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Exploring the Extreme Transport Conditions through Membranes by Molecular Dynamics Simulations

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1. Introduction

One of the most striking problems in the study of the diffusion processes in microporous materials is the frequent discrepancy between the values of diffusivities measured by conventional uptake methods and microscopic methods (*e.g.* PFG-NMR) [1]. While the uptake experiments observe macroscopic properties of mass transport, the microscopic techniques monitor diffusion processes on displacement scales much smaller than the crystal size. Despite the importance of elucidating the causes of the mentioned differences, the influence of surface barriers on diffusion have been scarcely studied by both experimental and theoretical techniques. Depending on the relative values of permeability (multiplied by the width of the membrane) and diffusivity, two extreme transport conditions can be distinguished: diffusion-limited transport and desorption-limited transport [2] (Fig.1). In particular, the influence of the surface on the diffusion becomes critical in the case of relatively small zeolite membranes; in this condition, fluxes are controlled by the rates of desorption from the zeolites. It is very important to determine whether the system under study falls into the diffusion-limited transport or desorption-limited transport in order to ensure that the most important property is being studied. In practice, frequently, systems fall between the two extremes. It is the idea of this paper to present an extensive MD study of the molecular diffusion in membranes in the presence of surface barriers.

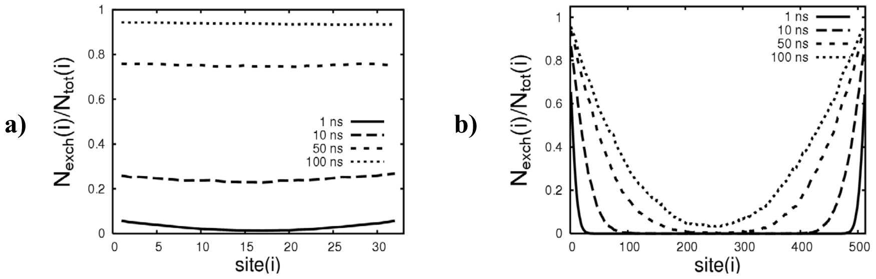

Fig.1. Concentration profiles (of exchanged particles) for the two extreme transport conditions, a) desorption-limited transport, b) diffusion-limited transport.

2. Results and Discussion

To study the evolution of the normal diffusion system under extreme transport conditions in a wide range of values, simulations were performed at loading (θ) = 0.25, 0.50, 0.75, and at three temperatures (T), 150, 200, 300 K. The exchanged particle profiles were obtained at five subsequent times (1, 10, 50, 100 ns). We considered different lengths of the channel, λ =1, 2, 4, 8, 16 (where $\lambda = L/L_0$ and L_0= 13.744 nm). The internal energy barriers between adsorption sites (spaced every 0.4242 nm) and the energy surface barriers were kept constant. At the same T and θ, only the length of the channel can affect the transport conditions in the system. For λ = 1 and at all temperatures, the profiles are very flat indicating a homogenous concentration of molecules independent of the position inside the channel. At T= 150 K and λ= 1 (in the limit of a very thin membrane), the influence of the surface barrier is critical and the desorption in the marginal sites is the determinant factor on the diffusion. When λ is increased, the profiles tend to the classical shape for a normal diffusion regime. According to the relative value of the permeability multiplied by the length of the channel ($\alpha_{\mathrm{Fick}}\ L$) and the diffusion coefficient (D_{Fick}), three diffusional regions can be distinguished (Fig. 2). In region I ($\alpha_{\mathrm{Fick}}\ L \ll D_{\mathrm{Fick}}$) desorption-limited transport is observed. In region II, different combinations of θ, T and λ produce transport regimes with a similar influence of desorption on the boundaries and intracrystalline diffusion ($\alpha_{\mathrm{Fick}}\ L \approx D_{\mathrm{Fick}}$). Finally, in region III ($\alpha_{\mathrm{Fick}}\ L \gg D_{\mathrm{Fick}}$) the diffusion-limited transport is observed. The $\alpha_{\mathrm{Fick}}\ L/D_{\mathrm{Fick}}$ ratio varies between 0.25 (θ = 0.25, T=150 K, λ= 1) and approximately 100 (θ = 0.75, T= 300 K, λ= 16), clearly representing both extreme transport conditions. Diffusion coefficients and permeabilities were obtained from fitting the concentration profile by Fick's second law solution. At the same conditions of T and θ, both quantities remain essentially constant within the margins of error of our fitting. Diffusion coefficients increase with T and decrease with θ, permeabilities increase with T and remain approximately constant with θ. In tracer exchange conditions, the transport coefficients (D_{Fick}) should exactly agree with the self-diffusion coefficients derived from Einstein's equation. According to our calculations, $D_{\mathrm{E}} \approx D_{\mathrm{Fick}}$. Values of permeabilities using Transition State Theory (α_{TST}) are in the same order of magnitude as α_{Fick}.

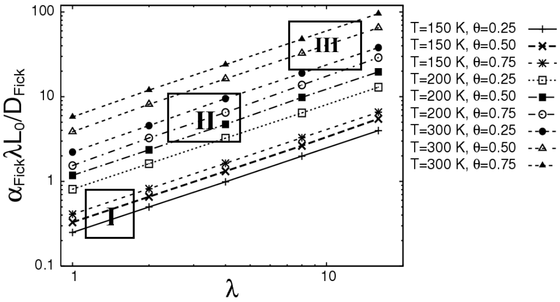

Fig. 2. $\alpha_{\mathrm{Fick}}\ L/D_{\mathrm{Fick}}$ ratio for the simulated systems

Refererences

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