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Entropic Barriers for the Diffusion of Molecules under Confinement

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1. Introduction

The diffusion of molecules under the confinement of a solid structure, *e.g.* a zeolite, can be characterised as a random walk between positions of preferred residence, the adsorption sites. The preferred residence can be caused by a strong attractive host-guest interaction, like *e.g.* benzene molecules close to the cations in zeolite NaY [1], and, furthermore, by differences in the accessible space for the molecules, *i.e.* when relatively spacious regions are separated by narrow pathways, which can be visualised as a “bottleneck”. In order to move from one adsorption site to another, in the first case, the molecule needs to have sufficient kinetic energy to overcome the attractive forces of the host, *i.e.* it needs to overcome an *energetic* barrier. In the second case, the undirected movement in the spacious region lasts a certain time until the molecule “finds” the way through the bottleneck, *i.e.* it needs to overcome an *entropic* barrier [2].

The barriers separating the adsorption sites carry usually a combination of both energetic and entropic character. Since a minimum of the residence probability, $p(x)$, on the “reaction” coordinate, x, is the criterion for a barrier between adsorption sites, the connection between the residence probability and the energy and the entropy, respectively, becomes clear within the relation $p(x) \propto Z(x) = \exp\{-A(x)/k_B T\}$, where Z is the partition function, $A = U - TS$ the Helmholtz free energy, k_B the Boltzmann constant, T the temperature, and finally U the internal energy and S the entropy.

In many cases, the energetic part dominates the temperature dependence of the diffusion coefficient, which approximately follows the Arrhenius law, $D(T) = D_0 \exp\{-E_A/k_B T\}$. The quantity E_A is called the “activation energy” and is related to the height of the energetic barrier. Using molecular dynamics simulations, we will discuss cases where the entropic part dominates which leads to significant deviations from the Arrhenius-type temperature dependence of the self-diffusion coefficient.

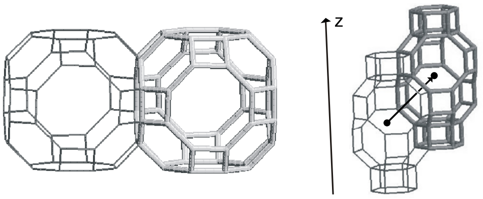

Figure 1: The crystal structures of zeolite LTA (left) and CHA .

2. Ethane in zeolite LTA

Zeolite LTA has a cubic structure with large cages which are connected by narrow windows with a free diameter of ≈ 4.1 Å (see Fig. 1). Small molecules like ethane tightly fit into this window. Due to the combination of large cages and narrow windows, the windows have a strong character of entropic barriers.

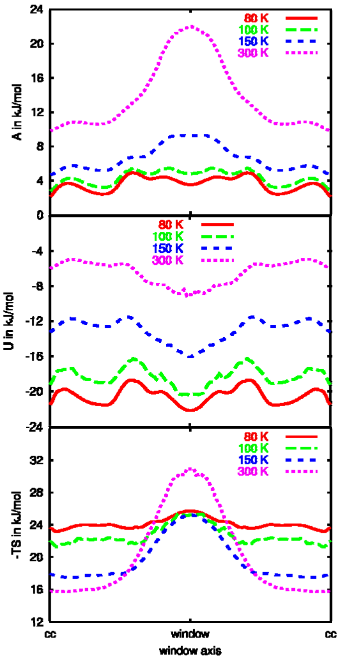

Figure 2: Profiles of the free energy *A* and the contributions *U* and -*TS* for ethane in zeolite LTA on an axis from one cage center (cc) through the window to the neighbouring cage.

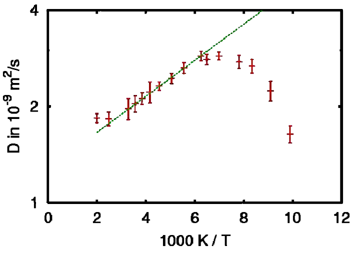

Figure 3: Arrhenius plot of the temperature dependence of the self-diffusion coefficient of ethane in zeolite LTA.

Figure 2 shows profiles of the free energy, the internal energy and the entropy in the cage along an axis from one cage center to the neighbouring one through the window. The barrier in the window which is present at $T = 300$ K (and less pronounced at 150 K) is of entropic nature which can be seen from the contribution of -*TS* to the free energy [2].

The accretion of the barrier has an effect on the temperature dependence of the self-diffusion coefficient, *D*, which is shown in Figure 3. *D decreases* with increasing temperature between 150 K and 300 K. The probability to reach the window decreases with increasing *T*, because more and more of the free volume in the large cage becomes accessible [2]. This extreme case of an inverted temperature dependence is exceptional, however, further studies have shown that a similar behaviour is found also in other host-guest systems.

3. Zeolite CHA

Zeolite chabazite (CHA) has smaller cages and slighltly narrower windows than zeolite LTA. The simulations predict an analogous but less pronounced temperature dependence of *D* for smaller molecules like chlorine which can pass the window easier than ethane.

4. Alkanes in Zeolite MFI

Entropic effects are furthermore observed if internal degrees of freedom of the molecules are constrained by the confinement. This is the case, *e.g.*, for alkanes in zeolite MFI. The aliphatic molecules are forced to sprawl in the channels of this zeolite while more spacious regions allow the chains to ball.

5. Conclusion

Entropic barriers are an important effect of the confinement. The temperature dependence of the self-diffusion coefficient is influenced by the entropic effects and deviations from the Arrhenius law occur. In rare cases *D* even decreases with increasing *T*.

References

[1] S.M. Auerbach, International Reviews in Phys. Chem. **19** (2000) 155-198

[2] A Schüring, S.M. Auerbach, S. Fritzsche and R. Haberlandt, J. Chem. Phys. **116** (2002) 10890-10894