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Correlating self- and transport diffusion in the Knudsen regime

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Abstract

Comparing the rates of molecular diffusion in porous materials under different regimes of measurement may provide valuable information about the underlying mechanisms. After quite generally explaining the benefit of such a procedure, we refer to a case which in the last few years has raised controversial discussion within the community, viz. the comparison of diffusion phenomena in pores of varying roughness in the so-called Knudsen regime. Knudsen diffusion represents the limiting case of molecular diffusion in pores, where mutual encounters of the molecules within the free pore space may be neglected and the time of flight between subsequent collisions with the pore walls significantly exceeds the interaction time between the pore wall and the molecules. In our studies, the coefficients of self- and transport diffusion are found to be in satisfactory agreement, which contradicts previous literature data. A number of effects which might becloud this relationship are discussed.

Keywords: Knudsen diffusion, Koch curve, surface roughness, Levy walks, transmission probability, anomalous diffusion

1. Introduction

Nanostructured porous materials have found widespread application in diverse fields of technology, notably in matter conversion by heterogeneous catalysis [1, 2] and matter separation [3, 4]. In most of these cases, the technical performance decisively depends on the rate how fast the molecular species involved exchange between the "active" parts of the porous materials (i.e. the regions of molecular separation and/or conversion) and the surrounding atmosphere. For speeding up this process, a new generation of high-tech materials is being designed, in which a microporous bulk-phase, responsible for the elementary processes of conversion and separation, is traversed by a network of larger pores, the so-called transport pores, which ensures fast exchange with the surroundings [5-7].

While the modeling of molecular propagation in micropores is complicated by the fact that on their whole trajectories the molecules are subject to the permanently varying potential field, exerted by the micropore walls due to their persistent immediate vicinity, the situation in transport pores is much simpler. Under the conditions met for pores with diameters between a few nanometers till hundreds of nanometers, typical of the transport pores, for not too large pressures the molecular trajectories essentially consist of periods of free ballistic flight between subsequent encounters with the pore surface. The total duration of rest on the pore surface and the number of mutual molecular collisions are negligibly small in comparison with the time of flight and the number of collisions with the surface, respectively. This type of molecular propagation is referred to as Knudsen diffusion [8]. The stochastic character of the overall process is caused by the fact that after collision with the pore wall, the direction in which a molecule continues its trajectory results in a probabilistic rather than a deterministic way.

Note that this mechanism, 150 years after its introduction [9], is completely correctly described by Fick's equations. Fick's equations, as introduced in analogy with Fourier's law of heat conduction and Ohms law of electricity, correlate molecular fluxes with the concentration gradients of the involved molecules measured within the system where the fluxes are observed. However, only in the last few decades, in particular owing to the introduction of spectroscopic techniques of diffusion measurement like pulsed field gradient (PFG) NMR [10, 11], Quasi-Elastic Neutron Scattering [10-13] and IR/interference microscopy [14, 15], the direct observation of molecular diffusion within the porous materials under study has become possible.

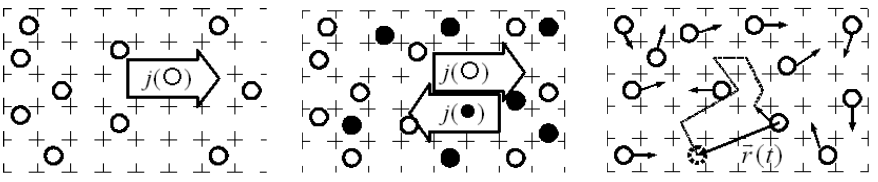
Up to this time, the researchers had to confine essentially to studying flux rates through porous materials as a function of the gradient of the concentration in the surrounding atmosphere [16]. The coefficients of proportionality resulting in this way from a comparison between the fluxes (through the porous material) and the generating concentration gradient (in the outer gas phase) have generally been referred to as "effective" diffusivities. If we stick to the assumption of Knudsen diffusion, i.e. that there are no effects of adsorption (i.e. of particle accumulation close to the surface) the absolute values of the concentrations (and hence of their gradients) inside and outside of the porous material are related to each other like the volume of the pores to that of the total porous materials (i.e. including the holes and the matrix). Correspondingly, the thus defined effective diffusivities are by this ratio ("the void fraction") smaller than the diffusivities in the strict sense of Fick's law.

