusivity within the 1D channels of AFI is significantly lower than that of pure fluid, and is also below the Knudsen diffusion value for a smooth 7.3 Å diameter tube. Each diffusing species within AFI experiences an undulating zeolite matrix structure, as has been emphasized earlier [23]; this is the reason that the diffusivities are significantly lower than that of a smooth tube. For Ne, the smallest molecule considered, the $D_{i,self}$–c_i trend for any zeolite appears to run parallel to that for the pure fluid, with the hierarchy roughly dictated by the characteristic channel or window size. More strongly confined molecules exhibit sharp maxima in the case of LTA, CHA and DDR. These three zeolites are

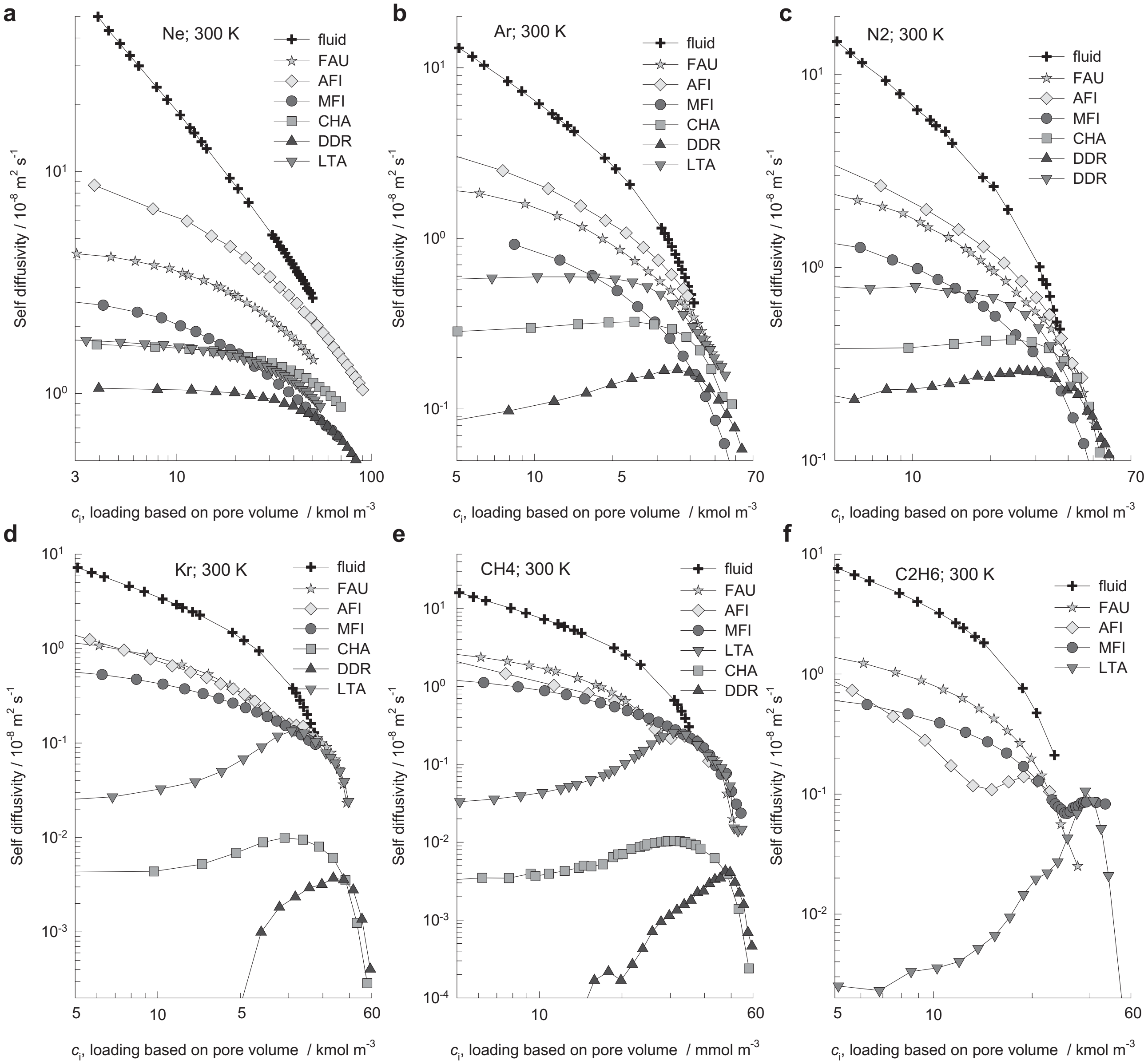

Figure 5. MD simulations of the self-diffusivities $D_{i,\text{self}}$, as a function of c_i, the molar loading based on pore volume, of: (a) Ne, (b) Ar , (c) N_2, (d) Kr, (e) CH_4, and (f) C_2H_6 in pure fluid, AFI, FAU, MFI, LTA, CHA and DDR.

particularly suited for use in diffusion selective separations, such as air purification and removal of CO_2 from natural gas. Fig. 5 provides a useful guide for screening zeolites for diffusion selectivity.

4 Influence of Cations on Self-Diffusivities in FAU and LTA Zeolites

The foregoing simulation results for $D_{i,\text{self}}$ were for all-silica zeolites. We also studied the influence of the presence of cations on the diffusivities in FAU and LTA. The force field information given by Calero et al. [8, 11] was used for this purpose. Fig. 6a compares the $D_{i,\text{self}}$ for methane, ethane and propane in all-silica FAU with FAU (106 Si, 86 Al, 86 Na^+) at 300 K. The presence of cations reduces the $D_{i,\text{self}}$ only slightly. Also, the trends in the loading dependence remain unchanged. These results, including cations, are in reasonably good quantitative agreement with the PFG NMR measurement data of Caro et al. [4] for NaX zeolites (see Fig. 6b). The presence of cations on the $D_{i,\text{self}}$ of CH_4 in LTA was investigated for two cases: LTA (96 Si, 96 Al, 96 Na^+), and LTA (96 Si, 96 Al, 32 Na^+, 32 Ca^{++}); see Fig. 6c. The presence of 96 Na^+ reduces the $D_{i,\text{self}}$ for methane by about one order of magnitude below the value for all-silica LTA (192 Si), and the increase in the $D_{i,\text{self}}$ for the initial range of loadings appears to be much

