Effects of Surface Roughness on Self- and Transport Diffusion in Porous Media in the Knudsen Regime

Kourosh Malek and Marc-Olivier Coppens

Delft Department of Chemical Technology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
(Received 26 April 2001; published 31 August 2001)

The effect of surface roughness on Knudsen diffusion in nanoporous media is investigated by means of dynamic Monte Carlo simulations in three-dimensional rough fractal pores. These simulations yield new insight and explain a number of apparent inconsistencies by revealing a striking difference between the roughness dependence of *transport* diffusion and gradientless (*self-* or *tracer*) diffusion. Both analytical and simulation results show a significant roughness dependence of self-diffusion in the Knudsen regime. Transport diffusion, on the other hand, is roughness independent, as the fluxes do not depend on the detailed residence time and molecular trajectories.

Disordered nanoporous materials with a vast pore network and a rough internal pore surface are extensively used in technical applications, such as heterogeneous catalysis [1–3], fuel cells [4], adsorption [5], and separations [6]. Many of these processes are diffusion controlled, so that a correct assessment of their efficiency depends on more accurate determinations of the dependence of diffusion on the topological and morphological textural parameters. Effects of pore interconnections, i.e., the *topology* of the pore network, can be accounted for through methods such as percolation theory, the effective medium approximation, renormalization group theory, and Monte Carlo simulations [1,2]. Pore shape and surface *morphology* may also play a crucial role, which is, nevertheless, typically ignored because of greater difficulties in modeling it realistically [7]. In many applications involving gases, however, Knudsen diffusion [8,9] plays a dominant role, meaning that molecule-surface collisions are at least as frequent as intermolecular collisions, so that pore surface morphology may have an important effect on diffusion and therefore on reaction efficiencies of diffusion limited catalytic processes [10].

In this Letter, we study the effect of surface roughness on Knudsen diffusion through dynamic Monte-Carlo simulations in three-dimensional rough pores. We demonstrate that there is a fundamental difference between gradientless *self-* or *tracer* diffusion and *transport* diffusion, i.e., diffusion under the influence of a concentration gradient. This difference is well appreciated and understood for ordered microporous zeolites with subnanometer sized regular pores [11], but not in disordered nanoporous materials, where we show for the first time how and why it comes into play when surface roughness is significant. The effect is studied for pores with fractal surface roughness within a realistic finite range, because it has been demonstrated by adsorption [12] and small-angle x-ray scattering [13] that many disordered porous catalysts and sorbents prepared by common sol-gel synthesis have a fractally rough internal

surface within a finite scaling regime and down to molecular scales [14].

The effect of surface irregularity has been studied to some extent, yet not systematically. Apart from the apparent complexity of realistic roughness models [1,7], experiments showed that shallow roughness on scales much smaller than the scale of the interstices or pores was not found to play a major role [15]. However, as mentioned earlier, fractal surface roughness in mesoporous materials is common and may include major perturbations on scales typically ranging from subnanometer scales up to the size of the pores, so that the outer cutoff of this scaling regime is a significant parameter.

A quantitative study of the influence of the fractal surface morphology on diffusion and reaction was started by Coppens and Froment [14]. A mean-field approximation predicts an inverse proportionality of the Knudsen diffusivity with the geometrically accessible area, so that, for a fractal self-similar surface with outer cutoff $\delta_{\max}$ and fractal dimension $\mathcal{D}$,

$$D_K = D_{K0}(\delta')^{\mathcal{D}-2}, \tag{1}$$

where D_{K0} is the Knudsen diffusivity in a smooth porous medium with the same topology as the real, rough medium, and $\delta' = \delta/\delta_{\max}$ is the normalized effective diameter of a molecule of size δ. The nonuniform accessibility of the surface could be accounted for in a more refined model, which uses a first-passage time perturbation approach [16], leading to

$$\frac{D_K}{D_{K0}} = \frac{1}{1 + \alpha[1 - (\delta')^{\beta}]}, \tag{2}$$

in which α and β are constants which can be calculated from the fractal adsorption dimension of the surface, $\mathcal{D}$, and a parameter p_0, the so-called return probability, i.e., the probability for a molecule to leave a fjord it has entered already. Expressions for $\alpha(\mathcal{D}, p_0)$ and $\beta(\mathcal{D}, p_0)$ are given in [16].

