diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

A "coarse-grained" model based on a cellular automaton for the study of diffusion in microporous materials.

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1. Introduction

It is well-known that in molecular liquids diffusion coefficients are in the range 10^{-9} - 10^{-8} m^2s^{-1}, while in microporous materials such as zeolites this range is much larger, spanning from 10^{-8} m^2s^{-1} (for example methane in silicalite-1) to 10^{-19} m^2s^{-1} (for example benzene in zeolite Ca Y) or even smaller.

The phenomenon is made complex if the concentration (or loading) is considered: high loadings make the diffusion coefficient smaller and smaller, following different trends [1].

Classical Molecular Dynamics (MD) computer simulation technique made it possible to study diffusion of small molecules in zeolites [2] for times not exceeding some tens of nanoseconds and for systems including not more than 10000 particles.

These limitations stimulated the interest to develop models able to reach mesoscopic scales through a *coarse-graining* process of atomic scale models.

Actually the coarse-graining scheme usually involves the evaluation of the free energy of an adsorbed molecules using detailed atomistic models to characterize adsorption sites and the possible presence of energy barriers to diffusion, and to use these results as an input for a lattice model of the considered system (see, for instance, [3]).

This permits to study a much larger system (with a large number of adsorption sites) for a much larger time, because the calculation is greatly simplified as the integration of equations of motion is avoided.

2. Theory and calculations

In this poster we propose a scheme to build a cellular automaton, whose evolution rule is representative of the dynamics of diffusion of simple molecules in zeolite ZK4, a dealuminated model of LTA zeolites. They are characterised by nearly spherical cavities of about 12 Å diameter connected by six windows of about 4 Å diameter, with an overall cubic symmetry.

The basic idea of our model is based on the correspondence between the atomistic model of ZK4 and a cubic lattice of identical cells, each one connected to other six cells though windows allowing the passage of one molecule at time from a cell to another.

A cell, representing a cavity of ZK4, can contain up to a maximum number of particles (for instance, 16 for methane or 8 for Xe). The connectivity between adjacent cells characterises the molecular migration process, which is represented by synchronous attempted jumps, which are accepted stochastically with a given probability weight and with the restrictions of a maximum number of particles per cell.

To verify the proposed model preliminary calculations have been performed on a relatively small system including 32764 cavities and simulating the diffusion of Xe. As probability weights the cell-to-cell transfer frequencies obtained from NMR experiments at different loadings [4] were used. The results are in agreement with the experimental equilibrium distributions.

3. Conclusion

The cellular automaton designed to simulate at mesoscopic scale the dynamics of simple molecules in LTA zeolites was able to capture the main features of the diffusive process and of the resulting equilibrium distributions. Work is in progress to relate the diffusion coefficient to the fluctuations of average number of particles per cell and to extend the model to zeolites of different connectivity between cells.

References

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