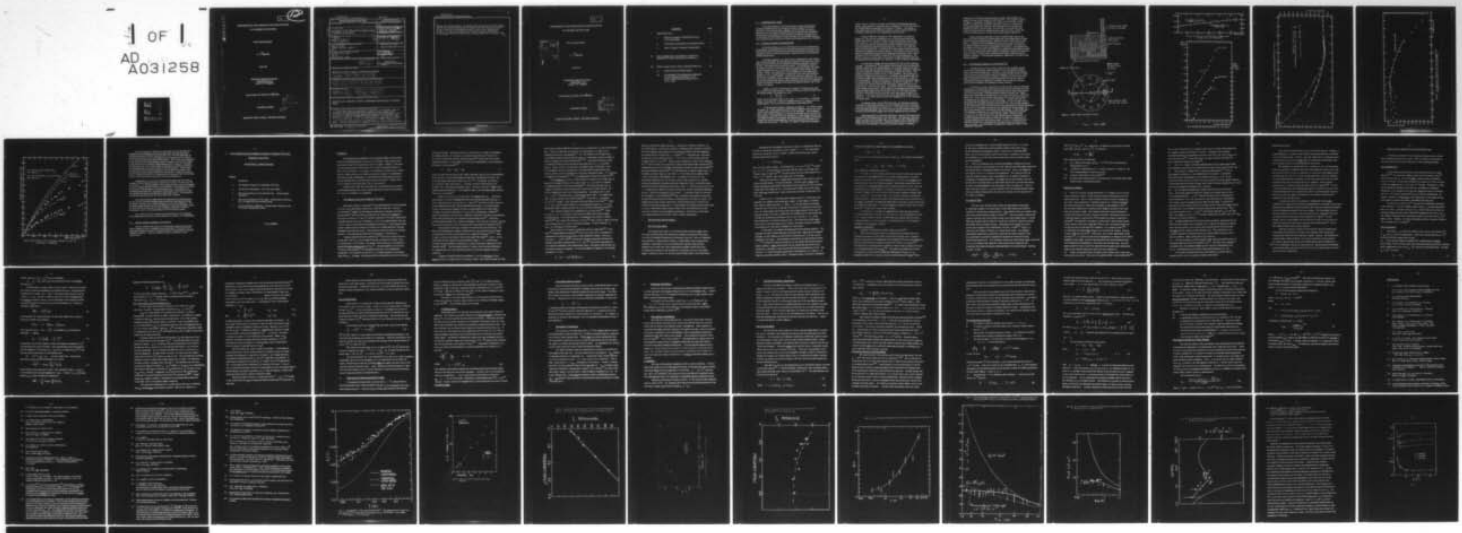
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EXPERIMENTS ON THE FORMATION AND SURFACE STATES OF ADSORBED HELIUM FILMS

Final Technical Report

by
D. F. BREWER

July 1976

EUROPEAN RESEARCH OFFICE
United States Army
London N.W.1, England

Grant Number DA-ERO-124-74-C-G0046

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This report contains a summary of results on 1) relaxation times in monolayer and submonolayer ^{3}He films adsorbed on Vycor porous glass, 2) density of adsorbed helium deduced from capacitance measurments, and 3) progress on a modified POMERANCHUK cooling project. For the first item the report summarizes several recently developed phenomenological models in an attempt to explain some of the properties of ^{3}He in Vycor porous glass. Several experiments are suggested which may help in discrimination

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between the various models. The second item refines this research groups view on the correlation between the density and the dielectric constant of the system under investigation based on some recent experimental evidence. In the third portion of the report contains information on the groups efforts to extend their cooling range down to helium 1.2mK.

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(1) Sussex University Internal Report

(2) Proceedings of 14th International Conference on Low Temperature Physics, LT.14 (North-Holland/American Elsevier 1975) Vol.1, p.463

I. EXPERIMENTAL WORK

In the Final Report for 1974 we described at length some detailed results on relaxation times in monolayer and sub-monolayer ^{3}He films adsorbed on Vycor porous glass, together with the situation concerning experiments on the density of adsorbed helium as deduced from capacitance measurements and progress on the modified Pomeranchuk cooling project. All three sets of experiments have been continued with considerable success, and we present here a summary of results and of analysis as so far completed.

I.1 Dielectric constant of adsorbed helium

In previous reports, we have described this work as a measurement of the density of adsorbed helium, but the results presented below lead to the conclusion that the correlation between density and dielectric constant is not understood, and we therefore now prefer to describe them only as dielectric constant experiments.

As already explained, the experimental arrangement is quite simple, and consists essentially of a parallel-plate capacitor containing Vycor porous glass into which helium can be condensed at pressures between 0 and about 35 atm., and temperatures between 1K and 4K. The difficulties which we described in Section I.1 of the last report have been eliminated by the means of shielding proposed there, and we have confidence in the validity of our results. Figure 1 is a diagram of the final design of the low temperature capacitance cell. Measurements of capacitance were made with a MOSFET oscillator at a frequency 20MHz. The effective dielectric constant is the ratio of the capacitances with and without dielectric material between the plates, and because of the porous nature of the material this has then to be interpreted to give the dielectric constant of the body of the porous material, and of the helium in the pores.

Figure 2 is a plot of the dielectric constant ϵ' of porous Vycor and of ϵ_v of the Vycor glass material. The first of these is derived directly from the measurements, the second is given by

$$\epsilon_v = \frac{(\epsilon' - 1)}{1 - \upsilon} + 1 \qquad (1)$$

where υ is the fractional volume of the voids, i.e. the porosity. As already stated, the temperature variation is unusually large, for a reason which we cannot explain. We are at present examining various possibilities.

A ^{4}He adsorption isotherm which was carried out at T=1.995K is shown in Figure (13). Equal quantities of the ^{4}He were condensed into the cell, each quantity being represented by a division on the abscissae. They condensed from a fixed volume of pipework in a period determined by the time taken for the pressure, measured with an oil manometer, to drop between fixed limits. The vapour pressure of the sample was measured with a Wallace and Tiernan Gauge which was calibrated against a mercury manometer and found to be accurate to within ½ torr. The 'dielectric constant' values were calculated

using a value of υ equal to that used in analysing the filled pores data (see below); thus (apart from the points which correspond to ^{4}He with filled pores) the ordinate does not represent a true dielectric constant. The change in slope which occurs in the "dielectric constant" curve is characteristic and is probably associated with the completion of the first layer.

Values of dielectric constant for ^{4}He "filled pores" are shown in Figure (4). The value of υ was taken to be 0.3 from our previous work. Suitably normalized, our bulk ^{4}He data are also shown (some of the points taken around T_λ are omitted for clarity) and are compared with the values of the dielectric constant obtained from the known density measurements. The well established value for the polarizability, 0.123 (c.g.s. units) was used to convert the density. Agreement of the bulk values is extremely good, and gives us confidence in our basic results. The points for helium in Vycor show an increasing discrepancy as the temperature increases, which must be attributed to the characteristic properties of the restricted geometry. The density maximum is much closer to the normal lambda temperature than are the temperature of the specific heat maximum, or that of onset of superfluidity.

The dielectric constant was also measured for ^{4}He at near monolayer coverage. The quantity of ^{4}He to condense was estimated from the adsorption isotherm (Figure (3), and corresponded to two divisions along the abscissae. This may be less than the quantity needed for a complete monolayer, especially if only the 'dielectric constant' curve is taken as a guide (see above). The analysis required an estimate of υ for a ^{4}He monolayer. By assuming it to consist of a single layer of atoms 3.6 Å in diameter, and using the value for the specific surface area obtained previously in this laboratory, a value of 0.06 was deduced. Values of the dielectric constant obtained using this figure, but uncorrected for the effect of desorption, are shown in Figure (15). This correction was important because the dead spaces, especially those at low temperatures, were relatively large. It was also difficult to estimate because of the complex cell geometry, and the effect of the changing temperature profile along the sample lines as the level of liquid ^{4}He in the ^{4}He dewar dropped. Because of these difficulties the correction was only accurate enough to be indicative. It was only worked out at 4K, and is represented by the arrow in Figure (6); it is evident that the temperature dependence for a ^{4}He monolayer is at least small.

In absolute terms, both the ^{4}He 'full pores' and monolayer dielectric constants are interesting because they are both higher than can be accounted for by the increased density of ^{4}He in Vycor. This might be due to the effects of the particular geometry of the Vycor cavities, but the measurements under pressure described below suggest that another explanation may be correct.

Measurements of the dielectric constant as a function of pressure were carried out at the temperatures 1.41K and 2.08K. The pressure, which was applied via one of the two sample lines, was measured with a Budenberg dial gauge connected to the other line. Pressures could be read to within $\frac{1}{2}$ p.s.i. In this way it was possible to correlate any sudden changes in frequency

(indicative of a ^{4}He liquid-solid transition in Vycor) with blockage of the sample lines due to the formation of solid bulk ^{4}He. The results are shown in Figure 6, calculated according to two models, in one of which ("single sphere") the filled Vycor pores are assumed to behave as a collection of non-interacting spheres, while the other assumes that the internal field connection is zero. In either case, the variation in ϵ is much less than would be expected from the statistical layer model of the film, unless 60% of it were incompressible. We thus need to seek another explanation.

Another possible explanation is that an induced dipole exists in the atoms of the first monolayer, resulting from the very strong adhesive forces, which lead to the enhanced dielectric constant of the first layer and the filled pores. A difficulty with this suggestion is that it is not clear in detail how the induced dipoles could orient in the applied eleotric field, since they may be expected to remain always perpendicular to the surface. It is possible that this could occur if the atoms move slightly in a sharply varying surface potential. If so, then the anomalously small variation of dielectric constant with pressure shown in Figure 6 must be due to inhibition of the dipole orientation as the pressure increases. This somewhat speculative explanation is currently being further explored.

