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Temperature dependence of the relaxation time in dilute ^{3}He gas: An investigation of the He-He potential*

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The first measurements of the temperature dependence of the intrinsic dipolar relaxation time T_{1B} due to binary collisions in dilute ^{3}He gas are reported. Experimental conditions sufficiently pure to observe T_{1B} were obtained by coating bare Pyrex sample cells with clean neon gas. The experiments were performed at low temperatures (1.7 to 19.0 K) where the colliding atoms have correspondingly low energy, so the effect of the long-range attractive forces is strongly felt and the measurements are sensitive to the depth and nature of the helium attractive well. Calculations of T_{1B} using the best available helium potentials have been fitted to the experimental results to test the parameters which describe the potential. The data favor a potential of the Bruch-McGee form, but having a slightly deeper attractive well of 11.5 K.

I. INTRODUCTION

Nuclear-spin relaxation in dilute gases has long been recognized as a sensitive means of studying the dependence of intermolecular forces on molecular orientation.[1] The NMR relaxation rate of molecular systems is related by a well-established theory[2] to the correlation time for molecular reorientation, which can be calculated in terms of the intermolecular potential. Unfortunately, even in the simplest molecular systems neither the isotropic nor the anisotropic parts of the potential are well known, and in practice only very crude functional forms of the potential have been used. Nevertheless, it should be possible to perform realistic calculations for the simplest systems, and in fact Riehl *et al.*[3] and Lalita and Bloom[4] have successfully obtained information on the H_2–rare-gas potential by NMR experiments on gaseous mixtures.

By contrast, from the point of view of simplicity, an ideal system to study is dilute ^{3}He gas in which the well-known dipole-dipole interaction dominates the nuclear-spin relaxation. The relaxation rate is directly related to the cross section for spin transitions caused by the dipolar coupling, and the cross section can be calculated in terms of adjustable parameters in the functional form of the isotropic part of the helium potential. Precise measurements of the relaxation time can therefore be used to test the theory of nuclear-spin relaxation in a fundamental system, and also provide an independent experimental check of the parameters in the helium potential. Since very good agreement with the theory of relaxation is expected, we hope to stress the nuclear-spin relaxation time measurements as a unique probe of the potential.

In the simplest picture, the central part of the interatomic potential is a sum of two contributions: a long-range electromagnetic attraction and a short-range repulsion. Much of the empirical information about the central potential comes from conventional techniques such as experiments to measure virial coefficients, transport properties (viscosity, diffusion, and thermal conductivity), and also beam scattering experiments. Exact theoretical calculations, particularly of the short-range part of the interaction, are extremely difficult multielectron problems and have been attempted only for simple systems such as H-H, He-He and H_2-He.

The helium potential has received much experimental and theoretical attention, and several potentials exist in the literature. A theoretical calculation of the He-He interaction was performed by Shafer and McLaughlin[5] who obtained a well depth of 12.0 K, slightly deeper than the empirically determined values. Semiempirical potentials are obtained by fitting experimental data to a function of interatomic separation r in order to obtain values for adjustable parameters. The form usually chosen for the repulsive part is an $\exp(-r)$ term, and for the long-range attraction an induced-dipole–induced-dipole (r^{-6}) plus an induced-dipole–induced-quadrupole (r^{-8}) term. The potentials give a range of depths of the attractive well from 10.3 to 12.0 K at a separation of $r \simeq 2.9$ Å. Experimental accuracy is not sufficient to determine the well depth to better than 1.0 K.

Empirical information about the helium potential has been provided by measurements of several different physical properties[6] including second virial coefficients in the range 1.5–1500 K, coefficient of viscosity in the range 1.5–2000 K, diffusion and spin diffusion between 1.2 and 700 K, and thermal conductivity in the range 100–800 K. Most of the data covers the high-temperature regime, with relatively sparse information in the region below

10 K where experiments would be more sensitive to the attractive well. Scattering experiments[7] have been done at energies only as low as five times the well depth.

The NMR measurements reported in this work have comparable accuracy to the other transport property measurements and have been made at low temperatures (1.7–19.0 K), where the relaxation rate is sensitive to the effect of the long-range attractive forces and information can be obtained on the nature and depth of the helium attractive well. In addition, these measurements should provide an upper limit for other contributions to the relaxation, such as the contribution from spin rotation which dominates T_1 in the heavier inert gas ^{129}Xe.[8]

It is possible to perform an accurate calculation of the nuclear-spin relaxation rate from first principles in terms of the interatomic helium potential which determines the cross section for nuclear-spin reorientation in binary collisions.[9] The relaxation rate is proportional to the thermal average of the product of the nuclear spin-flip scattering cross section σ and relative velocity v of the atoms,

$$1/T_1 = n\langle \sigma v\rangle \, , \qquad (1)$$

where n is the number density of helium atoms.

