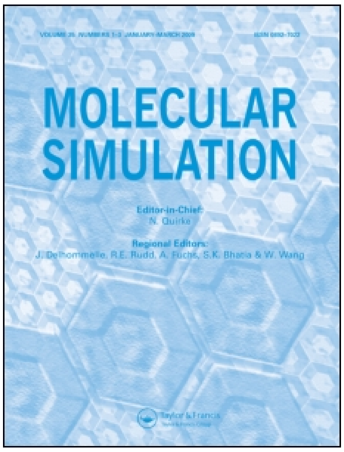

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Self-diffusion of *n*-alkanes in MFI type Zeolite using Molecular Dynamics Simulations with an Anisotropic United Atom (AUA) Forcefield

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We have investigated the effect of different guest–host forcefields, an united atoms and an anisotropic united atoms forcefields, on the self-diffusion of *n*-alkanes in MFI zeolite. The trend of the self-diffusion factor at infinite dilution is slightly affected by the choice of the forcefield: a small increase of the self-diffusion factor versus alkane chain length is observed with the UA forcefield between *n*-hexane and *n*-octane, whereas a decrease is observed with the AUA forcefield. We also investigated the effect of extraframework cations on diffusivities by introducing atomic defects that act as "obstacles" to molecular diffusion. A better quantitative agreement with self-diffusion data from QENS experiments is then observed, although the steep decrease of the diffusivity experimentally observed between *n*-hexane and *n*-octane is not reproduced.

Keywords: Self-diffusion; Zeolite; Alkanes; Anisotropic united atoms

INTRODUCTION

Zeolites and other open framework inorganic materials are gaining increasing importance in industrial applications such as molecular sieving and catalysis. A crucial role is played in these processes by adsorption and transport of the guest molecules. During the last decade, molecular simulation (Molecular Dynamics, MD or Monte Carlo, MC) has become a powerful tool to investigate equilibrium and transport properties at an atomistic length and timescale [1]. While molecular simulations of equilibrium adsorption have reached a state where the predicted quantities (adsorption isotherms, isosteric heats) are in reasonable agreement with experiments for all but the most complex guest–host systems [2], this is still not the case for transport properties [3]. The case of alkane diffusion in silicalite is a very interesting one. Jobic [4] has reported diffusivity measurements (by QENS) of alkane molecules in ZSM-5 (MFI type zeolite). While the QENS data are comparable to MD results obtained for short alkanes (up to C_6) in purely siliceous silicalite-1, a large discrepancy is observed for longer alkanes [5]. The experimental diffusivities steeply decrease with the alkane length. A step is observed between C_6 and C_8 accompanied by a decrease of an order of magnitude in diffusivity and a weak loading dependence. This very large discrepancy was tentatively attributed by Jobic [4] to the use of rigid frameworks in the simulations, and to the use of the united atom (UA) potential scheme.

Previously [6], we investigated in detail the effect of zeolite flexibility on tracer diffusion of methane, *n*-butane, *n*-hexane and *n*-octane. We have shown that the effect of framework flexibility depends on the sorbate length and loading. Diffusion was enhanced in flexible frameworks only for the shortest alkanes, namely methane and *n*-butane and at low loadings. At low loadings, the enhancement of diffusion was caused by a weak modification of sorbate–zeolite potential energy surface. Therefore, a flexible framework seems to be required for quantitative studies of self-diffusion of small molecules at low loading. At high loadings, diffusion was mostly controlled by sorbate–sorbate interactions and the sorbate–zeolite interaction modifications caused by flexibility became negligible. The dependence of the self-diffusion with alkane length remained unchanged compared to rigid

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framework simulations. The self-diffusion coefficient smoothly decreased from methane to *n*-hexane in reasonable agreement with QENS data. For longer alkanes (above C_7) the MD results did not reproduce the experimentally observed steep decrease of diffusivity. In this work, we use a different forcefield, namely the anisotropic united atom (AUA) intermolecular potential developed in a previous work on adsorption of hydrocarbons in zeolites, in order to test the above mentioned hypothesis of a forcefield dependence of the alkane diffusivity in MFI zeolite. In a second part of this work, we also investigate the effect of extraframework cations on diffusivities. All previously published MD results use a purely siliceous model of MFI (corresponding to silicalite-1). As the experiments have been performed on a ZSM-5 sample with $Si/Al = 35$, one may wonder whether or not this makes any difference in the alkane diffusivity behaviour.

