Relaxation of Nuclear Magnetization of Liquid ^{3}He in Confined Geometries

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We present a model for the relaxation of the magnetization of ^{3}He in contact with a solid substrate, leading to an explanation of the generally seen linear dependence of T_1 on temperature. The temperature dependence of the ^{3}He relaxation time results from the localization of the relaxation to the interfacial layer of ^{3}He. The model, tested for experiments on a fluorocarbon substrate, fits the data over three decades of temperature, with one adjustable parameter.

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The role played by surfaces in enhancing the thermal relaxation of liquid ^{3}He magnetization has been a perplexing problem since the earliest measurements of these properties in the liquid.[1] The question is closely related to the important technical problem of heat transfer between liquid ^{3}He and solids. Kelly and Richardson emphasized the role of the surface through studies of liquid ^{3}He confined in the pores of powdered materials. They found that the nuclear magnetic relaxation time, T_1, of the ^{3}He passed through a broad maximum around 1 K and decreased in proportion to the temperature below this.[2] This unexpected observation of a rate which increased with decreasing temperature was confirmed in measurements on a large variety of materials.[3,4] These measurements indicated that this behavior is probably universal. In bulk liquid the relaxation time should actually increase as T^{-2} as a consequence of its Fermi-liquid behavior. In experiments performed with a full cell of ^{3}He in contact with a substrate, relaxation rates were observed to increase with the ratio of surface to volume. Following a seminal theory of the role of magnetic interaction in heat transfer by Leggett and Vuorio,[5] theories by Beal-Monod and Mills[6] and by Albers and Wilkins[7] noted the importance of magnetic coupling to spins in the substrate as a mechanism for relaxing the ^{3}He magnetization.

Further measurements of the magnetic properties revealed that at very low temperatures the liquid ^{3}He displayed magnetic susceptibility which was strongly enhanced over the expected Pauli value seen in bulk-liquid measurements. Hydrodynamic[8] and magnetic[9] measurements on thin films of He have shown that the first layer of He on a substrate is immobile. In many respects this layer can be thought of as a solid layer with a density similar to that in bulk solid ^{3}He at a pressure of 100 bars. The experiments of Ahonen *et al.*[10,11] convincingly argued that the enhanced susceptibility could be attributed to several layers of ^{3}He adjacent to the substrate. The surface susceptibility obeyed a Curie-Weiss law with a Weiss constant Δ of order $\frac{1}{2}$ mK. Bozler and co-workers[12,13] introduced a model of two-dimensional ferromagnetism to account for their measurements of the surface magnetism. Their measurements of a shift of the nuclear resonance frequency demonstrated the localization of the enhanced magnetization.

The measured equilibrium magnetization M_{tot}^0 in an applied field H_0 is fitted by the equation

$$M_{\text{tot}}^0 = M_{\text{Pauli}} + fCH_0/(T-\Delta), \tag{1}$$

where the equilibrium magnetization at zero temperature of the bulk liquid is M_{Pauli} and f is the fraction of the total number of ^{3}He atoms in the surface layers. The susceptibility of the bulk liquid extrapolated to zero temperature, χ_0, has been measured[14] and defines the magnetic Fermi temperature T_{F}^{**} through the relation $\chi_0 = \frac{3}{2}(C/T_{\text{F}}^{**})$ where C is the Curie constant for ^{3}He. For our experiments, $T_{\text{F}}^{**} = 540$ mK.[1] We define a temperature T_{es}, the temperature at which the excess susceptibility originating in the solid layer becomes comparable to that of the bulk liquid: $T_{\text{es}} = fCH_0/M_{\text{Pauli}} = \frac{2}{3}fT_{\text{F}}^{**}$. Equation (1) can then be rewritten

$$M_{\text{tot}}^0/M_{\text{Pauli}} = 1 + T_{\text{es}}/(T-\Delta). \tag{2}$$

Bulk solid ^{3}He also displays a Curie-Weiss susceptibility, although the intercept has a different value and sign from those seen in the solid layer. Recent measurements[15] in bulk solid give $\Delta = -1.6$ mK, while we measure $\Delta = 0.55$ mK for the solid layer. T_{es} was determined from continuous-wave susceptibility measurements to be 1.8 mK. The fraction of atoms f displaying a Curie-Weiss susceptibility is then 5.0×10^{-4}.

