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Effects of Surface Roughness on Transport Properties of Porous Media

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1. Introduction

Disordered nano-porous solids play nowadays a key role in several industrial processes. Both equilibrium and dynamic processes, that take place within nano-pores, are sensitive functions of the topology and the geometrical disorder of the pore matrix. Thorough analysis of adsorption data, implementation of modern techniques (such as AFM, MRI) but mainly the wide use of neutron or x-ray small angle scattering techniques have unveiled that in many cases the surface of widely used nanoporous materials cannot be described in Euclidian terms and fractal geometry approaches must be adopted. It is nowadays quite common that the fractal dimension is used as an index of surface irregularity, however its effect on dynamic processes is far from being defined. This work focuses on the effect of surface irregularity on Knudsen and molecular diffusion as well as on the flow of incompressible fluids, by means of simulations within a set of custom made single pores characterized by varying fractal irregularity.

2. Determination of transport properties

A single regular rectangular pore of cross section w^2 and its irregular counterparts having the same pore volume and statistically self-similar Koch surfaces (Fig. 1) with fractal dimension log13/log3 (1st-3rd approximation, outer cut-off at $w/3$) were used as model systems for our three-dimensional simulations.

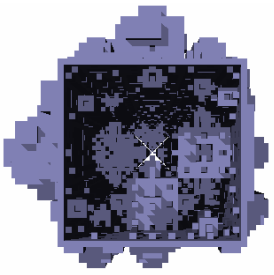

Fig 1. Model Koch surface pore (3rd approximation)

The Knudsen diffusivity, D_K, of inert tracers in the porous structures is determined from the one-dimension mean-square displacement (m.s.d.) of a statistically sufficient number of identical point-like molecules [1], according to Einstein's relation. Additionally, Knudsen diffusivities are determined from the transmission probability (t.p.), which corresponds to the probability for a molecule entering the pore at one end to leave from the opposite end. Since it has been reported that entrance effects could affect this probability we have performed the calculations by counting molecules that have reached a point located deeply into the pore.

In both cases diffusivities are reported (Table 1) in the reduced form D_K/D_{KC}, where D_{KC} is the Knudsen diffusivity in a regular (smooth) cylindrical pore with equal cross section.

Molecular diffusivities, D_M, are calculated by the "blind"' random walk method [2]. In short, the walker is placed at a random void space pixel and its trajectory is monitored vs time. At every time t a random trial move, of length l, to one of the six neighbouring pixels is performed and the time is increased by δt. Assuming D_0 the bulk diffusivity (without the pore confinement), δt is selected to satisfy the condition $l^2=6D_0\delta t$, while if the trial position lies in the solid phase the move is not allowed. The procedure is repeated for a sufficiently large number of time steps, the diffusivity is computed by the Einstein relation and expressed in dimensionless form as D_M/D_0 (Table 1).

The superficial velocity of a viscous fluid in a porous material is described by Darcy's law, while the creeping flow of a Newtonian incompressible fluid within the pore space is described by the Stokes equation coupled with the continuity equation. The Darcy permeability coefficient, k, depends on the spatial distribution of solid and void phase, thus in order to determine k one needs to determine first the superficial velocity by calculating the flow field with the appropriate boundary conditions. The numerical solution is achieved by the use of a finite-difference scheme in conjunction with the artificial compressibility relaxation algorithm [3]. The calculated permeability coefficients are reported dimensionless (over the pore cross-section, w^2) in Table 1.

3. Conclusion

Table 1: Single pore transport coefficients

Surface	D_K/D_{KC}		D_M/D_0	k/w^2
	m.s.d.	t.p.		
Regular	0.99	0.97	1	0.035
Koch 1st appr.	0.45	0.44	0.86	0.010
Koch 2nd appr.	0.34	0.35	0.80	0.007
Koch 3rd appr.	0.30	0.31	0.78	-

As expected, diffusivities (D_K or D_M) decrease as surface irregularity increases; however, disorder affects more D_K than D_M. This can be explained after recalling that in Knudsen regime the molecular trajectories consist of segments with ends at the solid-void interface resulting in a strong dependence on the pore space topology, while in molecular diffusion the inter-molecular collisions form a noisy trajectory and the pore geometry influence is partially masked. We may also note that contrary to recent findings [4] a very good agreement between the two methods of calculation (m.s.d. and t.p.) is observed, indicating that both can be safely used for the determination of D_K. It is finally observed that irregularity affects more Darcy permeability than diffusivity. As k strongly depends on the hydraulic radius, r_h, ($r_h=V_p/A$, where V_p is the pore volume and A the specific surface area) this observation can be explained by the fact that wall irregularity dramatically increases A (while V_p remains unaffected) leading to a significant decrease of the hydraulic radius.

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