SINGLE FILE DIFFUSION AND LASER POLARIZED TRACER EXCHANGE NMR IN PEPTIDE NANOTUBES

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Introduction

Nanotube materials have a vast range of potential applications, including molecular separation, environmental remediation, drug delivery and catalysis. Suitability for a particular application can be optimized by tuning the interactions and molecular transport dynamics inside the tubes or near the tube openings. Restricted diffusion in one-dimensional (1D) channels, where the diffusing particles are too large to pass one-another, leads to single-file diffusion (SFD). The distinguishing feature of SFD is that the mean-square displacement (MSD) is proportional to the square root of the diffusion time, $\mathrm{MSD} = 2F\sqrt{t}$, where *F*, the single-file mobility, depends on the loading, channel structure, guest-host interactions. In SFD, the motions of the diffusing particles are necessarily correlated, and hence SFD is slower than "normal" 1D diffusion, where $\mathrm{MSD} = 2Dt$. Here we summarize the results of a laser polarized tracer exchange NMR study in L-alanyl-L-valine (AV) peptide nanotubes.

Experimental

The spin-exchange optical pumping system is described in Ref. [1]. Experiments were performed using a modified single-channel Bruker wide-line NMR probe. The volume of sample holder within the detection coil region is approximately 6 μl which can accommodate roughly 10mg of AV sample. The 3.2mm (O.D.) PFA tubing was connected to the inlet and outlet of the sample holder with gas-tight fittings. In the laser polarized tracer exchange method, the adsorbed phase ^{129}Xe is selectively saturated using a train of shaped radiofrequency pulses. Freshly polarized ^{129}Xe atoms flow into the sample region and diffuse into the nanotubes. SFD limits the build-up of the ^{129}Xe longitudinal magnetization in the nanotube phase.

Results and Discussion

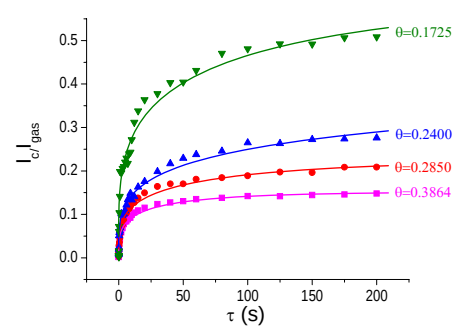
Saturation-recovery experiments were conducted at T=-10°C at a series of Xe pressures. Typical data, obtained after dividing by the integrated gas phase signal, are presented in the figure. Fitting yielded the steady-state amplitude and R_n. Invoking a 2-site exchange model and assuming Langmuir adsorption at pressure *p* and "coverage" θ, the following master equations for the nuclear spin Zeeman order in the gas and channel phases (I_z, I_{zc}) can be derived.

$$\frac{dI_z}{dt} = -k_a p(1-\theta) I_z + k_d \theta I_{zn} - I_z R + G(I_{zi} - I_z)\,; \quad \frac{dI_{zc}}{dt} = k_a p(1-\theta) I_z - k_d \theta I_{zn} - I_{zn} R_n$$

The solution of these equations, assuming long channels of average length $\bar{l}$ and excess laser polarized Xe gas, yields

$$I_{zc}(t) = \frac{1}{2}\left(I_{zi}/\bar{l}\right)\sqrt{F}\,\pi\,\Gamma^{-1}(1/4)\int_0^t u^{-3/4} e^{-uR_n}\,du$$

A similar expression can be derived from diffusion propagator theory [2] but does not yield the signal amplitude relative to the gas. The data agree qualitatively with the $\theta^{-1/2}(1-\theta)^{3/2}$ dependence predicted by the hard-spheres model for *F*.



Laser polarized tracer exchange curves as a function of the channel filling factor, θ, obtained at at T=-10°C

Conclusions

We have reported the first observation of molecular transport in peptide nanotubes. The tracer exchange-recovery inside AV channels following NMR saturation exhibits the clear signature of SFD, where $\mathrm{MSD} \propto \sqrt{t}$.

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References
[1] A.L. Zook et al., J. Mag. Reson. **159**, 177 –184 (2002).
[2] S. Vasenkov and J. Karger, Phys. Rev. E **66**, 052601 (2002).