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## Nuclear Magnetic Relaxation of $^3\text{He}$ Gas. II. $^3\text{He}$ - $^4\text{He}$ Mixtures

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Longitudinal relaxation times  $T_1$  have been measured in  $^3\text{He}$ - $^4\text{He}$  gas mixtures, using pulsed NMR, in the temperature range 0.6-15 K. Helium-3 number densities of the order of  $10^{24}$  atoms  $\text{m}^{-3}$  were used. Relaxation takes place on or near the walls of the Pyrex sample cells and measurements of  $T_1$  give information about the surface phases. A cryogenic precoating of solid molecular hydrogen was used to reduce the helium-substrate binding energy from  $\sim 100$  K on Pyrex to  $\sim 13$  K for  $^3\text{He}$  and 15 K for  $^4\text{He}$ . The  $T_1$  data at high temperatures were similar to those observed previously in the pure  $^3\text{He}$ - $\text{H}_2$  system. The presence of  $^4\text{He}$  generally caused  $T_1$  to rise on cooling below 2 K due to the preferential adsorption of  $^4\text{He}$  over  $^3\text{He}$  at the surface. However,  $^3\text{He}$  atoms that go into quasiparticle states in the superfluid helium film can be an extra source of relaxation. In uncleaned cells, relaxation probably takes place in quasiparticle states at the free surface of the superfluid film, which are bound with an energy of  $5.1 \pm 0.3$  K. Baking the Pyrex cells under vacuum and rf discharge cleaning the walls before sealing in the sample gas were found to increase the bulk gas  $T_1$  by two or three orders of magnitude. In a cleaned, sealed cell a  $T_1$  of  $\sim 8$  h was measured at 7.7 MHz and 0.8 K. In this case relaxation is probably occurring two or three helium layers away from the helium-hydrogen interface. It may be possible to observe a predicted minimum in the intrinsic dipolar  $T_1$  of the bulk gas by using a  $^4\text{He}$  wall coating to suppress wall relaxation effects (which usually dominate the nuclear relaxation of the bulk gas).

### 1. INTRODUCTION

It is important to study and gain understanding of nuclear magnetic relaxation processes in  $^3\text{He}$  gas for a number of reasons: (1) long nuclear spin-lattice relaxation times  $T_1$  are required if one is to produce a nuclear spin-polarized gas of  $^3\text{He}$  atoms and keep the gas in a nonequilibrium state for long enough to make measurements on it (a gas in which all of the

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We studied relaxation processes in the gas using pulsed NMR at  $\sim 1$  and  $\sim 7.5$  MHz. A cooled GaAsFET preamplifier that has been previously described<sup>6</sup> was used in order to achieve the required sensitivity at the lower  $^3\text{He}$  number densities. The experimental setup and sample preparation have been given in detail in a companion paper,<sup>7</sup> hereafter called I.

In I we presented our data on pure  $^3\text{He}$ , with and without cryogenic wall coatings, both in sealed and unsealed cells. That work also includes much of the theoretical background needed for the present work and it contains many references to earlier work on relaxation in  $^3\text{He}$  gas performed by other groups.

In the present work we present data on  $^3\text{He}$ - $^4\text{He}$  mixtures, using  $\text{H}_2$  wall coatings, and, based on our findings, we comment on the prospects of observing the  $T_1$  minimum in the intrinsic dipolar relaxation time of the bulk gas predicted by Shizgal.<sup>4,5</sup> Some of our mixture data have been reported briefly.<sup>8</sup> Before presenting the mixture data, we summarize the pertinent results of paper I.

## 2. SUMMARY OF THE THEORY OF RELAXATION PROCESSES AND OF WORK ON PURE HELIUM-3

### 2.1 Relaxation Processes

A number of bulk gas relaxation processes must be considered when interpreting  $T_1$  data: (1) the dipole-dipole interaction between nuclear spins, which is effective during binary collisions; (2) the spin-rotational coupling effect; and (3) the diffusion of spins in the macroscopic field gradients that exist across the sample due to imperfections in the coil winding of the NMR magnet solenoid. In all our experiments these bulk relaxation mechanisms were insignificant compared with wall relaxation mechanisms, primarily because of the low  $^3\text{He}$  number densities used. We consider fully the possibility of observing interesting features of the bulk dipolar  $T_1$  (mechanism 1) in Section 6.

In almost all of the range of temperatures and  $^3\text{He}$  number densities covered in our experiments the observed bulk relaxation was caused by processes occurring at or near the walls of the sample cell, where there are strong local magnetic fields due either to paramagnetic impurities embedded in the glass or adsorbed on the surface, or to the nuclear dipole moments of the neighboring  $^3\text{He}$  adatoms on the surface.

When wall relaxation is important, a number of regimes must be considered, depending on the surface cleanliness of the wall, the correlation time for local magnetic fields at the surface  $\tau_c$ , and the sticking time of adatoms on the surface  $\tau_s$ .

In the "dirty" wall limit the surface is sufficiently dirty that  $T_1$  is determined by the time needed for an atom to diffuse to the walls (the mean free path for  $^3\text{He}$  atoms was always much shorter than the cell dimensions in our experiments, so we were always in the diffusive limit), since in a much shorter subsequent time it will make enough collisions with the wall to flip its spin. For a spherical sample cell, this time is of the order of  $R^2/\pi^2 D$ , where  $R$  is the radius of the sample cell and  $D$  is the three-dimensional diffusion coefficient for  $^3\text{He}$  atoms. This time is at least two orders of magnitude smaller than the observed longitudinal relaxation times for all number densities, temperatures, and surface treatments used; therefore, we conclude that the data were taken in the "clean wall" limit.

If the cell walls are sufficiently free of magnetic impurities, an average  $^3\text{He}$  atom will diffuse to the wall, but will make too few collisions with the wall to relax its spin before returning to the bulk gas; therefore, the average atom must make many visits to the wall before its spin is flipped. Collisions most effective in causing relaxation are those that result in adsorption. The sticking time for  $^3\text{He}$  atoms in an adsorbed phase is given by

$$\tau_s = 4(N_{3Ad}/A)(V/N_{3B})(1/S\langle v \rangle) \quad (1)$$

where  $N_{3B}$  is the number of  $^3\text{He}$  atoms in the bulk,  $N_{3Ad}$  is the number in the adsorbed phase,  $V$  is the volume of the cell,  $A$  is its effective surface area,  $S$  is the probability that a colliding atom will stick to the surface, and  $\langle v \rangle = (8k_B T/\pi m)^{1/2}$  is the mean thermal velocity of atoms in the bulk gas.

We must consider two cases in this clean wall limit: (1)  $\tau_s \gg \tau_c$  and (2)  $\tau_s \ll \tau_c$ . If the sticking time for spins in the adsorbed phase is much greater than the correlation time of local fields at the surface (case 1), then there is a characteristic relaxation time in the adsorbed phase,  $T_{1Ad}$ . If  $\tau_s \ll T_{1Ad}$ , then the relaxation time observed is just  $T_{1Ad}$  divided by the fraction of time an average spin spends in the adsorbed phase:

$$T_1 = T_{1Ad}(N_{3B}/N_{3Ad}) \quad (2)$$

provided that  $N_{3B} \gg N_{3Ad}$ .

If the sticking time is much less than the correlation time of local fields that would be seen by an adsorbed spin if  $\tau_s$  was infinite (case 2), then  $\tau_s$  effectively becomes the correlation time and one can write for the observed  $T_1$

$$\begin{aligned} T_1^{-1} &= \gamma^2 \langle \Delta B_{loc}^2 \rangle \tau_s (N_{3Ad}/N_{3B}) \\ &= \gamma^2 \langle \Delta B_{loc}^2 \rangle (4V/A\langle v \rangle S) (N_{3Ad}/N_{3B})^2 \end{aligned} \quad (3)$$

assuming that  $\omega_0 \tau_s \ll 1$ , where  $\omega_0$  is the Larmor frequency, and that

$\gamma^2 \langle \Delta B_{\text{loc}}^2 \rangle \tau_s^2 \ll 1$ , where  $\langle \Delta B_{\text{loc}}^2 \rangle$  is the mean square local field at the surface and  $\gamma$  is the nuclear gyromagnetic ratio of  $^3\text{He}$ .<sup>10</sup>

At high temperatures, where there is only a small fraction of a complete helium monolayer adsorbed on the surface, the ratio  $N_{3\text{Ad}}/N_{3\text{B}}$  can be obtained by taking the bulk phase to be an ideal 3D gas in the classical limit and the adsorbed phase to be an ideal classical 2D gas. Equating the chemical potentials of the gases, one obtains

$$N_{3\text{Ad}}/N_{3\text{B}} = \lambda_3(A/V)(m_3^*/m_3) \exp(\Delta W_3/k_B T) \quad (4)$$

where  $m_3^*$  is the effective mass of the  $^3\text{He}$  adatom,  $m_3$  is the mass of the bulk  $^3\text{He}$ ,  $\Delta W_3$  is the adatom-substrate binding energy, and  $\lambda_3 = h(1/2\pi m_3 k_B T)^{1/2}$  is the thermal de Broglie wavelength for  $^3\text{He}$  atoms, which is 10 Å at a temperature of 1 K. The ratio  $N_{3\text{Ad}}/N_{3\text{B}}$  is a function of temperature, but is independent of  $N_{3\text{B}}$ . On cooling,  $N_{3\text{Ad}}$  increases (we assume that  $N_{3\text{B}}$  remains unaltered) and the observed  $T_1$  [given either by eq. (2) or (3)] decreases. A complete monolayer will be formed at a temperature  $T$  given approximately by

$$k_B T = \Delta W_3 / \ln(Vs_0/N_{3\text{B}}\lambda_3) \quad (5)$$

where  $s_0$  is the areal density of helium at monolayer completion. Once a monolayer has formed, Eq. (4) is no longer applicable and  $N_{3\text{Ad}}$  becomes relatively insensitive to temperature and bulk  $^3\text{He}$  number density. The observed longitudinal relaxation time then becomes either proportional to  $n_{3\text{B}} = N_{3\text{B}}/V$  or to  $n_{3\text{B}}^2$ , depending on whether case 1 or case 2 is applicable, given that  $T_{1\text{Ad}}$  in Eq. (2) is independent of  $N_{3\text{Ad}}$  (which is true if relaxation is taking place by single-particle processes).