I.2 Pomeranchuk refrigeration with adsorbed ^{3}He

In the past year, we have firstly carried out with complete success conventional Pomeranchuk cooling of liquid ^{3}He into the superfluid phases, using a reconstructed apparatus. Secondly we have installed the off-melting curve cell and carried out experiments which appear to show (i) that the basic requirements for the process are satisfied, allowing us to look for the polar phase of superfluid ^{3}He without solid being present, (ii) that the range of Pomeranchuk cooling is significantly extended, and (iii) that the method is particularly advantageous for adapting to indirect cooling.

For the first of these experiments we made several small but important alternations to the apparatus, including improved thermal anchoring of the ^{4}He compression line and enlarging the channel connecting the main compressional cell to the strain gauge, which had become blocked with solid ^{3}He. These improved the performance considerably, but we were still unable to cool below about 5mK. After several further experiments which included examination of the operation of the bellows at room temperature, it became clear that the particular bellows configuration used was unstable. In order to reduce as far as possible the dead space occupied by bulk liquid ^{3}He, they had been designed so that compression of the ^{3}He was achieved by compressing the bellows themselves. In this case, it is possible for them to move sideways and scrape against the side of the container with considerable frictional heating. A more stable (and conventional) arrangement is to compress the ^{3}He by extending the bellows (i.e. the ^{3}He is on the outside rather than the inside). When the stable arrangement was used the main frictional heating problem disappeared. In several subsequent experiments we were able to reduce the temperature at melting pressures from about 32mK to below 1.2mK (i.e. through both the A and the B transitions of superfluid ^{3}He) and keep it there for periods of the order of an hour. The conventional Pomeranchuk cooling has therefore been completely successful.

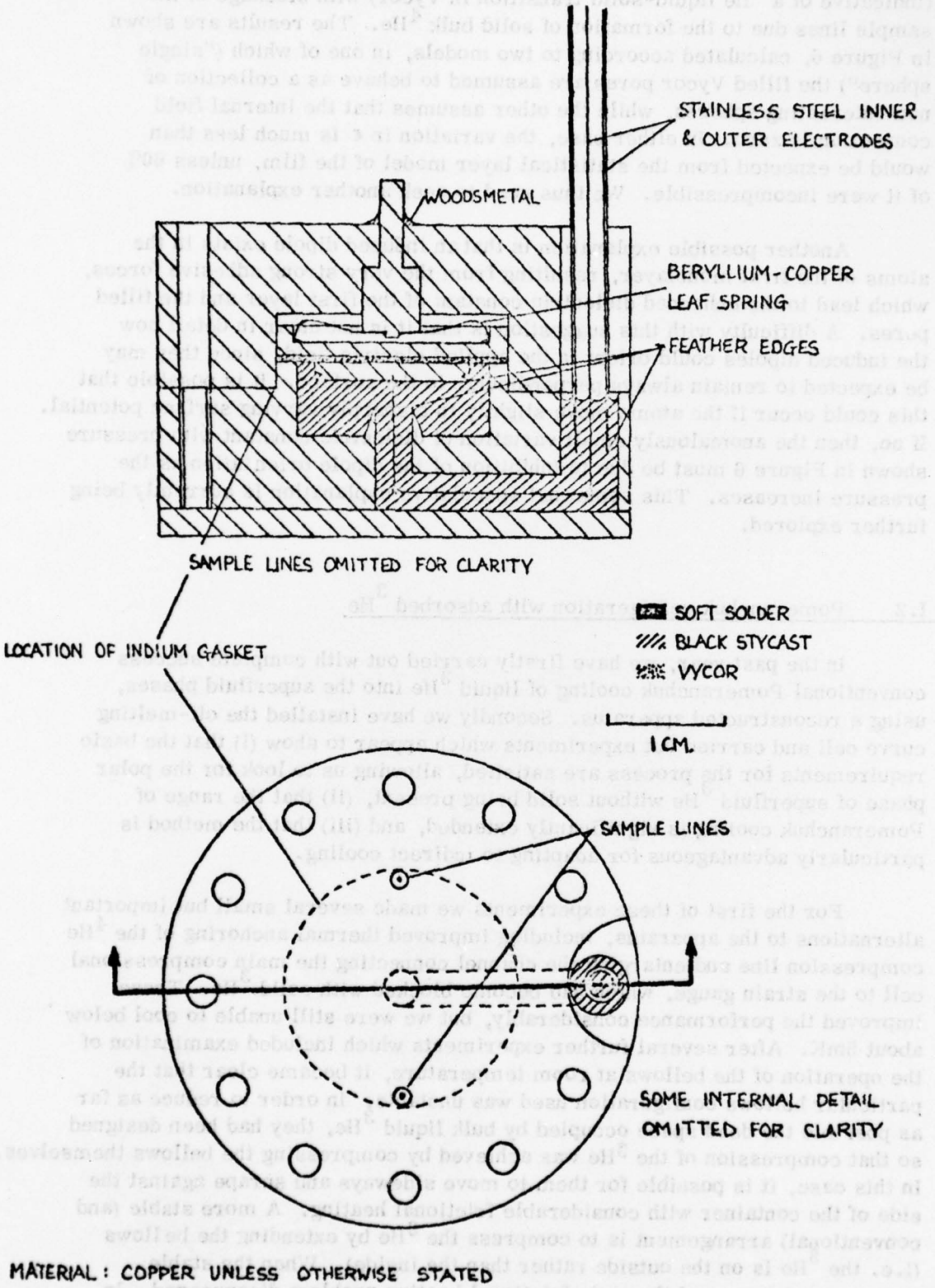
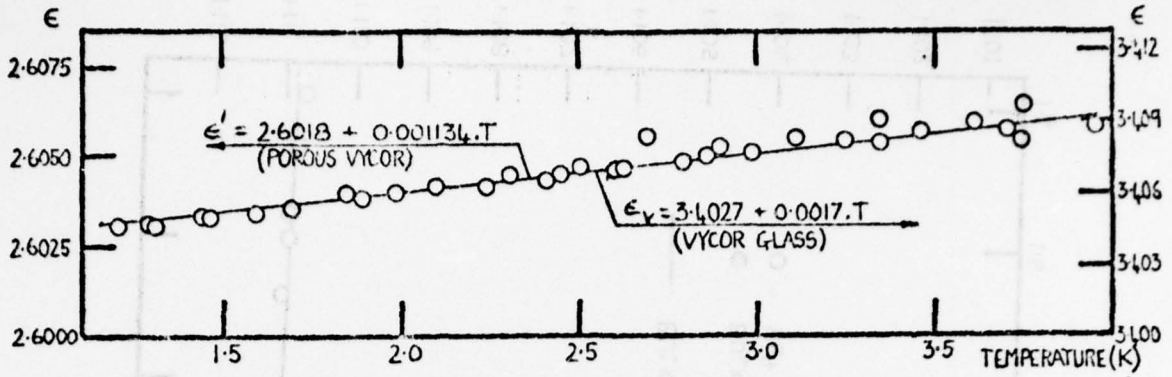
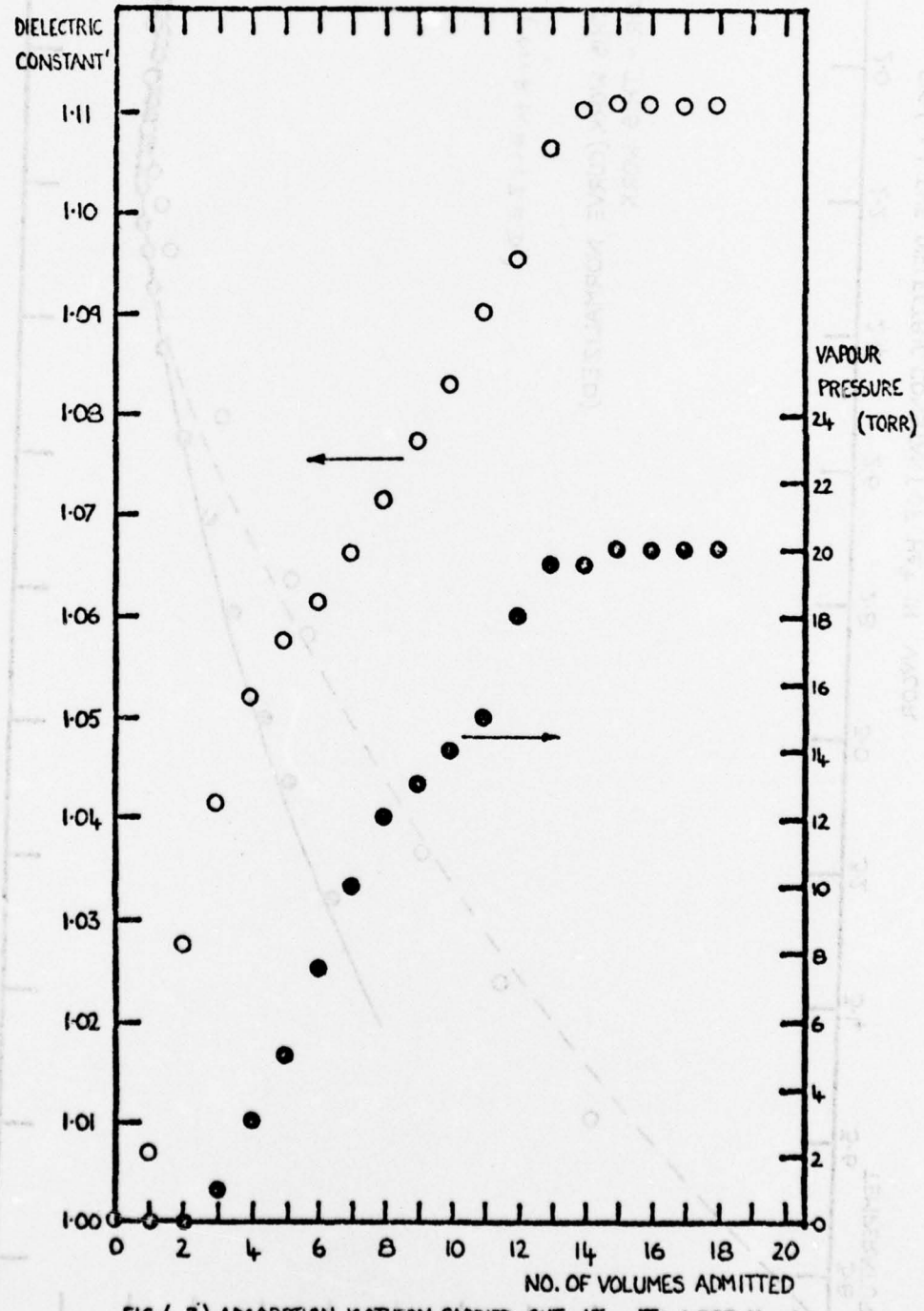