MODELS AND METHODS

MD simulation is used to compute diffusivity of several *n*-alkane molecules in MFI zeolite. We used a rigid framework and took the atomic coordinates of the orthorhombic structure from Olson and coworkers [7]. MD algorithms and tools are fully detailed in our previous paper [6].

The AUA model was used to describe the adsorbate molecules [8,9]. Intramolecular interactions include bond-bending and torsion potentials as well as non-bonded interactions described by a Lennard–Jones (LJ) 6–12 potential. More details on the intramolecular potential parameter values are given in a previous work [10]. Guest–guest intermolecular interactions are calculated by a LJ potential, the parameters of which are taken from Ungerer and coworkers [10].

The guest–host potential is of the "Kiselev type" [2,11]. It contains a single effective LJ term that acts between the oxygen atoms of the framework and each of the AUA of the guest molecules. The zeolite oxygen atom parameters obtained from a previous fit of *n*-butane adsorption data in silicalite-1 [12] are equal to $\sigma_O = 3.00\,\text{Å}$ and $\varepsilon_O = 93.53\,\text{K}$. The hydrocarbon–zeolite cross interaction parameters were determined from Lorentz–Berthelot combining rules. No further readjustment of the potential parameters was undertaken in this study.

In the second part of this study, we have built a model of ZSM-5 MFI, in which extraframework cations were present in the system, due to the finite value of the Si/Al ratio. According to Beerdsen *et al.* [13], we assumed that the preferred location of aluminium atoms in ZSM-5, which determines cations location, is in site T12. Therefore, our model consists of placing "atomic defects" in the straight channels of MFI, near the intersections with zig-zag channels, as depicted in Fig. 1.

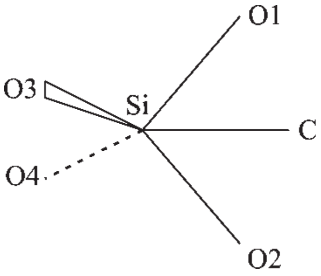

FIGURE 1 Positioning of the "pseudo-cations". The Si atom is located at position T12. Oxygen atoms are labelled O1–O4 and pseudo-cation is designed by C. O1 and O2 atoms are in the straight channel. Cation is in the plane (O1,Si,O2), on the bisector of the angle O1–Si–O2 at a distance of 1.605 Å of Si.

Because of the non-polar nature of *n*-alkane molecules, we believe that the electrostatic part of the host–guest interaction energy need not be taken into account to start with. We, thus, simply modelled the cations as fixed neutral atoms and used, for simplicity reasons, the size and energy parameters of the oxygen atom. In this crude model, we have thus introduced atomic defects that act as "obstacles" to molecular diffusion. A detailed description of the energetics of the actual cations found in a ZSM-5 framework are not taken into account for the time being. The number of atomic defects introduced in the system is of 2 atoms per unit cell, corresponding to an equivalent Si/Al ratio of 47. This should be compared with $Si/Al = 35$ of the experimental samples [4].

RESULTS AND DISCUSSION

Diffusion Coefficients: Forcefield Effect

We report in Fig. 2 the computed diffusion coefficients for *n*-alkanes ($n = 4$, 6, 8 and 10) at zero