The relaxation of the ^{3}He magnetization in confined geometries occurs at the substrate surface.

Displacing the ^{3}He from the surface with a monolayer of ^{4}He reduces the relaxation rates by an order of magnitude. Spin transport in the liquid and across the liquid-solid ^{3}He interface is sufficiently rapid that the bottleneck is the surface relaxation process. Mass diffusion in liquid ^{3}He is extremely fast; the time for diffusion across a 2000-Å pore is of the order of nanoseconds at 1 mK. The time scale for spin transport across the interface between the liquid ^{3}He and the solid layer is not well understood. It is thought to be an atomic exchange process occurring on the nanosecond scale.[16] T_1 in confined geometries occurs on the time scale of seconds or tenths of seconds and the bulk relaxation on the scale of hundreds of seconds.

A universal feature of measurements of T_1 in confined geometries is the proportionality of T_1 to temperature ($T < 0.3$ K). This is a straightforward consequence of the localization of a *temperature-independent* relaxation process to the surface layer. The boundary relaxation process becomes more efficient as the temperature decreases because the equilibrium surface magnetization becomes large while the liquid polarization remains constant.

The magnetization current, j, from the liquid into the solid layer contributes to the rate of change of surface magnetization: $dM_s/dt = -\rho(M_s - M_s^0) + j$. The rapidity of spin transport by atomic exchange across the interface ensures continuity of the quantity[17] $(M - M^0)/\chi_0$. Dividing by the applied field H_0, we get

$$\frac{M_s - M_s^0}{M_s^0} = \frac{M_{\text{liq}} - M_{\text{liq}}^0}{M_{\text{liq}}^0} = \frac{M_{\text{tot}} - M_{\text{tot}}^0}{M_{\text{tot}}^0}. \qquad (3)$$

The bulk relaxation rate is small so that $dM_{\text{liq}}/dt \simeq -j$. Using Eq. (3) to get an expression for the rate of change of the total magnetization,

$$dM_{\text{tot}}/dt = dM_s/dt + dM_{\text{liq}}/dt = -\rho(M_s - M_s^0)$$
$$= -\rho(M_s^0/M_{\text{tot}}^0)(M_{\text{tot}} - M_{\text{tot}}^0),$$

we can now identify $1/T_1$:

$$-\frac{1}{M_{\text{tot}} - M_{\text{tot}}^0}\frac{dM_{\text{tot}}}{dt} = \frac{1}{T_1} = \rho\frac{M_s^0}{M_{\text{tot}}^0}. \qquad (4)$$

In experiments in our laboratory,[18-21] we have been able to characterize the surface process which determines the rate ρ for one particular case. We have studied a system consisting of fluorocarbon powder substrate, DLX-6000,[19] immersed in liquid ^{3}He. The details of this study are available elsewhere[20,21] but we will state some of our results. In the system we studied, the dipole-dipole interaction between the ^{3}He and ^{19}F spins couples[4,18,19,22] the two spin reservoirs. The exchange motion of the ^{3}He atoms introduces fluctuations into this dipole-dipole interaction. Fluctuations at the Larmor frequency will induce resonant transitions in the nuclear spin state which alter the Zeeman energy of the spin. The spectrum of fluctuations of the interactions will be described by the spectral density function, $J(\omega)$. Because the dipole-dipole energy depends on the relative spatial position of the two dipoles, the change in Zeeman energy can be taken up by the exchange energy reservoir.

