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Transport into zeolite nanosheets: Diffusion equations put to test

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Ultrathin porous materials, such as zeolite nanosheets, are prominent candidates for performing catalysis, drug supply, and separation processes [1, 2] in a highly efficient manner due to exceptionally short transport paths. Predictive design of such processes requires the application of diffusion equations that were derived for macroscopic, homogeneous surroundings to nanoscale, nano-structured host systems. Because of the obvious dissonance between requirements and assumptions, we tested analytical solutions of Fick's diffusion equations for their applicability to methane transport into two different zeolite structures (Figure 1b) under instationary conditions. The two central questions were: Do the conventional diffusion equations break down at the nanoscale? And, what is the reason to the (possible) limitation of applicability?

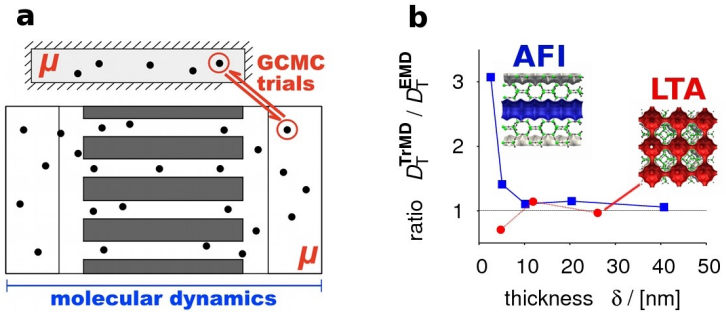

Figure 1: (a) Scheme of TrMD. (b) Deviation of TrMD transport diffusivities from EMD predictions.

Computationally demanding transient molecular dynamics (TrMD) simulations were performed, paralleling conditions of diffusion experiments with constant sorbate supply (Figure 1a). Transient concentration profiles from TrMD were fitted to standard analytical solutions of Fick's diffusion equations [3] to yield transport diffusivities, D_T, and surface permeabilities, α:

$$c(t,z)/c_\infty = 1 - \sum_i^\infty \{2L \exp[-\gamma_i^2 D_T t/(\delta/2)^2] \cos[\gamma_i z/(\delta/2)]/[(\gamma_i^2 + L^2 + L)\cos\gamma_i]\}, \qquad (1)$$

where δ denotes the sheet thickness, $L = (\delta/2)\alpha/D_T$ and γ_i the positive roots of $L = \gamma_i \tan\gamma_i$. The resulting transport diffusivities relative to equilibrium molecular dynamics (EMD) predictions highlight that TrMD data can significantly exceed EMD values at small nanosheet thicknesses (Figure 1b). This represents a size limitation to the applicability of Fick's laws because transport coefficients must not vary with primary geometric parameters. We observe the effect only for smooth pores (AFI); for cage-type zeolites (LTA), the effect is absent. Therefore, we conjecture that the molecular explanation is found in a memory effect. Entering molecules cannot equilibrate in the first cage, perform a cascade of jumps across several cages ("multijumps"), and, thus, violate random walk theory on the length scale of a single zeolite cage.

References

[1] J. Caro, M. Noack: *Zeolite membranes – Recent developments and progress*. Microporous Mesoporous Mater. **115**, 215–233 (2008)

[2] P.S. Wheatley, A.R. Butler, M.S. Crane, S. Fox, B. Xiao, A.G. Rossi, I.L. Megson, R.E. Morris: *NO-releasing zeolites and their antithrombotic properties*. J. Am. Chem. Soc. **28**, 502–509 (2006)

[3] J. Crank: *The mathematics of diffusion*. Oxford University Press, UK (1975)

[4] N.E.R. Zimmermann, T.J. Zabel, F.J. Keil: *Transport into nanosheets: Diffusion equations put to test*. J. Phys. Chem. C **117**, 7384–7390 (2013)