NMR Studies of $^3$He Films on Boron Nitride

Y. Tang, N. S. Sullivan
Department of Physics, University of Florida, Gainesville, Fl 32611, USA
E-mail: sullivan@phys.ufl.edu

Abstract. We report the results of NMR studies of the dynamics of $^3$He adsorbed on hexagonal boron nitride. These studies can identify the phase transitions of the 2D films as a function of temperature. A thermally activated temperature dependence is observed for $2.6 < T < 8$ K compared to a linear temperature dependence for $0.7 < T < 2.6$ K. This linear dependence is consistent with that expected for thermal diffusion in a fluid for coverages of 0.4 - 0.6 of a monolayer.

1. Introduction
Helium-three monolayer and submonolayer films are of great interest because the different phases and microscopic dynamics that occur are dominated by quantum effects that lead to new phenomena in reduced dimensions at low temperatures[1, 2]. In addition the films are ideal for testing our understanding of the quantum dynamics and spin ordering in two dimensions from first principles[3]. At low temperatures it had been postulated that the large quantum mechanical zero-point kinetic energy of the $^3$He atoms could be sufficient to prevent the system from condensing as a 2D liquid in some scenarios[4], leading to a unique quantum gas at extremely low temperatures. Experimental studies by Bhattacharyya and Gasparini [5, 6] offered evidence for such a phase but the majority of experiments [7–9] and the most recent theoretical treatments[10–12] do not support the existence of a low temperature gas phase. Recent thermodynamic measurements by Sato et al. [13, 14], however, for $^3$He adsorbed on bare graphite (and on $^4$He plated graphite), have provided new evidence in support of a self-bound state for very low coverages at very low temperatures. We have carried out NMR studies at much higher coverages of 0.41 and 0.62 of a full monolayer and at higher temperatures to determine the microscopic dynamics of the $^3$He atoms and the mechanisms of diffusion at coverages near the fluid-solid phase transition region[12, 15]. At these coverages NMR studies by Crane and colleagues[16] for $^3$He on BN showed evidence of a mixed coverage of fluid and solid components with the solid melting near 1.6K to form a dense fluid state with appreciable orientational order imposed by the substrate. We have carried out studies using a much higher NMR frequency which should help distinguish between the fluid and solid components.

In addition to measuring the diffusion in the fluid phase, NMR studies can be used to determine the spin exchange rates in the solid phases. Below monolayer coverage, the $^3$He monolayer forms a commensurate $\sqrt{3} \times \sqrt{3}$ solid structure that provides a unique testing ground for the multi-particle exchange model [17, 18] invoked to explain the magnetic properties of bulk $^3$He and $^3$He films [15, 19, 20]. For example, coverages less than the ideal commensurate structure lead to a reduced probability of 3-particle exchange compared to the 2-particle exchange and
this results in a much higher effective magnitude for the overall tunneling rate that can be seen in the $^3$He nuclear spin lattice relaxation times[21].

2. Experimental considerations

We used powdered hexagonal boron nitride (h-BN)[22] as the substrate for the helium film[23]. h-BN has similar structure and dimensions to graphite but is an insulator rather than a semimetal and has a smaller magnetic susceptibility ($-4.8 \times 10^{-7}$ emu/g)[24] than graphite ($-170 \times 10^{-7}$ emu/g)[25]. The electron micrograph of Fig. 1 shows that the substrate material consists of an assembly of small platelets of sizes in the $0.5 - 2.0 \mu$m range and thicknesses of $0.05 - 0.10 \mu$m. The samples were prepared by baking under vacuum[26, 27] before being introduced to the sample chamber which contained a brush of fine copper wires that penetrated the powdered h-BN to ensure thermal contact with a rod extending from a dilution refrigerator. A precise amount of $^3$He gas was introduced to the sample to produce the desired coverage which was inferred from previous adsorption isotherm studies used to characterize the same material[26].