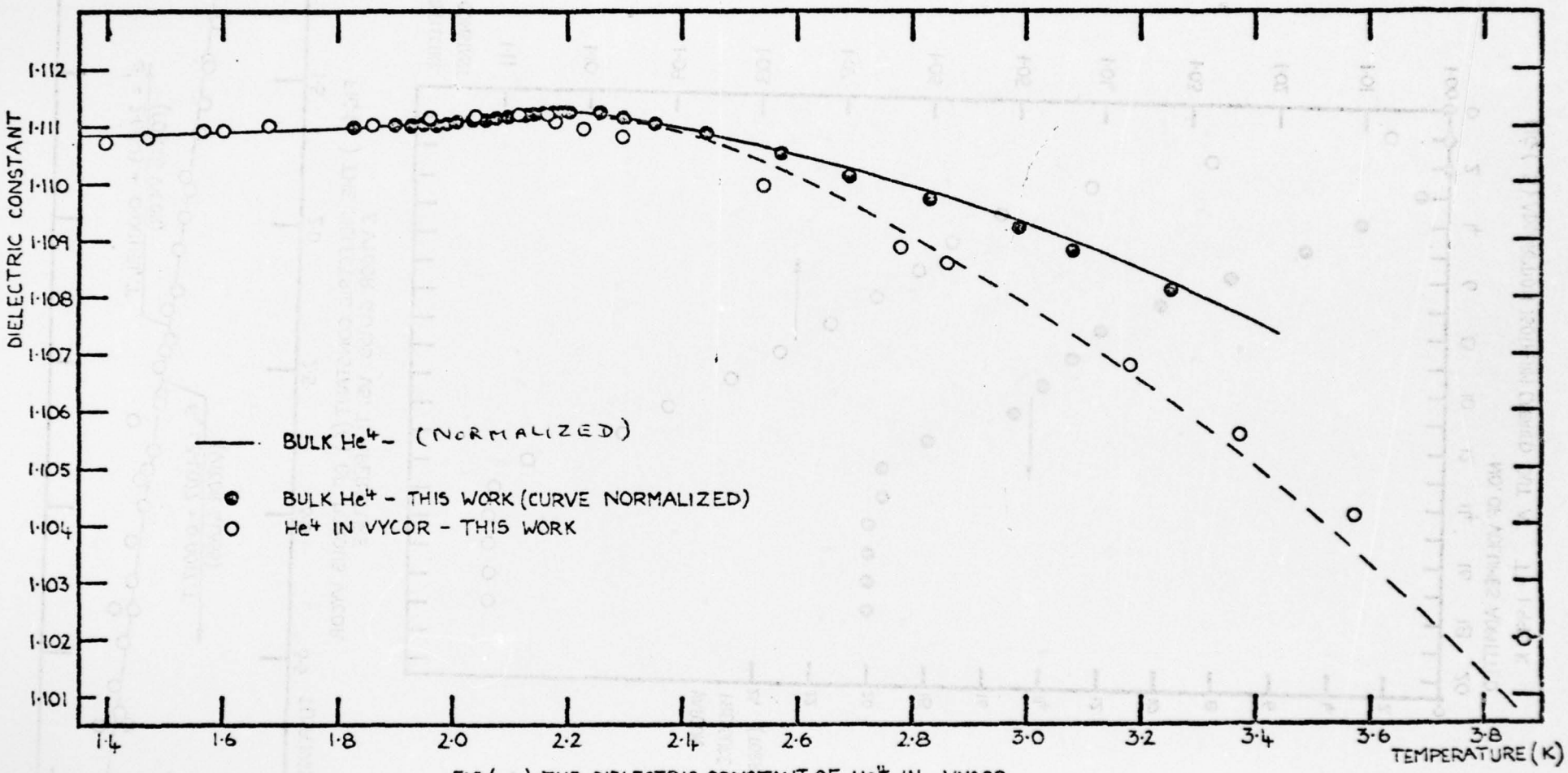
FIG 1 The cell



FIG(2) THE DIELECTRIC CONSTANT (ϵ) OF POROUS VYCOR & VYCOR GLASS VS. TEMPERATURE



FIG(3) ADSORPTION ISOTHERM CARRIED OUT AT T= 1·995 K



FIG(4) THE DIELECTRIC CONSTANT OF He^4 IN VYCOR

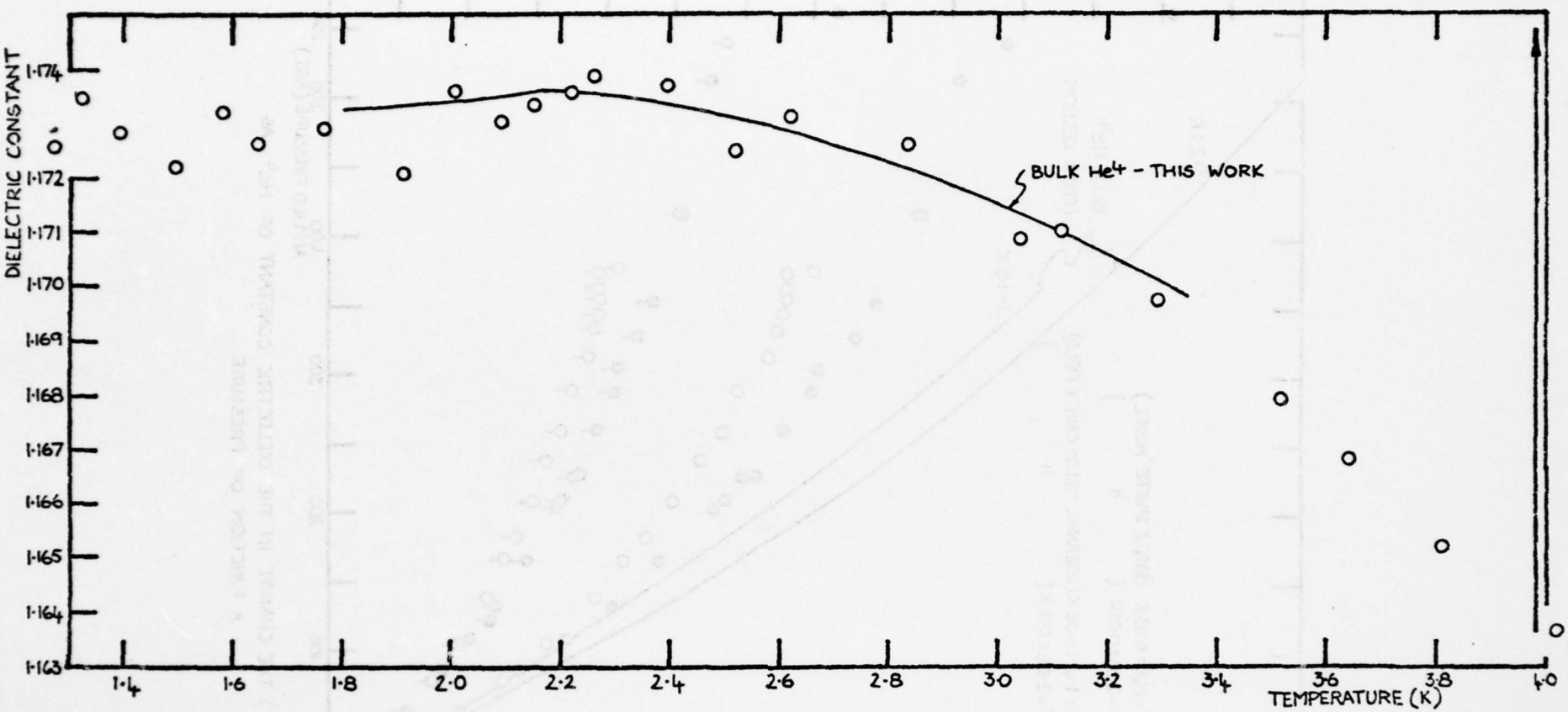


FIG (5) THE DIELECTRIC CONSTANT OF THE He^4 MONOLAYER (UNCORRECTED FOR THE EFFECT OF DESORPTION)