An estimate of the relaxation time of a dilute gas of ^{3}He atoms can be obtained by considering the effect of binary collisions which occur incoherently at an average frequency v . In this model[10,11] the spin system dissipates absorbed rf energy via collisional modulation of the dipolar interaction. The duration of a collision of order d/v, where d is the distance of closest approach and v the thermal velocity, is sufficiently small so that the short correlation time limit is satisfied for fields attainable with laboratory electromagnets. The relaxation rate is

$$T_1^{-1} = n\left(\frac{m}{kT}\right)^{1/2} \frac{\hbar^2\gamma^4}{d^2} \propto \frac{P}{T^{3/2}} \, , \qquad (2)$$

where P is the gas pressure and n is the number density of helium atoms. Evaluation of the expression at 1 atm pressure shows T_1 to be about 10^7 sec at room temperature and about 10^4 sec at 4.2 K.

These very long times indicate how weak the intrinsic relaxation mechanism is. It is difficult to prepare experimental conditions which are sufficiently pure that bulk gas relaxation can be observed. Indeed, other NMR and optical pumping experiments on ^{3}He gas have observed relaxation due to impurity effects,[12] wall relaxation,[13,14] or magnetic field gradients.[15]

Paramagnetic impurities such as oxygen molecules are expected to make a significant contribution to $^1T_1$ when their fractional concentration reaches $[\gamma(^3\mathrm{He})/\gamma(\mathrm{O}_2)]^2 \sim 10^{-6}$. When making measurements at or above 77 °K, it is difficult to avoid concentrations of this magnitude, but at 4.2 K where the data reported was recorded, all the impurities except ^{4}He will be condensed out on the walls.

Wall effects are more difficult to estimate because the probability of relaxation at the wall depends on the nature of the surface and on the bulk gas pressure which affects the total time a ^{3}He atom resides near the wall. It can be shown, however, that in the limits of very large and very small probability of spin relaxation at the wall, the wall relaxation time is proportional to density.[16] In the case of interest to this work, namely very weak wall relaxation, it is possible to separate the bulk gas and wall relaxation contributions by means of their density dependence.

Since the relaxation rates add, the observed relaxation rate can be written

$$\left(\frac{1}{T_1}\right)_{\mathrm{obs}} = \frac{1}{T_{1B}} + \frac{1}{T_{1W}} = C_1\rho + \frac{C_2}{\rho} \, . \qquad (3)$$

On the basis of this phenomenological model, a plot of ρ/T_1 vs ρ^2 yields a straight line with slope C_1. The basic experimental task was to prepare experimental conditions in which C_2 was suppressed sufficiently that bulk gas relaxation could be observed. Improved methods of gas purification and surface-cleaning techniques using wall coatings of solid neon which were developed in this work, provided reproducible weakly relaxing surfaces and permitted for the first time observation of T_{1B} in ^{3}He gas. Experiments have also been performed to study the wall relaxation specifically, and the results will be discussed in a separate paper.

The following section of this paper briefly discusses the theory of T_1 in dilute ^{3}He gas and also presents the helium potentials used in the calculations. The experimental techniques of sample preparation and also measurement of very long NMR relaxation times are then described in Sec. III. Results of the T_1 measurements are presented in Sec. IV, and the fitting procedure to test the adjustable parameters in the potential is described. This is followed in the final section by a brief summary.

II. THEORY OF LONGITUDINAL SPIN RELAXATION IN DILUTE ^{3}He GAS

The calculation of T_{1B} using simple collisional models described above is suitable only for an order-of-magnitude estimate and does not allow a detailed interpretation of T_1 in terms of the atomic and kinetic properties of the gas.

Because of the simplicity of the dipolar coupling, it is possible to perform an exact calculation of T_{1B} from first principles using the best available helium potentials to describe the scattering of He atoms. The temperatures at which the nuclear spin-relaxation experiments were performed restrict the relative energy of a colliding pair of atoms to very low energies, and this permits a computational simplification since it is necessary to include only the lowest partial waves in treating the scattering problem.

A formal kinetic theory for the calculation of T_{1B} in dilute monatomic gases was developed by Chen and Snider.[17] The essential quantity in their theory is the cross section $\sigma(E)$ for spin transitions resulting from the collisions of pairs of atoms interacting via the spherical potential and the dipolar coupling which is responsible for spin flips. The relaxation rate is then obtained from

$$T_{1B}^{-1} = n\left(\frac{2/\pi\mu}{(kT)^3}\right)^{1/2}\int_0^\infty e^{-E/kT}\,\sigma(E)E\,dE\,, \qquad (4)$$

where E is the relative energy of a colliding pair of reduced mass μ and n is the number density of the gas.

The kinetic formulation has the advantage that the dynamics of the binary collisions are accurately taken into account. In addition, realistic forms of the He-He potential can be used to evaluate the cross section, so that a comparison of the calculated and measured values of T_{1B} can provide a test of the form of the potential used.