It is noteworthy that this – historically caused – ambiguity in the definition of diffusivities implies the risk of misinterpretations, the more, since the term "effective" may be used in quite different senses. Examples include the necessity of different definitions of the factor of tortuosity. As a key parameter for describing the enhancement of molecular trajectories in porous media in comparison with the free fluid, it is defined as the ratio of the corresponding diffusivities in the free fluid and the porous system, provided both diffusivities are based on the strict definitions by Fick's laws. This is today common practice in the rather extensive field of applying PFG NMR to characterizing the porosity of a large variety of materials [17-21]. In order to obtain the same tortuosity factors when using "effective" diffusivities in the above explained sense, one has to keep in mind that this ratio has to be additionally multiplied (i.e. the effective diffusivity has to be divided) by the void fraction.

Sometimes existing discrepancies may be ruled out by simply deleting differences in the definitions. Having this in mind, we have referred to this ambiguity in diffusion terminology with respect to the key issue of this contribution, viz. the correlation of transport diffusion and self-diffusion under Knudsen conditions. After correlating self-diffusion and transport diffusion quite generally in the next section within the safe boundaries of the celebrated central limit theorem, in section 3 we shall talk about possible pitfalls which might obscure or prohibit the application of these principles to the systems under study, i.e. in straight tubes with surfaces, whose roughness may be deliberately enhanced. Having all these limitations in mind, section 4 presents coincidence between the coefficients of transport diffusion and self-diffusion. We conclude in section 5 with an encouragement of the experimentalists to take profit of the most recently provided options to get access to tailored nanotubular materials and to confirm the predicted results experimentally.

2. Correlating transport diffusion and self-diffusion via the central limit theorem

Figure 1 schematically shows the situation typical of the main types of diffusion experiments with porous materials.



(a) (b) (c)

Figure 1: Microscopic situation corresponding to the measurement of transport diffusivity (a) and self-diffusivity (b,c). The flux of the labelled molecules (●) in (b) is counterbalanced by that of the unlabelled molecules (○). If the mobility of the unlabelled molecules is unaffected by the presence of the labelles molecules, the fluxes in (a) and (b) are equal and the transport and the self-diffusivities coincide [11].

In all our considerations, the porous system is assumed to provide a rigid reference system, so that molecular propagation may be recorded with respect to this frame without any additional complications. Figure 1(a) represents the situation of measuring transport diffusion, where the transport diffusivity D_{T} is defined as the factor of proportionality between the flux (density) j and the (negative) concentration gradient in Fick's famous 1st law:

$$j = -D_{\mathrm{T}} \frac{\partial c}{\partial x}. \tag{1}$$

The analogous procedure may also be applied to systems in equilibrium, if a part of the molecules is labeled. In this case, by considering the flux and the concentration of only the labeled molecules, in complete analogy with Eq. (1) we can define the tracer- or self-diffusivity D [22]:

$$j^* = -D\frac{\partial c^*}{\partial x}. \qquad (2)$$

Albert Einstein's feats of 1905 include the demonstration that the self-diffusivity may be defined on the basis of the measurement of the time dependence of the molecular mean square displacement, yielding in the one-dimensional case [23]

$$\langle x^2(t)\rangle = 2Dt. \qquad (3)$$

The equivalence between Eq. (2) and (3) holds under the conditions of the central limit theorem [24], i.e. succeeding jump lengths are uncorrelated and their distribution behaves normally with finite moments. Under this condition, the probability of molecular displacement in a given direction approaches a Gaussian, with the molecular mean square displacement characterizing the distribution width linearly increasing with the observation time. This, however, is exactly the message of the Einstein relation, Eq. (3).