Thus far we have assumed that  $^4\text{He}$  is not present in the system. It is clear from Eq. (5) that in order to delay the formation of a  $^3\text{He}$  monolayer on cooling one must choose a substrate with a low binding energy. The theoretical estimate of the binding energy for a  $^3\text{He}$  atom on a semiinfinite surface of solid molecular hydrogen is  $\sim 13$  K.<sup>9</sup> This value is consistent with measurements made in Paris<sup>10</sup> and with our data<sup>7</sup> (only a few  $\text{H}_2$  layers are needed to prevent the van der Waals potential of the Pyrex from showing through<sup>10</sup>). This value is approximately an order of magnitude smaller than the binding energy for helium on Pyrex. Use of a cryogenic coating of  $\text{H}_2$  therefore delays the formation of a helium monolayer on cooling and results in an increase in the value of  $T_1$  that is observed at a given temperature. If long relaxation times are required at temperatures below  $\sim 2$  K, then  $^4\text{He}$  is the ideal coating to use, since  $^4\text{He}$  is adsorbed in preference to  $^3\text{He}$  on cooling. The effect of  $^4\text{He}$  in the system is discussed fully in Section 3. We first summarize our pure  $^3\text{He}$  data.

## 2.2. Results for Pure $^3\text{He}$

It was possible to study the thermodynamics of  $^3\text{He}$  adsorbing on  $\text{H}_2$  by using an unsealed cell.  $T_1$  was measured as a function of temperature and bulk number density. The cryogenic wall coating of solid  $\text{H}_2$  was found to delay the formation of a  $^3\text{He}$  monolayer on cooling.  $T_1$  was seen to drop on cooling and our measurements were consistent with a binding energy of  $\sim 13$  K for a  $^3\text{He}$  atom to a hydrogen surface. At temperatures below  $\sim 2$  K a complete  $^3\text{He}$  monolayer formed on the  $\text{H}_2$  coating. Once the monolayer was formed,  $T_1$  was independent of temperature, but was proportional to the bulk  $^3\text{He}$  number density. This suggests that  $\tau_s \gg \tau_c$  and Eq. (2) is applicable. It also suggests that  $N_{3\text{Ad}}$  is independent of bulk number density as  $n_3$  is varied over a factor of almost 60. This is consistent with a simple approximate calculation, which yields the value of  $6.3 \times 10^{-2} \text{ \AA}^{-2}$  for  $s_0$  for  $^3\text{He}$  on  $\text{H}_2$  (the completed  $^3\text{He}$  monolayer is therefore thought to be a dense fluid).<sup>7</sup> Taking this value for  $s_0$  and taking the effective surface area of the cell to be twice its geometrical area (there is evidence that for Pyrex cleaned with a discharge the ratio of effective area to geometrical area is not larger than 4),<sup>10</sup> we obtained a value for  $T_{1\text{Ad}}$  of  $\sim 20$  msec. Since this value is the same order of magnitude as that obtained in this cell before the  $\text{H}_2$  coating was added, we believe that the mean square local fields at the surface were approximately the same in both cases. This means that the local fields were probably caused by macroscopic paramagnetic impurities in the glass (local fields caused by surface impurities of microscopic dimensions would be greatly reduced a few  $\text{H}_2$  layers from the Pyrex surface).

Baking the Pyrex sample cells under vacuum and using an rf discharge in  $^3\text{He}$  gas to clean the walls before sealing in the sample gas were found to increase the bulk gas  $T_1$  by up to three orders of magnitude. Once a  $^3\text{He}$  monolayer was formed on the  $\text{H}_2$  coating in these cleaned, sealed cells the measured  $T_{1\text{Ad}}$  was  $\sim 2$  sec at 7.5 MHz. Relaxation at the surface is thought to be dominated by the nuclear dipolar interaction between adsorbed spins. Using a two-dimensional relaxation theory, the data, over a wide range of Larmor frequencies, are consistent with a correlation time of  $\sim 2 \times 10^{-9}$  sec and this time is consistent with the idea that the adsorbed phase of  $^3\text{He}$  on  $\text{H}_2$  really is a dense fluid and not a solid (the completed monolayer for  $^3\text{He}$  on graphite, which is more strongly bound than on  $\text{H}_2$ , is solid<sup>11</sup>).

## 3. MIXTURES OF HELIUM-3 AND HELIUM-4

In this work we present and discuss relaxation time data taken using Pyrex cells containing mixtures of  $^3\text{He}$ ,  $^4\text{He}$ , and  $\text{H}_2$ . In our notation we

use subscripts 3 and 4 to distinguish between the two helium isotopes and use no numerical subscript when considering, for example, the total bulk number density,  $n = n_3 + n_4$ .

Longitudinal relaxation times were measured at temperatures between 0.6 and 15 K. The  $^3\text{He}$  number densities  $n_3$  used were of the order of  $10^{24}$  atoms  $\text{m}^{-3}$ . The bulk  $^3\text{He}$  number densities remained almost constant over the temperature range used, since the bulk liquefaction point for  $^3\text{He}$  was never reached.

In all experiments a cryogenic precoating of solid molecular hydrogen was used. Enough hydrogen was added to form  $\sim 20$ - $30$  geometrical layers of solid  $\text{H}_2$ . This coating was formed on the surface of the Pyrex cell at all temperatures below  $\sim 6.5$  K. It served to delay the formation of a helium layer on cooling, since it reduced the helium-substrate binding energy.

The  $^4\text{He}$  number densities  $n_4$  used were in the range  $\sim 10^{22}$  to  $\sim 5 \times 10^{25}$  atoms  $\text{m}^{-3}$  at temperatures above the  $^4\text{He}$  liquefaction temperature. The role of the  $^4\text{He}$  is to lengthen the observed  $T_1$  below  $\sim 2$  K. It can do so in a number of ways: (1) by dilution; (2) by preferential adsorption; and (3) by the buildup of a superfluid film on the surface of the  $\text{H}_2$ . At high temperatures, where only a small fraction of a completed helium monolayer is on the surface, the addition of  $^4\text{He}$  has no effect on the observed  $T_1$ , since the ratio  $N_{3B}/N_{3Ad}$  is unaltered. However, at lower temperatures, where a complete helium monolayer has formed, addition of  $^4\text{He}$  will serve to dilute the  $^3\text{He}$  atoms in the adsorbed phase, thus reducing  $N_{3Ad}$ , but the number of spins in the bulk  $N_{3B}$  will be almost unchanged. As  $N_{3B}/N_{3Ad}$  increases due to addition of  $^4\text{He}$ , the observed  $T_1$  increases [Eq. (2) or Eq. (3)]. This will happen regardless of any preferential effect. In practice, at low temperatures  $^4\text{He}$  atoms are more tightly bound to a substrate than  $^3\text{He}$  atoms, since their zero-point motion is less. This results in an increase in the ratio  $N_{3B}/N_{3Ad}$  over that obtained from the dilution effect alone. Also, on further cooling, the observed  $T_1$  will increase as the preferential effect becomes more pronounced. The difference in binding energies,  $\Delta W_4 - \Delta W_3 \approx 2$  K, is calculated for single-atom states in the holding potential of a semiinfinite crystal of  $\text{H}_2$ .<sup>9</sup> This difference results from the extra zero-point motion of the  $^3\text{He}$  atom in the direction normal to the surface. However, when a helium film starts building up, one must also consider zero-point motion in the lateral directions and this will result in a larger preferential effect. At low temperatures a superfluid film of  $^4\text{He}$  will form on the hydrogen-coated sample cell walls and this may further exclude  $^3\text{He}$  atoms from the region where relaxation is taking place.

The buildup of the superfluid film on the surface might have a detrimental effect on the observed relaxation times. The  $^3\text{He}$  atoms can go into quasiparticle states in the film<sup>12</sup> and on its surface,<sup>13</sup> causing the number

of spins close to the surface (within  $\sim 100 \text{ \AA}$  of the  $\text{H}_2$  surface) to increase. If local magnetic fields are strong in this region near the surface, the relaxation could be caused by spins entering these quasiparticle states and in this case the observed  $T_1$  would decrease on addition of  $^4\text{He}$ .

### 3.1. Thickness of the $^4\text{He}$ Film

In I we deduced (by equating the chemical potentials of the bulk and the adsorbed phase) that at the temperatures used in our experiments only one monolayer of  $^3\text{He}$  would be formed on the  $\text{H}_2$  surface, and our experimental data were consistent with this. Since the adatom-substrate van der Waals interaction potential is the same for both helium isotopes, one might expect  $^4\text{He}$  also to form one monolayer on cooling. However, for a given number density,  $^4\text{He}$  liquefies at a higher temperature than  $^3\text{He}$  and in our experiments a superfluid film built up on the hydrogen-coated surface at temperatures below 2 K.

The thickness of the superfluid film as a function of temperature can be estimated using the Frenkel-Halsey-Hill (FHH) isotherm<sup>14</sup>:

$$P_4/P_{40} = \exp[-(\Delta\alpha/T)(D_0/d)^3] \quad (6)$$

where  $\Delta\alpha = \alpha_{\text{H}_2} - \alpha_{\text{He}}$  and  $D_0$  are van der Waals parameters, the attractive part of the adatom-substrate potential being given by

$$V(z) = -\alpha_{\text{sub}} k_B (D_0/z)^3$$

$P_4$  is the pressure of the  $^4\text{He}$  in equilibrium with a slab of thickness  $d$  on a hydrogen substrate and  $P_{40}$  is the saturated vapor pressure of  $^4\text{He}$  at a temperature  $T$ .

The film thickness as a function of temperature is calculated by putting  $N_4$  of the  $^4\text{He}$  atoms into a cell of volume  $V$  and effective surface area  $A$ . Ignoring the effect of any  $^3\text{He}$  present in the system, the partial pressure of  $^4\text{He}$  in the cell is given by

$$P_4 = (N_4 - n_{4l}Ad) k_B T / V \quad (7)$$

where  $n_{4l}$  is the number density of bulk liquid  $^4\text{He}$ .

Substituting for  $P_4$  in Eq. (6), we obtain

$$(d/D_0)^3 = (\Delta\alpha/T) / \{\ln[VP_{40}/(N_4 - n_{4l}Ad)k_B T]\} \quad (8)$$

Values of  $d$  as a function of temperature have been calculated<sup>16</sup> from this equation using our experimental parameters and taking  $D_0 = 3.6 \text{ \AA}$ ,  $\Delta\alpha = 7 \text{ K}$ ,<sup>9,15</sup> and  $n_{4l} = 2.18 \times 10^{28} \text{ m}^{-3}$ . The calculation shows that for all cells but two (which only contained enough  $^4\text{He}$  to form  $\sim 15$  layers or less on the surface, given that the effective surface area was twice the geometrical one\*)

\* The effective surface area for adsorption is taken to be twice the geometrical surface area throughout this work.<sup>10</sup>

the film thickness builds up rapidly on cooling, the temperature at which this happens being given approximately by that at which  $(N_4/V)k_B T$  is equal to the saturated vapor pressure of  $^4\text{He}$ . The gravitational potential energy of a  $^4\text{He}$  atom is equivalent to  $\sim 5 \text{ mK m}^{-1}$ , which, for a 2-cm-diameter cell, corresponds to a  $100 \mu\text{K}$  advantage in putting a  $^4\text{He}$  atom at the bottom rather than the top of the cell. The substrate-atom potential is such that if the film is between 100 and 150 Å thick, it is energetically more favorable for an atom to go onto the bottom of the sample chamber than to thicken the film at the top, and a liquid drop will form.

