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The Probability that a Molecule Enters a Porous Crystal

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1. Introduction

What is the probability that a molecule on the surface of a porous zeolite crystal will be able to enter the intracrystalline space? This question is of importance for practically all applications of zeolites and is often connected with the term "surface barrier". The flux of particles from the gas phase arriving at the surface is reduced by this entering probability. Separation processes make use of the fact that too big molecules can not pass the narrow pores while a smaller species easily reaches the region of strong adsorption inside the crystal. When zeolites act as catalysts, a fast access of the reactants to the pores is crucial for the catalytic performance. It is desired to estimate the entering probability since it is an important parameter for industrial processes involving zeolites. This contribution presents an analytical formula to calculate the entering probability through the intracrystalline self-diffusion coefficient in the case of an ideal crystal surface [1].

2. Theory

The entering probability (sometimes named sticking probability) is defined as the ratio between the number N_{in} of entering and the number N_{enc} of molecules encoutering the surface of the porous crystal, hence

$$P_{enter} = \frac{N_{in}}{N_{enc}} . \qquad (1)$$

The number of molecules passing a barrier is proportional to the number of molecules available. The proportionality coefficients are transition rates, which can be calculated using transition-state theory (TST). As such, Eq. (1) may be transferred into a ratio of transition rates, respectively, as a ratio between configuration integrals in the transition states. The intracrystalline self-diffusion coefficient is given in terms of transition rates as

Figure 1: The potential energy landscape in the transition region gas-adsorbent.

$$D = k_D L^2 = L^2 k_{des} \exp(\Delta E / k_B T) \qquad (2)$$

Between the rate of desorption, k_{des}, and the rate of intracrystalline diffusional jumps, k_D, a Boltzmann factor with k_B being Boltzmann's constant and T the temperature, has to be considered, which takes into account for a change in the (free) energy in the pore region (see Fig. 1). The equilibrium constant, K, which is the ratio between the concentrations in the zeolite and the gas phase may be written also as the ratio between the configuration integrals in these regions.
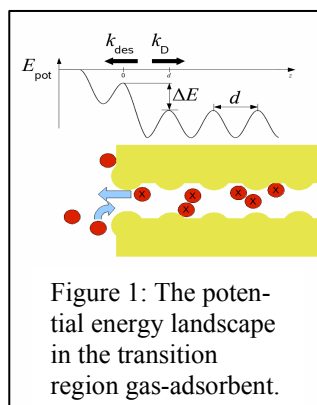
Using these relations, we may transform Eq. (1) into a relation which contains as variables the intracrystalline self-diffusion coefficient, D, the equilibrium constant, K, and the energy difference ΔE, so that we obtain

$$P_{\text{enter}} = \left(1 + \frac{L\sqrt{k_{\text{B}}T/2\pi m}}{KD\exp(-\Delta E/k_{\text{B}}T)}\right)^{-1}. \qquad (3)$$

3. Results from MD simulations

All quantities occuring in Eq. (3) can be obtained independently from the MD simulations. P_{enter} is calculated directly from the molecular trajectories using Eq. (1). ΔE is accessible in MD simulations from the potential energy landscape. In the considered case, ethane as diffusing molecule and zeolite Si-LTA as a host, ΔE was practically zero and had, thus, no influence on the result. However, in other cases a large influence may result due to the appearance of ΔE in the Boltzmann factor. Fig. 2 shows a comparison between the results obtained by Eq. (1) and Eq. (3) as a function of D. D and P_{enter} span over several orders of magnitude. In all cases, there is excellent agreement between both results.
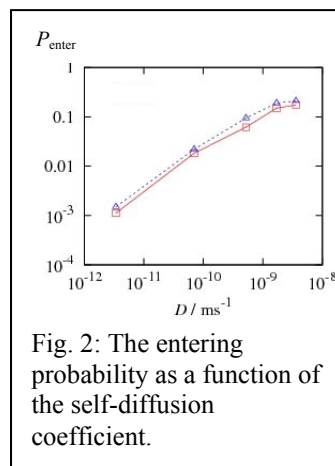
Fig. 2: The entering probability as a function of the self-diffusion coefficient.

4. Conclusions

The relation between the quantities given by Eq. (3) improves the understanding of surface barriers and sets it into relation to the resistance given by the intracrystalline diffusion. It helps to explain the reported low values of the entering probability of benzene on silicalite ($1.7 \cdot 10^{-6}$) [2] and the high values reported from MD simulations in Ref. [3]. In the latter case, the self-diffusion coefficient of the considered molecule (n-butane) was much larger. Additionally, real crystals have been considered in the experiment where additional effects due to blocked pores occur. The discrepancies between the results of Refs. [2] and [3] may thus be explained by 1. the difference in the diffusion coefficients, 2. the surface energy effect, and 3. the effects of pore blockage occuring for real crystals.

References
[1] A. Schüring, *J. Phys. Chem. C* 2007, in press.
[2] A. Jentys, H. Tanaka, J. A. Lercher, *J. Phys. Chem. B* 109 (2005), 2254.
[3] J.-M. Simon, J.-P. Bellat, S. Vasenkov, J. Kärger, *J. Phys. Chem. B* 109 (2005) 13523.