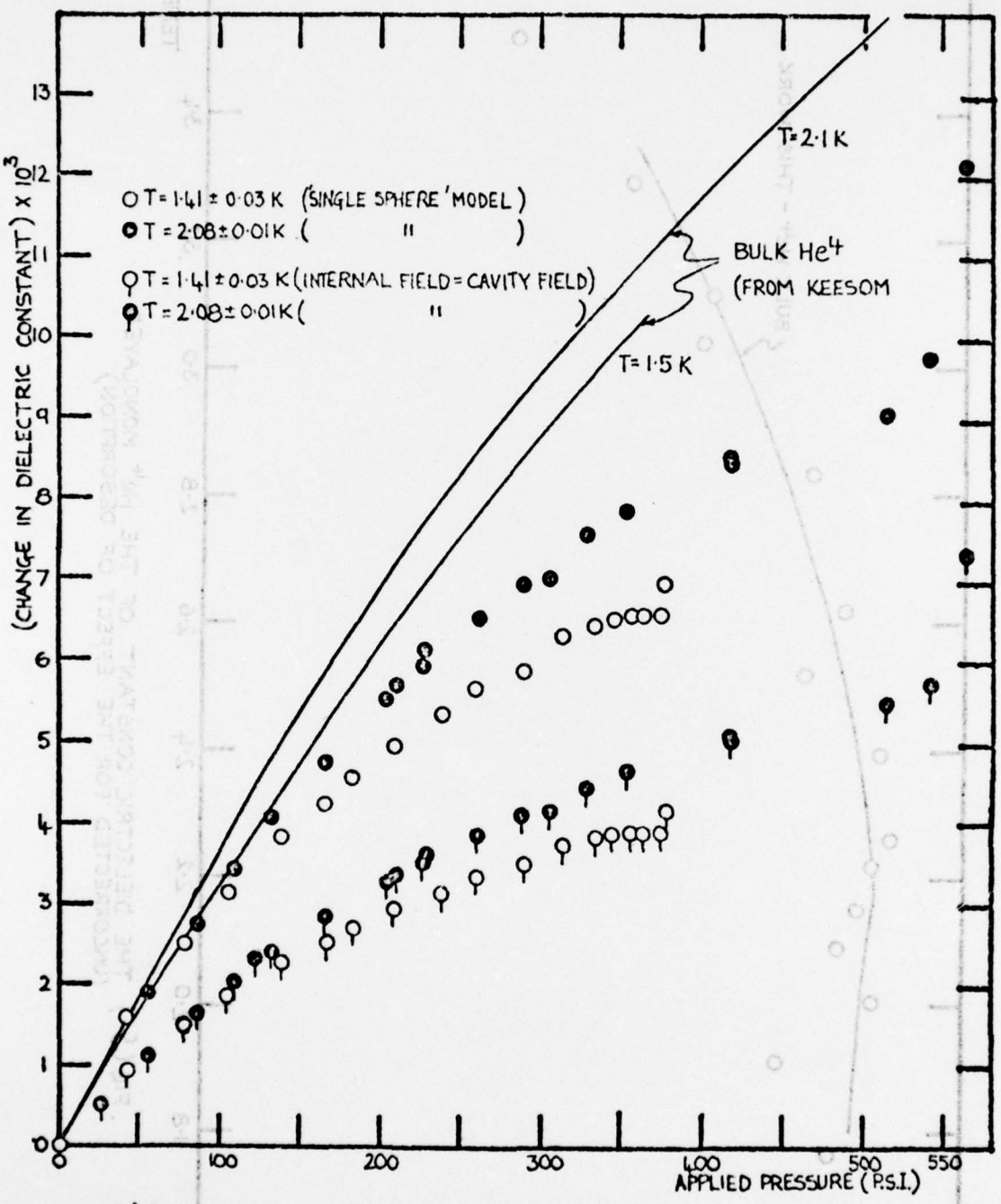


FIG (6) THE CHANGE IN THE DIELECTRIC CONSTANT OF He^4 AS A FUNCTION OF PRESSURE

The next step was to replace the conventional cell with the specially designed version containing Vycor porous glass discs and incorporating a hydraulically operated needle valve on the ^{3}He cell. With this apparatus we were able to carry out a series of experimen ts to measure the pVT relation of the combined bulk liquid/adsorbed ^{3}He system. The pressure was monitored in the usual way with a strain gauge pressure transducer, and volume changes by the movement of the bellows, again measured with a capacitive technique. Solidification in the Vycor pores should be detected by an apparent increase in the compressibility at pressures below the melting pressure. Unfortunately during these runs the dilution refrigerator was not operating properly, and we were able to take measurements only at about 95mK. These did, however, seem to confirm that there is a melting line for the adsorbed ^{3}He which is about 10 p.s.i. below the bulk melting curve at the same temperature.

Subsequently we carried out a Pomeranchuk experiment which gave a cooling of 15mK without formation of bulk solid, with only 10% of the total ^{3}He in the Vycor. For various reasons we were again not able to start compression at a lower temperature than 105mK, but we reached a low temperature of 20mK, the last part of the process on the bulk melting curve. This represents an important enhancement over conventional Poleranchuk cooling which we hope will continue into the lower temperature region below 20mK. The reasons for the high starting temperature are not entirely clear at present.

The success of these experiments has emphasized an important point, namely that this modified cooling process provides an outstanding advantage for indirect cooling, and we shall incorporate this into our programme. The advantage arises from the fact that the inhibition of bulk solid formation around the heat transfer surfaces prevents the consequent reduction in interface conductance, which is a serious problem in the conventional method.

The results of the pVT measurements outlined above were presented at the Manchester Solid State Physics Conference in January 1976 (unpublished).

I.3 Nuclear magnetic resonance measurements

We have continued our extensive measurements of spin-spin and spin-lattice relaxation times in monolayer and submonolayer ^{3}He films on Vycor, and further analysed our previous measurements of the susceptibility and spin diffusion coefficient. These are reported in detail in Sections III and II respectively.

II. Some Considerations of the Magnetic Properties of Multilayer ^{3}He Films Adsorbed on Vycor Glass

Internal Report - Sussex University

Contents

Introduction

1. The Magnetic Properties of Multilayer ^{3}He Films
2. The Nuclear Susceptibility - the 'Two-Fluid' Model
3. Spin-Spin Equilibrium in the Saturated Film - various models discussed.
4. Spin-Lattice Relaxation in ^{3}He Films - contrasting the behaviour of T_1 in single layer and multilayer films.
5. The Spin Diffusion Coefficient - with particular reference to the 'Two-Fluid' susceptibility model.

D. J. Creswell

Introduction

The following notes summarise several phenomenological models which have been developed during the last year in a n attempt to explain some of the properties of liquid ^{3}He contained in porous Vycor glass. Multilayer ^{3}He films are fascinating systems in which layers of very different quantum degeneracy exist in close proximity. For example, it is not known, when inter-layer motion occurs, whether particles carry their mean thermal energy and 'susceptibility' with them (quantum assimilation) or even whether the Landau approach can be used in situations where translational invariance is violated[1]. Effects which may be relevant to superfluid liquid ^{3}He are also apparent.

It will be clear from these notes that more experimental data is needed to discriminate between the variou s models discussed, and several experiments which may prove definitive are suggested.

I. The Magnetic Properties of Multilayer ^{3}He Films

Adsorption isotherm experiments[2] have established that the first adsorbed layer has a very high density appropriate to solid ^{3}He at 400 atm. Thermal measurements[3] suggest that the dominant excitations are phonons and N. M. R. measurements[4] show that the correlation time for atomic motion within the first layer is between 10^{-7} and 10^{-6} seconds, both pieces of evidence endorsing the conclusion that the first layer is solid like. In view of the tight-binding to the wall (~50 K), atoms are precluded from jumping out of this layer, and the spatial extent of their wavefunctions is probably so restricted as to inhibit significant exchange coupling with second layer atoms. The properties of this first layer are believed, therefore, to be substantially unaffected by adsorption of a second layer.

Magnetic experiments on the second layer[5] have been carried out by pre-plating with a ^{4}He layer and it is found the atoms are much more mobile, with a correlation time $\sim 10^{-9}$ seconds. The density of the second layer is equivalent to liquid/solid on the melting curve (32 atm.)[2]. The susceptibility of a two-layer ^{3}He film is best explained[6] by assuming the first layer to be magnetically independent, and treating the second layer as an antiferromagnetic Curie-Weiss solid with T_N = 36 mdeg., which agrees with correlation time above if the dominant

motion is exchange. Adsorption isotherm measurements have shown that following the addition of more layers (which are essentially like bulk liquid ^{3}He under the S.V.P.) the second layer itself is depleted somewhat[2] and may therefore become liquid-like in nature. In fact down to 0.4 K the total susceptibility χ can be adequately described by the expression[6,7]

$$\chi = c_1\chi_1 + c_2\chi_2 + c_f\chi_f \qquad (1)$$

where c_i is the relevant mass in each region of the film, χ_1 is the (Curie) susceptibility of the monolayer, χ_2 the susceptibility of liquid ^{3}He (extrapolated) at 32 atm. and χ_f the bulk liquid susceptibility under the S.V.P.[8]. Treating the second layer on a molecular field model with T_N = 36 mdeg. of course works equally well. In either case, to get perfect agreement (Fig. 1) one has to allow for a slight density enhancement of the third layer; the magnetic profile is still changing slightly until the fourth layer is reached[6].

