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NMR Studies of the Dynamics of 1D ^{3}He in ^{4}He Plated MCM-41

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Abstract

Pulsed NMR techniques have been used to study the dynamics of ^{3}He confined to the interior of the hexagonal nanochannels of MCM-41 for which the walls were coated with a monolayer of ^{4}He as determined by isotherm measurements. The ^{3}He was added afterward to form a 1D ^{3}He line density of about 0.1 A^{-1}, corresponding to a Fermi temperature of $T_F \sim 120$ mK. A distinct and appreciable departure from the Curie law was observed for the nuclear spin magnetization below 0.5 K. The temperature dependence of the nuclear spin–lattice relaxation times, T_1, for temperatures $0.05 < T < 2.5$ K, followed the expected linear behavior at low temperatures, and a peak was observed at $T \sim 2T_F$ consistent with the Luttinger liquid theory as predicted by Polini et al. (Phys Rev Lett 98:266403, 2007). The observed temperature dependence of the nuclear spin–spin relaxation times, T_2, differed considerably from that observed for T_1, with a minimum at $T = 0.8$ K, similar to the tendency reported by Matsushita and colleagues.

Keywords Luttinger liquid · Magnetic resonance · One dimension

1 Introduction

The confinement of quantum fluids (^{3}He, ^{4}He, H_2, HD) to nanoscale dimensions where the thermal de Broglie wavelength is comparable to the channel size has been predicted [1–4] to lead to new quantum states. In particular, strong correlations in 1D make all excitations collective and the properties of the system must be described in terms of Tomonaga–Luttinger liquid (TLL) physics [5–8]. Exploring these quantum states beyond electronic materials has generated a considerable

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interest. Wada et al. [7, 8] have explored the existence of superfluidity in 1D ^{4}He in nanotubes, and the effects of degeneracy have been reported for ^{3}He in FSM-16 [9–12]. Yager et al. [13] have used NMR to show the spatial correlations of ^{3}He in MCM-41 scale with time t as $t^{1/2}$ at long times. Birchenko et al. [14, 15] have also reported on NMR studies of ^{3}He on nanostructured MCM-41 for temperatures above 1.4 K and notably observed two components for the spin diffusion which is consistent with our nuclear spin–spin relaxation studies at high temperatures [16]. Gatica et al. [17] have pointed out that in real experiments many quasi-1D fluids can exhibit higher-dimensional character as some degree of translational motion will exist. The advantages of the ^{3}He systems are that the density can be varied accurately over a wide range, the transverse dimension can be varied by preplating with ^{4}He (or Ne or Ar [18]), and the system is free from impurities to a very high degree. In this report, we discuss the use of NMR methods to observe the magnetization and the dynamics of ^{3}He atoms in ^{4}He preplated MCM-41 in the region of the estimated Fermi temperature.

2 Experimental Methods

We used MCM-41 supplied by Sigma-Aldrich [19] with a pore size specified as 2.1–2.7 nm and tubular lengths varying in the range of 100–300 nm. The MCM-41 was compressed lightly into a cylindrical polycarbonate NMR cell with one end of the MCM-41 pressed against a silver plate that was an integral part of the refrigerator. ^{4}He for preplating and the ^{3}He sample were admitted via a capillary entering the opposite end [20].

Prior to the NMR studies, an in situ ^{3}He isotherm of the MCM-41 was carried out at 1.5 K. The results plotted in Fig. 1 showed an anomalous minimum near the isotherm rise and was quite different from the isotherm measured at 2.5 K in a separate experiment [16]. Because of the small volume of the NMR cell, isotherm measurements in our case do not provide an accurate measurement of the monolayer completion. We therefore used the observation that the nuclear spin–spin relaxation times, T_2, are very different for ^{3}He adsorbed on the wall and the mobile ^{3}He beyond the wall [16]. This result can be used to provide a quantitative measure of the amount of ^{3}He needed to cover the walls of the MCM-41 instead of relying on the isotherm measurement alone. A correction can be made for the amount for ^{4}He coverage needed for the same wall by using the results of Goellner et al. [21].