We have now performed dynamic Monte Carlo simulations of both self- and transport diffusion in model pores with a stochastic fractal surface with outer cutoff δ_{max} and inner cutoff δ_{min}. A model pore is constructed from N segments of length δ_{max}. The pore surface consists of the statistical Koch curves with $\mathcal{D} = \log 5/\log 3$ [17] also used by Sapoval [18] for two-dimensional (2D) simulations, or the statistically self-similar Koch surfaces with $\mathcal{D} = \log 20/\log 3$ for three-dimensional (3D) pores (Fig. 1), used in our earlier work [19]. The pore width, length, and the number of generations n (outer/inner cutoff) are varied. In our computations, the molecules are represented by point mass particles, so that the results are approximate to order $\delta \sim \delta_{max}/3^n$; features smaller than $\sim\delta$ are not "seen" by a molecule of size $>\delta$. While a complete analysis of the collision and diffusion dynamics should involve the interactions between the molecules and the surface atoms, which can be done by molecular dynamics [6,20], our goal is to present the sole effect of geometrical factors and the differences between self- and transport diffusion, which is why we take a purely mesoscopic, geometrical approach. The irregularity or roughness factor, ζ, of the pore at any generation is characterized by the ratio of perimeter length (2D) or surface area (3D) to perimeter length or surface area of a smooth pore with the same cross section. The numerical simulation of the gas motion proceeds as follows: Initially, a point particle is released at a uniformly chosen random position inside a pore. Then, the molecule is allowed to follow a straight line in a random direction, until it leaves the pore or collides with its wall. Immediately after a collision, a new random direction is selected according to Lambert's cosine law [8,9].
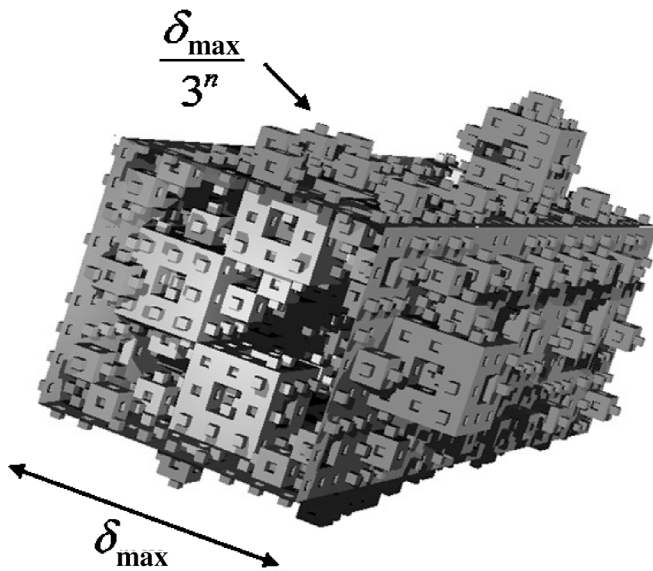

FIG. 1. Part of a typical 3D model "Koch pore" with square cross section and three generations of self-similarity. Extensions to other cross sections are possible.

For the simulation of self- and transport diffusion in long pores, periodic boundary conditions over a number of fractal segments were used to reduce the heavy computer memory requirements; molecules leaving a sequence of segments at one end reenter the opposite end. Then, the self-diffusivity is evaluated using Einstein's relation

$$D_s = \lim_{t\to\infty} \frac{1}{\alpha t}[|\vec{l}(t) - \vec{l}(0)|^2], \qquad (3)$$

in which α is 4 or 6 for two- or three-dimensional calculations, respectively, and $\vec{l}(t)$ is the position of a molecule at time t. For each set of parameters, ensemble averages are performed over a large number of simulations, until convergence is obtained. Transport diffusion is simulated by imposing a concentration gradient over a pore with a finite length. A crucial point in the latter simulations is the elimination of "entrance effects," i.e., the removal of molecules that cannot enter deeply into a pore. This effect eliminates the artificiality of the shape of the inlet, allowing the molecules to equilibrate after crossing a few (1–5) segments. Transport diffusion is then considered over the pore stretching out from the equilibration length until the other pore end, and with respect to the imposed concentration gradient over this same piece. It is worth noting that such entrance effects may also occur in real porous media. The transport diffusivity, D_t, is estimated from the transmission probability, f_t, which is the fraction of equilibrated molecules leaving the pore at the other end:

$$\phi = \frac{f_t C_A \overline{u}}{4}, \qquad D_t = -\frac{\phi}{\vec{\nabla}C}, \qquad (4)$$

where C_A is the inlet concentration and $\overline{u}$ is the average velocity of the molecules. In all simulations, the amount of fractal segments N was chosen large enough not to influence the results. In the case of self-diffusion, trajectories are started in the middle, and in transport diffusion studies at the pore mouth. After a large number of collisions, and using periodic boundary conditions, the end-to-end square displacement l^2 as well as the total length of the trajectory L are calculated. This allows us to calculate the self-diffusivity D_s by equation (3). A typical example of part of a trajectory in a 2D pore with $n = 2$ generations is shown in Fig. 2a, but most calculations are performed in 3D. As expected, the number of collisions increases with the irregularity.

At first, consider the probability distribution of the individual trajectories, as shown in Fig. 2b; it is shown to be well approximated by a Lévy-type power law distribution [17,21] with an outer cutoff on the order of δ_{max} and an inner cutoff on the order of δ. The relative number of short paths increases when the irregularity is increased. Deviations occur for very long paths, which are influenced by the detailed shape of the generator, as a result of inner cutoff effects.

The main results are presented in Fig. 3a, which shows the roughness dependence of the self- and transport
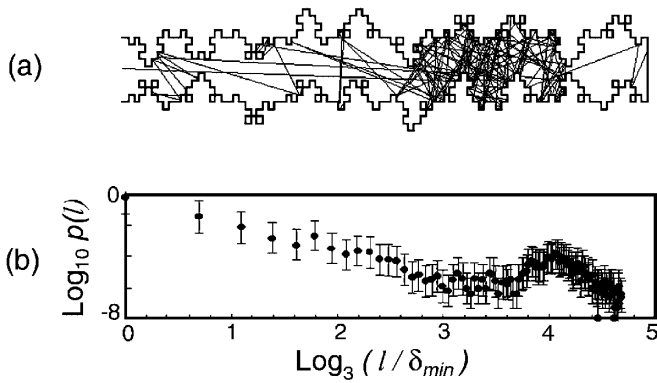
(a)

(b)

FIG. 2.   (a) Typical molecular trajectory generated in a 2D computer simulation. (b) Probability distribution $p(l)$ of the individual trajectories for a 3D "Koch pore," 3rd generation ($n = 3$), pore width $d = \delta_{max}$.

diffusivity in 3D pores. There is clearly a large influence of roughness on self-diffusion; the self-diffusivity decreases as the fractal scaling range widens, i.e., with increasing roughness or decreasing δ. On the other hand, the transport diffusivity does not vary with ζ and is therefore independent on roughness. This is a result of the fact that the transport fluxes are independent on the residence time of individual molecules; only the concentration gradient over the pore and the average pore cross section matter, implying that in a long enough pore and in a finite concentration gradient transport diffusion should not be a function of wall surface irregularity, as our simulations show. Self-diffusion, on the other hand, is a

direct function of the individual molecular trajectories, the total trajectory length, or residence time. Trajectory lengths will increase with increasing surface irregularity, and depend on molecular size and shape [19]. The effect of pore diameter d on self- and transport diffusivity is presented in Fig. 3b. For wider pores, the effect of roughness on self-diffusivity is less pronounced. Simulation results in a wide two-dimensional model pore similar to that used by Sapoval and co-workers [18] show little dependence on surface roughness, in agreement with their results (Fig. 3b). The surface irregularity in these pores is such that the largest irregular features are considerably smaller than the pore diameter. Experiments show that this requirement is not met for many industrial nanoporous sorbents and catalyst supports [22], where the fractal perturbations reach up to the size of the local channel diameter. The latter is a result of the fact that pores in sol-gel based materials are interstices between primary, fractally rough aggregates. Sapoval's model would be more appropriate for certain leached materials; our more general results, however, show a significant roughness dependence for self-diffusion in nanopores with roughness up to the size of the pores themselves ($\delta_{max} \sim d$), a typical situation in sol-gel synthesized disordered materials.