Below 0.4 K, however, the prediction of the liquid-model (χ_2 = bulk liquid susceptibility at 32 atm) is significantly lower than the experimental value (Fig. 1). Three explanations have been put forward. The first[7] attributes the discrepancy to a partly solidified second layer with the solidified part having a Curie susceptibility. Second, the second layer might be treated as a homogeneous Curie-Weiss solid, although at the lowest temperatures $T \sim T_N$ so exact calculations are difficult[6]. Third, the second layer is treated as a liquid but is believed to enhance the susceptibility of the central liquid region via a substrate-mediated interaction[9]. In section 2 we discuss these models from a different standpoint, with particular reference to the last because of its relevance to ultra-low temperature experiments on superfluid ^{3}He[10].

The properties of the spin relaxation times in the saturated (full-pores), ^{3}He film are interesting from a number of points of view, but particularly so in relation to the behaviour of these same parameters in a single ^{3}He monolayer[11,12]. Both T_1 and T_2 are very much shorter than the bulk liquid ^{3}He values[13], and are, in fact, comparable with the values seen in the monolayer (Figs. 2 - 5). It follows that the entire film is relaxing (or dephasing) as a result of processes taking place in the adsorbed layers[5]. The interesting question of course, is how the spin information is communicated to the rest of the film in such a way that the magnetic profile is preserved.

A number of features should be mentioned. T_1 for the monolayer is very unusual in that T_1 is vaguely linear in frequency (Fig. 2), also passing through the origin

and therefore making it difficult to estimate the correlation time (τ_c) and second moment (M_2). The linear behaviour is believed to be related either to a range of τ_c's resulting from surface heterogeneity[14], or to the anisotropy of the dipole interaction which becomes important because atoms are constrained to move on planes at arbitrary angles to the main-field direction[12,15]. In the saturated film T_1 goes as (frequency)^2 which is characteristic of most liquid-like ($\omega\tau_c \ll 1$) systems (Fig. 3). Since, however, the monolayer is still the origin of relaxation, either the heterogeneity has been smoothed out or the dimensional constraint has been removed and the system is behaving as a truly three dimensional entity. T_1 recoveries are slightly non-exponential[11,12] T_1 is independent of temperature below 1 K[16].

In the monolayer T_2 rises ("10/3" fashion) as frequency is increased (Fig. 4) However the change takes place in a regime where $T_1 \gg T_2$ so that it is difficult to attribute the effect to life-time broadening[12]. In the saturated film (Fig. 5) a single well-defined T_2 exists but there is no such increase with frequency, and in fact a slight drop occurs at the lowest frequencies. According to the T_1 data, $\tau_c = 1.5 \times 10^{-7}$ seconds so that T_2 should rise around 1 MHz. It is possible that there are two branches to the spectral density[17], so that the τ_c, appropriate to T_2 is $\gg 10^{-7}$ seconds, or that extraneous local field effects are present[18]. Since $T_1 \gg T_2$ in a system which is known to be predominantly liquid ($\omega\tau_c \ll 1$) it is dangerous to infer anything from the ratio T_1/T_2 in these adsorption systems[19].

Fig. 6 shows the temperature dependence of T_2 at full-pores[16]. Plots of $\ln T_2$ vs. $1/T$ are non-linear so that the data cannot be fitted with a single activation energy. In fact the behaviour is reminiscent of the behaviour of both solid ^{3}He[20] and a single ^{3}He monolayer on Vycor[12], with a 'plateau' region occurring at low temperatures as a result of exchange tunnelling. Various models for T_2 and T_1 are discussed in sections 3 and 4.

Experiments on the transport coefficients (thermal conductivity[21], mass flow[22] and spin diffusion coefficient[23]) have been carried out to investigate the modification of Landau-type properties in the collisionless regime. The mean-free-path $\lambda = .3/T^2$ (in $\mathring{A}$)[24] and therefore becomes comparable with the pore-diameter d ($\sim$60 $\mathring{A}$) at approximately 0.1 K. Rice[25] has derived expressions for the transport coefficients in the collisionless regime, allowing for both specular and non-specular boundary conditions. For the spin-diffusion coefficient D, the limiting expression ($\lambda \gg d$) is

$$D = \frac{1}{3}(1 + Z_o/4)\,\frac{(\nu+1)}{(\nu-1)}\,V_F\,d \qquad (2)$$

where Z_o is the usual Landau parameter, ν the specular reflection coefficient, V_F the Fermi velocity, and d the pore diameter (assuming perfect cylindrical channels). All of the transport experiments are in qualitative agreement with this suggesting that Landau theory is valid in the $\lambda \gg d$ regime[23]. To get numerical agreement, the data have to be scaled by a factor $F = \epsilon X$, where ϵ is the porosity and X the tortuosity factor for Vycor[26]. There is some confusion as to the correct definition of F[27] and the values used in the three transport experiments differ considerably[28], although there may be fairly obvious experimental reasons for these discrepancies[29]. In the spin diffusion experiment[23] F is determined by scaling the results (Fig. 7) to the high temperature region ($\sim$0.2K) where $\lambda \ll d$ and the particles diffuse within a pore at the ordinary bulk diffusion rate. F is taken to be $0.09 \pm 80\%$, the uncertainty arising from the low accuracy of the results around 0.2 K. Notwithstanding some possible adjustment from the scaling factor there is still discrepancy between data and the predictions of Rice theory (Fig. 7). The shape of the curve in the $\lambda \sim d$ regime is very different from the lie of the data, and the experimental limiting value is $\sim$half the value given by Eq. (2) with $\nu = 0$ (non-zero values of ν increase the discrpancy). Rolt has indicated[16] that, to explain certain features of the data, the adsorbed layers should be treated as an integral part of the film as a whole. He suggests that the discrepancy between data and Rice theory may be related to the presence of the slow moving layers. It is the purpose of the final section of these notes to derive a model which takes account of effects due to the adsorbed layers with particular reference to the spin diffusion experiment. References are also made to the application of this new model to other transport experiments.

2. THE NUCLEAR SUSCEPTIBILITY

The 'Two-Fluid' Model

For temperatures below 0.1 K the quasiparticle coherence length (mean-free-path) becomes comparable with the pore diameter allowing the ^{3}He system to become increasingly dominated by the presence of the wall. Since (by definition) the properties of a quasi-particle system are determined by inter-quasi-particle collisions, and because, at very low temperatures, <u>all</u> inter-quasi-particle collisions occur at the wall, where (ignoring interactions with the first layer) the quasiparticle density is that appropriate to bulk liquid at 32 atm. the system might be expected to take on the characteristics of bulk helium at that high density.

Justification for treating the second layer region as a liquid stems from the fact that (to explain the spin diffusion data) it appears $\nu = 0$. The relationship between the second layer surface density σ and the sticking time $\tau_\perp$ for jumps into the central liquid region is

$$\sigma = (1 - \nu) \frac{1}{4} N V_F \tau_\perp \tag{3}$$

where N is the number density. It is known that $\sigma \simeq 6.5 \times 10^{14}/cm^2$ [2], giving $\tau_\perp \sim 3 \times 10^{-11}$ seconds which is comparable with the 'time' for exchange interactions to occur in liquid ^3He[30], but much shorter than the values expected for a solid ($\sim 10^{-9}$ seconds, with a Neel temperature of 36 mdeg)

These ideas have led to a simple phenomenological model which we refer to as the 'two-fluid' model. It says the following. Particles which collide in the central liquid region are ordinary bulk liquid particles and they have the properties of bulk liquid ^3He atoms at S.V.P. Particles which collide (only) in the second layer region are 'second layer' atoms and have the properties of bulk liquid ^3He at 32 atm.

Above 0.4 K, $\lambda \sim$ the interatomic spacing so that the 'second layer type particles' are confined to the second layer region. In this regime a statistical layer model is appropriate (Eq. 1). When $\lambda \gg d$ the only effective scattering collisions occur at the wall, so that the 'second layer' is extended over the whole pore. At intermediate temperatures the central region consists of two types of particles namely a fraction $f c_L$ which have not collided since last leaving the wall (to which we ascribe the properties of layer 2) and a fraction $(1 - f) c_L$ which have collided and are therefore bulk particles. The system then behaves as if there were two non-interacting Fermi systems, with some particles continually traversing the pore and others colliding in the bulk region.

To determine f we consider the following detailed balancing argument. The dominant interaction in both bulk liquid and second layer regions is ferromagnetic exchange, so that an $\uparrow$ spin can only leave the second layer if an $\uparrow$ spin arrives (similarly for $\downarrow$ spins). At intermediate temperatures an (approximate) fraction $f = e^{-d/\lambda}$ particles leaving the second layer at any instant will traverse the pore without collision. These particles have the net polarization appropriate to the second layer and cause an equal fraction with the same polarization to leave. The fraction $(1 - f)$ with polarization appropriate to bulk liquid (S.V.P.) induce $(1 - f)$ similarly polarized particels to leave. A dynamic balance is therefore maintained

so that at any instant the central region has a susceptibility contribution

$$f\chi_2 + (1 - f)\chi_L$$

The second layer itself maintains its susceptibility χ_2. The total film susceptibility is then

$$\chi_t = c_1\chi_1 + c_2\chi_2 + fc_L\chi_2 + (1 - f)c_L\chi_L \qquad (4)$$

Fig. 1 shows the result of this analysis.

In reality of course a single particle will eventually collide and objections may be raised at the suggestion that two non-interacting systems are present. However the particles are of course indistinguishable and it is just because of the spin-conserving constraint of the ferromagnetic interactions (which is one of the consequences of indistinguishability) that it becomes immaterial (as far as the net polarization is concerned) whether one imagines a particle traversing the pore for ever or whether after several traverses it collides, thereby becoming a bulk atom, provided at the same time another 'second layer' particle is created elsewhere in the film. The essential feature of the model is that there is a difference in the result of collisions occuring in the high density second layer compared with those occurring in the bulk region. The known magnetic properties of bulk ^{3}He at various densities[8] would tend to support this contention.