#### 4. THE ROLE PLAYED BY THE HELIUM-4

When bulk nuclear magnetic relaxation takes place as spins visit the walls of the sample chamber, the observed longitudinal relaxation time is determined in part by  $N_{3Ad}$ , i.e., the number of spins in the region near the walls where there are strong local magnetic fields causing relaxation.

At high temperatures the addition of  $^4\text{He}$  has no effect on the ratio  $N_{3B}/N_{3Ad}$  (it is easy to see this by equating the chemical potentials of the gas mixtures) and theoretically it should have no effect on  $T_1$ . At temperatures where interactions in the adsorbed phase become important, the addition of  $^4\text{He}$  dilutes the adsorbed phase, leaving  $N_{3B}$  almost unchanged. This causes  $T_1$  to increase. Preferential adsorption of  $^4\text{He}$  over  $^3\text{He}$  will enhance this expulsion of spins from the adsorbed layer and will cause the observed  $T_1$  to rise further on cooling.<sup>17</sup>

Once a superfluid film forms on the  $\text{H}_2$  surface, the situation becomes more complicated. We consider this situation below.

##### 4.1. $^3\text{He}$ Quasiparticles in Superfluid $^4\text{He}$ : The Effect of an External Potential

In the low-temperature regime a superfluid  $^4\text{He}$  film builds up on the surface of the sample cell as the sample is cooled. This film builds up on the sample cell walls at a temperature above that of bulk phase separation, as observed by Laheurte.<sup>18</sup> Once the film has built up, it is possible for  $^3\text{He}$  atoms to go into quasiparticle states in the bulk of the film or on its surface (at the gas-liquid interface). Our experimental parameters were such that the bulk  $^3\text{He}$  number density was not significantly changed when bulk liquefaction of  $^4\text{He}$  occurred.

The low-temperature thermodynamic properties of dilute mixtures of  $^3\text{He}$  in bulk superfluid  $^4\text{He}$  are described in a review article by Ebner and

Edwards.<sup>12</sup> We use much of their notation in the following. The situation is modified somewhat by the presence of a wall, which provides an external potential. We follow closely the analysis of Himbert and Dupont-Roc<sup>19,24</sup>. The energy change when a single <sup>3</sup>He atom initially at rest and far away is added to some stationary liquid <sup>4</sup>He is given by

$$\varepsilon(\mathbf{p}) = -E_3 + (p^2/2m_3^*) \quad (9)$$

where  $-E_3$  is the energy with which the impurity is bound in the liquid and  $m_3^*$  is its effective mass.  $m_3^*$  is known from experiment to be  $\sim 2.3 m_3$ .<sup>12</sup> The energy  $E_3$  is a function of the <sup>3</sup>He concentration  $x_3$  and of the chemical potential of the <sup>4</sup>He,  $\mu_4$ . We consider the limit  $x_3 \rightarrow 0$  and use the relation<sup>12</sup>

$$dE_3/d\mu_4 = -(1 + \alpha) \quad (10)$$

where  $(1 + \alpha)$  is the ratio of the volume occupied by a <sup>3</sup>He atom to that occupied by a <sup>4</sup>He atom in the liquid.  $\alpha$  is positive due to the extra zero-point energy of the <sup>3</sup>He atom. It is a slowly varying function of  $x_3$ ,  $T$ , and pressure  $P$ . We take it to be constant and use a value of 0.25 (that which corresponds to a temperature of  $\sim 1$  K and zero  $x_3$  and  $P$ ). Integrating Eq. (10) at  $x_3 = 0$ , we obtain

$$\begin{aligned} E_3(P, T) &= E_3(P=0, T=0) - (1 + \alpha)[\mu_4(P, T) - \mu_4(P=0, T=0)] \\ &= E_{30} - (1 + \alpha)[\mu_4(P, T) + L_4] \end{aligned} \quad (11)$$

where  $L_4 = 7.17$  K is the latent heat of <sup>4</sup>He at zero temperature and  $E_{30} = 2.8$  K is the quasiparticle binding energy at zero  $T$  and  $P$ .<sup>12</sup>

We now introduce an external potential  $V(z)$ , which is that due to the van der Waals interaction between the helium atoms and the substrate minus that created by the helium which the substrate has replaced;  $z$  is the distance from the substrate along the surface normal. The potential energy of a <sup>3</sup>He quasiparticle is altered in two ways by this external potential: (1) the potential  $V(z)$  leads to a density variation in the <sup>4</sup>He film, the density being a maximum near the surface, and this causes a change in the quasiparticle binding energy through Eq. (11); and (2) the external potential contributes directly to the quasiparticle binding energy. We can consider the density variation in the fluid due to the external potential as being similar to a pressure variation and replace  $\mu_4(P, T)$  in Eq. (11) with  $\mu_4(T) - V(z)$ , where  $\mu_4(T)$  is a constant throughout the film, i.e., independent of  $z$ . The <sup>3</sup>He quasiparticle binding energy thus obtained must then be augmented by  $-V(z)$  to give

$$\begin{aligned} -E_3(z, T) &= V(z) - \{E_{30} - (1 + \alpha)[(\mu_4(T) - V(z) + L_4)]\} \\ &= -E_{30} - \alpha V(z) + (1 + \alpha)[\mu_4(T) + L_4] \end{aligned} \quad (12)$$

If  $V(z) < 0$ , the term  $-\alpha V(z)$  provides a repulsive part to the potential of a <sup>3</sup>He quasiparticle in liquid <sup>4</sup>He. This equation tells us how the potential

energy of a  $^3\text{He}$  quasiparticle varies with its position in the film. We make use of this equation in Section 5.

#### 4.2. Surface Quasiparticle States

There are  $^3\text{He}$  quasiparticle states that exist at the surface of the film. Andreev<sup>20</sup> proposed the existence of these states in order to explain the large reduction in the surface tension of pure superfluid  $^4\text{He}$  at low temperatures that resulted from the addition of small quantities of  $^3\text{He}$ . The surface tension data could be explained by assuming that surface quasiparticle states exist at the gas-liquid interface with a potential energy 2.2 K lower than that of the states in the bulk<sup>13</sup>. The energy change in putting a  $^3\text{He}$  atom from outside the film into a surface quasiparticle state is

$$\varepsilon(\mathbf{p}) = -E_{3s} + (p^2/2m_{3s}^*) \quad (13)$$

where  $E_{3s} = 2.8 + 2.2 \text{ K} = 5 \text{ K}$  and the surface quasiparticle effective mass  $m_{3s}^*$  is  $\sim 1.4m_3$ .

The existence of surface quasiparticle states was verified theoretically by Lekner<sup>21</sup> and the most recent calculations of the binding energy are in good agreement with experiment (see ref. 13 for a review of the subject and other references). Experiments on films less than 50 Å thick<sup>22</sup> have shown that the difference in the binding energies of the surface and the bulk quasiparticle states might be less than 2.2 K for thin films.

### 5. EXPERIMENTAL RESULTS AND INTERPRETATION

In this section we present relaxation time data for  $^3\text{He}$ - $^4\text{He}$ - $\text{H}_2$  mixtures in open and sealed cells. Transverse relaxation was dominated in all cases by diffusion of spins in the macroscopic field gradient across the sample. This mechanism is discussed briefly in I. We restrict our discussion here to longitudinal relaxation. A rigorous cleaning procedure was used on the sealed cells, which in general produced much longer  $T_1$  than those observed with the open geometry (for which no rigorous cleaning was attempted). In almost all cases wall relaxation processes dominated the longitudinal relaxation.

#### 5.1. Longitudinal Relaxation Times in $^3\text{He}$ - $^4\text{He}$ Gas Mixtures in an Open Sample Chamber with a Cryogenic Wall Coating of Solid Molecular Hydrogen

We measured  $T_1$  using pulsed NMR at 7.5 MHz. The experimental setup and sample preparation are described in detail in paper I. In all

experiments enough hydrogen was added to form  $\sim 20$  geometrical layers on the walls of the 2-cm-diameter Pyrex cell and filling capillary. A cryogenic wall coating of solid  $H_2$  was formed at temperatures below  $\sim 6.5$  K.

We measured  $T_1$  as a function of temperature for various  ${}^3\text{He} : {}^4\text{He}$  ratios (ratios and concentrations are defined in terms of numbers of atoms throughout this work). Once gas had been added, the valve to the sample cell was closed and measurements were made, keeping the number of atoms in the cell constant. The bulk  ${}^3\text{He}$  number density  $n_3$  was almost constant with temperature.

Increasing amounts of  ${}^4\text{He}$  were added to the cell, which was initially filled with pure  ${}^3\text{He}$  with  $n_3 = 3.1 \times 10^{24} \text{ m}^{-3}$ . The results are shown in Fig. 1. The pure  ${}^3\text{He}$  data exhibit the features mentioned in Section 2. The  $T_1$  dropped on cooling as  ${}^3\text{He}$  atoms were adsorbed on the  $H_2$  coating and then reached a plateau once a complete helium monolayer had formed. In this low-temperature plateau region  $T_1$  was proportional to  $n_3$  for pure  ${}^3\text{He}$  measurements. Once a complete monolayer of  ${}^3\text{He}$  had formed, the ratio  $N_{3B}/N_{3Ad}$  was  $\sim 750$ . The pure  ${}^3\text{He}$  data in Fig. 1 are part of the set given in paper I. For all the mixture data shown in Fig. 1 the cell contained enough  ${}^4\text{He}$  to form a saturated  ${}^4\text{He}$  film, probably between 100 and 200 Å

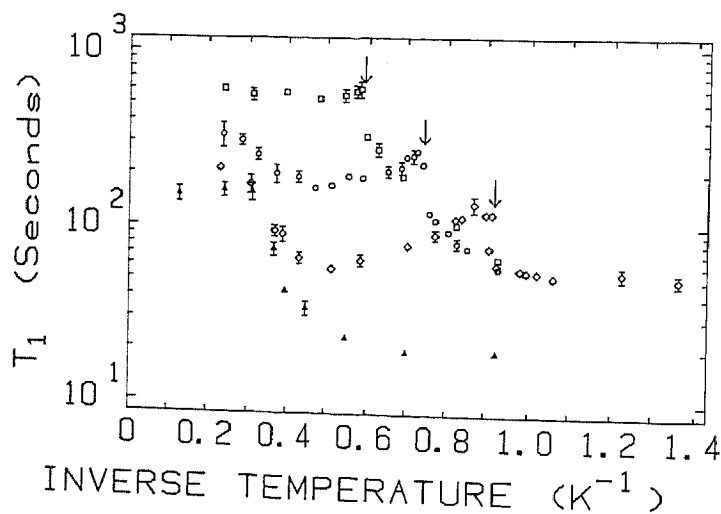


Fig. 1. Longitudinal nuclear magnetic relaxation times of  ${}^3\text{He}$ - ${}^4\text{He}$  mixtures contained in a solid  $H_2$ -coated Pyrex cell. The Larmor frequency is 7.5 MHz. In all samples the  ${}^3\text{He}$  bulk number density is  $3.1 \times 10^{24} \text{ m}^{-3}$ . The  ${}^3\text{He} : {}^4\text{He}$  atomic ratios are as follows: (▲) pure  ${}^3\text{He}$ ; (◊)  ${}^3\text{He} : {}^4\text{He} = 1 : 1$ ; (◻)  ${}^3\text{He} : {}^4\text{He} = 1 : 16$ . The arrows indicate the temperature at which a superfluid  ${}^4\text{He}$  film builds up rapidly on the  $H_2$  wall coating.

thick, and a liquid drop. The arrows in Fig. 1 indicate the temperatures at which the superfluid film rapidly builds up as the  $^4\text{He}$  liquefies [as obtained using Eq. (8)].

