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### Nuclear spin-lattice relaxation in $^3\text{He}$ - $^4\text{He}$ mixtures

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Spin-lattice relaxation times  $T_1$  in  $^3\text{He}$ - $^4\text{He}$  solutions have been measured at temperatures between 1.5 and 3.3 K and for molar concentrations of 10%, 1%, and 0.1%. Little concentration dependence was observed. Below the lambda point,  $T_1$  increases rapidly with increasing temperature; above, it is fairly constant. The data are well described by a wall relaxation mechanism, in which  $T_1$  depends upon the time for the  $^3\text{He}$  spins to diffuse to the walls. We discuss a theory for diffusion in dilute solutions at high temperatures where the diffusion coefficient is primarily determined by  $^3\text{He}$ -roton scattering.

Spin-polarized  $^3\text{He}$  and  $^3\text{He}$ - $^4\text{He}$  mixtures have attracted recent attention because of the striking dependence of the transport coefficients on the magnetic polarization.<sup>1</sup> Tests of theoretical predictions require large polarizations (in excess of thermal equilibrium) which persist over extended periods of time. These conditions are difficult to realize experimentally, and a proper understanding of the fundamental processes governing spin relaxation is necessary to make progress on this problem.

Relaxation of nuclear magnetization in liquid  $^3\text{He}$  is strongly affected by interactions occurring at the walls of the container.<sup>2</sup> Relaxation rates for pure liquid  $^3\text{He}$  in contact with high surface area substrates are reduced by coating the solid surfaces with  $^4\text{He}$  (Ref. 3). This raises several important questions. How are the relaxation processes in  $^3\text{He}$  affected by the presence of  $^4\text{He}$ ? Under what conditions will a bulk relaxation mechanism dominate over a surface mechanism? Some of these effects may be elucidated by NMR measurements of the  $^3\text{He}$  nuclear spin-lattice relaxation time  $T_1$  in  $^3\text{He}$ - $^4\text{He}$  mixtures.

We have performed  $T_1$  measurements in  $^3\text{He}$ - $^4\text{He}$  solutions with  $^3\text{He}$  molar concentrations of 10%, 1%, and 0.1% over a temperature range between 1.5 and 3.3 K and found little concentration dependence in the  $T_1$  values. The results are well described by a model in which  $T_1$  is determined by the time required for  $^3\text{He}$  magnetization to diffuse to the walls where very rapid relaxation occurs. We show that the results are essentially proportional to the normal fluid density of pure  $^4\text{He}$ , and discuss a theory in which the diffusion coefficient is primarily determined by  $^3\text{He}$ -roton scattering at these temperatures and concentrations.<sup>4</sup> We also observe surprisingly fast wall relaxa-

tion rates.

Earlier experimental studies of  $T_1$  in  $^3\text{He}$ - $^4\text{He}$  solutions have focused on the behavior below the lambda point<sup>5</sup> or immediately around it.<sup>6</sup> The variability in the results is substantial.

The nuclear relaxation time  $T_1$  was measured by NMR in a 3.0 T magnetic field. The pulse sequence consisted of a train of 4- $\mu\text{sec}$  saturation ( $\sim 90^\circ$ ) pulses followed by a single 4- $\mu\text{sec}$  pulse occurring after a variable time delay  $\tau$ . The separation between the saturation pulses was 1 sec a time shorter than  $T_1$ . The resulting free-induction decay (FID) signal was digitized and integrated for each value of  $\tau$  to obtain the magnetization as a function of  $\tau$ .  $T_1$  was determined by fitting an exponential to the magnetization recovery curve,  $M(\tau) = M_0[1 - A \exp(-\tau T_1)]$ , where the adjustable parameters are  $M_0$ , the equilibrium magnetization;  $A$ , a factor ( $\sim 1$ ) which compensates for incomplete initial saturation; and  $T_1$ , a time constant which we call the spin-lattice relaxation time, even in the absence of a bulk relaxation mechanism.