The interaction between ^{3}He atoms is taken as the sum of the ground-state electronic interaction $V_0(r)$ and the anisotropic dipolar interaction between nuclei,

$$V(r) = V_0(r) + V(\vec{r}, \vec{I}_1, \vec{I}_2)\,, \qquad (5)$$

$$V(\vec{r}, \vec{I}_1, \vec{I}_2) = \frac{3\gamma^2\hbar^2}{r^5}\left((\vec{I}_1\cdot\vec{r})(\vec{I}_2\cdot\vec{r}) - r^2\,\frac{\vec{I}_1\cdot\vec{I}_2}{3}\right),$$

where $\vec{r}$ is the relative position vector of atoms with spins I_1 and I_2. In the center-of-mass system the Hamiltonian is

$$\mathcal{H} = -(\hbar^2/2\mu)\nabla^2 + V(r)\,. \qquad (6)$$

The cross section can be obtained by performing a standard partial-wave analysis of the scattering. Since we are considering the collision of identical spin-$\frac{1}{2}$ particles, the total wave function Ψ is antisymmetric. It is expanded as a product of space and spin variables, with the spin part expressed in terms of total spin $\vec{I} = \vec{I}_1 + \vec{I}_2$. Because the $I = 0$ state does not contribute to the relaxation, the space part of Ψ must be antisymmetric (since the $I = 1$ spin state is symmetric) and the partial waves required in the calculation are restriced to odd values of l. Over the entire range of energy, the number of partial waves required to achieve convergence is small, and at very low energy ($E < 5 \times 10^{-4}$ eV), $\sigma(E)$ is effectively given by the $l = 1$ partial wave only. Since the dipolar coupling is many orders of magnitude smaller than the spherical potential, it is possible to calculate the partial-wave scattering amplitudes within the distorted-wave Born approximation. The details of the calculation are given by Shizgal.[9]

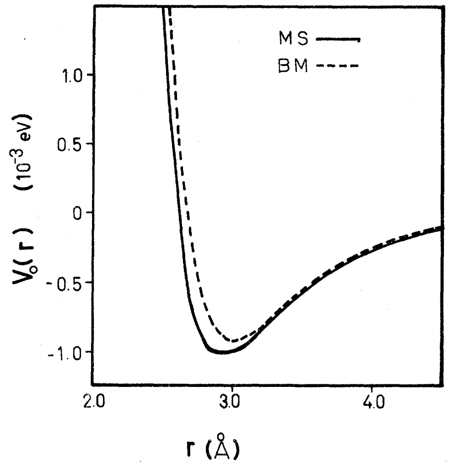

FIG. 1. $V_0(r)$ vs r for the MS and BM helium potentials.

The properly symmetrized cross section was computed numerically in the energy range 0–0.07 eV using the best available He-He potentials, in particular the forms obtained by Beck, Bruch and McGee (BM), and McLaughlin and Shafer (MS). The latter two potentials are plotted versus relative separation r in Fig. 1.

The Beck potential[18] is a fit of second-virial-co-

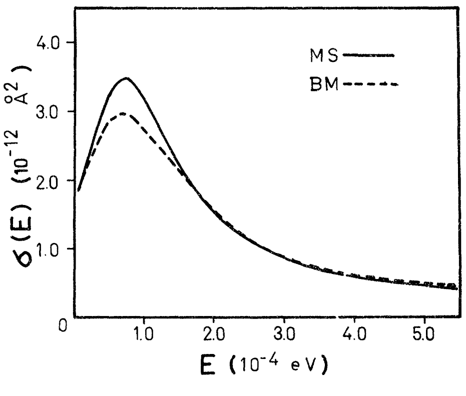

FIG. 2. Calculations of cross section $\sigma(E)$ for spin transitions caused by the dipolar coupling vs energy, using the MS and BM helium potentials.

efficient data in the temperature range 25–1500 K by the functional form

$$V_0(r) = A\exp(-\alpha r - \beta r^6) - \frac{0.869}{(r^2+a^2)}\left(1 + \frac{2.709 + 3a^2}{r^2+a^2}\right), \tag{7}$$

where $a = 0.675$ Å, $\alpha = 4.390$ Å^{-1}, $\beta = 3.746\times10^{-4}$ Å^{-6}, $A = 398.7$ eV.

Bruch and McGee[6] have fitted transport properties and second-virial-coefficient data in the range 1.5 - 2000 K by the functional form

$$V_0(r) = A\{\exp[2c(1-x)] - 2\exp[c(1-x)]\}, \quad r \le r_2$$
$$x = r/r_{\text{min}} \tag{8}$$
$$V_0(r) = -1.47r^{-6} - 14.2r^{-8}, \quad r > r_2$$

and obtained $A = 1.484\times10^{-15}$ erg, $r_m = 3.0238$ Å, $r_2 = 3.6828$ Å, and $c = 6.12777$.

The MS potential[5] is a fit of calculations of the He-He interaction to the functional form

$$V_0(r) = \exp(a + br + cr^3) + d/r^6 + e/r^8, \tag{9}$$

where $a = 15.480$, $b = -2.2928$, $c = -2.5443\times10^{-3}$, $d = -4.8696\times10^5$, and $e = -4.9513\times10^6$. $V_0(r)$ is in K and r in bohrs.

