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A CTRW interpretation of simulated single-file diffusion in zeolites

Pierfranco Demontis, Giuseppe B. Suffritti
Dipartimento di Chimica, Università degli studi di Sassari and Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Unità di ricerca di Sassari, Via Vienna, 2, I-07100 Sassari, Italy, E-mail: pino@uniss.it

1. Introduction

Single-file diffusion of molecules adsorbed in the channels of zeolite is a phenomenon occurring at different time and length scales, which is difficult to simulate by standard methods, because it often occurs for large molecules adsorbed in microporous materials showing parallel non-crossing channels, with large energy barriers to diffusion..

Two interesting examples are given by water adsorbed in two different Li containing zeolites, Li-ABW [1] and bikitaite [2], which show parallel straight channels where hydrogen-bonded linear chains of water molecules run along the axis of the channels, parallel to regular rows of lithium ions sticking to the channel surface.

Extensive Molecular Dynamics (MD) simulations of the dynamical of water in these zeolites at different loading and temperature were performed by this research group. It resulted that the energy barrier for water molecules to cross one another in the same channel is much larger than *kT* event at any reasonably high temperature, so that the diffusion resulted single-file in all the simulation conditions.

The simulation details and results are reported in Refs. [3] and [4], were it was shown that for time scales ranging from a few to some hundreds of picoseconds depending on temperature and loading the mean square displacement (MSD) is proportional to the square root of time as expected for single-file diffusion.

2. Theory and calculations

In this poster we report a comparison of the simulated systems with the prediction of Continuum Time Random Walk theory (CTRW) [5]. A key quantity of the theory is the propagator $W(x,t)$, which yields the probability of finding a particle, which was in $x = 0$ at $t = 0$, in the position x at time t. The analytical form of $W(x,t)$, was derived in the frame of CTRW theory, for the single-file diffusion of a point particle subject, among other few examples, to constant friction and to an elastic force centred at any point x'. In these cases, $W(x,t)$ results to be a special function or involves special functions, and its numerical computation is not trivial.

In the considered systems, the water molecules are structured, but at the simulated temperatures (higher than 400 K) they are free to rotate, so that they can be considered spherical to a good approximation. The effective potential acting on the water molecules along the channel axis is in both zeolites is approximately sinusoidal, with barriers in the range 13 - 19 kJ/mol, and at the simulated temperatures they are overcome rather easily.

Therefore, the propagator resulting from simulations should be somehow intermediate between the theoretical one for uniform friction and that for molecules subject to a harmonic potential.

For each simulation we evaluated the propagator twice: for time intervals corresponding to the full duration of the simulation (full-time propagator) and corresponding to the validity of the MSD proportional to $t^{1/2}$ rule ($t^{1/2}$ propagator), respectively.

The comparison shows that indeed the agreement is reasonably good in both cases for the $t^{1/2}$ propagator, and the details are discussed. The behaviour of the full time propagator, which becomes multimodal for fixed t at low loadings, is reported and briefly commented.

3. Conclusion

The propagator for single-file diffusion derived in the frame of the CTRW theory was compared with the ones evaluated from MD simulations of water adsorbed in two different zeolites. Comparison of the simplified theory with realistic system results shows that the agreement is reasonably good at short times, but is challenging for the theoretical developments if long-time behavior is considered.

References

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