Let us now compare the microdynamic situations in experiments, in which the transport diffusion (Fig. 1(a)) and the self-diffusion (Figs. 1(b) and (c)) are investigated. Let us in particular compare the fluxes (of the molecules represented by empty circles) in Figs. 1(a) and (b). Generally, the molecules diffusing in Fig. 1(a) from left to right, i.e. propagating from regions of higher to lower concentration, will experience a situation different from those shown in Fig. 1(b), where the concentration remains uniform. Not unexpectedly, therefore, the molecular fluxes (and hence also the corresponding diffusivities, since we have implied identical concentration gradients) under the conditions of transport diffusion and self-diffusion may be different. This is the situation well known, e.g., from the study of zeolitic adsorbate-adsorbent systems [11, 25-27]. By the same chain of arguments, however, one has to conclude that the fluxes and hence the diffusivities must coincide if the diffusants do not interact with each other since then their microdynamic situation in Figs. 1(a) and (b) are completely identical.

Hence experimental techniques like QENS, which bear the potentials to measure both transport diffusion and self-diffusion [12, 28], may provide important information about the microdynamic situation of molecular transportation. This information is of benefit for both an optimization of the operation conditions for a given nanoporous material and for further improvement of the pore architecture with respect to its application in matter separation or heterogeneous catalysis.

Since, by definition, under the conditions of Knudsen diffusion any mutual interaction of the diffusants is excluded, on the basis of these considerations transport and self-diffusion in the Knudsen regime have to coincide. Most astonishingly, however, in a series of papers [29-31], this requirement seems to be violated in dynamic Monte Carlo Simulations. In view of the very fundamental relevance of this discrepancy, we are going to present our considerations, which have been prompted by the rather puzzling message of the diverging trends in the coefficients of transport diffusion and self-diffusion reported in the literature. These results have been presented to the public on the occasion of the International Meeting of the German Physical Society in March 2005 and are described in more detail in [32, 33].

3. Knudsen diffusion in pores with varying surface roughness: a consistency check of the self-diffusivities

We have used both scaling arguments and numerical simulations to explore the general laws of Knudsen diffusion in pores of varying surface roughness. Figure 2 illustrates the way to generate the pores considered in our studies for the numerical simulations. The particle starts at the left side of the pore when transport diffusion is considered, or in the middle when self-diffusion is considered. Each particle performs a random trajectory inside the pore, where it moves with constant velocity u_0 along the trajectory. After hitting a boundary, the particle moves in a new direction chosen according to Lambert's cosine law, where the new angle θ to the surface normal vector occurs with the probability $dP(\theta,\varphi) \sim \cos\theta d\Omega$ where $d\Omega = d\theta$ in $d=2$ and $d\Omega = \sin\theta d\theta d\varphi$ in $d=3$. The 2d- and 3d-pores of different roughness that we consider are built by sticking together n units of equal length and width h, with n up to 2000, which leads to a total length $L = nh$ of the pores. For the smooth pores (generation $\nu = 0$) this unit is a square in $d = 2$ and a cube in $d = 3$. For higher generations ν, the boundary of each unit is created iteratively by a random generalized Koch curve, where in each generation the smooth segments are replaced by a random Koch curve generator of length $h/2$ as shown in Figs.

