Restricted diffusion of polarised ^{3}He gas in aerogels

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Abstract

Polarised ^{3}He is used to non-destructively probe by NMR the structure of silica aerogels. Using laser optical pumping large spin-echo signals are obtained with small amounts of gas, even at low magnetic field. Attenuation induced by applied field gradients is measured for equivalent ^{3}He pressures ranging from 5 mbar to 3 bar. Systematic diffusion studies are performed by NMR on custom-made (98% porous) and commercial (97% porous) aerogels used by research groups to study quantum fluids in confined geometries. The observed pressure dependence suggests a non-uniform structure of both aerogel samples on length scales up to tens of microns.

Key words: Silica aerogel ; NMR ; spin diffusion

NMR diffusion studies are standard methods used to probe the microscopic structure of porous media. Measurements using a low density gas have been shown to potentially provide small-scale information on silica aerogels of the kind used in low temperature experiments [1–3]. This initial study of the effect of the gas pressure in a single aerogel sample revealed a non-uniform distribution of density of silica strands in this system, in contrast with the well-defined mean free path value obtained for diffusion in ^{3}He-^{4}He dilute solutions [4]. We present an extended study over a broader range of gas pressures and in a second sample of different characteristics and origin.

The experiments are performed at room temperature and low magnetic field (2 mT) using hyperpolarised ^{3}He gas produced by laser optical pumping and transferred into the experimental cells using a dedicated peristaltic compressor [5]. Pressures P_3 =12–120 mbar are used for experiments with pure ^{3}He gas. Partial pressures P_3 of order 30 mbar of polarised ^{3}He mixed with various amounts P_{N2} of nitrogen (up to 1.2 bar) are used to study diffusion at high gas densities. Two samples have been studied. Sample "M" (prepared and provided by N. Mulders [2,3]) is a 98% porous (22.9 m^2/cm^3) aerogel sample grown in a cylindrical glass cell (1.2 cm diameter, 3.7 cm height). Sample "A" (provided by G. Eska from Airglass, Staffanstrop, Sweden), is a 97% porous (18.4 m^2/cm^3) aerogel cylindrical sample enclosed in a matching PMMA container (1.25 cm diameter, 1.1 cm height). An identical empty container is used as a reference cell for free diffusion measurements.

Spin diffusion is measured as described in [2,3] using a standard CPMG $\pi_x/2$–$(\pi_y)_n$ spin-echo sequence with period τ. Large (∼10 cm) tipping coils are used to generate homogeneous pulses with negligible magnetisation loss (less than 10% after 1000 echoes in the absence of applied gradient). Small (∼1 cm) detection coils are used for optimal signal to noise ratio with small samples. Pulsed field gradients G=0–10 μT/cm are applied along the common axis of the cells and of the main field. The frequency spectra of the recorded echoes provide 1-D images of the gas magnetisation in the samples (figure 1, top). The shape of cell A is fairly well reproduced considering the spatial NMR resolution $2\pi/(\gamma G\delta)$=0.7 cm (γ=$2\pi\times$32.43 MHz/T is the gyromagnetic ratio of ^{3}He nuclei and δ the gradient duration). The strongly reduced sensitivity of the detection coils for the ends of cell M is responsible for its smeared profile. The local magnetisation is found to ex-

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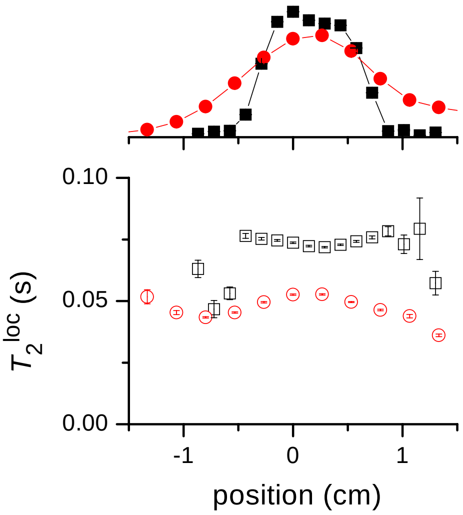

Fig. 1. Top : variations of signal intensities along the gradient axis in aerogels M (circles) and A (squares). Bottom : corresponding local decay times $T_2^{\rm loc}$ of a spin-echo train with τ=6 ms and G=9 μT/cm.

ponentially decay, with slightly non-uniform lifetimes (±10% see figure 1, bottom). This is small enough to accurately ascribe a single exponential decay time T_2 for the average magnetisation in the cell.