At high temperatures the adsorbed phase was a 2D gas mixture, which was in equilibrium with the bulk 3D gas mixture. Given that the correlation time  $\tau_c$  is much less than the sticking time in the adsorbed phase  $\tau_s$ , we would expect the observed  $T_1$  to be given by Eq. (2). The ratio  $N_{3\text{Ad}}/N_{3\text{B}}$  is given by Eq. (4) and should be independent of the  $^4\text{He}$  concentration, the ratio  $N_{4\text{Ad}}/N_{4\text{B}}$  being given by Eq. (4) with subscripts 3 replaced by subscripts 4;  $\Delta W_4$  is  $\sim 15$  K, as opposed to  $\sim 13$  K for  $\Delta W_3$ . If  $T_{1\text{Ad}}$  is a slowly varying function of temperature, and it is dominated by single-particle processes (we would expect this to be the case in the noninteracting 2D gas limit), then one might expect a slope of  $\sim -\Delta W_3$  ( $-13$  K, neglecting the  $T$  dependence of  $\lambda_3$ ) if we plot  $\ln T_1$  versus  $1/T$ , with  $T_1$  independent of total bulk number density  $n$ . However, we measured a variety of slopes, depending on the  $^4\text{He}$  content, whose magnitudes were all less than 13 K. Also,  $T_1$  was a function of  $n$ . This result is similar to that of our pure  $^3\text{He}$  data<sup>7</sup> and our interpretation is the same: at temperatures above  $\sim 6.5$  K the hydrogen began to desorb from the surface, enabling the spins to "see" the Pyrex walls; also, we expect that there were other contributions to the observed bulk relaxation; for example, as the temperature was raised and the bulk diffusion coefficient increased it was possible that some relaxation was taking place in the filling line.

On cooling from the highest temperatures,  $T_1$  dropped due to the building up of a monolayer (a mixture of  $^3\text{He}$  and  $^4\text{He}$ ) on the  $\text{H}_2$  surface.  $T_1$  was observed to rise on cooling below  $\sim 2$  K due to (1) the preferential absorption of  $^4\text{He}$  over  $^3\text{He}$  and (2) the buildup of a superfluid film of  $^4\text{He}$  on hydrogen. In Fig. 2 we plot  $T_1$  as a function of total bulk number density  $n = n_3 + n_4$  at temperatures cold enough that a monolayer of a  $^3\text{He}$ - $^4\text{He}$  mixture was formed, but not cold enough for a superfluid  $^4\text{He}$  film to be present. The dashed line in the figure shows  $T_1$  versus  $n = n_3$  for pure  $^3\text{He}$  data in the low-temperature plateau region, where a complete monolayer has formed. In this region  $\tau_c \ll \tau_s$  for the pure  $^3\text{He}$  data. Taking  $T_{1\text{Ad}}$  to be the same for both the pure  $^3\text{He}$  and the mixture runs, one would expect these two curves to be coincident in the absence of a preferential effect (in this situation the  $^3\text{He}$  concentration would be the same in the bulk and in the surface phase, and we would expect the areal number density at monolayer completion to be only a few percent larger for the mixture than for pure  $^3\text{He}$ ). However, from our data we deduce that  $^4\text{He}$  is adsorbed preferentially in this region; for example, at  $\sim 2$  K the sample with a 20%  $^3\text{He}$  concentration in the bulk gas has only a 10%  $^3\text{He}$  concentration in the adsorbed layer.

in the region where the film builds up rapidly), we deduce that the data were taken with the sample in thermal equilibrium.

1. At temperatures above that of the rapid buildup  $T_1$  increases as  $^4\text{He}$  is added, because this does not significantly increase the film thickness, but reduces the number of  $^3\text{He}$  spins in the film.

2. As the film builds up from  $\sim 10$  to  $\sim 100$  Å, either by adding  $^4\text{He}$  or by cooling [Eq. (8) shows that a temperature change of as little as 0.02 K is required for this to occur], two competing effects are at work. The number of  $^3\text{He}$  atoms within about 10 Å of the  $\text{H}_2$  substrate continues to be reduced, thus increasing  $T_1$ , but the thickening film dissolves more  $^3\text{He}$  in it and also *on* it (surface states). This second effect eventually predominates,  $^3\text{He}$  atoms in surface quasiparticle states probably being the most important source of relaxation, as discussed below.

3. When the film saturates at 100–200 Å (the film thickness at a given point in the cell being determined by its height above the free surface of the bulk liquid drop),  $T_1$  is observed to be independent of the  $^4\text{He}$  content of the cell. Since further addition of  $^4\text{He}$  merely increases the size of the bulk liquid drop in equilibrium with the film, we deduce that  $^3\text{He}$  atoms in the liquid drop are not an important source of relaxation. The common curve followed by all samples after bulk liquefaction levels off at about 50 sec below 1 K.

Figure 2 applies to regime 1. The two competing effects present in regime 2 explain the maximum in  $T_1$  near the arrows in Fig. 1 and the crossing of the curves. On cooling a sample with less  $^4\text{He}$ ,  $T_1$  will at first be shorter due to more  $^3\text{He}$  in the 10-Å film. However, further cooling will thicken the film in the sample with more  $^4\text{He}$  first. This will draw extra  $^3\text{He}$  to the surface, making  $T_1$  shorter than in the sample with less  $^4\text{He}$ .

Table I gives a number of  $^3\text{He}$  quasiparticle parameters appropriate for a superfluid  $^4\text{He}$  film 100 Å thick on a surface area of twice the geometrical surface area of the cell. The number density of  $^3\text{He}$  quasiparticles in the bulk liquid  $n_{3l}$  can be obtained by treating the  $^3\text{He}$  quasiparticles as a noninteracting 3D gas to give

$$n_3/n_{3l} = (m_3/m_3^*)^{3/2} \exp(-E_3/k_B T) \quad (15)$$

where we take  $E_3 = E_{30} = 2.8$  K once a saturated film has built up; and the areal density of surface  $^3\text{He}$  quasiparticles  $s_{3s}$  is given by

$$\begin{aligned} s_{3s}/n_3 &= (N_{3s}/A) V / N_{3B} \\ &= \lambda_3 (m_{3s}^*/m_3) \exp(E_{3s}/k_B T) \end{aligned} \quad (16)$$

The Fermi temperature of the bulk quasiparticles  $T_F$  is given by

$$T_F = \hbar^2 (3\pi^2 n_{3l})^{2/3} / 2m_3^* k_B \quad (17)$$

TABLE I  
Helium-3 Quasiparticle Parameters<sup>a</sup>

$T$ , K	1.67	1.5	1.2	1.0	0.7
$T^{-1}$ , K <sup>-1</sup>	0.6	0.667	0.833	1.0	1.43
$n_{3s}/m_{3s}$	$5.34 \times 10^{-2}$	$4.43 \times 10^{-2}$	$2.78 \times 10^{-2}$	$1.74 \times 10^{-2}$	$5.25 \times 10^{-3}$
$n_{3s}/N_{3s}$ , m <sup>-2</sup>	$4.41 \times 10^7$	$3.00 \times 10^7$	$1.17 \times 10^7$	$4.62 \times 10^6$	$4.54 \times 10^5$
$N_{3B}/N_{3s}$	$8.19 \times 10^3$	$6.79 \times 10^3$	$4.26 \times 10^3$	$2.67 \times 10^3$	$8.04 \times 10^2$
$N_{3B}/N_{3s}$	$6.76 \times 10^4$	$4.60 \times 10^4$	$1.79 \times 10^4$	$7.08 \times 10^3$	$6.96 \times 10^2$
$n_{3s}$ , m <sup>-2</sup>	$5.81 \times 10^{25}$	$7.00 \times 10^{25}$	$1.11 \times 10^{26}$	$1.78 \times 10^{26}$	$5.90 \times 10^{26}$
$s_{3s}$ , m <sup>-2</sup>	$7.93 \times 10^{16}$	$1.03 \times 10^{17}$	$2.65 \times 10^{17}$	$6.71 \times 10^{17}$	$6.83 \times 10^{18}$
$x_{3s}$ , %	0.27	0.32	0.51	0.82	2.7
$T_1$ , K	$5.02 \times 10^{-2}$	$5.68 \times 10^{-2}$	$7.7 \times 10^{-2}$	0.106	0.235
$T_1$ , K	$2.5 \times 10^{-2}$	$3.6 \times 10^{-2}$	$9.2 \times 10^{-2}$	0.234	2.3
$N_{3B}/N_{3s}$	8.25	6.77	4.20	2.65	0.865

<sup>a</sup>Values appropriate for a superfluid <sup>4</sup>He film 100 Å thick on an effective surface area of twice the geometrical area of the cell.

and that of the 2D gas of surface quasiparticles  $T_0$  is given by

$$T_0 = \hbar^2 \pi s_{3s} / m_{3s}^* k_B \quad (18)$$

We see from Table I that the three-dimensional gas is always nondegenerate [which means that Eq. (15) is always valid] and that the two-dimensional gas is nondegenerate at all but the lowest temperature. However, at 0.7 K the calculated areal density of the surface quasiparticles is higher than our calculated areal density for <sup>3</sup>He on H<sub>2</sub>, and since the surface quasiparticles are more weakly bound than on H<sub>2</sub>, one would expect the surface to be saturated with spins before this areal density was reached.