Temperatures between 1.5 and 3.3 K were obtained by pumping on a  $^4\text{He}$  pot and were regulated by an electrical heater to within  $\pm 15$  mK. Pure  $^3\text{He}$  (99.8% pure) and the solutions were introduced into a cylindrical cell molded from Stycast 1266 (Emerson & Cuming, Inc. Gardena, CA) with a 0.2-in radius and a 0.62-in. length. The rf coil surrounding the cell was embedded in the epoxy. Thermal contact between the cell and the  $^4\text{He}$  pot was achieved by heat sinking the coil to a copper can which was attached to the pot by a copper braid. The temperature of the cell was monitored with a carbon glass resistor (CGR) mounted near the can. The CGR was calibrated by measuring

the saturated vapor pressures of pure  $^3\text{He}$  with a capacitive sensor (Baratron). For most of the  $T_1$  measurements, the cell was open to the Baratron. (There was little difference in  $T_1$  when the cell was closed.)

The values of  $T_1$  for  $^3\text{He}$ - $^4\text{He}$  solutions at saturated vapor pressure are shown in Fig. 1 for 10%, 1%, and 0.1% concentrations. The relaxation times are independent of molar concentration above 1.5 K to within the experimental accuracy  $\pm 10\%$ . Below the lambda point,  $T_1$  increases rapidly with increasing temperature; above, it remains fairly constant.

In this system, two primary mechanisms for nuclear relaxation may occur:  $^3\text{He}$ - $^4\text{He}$  scattering in the bulk liquid<sup>7</sup> or  $^3\text{He}$  interactions with the cell wall.<sup>2</sup> If a bulk relaxation mechanism is dominant, then  $T_1$  should exhibit the following behavior<sup>7</sup> at temperatures much greater than the Fermi temperature:

$$\frac{1}{T_1} = \frac{n_3}{T^{1/2}} \frac{(2\pi^5)^{1/2}}{3} \frac{m^*^{1/2}(\gamma^2 \hbar)^2}{a_0^2} = \frac{X}{11} \frac{1}{T^{1/2}}, \quad (1)$$

where  $T_1$  has units of hours,  $X$  is the molar percent concentration of  $^3\text{He}$ ,  $a_0$  is the atomic radius ( $\sim 2 \text{ \AA}$ ),  $n_3$  is the number of  $^3\text{He}$  atoms per volume,  $m^*$  is the effective mass of  $^3\text{He}$  in the presence of  $^4\text{He}$ , and  $\gamma$  is the gyromagnetic ratio. For pure  $^3\text{He}$ , this relation yields a value for  $T_1$  of about 800 sec at 2.5 K, which agrees with previously reported measurements.<sup>8</sup> For a 10% solution,  $T_1$  is predicted to be 1.7 h; for 1%,  $T_1 = 17$  h; for 0.1%,  $T_1 = 170$  h. These long bulk relaxation times were not observed in this experiment.

A wall relaxation mechanism, however, does account for the data. We compared our observations with a model in which  $T_1$  is determined by the time for the  $^3\text{He}$  spins to diffuse to the walls, where all relaxation is assumed to occur. By solving the three-dimensional diffusion equation with cylindrical boundaries, a solution for the time

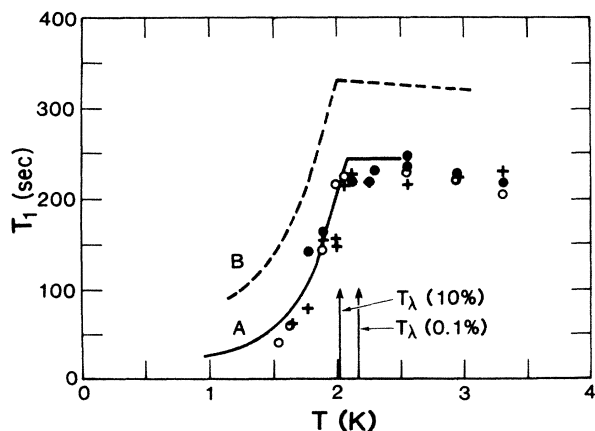


FIG. 1. Spin-lattice relaxation time  $T_1$  as a function of temperature for  $^3\text{He}$ - $^4\text{He}$  solutions. Experimental data for three molar concentrations  $X$  are shown: 10% ( $\bullet$ ), 1% ( $+$ ), and 0.1% ( $\circ$ ). The solid curve (A) represents values of  $T_1$  obtained from fits to the solution of the diffusion equation, using experimental values for  $D$  with  $X=9\%$  (Ref. 9). Similarly, the dashed curve (B) pertains to  $X=13.7\%$ , but  $D$  was measured by different authors.<sup>10</sup>

