A Combined Atomistic Simulation and Quasielastic Neutron Scattering Study of the Low-Temperature Dynamics of Hydrogen and Deuterium Confined in NaX Zeolite

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1. Introduction

Atomistic MD simulation can address comparable time and length scales of molecular motion as the QENS technique [1,2]; they are, therefore, complementary and can form a basis for illuminating comparisons. In modeling hydrogen and deuterium confined within zeolite pores, a classical treatment of the energetics is not entirely satisfactory. In this work we carry out a simultaneous study of the sorption thermodynamics and kinetics of hydrogen and deuterium in the zeolite NaX by means of QENS experiments and equilibrium MD simulations, taking into account the quantum mechanical effects.

2. Experimental Method

The adsorption isotherm of H_2 in NaX at 77 K was measured volumetrically by means of an in-house built apparatus. The quasielastic neutron scattering experiments were carried out at the ILL (Institut Laue-Langevin, Grenoble, France) to determine the self (D_s) and transport (D_t,) diffusion coefficients for D_2 in NaX. Taking into account the data treatment and the values from refinements using different jump diffusion models [3], typical mean errors of 20% and 50% were estimated for D_s and D_t, respectively.

3. Simulation Method

For all sorbate-sorbate and sorbate-sorbent atom interactions Feynman's effective quadratic potential, U_q, [4,5] was used

$$U_q\left(r_{ij}\right) = U_{LJ}\left(r_{ij}\right) + \frac{\beta\hbar^2}{24m_r}\left[\frac{\partial^2 U_{LJ}\left(r_{ij}\right)}{\partial r_{ij}^2} + \frac{2}{r_{ij}}\frac{\partial U_{LJ}\left(r_{ij}\right)}{\partial r_{ij}}\right]$$

where r_{ij} is the position vector distance between the centers of mass of molecules i and j. In place of the atomic mass, the reduced mass, m_r, must be used.

To reconstruct a digital NaX crystal, the unit cell geometric characteristics, X-Ray diffraction data and the symmetry operations of the relevant space group were used to obtain the position vectors of all framework atoms [6]. The simulated equilibrium sorption experiments of H_2 and D_2 in NaX were performed by employing a Grand Canonical Monte Carlo (GCMC) algorithm. Equilibrium molecular dynamics (MD)

simulation was carried out in the microcanonical (*NVE*) ensemble; the self, transport and collective diffusion coefficients were calculated [5].

3. Results and Discussion

The experimental and simulated self diffusion coefficients for H_2 and D_2 are compared (Figure 1a), showing an increase of the self diffusivity as the loading increases; this can be explained on the basis of calculating, via GCMC, the partial molar configurational internal energy of the sorbed phase [5]. In Figure 1b, it is shown that the strongest sorption sites with lower energy inside the zeolite pores are firstly populated by the sorbate molecules, while as the loading increases the new sorbed molecules are free to move inside pores.
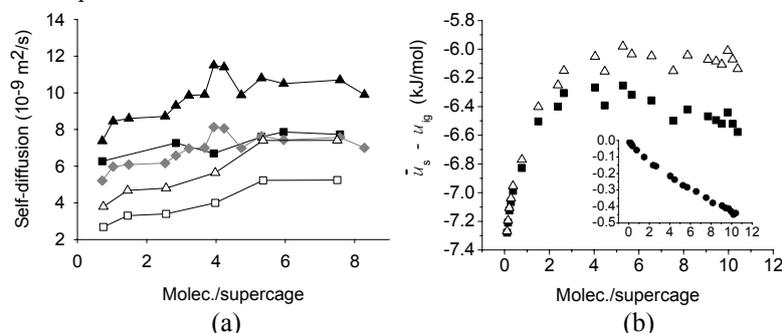
Figure 1. (a) Self diffusivities measured by QENS for H_2 (open triangles) and D_2 (open squares) and computed by MD (filled symbols) as a function of their loading in NaX; (b) Partial molar configurational internal energy of sorbed phase calculated for H_2 via GCMC simulation vs. loading, shown as total (filled squares), and separated into sorbate-sorbent (open triangles) and sorbate-sorbate interactions (inset).

Computed and experimental transport diffusivities exhibit a very large increase with the loading and are in very good agreement, except for higher loadings [5]. This discrepancy is expected, since in our calculations the experimental and simulated isotherms exhibit different saturation values. It also appears that the corrected diffusivity is not constant, contrary to the assumption often made in the interpretation of macroscopic data.

References

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