Pulsed NMR techniques were used to measure the $^3$He nuclear spin-spin and spin-lattice relaxation times. The NMR setup shown in Fig. 2 uses a tuned system matched at low temperatures to close to 50 $\Omega$. A $3\lambda/2$ $50 \Omega$ cable was used to connect the tuned circuit to a hybrid-tee bridge at room temperature that had a second fine tuning stage. The latter stage was important to correct for the small shift in tuning as the sample cell was cooled. A high magnetic field, corresponding to a Larmor frequency $\omega_L/(2\pi) = 200$ MHz, was chosen so that $\omega_L$ was much larger than the typical motional frequencies[28] of the $^3$He atoms. For this choice the relaxation times of the solid component are expected to be much higher than the fluid component as the exchange induced relaxation time in the solid grows exponentially with Larmor frequency[28]. This choice therefore simplifies the analysis of the relaxation data. (Crane et al.[16] used Larmor frequencies of 2.7 and 4.5 MHz.) The relaxation times were measured using standard $90^\circ - \tau - 90^\circ$ and $90^\circ - \tau - 180^\circ$ pulse sequences followed by signal averaging (50 - 5000 times) to obtain adequate signal/noise ratios.

3. Results

The decay of the NMR echoes following repeated pulse sequences as a function of repeat time $\tau_r$ show two distinct components, a fast component with a relatively large amplitude and a
slow component with a much smaller amplitude. A typical decay for the echo amplitude $E(\tau_r)$ is shown in Fig. 3 for $x = 0.62$ at $T = 1.9$K. These two components are expected from the results of Crane[16] for this temperature range if the $^3$He forms a mixed state of fluid and solid. The surprising result from this study is the relatively small amount of solid component for temperatures $T > 0.7$K. From the flat geometry of the BN platelets we would expect an adsorbed solid component at the edges (where there are much stronger adsorption sites) to correspond to $\sim 5\%$ of the total area. This “edge” component would appear to account for an appreciable fraction of the long relaxation time component.

![Figure 3. Typical decay observed for the NMR echo amplitudes for $x = 0.62$ at 1.9 K with $E(\infty) - E(\tau_r) = 121e^{-\tau_r/1.57} + 29e^{-\tau_r/11}$ shown by the solid line. The fast decay is attributed to a fluid component and the slower decay to a solid component.](image)

The observed temperature dependence of the nuclear spin-lattice relaxation times for the fast decay component of the relaxation is shown in Fig. 4 for two different coverages, 0.62 and 0.41 of a full monolayer. Three different temperature regimes are observed. In the high temperature regime, $2.6 < T < 8$ K, there is a clear thermal activation with an energy $E_A = 31 \pm 2$ K, corresponding to the binding of the $^3$He atoms to the surface and in good agreement with other studies[29]. The sharp minimum for the 0.62 coverage is a standard BPP minimum[30] given by $T_{1(\text{min})} \approx \omega_L/M_2$ where $M_2 = 1.8 \times 10^9$ s$^{-2}$ is the calculated NMR second moment for a full monolayer of $^3$He in BN (and includes the $^3$He-B and $^3$He-N nuclear spin-spin interactions).

The most interesting and unexpected region is for intermediate temperatures, $0.7 < T < 2.6$ K, for which a linear dependence on temperature is observed, and most remarkably there is very little variation in the magnitude of $T_1$ for an appreciable change in the amount of $^3$He added to the total surface coverage. These two features support a model where the surface is covered with patches of fluid of constant areal density but varying in overall size and co-existing with solid patches. Following Crane[16] the patches are believed to be nucleated at specific sites and grow continuously as the temperature decreases. If this region consisted of continuous fluid covering all the surface area of the h-BN platelets one would expect a very strong change in the absolute value of $T_1$ with $^3$He coverage since the NMR second moment $M_2$ scales as $\sum_{\text{pairs}(ij)} R_{ij}^6$. These studies show that the fluid component is close to constant in density but it is distinct from the dense self-bound liquid state observed by Sato et al.[13] for very low coverages. At low temperatures, $T < 0.7$ K, the solid component begins to dominate the relaxation, and we observe the onset of a stronger temperature dependence (shown by the dotted line in Fig. 4) which is attributed to the relaxation determined by the solid $^3$He to substrate interactions.

