A new theoretical insight on time-dependent diffusion coefficient

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In NMR, measuring the time-dependent diffusion coefficient $D(t)$ is an efficient tool to probe the geometry of porous media[1,2,3]. Although the diffusive motion is well understood in single-scale domains (slab, cylinder, and sphere)[4], many issues remain unclear for multi-scale porous structures like sedimentary rocks, cements, or biological tissues. To get a better theoretical insight onto restricted diffusion in multi-scale geometries, we study the spin-echo signal attenuation due to diffusion in circular and spherical layers, $\{x \in \boldsymbol{R}^d : L-l<|x|<L\}$, presenting two geometrical lengths, the radius L and the thickness l. Since the Laplace operator eigenbasis is known explicitly, many analytical results can be derived, in particular, the closed form for the time-dependent diffusion coefficient,

$$D(t)/D = \sum_{k=0}^{\infty} \lambda_{1k} B^2_{00,1k}\, w(D\, t\, \lambda_{1k}/L^2),$$

where D is the free diffusion coefficient, λ_{nk} the Laplace operator eigenvalues (here, only λ_{nk} with n=1 are involved), $\lambda_{1k}B^2_{00,1k}$ the explicit weighting coefficients[5]. The function $w(p)$ is determined by the temporal profile (or waveform) of the applied magnetic field gradient, e.g.,

$$w(p) = 12(1/p^2 - (\exp(-p) - 4\exp(-p/2) + 3)/p^3)$$

for the simple bipolar gradient (two rectangular pulses of duration $\delta = t/2$). For thin layers ($l << L$), a perturbative analysis gives surprisingly accurate results, e.g. $\lambda_{10} \approx 1$ and $\lambda_{1k} \approx \pi^2 k^2 (L/l)^2$ for circular layers. The "gap" between λ_{10} and λ_{11} is bigger for larger separation between two geometrical lengths L and l. A new, intermediate diffusion regime emerges for $l << (2Dt)^{1/2} << L$, when the echo time t is long enough for particles to travel between two boundaries, but still insufficient for exploring the whole domain. This diffusion time t appears as an experimental "yardstick" for probing geometrical lengths of the confinement. This intermediate regime resembles the tortuosity regime in porous media.

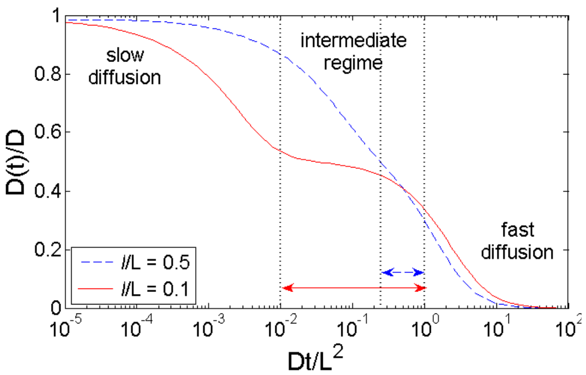

Fig. 1: Time-dependent diffusion coefficient $D(t)$ for thick (l/L = 0.5, dashed blue line) and thin (l/L=0.1, solid red line) circular layers. For thick layer, the scale window 0.25 << Dt/L^2 << 1 (shown by vertical dotted lines) is too narrow, so that a mere transition between slow and fast diffusion is observed, as for the disk. For thin layer, the scale window 0.01 << Dt/L^2 << 1 is large enough to reveal the new intermediate regime. At this time and length scales, restricted diffusion in a two-dimensional thin layer is effectively one-dimensional so that the apparent diffusion coefficient is reduced by factor 2, a kind of "tortuosity" of the thin layer.

In conclusion, we considered restricted diffusion in model two-scale geometries. In a single mathematical frame, we observed the transition from the slow diffusion to a new intermediate regime (analogous to the tortuosity regime in porous media), and then to the fast diffusion. These features should appear and be relevant for natural multi-scale structures.

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