The sharp drop in  $T_1$  below the bulk liquefaction temperature is associated with the appearance of a new relaxation mechanism. We suggest that relaxation is taking place in surface quasiparticle states and give our reasoning below. On further cooling,  $T_1$  drops more slowly as the number of surface quasiparticles increases. We see from Eq. (16) that

$$N_{3B}/N_{3s} \propto T^{1/2} \exp(-E_{3s}/k_B T) \quad (19)$$

since the thermal de Broglie wavelength is proportional to  $T^{-1/2}$ . In Fig. 3 we plot  $\log_1(T_1/T^{1/2})$  versus  $1/T$ , where  $T_{1c}$  is the value of  $T_1$  along the common curve of Fig. 1, followed by all samples after bulk liquefaction. We obtain a straight line at high temperatures with a slope of  $-5.1 \pm 0.3$  K. The data deviate from the straight line at temperatures below  $\sim 1.2$  K. These data are highly suggestive of the surface quasiparticle relaxation mechanism, since the slope is consistent with the value of  $-E_{3s}$  obtained from the surface tension data<sup>17</sup>. If bulk gas relaxation is taking place as spins visit the two-dimensional quasiparticle gas at the liquid-gas interface, then the

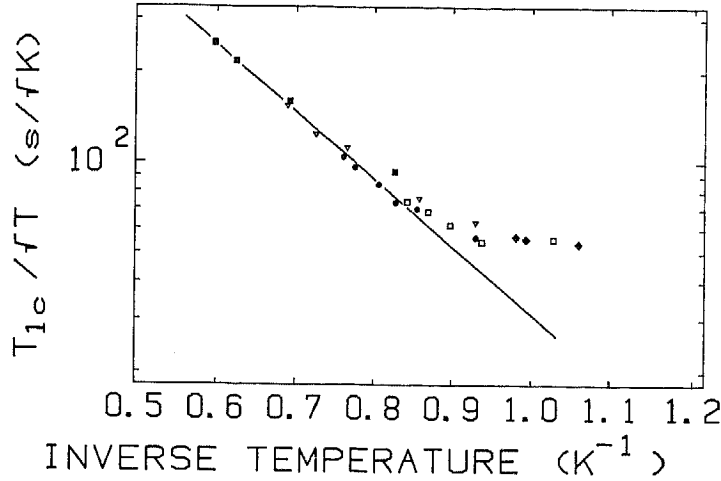


Fig. 3. Temperature dependence of the value of  $T_1$  along the common curve that occurs after a saturated superfluid film has built up on the  $\text{H}_2$ -coated surface. The Larmor frequency is 7.5 MHz. Here  $n_3 = 3.1 \times 10^{24} \text{ m}^{-3}$ . ( $\blacklozenge$ )  $^3\text{He}:^4\text{He} = 1:1$ ; ( $\square$ )  $^3\text{He}:^4\text{He} = 1:2$ ; ( $\bullet$ )  $^3\text{He}:^4\text{He} = 1:4$ ; ( $\nabla$ )  $^3\text{He}:^4\text{He} = 1:8$ ; ( $\blacksquare$ )  $^3\text{He}:^4\text{He} = 1:16$ . We obtain from the slope at the higher temperatures a value for the surface quasiparticle binding energy of  $5.1 \pm 0.3 \text{ K}$ .

observed  $T_1$  will be given by

$$T_{1c} = (N_{3B}/N_{3s})T_{1s} \quad (20)$$

where  $T_{1s}$  is the characteristic relaxation time in the surface quasiparticle phase. Our measured value of 323 sec for  $T_{1c}$  at 1.67 K corresponds to a value of 4.8 msec for  $T_{1s}$ , taking the value of  $N_{3B}/N_{3s}$  from Table I. This assumes that the sticking time in the surface quasiparticle states is much longer than the correlation time for local magnetic fields seen by the surface quasiparticles and that  $T_{1s}$  is caused by single-particle processes.

We suggest that  $T_{1c}$  levels off at low temperatures because interactions between the  $^3\text{He}$  surface quasiparticles become important and that the surface becomes full. Assuming that  $T_{1s}$  is independent of temperature, then we deduce from the plateau value of  $T_{1c}$  ( $\sim 50 \text{ sec}$ ) that the areal density of completion is  $4.57 \times 10^{17} \text{ m}^{-2}$  (smaller than that of monolayer completion of  $^3\text{He}$  on  $\text{H}_2$  by just over a factor of ten). If this is indeed the mechanism, then  $T_{1s}$  is smaller than the  $T_{1Ad}$  of the adsorbed phase by about a factor of five. It is probable that  $\langle \Delta B_{loc}^2 \rangle$  is the same order of magnitude in both cases (since it is probably caused by macroscopic magnetic impurities in the glass, in which case its magnitude would be changed very little as spins are moved  $100 \text{ \AA}$  away from the  $\text{H}_2$  surface); however, the correlation times for local fields could be very different in the two cases.

analyzing the composition of the  $^3\text{He}$  sample gas using an Anavac-2 residual gas analyzer, we discovered that it contained  $\sim 1\%$   $^4\text{He}$  impurity. Therefore we suggest that the latter cell contained a  $^3\text{He}$ : $^4\text{He}$  ratio of  $\sim 100:1$ . Both cells contained enough hydrogen to form  $\sim 17$  geometrical layers of solid  $\text{H}_2$ . The lowest  $^3\text{He}$  number density corresponds to  $\sim 70$  full monolayers on an effective surface area of twice the geometrical one.

At temperatures above  $\sim 2$  K the data are very similar to those taken with the pure  $^3\text{He}$ - $\text{H}_2$  sealed cells from Paris (see paper I for details). Relaxation times in both sets of data are the same order of magnitude ( $\sim 10^5$  sec at 4.2 K) and in all cases  $T_1$  falls on cooling with a slope of  $\sim -20$  K. We would expect the ratio  $N_{3B}/N_{3Ad}$ , and thus  $T_1$  [Eq. (2) or (3)], to be independent of  $N_{3B}$  and of the total number of  $^4\text{He}$  atoms  $N_4$  in this region of temperature. The data here and in paper I suggest that this is true. However, it is impossible to say with certainty, since both  $\langle \Delta B_{loc}^2 \rangle$  and the ratio of effective to geometrical surface area may be different in the various cells. From the slope we deduce that  $\tau_s \ll \tau_c$  at high temperatures.

On cooling below 2 K,  $T_1$  rises in both cells of Fig. 4 as  $^4\text{He}$  atoms exclude  $^3\text{He}$  atoms from the region of the sample, near the  $\text{H}_2$  coating, where relaxation is taking place. Using Eq. (8), we calculate that for the cell filled with a pressure of 2 Torr of  $^4\text{He}$  at room temperature, the  $^4\text{He}$  starts to condense at  $\sim 0.8$  K, is half-condensed by  $\sim 0.7$  K, and by 0.6 K 93% is condensed. In this cell  $T_1$  reaches a maximum value of  $\sim 3 \times 10^4$  sec at  $\sim 0.8$  K and then falls slowly on further cooling. This cell contains enough  $^4\text{He}$  to form a film  $\sim 40 \text{ \AA}$  thick on an effective surface area of twice the geometrical area of the cell.

In Fig. 5 we show  $T_1$  data for this same cell (filling pressures 10 Torr of  $^3\text{He}$ , 2 Torr of  $^4\text{He}$ , and 1.5 Torr of  $\text{H}_2$ ) taken at two different frequencies. The 7.7-MHz data were taken at Sussex and the 45-kHz data were taken in Paris, using an optical pumping technique to initially polarize the spins in the low-frequency experiment. We see from these data that in the high-temperature region  $T_1$  is independent of frequency. This is consistent with our results on the pure  $^3\text{He}$  cells from Paris.<sup>7</sup> In this region the root mean square local field at the surface, which is causing relaxation, is independent of frequency and our data are consistent with a value of  $\sim 4 \times 10^{-4}$  T for  $\langle \Delta B_{loc}^2 \rangle^{1/2}$  using Eqs. (3) and (4) and taking a value of 13 K for  $\Delta W_3$  and a value of unity for both  $S$  and  $m_3^*/m_3$ .<sup>7</sup>

The shape of the low-temperature data in Fig. 5 is similar to data obtained by the French group on a whole series of  $^3\text{He}$ - $^4\text{He}$ - $\text{H}_2$  mixture cells.<sup>19,23,24</sup> They observed  $T_1$  to rise on cooling below 1 K with a slope of  $\sim -7.4$  K and once a superfluid film had built up,  $T_1$  dropped slowly with decreasing temperature with a slope of  $\sim -0.5$  K. In the weakly temperature-dependent region  $T_1$  was found to be independent of the  $^4\text{He}$  content of

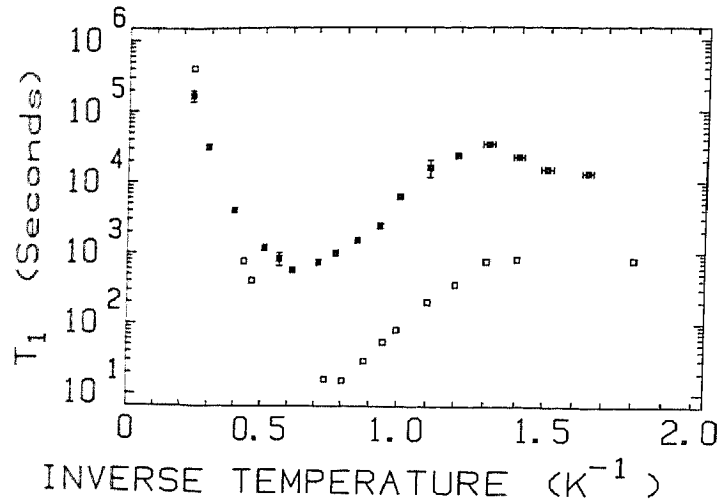


Fig. 5. Values of  $T_1$  measured in the same sealed cell at frequencies of (□) 45 kHz and (■) 7.7 MHz. Here  $n_3 = 3.3 \times 10^{23} \text{ m}^{-3}$ ,  ${}^3\text{He} : {}^4\text{He} = 5 : 1$ .

the cell; however, the temperature at which the slow drop started was higher for cells containing larger amounts of  ${}^4\text{He}$ . By varying the  $\text{H}_2$  content of the cells, they deduced that, once a superfluid film had built up,  ${}^3\text{He}$  atoms were excluded from the part of the  ${}^4\text{He}$  film of the order of two or three helium layers from the helium-hydrogen interface, given that the effective surface area was twice the geometrical one.

With the above results in mind, we consider the low-temperature part of the data in Fig. 5. The  $T_1$  rises quite rapidly on cooling from  $\sim 1.3$  to  $\sim 0.8$  K with a slope somewhere between 7 and 10 K. In this temperature region a thin  ${}^4\text{He}$  film builds up on the  $\text{H}_2$  surface and it is probably only two or three layers (one layer =  $3.6 \text{ \AA}$ ) thick by 0.8 K. The first layer is probably all  ${}^4\text{He}$  (this certainly would be the case on a glass surface<sup>17</sup>) and  ${}^3\text{He}$  atoms are probably being expelled from a second and third layer.