evolution of the magnetization can be constructed:

$$M(t) = M_0 \left\{ 1 - \frac{8}{\pi^2} \sum_{k,m} \frac{[1 - (-1)^k]^2}{k^2 x_m^2} \times \exp\{-D[(k\pi/L)^2 + (x_m/R)^2]t\} \right\}, \quad (2)$$

where  $D$  is the diffusion coefficient;  $R$  is the radius of the cell;  $L$  is the cell length;  $k$  and  $m$  are indices ranging from one to infinity; and  $x_m$  is the  $m$ th root of the Bessel function  $J_0(x)$ . Using values of the spin-diffusion coefficient reported in the literature for  $^3\text{He}$ - $^4\text{He}$  solutions,<sup>9-12</sup> the magnetization as a function of time may be obtained.

Although diffusive behavior is not strictly exponential, values for  $T_1$  may be estimated by fitting an exponential to the magnetization curve, Eq. (2). The leading term ( $k=m=1$ ) in the summation is at least five times greater than the next one ( $k=1, m=2$ ). To first approximation,  $T_1$  may be regarded as the reciprocal of the diffusion coefficient modified by a geometrical factor. Because of noise at large values of  $\tau$ , our magnetization recovery curves are consistent with the recovery predicted by the solution to the diffusion Eq. (2) as well as a pure exponential.

The  $T_1$  values obtained from fits to the solution of the diffusion equation are shown with the data in Fig. 1. Curves A and B represent the  $T_1$  values estimated from the diffusion coefficients for 9% (Ref. 9) and 13.7% (Ref. 10) solutions. Curve A (9%) coincides with the data. Other measurements of  $D$  by the same authors (Chang and Rorschach) for 5% and 14% solutions yield little concentration dependence of  $T_1$  at these high temperatures. Curve B (13.7%), however, has the same overall shape as our data, but is displaced upward by about 100 sec. The measurement of  $D$ , performed by different authors (Harrison and Hatton) did not extend to lower concentrations.

It is important to note that the values of the spin-diffusion coefficient differ in the literature, although they were all obtained by spin-echo methods. For example, Chang and Rorschach's data for 14% solutions exceed Harrison and Hatton's data for 13.7% solutions by a factor of 2. Nevertheless, the overall qualitative high concentration and temperature behavior of  $D$  are the same in both cases; below the lambda point,  $D$  rapidly decreases with increasing temperature and depends on concentration, but above the lambda point, the diffusion curves for different concentrations merge and are relatively insensitive to temperature. At low concentrations (i.e.,  $X < 10\%$ ),  $D$  has essentially no concentration dependence<sup>11</sup> above 1.5 K. This is in agreement with our  $T_1$  data, assuming a wall relaxation mechanism.

We can understand the temperature dependence of  $T_1$  using a theory developed by Khalatnikov and Zharkov<sup>4</sup> for the diffusion of a dilute gas of  $^3\text{He}$  in superfluid  $^4\text{He}$ . The diffusion of the  $^3\text{He}$  impurity atoms is limited by impurity-rotor scattering with the cross section  $\sigma_{ir}$ . At high temperatures,  $T > 1.7$  K, the thermally excited rotors form a dense gas through which the  $^3\text{He}$  atoms diffuse. A classical mean-free-path argument for the diffusion coefficient  $D$  yields  $D \sim \bar{v}_i l$ , where  $\bar{v}_i = \frac{8}{3} (2k_B T /$

