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### Adsorption and diffusion in zeolites: the pitfall of isotopic crystal structures

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## Adsorption and diffusion in zeolites: the pitfall of isotypic crystal structures

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The influence of isotypic crystal structures on adsorption and diffusion of methane in all-silica LTA, SAS and ITE zeolites is studied. Results obtained with the experimental structures are compared with structure predictions and approximations that are commonly employed. The results indicate that diffusion coefficients are much more affected than Henry coefficients. In fact, orders of magnitude deviations in the diffusivity can be observed and a systematic parameter study finally gives rise to the correlation between structure sensitivity and diffusion-window size.

**Keywords:** Monte Carlo simulations; zeolite isotypes; adsorption; diffusion; methane

Molecular simulations have become an important tool to study and predict the properties of adsorbed molecules in zeolites. The crystal structure, beside the force field [1], represents an important input to the simulations. All-silica zeolites are investigated most often. Crystallographic studies on the true siliceous structure provide the atoms' positions in the unit cell (procedure *i*). If experimental data are yet not available, two principle routes exist for obtaining the input structure. Either the database of the International Zeolite Association (IZA) can be accessed which, for every framework type, offers a prediction of the siliceous material on the basis of theoretical considerations (procedure *ii*). Or a synthesised structure which is not purely siliceous can be converted by, for example, substituting the aluminium atoms of an aluminosilicate by silicon atoms (procedure *iii*). Each of these procedures gives small structural differences for the same framework type. In this context, it is interesting that a PFG NMR study by Hedin et al. [2] has indicated that the self-diffusion coefficient of propylene in different LTA-type zeolites is quite sensitive to compositional and structural differences. To investigate the influence of these structural differences, we have performed Monte Carlo simulations of methane in different zeolite structures of the same framework type – following procedures *i*, *ii* and *iii* – in order to assess the influence of these structure variations on the thermodynamics and mass transport of guest molecules.

Henry coefficients,  $K_{\text{H}}$ , and self-diffusion coefficients at zero loading,  $D$ , are calculated for methane, modelled as a united atom [3], in siliceous structures of the frameworks LTA, SAS and ITE (300 K). Apart from the IZA structures

[4], the zeolites investigated here include the all-silica materials, as experimentally determined by Corma et al. (LTA), Wragg et al. (SAS) and Cambor et al. (ITE) [5–7], as well as an aluminosilicate (LTA by Pluth and Smith) and a magnesioaluminophosphate (SAS by Patinec et al.) [8,9]. The latter two are converted to purely siliceous structures according to procedure *iii* as mentioned above. Note that a detailed description of the methodology is found in the Supplementary Material.

The chosen framework types belong to the group of cage-type zeolites [10]. Their pore structure includes wide regions (cages) and very narrow regions (windows) which, together, form large entropic diffusion barriers to methane molecules. The windows are in fact so small that a methane molecule just fits into them (kinetic diameter of a methane bead:  $\sigma_{\text{CH}_4}^{\text{LJ}} = 3.72 \text{ \AA}$ ; diameter of the windows, determined as the largest hard sphere that fits [11]:  $d \approx 4 \text{ \AA}$ , compare Table 1). It is important to mention that, in our simulations, we use a rigid zeolite model. Including flexibility may quantitatively change our results, in particular for the here studied cage-type zeolites. More details on the effects of zeolite flexibility can be found in Ref. [12].

The influence of the crystal structure on the adsorption properties is moderate, see Table 1. Henry coefficients differ between –32% (LTA Pluth and Smith) and +23% (ITE Cambor et al.) from the corresponding  $K_{\text{H, IZA}}$  of a given framework type. A larger Henry coefficient can, obviously, be correlated with a smaller unit cell and thus cage because the average potential in the zeolite cage becomes denser but more attractive in consequence

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Table 1. Henry coefficients and self-diffusivities at zero loading (methane, 300 K).