In addition a Lennard-Jones (6-12) potential with $\epsilon = 0.887\times10^{-3}$ eV and $\sigma = 2.56$ Å was tried.

Calculated values of σ using the MS and BM potentials are shown in Fig. 2. At high energies $E > 10^{-3}$ eV, all potentials give an E^{-1} dependence with slight differences in magnitude, whereas below 10^{-3} eV there is a greater difference in the numerical results, although all potentials indicate a maximum near 10^{-4} eV.

T_{1B} is readily obtained from Eq. (4). The results suggest that the temperature dependence of T_{1B} is sensitive to the form of the spherical potential and, in particular, the details of the attractive well.

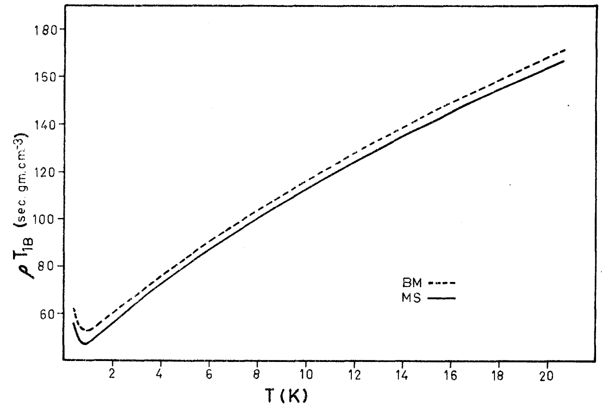

FIG. 3. Temperature dependence of T_{1B}. Calculations were performed using the MS and BM potentials.

Figure 3 shows the calculated values of T_{1B} in the range 0–20.0 K. At temperatures $T > 10$ K the value of $T_{1B}T^{-1/2}$ approaches a constant.

Perhaps the most interesting feature of the temperature dependence is the minimum in the neighborhood of 1.0 K. Although data was not obtained at low enough temperature to pass through the minimum, it is interesting to discuss the effect.

The source is in part due to the cross-section maximum in Shizgal's calculation. [A T_1 minimum would naturally result from the average over energy in Eq. (4).] A simple physical picture of the cross-section maximum can be described as follows. Shizgal's calculations show that only the $l = 1$ partial wave contributes to $\sigma(E)$ at low energies. For p-wave scattering the effective potential is $V_0(r)$ plus the centrifugal barrier for the $l = 1$ wave. Although it is tempting to describe the maximum as a p-wave resonance, Shizgal points out that the $l = 1$ phase shift does not equal $\frac{1}{2}\pi$ at the energy where the maximum occurs, and in fact the potential must be far more attractive before a resonance appears. Qualitatively, the maximum in σ occurs because the wave function is concentrated in the region of the well due to the attractive part of $V_0(r)$. The collision time is effectively increased, leading to a greater probability of a nuclear-spin flip during the collision. Eventually at sufficiently low energies the atom is scattered off the centrifugal barrier and the spin-flip transition probability is reduced since the distance of closest approach of the pair is larger. The T_1 minimum (relaxation-rate maximum) occurs as the temperature is varied through the range in which the most probable energy in the Maxwell-Boltzmann energy distribution roughly matches the height of the centrifugal barrier.

There will also be a contribution to the relaxation from the transient spin-rotation interaction associated with effects of electric polarization during a collision. In brief, there is a distortion of the charge clouds due to the Van der Waals interaction during a collision; the rotation of the distorted charge distortion creates a fluctuating field at the nucleus which can excite spin transitions.

It is possible to calculate a cross section for spin transitions owing to the spin-rotation coupling[19] and estimate the strength of its contribution to T_{1B}. The calculation is formulated in the same manner as in the previous case of dipolar coupling. Figure 4 shows a plot of dipolar and spin-rotation cross sections for ^{3}He. It is evident that at low temperature there should be only a negligible contribution from the spin-rotation coupling.

A further contribution to the relaxation could arise from magnetic field gradients through which

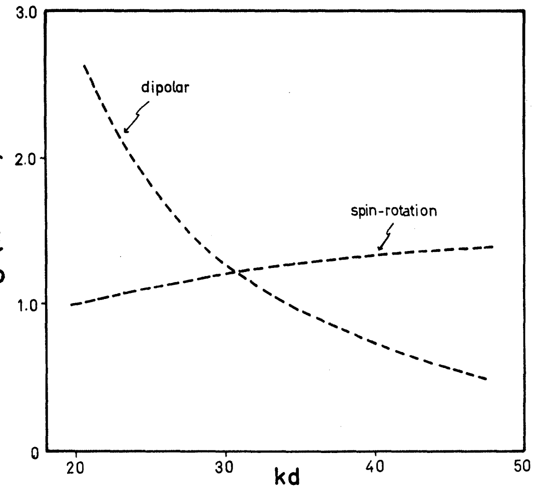

FIG. 4. Cross sections for spin transitions via the dipolar and the spin-rotation interactions. k is the magnitude of the relative wave vector and d is the distance of closest approach. At $kd = 31$, relative energy is 0.2 eV.