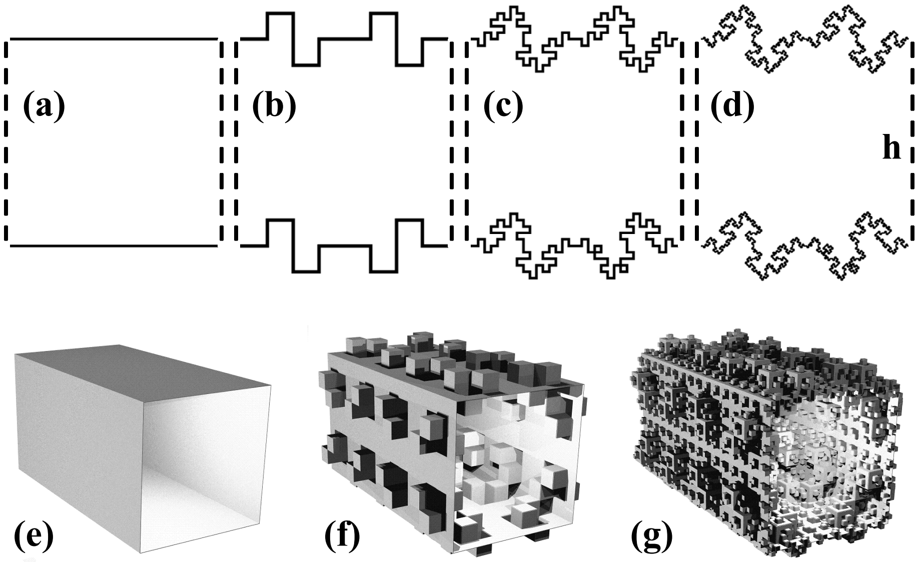


Figure 2: Examples for the realizations of the pore geometry generated by a generalized random Koch curve of length $h/2$ in two (a-d) and three (e-g) dimensions. a-d: the smooth unit and the units after generation $\nu = 1$, 2 and 3, respectively. e-g: the smooth 3d-pore and examples of 3d-pores after iteration steps $\nu = 1$ and 2. The presented 3d-pores consist of n = 2 units.

2(a-d), and 2(e-g). The highest iteration, ν = 3, yields the highest roughness considered in this study. By the chosen way of pore construction, the volume of the pores does not change with varying surface roughness. In the numerical simulations, pore width h and velocity u_0 were set equal to 1.

A first check whether the reasoning of the previous section using the central limit theorem does in fact apply may be based on a discussion of the distribution $P(|x|)$ of the flight lengths $|x|$ parallel to the channel. Figure 3 shows that asymptotically $P(|x|)$ decays as

$$P(|x|) \sim |x|^{-(1+\beta)}, \qquad (4)$$

where β is equal to 2 in the two-dimensional pore, and equal to 3 in the three-dimensional pore, independent of the pore roughness.

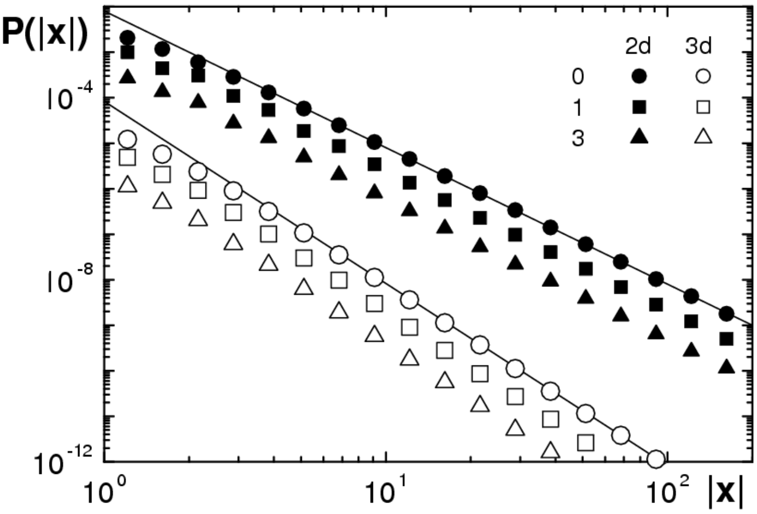


Figure 3: Flight-length distribution $P(|x|)$ as a function of the flight length $|x|$ parallel to the channel for the 2d-pores (filled symbols) and 3d-pores (open symbols) with increasing roughness ν = 0 (circles), ν = 1 (squares) and ν = 3 (triangles). The 3d-data are shifted down by a factor of 100. The lines of slopes -3 and -4 are guides to the eye.