Starting with the coverage of 0.480 mmoles (the start of the major step in the isotherm), an all ^{3}He sample with 0.528 mmoles (an approximate 10% excess over monolayer coverage) was prepared, and the two distinct nuclear spin–spin relaxation times shown in Fig. 2 were observed. The solid red line in Fig. 2 is the sum of two exponential relaxation times. The slow relaxation is identified with a mobile gas component in the core of the nanotubes and the fast relaxation with the wall component. This two-component relaxation is very similar to the observations made by Birchenko et al. [15] although they proposed no explanation. The slow component corresponds in amplitude to 6.5% of the ^{3}He added, so that the monolayer

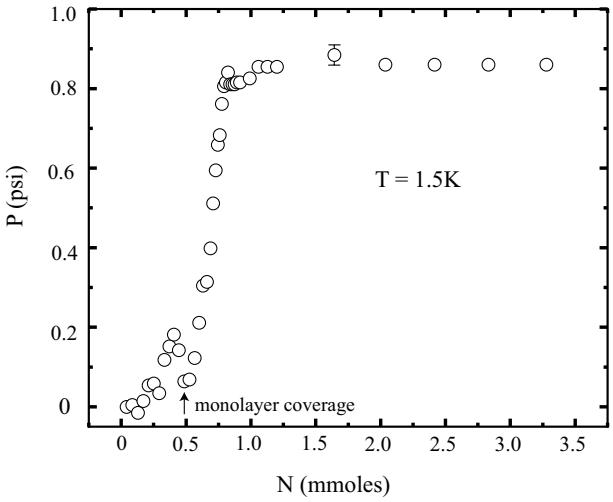

Fig. 1 In situ isotherm for ^{3}He adsorbed on MCM-41 at 1.5 K. Completion of the monolayer coverage marked by the indicator was identified from the existence of two distinct nuclear spin–spin relaxation times [16] (Color figure online)

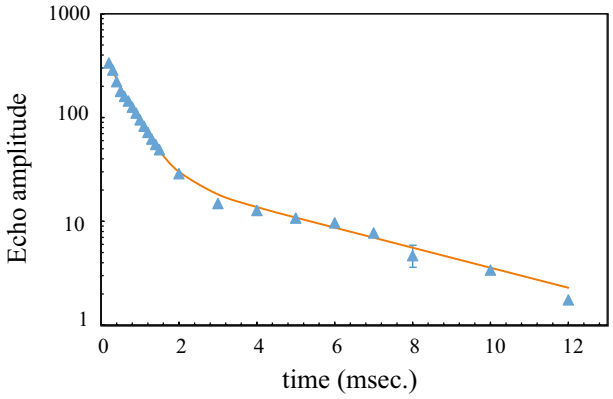

Fig. 2 Relaxation of ^{3}He NMR echoes at 2.5K, in an experiment without ^{4}He preplating, demonstrating two components: (i) a fast relaxing wall layer and (ii) a slow relaxing mobile contribution (7.3%) attributed to atoms in the center of the nanotubes [16]. The solid red line is a best fit for the sum of two independent relaxation times (Color figure online)

coverage for this preparation of MCM-41 was 0.495 mmoles. A small correction needs to be made to determine the ^{4}He coverage. This correction, which is expected to be of the order of 2% from studies of adsorption on grafoil [21], is not known for MCM-41. Taniguchi et al. [22] observed a difference of 17% for FSM-16, which has much smaller pores than MCM-41. This correction was not made in determining the ^{4}He coverage needed for a monolayer, and therefore, a small fraction of the wall remained uncovered completely by ^{4}He and was replaced by ^{3}He instead.

After warming and recooling, 0.495 mmoles of ^{4}He was admitted to the NMR cell for preplating. A small additional amount of ^{3}He was then added afterward to create a mobile core of atoms with a linear density of approximately 0.10 $(\text{Å})^{-1}$. This density would result in a Fermi temperature of 125 mK if the effective mass $m^* = 1.6$ m for 1D ^{3}He as is the case for 2D ^{3}He [23].

Standard $90°-\tau-180°$ pulsed NMR techniques were used to determine the temperature dependence of the dynamics of the ^{3}He in the interior of the MCM-41 nanotubes for applied magnetic fields of 1.5 T. Low-amplitude long-length RF pulses were used to minimize the RF heating, and the temperature of the NMR coil was allowed to float relative to the sample. With a separation time between RF pulses longer than the spin–lattice relaxation time, the echo at time $t = 2\tau$ was used to determine the nuclear spin–spin relaxation time T_2 by varying τ. The nuclear spin–lattice relaxation time, T_1, was measured by varying the repetition time between pulse sequences. Further experimental details on the cell design and NMR configuration can be found in reference [20].