$\pi m_i)^{1/2}$  is the average velocity of the  $^3\text{He}$  atoms;  $l^{-1} \sim N_r(T) \sigma_{ir}$  is the inverse of the mean-free path;  $m_i$  is the mass of a  $^3\text{He}$  atom in  $^4\text{He}$ ; and  $N_r(T)$  is the number of density of the rotons. A similar structure appears in the full expression for  $D$ , derived by Khalatnikov and Zhar'kov, for  $n_3 \ll N_r(T)$ :

$$D = \frac{32}{9\pi} \frac{p_0^2}{3m_3} \frac{1}{\rho \bar{v}_i \sigma_{ir}} \frac{\rho}{\rho_n(T)}, \quad (3)$$

where  $\rho_n(T) \approx p_0^2 N_r(T) / 3k_B T$  is the normal fluid density of pure  $^4\text{He}$ ,  $\rho = 0.145 \text{ g/cm}^3$  is the  $^4\text{He}$  density,  $p_0 = 1.91 \hbar \text{ \AA}^{-1}$  is the roton momentum, and  $m_3$  is the bare mass of  $^3\text{He}$ . The impurity-roton scattering cross section is

$$\sigma_{ir} = \frac{m_i m}{2\pi \hbar^4} |U_{ir}|^2, \quad (4)$$

where  $m = m_i \mu / (m_i + \mu)$  and  $\mu$  is the roton "mass." The potential  $U_{ir}$  is an adjustable parameter with a very weak temperature dependence, and may be expressed as  $U_{ir} = 2\pi \hbar^2 a_{ir} / m$ , where  $a_{ir}$  is a scattering length. An estimate of  $D$  based on these expressions can be compared with measured values of  $D$  to obtain a value for  $a_{ir} \sim 5\text{--}6 \text{ \AA}$ . These expressions represent the *collective* motion of the  $^3\text{He}$  and  $^4\text{He}$  atoms; the scattering does not occur between hard-sphere He atoms of radius  $2 \text{ \AA}$ .

The essential aspects of our  $T_1$  data are revealed in Eq. (3) for the diffusion coefficient. From Eq. (2),  $T_1$  can be expressed approximately as  $T_1 = s^2 / D$ , where the geometrical factor is  $1/s^2 = (\pi/L)^2 + (x_1/R)^2$ . Therefore,  $T_1(T)$  is proportional to  $\rho_n(T)$ . For  $1.7 \text{ K} < T < 2.17 \text{ K}$ , the temperature dependence of  $T_1$  is dominated by  $\rho_n$ ; thus,  $T_1$  varies as  $e^{-\Delta/T}$ . For  $T \geq T_\lambda$ ,  $\rho_n(T)$  equals  $\rho$  and  $T_1 \sim T^{1/2}$ . Thus, a kink in  $T_1$  should exist at the lambda point. In Fig. 2, the  $T_1$  data and the experimental values of the normal fluid density  $\rho_n$  for pure  $^4\text{He}$  are shown as a function of temperature.<sup>13</sup> The  $\rho_n$  values, which were measured in  $\text{g/cm}^3$ , are multiplied by an estimated factor 1580 to indicate the relationship between  $\rho_n$  and the  $T_1$  data. This value can also be calculated from the expression for  $T_1$ , where  $s = 0.2 \text{ cm}$  and  $a_{ir} \sim 5\text{--}6 \text{ \AA}$ . As the  $^3\text{He}$  concentration increases, the lambda point shifts towards decreasing temperatures. At lower temperatures, where the roton density is small, or at higher concentrations, our model predicts that  $T_1$  should be more affected by  $^3\text{He}$ - $^4\text{He}$  scattering, and hence should depend on concentration. For comparison, we show in Fig. 2 our measurements for pure  $^3\text{He}$  (dashed line); obviously, the presence of  $^4\text{He}$  has a profound effect on  $T_1$ .

