Analysis of Argon Diffusion in Zeolite Imidazolate Framework-8: Preliminary Calculations

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1. Introduction

Recently, Zeolitic Imidazolate Frameworks (ZIFs) are receiving considerable attention within the survey of porous materials due to their high framework porosity, thermal and chemical stability, and amenability to pore functionalization [1].

In the present work, the self-diffusion coefficient, D_S, of argon inside the metal-organic framework of ZIF-8 [1], see Fig. 1, is computed by molecular dynamics simulations. At the same time, special attention is focused on the study of equilibrium density profiles obtained via grand-canonical Monte Carlo. This is the first step to establish a connection between the spatial distribution of the sorbate inside each pore and its diffusivity, enabling the construction of coarse-grained models to reproduce the very essential aspects of the system dynamics.

2. Model Description

In these preliminary calculations, the host framework has been approximated as rigid, and guest-host interactions have been modelled as 12-6 Lennard-Jones potentials, obtained by combining the DREIDING force-field [2] (assumed for the host) and a model of argon by García-Pérez *et al.* [3] (assumed for the guest species) through the Lorentz-Berthelot rules.

3. Results

At room temperature, D_S of argon in ZIF-8 exhibits a trend very similar to that of methane in Linde Type A zeolites [4]: it increases from low to high loadings, then reaches a maximum

Fig. 1: Atomic structure of ZIF-8 sorbent.

and starts decreasing until saturation of the system (see Fig. 2). In fact, the structure of ZIF-8 framework, with its large and highly occupied cages (pore diameter ~11.6 Å), linked by narrow and poorly occupied windows (with diameter ~3.4 Å), suggests in advance the presence of the observed maximum in the profiles of D_S *vs.* concentration
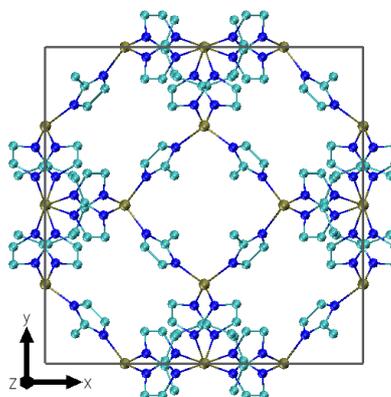
[5]. The positioning of such a maximum at high densities could be related to the long distance between the windows and the preferred adsorption sites (arranged along the edges of a cubic shell around the cage centers) which, together with the high cage capacity (more than 30 argon atoms per cage) causes the regions closest to the windows to remain poorly occupied for a large range of concentrations, so that diffusion keeps on increasing until the cores of the cages are close to saturation.
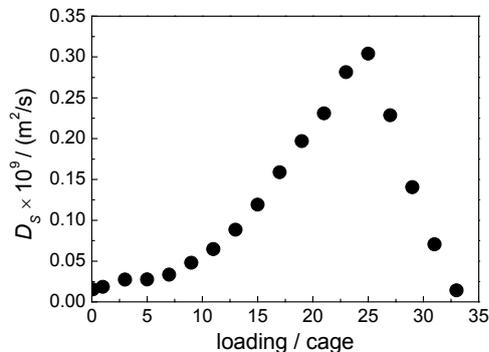

Fig. 2: Self-diffusivity trend of argon in ZIF-8 *vs.* concentration at 300 K.

4. Conclusions

A preliminary study of diffusion of argon in ZIF-8 has been carried out via molecular dynamics simulations, in order to define the most general features of the migration process in such a material, and the obtained results have shown to be explainable on the basis of the host structure and static equilibrium properties.

The complex arrangement of sorbed atoms in the inner pore space represents an attractive challenge for the formulation of a coarse-grained model of the system dynamics [6,7]. In the progressing work more in-depth analysis are being performed to help in capturing the most relevant traits of the diffusion mechanism.

References

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