By definition, the time of each jump is proportional to the jump length l Thus, for very large jumps, we have $x \approx l \sim t$, so that Eq.(4) defines a Levy walk in one dimension [34-36]. For such Levy walks, the mean square displacement is known to scale as [34-36]

$$< x^2(t) >= 2D_S(t)t \qquad (5)$$

where only for β > 2 the self - diffusion coefficient $D_S(t) = D$ is a time-independent constant, so that Eqs. (3) and (5) coincide. For the two-dimensional model pores, i.e. for β = 2, however, $D_S(t)$ scales with ln$t$. Under such conditions, Eq. (3) does not hold anymore, and the central limit theorem is no more applicable. This special behaviour is caused by the fact that in the straight model pores considered, flights of infinite extension may become possible. Convergence to the situation described by the central limit theorem depends on the relative probability by which such infinitely large flights may occur. In two-dimensional pores, parallelism with the pore axis, as a prerequisite for extremely large jumps depends on only one angle θ, while in three-dimensional pores the two angles θ and φ have to attain the appropriate values, which will occur with a correspondingly smaller probability. It is not unexpected, therefore, that correlating transport diffusion and self-diffusion in the conventional way fails to provide any reasonable result for two-dimensional model pores, while in the case of three-dimensional pores satisfactory agreement might be attained.

To test these predictions, we have determined the particle mean square displacements for different pore geometries with starting points in the middle of the channel by numerical simulations. The results are displayed in Fig. 4, where we have plotted $<x^2(t)>/(t\ln t)$ for the 2d-pores and $<x^2(t)>/(2t)$ for the 3d-pores. In both cases, in complete agreement with our scaling considerations, with increasing observation time constant values are approached. In the case of the 3d-pores, these values represent the self-diffusivities. They notably decrease with increasing surface roughness. Following the arguments of the previous section, these self-diffusivities should coincide with the transport diffusivities, which shall be considered more closely in the subsequent section.

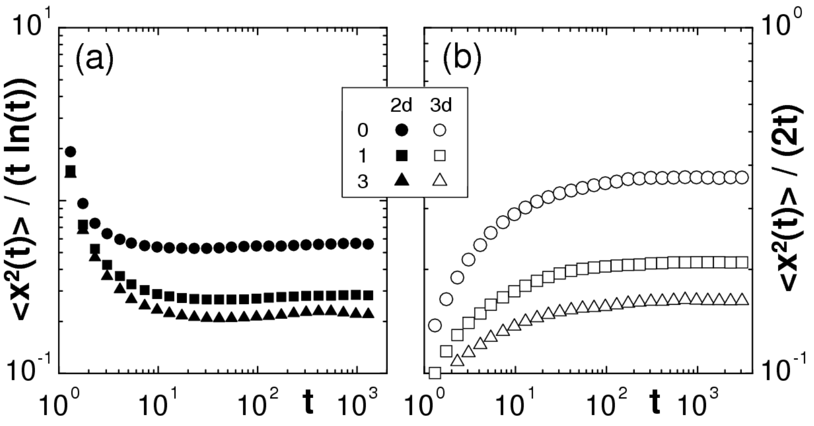


Figure 4: The appropriately scaled mean square displacements from numerical simulations, viz. $<x^2(t)>/(t\ln t)$ for the 2d-pores (a) and $<x^2(t)>/(2t)$ (coinciding with the self-diffusivity as defined by Eq. (3)) for the 3d-pores (b), attain constant values, as predicted by scaling arguments. The surface roughness increases with increasing iteration parameters $\nu = 0$ (circles), $\nu = 1$ (squares) and $\nu = 3$ (triangles).

4. Simulating transport diffusion

For attaining the situation illustrated by Fig. 1(a), to the system under study, i.e. to the pores exemplified, e.g., by Fig. 2, a fixed concentration gradient c_0/L is applied by considering the concentrations $c = c_0$ on the left hand side (i.e. for $x \leq 0$) and $c = 0$ on the right hand side ($x \geq L$) of the pore, respectively. Particles start at the left boundary, perform a random trajectory between the system walls and are thought to be absorbed when they hit either the left or the right boundaries. After some relaxation time, this leads to a constant current (density) j, which yields the transport diffusivity D_T by use of Fick's 1st law, Eq. (1), via

$$D_{\mathbf{T}} = j / \left|\frac{\partial c}{\partial x}\right| = jL / c_0 . \tag{6}$$

