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Self- and Transport Diffusion in Narrow Pores with Different Roughness

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1. Introduction

We study molecular diffusion in nanopores with different types of roughness in the Knudsen regime in d=2 and d=3. We show that the diffusion can be mapped onto Levy walks and discuss the roughness dependence of the diffusion coefficients D_s and D_t of self- and transport diffusion, respectively. We use scaling arguments and numerical simulations to understand how both types of diffusion depend on the surface roughness of the pore [1]. We find that the diffusion is anomalous in d=2 and normal in d=3. Both diffusion coefficients decrease significantly when the roughness is enhanced.

2. Simulation

We simulate random diffusion trajectories in rough pores [2]. Each particle has a constant velocity u along the trajectory. At the pore boundaries, it is reflected according to Lambert's law. Smooth pores (generation ν=0) are built by sticking together n units (squares in 2d and cubes in 3d) of equal length and width. For higher roughness (ν=1-3), the boundary of each unit is iterated by a random generalized Koch curve.

In the self-diffusion problem, we calculate the mean square displacement $<x^2(t)>=2D_st$, where D_s is the self-diffusion coefficient. It can be calculated from the distribution $P(|x|)$ of the jump lengths $|x|$ parallel to the channel. Fig. 1 shows that asymptotically $P(|x|)$ decays as $P(|x|)\sim|x|^{-(1+\beta)}$ with β=2 for d=2 and β=3 for d=3, irrespective of the pore roughness. Hence, the particle performs a 1d Levy walk [3]. Accordingly, we expect that in d=2, where β=2, the diffusion is anomalous with a diffusion coefficient $D_s\sim\ln t$ that tends to infinity with increasing t. For a direct analytical calculation of D_s in d=2 see [1]. In d=3, β=3 and we expect normal diffusion with $D_s=const$ and $<x^2>\sim t$.

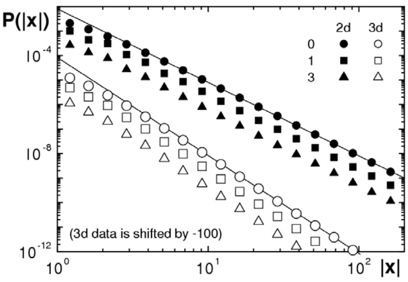

Fig. 1: The distribution $P(|x|)$ for 2d and 3d pores of roughness ν=0,1,3.

In Fig. 2 we see in agreement with the theory that for large t the scaled mean square displacement $<x^2(t)>/(t\ln t)$ reaches a plateau in d=2 and $D_s=<x^2(t)>/(2t)$ reaches a plateau in d=3. The figure also shows that with increasing boundary roughness, the diffusion is considerably slowed down in both cases.

For transport diffusion, a concentration gradient is applied between the concentrations c_0 at the left side and 0 at the right side. Particles start at the left side, perform a random trajectory between the walls and are absorbed when they hit one side of the pore, leading to a constant current. Using Fick's law, the current density $\vec{j} = -D_t \vec{\nabla} c = D_t c_0 / L \vec{e}_x$ defines the transport diffusion coefficient D_t.

Since the relaxation into a stationary state is time-consuming, it is common to derive D_t from the probability f_t, that a particle that starts at the left wall leaves the system at the right wall [4]. To calculate f_t, many random trajectories are simulated that start at x=0 and end when $x \leq 0$ or $x \geq L$ is reached. Since $|\vec{j}| = c_0 f_t < u_x >$, with the velocity in x-direction u_x, we obtain D_t=$<u_x>f_t L$.

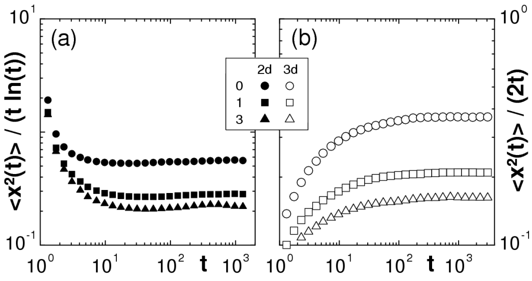

Fig. 2: (a) The scaled mean square displacement $<x^2(t)>/(t \ln t)$ in 2d and (b) D_s=$<x^2>/(2t)$ in 3d.

By simple scaling arguments [1], we can calculate D_t from D_s, i.e. D_t~ln$L$ in d=2 and D_t=$const$ in d=3. In Fig. 3, we plot $f_t(L)L/\ln L$ in 2d and D_t=$f_t L<u_x>$ in 3d for different roughness ν. Again, all curves reach a plateau for large values of L. We see that D_t decreases strongly with increasing roughness of the pore, and that $D_s \approx D_t$ in d=3 in remarkable disagreement with Ref. [5].

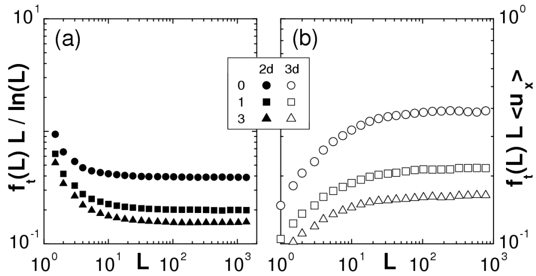

Fig. 3: (a) The scaled probability $f_t(L)L/\ln L$ in 2d and (b) $D_t = f_t L<u_x>$ in 3d.

3. Conclusion

In summary, we have given a description of self- and transport diffusion in the Knudsen regime in 2d and 3d pores. Using Lambert's law, we have shown that both kinds of diffusion strongly decrease with increasing roughness. These results are in marked contrast to earlier investigations [5], where the transport diffusion coefficients were found to be insensitive to the surface roughness. Moreover, we have shown that logarithmic corrections appear to the diffusion coefficients in d=2 that are absent in d=3.

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