We can now compare the MC results with the analytical solution for self-diffusion in a random 3D fractal pore model on the basis of Eq. (2). In this case, p_0 is the ratio of the area of a fjord's opening to the area of its (unperturbed) walls [16] so that $p_0 = 1/5$. The result in 2D is compared with the simple mean-field expression, Eq. (1), which ignores the nonuniformity of the surface accessibility to diffusing molecules. Figure 4 compares simulation results and analytical calculations. The agreement with analytical results based on a first-passage time approach is
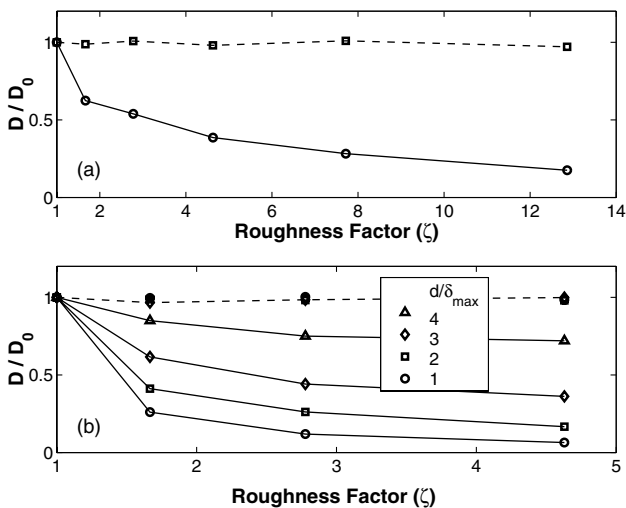

FIG. 3.   Roughness dependence of the normalized self- (solid line) and transport (dashed line) diffusivities in (a) 3D pore with a rough surface, pore width $d = \delta_{max}$, and (b) 2D fractal pores with different widths; triangles are for a simulation in a wide pore, $d = 4\delta_{max}$, similar to the pore used in [18]. D_0 is the diffusivity in a smooth pore.
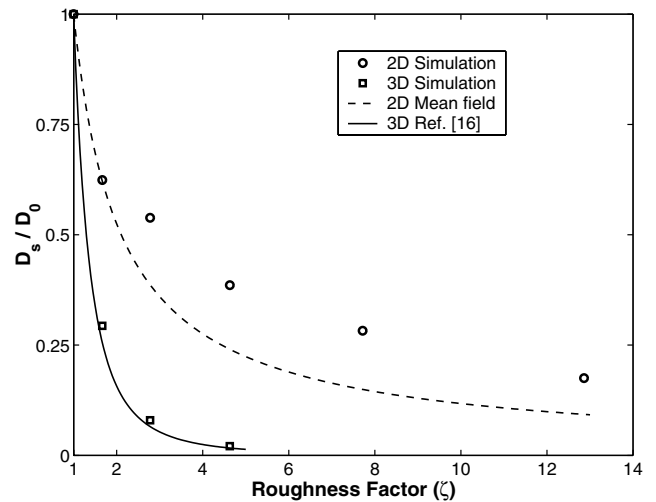

FIG. 4.   Self-diffusion vs roughness factor. Symbols are Monte Carlo simulation results; lines correspond to analytical calculations in 2D (dashed line) and 3D (solid line).

excellent, and even the mean-field approximation is rather good.

It is interesting to draw a parallel with diffusion in crystalline, microporous zeolites, where the qualitative difference between the dependence of self- and transport diffusion on occupancy is well known [23]. When the size of the molecules is similar to the pore size, which is often the case for zeolites, diffusion of these molecules is activated, and can be approximated by site-to-site hops on a lattice. Two molecules cannot occupy the same lattice site, and molecules cannot easily pass each other. In the simplest case of pure Si zeolites with equivalent adsorption sites, the self-diffusivity decreases with occupancy in a monotonous way, because at higher occupancy molecules are trapped for longer times. Transport diffusion on a lattice of equivalent sites, on the other hand, is occupancy independent, even if the residence times of individual molecules are much longer at higher occupancies. Although the details of the diffusion mechanism are clearly different, the trapping because of adsorption in zeolites, with hops in between successive adsorption times, is qualitatively comparable to the geometrical trapping by surface indentations in mesoporous media, where the same qualitative behavior for self- and transport diffusion as a function of increasing roughness is observed.