Using the values of  $d$  calculated from Eq. (8), one can calculate  $P_4/P_{40}$  from Eq. (6). The partial pressure of  ${}^4\text{He}$  in the sample becomes 90% of the saturated vapor pressure of  ${}^4\text{He}$  around 0.73 K. Since the sample does not have enough  ${}^4\text{He}$  to form a bulk liquid drop, the film can never become truly saturated. Once a film has formed, addition of extra  ${}^4\text{He}$  would always cause the film to thicken, whatever the temperature. Both  $P_4(T)/P_{40}(T)$  and  $\mu_4(T)$  [which can be calculated from the chemical potential of an ideal gas of  ${}^4\text{He}$  atoms at a pressure  $P_4(T)$ ] for this cell are plotted in ref. 16.

As  $P_4/P_{40}$  approaches unity, the chemical potential of the  ${}^4\text{He}$  becomes independent of temperature and equal to  $-L_4$ . In this region  $T_1$  falls with

decreasing temperature. It is not clear from our data whether the drop is exponential with temperature. If it is, then the slope is around 2 or 3 K. The 45-kHz slope is much smaller than this.

Substituting the appropriate numbers into Eq. (12), we obtain for the potential of a  $^3\text{He}$  quasiparticle in the superfluid film near a surface

$$E_3(z, T) = 2.785 + 0.25V(z) - 1.25[\mu_4(T) + 7.17] \quad (21)$$

If we postulate that relaxation is taking place in the bulk of the superfluid film, near the helium-hydrogen interface, at a point where the potential due to the wall is  $V(z)$  and that the characteristic relaxation time in that region is independent of temperature, then we expect the observed  $T_1$  to be proportional to  $\exp[-E_3(z, T)/k_B T]$ . We plot this function in Fig. 6, for different values of  $V(z)$ . The  $\mu_4(T)$  is calculated from the ideal gas expression [ $\mu_4(T) = T \ln(n_4 \lambda_4^3)$ ] using a pressure of  $P_4(T)$  obtained from Eq. (6). The positive slope is  $\sim 8.5$  K, which is consistent with our measured slope, and the negative slope is given by putting  $\mu_4(T) + 7.17 = 0$  in Eq. (21), i.e., the slope is  $-[2.785 + 0.25V(z)]$ , which is  $\sim -2.5$  K for a value of  $V(z) = -1$  K (appropriate for a distance of  $\sim 2$  layers from the hydrogen coating) and this is consistent with our 7.7-MHz data.

At temperatures between 0.8 and 1.5 K a thin helium film is formed on the  $\text{H}_2$  surface. The chemical potential of the  $^4\text{He}$  in the film  $\mu_4$  is a function of temperature in this region. It becomes less negative on cooling

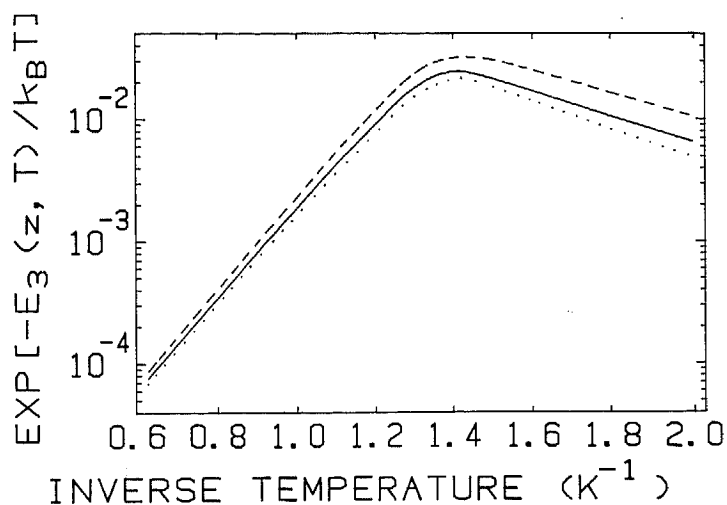


Fig. 6. Plot of  $\exp[-E_3(z, T)/k_B T]$  versus  $1/T$  for different values of the external adatom-substrate potential  $V(z)$ : (---)  $-2$  K, (—)  $-1$  K, (···)  $-0.5$  K. See text for details.

and approaches  $-L_4$  as  $T \rightarrow 0$ . On cooling below 2 K, the chemical potential of the  $^4\text{He}$  atoms in the film increases and this causes the  $^3\text{He}$  quasiparticle binding energy in the film to decrease [Eq. (10)]. The  $^3\text{He}$  quasiparticle become less tightly bound on cooling. Therefore, as we cool, the number of spins in the region where relaxation is taking place decreases as  $T$  increases. Our data are consistent with the idea that relaxation is taking place two or three helium layers from the helium-hydrogen interface.

If relaxation was taking place in a film 10 Å thick, our observed  $T_1$  would correspond to a relaxation time in the film of  $\sim 7$  sec at 7.7 MHz. It is difficult to say much about the mechanism involved. It is clear that the mechanisms at high and low temperatures are different, since there is a frequency dependence of  $T_1$  in the low-temperature region, but not at high temperatures. The relaxation time is the same order of magnitude as that observed in the adsorbed phase of  $^3\text{He}$  on  $\text{H}_2$  as described in I. In that paper we suggested that in the  $^3\text{He}/\text{H}_2$  system relaxation is caused by dipole-dipole coupling between  $^3\text{He}$  spins adsorbed on the hydrogen-coated surface. The situation is less clear when a superfluid film of  $^4\text{He}$  is present, partly because of the uncertainty in the region of the sample where relaxation is taking place. However, we think relaxation could be due to diffusion of spins in the local magnetic fields near the surface caused by macroscopic magnetic impurities in the glass. We note that slopes of  $\sim -5$  K were not observed with the cleaned sealed cells whose data are presented in this subsection and we conclude that  $^3\text{He}$  quasiparticle states at the free surface of the helium film are not a source of relaxation in these cells. This means that the local magnetic fields near the hydrogen surface are much stronger than those 50 Å away. This is consistent with the data in ref. 24, from which we conclude that relaxation is probably taking place two or three helium layers from the helium-hydrogen interface.

In the bulb filled with 30 Torr of nominally pure  $^3\text{He}$  and 1.65 Torr of  $\text{H}_2$  (Fig. 4) there were only enough  $^4\text{He}$  impurity atoms to form  $\sim 2$  layers on the  $\text{H}_2$ -coated walls. On cooling below 1 K,  $T_1$  rises slowly with a slope of  $\sim 2$  K due to the preferential adsorption of  $^4\text{He}$  at low temperatures. There is possibly just a single monolayer of a helium mixture on the surface at these temperatures.

### 5.3. Longitudinal Relaxation Times in a "Dirty" Sealed Cell

In Fig. 7 we show  $T_1$  data taken using a sealed cell cleaned (by baking under vacuum and using an rf discharge) in the manner previously described,<sup>1</sup> and then filled at room temperature with 567 Torr of  $^3\text{He}$  ( $n_3 = 1.9 \times 10^{22} \text{ m}^{-3}$ ), 61 Torr of  $^4\text{He}$  (including a 1%  $^4\text{He}$  impurity concentration in the  $^3\text{He}$ ), and 1.87 Torr of  $\text{H}_2$ . The diameter of the sample cell was

and approaches  $-L_4$  as  $T \rightarrow 0$ . On cooling below 2 K, the chemical potential of the  $^4\text{He}$  atoms in the film increases and this causes the  $^3\text{He}$  quasiparticle binding energy in the film to decrease [Eq. (10)]. The  $^3\text{He}$  quasiparticles become less tightly bound on cooling. Therefore, as we cool, the number of spins in the region where relaxation is taking place decreases as  $T_1$  increases. Our data are consistent with the idea that relaxation is taking place two or three helium layers from the helium-hydrogen interface.

If relaxation was taking place in a film  $10 \text{ \AA}$  thick, our observed  $T_1$  would correspond to a relaxation time in the film of  $\sim 7$  sec at 7.7 MHz. It is difficult to say much about the mechanism involved. It is clear that the mechanisms at high and low temperatures are different, since there is a frequency dependence of  $T_1$  in the low-temperature region, but not at high temperatures. The relaxation time is the same order of magnitude as that observed in the adsorbed phase of  $^3\text{He}$  on  $\text{H}_2$  as described in I. In that paper we suggested that in the  $^3\text{He}/\text{H}_2$  system relaxation is caused by dipole-dipole coupling between  $^3\text{He}$  spins adsorbed on the hydrogen-coated surface. The situation is less clear when a superfluid film of  $^4\text{He}$  is present, partly because of the uncertainty in the region of the sample where relaxation is taking place. However, we think relaxation could be due to diffusion of spins in the local magnetic fields near the surface caused by macroscopic magnetic impurities in the glass. We note that slopes of  $\sim -5$  K were not observed with the cleaned sealed cells whose data are presented in this subsection and we conclude that  $^3\text{He}$  quasiparticle states at the free surface of the helium film are not a source of relaxation in these cells. This means that the local magnetic fields near the hydrogen surface are much stronger than those  $50 \text{ \AA}$  away. This is consistent with the data in ref. 24, from which we conclude that relaxation is probably taking place two or three helium layers from the helium-hydrogen interface.

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### 5.3. Longitudinal Relaxation Times in a "Dirty" Sealed Cell

In Fig. 7 we show  $T_1$  data taken using a sealed cell cleaned (by baking under vacuum and using an rf discharge) in the manner previously described,<sup>7</sup> and then filled at room temperature with 567 Torr of  $^3\text{He}$  ( $n_3 = 1.9 \times 10^{25} \text{ m}^{-3}$ ), 61 Torr of  $^4\text{He}$  (including a 1%  $^4\text{He}$  impurity concentration in the  $^3\text{He}$ ), and 1.87 Torr of  $\text{H}_2$ . The diameter of the sample cell was

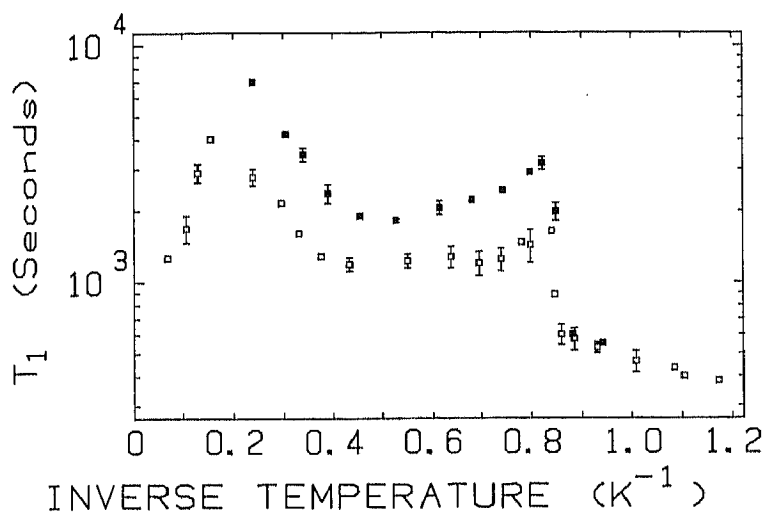


Fig. 7. Values of  $T_1$  measured in a "dirty" sealed cell containing an  $^3\text{He}$ - $^4\text{He}$ - $\text{H}_2$  mixture at frequencies of (■) 1.16 and (□) 7.66 MHz. Here  $n_3 = 1.9 \times 10^{25} \text{ m}^{-3}$ ,  $^3\text{He} : ^4\text{He} = 9 : 1$ .