Relaxation through motion of unlike dipoles in a homogeneously mixed system is well known.[23] If we ignore bulk relaxation processes and consider the ^{3}He and ^{19}F spin systems to be relaxed only by dipolar motion at the interface we obtain

$$\begin{pmatrix} \dot{H} \\ \dot{F} \end{pmatrix} = A \begin{pmatrix} H - H^0 \\ F - F^0 \end{pmatrix}, \qquad (5)$$

where we refer to ^{3}He and ^{19}F magnetizations, respectively, as H and F. The elements of the 2 by 2 matrix A are products such as in Eq. (4). For the case of dipole-dipole relaxation the rate parameter ρ_{He} is $\rho_{\text{He}} = \langle 1/r^6 \rangle_{\text{He}} (\gamma_{\text{He}}\gamma_{\text{F}}h)^2 J(\omega)$. ρ_{F} is obtained by interchanging the subscripts He and F. In this expression r is the distance between dipoles so that $\langle 1/r^6 \rangle = \pi\alpha/2a^4$, where α is the surface density of dipoles and a is the distance of closest approach between dipoles. The Larmor frequencies are given by $\omega_{\text{He}} = 2\pi\gamma_{\text{He}}H_0$ and $\omega_{\text{F}} = 2\pi\gamma_{\text{F}}H_0$. The spectral density function, $J(\omega)$, will be discussed below. In the low-temperature limit the ^{19}F T_1 ($T_{1,\text{F}}$) greatly exceeds that of the ^{3}He ($T_{1,\text{He}}$). In this case the eigenvectors of the coupled system are the two relaxation rates: $1/T_{1,\text{He}} = \rho_{\text{He}} \times (H_s^0/H_{\text{tot}}^0)$ and $1/T_{1,\text{F}} = \frac{3}{4}\rho_{\text{F}}(F_s^0/F_{\text{tot}}^0)$. The coupling between the ^{19}F and ^{3}He spin systems predicted by Eq. (5) has been explicitly observed in the experiments by Friedman, Millet, and Richardson[18] and Hammel *et al.*[4]

The temperature dependence of the rate constants is determined by the spectra density fluctuation $J(\omega)$, which is not well understood in the context of the two-dimensional layer of solid ^{3}He. Two similar systems whose spectral density functions provide some insight are that for hydrodynamic motion in a two-dimensional film of ^{3}He which has been discussed by Cowan[24] and that for bulk solid ^{3}He. A feature common to both of these is that they are temperature independent. In this case, the entire temperature dependence of the observed relaxation rate must arise from the factor which multiplies the rate constant. The spectral density function which Cowan proposes is inversely proportion-al to frequency, a feature which would explain the frequency dependence which is observed experimentally. Additionally, the magnitude of the rate which we would predict for our system using this function is in good agreement with our measurements.

For the substrate ^{19}F spins, the surface magnetization and the bulk magnetization have the same temperature dependence so that the ratio of the two is temperature independent. This is in agreement with our measurements in which the ^{19}F relaxation time changes by less than a factor of 2 over two decades of temperature.

However, for liquid ^{3}He the ratio is temperature dependent in the temperature regime below T_F^{**} (where the liquid displays a Pauli susceptibility) and above the temperature T_{es}. Below T_{es}, it again becomes temperature independent when the magnetization of the overlying liquid becomes small compared to that of the surface. From Eqs. (2) and (4) we would expect the ^{3}He relaxation rate to go as

$$\frac{1}{T_{1,\mathrm{He}}} = \rho_{\mathrm{He}} \frac{T_{es}/(T-\Delta)}{1+T_{es}/(T-\Delta)} = \rho_{\mathrm{He}} \frac{1}{1+(T-\Delta)/T_{es}}. \quad (6)$$

If we use a spectral function similar to that of Cowan with $\rho_{\mathrm{He}} = \mathrm{const} \times \omega^{-1}$ we obtain the dashed lines shown in Fig. 1 when the constant is adjusted to the value 2.6×10^7. This corresponds in Cowan's model to a plausible distance of closest approach between ^{19}F and ^{3}He dipoles of approximately 2 Å. The remaining parameters Eq. (6) are independently determined by experiment.

