

## Commensurate diffusion effects of n-heptane in silicalite-1

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Step isotherms in silicalite-1 have been evidenced experimentally for many adsorbates. To understand the origin of these phenomena, molecular simulations as molecular dynamics (MD) and mainly Monte Carlo (MC), were performed on these systems. Depending on the specificities of the adsorbates, different explanations were proposed. For atomic species like argon atoms adsorbed at low temperatures (200 K), it was shown that the step was the result of a condensation effect within the zeolite pores. On the contrary, for chain molecules like n-heptane and n-hexane the step was attributed to commensurate effects, the characteristic length of the channel being of the same size of the chain molecules. In a recent article [1] we presented the study of the n-heptane adsorption in silicalite-1 at 300 K using MD. As expected, we obtained a step at 4 molecules per unit cell. Contrary to what was generally admitted we showed that the step was not the consequence of a commensurate freezing but of a commensurate locking of molecules trapped in sinusoidal channels. This result is particularly meaningful for the understanding of the diffusion phenomenon within the pores.

In a previous article Jobic et al. [2] reported self-diffusion coefficients,  $D$ , of n-heptane obtained from quasi-elastic neutron scattering and from MD simulations. They observed at the step, a strong inflection in the MD results while such an effect is not evident for QENS data. In agreement with these authors, we observed by MD that  $D$  is increasing after the step. We observed that this effect is mainly due to the contribution of the  $y$  component of  $D$ , where the  $y$  direction is orientated along the straight channel. The mean square displacements (MSD) in the  $y$  direction are plotted for different loadings on Figure 1. After the ballistic regime that lasts about 5 ps, the profile at low loading shows a linear dependence on time,  $t$ , typical of the diffusional regime. At higher loadings there is

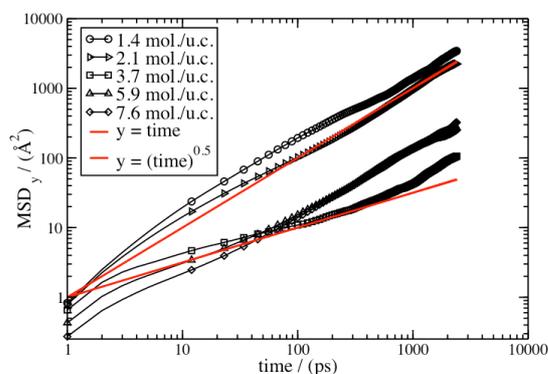


Figure 1: The mean square displacement as a function of the time ( $t$ ) in a logarithmic scale for different loadings.

an intermediate regime close to a dependence on  $t^{0.5}$ , characteristic of single file diffusion. This regime lasts much longer time as the system goes closer to the step zone (about 800 ps at 3.7 mol./u.c.). This can be considered as a characteristic of this step zone. For higher loadings the dependence in  $t^{0.5}$  is much shorter. By analyzing the conformation and the intramolecular potential energy of the heptane molecule, we attributed the single file diffusion regime and the increase of  $D$  after the step to a commensurate locking. N-heptane molecules are compressed within the sinusoidal channels and the other molecules are able to move freely within the straight channels. The picture is different before the step when molecules are not compressed. These results are a good example of the strong consequences of the commensurate effects on the diffusion process inside structured materials.

### References

- [1] Floquet, N.; Simon, J.-M.; Coulomb, J.-P.; Bellat, J.-P.; Weber, G.; Andre, G. *Microporous Mesoporous Materials* 122 (2009) 61.
- [2] Jobic, H.; Laloué, N; Laroche, C.; van Baten, J.M.; Krishna, R. *J. Phys. Chem. B* 110 (2006) 2195.