Since the relaxation of the particle flow into a stationary state is very time-consuming, it has become common practice to derive D_T from the (transmission) probability f_T that a particle starting at the left boundary will leave the pore through the right boundary [37]. With this probability, the particle flux (density) may be represented as

$$j = c_0 f_{\mathbf{T}} < u_x > , \tag{7}$$

where $<u_x>$ is the mean velocity in x-direction. Combination with Eq. (6) yields

$$D_T =< u_x > f_T L . \tag{8}$$

For calculating the transmission probability f_T, N random trajectories are considered that start at $x = 0$ and end when either $x = 0$ or $x = L$ is reached. Then f_T results as the ratio between the number of trajectories leaving the pore at the right boundary and N.

Similarly as in the previous section where the self-diffusivity had to be shown to remain invariant with varying time as a check of self-consistency, with Eq. (8) now the transport diffusivity has to be shown to remain constant with increasing pore length L. Since the particle velocity saturates for large pores, constancy of D_T with varying pore length implies that f_T scales inversely proportional to the pore length. Figure 5 shows the results of our simulations, in which the pore length has been varied over more than three orders of magnitude. It results in particular that the 3d-pores behave exactly as predicted, i.e. that $<u_x> f_T L$ remains constant, which, according to Eq. (8), is nothing else than the transport diffusivity. With the 2d-pores, however, constancy is only attained after division of this quantity by $\ln(L)$.

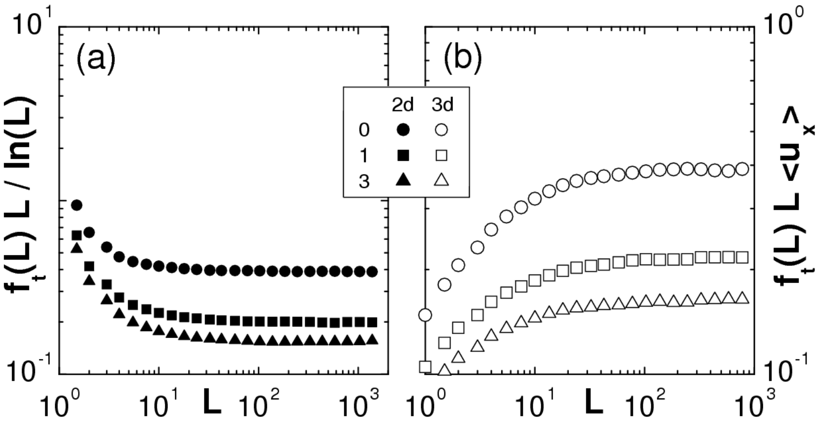


Figure 5: While in 2d-pores, constancy with varying pore length L is attained by multiplying the transmission probability f_T with $L/\ln(L)$ (a), in 3d-pores f_T is found to scale with $1/L$ so that a plot of $<u_x> f_T L$ (which, according to Eq. (8), coincides with the transport diffusivity) becomes invariant with the pore length L (b).

Thus, in complete analogy with the consideration of self-diffusion, also transport diffusion in 3d-pores totally complies with the general pattern illustrated in section 2. It is noteworthy that the anomalous scaling behaviour of the transmission probability f_T (i.e. of transport diffusion) in 2d-pores in space nicely corresponds with the anomalous behaviour of the mean-square displacement, i.e. of self-diffusion, in such pores with respect to time: If the time dependence of the (self-) diffusivity is transferred into the space dependence of the (transport) diffusivity by implying the scaling relation $t \sim L^2$, the logarithmic scaling of the self-diffusivity with time corresponds even quantitatively with the logarithmic scaling of the transport diffusivity with the pore length L [32].

Comparison of Figs. 4(b) and 5(b), i.e. of the self-diffusivities and the transport diffusivities in 3d pores, yields satisfactory agreement in both the absolute values and the trends with increasing surface roughness. This result is in complete agreement with the general considerations presented in section 2. Moreover, it is also in agreement with the message of Refs. [29-31] with respect to the influence of surface roughness on self-diffusion. It totally disagrees, however, with the statement about the transport diffusivities which in Refs. [29-31] are claimed to remain unaffected by the surface roughness and hence to deviate from the self-diffusivities. We shall come back to discussing possible reasons of this discrepancy in the following conclusions.

