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Diffusion via the Space Discretization (DSD) Method to Study the Concentration Dependence of Self-Diffusion under Confinement

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1. Introduction

We have applied a recently developed second-order Markov process method [1] to periodic model pore systems, introducing a *minimum-crossing surface* concept (MCS); namely, the system is discretized into regions by drawing *dividing surfaces* at a fixed constant distance along the considered coordinate direction (here, x), respecting the periodicity; among all the possible sets of dividing surfaces we choose the one through which the absolute crossing rate is minimal, the MCS. In this way, an *unequivocal* decomposition of the self-diffusion coefficient is obtained along x, through the parameters α and ζ, according to the expression:

$$D_S = \frac{1}{2}\langle |v_x| \rangle \alpha\zeta \,, \tag{1}$$

with $\langle |v_x| \rangle \alpha = l/\tau$ and $1/\zeta = \lim_{n\to\infty} d(1/P)/d(nl)$, where τ is the mean time spent by a particle inside a region and P is the transmission probability that a particle exits a region via the MCS opposite to the one through which it entered [1], computed over an increasing number n of regions coarse grained together, where the single regions have extent l along x. The α parameter accounts for the efficiency of the thermal speed (with respect to the bulk fluid where $\langle |v_x| \rangle = l/\tau$) in bringing about transitions across the MCSs, while the ζ parameter accounts for the particle-particle collisions and the tortuosity of the system.

2. Results

On the basis of our formulation, we have determined two scenarios that can lead to a maximum in the dependence of the self-diffusivity on concentration, under thermodynamic equilibrium and constant temperature.

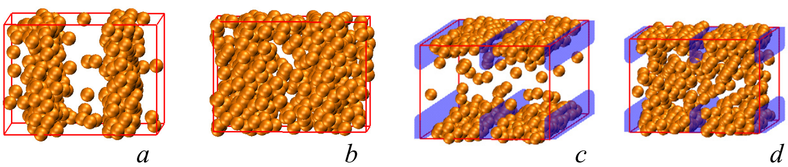

Fig. 1: Case 1: potential wells along the x direction at low (a) and high (b) density. Case 2: potential wells along the z direction behind uncrossable walls normal to the x direction at low (c) and high (d) density.

A case study is performed in these conditions, using a system of purely repulsive soft spheres.

- **Case 1**: a x-dependent periodic potential generates an array of dense regions (in the potential wells) at equilibrium along the x direction;

- **Case 2**: a z-dependent periodic potential generates an array of dense regions (in the wells), which are screened from diffusion by uncrossable walls normal to the x direction.

In Fig.1 we see the inhomogeneity of the sorbate probability density profile (a, c) and how this smoothes out at a higher density (b, d) due to the loading redistribution process. In both cases the MCS is a plane perpendicular to the x direction, located at the two extremities and in the center of the box; the loading redistribution process raises the portion of particles that can cross the MCS, causing the α parameter to grow (Fig. 2).

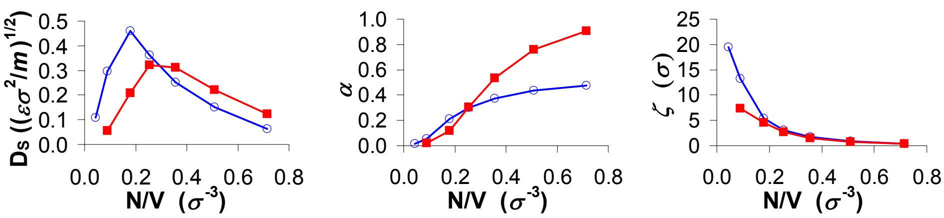

Fig. 2: Self diffusivity (left), α parameter (center), ζ parameter (right), for case 1 (solid squares) and case 2 (open circles).

The ζ parameter is always a monotonically decreasing function of loading (Fig. 2), since the probability P to cross a whole region and exit through the MCS opposite with respect to the entrance one can only decrease if the number of particles inside the region grows. When working at constant temperature, then, a maximum in self-diffusivity can only occur from an increase in the α parameter and, in particular, only if this increase is bigger than the decrease of the ζ parameter, see Eq. 1.

3. Conclusions

Application of our DSD method to a model pore system for two different potential distributions was proved to give insight on the presence of a maximum in the self-diffusion as a function of sorbate concentration for both cases (Fig. 2): A maximum could be found: 1. in the case of potential wells along the diffusive direction (Fig. 1 a, b), 2. in case of potential wells perpendicular to the diffusive direction and located behind uncrossable walls partly blocking diffusion along the considered direction (Fig. 1 c, d). Adaptation of the DSD method in a real system (MCM-22 zeolite) where a maximum in self-diffusivity has been observed [2], is in progress.

References

[1] M. Sant, G. K. Papadopoulos, D. N. Theodorou, J. Chem. Phys. 128, (2008) 024504-1.

[2] M. Sant, J-M Leyssale, G. K. Papadopoulos, D. N. Theodorou, submitted to *J. Phys. Chem. B*.