the spins diffuse. Relaxation by this mechanism has been observed in optical pumping studies of ^{3}He gas at very low density.[15,20] The relaxation time can be estimated by a random-walk argument, in which the spin experiences a changing magnetic field of mean square value $\langle \delta H^2 \rangle$ at intervals of time τ equal to the average time necessary to diffuse through δH. Schearer and Walters[20] have estimated this relaxation time to be

$$T_1^{-1} = G^2 \langle u^2 \rangle \tau / H_0^2 \qquad (10)$$

where G is the magnetic field gradient and u the thermal velocity of atoms which make collisions on the average at intervals τ. In the field gradients experienced in this work ($G \simeq 10^{-3}$ G in 1 kG) the time constant T_1 is of order 10^{15} sec so that contributions to the relaxation rate due to this mechanism can be completely neglected.

III. EXPERIMENTAL TECHNIQUE

The very long relaxation times were measured by the technique of adiabatic fast passage (AFP). In a sample of pure ^{3}He gas the adiabatic conditions

$$\gamma H_1 \gg \frac{1}{H_1}\frac{dH}{dt} \gg \frac{1}{T_1} \qquad (11)$$

are easily satisfied with a sweep rate of 0.1 G/sec and rf fields of about 60 mG. The usual technique of observing signals in an initial and return sweep through resonance[2] was modified so that the entire T_1 measurement could be made in a period of time of about 2.5 T_1's. Initially the system was polarized off resonance to achieve equilibrium and then swept through resonance to a resting field in order to invert the magnetization. Subsequently the magnetization was sampled nondestructively by cycling the field back to resonance and then returning it to the resting field. The magnetization continues on its original relaxation curve, and as long as the adiabatic conditions are satisfied, there is negligible loss of magnetization each time the signal is monitored.[21] The method was compared to the usual technique at a suitable high density where the relaxation time was short, and the two results agreed within experimental error.

It is important to ensure that H_1 is greater than the local field H_L and also the field gradient δH over the sample. Otherwise all the spins are not inverted at the same time during the sweep and the signal strength is reduced by the factor H_1/H_L or $H_1/\delta H$, respectively. Weak rf fields may also create a nonuniform magnetization in the sample which will persist until smoothed by diffusion.

At the sample chamber surface, local fields H_S which are responsible for wall relaxation may not be small compared to H_1, and it may be necessary to consider their effect on the adiabatic passage. On resonance the magnetization is polarized along the effective field in the rotating frame and has energy levels proportional to $(H_1^2 + H_S^2)^{1/2}$. Transitions between these levels can easily be excited by the local surface fields and the relaxation rate may be very strong. Therefore, the time of the passage through resonance must be short compared to $T_{1\rho}$ (walls), which is the wall relaxation time in the rotating frame.

A simple twin-T rf bridge spectrometer operating at 3.5 MHz was used to monitor the AFP signal from a sample of ^{3}He gas contained in a Pyrex bulb. The bridge operated at room temperature, but a large fraction of the total capacitance in the tuned circuit was soldered directly in parallel with the coil in order to reduce the noise temperature of the circuit. The signal was amplified by a tuned rf amplifier, detected and fed directly to a chart recorder.

All measurements were made in a 12-in. Varian magnet with a 2.25-in. pole gap in which the field was constant to 7 parts in 10^6 per cm^3 at the optimum place in the gap.

A variable-temperature cryostat was constructed in which ^{4}He exchange gas stabilized temperature in the range 1.2–20 K. The temperature was monitored by a carbon resistor.

Samples of ^{3}He gas were obtained from the Monsanto Corporation with a quoted isotopic purity of 99.8 mole % and less than 0.1 mole % of other gases such as nitrogen and oxygen.

Since this gas was not sufficiently pure to use directly, it was cleaned by storing it in a 4-l pyrex bulb lined with a permanent getter. The getter was made by slowly evaporating a thin surface of misch metal[22] on the inside of the bulb in an argon atmosphere. The mish-metal surface is highly reactive with oxygen and was an effective trap. Gas from the storage tank was admitted to additional purification stages in the gas line. (A charcoal absorption trap cooled to 77 K was used in conjunction with the getter to take out nitrogen and residual heavier contaminants.) The clean gas was then passed through the leak valve at a slow rate into the metal tubes and collected in the sample chamber, which had been cooled previously to 1.2 K. The sample chamber consists of an approximately spherical bulb of volume 1 cm^3 blown at the end of a $\frac{1}{2}$-m length of 0.5-mm capillary. (The capillary also served as a final trap since the gas was admitted slowly enough that impurities could condense on the walls.) Pyrex was chosen for the sample chamber since it appears to be a weakly relaxing surface for ^3He spins at low temperature where diffusion of atoms into the walls is not an important relaxation mechanism.[14]

The cells themselves were cleaned at first by a method suggested by Horvitz,[23] who used a complicated procedure of baking under vacuum and rf discharge in low pressure of ^4He to drive impurities off the surface. Although some success was achieved with this method,[16] it was eventually abandoned not only because the process itself was extremely tedious but also because reproducible cleanness could not be obtained in successive series of experiments.