For free gas diffusion, the expected relation between T_2, G and the diffusion coefficient D is T_2=$12/(\gamma G\delta)^2 fD$, in which f is a numerical pulse shape factor (f=3-2δ/τ for negligible gradient rise-time). Scattering on N_2 molecules leads to an effect of the gas composition, which is accounted for using the equivalent pressure $P_3^{\rm eq} = P_3 + P_{\rm N2} D_3^1/D_{\rm N2}^1$, with D_3^1=1895 cm^2/s (resp. $D_{\rm N2}^1$=780 cm^2/s) the diffusion coefficient of ^{3}He (resp. of ^{3}He atoms in N_2) at 1 mbar and 293 K. $1/D$ and hence T_2 are expected to linearly depend on $P_3^{\rm eq}$. Data for the empty reference cell obtained at various G and τ collapse on a straight line, with a slope corresponding to the expected value $1/D_3^1$ (figure 2). This provides a consistency check for our apparatus and measurement technique.

In figure 2 we have also plotted all aerogel data in reduced units introducing $1/D_{\rm eff}$=$T_2(\gamma G\delta)^2 f/12$ ($D_{\rm eff}$ is an effective diffusion coefficient). The new data for cell M are consistent with our previous ones [2,3] and extend over a wider pressure range. Results in the other aerogel (cell A) show a strikingly stronger departure from the free diffusion behaviour, revealing a much more restricted gas diffusion.

The non-linear variation of decay times with pressure rules out a uniform density of scattering centres (the silica strands) in the aerogels. For both of them, a broad distribution of local mean free paths at scales smaller than our imaging resolution (over a range 0.1–100 μm) has to be assumed to account for the experimental observations [3]. These consistent results confirm the discrepancy with diffusion measurements in dilute solutions [4].

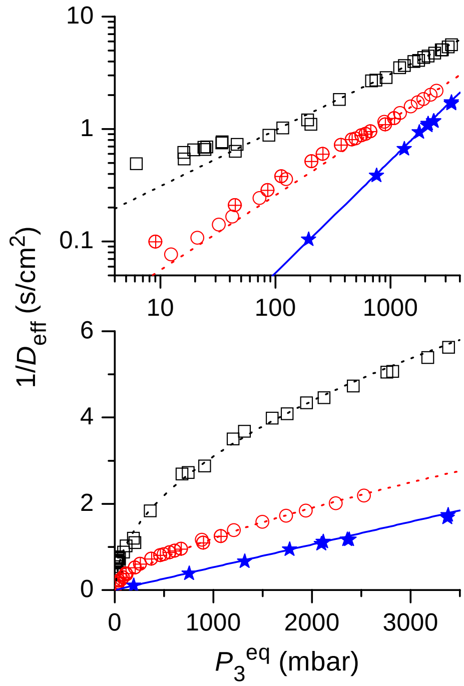

Fig. 2. The reduced data $1/D_{\rm eff}$ (see text) are plotted as a function of the equivalent ^{3}He pressure $P_3^{\rm eq}$ both in linear and semi-logarithmic scales. Stars: measurements in the empty reference cell (free diffusion). Circles (resp. squares): measurements in aerogel sample M (resp. A). Crossed circles correspond to previous measurements [2,3]. The solid line $P_3^{\rm eq}/D_3^1$ corresponds to the nominal free diffusion coefficient. The dotted lines are phenomenological power laws with exponents 0.5 (cell A) and 0.66 (cell M). $1/D_{\rm eff}$ values are 2.5–5 times larger in cell A than in cell M.

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