

# diffusion-fundamentals

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## Diffusion of *n*-Pentane in Zeolite ZK5

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### 1. Introduction

Zeolite ZK5 has an interesting framework topology (Fig. 1) which contains two different types of cages, gamma ( $\gamma$ ) and alpha ( $\alpha$ ) cages, connected via eight-membered oxygen rings with a free diameter of 3.9 Å. Recently, Magusin *et al.* [1] have investigated *n*-pentane in zeolite ZK5 using 1D- and 2D-exchange <sup>13</sup>C NMR techniques. Diffusion takes place by rare jumps between neighbouring cages. For an interpore distance of ~10 Å these hopping rates correspond to intra-zeolite self-diffusion coefficients between 10<sup>-18</sup>-10<sup>-15</sup> m<sup>2</sup>s<sup>-1</sup> [1]. Though the methyl and methylene groups fit through the eight-membered oxygen ring, the diffusion of *n*-alkanes with *n*>2 is known to be much slower than for methane and ethane [2]. This results from the C-C-C bond angle. The slow exchange of the guest molecules between the neighbouring cages through the eight-membered oxygen ring is

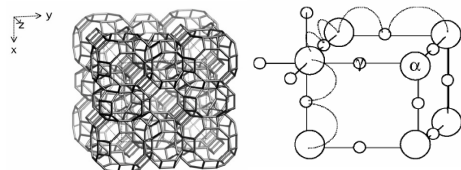


Fig. 1: KFI topology type of framework structure viewed along [001] and schematic illustration of half of the cubic pore structure. The  $\alpha$  and  $\gamma$  cages are indicated by large and small circle, respectively [1].

in the center of this work. We study the system using molecular dynamics (MD) simulations and transition-path sampling (TPS). For the first method, the determination of diffusion coefficients is in the considered case only feasible at high temperature. The Arrhenius law is used to extrapolate the diffusion coefficient to lower temperatures. TPS allows the calculation of transition rates also at lower temperatures.

### 2. Model

The united-atoms approximation is used in which the CH<sub>3</sub> and CH<sub>2</sub> groups are treated as spherical force centers. They interact with the corresponding force centers in other pentane molecules and with the zeolite lattice atoms by Lennard-Jones pair potentials [3]. The loading is set to one molecule per cage according to the experimental conditions in Ref. [4]. The lattice is assumed to be rigid whereas the pentane molecule is flexible. C-C bonds are modeled by harmonic potentials. The self-diffusion coefficient has been calculated from the mean square displacement using the momentum method proposed in

ref. [5]. The determination of hopping rates between the cages by use of the TPS method is subject of ongoing work. MD simulations are carried out at high temperature,  $T$ . Using the Arrhenius equation,  $D = D_0 \exp(-E_a/RT)$ , where  $D_0$  is a pre-exponential factor [6], the activation energy,  $E_a$ , can be computed and diffusion coefficients at lower temperatures can be extrapolated.

### 3. Results and Discussion

In the previous work, the rotational motion of  $n$ -pentane in the  $\gamma$ -cages of zeolite ZK5 has been studied. In addition, the effect of confinement on molecular orientation has been investigated by the distribution of intramolecular vectors of the pentane molecule. Fig. 2

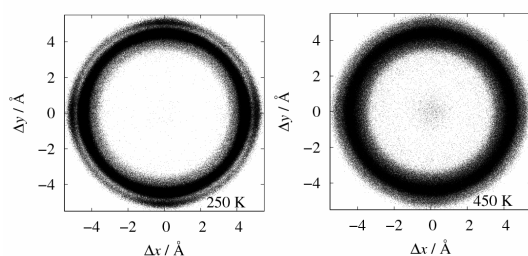


Fig. 2: Orientations of the molecule in the cage represented by projection of the intramolecular vectors  $C_{15}$  (end-to-end) at low (250 K) and high (450 K) temperature, respectively. Each dot represents one orientation registered from the trajectories.

shows some configurations of the molecule trying to escape from the  $\gamma$ -cage to a neighbouring  $\alpha$ -cage at high temperature. An energetic barrier occurs in the transition state between two cages which is formed by the eight-membered oxygen ring. The experimental value of the activation energy,  $E_a = 28 \pm 5 \text{ kJ mol}^{-1}$  was obtained from 1D- and 2D-exchange  $^{13}\text{C}$  NMR measurements in ref. [1]. From MD simulations, the activation energy can be explicitly obtained by fitting the temperature dependence of the diffusion coefficient at high temperature to the Arrhenius equation. In preliminary results, the fitted activation energy value of  $57 \pm 5 \text{ kJ mol}^{-1}$  overestimates the experimental value ranging  $28 \pm 5 \text{ kJ mol}^{-1}$ . The reason could be the constraints of the lattice during simulations or the interaction parameters used. The extrapolated self-diffusion coefficient at 300 K is on the order of magnitude of  $10^{-18} \text{ m}^2 \text{ s}^{-1}$ , which approximately agrees within the range of values ( $10^{-18}$ -  $10^{-15} \text{ m}^2 \text{ s}^{-1}$ ) concluded from the experiment [1].

### 4. Conclusions

Extremely slow diffusion in zeolites is explored by MD simulations at high temperature and transition-path sampling. In first results for  $n$ -pentane in zeolite ZK5, good agreement is found between the values extrapolated using the Arrhenius law and the experimentally determined values from Ref [1].

### References

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