A far simpler and more reliable technique was to deposit a surface coating to cover residual impurities instead of attempting to remove them from the walls. Clean surfaces, which could be reproduced from run to run were achieved by coating the sample chamber walls with enough clean neon gas to build up several monolayers and cover any impurities. In effect, a neon container was created, whose surface was extremely weak in relaxing ^3He spins.

The neon was admitted at a pressure of 2 mm at room temperature just before beginning to precool the apparatus. As the system cooled during the liquid-helium transfer, the neon condensed on the walls, forming a layer over the impurities and higher-boiling-point gases which were not removed by the traps. Further improvement was made by annealing the neon coating, i.e., heating the surface to about 18 K for several hours.[24] T_1 values measured after the annealing process were consistently 15% longer than those on unannealed surfaces at the same conditions of temperature and density.

Neon was chosen as the coating substance since it is spinless, has a low dielectric constant, and a low boiling point. Argon may also be suitable. Below 4.2 K it may be possible to use ^4He since it is preferentially absorbed in this temperature range owing to its slightly larger isotopic mass.[25] Barbé *et al.*[15] have successfully used a coating of H_2 to reduce ^3He wall interactions in low-density pumping experiments.

These preparations were successful in allowing observation of pure-gas relaxation at high densities ($\rho < 5.0 \times 10^{-2}$ g/cm^3) but eventually a lower limit was reached around 1.0×10^{-2} g/cm^3 at which the wall relaxation rate was roughly equal to that of the bulk gas. An estimate of sample chamber purity could be obtained from the expression for the wall relaxation time T_{1W}[16]

$$T_{1W} = 4R/3\alpha\bar{v} \tag{12}$$

where $\bar{v}$ is the thermal velocity of ^3He atoms in a spherical cell of radius R and α is the wall relaxation probability. In the uncoated Pyrex cells of radius 0.5 cm, the limiting value of T_{1W} at 4.2 K and a density of 1.0×10^{-2} g/cm^3 was roughly 3×10^3 sec, whereas in the annealed neon coated cells at the same conditions, T_{1W} was consistently 2×10^4 sec. Using Eq. (12), $\alpha = 1.5 \times 10^{-8}$ for the bare Pyrex surfaces and is equal to 2×10^{-9} for the coated surfaces.

IV. RESULTS AND DISCUSSION

The measurements reported in this paper were taken at a field of 1.0 kG in sample chambers coated with neon gas over a temperature range of 1.7–19.0 K and at densities at which the mean free path was much larger than the atomic diameter, so that the dilute gas limit was a good approximation: ($\rho < 5.0 \times 10^{-2}$ g/cm^3). In this regime, the bulk gas relaxation rate scales with density, as observed previously.[16] It is important to realize, however, that since wall relaxation was present in varying strengths in all measurements taken at lower densities especially ($\rho < 1.0 \times 10^{-2}$ g/cm^3), its contribution could not be ignored. The phenomenological approach outlined earlier [Eq. (3)] was used to separate the wall and bulk gas relaxation. This theory can lead to serious systematic errors if other relaxation mechanisms dependent on density are present, but there is empirical justification for using Eq. (3) in the density range observed since plots of ρT_1^{-1} vs ρ^2 always yielded straight lines (Fig. 5). At higher densities the effects of three-body collisions may become important, and it may be necessary to consider a term $C_3\rho^2$ which describes the effect in a phenomenological way. There was, however, no evidence of any contribution from three-body collisions when the results

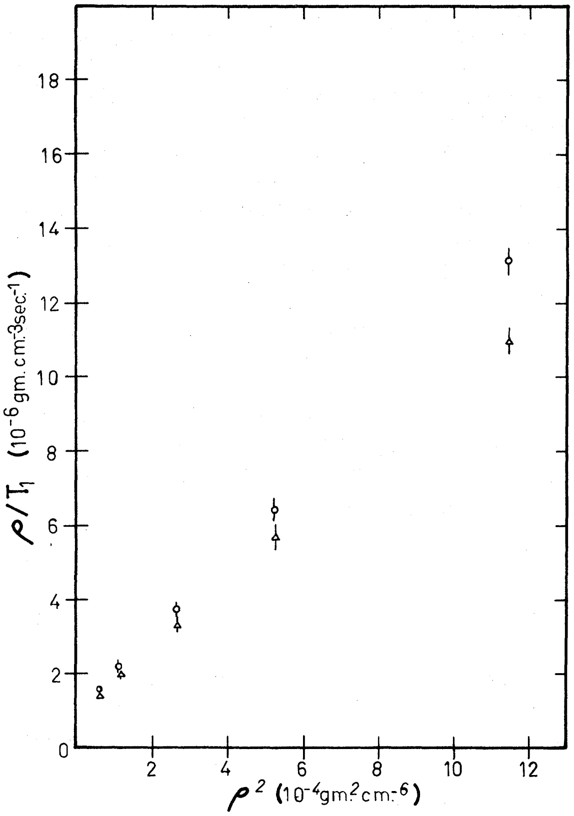

FIG. 5. ρ/T_v vs ρ^2. Measurements were taken at 1.0 kG. Triangles, 8.5 K; circles, 6.5 K.

were analyzed with the additional term in Eq. (3).[26]

Measurements were made at at least three densities for each temperature, and the recovery of the signal was observed to be exponential. Values of T_1 were obtained by fitting the data by the equation $\ln y = mt + b$.