1.6 cm. The cell was used when making the signal-to-noise ratio measurements at 1 MHz reported previously.<sup>6</sup>

This sample was prepared in an attempt to measure the  $T_1$  minimum edicted for the intrinsic dipolar relaxation of the bulk gas. The attempt as unsuccessful; nevertheless, the data in Fig. 7 have interesting features.

The relaxation times measured in this cell were much shorter than expected. Since this cell was cleaned in the same manner as those that produced the  $T_1$  values in Fig. 4, we might have expected  $T_1$  of  $\sim 10^5$  sec at 4.2 K (at this temperature  $T_1$  should be independent of the bulk  $^3\text{He}$  number density). However, the observed  $T_1$  values were more than an order of magnitude shorter than this at 4.2 K. We expect that the oxygen impurities in the  $^3\text{He}$  sample gas were responsible for the increased local magnetic fields present at the surface of the cell. The sample gas was guaranteed to have less than 0.1% oxygen impurity. However, at these high  $^3\text{He}$  filling pressures (50 times larger than that for the  $n_3 = 3.3 \times 10^{23} \text{ m}^{-3}$  sample of Fig. 4) a 0.1%  $\text{O}_2$  concentration would be significant. Since this sample contained enough  $^3\text{He}$  to form  $\sim 5000$  monolayers on an effective surface area of twice the geometrical area of the cell, then a 0.1%  $\text{O}_2$  impurity concentration would be enough to form approximately five layers of  $\text{O}_2$  on the surface of the cell. Any  $\text{O}_2$  impurity would condense out on the walls before the  $\text{H}_2$  on cooling and then would be covered with solid  $\text{H}_2$  at lower temperatures, the hydrogen keeping the  $^3\text{He}$  atoms  $\sim 10 \text{ \AA}$  away from the

oxygen. The magnetic field 10 Å away from an oxygen molecule is  $\sim 10^{-3}$  T which is around an order of magnitude larger than the local fields causing relaxation in the clean cells. Increasing the local field by an order of magnitude would result in a two-orders-of-magnitude reduction in  $T_1$ .

The frequency dependence of the  $T_1$  data in Fig. 7 offers another clue to the major source of the relaxation. The increase of  $T_1$  at low frequencies (the opposite of a spectral density effect) suggests that the local fields near the surface are caused by paramagnetic impurities (possibly  $O_2$ ) on or near the glass surface, since the local fields increase with increasing frequency.

The general shape of the data in Fig. 7 is the same as that for the open cell of Fig. 1. The sharp drop in  $T_1$ , associated with the bulk  $^4\text{He}$  liquefaction and the buildup of a saturated superfluid film on the surface, is again present, as is the slow drop on further cooling. Since  $T_1$  becomes frequency-independent at low temperatures, we suspect a source of relaxation different from that which dominates at temperatures above that of bulk liquefaction.

The slope in a  $\ln T_1$  versus  $1/T$  plot is  $\sim -7$  K at high temperatures, which is comparable with that in Fig. 1 for the same total bulk number density. We do not have a good explanation of the slope. Mechanisms other than the wall effect may be important.  $T_1$  drops on warming above 6.5 K. In this region  $H_2$  desorbs from the walls, leaving the glass (or oxygen) surface exposed. Spins can relax more effectively on the "bare" substrate, where local magnetic fields are stronger than those at the hydrogen surface. Also,  $^3\text{He}$  atoms are more strongly bound to a Pyrex surface than to a hydrogen surface.

Once a saturated superfluid film has formed, longitudinal relaxation could well be taking place in the quasiparticle states at the free surface of the film.  $T_1$  is  $\sim 500$  sec at 1 K, as opposed to 50 sec for the samples in Fig. 1. The fact that  $n_3$  is  $\sim 10$  times as great in the sealed sample suggests that the characteristic relaxation time in the surface quasiparticle states is the same in both cells (the states having become full at this temperature). This is probably a coincidence, since the relaxation time is related to the magnetic cleanliness of the walls.

## 6. PROSPECTS FOR THE OBSERVATION OF THE BULK GAS $T_1$ MINIMUM

Longitudinal relaxation times caused by wall effects are often proportional to the bulk spin density (this is certainly true when a complete  $^3\text{He}$  monolayer has formed on the  $H_2$  coating in the pure  $^3\text{He}$  experiments, for example). Intrinsic relaxation in bulk  $^3\text{He}$  gas is due to the dipole-dipole interaction between nuclear spins (which is effective during binary collisions) and the  $T_1$  values produced by this mechanism are inversely propor-

tional to  $n_3$ . Therefore, by working at much higher number densities than ours ( $\sim 10^{27} \text{ m}^{-3}$ ) it is possible to observe intrinsic bulk relaxation. The experimental results of Chapman and Richards<sup>25,26</sup> are in good agreement with the theoretical results of Shizgal<sup>4,5</sup> for the bulk dipolar relaxation times ( $T_{1B}$ ). Shizgal predicts that  $n_3 T_{1B}$  should go through a minimum of  $\sim 10^{31} \text{ sec m}^{-3}$  at a temperature of  $\sim 0.8 \text{ K}$ , which corresponds to a value for  $T_{1B}$  of  $\sim 10^4 \text{ sec}$  for  $n_3 = 10^{27} \text{ m}^{-3}$  and  $10^7 \text{ sec}$  for  $n_3 = 10^{24} \text{ m}^{-3}$ . This minimum has not been observed experimentally, since with the number densities used previously the liquefaction temperature of the  $^3\text{He}$  was  $\sim 1.5 \text{ K}$ , which was too high to observe the minimum.

In order to keep the  $^3\text{He}$  in the gaseous state to  $\sim 0.8 \text{ K}$ , one must use bulk  $^3\text{He}$  number densities  $\sim 10^{25} \text{ m}^{-3}$ . Use of low number densities to measure bulk gas relaxation times was previously a problem for two reasons: (1) poor spectrometer sensitivity prohibited the use of such small number densities; and (2) wall effects were dominant at low number densities. We are now able to get exceptional signal-to-noise ratios for low gas densities by using a cooled GaAsFET amplifier in our NMR spectrometer.<sup>6</sup> Also, by using a superfluid  $^4\text{He}$  wall coating, with possibly an  $\text{H}_2$  precoating, it is possible to produce long wall relaxation times at temperatures below  $1 \text{ K}$ , if the glass cell is suitably cleaned.

Using a  $^3\text{He}$  number density  $n_3$  of  $2 \times 10^{25} \text{ m}^{-3}$ , one would expect a value for  $T_{1B}$  at the minimum to be  $\sim 5 \times 10^5 \text{ sec}$ . The longest wall relaxation time (called here  $T_{1W}$ ) measured at  $0.8 \text{ K}$  was  $\sim 3 \times 10^4 \text{ sec}$  in a sample with  $n_3 = 3.3 \times 10^{23} \text{ m}^{-3}$  ( $T_{1B}$  should be  $\sim 3 \times 10^7$  at these number densities). One might hope that  $T_{1W}$  scales linearly with  $n_3$ , giving a value of  $\sim 2 \times 10^6 \text{ sec}$  for  $T_{1W}$  when  $n_3 = 2 \times 10^{25} \text{ m}^{-3}$ . Since relaxation rates add to give the total rate, when more than one mechanism is contributing to the relaxation (assuming rapid spin transfer between the relaxing regions), then one might expect bulk relaxation to dominate with  $n_3 = 2 \times 10^{25} \text{ m}^{-3}$ . The  $^3\text{He}$  gas at this number density will start to liquefy on cooling at  $\sim 0.7 \text{ K}$ , and so will remain in the gaseous state in the temperature region near the predicted  $T_{1B}$  minimum.

The data from the cell produced in order to try to observe the  $T_1$  minimum are shown in Fig. 7 and are discussed in Section 5.3. The cell contained enough  $^4\text{He}$  to form a saturated superfluid film around  $1 \text{ K}$ . The short  $T_1$  values we measured were due almost certainly to oxygen impurity in the  $^3\text{He}$  sample gas; therefore, it should be possible to purify the sample gas using a getter or cold trap before filling the cell and thus achieve longer  $T_1$  than those of Fig. 7. The main question to be answered is, "Is the wall relaxation time measured at low temperatures proportional to the bulk  $^3\text{He}$  number density?" If this is so, then it should be possible to observe the intrinsic bulk  $T_1$  minimum by using a superfluid  $^4\text{He}$  wall coating to suppress

wall relaxation at low temperatures. However, if the superfluid film does not become saturated with  $^3\text{He}$  spins at these number densities, then increasing  $n_3$  will cause more spins to dissolve in the film, resulting in an observed  $T_1$  that is independent of  $n_3$ . More work is needed to determine the number density dependence of the low-temperature values of  $T_1$ .

We see from Fig. 5 that  $T_1$  is an increasing function of frequency at low temperatures. Hence it may be possible to decrease the wall contribution to  $T_1$  by working at frequencies higher than 10 MHz. The bulk dipolar  $T_1$  is independent of frequency, since the time over which the nuclear dipolar interaction is present during collisions is much shorter than an inverse Larmor frequency. Measurements of  $T_{1B}$  in the region of the minimum would give information about the He-He electronic interaction potential.

## 7. CONCLUSIONS

We have studied the effect of  $^4\text{He}$  on the longitudinal nuclear magnetic relaxation times of  $^3\text{He}$  gas at low temperatures using pulsed NMR. An undercoating of solid molecular hydrogen was used in all experiments. We used both open Pyrex cells (into which we could put shots of gas, enabling a range of number densities to be studied during a run) and sealed Pyrex cells (which were cleaned by heating to  $\sim 450^\circ\text{C}$  under vacuum and using an rf discharge in  $^3\text{He}$  before sealing in the sample gas).