It should be clear that it is not suggested in the model that all particles leaving the second layer have the characteristics (i.e. the net polarization) of that layer. In fact it followis from the detailed balancing argument that the fraction of such particles is f. The parameter f represents therefore a sort of quantum mechanical accommodation coefficient.

Objections to the Model

A number of objections have been raised to the model[31]:

(i) Given that the dynamic balance is preserved in the model by the ferromagnetic spin conserving interaction, what turns up the first spin? A similar problem arises in both ferromagnetism and in superfluid ^{3}He where the Hamiltonian has the properties that if two spins can pair then a lot more may as well[32]. The details of the pairing process are however related to the existence of non-spin conserving interactions such as $\mathcal{H}_{dip}$[32]. Non-spin-conserving terms are also important in any situation of disequilibrium (following a 90° pulse in a T_1 experiment would be one example). Suppose in an experiment in bulk ^{3}He one

were to cool suddenly from a relatively high temperature where $\lambda \gg d$, then the approach to equilibrium would undoubtedly depend on the terms of $\mathcal{H}_{dip}$, but the equilibrium susecptibility would be related only to spin-independent terms such as the interatomic Van der Waal's force. It should be no surprise that switching on a Van der Waal's interaction at the wall has a similar effect on the susceptibility

(ii) There is a feeling that one is getting something for nothing in the model! One must remember that the situation is rather different from those high temperature experiments where accommodation effects are present. There is no suggestion that adjacent 'layers' are in thermal dis-equilibrium. The reason for the drop below the classical values of mean susceptibility etc. is simply the statistical consequence of indistinguishability. One might say that the presence of the wall has the effect of labelling those particles which collide with it, thereby introducing an element of distinguishablity with consequent removal of degeneracy. (The two fluids would then consist of particles labelled "wall" and particles labelled "bulk", with each collision rubbing off the old label and creating a new one appropriate to the region of collision!)

The Range of Effect

It is very clear that this model relates the susceptibility enhancement to a coherence length (or mean free path), so that little enhancement would be expected in a system large compared with λ. The question arises as to whether some other cause of size limitation might be present[31]. The susceptibility enhancement requires a net increase in the Zeeman energy of the central liquid region. It seems likely that the film itself (probably the second layer) should be required to provide this energy and the necessary entropy. Assuming that the specific heat of the second alyer is equal to that of bulk liquid at 30 atm., we find[32] $c/N_s kT \simeq 4$ where N_s is the number of surface (i.e. second layer) atoms. The magnetic enhancement would then be expected to cease when the energy required to turn up N_L bulk spins represented a significant imposition on the thermal energy stored in the second layer. In its attempt to polarize the entire liquid region, the second layer is, according to this argument, itself rendered more degenerate and presumably will ultimately become indistinguishable from the bulk liquid. Equating energies, we find

$$2N_s kT^2 = \left(\frac{\mu H}{kT_F(2)} - \frac{\mu H}{kT_F(L)}\right) N_L \qquad (T \ll T_F) \qquad (5)$$

where $T_F^{(2)}$ and $T_F^{(L)}$ are, respectively, the degeneracy temperatures of bulk liquid ^{3}He at 30 atm. and S.V.P.[8]. We then have

$$N_L/N_S = 1.7\left(\frac{kT}{\hbar\omega}\right)^2 \qquad (6)$$

This argument predicts the following:-

(i) At 1.6 MHz and 50 mdeg, $N_L/N_S \sim 2 \times 10^4$ so that one would expect enhancement in Vycor.

(ii) A reduction in enhancement as $T \to 0$ since entropies are dying out, this effect compensating the rapid increase in λ.

(iii) A greater enhancement at lower fields[34].

(iv) No appreciable enhancement for the specific heat of the liquid region (which would be open to experimental study).

Subsidiary Comments

(1) There is an obvious analogy between the $\lambda \gg d$ regime in Vycor and the electron system in metals, with the substrate potential playing the part of the lattice interaction. Just as a lattice-mediated electron-electron coupling can give rise to superconductivity, it should be possible for a substrate-mediated interaction to produce (or enhance the possibility of) superfluidity in ^{3}He[35]. One can easily imagine how a metastable state might be nucleated at the walls where the pressure is high. The stability of this state would presumable be related to the ability of the film to polarize the liquid. Bearing in mind the way in which the degree of polarization of ^{3}He depends on pressure, temperature and field[8], the application of equation 5 would predict a phase diagram qualitatively similar to that seen in superfluid ^{3}He at 2 mK! One unusual feature has laready been seen in superfluid ^{3}He confined to ~12 μ platinum powder[34]. It is found that the susceptibility drops as one cools into the A-phase, whereas in bulk a slight rise is seen[36]. While there may be other explanations of this phenomena[37], it could be that the normal susceptibility is enhanced by the effects suggested in this model, but that in the superfluid state the mechanism breaks down allowing the susceptibility to relax back to its true bulk value. Since the experiments were done at fairly low resonant field (50 gauss) some enhancement might be still expected despite the larger pore-size (equation 5).

(2) Similar polarization effects are seen in other systems where long range correlations are present. One such is the proximity effect of superconductivity[38],

where a material below its own transition temperature can induce superconductivity in a sample of normal metal simply by contact. Examples of ferromagnetic materials inducing ferromagnetism in materials above their own Curie temperature have also been seen[39], and in this context, one must remember that bulk ^{3}He is very close to becoming a ferromagnet[8].

(3) There is a number of obvious simplifications in the proposed model which may contribute to the fact that agreement between model and data is not perfect (Fig. 1)

(i) The parameter f should really be derived by integrating $e^{-X/\lambda}$ over all path lengths X allowing for a cosine distribution of desorption. Calculations have shown that by ignoring this we have underestimated χ_t by ~2%. In view of the uncertainty in the exact nature of the Vycor geometry with the possible existence of pores much smaller than the average (which would be strongly weighted in the f factor) we have not attempted too sophisticated an analysis.

(ii) We have ignored assimilations of bulk particles directly into the first layer. This seems justified in view of the expected correlation time for inter-layer motion (believed to $\gtrsim 10^{-7}$ secs) but the effect of such exchanges will become significant at very low temperatures where the monolayer susceptibility will be many orders of magnitude greater than the bulk liquid. To explain the discrepancy between model and data (at 40 mK) in terms of this effect alone requires approximately 1 in 20 incident particles to penetrate into the first layer. Since $\tau_\perp$ for the second layer is $\sim 3 \times 10^{-11}$ seconds this would give $\tau_\perp$ for the first layer the unlikely value of 6×10^{-10} seconds, much shorter than the value (10^{-7} secs) believed to be correct (Section 1).

(iii) A slight modification of the model has been examined, allowing for the fact that in the first collision after leaving the wall, residual wall effects may still be felt as the quasiparticle wave packet is still coherent with the wall interaction Only after the first collision is this coherence lost. The 'second layer' type particles would then be identified with those particles which have had not more than one collision. Again an increase in χ_t is expected.

(iv) We have ignored the extended density profile which was found necessary to explain the high temperature susceptibility data[6]. The 'third' layer should be accredited with a susceptibility slightly greater than that of bulk liquid at the S.V.P. Calculations show that we have again underestimated χ_t by ~3%.

All of these simplifications tend to underestimate χ_t and therefore it should be fairly easy to reconcile the residual discrepancy.

An alternative picture

In the previous model the first layer was essentially ignored, although, as already mentioned, it could be easily included (and perhaps should be so included at very low temperatures). However, since all of the spins are exchange-coupled, it is perhaps better to treat the entire film as a unique three-dimensional entity and to attempt to predict the wavefunctions for this system.

The standing wave eigenfunctions for a 'particle in a box' are well known. If one now switches on a highly localized but large binding interaction at the walls, the immediate effect is to nucleate particles (i.e. increase certain single particle wavefunctions) near the wall. However having allowed for hard-core repulsion (in a self-consistent field calculation), the attractive interaction seen by incident particles as they approach the wall becomes a repulsion, and the average potential seen by a particle looks rather like and S.H.O. potential[40]. In such a system the thermally active high quantum number particles near the top of the Fermi distribution will have wavefunctions which are macroscopically large near the walls, so that once again, the behaviour of the relevant particles will be dominated by the wall interaction.

In a sense this picture is predicting a 'condensation' of the active particles into a region near the wall, while simultaneously conserving overall mass by allowing the wavefunctions of those particles lower down the momentum distribution to have wavefunctions peaking in the central region. The relationship betweeen this type of picture, and the idea that the second layer is solidifying (or that its correlation time is increasing) as the temperature is reduced[7], is self-evident. Since it seems unlikely that one will be ever able to treat a system of hard-core particles and then make a quasi-particle transformation[1], the ad-hoc models probably deserve closer attention.

This type of picture is similar to the mean-free-path (two-fluid) model in that enhancement effects are related to the behaviour of the quasiparticle wavefunctions in the first and second layer regions. However, the big difference is in the range of effect predicted. In a larger system the average potential seen will be affected much less by the wall interaction and it is unlikely that a build-up of wavefunction could occur in the same way. Measurements on adsorption systems with larger pore-size would therefore allow one to discriminate between these alternative explanations.

3. SPIN-SPIN EQUILIBRIUM IN THE SATURATED FILM

To simplify a discussion of the dephasing mechanism in the saturated film we begin by using the layer model. This is obviously an abstraction at low temperatures where the film behaves as a three-dimensional entity.