Two related assumptions are made in this model for the diffusion coefficient: (1) The rotons are well defined just below and just above  $T_\lambda$ , and (2) the cross section is independent of temperature. The first point implies that roton-impurity scattering is possible above  $T_\lambda$ .<sup>14</sup> The second point is not strictly correct. In neutron scattering experiments on liquid  $^4\text{He}$ , the width of the roton spectral peak broadens continuously with temperature through  $T_\lambda$ . This implies that  $\sigma_{ir}$  depends on temperature. Although this dependence is much weaker than  $\rho_n(T)$ , it competes with the temperature dependence of  $\bar{v}_i$  above  $T_\lambda$ . Also at sufficiently high temperatures, hard-sphere scattering is important with a cross section  $\sigma_{34} = 4\pi a_3^2 = 5 \times 10^{-15} \text{ cm}^2$ ,

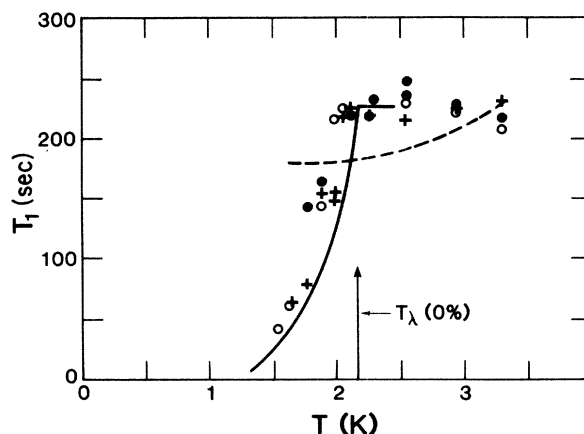


FIG. 2. Comparison of the  $T_1$  data for dilute solutions with the normal fluid density  $\rho_n$  for pure  $^4\text{He}$ . The symbols are the same as in Fig. 1. The solid curve represents measured values (Ref. 13) of  $\rho_n$  multiplied by a constant 1580 (see text). The dashed curve is experimental data for pure  $^3\text{He}$ .

this is 30 times smaller than  $\sigma_{ir}$ . Thus, the theory predicts that  $T_1$  is proportional to  $T^{1/2}$  for low concentrations over a small temperature range above  $T_\lambda$ , but decreases at high temperatures as  $T^{-1/2}$ . Within the accuracy of our experiment, we cannot distinguish this subtle behavior.

One surprising feature of our measurements is the exceptionally large relaxation rate ( $1/T_1$ ) at the walls. The rate implied by our data is at least  $2 \times 10^4 \text{ sec}^{-1}$ . But for pure  $^3\text{He}$  in contact with high surface area fluorocarbon substrates (teflon beads),<sup>15</sup> for example, the wall relaxation rate is about  $100 \text{ sec}^{-1}$ . (These experiments were performed at  $\sim 0.1 \text{ T}$ .) In solutions, this rate should be reduced even further, since the  $^4\text{He}$  would coat the cell walls. This discrepancy with our data is not understood.

Another noteworthy feature is the absence of an anomaly in our  $T_1$  data at the lambda point. A few  $T_1$  experiments have revealed unusual behavior at higher concentrations<sup>6</sup> near  $T_\lambda$ . Careful measurements of the spin-diffusion coefficient, however, do not exhibit anomalous behavior.<sup>9-12</sup>

In summary, we have found that the relaxation rate in  $^3\text{He}$ - $^4\text{He}$  solutions depends strongly on temperature and is approximately proportional to the spin-diffusion coefficient. This supports the view that the rate at which  $^3\text{He}$  magnetization relaxes is limited by the time for spins to diffuse to the walls of the container. At these temperatures and concentrations, the dominant scattering process occurs between  $^3\text{He}$  atoms and rotons. We show theoretically that  $T_1$  is basically proportional to the normal fluid density of pure  $^4\text{He}$ . The expected suppression of wall relaxation by a coating of  $^4\text{He}$  on the container walls was not seen for our cell material (Stycast 1266 epoxy). In fact, the wall relaxation rate is surprisingly rapid, and must be substantially reduced for experiments on highly polarized liquid  $^3\text{He}$  and  $^3\text{He}$ - $^4\text{He}$  mixtures.

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