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# Transport Barriers as Triggered by the Idealized Microscopic Crystal Surface and the Role of the Evaluation Protocol of Diffusion Experiments

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## 1. Introduction

Diffusion of gas molecules in nanoporous materials such as zeolites and metal-organic frameworks (MOFs) has a long research history [1]. However, many related phenomena still remain poorly understood. For example, the questions weather or not special transport barriers exist in the boundary layer of such crystals (surface barriers) and, if so, what these barriers depend on are controversial items. Interference microscopy and infrared microscopy experiments [1] as well as molecular simulations [2] provide evidence to the existence of such genuine barriers at the crystal surface. Regarding the nature of such barriers, Hibbe *et al.* [3] have recently shown that, for various alkanes penetrating the MOF Zn(tbtip), blocked pore entrances together with crystal defects primarily lead to the formation of severe surface barriers. In this study, we aim to show by means of a combination of molecular modelling approach and tracer-exchange simulations that the atomistic structure of the zeolite boundary layer and thus the potential prevailing there causes similar surface barriers.

## 2. Methodology

Equilibrium molar fluxes were computed on the basis of molecular simulations. The reversible flux between two adjacent cages of the zeolite (AFI type) was computed as well as the fluxes in the boundary layer, i.e. between the last cage of the zeolte crystal and the adsorption layer located at the external surface (1st step) and the flux from the surface layer to the gas phase (2nd step), see Fig. 1. The fluxes served as an input for the tracer-exchange simulations to eventually yield mass uptake and release curves, $M(t)/M_\infty$. The uptake curves were evaluated using two different protocols: a popular though approximate one neglecting surface transport limitation (§4.3.2. in ref. [4] resulting in an $D_{\mathrm{S,eff}}$) and a more accurate method including a surface permeability (§4.3.6., ref. [4], $D_{\mathrm{S}}$). Finally, an approximate estimate of the severity of surface barriers was determined on basis of the fluxes: $L_{\mathrm{crit}} = l_{\mathrm{bound}} \cdot j_{\mathrm{zeo}} / j_{\mathrm{bound}}$ (1 step) [2].

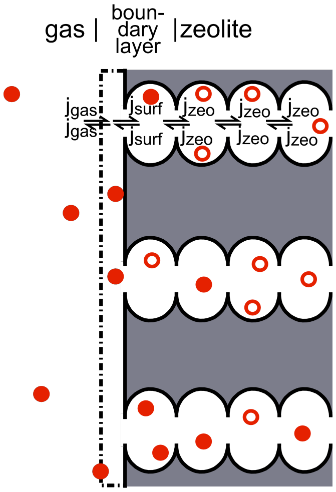

Fig. 1: Scheme of tracer exchange.

## 3. Results

Our results reveal typical convex concentration profiles similar to experiments [3] with a very slow approach of the $c_{\mathrm{surf}}$ saturation value. They are caused by lower boundary-layer fluxes in comparison to $j_{\mathrm{zeo}}$. This transport limitation (surface barriers) lead to smaller effective diffusion coefficients, see Fig. 2. However, $D_{\mathrm{S,eff}}$ approaches the true diffusivity ($D_{\mathrm{S}}$) as the crystal size increases. The tracer-exchange simulations including the 2nd adsorption step underline the importance of an accurate microscopic description of the entire boundary layer (Fig. 2). A tracer molecule can only be considered exchanged, if it has reached the gas phase from the surface layer, and, as evidenced by a slower increase of the 2-step $D_{\mathrm{S,eff}}$ *vs.* $L$, the surface barrier effect becomes the more important the more the microscopic nature of the crystal (or membrane) is taken into consideration.

At a crystal half-length of $L_{\mathrm{crit}}/2$, the deviation factor between the two diffusion coefficients is around 3. Regardless the magnitude and ratio of the fluxes, and thus irrespective the nature and pairing of guest molecules and host material as well as $T$ and $p$, the criterion always provides an estimate where the effective diffusion coefficient is 2 to 3 times smaller than the true one. It is important to stress that no other influence than the idealized (no silanol groups) crystal surface structure can cause the deviation of $D_{\mathrm{S,eff}}$ from $D_{\mathrm{S}}$ because we do not deal with nonidealities.

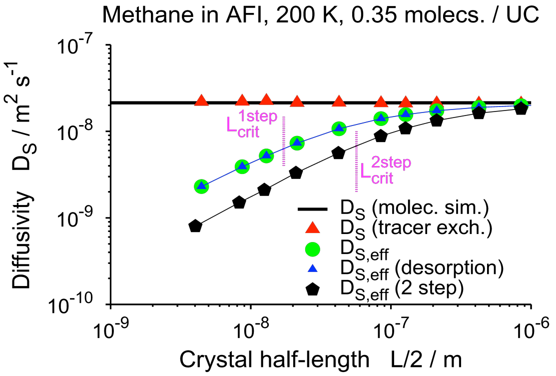

Fig. 2: Diffusivity, $D$, as functions of crystal half-width, $L/2$.

## 4. Conclusions

The 2-step simulation approach provides evidence to the existence of significant surface barriers and emphasizes the necessity of an accurate description of the boundary layer (2 step processes). The critical crystal length proves advantageous and reliable for assessing the limitation of more approximate evaluation protocols of diffusion experiments and simulations.

## References

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