In conclusion, both simulations and analytical calculations show that surface roughness can have a pronounced influence on self-diffusion of gases in the Knudsen regime, which frequently is the dominating diffusion regime in mesoporous materials. This is especially so when the pores are fractally rough with perturbations of the same order of magnitude as the local pore diameter, such as for typical sol-gel based catalysts and supports. Transport diffusion, on the other hand, does not significantly depend on roughness, because the fluxes are not influenced by the detailed residence time distribution. Flux-based experimental measurements of diffusion through pellets or membranes can therefore not reveal roughness effects. As expected for rough fractal media, the individual collision pathways are Lévy distributed within the scaling regime. Since catalytic efficiency is influenced by the surface geometry [14], these results are of great importance to catalysis. In future work, model reactions will be added and calculations will be performed for pore structures with different realistic cross sections.

[1] M. Sahimi, Rev. Mod. Phys. **65**, 1393 (1993).
[2] M. Sahimi, G. R. Gavalas, and T. T. Tsotsis, Chem. Eng. Sci. **45**, 1443 (1990).
[3] G. F. Froment and K. B. Bischoff, *Chemical Reactor Analysis and Design* (Wiley, New York, 1991), 2nd ed.
[4] P. J. Gellings and H. J. M. Bouwmeester, *The CRC Handbook of Solid State Electrochemistry* (CRC Press, Boca Raton, Florida, 1997).
[5] F. J. Keil, Catal. Today **53**, 245 (1999).
[6] L. F. Xu, M. Sahimi, and T. T. Tsotsis, Phys. Rev. E **62**, 6942 (2000).
[7] (a) P. Pfeifer and B. Sapoval, Mat. Res. Soc. Symp. Proc. **366**, 271 (1995); (b) S. K. Bhatia and J. S. Gupta, Rev. Chem. Eng. **8**, 177 (1992).
[8] M. Knudsen, Ann. Phys. 4F **28**, 75 (1909).
[9] P. Clausing, Ann. Phys. 5F **4**, 567 (1930).
[10] M.-O. Coppens and G. F. Froment, Chem. Eng. Sci **51**, 2283 (1996).
[11] J. Kärger and D. M. Ruthven, in *Diffusion in Zeolites and other Microporous Solids* (Wiley, New York, 1991).
[12] D. Avnir, D. Farin, and P. Pfeifer, Nature (London) **308**, 261 (1984).
[13] (a) H. D. Bale and P. W. Schmidt, Phys. Rev. Lett. **53**, 596 (1984); (b) P. W. Schmidt, J. Appl. Cryst. **24**, 414 (1991).
[14] (a) M.-O. Coppens, Catal. Today **53**, 225 (1999); (b) M.-O. Coppens and G. F. Froment, Chem. Eng. Sci. **50**, 1013 (1995); **50**, 1027 (1995).
[15] T. E. Holt and D. M. Smith, Chem. Eng. Sci. **44**, 779 (1989).
[16] M.-O. Coppens and G. F. Froment, Fractals **3**, 807 (1995).
[17] B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).
[18] (a) S. B. Santra and B. Sapoval, Phys. Rev. E **57**, 6888 (1998); (b) M. Filoche and B. Sapoval, Phys. Rev. Lett. **84**, 5776 (2000).
[19] M.-O. Coppens, in *Fractals in Engineering,* edited by J. Lévy-Vehel, E. Lutton, and C. Tricot (Springer, Berlin, 1997), 2nd ed., p. 336.
[20] (a) J. M. D. MacElroy and S.-H. Suh, J. Chem. Phys. **106**, 8595 (1997); (b) L. A. Pozhar, Phys. Rev. E **61**, 1432 (2000).
[21] (a) J. Klafter, G. Zumofen, and M. F. Shlesinger, Physica (Amsterdam) **200A**, 222 (1993); (b) J. Villermaux, Chem. Eng. Sci. **51**, 1939 (1996).
[22] M.-O. Coppens, Colloids Surf. A **187–188**, 257 (2001).
[23] (a) M.-O. Coppens, A. T. Bell, and A. K. Chakraborty, Chem. Eng. Sci. **53**, 2053 (1998); (b) D. S. Sholl and K. A. Fichthorn, Phys. Rev. Lett. **79**, 3569 (1997); Phys. Rev. E **55**, 7753 (1997).