The ratio H_s^0/H_{tot}^0 is only given by Eq. (2) for $T << T_F^{**}$ where the liquid susceptibility is constant. This factor becomes temperature independent at higher temperatures since the susceptibility of the liquid also obeys a Curie law above T_F^{**}. At low temperatures, the total magnetization is dominated by the magnetization of the surface layer. Well above T_F^{**} the magnetization which is to be relaxed by the surface layer is that of the liquid. The ratio of the two relaxation times in these limiting cases should be $f = 3T_{es}/2T_F^{**}$, the fraction of atoms in the surface layer. In this case we can write an approximate interpolation formula:

$$\frac{1}{T_{1,\mathrm{He}}} = \rho_{\mathrm{he}} \frac{1+3T/2T_F^{**}}{1+(T-\Delta)/T_{es}}. \quad (7)$$

This is plotted as a solid line in Fig. 1. In our analysis we have neglected the relaxation due to the dipole-dipole interaction between ^{3}He spins in the surface solid layer. The relaxation rate due to this mechanism may be comparable to the similar process resulting from the dipole-dipole interaction with the ^{19}F spins and has the same temperature dependence. In the case of systems where the substrate contains fewer magnetic spins which interact with the ^{3}He spins, the relaxation by means of the ^{3}He-^{3}He coupling may dominate. As the temperature and frequency dependence are determined by the same spectral density function, these would be unchanged. Only the magnitude of the T_1 would be affected.

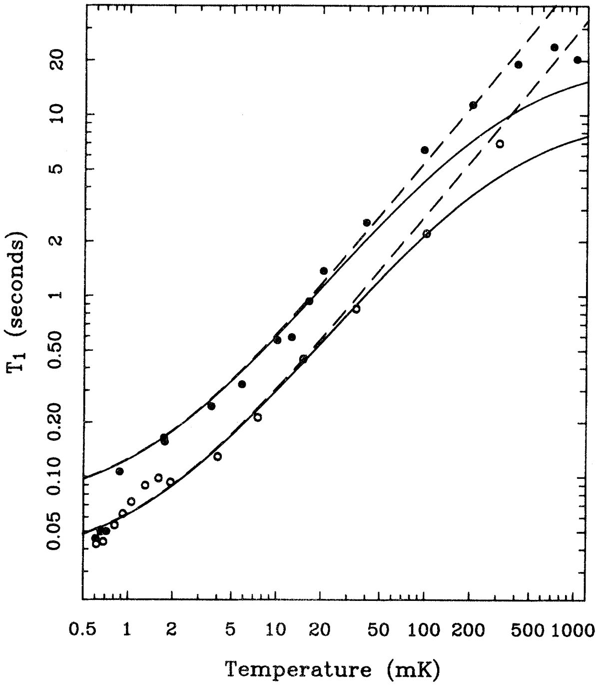

FIG. 1. Comparison of the predicted ^{3}He T_1 to our data taken at 2.067 MHz (open circles) and 4.135 MHz (closed circles). The single adjustable parameter adjusts the prediction to match the data at a single temperature and frequency. The dashed line results if the liquid susceptibility is taken to be temperature independent; the solid line takes into account the temperature dependence of the susceptibility at temperature comparable to or greater then T_F^{**}. T_{es} was determined by performing continuous-wave susceptibility measurements on the ^{3}He. The drop in the data below 1 mK results from the onset of superfluidity (Ref. 4) in the liquid ^{3}He.

We have discussed measurements of nuclear spin relaxation in a system of liquid ^{3}He in contact with a fluorocarbon substrate. Fluctuations in the dipole-dipole interaction across the liquid-solid interface resulting from the exchange motion of the ^{3}He atoms in the surface are responsible for the relaxation. The temperature dependence of the ^{3}He

T_1 results from the localization of the relaxation to the surface layer of ^{3}He which obeys a Curie-Weiss susceptibility. The total liquid susceptibility which must be relaxed by the surface is independent of temperature. The increasing rate at which spins are relaxed in the region of large magnitude results in a relaxation rate which increases with decreasing temperature. With use of a single adjustable parameter, our data are well fitted by the model over three decades of temperature.

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