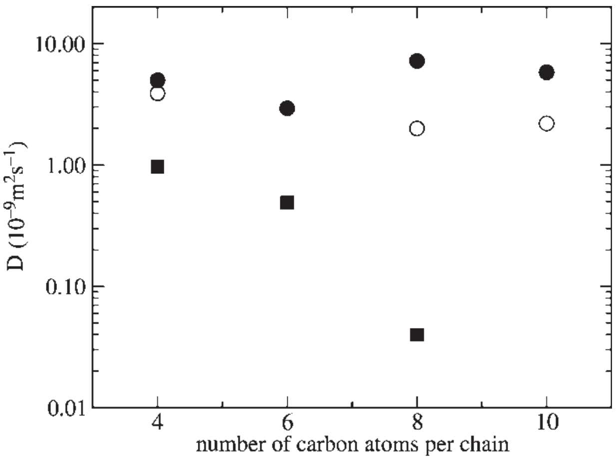

FIGURE 2 Self-diffusion of *n*-alkanes in silicalite-1 in $10^{-9}\,m^2\,s^{-1}$ obtained from MD simulations using different forcefields: UA (full circles) and AUA (open circles). MD data are compared with experimental results (full squares) from QENS [4].

TABLE I Self-diffusion coefficients of *n*-alkanes in silicalite-1

Adsorbat	*Force field*	D_x	D_y	D_z	D
n-C_4H_{10}	UA	2.2 ± 0.2	12.2 ± 2.0	0.61 ± 0.08	5.0 ± 0.8
	AUA	2.1 ± 0.3	8.9 ± 0.6	0.61 ± 0.09	3.9 ± 0.3
n-C_8H_{18}	UA	0.35 ± 0.07	19.15 ± 1.67	0.090 ± 0.039	6.53 ± 0.6
	AUA	0.34 ± 0.06	5.56 ± 1.20	0.104 ± 0.008	2.0 ± 0.4
n-$C_{10}H_{22}$	UA	0.057 ± 0.02	15.6 ± 0.6	0.047 ± 0.030	5.2 ± 0.2
	AUA	0.20 ± 0.04	6.37 ± 1.67	0.037 ± 0.013	2.2 ± 0.6

Comparison between UA and AUA molecular dynamics data from C_4 to C_{10}.

coverage (i.e. one molecule in the simulation box of 2 × 2 × 2 unit cell) and compare these results with the experimental QENS values of Jobic [4]. The use of the AUA forcefield clearly leads to a systematic decrease of the diffusion coefficient, as compared with the previously published UA results [6]. Interestingly enough this effect is somewhat larger for the larger alkanes. This leads to a better agreement between MD simulations and experiments, although there are still some discrepancies. The stepwise decrease of diffusivity for *n*-octane is still not reproduced.

We report in Table I the self-diffusion data along the different space directions, from C_4 to C_{10} at zero coverage obtained with UA and AUA forcefields. Whatever the forcefield used, diffusion occurs preferentially along the y direction (straight channels), then along the x direction (zig-zag channels) and finally along the z direction. The ratio of the self-diffusion components D_y/D_x increases with increasing chain length, indicating that diffusion along the y direction becomes the dominant mode when chain length increases. As can be seen in Table I, an important effect of the AUA forcefield relative to the UA forcefield is to decrease the self diffusion along the y channel, D_y. The decrease of D_y is more pronounced for long chains. This effect, combined with the fact that D_y/D_x increases with increasing chain length, leads to a larger decrease of the self-diffusion coefficient with longer alkanes.

We report in Fig. 3 the torsion angle distributions for C_4 and C_8 molecules. A torsion angle of zero degree corresponds to a *trans* conformation. Clearly, the change of the guest–host interactions modifies the internal conformation of the chains. When chain length increases, the torsion angle distribution exhibits more *cis* conformations with AUA (20% C_8 are in *cis* conformation) than with UA forcefield. In C_8, we observed 20% torsion angles in *cis* conformation with AUA forcefield and 12% with the UA forcefield. This may explain the change in diffusion, although a more thorough study would be necessary to conclude.

