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Anomalous Knudsen Diffusion in Simple Pore Models

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1. Introduction

Gas diffusion in mesoporous media is often in the Knudsen regime, cross sections of the pores being considerably smaller than the intrinsic molecular mean free path. Coppens [1] predicted the effect of fractal wall roughness on Knudsen self-diffusivity D_K in a channel. A "trapping" process was identified as the cause of reduction of D_K. Essentially, the trajectory of a particle consists of a sequence of chords in a hypothetical smooth pore, interrupted by excursions into fractal "fjords" in the actual pore wall. Assuming a constant velocity v, traversal of a single chord of length r, drawn from a probability distribution $f(r)$, takes a flight time $\tau_f = r/v$. Subsequently the particle is trapped during a waiting time τ_w, prior to following the next chord. Coppens predicted a reduction of the Knudsen diffusivity $D_K = D_K^{(o)} \Big/ \left(1 + \langle \tau_w \rangle / \langle \tau_f \rangle\right)$, giving formal expressions for the case of *fractal* wall roughness. This was quantified, both analytically and through kinetic Monte Carlo simulations [1][2] for pores with fractal Koch roughness in 2D (fractal lines) and 3D (fractal surfaces), respectively. Levitz [3] identified Knudsen self-diffusion in a slit pore (parallel planes) as *anomalous*, i.e. the mean squared displacement of particles has an asymptotic time dependence $\langle \xi^2(t) \rangle \sim t \ln t$, which is different from normal diffusion, where $\langle \xi^2(t) \rangle \sim t$. This behaviour relates to the fact that the chord length distribution obeys a power law $f(r) \sim 1/r^3$, i.e. the particles perform a Lévy walk [4]. The 2D model belongs to the same universality class as the 3D slit pore, i.e. asymptotically $f(r)$ has the same power law behaviour. This led us to explore the "taxonomy" of Knudsen diffusion, addressing both geometry and reflection rules. We will present results as well as a discussion on the validity of our previous 2D results.

2. Knudsen diffusion in various pore geometries

Consider two infinite parallel lines with spacing δ, which form a 2D "billiard". A particle travels at constant velocity and upon hitting a line it is reflected. The reflection angle θ determines the direction of the outgoing velocity vector relative to the surface normal. Diffuse reflection implies that θ is drawn from a probability distribution $p(\theta) \sim \cos\theta$. With $r = \delta / \cos\theta$ the requirement $f(r)dr = p(\theta)d\theta$ leads to a chord length distribution $f(r) \sim 1/r^2 (r^2 - \delta^2)^{1/2}$, which for large r behaves as $f(r) \sim 1/r^3$. This is the same power law as derived for a 3D slit pore [3]. For a 3D *cylindrical* pore with radius R a chord is characterized by two angles (θ, ϕ), where again θ is the angle between the outgoing velocity and the local surface normal at the collision point, and ϕ

is the azimuthal angle. Straightforward geometry leads to $r = 2R\cos\theta/(1-\sin^2\theta\cos^2\phi)$. Diffuse reflection implies an angular distribution $P(\theta,\phi) \sim \cos\theta$, independent of ϕ. We now need to solve $f(r)$ from $f(r)dr = P(\theta,\phi)d\Omega$, where $d\Omega = \sin\theta d\phi d\theta$. No closed expression was found, but an asymptotic treatment leads to $f(r) \sim 1/r^4$. We also examined the effect of the reflection law $p(\theta) \sim \sin\theta$. This gives rise to $f(r) \sim 1/r^2$ (2D parallel lines and 3D slit pore) and $f(r) \sim 1/r^3$ (3D cylindrical pore) respectively. The observed power laws $f(r) \sim 1/r^\mu$, with $\mu = 2, 3$ and 4 represent distinct instances of Lévy walks, with mean squared displacement $\langle \xi(t)^2 \rangle$ proportional to $t^2/\ln t$, $t \ln t$ and t respectively [5]. Clearly, only the latter case represents normal diffusion. We verified the time dependences explicitly by Monte Carlo simulations.

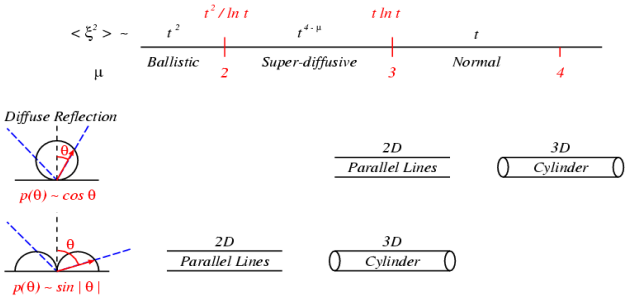

Figure 2 Classification of the time dependence of the mean squared displacement $<\xi(t)^2>$ in terms of the exponent μ, which governs the asymptotic behaviour of the chord length distribution $f(r) \sim 1/r^\mu$.

3. Discussion and Conclusions

While our results are interesting in their own right as physical models where the more formal notion of Lévy walks applies, they also raise questions regarding the validity of results obtained by us previously for the 2D (fractally perturbed parallel line) model. This can be rationalized as follows. The basic notion of the model is a delay introduced by temporary trapping of particles upon collision with a hypothetical smooth pore wall. This implies that the average time to cover a displacement ξ, essentially parallel to the pore axis for large t, increases from $\langle T_\xi^{(0)} \rangle$ to $\langle T_\xi \rangle = \left(1 + \langle \tau_w \rangle / \langle \tau_f \rangle\right) \langle T_\xi^{(0)} \rangle$, where τ_w and τ_f were introduced previously. Thus, behaviour of the *first passage time* is the key prediction of the theory. Simulations were carried out by launching particles in the middle of the pore of length, say, $2L$ and subsequently recording the time T_L required to reach either end. Only in the case of *normal* diffusion we have $D_K = L^2/2\langle T_L \rangle$, so $D_K / D_K^{(o)} = \langle T_L^{(0)} \rangle / \langle T_L \rangle$. Therefore, graphs of $D_K/D_K^{(o)}$ in [2] should be interpreted as those of $\langle T_L^{(0)} \rangle / \langle T_L \rangle$.

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