

## Transport in the Transition Region Gas/Adsorbent Studied by Molecular Dynamics Simulations

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### 1. Introduction

Molecular transport through the external surface of an adsorbent differs from the diffusion in the bulk of the adsorbent material. The effect of the surface transport on the overall diffusive transport in nanoporous materials increases with the surface-to-volume ratio of the adsorbent. For applications, e.g., catalysis, it is desirable to have an estimate showing whether surface effects may be neglected or must be considered, and, to which extent they influence the overall transport. We study such boundary effects using molecular dynamics simulations of tracer exchange in zeolite membranes [1,2]. Zeolites are crystalline nanoporous materials with well-defined pore sizes. Beside normal diffusion (ND), one-dimensional zeolite channels exhibit anomalous single-file diffusion (SFD) of the molecules. Both cases are considered in this contribution. In analytical considerations, the parameters needed to quantify the magnitude of boundary effects have been related to further system parameters. These relations have been verified by the simulation results [2-4].

### 2. Tracer-exchange simulations

As model system we consider a zeolite membrane to study both, diffusion in the crystal and through the crystal surface. The membrane is in sorption equilibrium with the surrounding gas phase and the exchange of (labelled) particles initially in the membrane by (unlabelled) particles from the gas phase is observed. Simulations of single-file diffusion have been carried out with a spherical model of neo-pentane in an analytical potential function describing the potential energy landscape of neo-pentane in the zeolite-like material  $\text{AlPO}_4\text{-5}$ . Simulations of normal diffusion were performed in the same potential landscape but with much smaller size of the diffusing particles allowing them to pass one another in the channels.

### 3. Results

From the tracer-exchange simulation one obtains concentration profiles of the exchanged particles. Typical examples are shown in Fig. 1. These profiles are fitted to the solutions of Fick's second law using appropriate boundary conditions. Beside the diffusion coefficient, additional parameters are needed to describe these concentration profiles correctly. In the case of SFD (Fig. 1 top), the inner part of the profile may be described by the analytical solution, but the range where this solution is valid is reduced

to a length  $L^* < L$ , where  $L$  is the thickness of the membrane. At the boundaries, equilibrium is reached faster compared to the inner part. This indicates a higher mobility of the molecules close to the boundaries. The length of this region is given by the parameter

$$l = (L - L^*) \lambda / 2 \quad (1)$$

where  $\lambda$  is the distance between adsorption sites in the channel.

On the other hand, for normal diffusion, it can be seen in Fig. 1 (bottom) that sorption equilibrium at the boundaries is reached slowly. This behaviour can be described with the boundary condition [5]

$$J(t) = \alpha(C_0 - C(t)), \quad (2)$$

where  $J(t)$  is the flux density through the zeolite surface at time  $t$ ,  $C_0$  the concentration needed to maintain equilibrium with the surrounding gas phase,  $C(t)$  the concentration at time  $t$ , and  $\alpha$  is a constant of proportionality.

From analytical considerations we obtained [3]

$$l^2 = 2L \lambda^2 (1 - \theta)^2 \theta, \quad (3)$$

where  $\theta$  is the fractional site occupancy, and [2]

$$\alpha = (D/\lambda) \exp(-\beta\Delta E), \quad (4)$$

where  $D$  is the self-diffusion coefficient and  $\Delta E$  is an energy difference occurring at the crystal boundaries, which can be obtained from force field calculations.

#### 4. Conclusions

Surface effects significantly influence the shape of the concentration profiles and, thus, the overall transport. The relative importance decreases with increasing system size. However, in applications like catalysis, where small crystals are employed, a significant effect is probable. With help of the relations Eqs. (3) and (4) presented here, the magnitude of these effects can be calculated.

#### References

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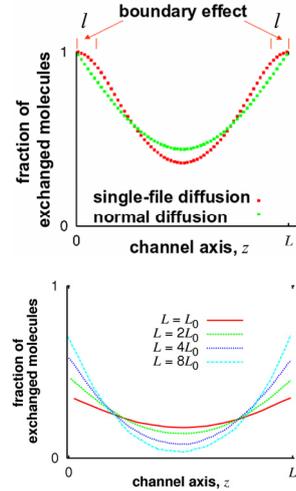


Figure. 1: Tracer-exchange concentration profiles. Top: SFD in comparison to ND with large value of  $\alpha$ , bottom ND, low value of  $\alpha$ .