Relaxation of bulk spins was taking place near the  $\text{H}_2$ -coated surface. In all the cells the high-temperature behavior of  $T_1$  was much the same as that observed in the  $^3\text{He}$ - $\text{H}_2$  cells.<sup>7</sup> Helium-4 became important below  $\sim 2$  K, where a superfluid film built up on the solid  $\text{H}_2$  surface and  $^4\text{He}$  atoms were adsorbed on the wall in preference to  $^3\text{He}$ . In the "dirty" cells that contained enough  $^4\text{He}$  to form a saturated film on the  $\text{H}_2$  surface we saw  $T_1$  drop on cooling as the film built up. Relaxation was probably taking place in the  $^3\text{He}$  quasiparticle states at the free surface of the saturated film. The data were consistent with a binding energy of  $5.1 \pm 0.3$  K for a  $^3\text{He}$  quasiparticle in one of these surface states.

Using a cleaned, sealed Pyrex cell containing enough  $^4\text{He}$  to form a film  $\sim 50$  Å thick, we saw  $T_1$  rise on cooling below 2 K and observed a maximum  $T_1$  of almost 8 h at a temperature of 0.8 K and a frequency of 7.7 MHz. In this sample relaxation was taking place probably two or three helium layers from the helium-hydrogen interface. This determines the time for which a spin-polarized gas of  $^3\text{He}$  atoms can be kept at temperatures below 1 K. It may be possible to observe a minimum in the intrinsic bulk dipolar  $T_1$ , which has been predicted theoretically, by using a  $^4\text{He}$  wall coating to suppress wall relaxation effects which usually dominate the nuclear relaxation of the bulk gas.

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### 5.2. Longitudinal Relaxation Times in Sealed Pyrex Cells Containing Mixtures of $^3\text{He}$ , $^4\text{He}$ , and $\text{H}_2$

The results of paper I showed clearly that by cleaning the Pyrex cell by baking to  $470^\circ\text{C}$  under vacuum ( $\sim 10^{-6}$  Torr) and using an rf discharge in  $^3\text{He}$  gas and then sealing in the required mixture of gases, it was possible to increase the  $T_1$  observed at low temperatures by a factor of between two and three orders of magnitude over values obtained with the open geometry. In this subsection we present data taken on sealed Pyrex cells produced at Sussex using a glass gas handling system built for the purpose.\*

The Pyrex sample cells were spherical and had a radius of  $\sim 1$  cm and a wall thickness of  $\sim 1$  mm. The  $T_1$  was measured at Sussex, using pulsed NMR at 7.7 MHz, and in Paris (data taken by M. Himbert and J. Dupont-Roc) at a frequency of 45 kHz, using an optical pumping technique to polarize the spins in order to enhance the signal.

Figure 4 shows the results of  $T_1$  measurements on two cells, one filled at room temperature with 10.1 Torr of  $^3\text{He}$ , 1.99 Torr of  $^4\text{He}$ , and 1.51 Torr of  $\text{H}_2$ , and the other filled with 30.1 Torr of  $^3\text{He}$  and 1.65 Torr of  $\text{H}_2$ . The  $^3\text{He}$  filling pressures correspond to  $^3\text{He}$  number densities of  $3.3 \times 10^{23}$  and  $9.8 \times 10^{23} \text{ m}^{-3}$ , respectively. The  $^3\text{He}:^4\text{He}$  ratio in the first cell was 5:1. On

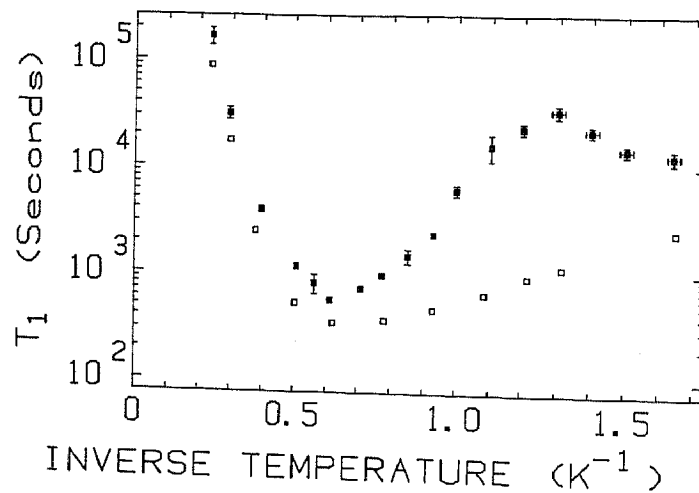


Fig. 4. Values of  $T_1$  measured at 7.7 MHz in sealed Pyrex cells containing  $^3\text{He}$ - $^4\text{He}$ - $\text{H}_2$  mixtures. (■)  $n_3 = 3.3 \times 10^{23} \text{ m}^{-3}$ ,  $^3\text{He}:^4\text{He} = 5:1$ ; (□)  $n_3 = 9.8 \times 10^{23} \text{ m}^{-3}$ ,  $^3\text{He}:^4\text{He} \approx 100:1$ .

\* We have benefited greatly from discussions with J. Brossel, V. Lefevre-Seguin, and others from the Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure in Paris concerning the design and operation of this system.

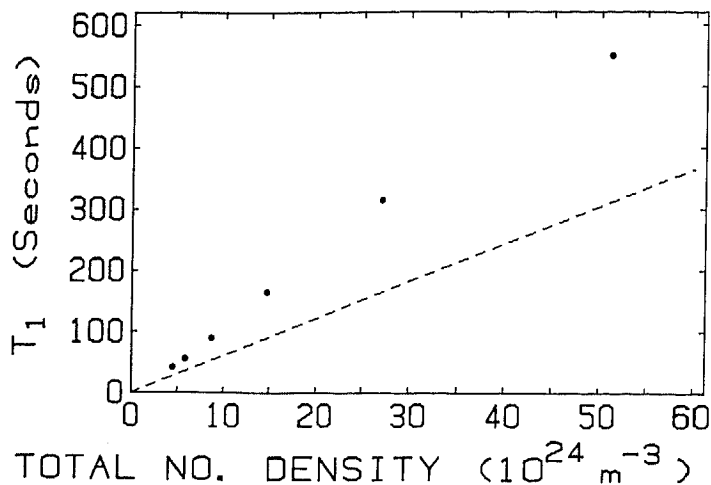


Fig. 2. Value of the minimum in  $T_1$  versus total bulk number density,  $n = n_4 + n_3$ . The frequency is 7.5 MHz. The dashed line shows the value of  $T_1$  obtained with pure  $^3\text{He}$  on a hydrogen surface at a temperature at which a complete  $^3\text{He}$  monolayer has formed on the hydrogen surface versus total bulk number density,  $n = n_3$ . The lines are not coincident, due to the preferential adsorption of  $^4\text{He}$  over  $^3\text{He}$  at low temperatures.

$T_1$  rises on cooling below 2 K as  $^3\text{He}$  is excluded from the region of strong local magnetic fields near the wall. An unsaturated superfluid  $^4\text{He}$  film (a film that exists with no bulk liquid present and is in equilibrium with a partial pressure of  $^4\text{He}$  that is less than the saturated vapor pressure) starts to form on the solid  $\text{H}_2$  surface. On cooling through the temperatures indicated by the arrows in Fig. 1, the film builds up rapidly and a drop of liquid forms in the bottom of the cell. Once a drop of bulk liquid has formed, the thickness of the film at a given point in the cell is determined by its height above the free surface of the liquid drop. The saturated film is probably around 100–200 Å thick at temperatures below that indicated by the arrows. A rapid drop in the value of the observed  $T_1$  is associated with bulk liquefaction.

As liquefaction takes place, the total number density in the bulk gas falls as it loses  $^4\text{He}$ . We have approximately

$$n = n_3 + P_{40}/k_B T \quad (14)$$

once a saturated film and a liquid drop have formed, where  $P_{40}$  is the saturated vapor pressure of  $^4\text{He}$  and  $n_3 \approx 3.1 \times 10^{24} \text{ m}^{-3}$  throughout the temperature range covered.

In the region of temperature where the  $^4\text{He}$  film builds up there are three regimes observable in Fig. 1. Since we observed no hysteresis (even

nuclei are in the same spin state exhibits macroscopic quantum effects, which are manifest in the transport properties of the gas and in the liquid-vapor equilibrium pressures<sup>1-3</sup>); (2) long free induction decay lifetimes  $T_2^*$  are needed if one is to use the  $^3\text{He}$  nucleus as a detector of small angular rotation rates in an NMR gyroscope; (3) nuclear relaxation in helium gas is often dominated by processes occurring at or near the walls of the sample cell and in this situation measurements of bulk gas relaxation times give information about processes happening near the cell walls, making possible the study of certain two-dimensional systems ( $^3\text{He}$  adsorbed on a hydrogen surface or  $^3\text{He}$  quasiparticles in superfluid  $^4\text{He}$ , for example); (4) if the intrinsic bulk relaxation can be observed at low temperatures (this involves using low bulk number densities and suppressing wall effects), one can probe the He-He interaction potential by measuring  $T_1$  in a temperature region  $\sim 0.8$  K, where the bulk dipolar relaxation time is predicted to go through a minimum.<sup>4,5</sup>

We have studied processes responsible for longitudinal nuclear relaxation ( $T_1$  processes) with a view to making  $T_1$  as long as possible. As well as being relevant for points 1, 3, and 4 above, this is also relevant for point 2, since an upper limit for  $T_2^*$  is of the order of  $T_1$ . We did not use highly polarized samples in our experiments (a typical polarization being of the order of the equilibrium polarization at  $\sim 0.1$  T and liquid helium temperatures).

We have measured  $T_1$  in samples of  $^3\text{He}$  gas contained in Pyrex bulbs as a function of temperature and bulk  $^3\text{He}$  number density. Helium-3 number densities between  $3 \times 10^{23}$  and  $6 \times 10^{25}$  spins  $\text{m}^{-3}$  and temperatures between 0.6 and 15 K were used.

In order to reduce the strength of the surface contributions to the relaxation rate (in almost all instances in this work surface relaxation was the dominant process), we tried surface cleaning techniques, which involved the use of an rf discharge in  $^3\text{He}$  gas, and also tried using cryogenic wall coatings: namely, solid molecular hydrogen, which forms a coating below  $\sim 6.5$  K, and  $^4\text{He}$ , which becomes adsorbed in preference to  $^3\text{He}$  at temperatures below  $\sim 2$  K, since its larger mass results in a lower zero-point energy (effectively, a smaller "quantum size").

We used two types of spherical Pyrex cells in these experiments. An open cell was used, which was connected to a Pyrex gas handling system situated at the top of the cryostat via a Pyrex filling capillary. Using this setup, we could study a range of number densities during a run. We also studied sealed Pyrex cells containing various mixtures of  $^3\text{He}$ ,  $^4\text{He}$ , and  $\text{H}_2$ , some produced in Paris,\* and some produced at Sussex.

\* Samples produced by V. Lefevre-Sequin and J. Brossel at the Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure in Paris.