4. Discussion

The nuclear spin-lattice relaxation time $T_1$ is given by[31]

$$\frac{1}{T_1} = \frac{2}{3} M_2 \sum_n n^2 J_n(n\omega_L)$$
where the $J_n(\omega)$ are the normalized spectral densities of the fluctuations of the $^3$He-$^3$He dipole-dipole interactions at frequency $\omega$. (Note that for the spectral densities we neglect the contributions of unlike spin-spin interactions such as $^3$He-$^{14}$N because, (i) they are reduced relative to the $^3$He-$^3$He contribution by $[\gamma(14N)/\gamma(3He)]^2 \sim 10^{-2}$ and $[\gamma(11B)/\gamma(3He)]^2 \sim 10^{-1}$, and (ii) as a result of their long relaxation times in the solid platelet, their spin magnetization would be saturated and thus ineffective[32] as far as the $^3$He relaxation is concerned. If $J_n$ can be characterized by a simple correlation time, $\tau$, then we have a simple Lorentzian $J(\omega) = \tau/[1 + (\omega \tau)^2]$. We have analyzed the data in terms of a sum of three relaxation rates $T_1^{-1} = T_{1H}^{-1} + T_{1I}^{-1} + T_{1L}^{-1}$ for the high, intermediate and low temperature regions, respectively. For the high temperature gas-like region we used a Lorentzian form with $\tau_H = 6.8 \times 10^{-8} \exp(31/T)$ which leads to the BPP minimum at 7.1 K. For temperatures below the minimum we can take $\omega_L \tau > 1$ and analyze the lower temperature data in terms of $T_1^{-1} = (4M_2/3\omega_L^2)(\tau_L^{-1} + \tau_I^{-1})$.

The best fit to the data for the intermediate temperature range is shown by the solid lines in Fig. 4. For this fit $\tau_I = (1.7 \pm 0.5)T^{-1}10^{-9}$ s (red line of Fig. 4) for coverage $x_1 = 0.62$, and $(1.4 \pm 0.5)T^{-1}10^{-9}$ s (blue line of Fig. 4) for coverage $x_2 = 0.41$. The linear temperature dependence is consistent with that reported by Crane (Fig. 7.2.2.14 of Ref. [16]) and interpreted in terms of a fluid component. The low temperature data had poor signal/noise and was fit empirically to $\tau_L = 2.1 \times 10^{-10}T^3$.

The most recent calculation of the spin diffusion for a fluid Fermi system in two dimensions has been given by Bruun[33] who finds a diffusion constant $D = k_BT/(4\pi^2 n h I_D)$ where $n$ is the areal density and $I_D = 2/[\ln(E_B/k_BT) - 0.42]^2 + \pi^2] \sim 0.22$. The characteristic time $\tau_c = r_n^2/D$ where $r_n$ is the mean separation of the $^3$He atoms. We find from Bruun’s theory $\tau_c = 2.4 T^{-1}10^{-9}$ s in reasonable agreement with the experimental results for $\tau_I$. The important point in this analysis is that both $\tau_I$ and $M_2$ are independent of the fractional coverage if the fluid forms patches (or puddles) of liquid. If the $^3$He were to spread uniformly across the platelets in this temperature regime there would be a much stronger concentration dependence which is not observed.

5. Conclusion
The linear temperature dependence and very weak variation of the nuclear spin-lattice relaxation times at intermediate temperatures with the number of $^3$He atoms adsorbed for monolayer films with fractional coverages $x = 0.41$ and $x = 0.62$ on hexagonal boron nitride support the interpretation that this phase consists of patches of liquid $^3$He at very close to constant areal density, with a small fraction of solid that becomes complete at 0.7K. Although the fluid density appears to be constant in this region there is no evidence that this is an incompressible liquid
state such as reported for much lower coverages and at lower temperatures by Sato et al.[13].

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