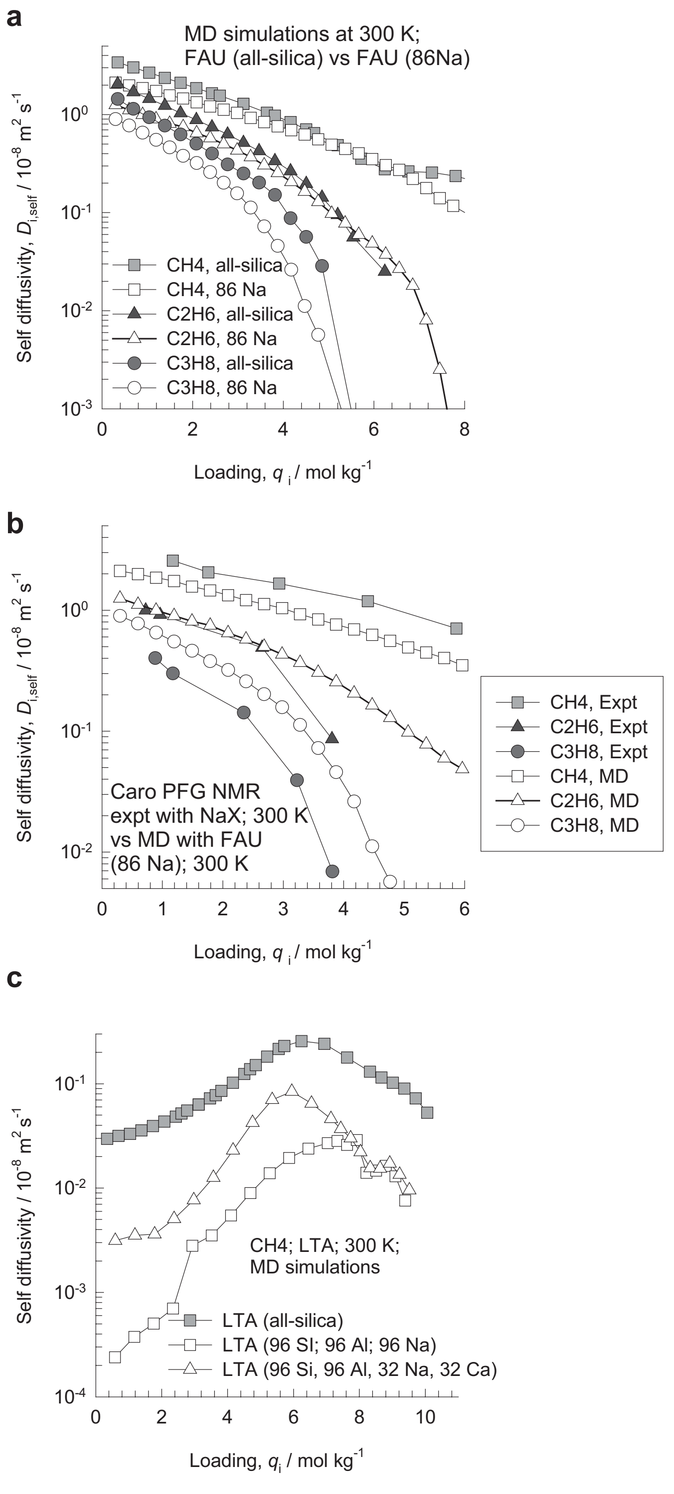

Figure 6. (a) Comparison of $D_{i,self}$ of methane, ethane and propane in FAU (all-silica) with FAU (106 Si, 84 Al, 86 Na^+) at 300 K. (b) Comparison of PFG NMR measurement data of Caro et al. [4] for $D_{i,self}$ of methane, ethane and propane in FAU (NaX) at 300 K with MD simulations for FAU (106 Si, 86 Al, 86 Na^+) at 300 K. (c) Comparison of MD simulations for CH_4 in LTA (all-silica) with LTA (96 Si, 96 Al, 96 Na^+) and LTA (96 Si, 96 Al, 32 Na^+, 32 Ca^{++}) at 300 K.

sharper. The $D_{i,self}$ for the situation with 32 Na^+, and 32 Ca^{++} lies intermediate between the all-silica and the 96 Na^+ case, indicating that the hindrance effect increases with the number of cations present. In general, it is much more difficult to obtain good quantitative agreement for simulated diffusivities with experimental results for LTA because the obtained values are very sensitive to the choice of force field.

5 Conclusions

MD simulations of the $D_{i,self}$ of all seven different molecules (CH_4, N_2, Kr, C_2H_6, C_3H_8, Ar, and Ne) in six different all-silica zeolite structures (MFI, AFI, FAU, CHA, DDR, and LTA) were performed. The following major conclusions can be drawn from the data.

- The $D_{i,self}$ in all zeolite structures is generally a strong function of loading q_i, and usually, but not always, exhibits a decreasing trend with increased q_i.
- The $D_{i,self}$ of any molecule in the large and medium pore-size zeolites, AFI, FAU, and MFI, invariably exhibits a monotonic decrease with increased q_i. These MD results are in line with the experimental data for Caro et al. [4] for CH_4, C_2H_6, and C_3H_8 in FAU (NaX) and MFI zeolites.
- For zeolite structures such as LTA, CHA, and DDR that consist of cages separated by narrow windows, the $D_{i,self}$ of strongly confined molecules (such as Ar, N_2, CH_4, Kr, C_2H_6, and C_3H_8) increases sharply with loading before decreasing as saturation is approached. The stronger the confinement, the sharper the increase in $D_{i,self}$. The MD simulations rationalize the experimental data of Cao et al. [3] for N_2, CH_4, and Kr in LTA-4A.
- The presence of cations reduces the $D_{i,self}$ for methane, ethane and propane in FAU to a small extent, but does not significantly alter the loading dependence in a qualitative sense. The presence of cations leads to a much more pronounced reduction in the $D_{i,self}$ for methane in LTA.

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Symbols Used

c_i	kmol m^{-3}	molar loading of species *i* based on pore volume
$D_{i,self}$	m^2 s^{-1}	self-diffusivity
q_i	mol kg^{-1}	molar loading of species *i*
V_p	m^3 kg^{-1}	pore volume

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