The temperature dependence of T_{1B} is plotted in Fig. 6 for comparison with calculations using the potentials described earlier. The sum of squared deviation between theory and experimental data was calculated for each potential and is presented in Table I.

Agreement with the calculated values is remarkably good. The BM potential, with a well depth of 10.8 K, fits the data closely in the range 3–19 K, but the calculated values are slightly higher at temperatures below this range. The Beck potential, with a more shallow well, deviates at each end of the measured range, underestimating at high temperature and overestimating at low temperature. The MS potential, which has the deepest well, gives the best fit at low temperature but underestimates at high temperature. The least value of the sum of squares was obtained with the BM potential.

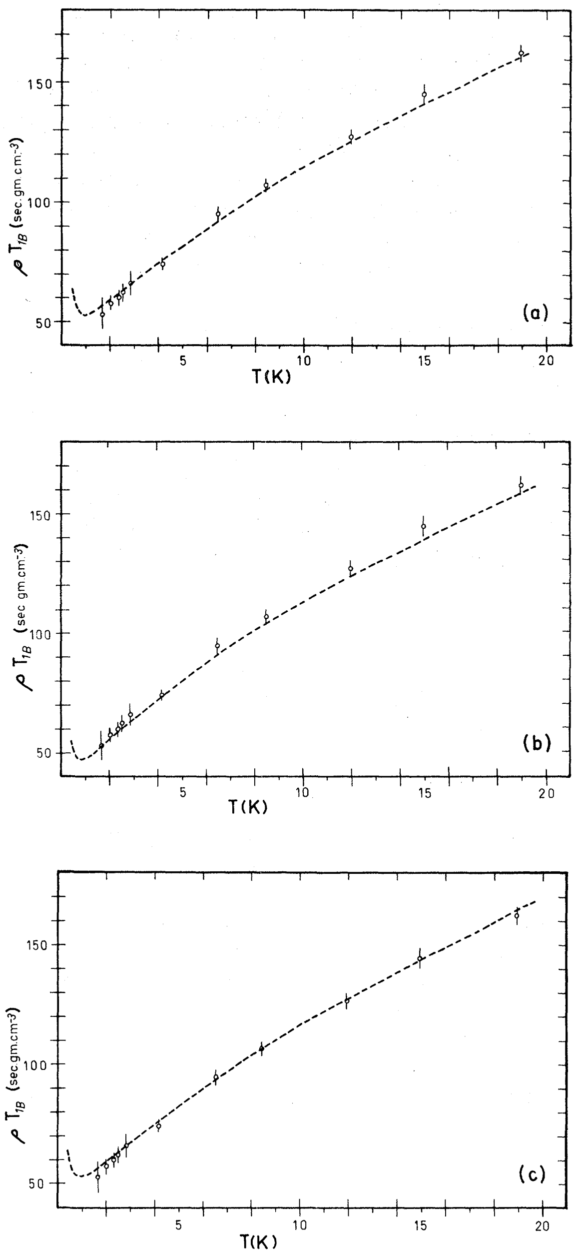

FIG. 6. Temperature dependence of T_{1B}. Broken curve, calculation of T_{1B} using (a) Beck potential, (b) MS potential, and (c) BM potential.

It is clear that relaxation via the dipolar coupling alone is sufficient to explain the relaxation. An upper limit can be placed on the relaxation rate for relaxation via the spin-rotation interaction by considering the agreement with experiment at high temperature where the spin-rotation cross section is largest. The empirically determined relaxation rate for bulk gas relaxation can be expressed as a sum of dipolar (T_{1D}) and spin-rotation

TABLE I. Results of fitting temperature dependence by calculations of T_{1B} using available helium potentials.

Potential	Adjusted parameters	Well depth (K)	Sum of squared deviations for ρT_{1B} [(sec g/cm^3)^2]
Beck	None	10.3	42.0
MS	None	12.0	94.0
BM	None	10.8	25.0
	d		
MS	−5.5	14.5	128.0
MS	−4.75	11.5	64.0
MS	−4.55	10.9	39.0
MS	−4.35	10.2	45.0
MS	−4.05	9.3	198.0
	A (10^{-15} erg)		
BM	1.563	11.2	11.7
BM	1.603	11.5	10.6
BM	1.643	11.8	11.5

(T_{1SR}) components

$$T_{1B}^{-1} = T_{1D}^{-1} + T_{1SR}^{-1} \ . \tag{13}$$

At 19.0 K and 10^{-2} g/cm^3, $T_{1B}^{-1} = (6.17 \pm 0.2) \times 10^{-5}$ sec^{-1}, so the upper limit of the spin rotation relaxation rate is roughly the experimental uncertanty 0.2×10^{-5} sec^{-1}.