Diffusion Coefficients: Pseudo-cations Effect

We report in Fig. 4 the computed diffusion coefficients for *n*-alkanes ($n = 4$, 6 and 8), with and without the "pseudo-cations" introduced in the system to model the finite value of Si/Al ratio in the experiments. The corresponding values (together with the x, y and z components of D) are given in Table II. The existence of pseudo-cations clearly has the effect of decreasing the diffusion coefficient with respect to the defect-free system. The decrease in D is slightly larger for C_8 (56%)

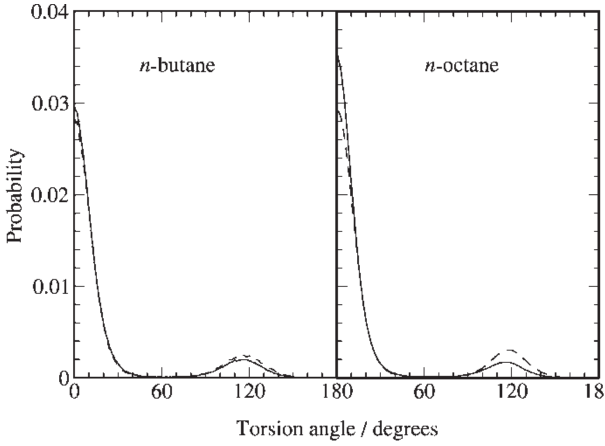

FIGURE 3 Torsion angle distribution in *n*-butane and *n*-octane with different forcefields: UA (full line) and AUA (dashed line).

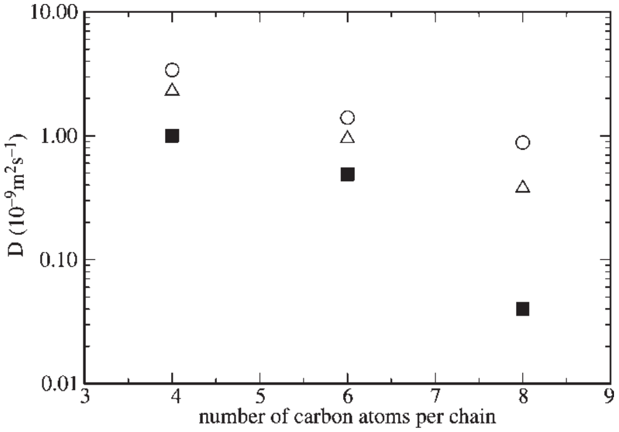

FIGURE 4 Self-diffusion of *n*-alkanes in silicalite-1 in $10^{-9}\,m^2\,s^{-1}$ computed with (triangle) and without (circle) pseudo-cations, from C_4 to C_8. MD data are compared with experimental results from QENS [4].

TABLE II Self-diffusion coefficients of *n*-alkanes in silicalite-1 computed with and without pseudo-cations, from C_4 to C_8

Adsorbat (loading)	*Defect*	D_x	D_y	D_z	D
n-C_4H_{10} (2/uc)	N	1.7 ± 0.4	7.9 ± 1.7	0.54 ± 0.08	3.4 ± 0.7
	Y	1.81 ± 0.3	4.63 ± 0.7	0.39 ± 0.05	2.3 ± 0.4
n-C_6H_{14} (2/uc)	N	0.48 ± 0.07	3.5 ± 0.4	0.12 ± 0.01	1.4 ± 0.2
	Y	0.37 ± 0.06	2.41 ± 0.3	0.08 ± 0.01	0.95 ± 0.2
n-C_8H_{18} (2.25/uc)	N	0.08 ± 0.06	2.5 ± 1.4	0.034 ± 0.018	0.88 ± 0.5
	Y	0.08 ± 0.04	1.03 ± 0.7	0.017 ± 0.01	0.38 ± 0.3

than for C_4 and C_6 (roughly 30% for both alkanes). Thus, introducing such defects in the framework reduces the discrepancy between MD and experiments, without explaining the steep drop in D for *n*-octane.

From data in Table II, it can be seen that the self-diffusion along the zig-zag channels, D_x, is almost unchanged. The net effect of the presence of pseudo-cations is to reduce diffusion in the y direction. Because the total self-diffusion coefficient is mostly controlled by the y component D_y when chain length increases, one may expect a more pronounced effect of the pseudo-cations with longer alkanes.

CONCLUSION

We have shown that a better quantitative agreement between MD simulation of diffusion coefficients and QENS experiments can be observed for short alkanes (C_n, $n \leq 6$) with the use of an AUA forcefield and a model in which the presence of extraframework cations is taken into account. The steep decrease of the self-diffusion coefficient between C_6 and C_8 is still not reproduced in the simulations.

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