5. Conclusions

We have considered molecular diffusion in channel pores with increasing roughness under the so-called Knudsen conditions, i.e. for negligible mutual molecular collisions and for flight times notably exceeding the periods of interaction with the pore walls. We have in particular used this system for elucidating items of difference and concordance between self-diffusion and transport diffusion as the two most important situations for the measurement of molecular motion in porous materials.

Most astonishingly, at first sight, molecular migration in the two-dimensional model pores considered is found to notably deviate from normal diffusion, i.e. from the behaviour expected on the basis of Fick's and Einstein's diffusion equations, corroborated by the central limit theorem. This anomaly, however, may be easily rationalized by understanding the given situation of molecular dynamics as a Levy walk. As a sufficient and necessary prerequisite for their adequacy with the relations of one-dimensional normal diffusion, the probability (density) $P(|x|)$ for the distance x between two subsequent wall collisions has to scale as $P(|x|) \sim |x|^{-(1+\beta)}$ with $\beta > 2$. With the two-dimensional model pores considered this condition is not fulfilled so that by very fundamental reasons, the simple case of normal diffusion does not apply. Most satisfyingly, the relations resulting by simple scaling arguments and notably deviating from those for normal diffusion, viz. an increase of the apparent self-diffusivity with the logarithm of time, and of the apparent transport diffusivity with the logarithm of the pore length, are nicely reflected by the numerical simulations.

In the case of the three-dimensional pores, however, which reflect a situation possibly occurring in the real nano-world, by the same scaling arguments complete compatibility with the laws of normal diffusion is predicted. For non-interacting particles, as implied in the considered case of Knudsen diffusion, this has to lead to equivalence between transport diffusion and self-diffusion, as illustrated in section 2 on the basis of Fick's and Einstein's diffusion equations. The numerical simulations (Figs. 4(b) and 5(b)) are in satisfactory agreement with this prediction. Transport diffusion and self-diffusion are found to be in accordance with respect to both their absolute values and their dependence on the surface roughness. Most recent progress in manufacturing silicon wafers with tubular pore structure and a large variability of the internal pore surface [38-40] provide excellent conditions for an experimental verification of the simulated dependences.

There are a number of reasons, which may be (and, partially, have been already) used to explain why in Refs. [29-31] the transport diffusivities have been found to remain unaffected by increasing surface roughness, contrary to our results. One reason might clearly be related to the fact that in these papers simulations refer to both two- and three-dimensional pores. Since, as explained in our sections 3 and 4, in the case of two-dimensional pores the resulting (apparent) self-diffusivities (via the Einstein equation (3)) and transport diffusivities (via Fick's law, Eqs. (1) and (6)) are a function of the observation time and the pore length, respectively, arbitrariness in the obtained data cannot be excluded. Moreover, in Ref. [31], during the simulations of transport diffusion, the molecular concentration within the pore close to its entrance to the gas phase is described to be larger than in the gas phase. If - following the convention of the so-called effective diffusivities, as discussed in the Introduction - the transport diffusivities reported in [29-31] refer to the gas phase rather than to the concentration within the system, the smaller values of the gas phase concentration would in fact lead to transport diffusivities larger than those defined in the (original) sense of Fick's law, so that they would also exceed the self-diffusivity. In this case, however, the origin of the (apparent) concentration enhancement at the pore orifice remains to be clarified. A third explanation of the differences might be related to the fact that, differing from our procedure, in Refs. [29-31] for determining the transmission probability f_T the trajectories of only those molecules have been considered which have already entered the pore over a distance of a couple of pore diameters. By comparison with the results of simulations taking into account the total particle flux [32, 33], we did not observe any indication for the necessity of such a procedure. In fact, we have observed the tendency that in this way too large transport diffusivities may result. We are sure, however, that in this vividly developing field of both fundamental and applied research further theoretical and experimental work will contribute to a better understanding of the origin of the still existing differences in our perspective on molecular dynamics in the microworld of nanoporous materials.

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