

Sub- and superdiffusive molecular displacement laws in disordered media probed by nuclear magnetic resonance techniques

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The two most obvious reasons why molecular transport can become anomalous are "obstruction" and "trapping" [1]. An example of the obstruction effect is single-file diffusion of molecules in zeolite pores [2]. Temporal trapping in the sense of a waiting time distribution occurs under more or less disordered topological constraints. Examples are fluids in random porous media [3], and, as a special scenario, polymers in entanglement networks [4]. In this sort of systems, trapping means that particles are temporally held up by constraints such as dead ends or loops not permitting displacements along the transport direction under consideration. This is the situation examined in the present study.

If the topological constraints are random or fractal in nature, one expects anomalous mean squared displacement laws, $\langle r^2 \rangle \propto t^\alpha$ with $\alpha \neq 1$, in the so-called scaling window, $a < \sqrt{\langle r^2 \rangle} < \xi$ [1]. The lower limit, a , is the elementary unit length on which the constraints become first perceptible. An example for a is the pore dimension in a porous medium. On the long-displacement side, it is the correlation length of the constraints, ξ , that limits the anomalous power-law regime. If the driving mechanism of transport is Brownian motion, one expects a subdiffusive power law in the scaling window, i.e. $\alpha < 1$. The superdiffusive counterpart arises for hydrodynamic dispersion due to the simultaneous action of tortuous coherent flow and Brownian motion.

Anomalous transport laws can be probed non-invasively by NMR techniques [5]. On a micrometer length scale, field gradient NMR diffusometry provides access to mean squared displacement data. With a "velocity compensation" variant, hydrodynamic dispersion can be examined. As an indirect method, field-cycling NMR relaxometry can be employed for studies of transport properties on a nanometer length scale.

The crossover from subdiffusive to superdiffusive displacements will be demonstrated with water molecules percolating through a porous glass depending on the flow rate. Subdiffusive displacement laws were also identified in polymer melts confined in mesoscopic pore spaces.

A typical sample series studied in this context is linear poly(ethylene oxide) incorporated in strands embedded in a quasi-solid and impenetrable methacrylate matrix. The strand diameters ranged from 8 to 60 nm. It will be shown that chain dynamics becomes dramatically different from bulk behavior. This so-called "corset effect" [6] occurs both above and below the critical molecular mass and reveals the frequency dependence signature of reptation ($T_1 \sim \nu^{3/4}$, that is limit II of the Doi/Edwards formalism corresponding to the mean squared segment displacement law $\langle r^2 \rangle \sim t^{1/4}$). The corset effect is traced back to the lack of the local fluctuation capacity of the free volume under nanoscopic confinements.

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