3 Results

In addition to measuring the relaxation times, the echo amplitudes as a function of τ were extrapolated back to $\tau \sim 0$ to determine the magnetization M as a function of temperature T. As shown in Fig. 3, there is a strong deviation of the product MT from Curie law behavior and the detailed variation is appreciably stronger than that expected for a 1D Fermi gas, implying that there is still appreciable transverse motion for the ^{3}He atoms with a single-monolayer ^{4}He wall coating.

The strongest evidence of 1D behavior is given by the temperature dependence of the spin–lattice relaxation time shown in Fig. 4. The solid red line is taken from

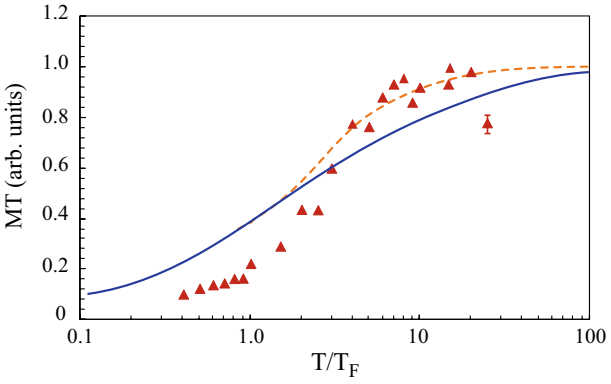

Fig. 3 Observed temperature dependence of the product of the nuclear spin magnetization M and temperature T as a function of temperature. The units are chosen to approach unity in the high-temperature limit. The solid line is the calculated dependence for a 1D Fermi system given in Fig. 2 of Ref. [11]. The broken line is the correction proposed by Matsushita et al. [11] that accounts for residual transverse motions and depends on the available space for transverse motion (Color figure online)

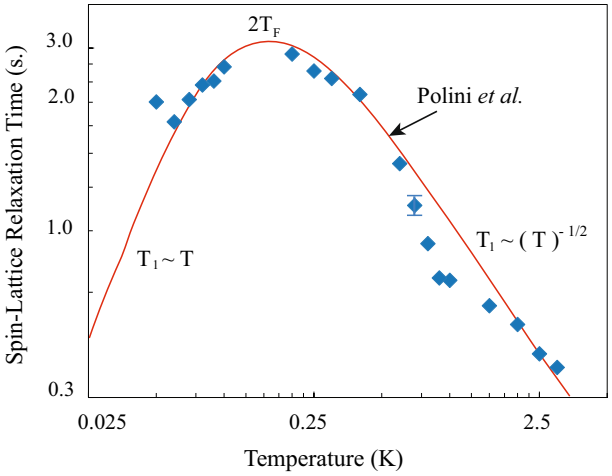

Fig. 4 Variation of the nuclear spin–lattice relaxation time with temperature for ^{3}He in MCM-41. There is a rounded maximum at $T = 2T_F$ as expected. The deviation from the behavior predicted by Polini et al. [24, 25] occurs at temperatures $T \sim 0.5$ K comparable to the energy for the first discrete excitation level for the transverse motion (Color figure online)

Polini et al. [24] but scaled to adjust T_F and the Yang parameter, $\gamma = (mg_{1D})/n\hbar^2$ (with g_{1D} the strength of the s-wave interaction potential and n the ^{3}He line density) to obtain the best overall fit. The fit shown in this figure is an improved fit compared to that given in Ref. [16] obtained by using a smaller value of γ. Polini et al. [24] showed that the temperature dependence of the spin-drag relaxation rate τ_{SD} at low temperatures ($T < T_F$) was given by

$$\tau_{SD}^{-1} = \frac{8}{9\pi}\gamma^2 \frac{T}{2T_F}\frac{k_B T_F}{\hbar} \tag{1}$$

for small nuclear spin polarizations. The linear temperature dependence of the nuclear spin–lattice relaxation at low temperatures is a signature of the 1D Fermi system. This can be simply understood using Fermi's golden rule to estimate the relaxation rate which shows that well below T_F the relaxation time is related to the nuclear spin polarization. A deviation from linear temperature dependence was predicted by Rainis et al. [25] for high spin polarizations which is beyond the present experimental results. The nuclear spin–lattice relaxation time is given by:

$$T_1 = \tau_{SD}^{-1}/M_2 \tag{2}$$

where M_2 is the NMR second moment. The best fit shown by the solid red line in Fig. 4 is obtained for a Fermi temperature $T_F = 95$ mK, $M_2 = 1.2\ 10^7 s^{-2}$, and $\gamma = 0.24$. The small value of γ deduced from this experiment is expected for a weak coupling [25], but a detailed theoretical calculation is needed to understand the value.

