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ABSTRACT BOOK

A COARSE-GRAINED MODEL FOR DIFFUSION IN ZEOLITES BASED ON CLUSTERING OF SHORT MD TRAJECTORIES

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Zeolites form a class of microporous aluminosilicates of great interest due to their multifarious applications in industry and everyday life. Their porous structure allows small molecules to be adsorbed and to diffuse inside crystals, and depending on the zeolite type and on the diffusant species a variety of behaviours is possible. Molecular Dynamics is now widely used in order to understand the microscopic mechanisms of adsorption and diffusion occurring within these materials as well as in MOFs and ZIFs [1]. A major drawback of MD for this kind of systems is its high computational cost, so that coarse-grained methods, speeding up simulations without losing the essential features of dynamics, are valuable tools for exploring the behaviour of guest molecules on time and space scales hardly, if at all, reachable with ordinary MD.

The first step in our proposed method is the clustering of MD trajectories to obtain a discretized version of the motion of adsorbed molecules within the zeolite. Each pore in the aluminosilicate is partitioned in a number of regions and each point in the original trajectory is mapped to the proper region based on a distance criterion. The regions correspond roughly to the main basins in the potential energy surface (PES).

This discrete trajectories in space are then mapped to moves-space trajectories: given a certain lag-time we replace the two discrete positions at the start and end of each interval with the corresponding discrete displacements. Using the free software EMMA [2] we then perform a statistical analysis of the trajectories and obtain the transition probabilities from each discrete move to each other as a transition matrix. This matrix is at the basis of the evolution rule of the model.

Considering the transitions between moves allows one to circumvent the inherent non-markovity of the space partition, at least to a reasonable degree of approximation. Simulating the motion of guest molecules as a simple random walk on the lattice of regions obtained in the first step of coarse-graining would be inaccurate due to the low barriers in the PES, especially at low loadings. By considering the transitions between moves, short time memory effects are naturally taken into account and this allows us to treat the dynamics of interest as a simple random walk in the moves-space, ruled by the transition matrix. The trajectory on this space then naturally implies a trajectory in the real discretized space.

Our method gives self-diffusivity, moves frequency and occupation probabilities of regions and pores in good agreement with the MD results for spherical, or roughly spherical, guest molecules, such as Ar, Kr, Xe and CH₄ in zeolite ZK4. The application to other molecular geometries and zeolite types is currently under study.

This suggests the algorithm can be successfully used for the simulation of massive zeolite-like systems, with various sorbates, for time scales substantially longer than previously possible on ordinary machines.

REFERENCES

[1] Smit B., Maesen T.L.M., *Chem. Rev.* 2008, 108, 4125-4184

[2] Senne M., Trendelkamp-Schroer B, Mey A., Schutte C, Noe F., *J. Chem. Theory Comput.*, 2012, 8 (7), 2223–2238