The Dephasing Zone

T_2 for the full-pores film is very much shorter than the T_2 of bulk liquid ^{3}He[13] and comparable (slightly longer) than the monolayer value[11]. The correlation time $\tau_{//}$ for motion within a single monolayer is believed to be 10^{-7} seconds. A solid-like treatment of a second layer of ^{3}He (adsorbed on ^{4}He) has suggested that τ_c is of order 10^{-9} seconds. Allowing for a return towards liquid-like behaviour when that layer is depleted on subsequent adsorption, it is concluded that for all layers above the first the correlation time is $\lesssim 10^{-9}$ seconds and therefore that $T_2 \gg$ several milliseconds. We identify, therefore, the first layer as the dephasing zone and assume that all spins dephase by interaction with (or assimilation into) that layer.

T_2 will then be related to $T_2^{(z)}$, the spin-spin equilibrium appropriate to the monolayer, and to the relative amount of time $\tau_\perp$ the spins spend there. Since, in a time t, particles will make $t/(\tau/c_1)$ visits to the zone and spent $c_1 t$ seconds relaxing, the time scale is effectively expanded by the ratio c_1, and this would be consistent with an approximate factor of two in the ratio $T_1/T_1^{(z)}$ (figs. 4 and 5). However, the exact relationship depends on a number of factors. Four situations can be envisaged[41].

The Four Regimes

(i) If the time, t_ω, for particles to diffuse to the wall is $\gg$ than either $T_2^{(z)}$ or $\tau_\perp$, then t_ω is the controlling factor. In the Vycor system this time is $\sim 10^{-9}$ seconds so that this regime does not apply.

(ii) If the specular reflection coefficient for assimilation into the first layer is high, so that particles make many traversals between second layer and bulk before assimilation occurs, then $\tau_\perp$ may become the controlling factor. Provided $\tau_\perp \gtrsim T_2^{(1)}$ we expect

$$T_2 = \tau/c_1 \qquad (7)$$

(iii) The regime $t_\omega \lesssim \tau_\perp \lesssim T_2^{(z)}$ has two subregions.

(a) $\tau_\perp \simeq \tau_\parallel$, where $\tau_\parallel$ is the correlation time for motion within the first layer.

In this situation a particle visits a layer for time τ and sees a local field $M_2^{\frac{1}{2}}$ which is virtually unchanging over the length of its stay. During this visit it dephases by an amount $\Delta\phi = \tau M_2^{\frac{1}{2}}$. The particle then leaves the zone for a time $(1 - c_1)/\tau c_1$, and then re-enters to find a local field of magnitude $M_2^{\frac{1}{2}}$ but probably of opposite polarity, so that it 'dephases' in the opposite direction. Averaged over many cycle times (τ/c_1) the particle makes tc_1/τ visits and dephases by $\overline{\Delta\phi(t)}$ where

$$\overline{\Delta\phi(t)} = f\left[\frac{tc_1}{\tau}\right]^{\frac{1}{2}} \Delta\phi \tag{8}$$

The parameter f is a numerical factor of order unity which can be related to the spectral density by the equation

$$f^2(\omega\tau) = \left[1 + \frac{10}{6} j(\omega\tau) + \frac{2}{3} j(2\omega\tau)\right] \tag{9}$$

where typically $j(\omega\tau) = 1/(1 + \omega^2\tau^2)$. By definition, T_2 is the time for which $\overline{\Delta\phi} = 1$, giving

$$T_2 = \frac{1}{c_1}\frac{1}{f^2}\frac{1}{M_2\tau} = \frac{1}{c_1} T_2^{(z)} . \tag{10}$$

The function f is of course chosen to reflect the frequency dependence of $T_2^{(z)}$ and will display the usual 10/3 effect. This analysis shows that if interactions near the monolayer are isotropic ($\tau_\perp \sim \tau_\parallel$) then T_2 is longer than $T_2^{(z)}$ by the relative amount of time spent in the dephasing zone.

(b) $T_2^{(z)} \gg \tau_\perp \gg \tau_\parallel$. During a single visit, a particle now experiences $(\tau_\perp/\tau_\parallel)$ jumps and dephases by an amount

$$\overline{<\Delta\phi>} = f(\omega\tau_\parallel)\left(\frac{\tau_\perp}{\tau_\parallel}\right)^{\frac{1}{2}} M_2^{\frac{1}{2}}\tau_\parallel \tag{11}$$

having visited a whole spectrum of sites. After leaving for time $(1 - c_1)\tau_\perp/c_1$ it re-enters the zone and again dephases by $<\Delta\phi>$. In time $t \gg \tau_\perp$ it will have made $(tc_1/\tau_\perp)$ visits and therefore dephased by

$$\overline{<\Delta\phi>} = \frac{tc_1}{\tau_\perp} f(\omega\tau_\parallel)\left(\frac{\tau_\perp}{\tau_\parallel}\right)^{\frac{1}{2}} M_2^{\frac{1}{2}}\tau_\parallel \tag{12}$$

giving the following expression for T_2,

$$T_2 = \frac{1}{c_1} \frac{1}{f(\omega\tau_{\parallel})} \left(\frac{\tau_\perp}{\tau_{\parallel}}\right)^{\frac{1}{2}} \frac{1}{M_2^{\frac{1}{2}}} = \frac{\tau_\perp^{\frac{1}{2}}}{c_1} (T_2^{(z)})^{\frac{1}{2}} \quad (13)$$

To fit the data with a second moment $M_2 = 4 \times 10^8$ (rad/sec)^2 [4], $\tau_\perp$ must be approximately 10^{-5} to 10^{-4} seconds which is consistent with the necessary requirement $\tau_\perp < T_2 \sim 10^{-3}$ seconds.

The Temperature and Field Dependence of T_2

We now examine these models in relation to the variation of T_2 with temperature and field. Changes might be expected in $\tau_\perp$, c_1, and $T_2^{(z)}$.

If $\tau_\perp$ is the controlling factor (model (ii)) then τ must be $\simeq$ several milliseconds, and must increase at higher temperatures. It is difficult to imagine a situation in which $\tau_\perp$ could increase with temperature, even if both quantum tunnelling and thermal activated motion are present. If one can justifiably take c_1 to be proportional to $\tau_\perp$ (as in equation 3) then the rather slow field dependence (at 0.1 K) could be understood. Since $\tau_\perp \sim T_2^{(z)}$ the temperature dependence might be complicated by the rise in $T_2^{(z)}$ with temperature, so that at higher temperatures regime (iii) becomes appropriate.

If situation (iii)(a) is operative the increase of T_2 with temperature could be attributed directly to the variation of $T_2^{(z)}$. The field dependence is however difficult to explain. T_2 for a monolayer increases monotonically with frequency, through the f factor, whereas T_2 for the saturated film shows a very slow drop with increasing field. One can attribute the difference only to an increase in c_1 with increasing field. At higher fields, therefore, one must move into regime (iii)(b) where the term $T_2^{(z)}$ enters as a square-root. The monotonically increasing behaviour cannot be rendered decreasing simply square-rooting. The difference would be ascribed to changes in the ratio $\tau_\perp^{\frac{1}{2}}/c_1$. The inferences one can draw from this now depend on whether $c_1 \propto \tau_\perp$ or whether c_1 and $\tau_\perp$ can vary independently. The former would require an increase in $\tau_\perp$ (and therefore c_1), the latter a drop in $\tau_\perp$ (with c_1 constant). Arguments can be put forward for both possibilities. On the basis of the field dependence of the bulk ^{3}He melting curve[4,2], a lengthening of $\tau_\perp$ might be expected. Allowing for the polarizing effects discussed in equations 5 and 6, the opposite might be expected.

The temperature dependence of T_2 on this model would also be consistent with $\tau_\perp$ getting longer as the sample is cooled. This may be evidence of a

progressive condensation (solidification) of the second layer onto the first layer[7]. Alternatively it may reflect the increasing dominance of the monolayer over the entire system. Since in any magnetic experiment the three components of the film are weighted according to their contributions to the susceptibility (rather than to the relative number of spins in each region) it may be more correct to replace c_1 by c_1/χ_t where χ_t is the (normalised) susceptibility of the whole film (Fig. 1). Expressions 10 and 13 then become (assuming $c_1 \propto \tau_\perp$):-

$$T_2 = \frac{\chi_t}{c_1} T_2^{(z)} \qquad (\tau_\perp \sim \tau_\parallel) \qquad (10')$$

and

$$T_2 = \left(\frac{\chi_t}{c_1}\right)^{\frac{1}{2}} T_2^{(z)\frac{1}{2}} \qquad (\tau_\perp \gtrsim \tau_\parallel) \qquad (13')$$

At high temperatures, of course, the respective equations are identical. The data cannot be fitted exactly to equation 10' over the entire temperature range although the order of magnitude variation is correct. However, up to 0.15 K the ratio $T_2/\chi_t^{\frac{1}{2}}$ is constant to within 2 %, suggesting that equation 13' might be correct with a temperature independent $T_2^{(z)}$ = 1.5 msecs. The faster variation of T_2 above 0.15 K is explicable on two grounds. Either, as $\tau_\perp$ shortens, one moves in regime (iii)(a) described by equation 10', or $T_2^{(z)}$ itself starts to increase (Section I). Measurements at lower temperatures would be useful in exploring the ratio $T_2/\chi_t^{\frac{1}{2}}$.