There are no simple prescriptions for direct inversion of transport property data to obtain parameters of the interatomic potential. Having chosen a particular form which satisfies the data as well as the potentials used, it is possible to test the sensitivity of T_{1B} to the potential by adjusting the parameters by trial and error and comparing with experiment. It may be argued that adjusting the potentials is unneccessary since the fits with all three potentials are remarkably good. But it is useful to see how sensitive T_{1B} is to the potential and if possible determine which potential and what value of well depth gives the best fit. The results of the fits with adjusted BM and MS potentials are also shown in Table I.

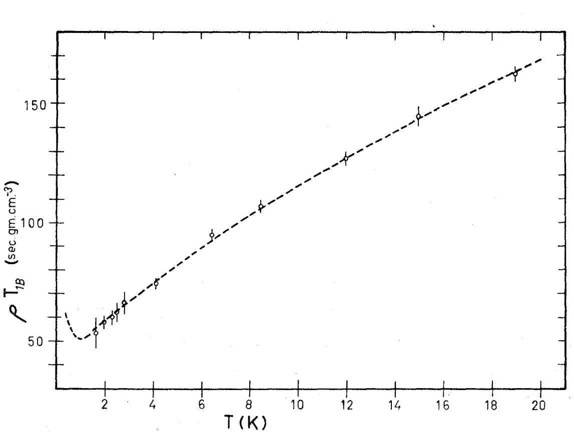

FIG. 7. Temperature dependence of T_{1B}. Broken curve, calculation using the best parameters of the BM potential.

Variations in the potentials were achieved by first determining the sensitivity of the well depth to each parameter and then varying the most sensitive parameter to obtain a desired depth. The depth could be changed by varying parameters in either the short-range or the long range part; only the short-range part of the BM potential was varied, whereas both parts of the MS potential were varied in turn.

Bruch and McGee did not quote errors for the parameters in their potentials; instead, they gave the accuracy to which the empirical data was fit by the potential, and it is not known how sensitive the potential is to the chosen data. The BM potential was tested with slightly deeper wells in order to improve the fit to the NMR T_1 data below 3 K. The best fit was obtained with a well depth of 11.5 K which was achieved by a 7% variation of the parameter A [Eq. (8)]. The NMR data is reproduced to within 3%, but it is not known how well the new adjusted potential fits the data originally used by Bruch and McGee. (See Fig. 7.)

Results are given in Table I for calculations of T_{1B} using the MS potential and variations obtained by adjusting the attractive part to achieve well depths between 9.3 and 14.5 K. The best fit is obtained for well depths slightly more shallow than the quoted value, but the high temperature results are consistently underestimated. An attempt was made to fit the data by making the potential less repulsive, but the high-temperature results were again far too low.

A two-parameter Lennard-Jones model is capable of fitting the results, over a restricted range, and can perhaps be used as a rough guess of the potential. The accepted Lennard-Jones helium parameters provide a good fit of the low-temperature data but seriously underestimate T_{1B} above 4.2 K. A better fit to the high-temperature data can be obtained only with values of well depth ϵ or range σ which are far out of line with the accepted values.

V. SUMMARY

The NMR relaxation time experiment has shown that a dipolar coupling can account for the observed relaxation in bulk ^{3}He gas, and that calculations using existing helium potentials can describe the results adequately. The data favor the Bruch-McGee potential, with a potential of that form having a slightly deeper attractive well than their original value providing the best fit.

It will be fruitful to extend the measurements to temperatures near 1.0 K to observe relaxation in the region of the T_{1B} minimum. Although the density of saturated ^{3}He vapor decreases rapidly below 1.5 K, the present equipment can be improved to reach the required sensitivity to make measurements in that temperature range. The noise observed in the experiment was of microphonic origin and stronger than the limiting thermal noise estimated from Nyquist's relation by about three orders of magnitude. The lowest density observed was 10^{-3} g/cm^3 at 1.4 K with a signal-to-noise ratio of 4; with improved design to reduce microphonic noise and increase amplifier gain, it should be possible to observe signals at 1.0 K where the saturated vapor density is 5×10^{-4} g/cm^3.[27] An obvious improvement in signal-to-noise ratio could be obtained by immersing the entire bridge in the liquid He bath. The bulk gas relaxation time at such low densities will be of order 10^5 sec; so it will be necessary to make measurements at higher fields where the wall relaxation rate is much weaker, since the spectral density for the fluctuating fields at the surface cuts off at a much lower frequency than in the bulk gas.

The relaxation could also be studied in sample chambers coated with other gases such as heavier rare gases, or H_2 or D_2 which have smaller dielectric constants than Ne and may be less efficient in relaxing ^{3}He spins.

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