Crystal structure	$a^a \times b^a \times c^a$	$d^a$	$K_H^b$	$D^c$
LTA				
IZA <sup>d</sup> [4]	$11.919 \times 11.919 \times 11.919$	4.14	4.18	$78.08_{4.30}$
Corma et al. <sup>d</sup> [5]	$11.867 \times 11.867 \times 11.867$	4.00	4.45	$27.39_{1.60}$
Pluth and Smith <sup>d</sup> [8]	$24.555 \times 24.555 \times 24.555$	4.00	2.85	$112.91_{4.05}$
SAS				
IZA [4]	$14.349 \times 14.349 \times 10.398$	4.21	6.87	$118.06_{5.70}$
Wragg et al. [6]	$14.104 \times 14.104 \times 10.188$	4.02	9.29	$7.72_{0.83}$
Patíneck et al. [9]	$14.322 \times 14.322 \times 10.424$	4.16	6.94	$160.84_{12.23}$
ITE				
IZA [4]	$20.753 \times 9.804 \times 20.009$	4.15	56.75	$155.72_{0.89}$
Camblor et al. [7]	$20.622 \times 9.724 \times 19.623$	3.79	69.99	$0.97_{0.09}$

<sup>a</sup>  $10^{-10}$  m. <sup>b</sup>  $10^{-3}$  mol Pa<sup>-1</sup> m<sup>-3</sup>. <sup>c</sup>  $10^{-12}$  m<sup>2</sup> s<sup>-1</sup> (errors as subscripts). <sup>d</sup> The unit cell of the 4A zeolite by Pluth and Smith accommodates  $2 \times 2 \times 2$  cages, whereas the structures by the IZA and by Corma et al. each accommodate a single cage.

of decreasing cage size, compare Figure 1. Clark and Snurr [13] as well as Castillo et al. [14] have shown that the crystal structure (silicalite) can strongly influence benzene as well as water adsorption because of the importance of electrostatic guest–host interactions. However, Castillo et al. [14] also showed that propane adsorption in silicalite is not influenced by the crystal structure. To sum up, it might thus be concluded that the sensitivity of adsorption to structure variations is weak, as long as relatively small non-polar molecules are considered.

The impact of structure variations on the diffusivity is much stronger than on adsorption. In particular, the differences between the diffusion coefficients obtained with the IZA structures and the ‘true’ all-silica crystals are large; the latter ones are smaller by factors of 2.9, 15.3 and 161 for LTA, SAS and ITE, respectively. Interestingly, an analysis of the free-energy and potential-energy profiles observed in different structures of the same framework type [ $-\Delta S/k_B = (\Delta F - \Delta U)/(k_B T)$ ] hardly vary. Significant changes manifest only for the potential-energy barriers.

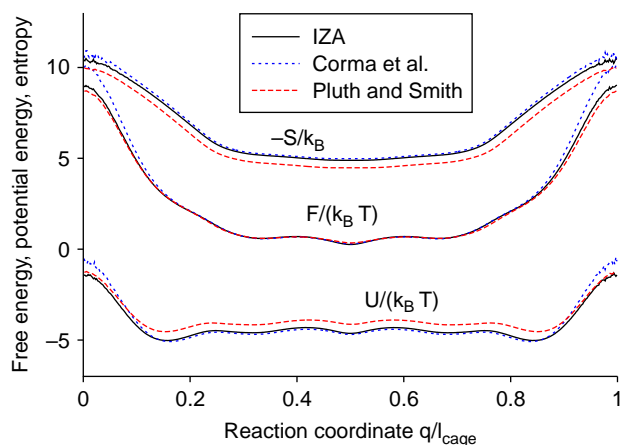


Figure 1. Free-energy, potential-energy and entropy profile of methane diffusing in different LTA structures.

In order to better understand the structure sensitivity of the guest diffusivity, a parameter study, using the LTA zeolites, is conducted in which either the unit-cell parameters,  $a = b = c = L_{UC}$ , are scaled proportionately or the Lennard-Jones size parameter of the guest–host interaction,  $\sigma_{O-CH_4}^{LJ}$ , is changed. From the results (Figure 2), it can be concluded that enlarging the window area by increasing the unit-cell size by a given fraction (filled symbols) has *precisely* the same effect on the diffusion coefficient as reducing the Lennard-Jones parameter by the same fraction (open symbols, for a given structure and thus symbol type, lie on the same trend line as the filled ones). Furthermore, the diffusivity is extremely sensitive to only small window-area changes because an enlargement of  $\approx 4\%$  can result in an order of magnitude larger diffusion coefficient. Most importantly, however, the differences between diffusion coefficients obtained in different structures decrease with an increasing window size. In other words, the structure sensitivity becomes the more prominent, the tighter the guest molecule fits into the window and the sensitivity will very likely be observed for any cage-type zeolite into which non-polar guest molecules diffuse.