The value of M_2 is close to what is expected for a 1D ^{3}He system, but it is two orders of magnitude less than that reported by Yager et al. [13] who assumed their values were due to magnetic impurities in the wall. In our case, the ^{4}He monolayer considerably reduces the contribution from wall impurities.

The temperature dependence of the nuclear spin–spin relaxation time shown in Fig. 5 is very different to that seen for the spin–lattice relaxation time. This difference is expected because the spin–lattice relaxation is determined by the high-frequency spectral motions, while T_2 is determined by low-frequency excitations. The high-temperature behavior can be calculated for a simple model of gaseous diffusion [16] using a chemical potential $\mu = k_b T \ln(n\lambda_{dB})$ where the thermal de Broglie wavelength $\lambda_{dB} = \sqrt{2\pi\hbar^2/(mk_B T)}$. This model yields a $T^{3/2}$ dependence for T_2 as shown by the solid red line in Fig. 5.

The minimum observed at $T = 0.8$K is similar to the behavior observed by Matsushita et al. [12] who reported observing a broad minimum around 150 mK for low coverages, while at high coverages a plateau region was reported below 150 mK. The observation of a minimum is significant because the low temperature values of T_2 are therefore larger than the minimum and the value expected for a rigid lattice, which can be the signature of some residual motional narrowing of the T_2 values at low temperatures. This unusual behavior resembles that seen for dilute ^{3}He impurities in solid ^{4}He [26, 27]. Small amounts of ^{3}He in the wall layer could lead to ^{3}He-^{4}He exchange, and this would be temperature independent until vacancies are created by thermal activation. The vacancies are very mobile and interfere with the exchange motion of the ^{3}He atoms. The broken line corresponds to a vacancy thermal activation energy of 5.6 K.

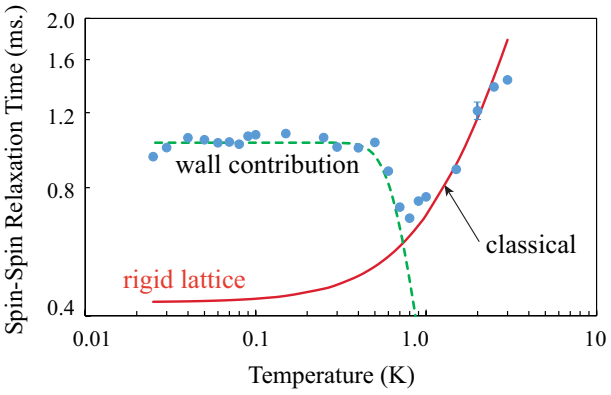

Fig. 5 Observed variation of the nuclear spin–spin relaxation time with temperature for ^{3}He in MCM-41. The solid red line is the temperature dependence calculated for a classical system [16]. The broken green line is for conjectured quantum tunneling of a small number of ^{3}He atoms in the ^{4}He wall layer with a downturn near 0.5K due to the formation of vacancies (Color figure online)

4 Conclusion

We have observed two new features for the temperature dependence of fundamental properties of ^{3}He constrained to the interior of ^{4}He plated nanotubes. Firstly, there is a strong reduction in the nuclear spin degeneracy below T_F, which is expected for a quasi-1D degenerate quantum fluid. The value of T_F is identified from previous measurements of the nuclear spin–lattice relaxation time [16]. Future experiments that further constrain the transverse freedom in the nanotubes will be needed to check agreement with the expected 1D temperature dependence. New information about the dynamics of the ^{3}He atoms was obtained from measurements of the nuclear spin–spin relaxation time which (in contrast to T_1 studies) probes the low-frequency spectrum of the ^{3}He motion. For the coverages of this experiment, we observe an unusual minimum in the relaxation time near $T = 0.8$ K, which is totally different from the temperature dependence observed for the nuclear spin–lattice relaxation time. This difference clearly shows that the dynamics cannot be described in terms of a unique correlation or diffusion time, and this is expected for a system governed by Tomonaga–Luttinger liquid physics. Future experiments are planned for samples using silver powder inter-dispersed throughout the MCM-41 to better thermalize the sample and at higher magnetic fields and lower temperatures which should reveal the expected deviation from linear T dependence at low temperatures.

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