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Single-file dynamics in nanotubular materials probed by a combination of hyperpolarized tracer exchange and diffusion NMR techniques

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Diffusion of adsorbed species in one-dimensional channels can follow the mechanism of single-file diffusion (SFD) when the cross-sectional dimensions are comparable to the sorbate size. SFD preserves the relative order of particles in a channel and is characterized by a square root time dependence of the mean squared displacement (MSD), i.e. $\langle r^2 \rangle \propto t^{0.5}$. This time-scaling has been confirmed in an assortment of contrived macroscopic single-file systems, but experimental reports of SFD in molecular systems are rare [1–3] and in some cases inconsistent [3, 4].

Here we report results of experimental studies of self-diffusion and tracer exchange of xenon in dipeptide nanotubes in which distinct signatures of single-file dynamics are obtained using two different NMR techniques applied to the same single-file host-guest systems. The combination of the two techniques allowed us to investigate the MSD time-scaling over a 5 orders of magnitude variation in diffusion time. In addition, the impact of channel blockages due to defects in the crystal structures on the time-scaling of the MSD was investigated by kinetic Monte Carlo simulations.

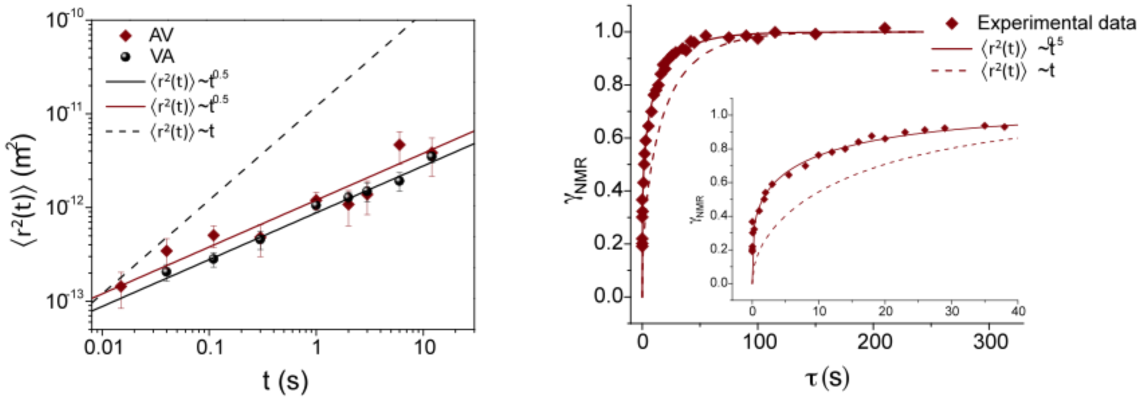

Figure 1: (Left) Time dependence of mean-squared displacements of Xe in l-alanyl-l-valine (AV) and l-valyl-l-alanine (VA) nanotubes probed by PFG NMR at 25 °C. (Right) Continuous-flow hyperpolarized tracer exchange data for Xe in AV, normalized to the steady-state. Curves represent the fully determined simple kinetic model for single-file and Fickian diffusion time-scaling, with no free parameters. Solid and dashed lines on both figures represent the $t^{0.5}$ and t time-scalings, respectively.

References

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