The occurrence of window-area differences between different structures of the same topology type stems partially from different unit-cell sizes, as the (almost) parallel trends of  $D$  over  $L_{cage}^2$  in the inset of Figure 2 suggest. On top of this ‘scaling effect’, differences in individual crystal atom positions can lead to large differences between diffusivities. This is indicated by the discrepancies between diffusivities obtained with the 4A structure by Pluth and Smith [8] and the other two LTA structures. The 4A structure exhibits much larger differences in atom positions from the IZA structure than the siliceous structure by Corma et al. [5] does (see Supplementary Material). Note that, in the Supplementary Material, we also show that (a) the structure sensitivity effects also occur at finite loadings and that (b) recrossing

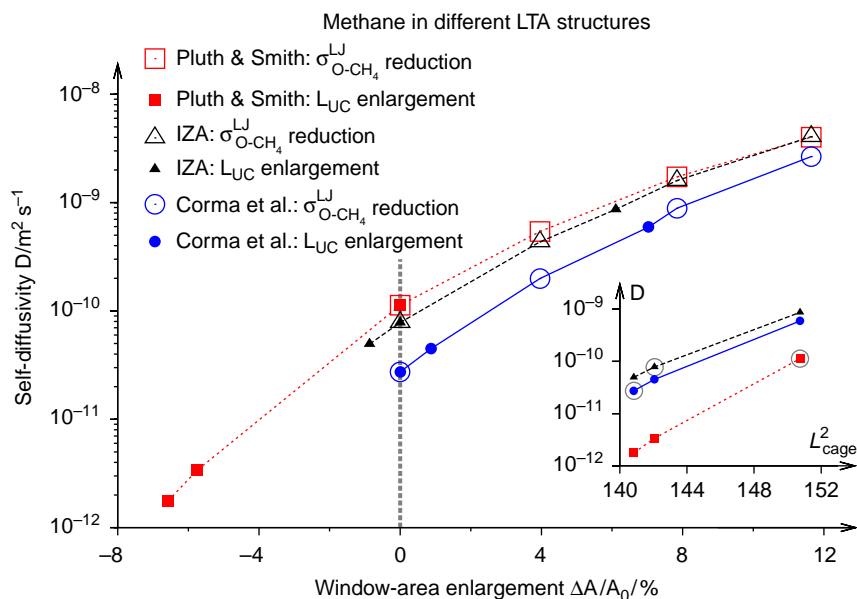


Figure 2. Self-diffusion coefficient,  $D$ , of methane in different LTA structures for varying relative window-area enlargement,  $\Delta A/A_0$ , where  $A_0$  denotes the window area for the original structure ( $L_{\text{UC},0}$ ) and original Lennard-Jones parameter ( $\sigma_{\text{O-CH}_4,0}^{\text{LJ}}$ ); thus,  $\Delta A/A_0 = [(L_{\text{UC}})^2 - (L_{\text{UC},0})^2]/(L_{\text{UC},0})^2$  for unit-cell enlargement and  $\Delta A/A_0 = -\left[\left(\sigma_{\text{O-CH}_4}^{\text{LJ}}\right)^2 - \left(\sigma_{\text{O-CH}_4,0}^{\text{LJ}}\right)^2\right]/\left(\sigma_{\text{O-CH}_4,0}^{\text{LJ}}\right)^2$  for interaction parameter reduction. The errors in  $D$  are, at the maximum, in the range of the largest symbol size. The inset shows the variation of  $D$  with the squared cage length,  $L_{\text{cage}}^2$ ; the large open circles indicate results obtained with the original structures.

rates (transmission coefficients) are not affected by the here probed structure variations.

In summary, we have investigated the influence of the crystal structure on adsorption and diffusion of methane in cage-type zeolites. In contrast to the Henry coefficient, the self-diffusion coefficient can, in fact, be extremely sensitive to very small structural differences supporting experimental observations [2]. At this point, it is important to stress that results for exactly the same zeolite framework type are being compared. We have certainly underestimated these subtleties in the past and, as there is no standard procedure to create all-silica structures when experimental data are still lacking, we suggest to include the actual crystal structure files used in simulation studies, for example in the Supplementary Material.

### Supplementary Online Material

Supplementary material associated with this note can be found, free of charge, in the online version.

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