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Cellular Automata Modeling of Diffusion under Confinement

Pierfranco Demontis, Federico G. Pazzona, Giuseppe B. Suffritti

Università degli Studi di Sassari, Dipartimento di Chimica, via Vienna 2,
07100 Sassari, Italy, E-Mail: fpazzona@uniss.it

1. Introduction

Both thermodynamic and transport properties of molecular species are strongly influenced by the effect of confinement exerted by microporous materials such as zeolites. The nature of particle-framework interactions, along with geometric effects (size, shape, and connectivity of the pores), provides the energy landscape for the transport process and plays a major role in determining the aptitude of the diffusing species to migrate from pore to pore. [1] Geometrical restrictions can cause a sharp separation on the time scales involved in the diffusion process: intracage motion (short times) and intercage migration (long times). [2]

Zeolites provide a three-dimensional framework (connected channels and cages with finite capacity) which, when reduced to its essential constituents, can be represented as a set of structured lattice points (cells) evolving in time according to well defined local rules: these are the basic ingredients of Cellular Automata (CA) models.

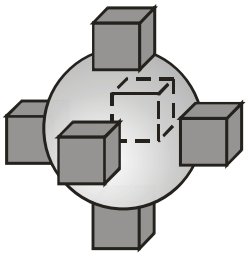

Fig. 1: a CA unit cell (cubic symmetry).

With their parallel, space-time discrete nature, CA algorithms represent a very convenient environment in which physical systems can be modelled in a reductionistic approach, in order to cover large scales of space and time. [3]

We constructed a CA satisfying detailed balance to model intercage diffusion and equilibrium properties of particles adsorbed in a ZK4 zeolite. [4, 5, 6]

2. The Model

The structure of our CA is constituted by L^3 cubically arranged cells (L is the number of cells per side of the cube) at constant temperature. N adsorbed particles can diffuse from cell to cell. A cell is pictured in Fig. 1, while in Fig. 2 a sketch of their connection is represented. A single cell has a total number of K adsorption sites, which can be grouped into 6 *exit sites* with potential adsorption energy ε_{ex}, and K–6 *inner sites* with energy ε_{in}. Each site can accommodate only one particle, and each cell can exchange particles with its 6 first-neighboring cells. Jumps may occur only between adjacent exit sites of adjacent cells, therefore the topology of the exit sites (dark grey cubes in Fig. 1) turns out to be

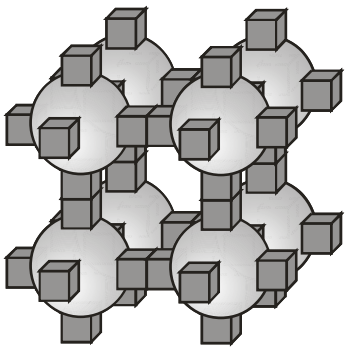

Fig. 2: some connected cells: a small 3D portion of the system.

automatically defined. Instead, a particle cannot migrate to another cell if it occupies an inner site, therefore we choose to neglect their spatial arrangement (this is why we represented them with the pale gray sphere in Fig. 1).

At each time step, the evolution of the system is given by a *randomization* procedure in which each cell (treated as a closed system) independently of each other can change the configuration of the guest particles, and a *propagation* procedure in which independent pairs of adjacent exit sites can synchronously exchange particles. The output of each operation is determined stochastically according to probabilities defined by Boltzmann's statistics. Each operation is carefully designed in order to satisfy detailed balance.

In our first calculations the particles interact with each other only by mutual exclusion. We found that a differentiation between ε_{ex} and ε_{in} is enough to produce various types of diffusivity profiles, while the adsorption isotherm is a dual-Langmuir isotherm. Even in this simple case, many features of the model (e.g., the separation between the mean life times of differently occupied cells and the relaxation time of local density fluctuations) turn out to behave in a way similar to that observed through Molecular Dynamics simulations.

The introduction of mutual interactions between particles is represented by a dependence of the energy parameters ε_{ex} and ε_{in} on the local density of each cell. This fact arises naturally when a systematic coarse-graining is performed to transfer the essential features of a cell *equipped with adsorption sites structured in space and pair interparticle potential* into a less structured cell such the one pictured in Fig. 1. The introduction of this dependence allows to use effective energy potentials as flexible parameters by means of which the model can exhibit a wide range of behaviors, and therefore opens a way to generate coarse-grained models of diffusion in zeolites.

3. Conclusion

We constructed a Cellular Automaton to capture the essential features of confinement by means of a probabilistic scheme satisfying detailed balance. The model works with few flexible parameters, which depend on local observables and rule the adsorption isotherm, the diffusivity profile, the separation of time scales.

References

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