All of the models (ii), (iii)(a), (iii)(b) are plausible. To discriminate between them more accurate measurements of T_2 should be made over larger frequency and temperature range both for full-pores and a single monolayer. The detailed relationship between T_2 and $T_2^{(z)}$ might then be established. It would also be instructive to measure T_2 for a single layer of ^{3}He adsorbed on ^{4}He - on the basis of these arguments T_2 is expected to be long (~ 1 second). If c_1 is itself field-dependent, the nuclear susceptibility may bot be uniquely defined. Measurements of χ against temperature over a range of frequency, scaled to the high temperature region, would be particularly useful.

Whichever model is correct, it seems clear that $10^{-7} < \tau_\perp \lesssim 10^{-3}$ seconds. It also seems likely that $\tau_\perp$ must change with field and temperature to explain the T_2 behaviour.

In this analysis we have assumed that effects due to extraneous fields (impurities etc.) were either absent, or present to the same extent in both full-pores and monolayer experiments. If the latter is the case, it remains unlikely that the very different frequency dependence of T_2 could be explained in terms of extraneous effects alone.

The Two-Fluid Model

In the analysis of T_2 given above we have assumed that the dephasing zone stays 'intact' as more layers are added. If this is so, then it makes sense to examine the ratio $T_2/T_2^{(z)}$. At low temperatures, however, it is probably more correct to treat the entire film as a three-dimensional entity and allow for the fact that the emotional behaviour in the zone may be completely transformed. The temperature and frequency response of $T_2^{(z)}$ itself may therefore be very different from that of a single monolayer.

A 'two-fluid-model' type of approach has been made, based on the equation

$$T_2^{-1} = f/T_2^{(1)} + (1 - f)/T_2^{(2)} \qquad (14)$$

$T_2^{(1)}$ and $T_2^{(2)}$, which have been treated as temperature-independent parameters, represent the spin-relaxation times of the two components. Since the 'second layer' type particles are the ones which are dominated by the presence of the adsorbed layers we expect $T_2^{(1)}$ to be less than $T_2^{(2)}$.

This analysis has shown that (i) for no values of $T_2^{(1)}$ and $T_2^{(2)}$ can the data be fitted to equation (14) with $f = e^{-d/\lambda}$ and $d = 60\,\text{Å}$. (ii) an almost perfect fit is obtained with $d = 10\,\text{Å}$ and $T_2^{(1)} = 1.6$ msecs. and $T_2^{(2)} = 2.9$, secs.

The interpretation of (ii) would presumably be that between the antiferromagnetic (dephasing) region and the ferromagnetic core, an intermediate zone of width $10\,\text{Å}$ exists, with the property that only collisions <u>within</u> this region can cause spins to lose coherence with the dephasing centre. Since, with three variable parameters, a good fit to the data is bound to occur, it will be necessary to make more precise measurements in large geometries to evaluate this idea.

4. SPIN-LATTICE RELAXATION IN ^{3}He FILMS

The significant feature of the T_1 data is that $T_1 \propto f^2$, characteristic of three-dimensional fluids, while the values of M_2 and T_c are appropriate to the monolayer density (section 1). Since the system is behaving in this three-dimensional

way it is probably wrong to attempt to relate $T_1^{(z)}$ to the T_1 of a single monolayer. However, bearing in mind that the second and higher layers have very short correlation times so that T_1 should be long and frequency-independent (T_1 for a layer ^{3}He on ^{4}He was ~1 second at 6 MHz) it is clear that over the range of frequency on Fig 3, the monolayer region is the relaxation zone[43].

The nature of the assimilation process is not understood in detail but must relate to the interlayer exchange motion (rather like the diffusion of exchange energy in solid ^{3}He[44]). The following points seem relevant.

1. Fluctuation Effects

Immediately after a 90° pulse the spin populations in the central region are equalised. If an incident ↓ particle penetrates the antiferromagnetic relaxation zone, then an ↑ spin will be injected into the central liquid region. Effectively the liquid has taken one step towards returning to its equilibrium polarization and the ↓ spin, while in the relaxation zone, stands some probability of being 'flipped-up' itself. One must remember that the newly released spins will eventually return to the zone. If this occurs in a region which has just experienced a net recovery (↓ to ↑) then an antiferromagnetic interaction with an incident particle will reverse the net polarity of this region. We therefore envisage each region of the zone fluctuating rapidly in net polarity, with the average rate of advance from ↓ to ↑ (caused by the relaxation process) proportional to (the number of visits)$^{1/2}$. Assuming the probability of recovery in a given visit (fluctuation) to be history-independent, the relation for T_1 becomes

$$\left[\frac{T_1}{\tau_\perp}\right]^{1/2} \frac{\tau_\perp}{T_1^{(z)}} \sim (1 - 1/e) \sim 0.6$$

giving
$$T_1 = (T_1^{(z)})^2 / \tau_\perp \qquad (15)$$

This equation would explain therefore the relationship between the frequency dependencies of the full-pores film and the monolayer. However, there are two features which are unsatisfactory. First, to give numerical agreement we must have $\tau_\perp \sim T_1 \sim$ tens of milliseconds, whereas the T_2 data indicate that $10^{-6} \lesssim \tau \lesssim 10^{-3}$ seconds. Second, equation (15) suggests that T_1 for the saturated film should be linear through the origin.

2. Uncorrelated Interlayer Motion

Since the excahnge interaction conserves spin it cannot itself produce relaxation and it is not obvious that interlayer exchange motion can ever produce a net change in the polarization of particles injected into the central region. The relaxation process may depend on (uncorrelated) single-particle quantum-tunnelling into the zone. Assuming visits to the zone are statistically independent, we may write

$$T_1 = T_1^{(z)} / c_1 \quad . \tag{16}$$

To explain the different frequency and temperature dependence in terms of c_1 alone (ie with $T_1^{(z)}$ equal to the monolayer value) the behaviour of c_1 would have to be very different from that expected from considerations of T_2 (Section 3). For example c_1 would have to decrease with frequency, and to be essentially independent of temperature (Section 1).

3. The Removal of Anisotropy

The appearance of an intercept in the T_1 v.f^2 plot suggests that the cause of the unusual feature of the monolayer (T_1 v. frequency passing through the origin) has been removed in the multilayer film. If that cause was surface heterogenity then, since spin-lattice relaxation occurs as a result of 'assimilation' into the monolayer, the range of correlation times should still have effect. An explaination can, however, be put forward on the basis of the removal of anisotropy effects.

In a single monolayer spins are constrained to lie and move on surfaces at fixed angles to the field axis. On some surfaces those components of $\mathcal{H}_{dip}$ capable of inducing relaxation are identically zero. Having made many circumnavigations of a pore circumference in time $\sim T_1$, a spin comes to two conclusions: First it sees a mean value of $< \mathcal{H}_{dip} >$ averaged over all surfaces. Second, it 'remembers' that, on some surfaces, it had to wait a lot longer for $\mathcal{H}_{dip}$ to change significantly and it therefore concludes that a range of τ_c's is present. It is shown elsewhere that a range of τc's can lead to a linear frequency dependence (12, 14). If, in the multilayer film, motion near the monolayer region is sufficiently isotropic ($\tau_\perp \sim \tau_{//}$) then this constraint will be removed and the system described by a single correlation time.

4. Extraneous Field Effects

There is no obvious way of explaining the different frequency dependencies of T_1 in the monolayer and multilayer films in terms of a field-dependent 'M_2'. Furthermore the value $M_2 = 2.5 \times 10^8$ (rad/sec)^2 derived from Fig 3 is that expected on the basis of intrinsic interactions alone.

One problem still unresolved is that if $M_2 = 2.5 \times 10^8$(rad/sec)^2 and $\tau_c = 1.5 \times 10^{-7}$ seconds, then T_2 should drop for frequencies below ~ 1MH$_z$. The constancy of T_2 (Fig 5) may be due to a low frequency 'hump' in the spectral density which is affecting T_2 but not T_1[45].

5. The Approach to Equilibrium

One of the most interesting problems concerns the shape of the recovery in time with particular reference to the way the susceptibility returns to its equilibrium value in which the susceptibility profile is maintained. Since relaxation is occurring in the highly polarized monolayer, the system may tend, in the early stages of recovery, towards the 'Curie' susceptibility, before approaching its degenerate equilibrium valve with a slower time constant. Non-exponential recoveries of this form are seen[46]. At 0.4 K the system is $\sim 30\%$ degenerate in a regime where the pore-diameter is many orders of magnitude smaller than the mean-free-path for non-spin-conserving (relaxative) interactions. It follows that the enhanced polarization seen at lower temperatures cannot be related to dynamic polarization effects alone. The 'two-fluid' model of course relates the enhancement to the number of spin conserving interactions, so that when $\lambda \gg d$ surface polarization effects may be possible.

A conclusion

The most self-consistent explanation of the T_1 data is as follows. The multilayer film behaves as three-dimensional fluid with a lorentzian type spectral density. Anisotropy effects seen in a single layer are removed. $\tau_c = 1.5 \times 10^{-7}$ sees and $M_2 = 2.5 \times 10^8$ (rad/sec)^2. Relaxation processes occurring in the monolayer region are communicated to the rest of the film via unspecified quantum mechanical motion.

Definitive experiments are likely to involve (i) the removal of the relaxation zone by a layer of ^{4}He (ii) separation of the inherent and polarizing properties of the first layer in larger geometries (provided $t_w \ll T_1$).

5. THE SPIN DIFFUSION COEFFICIENT

The basic idea behind the transport coefficient experiments in the $\lambda >> d$ regime has already been discussed. These experiments tend to show that the quasi-particle concept is valid in restricted geometries and the specular reflection coefficient $\nu \simeq 0$. The theories of Rice are approximately obeyed although the spin diffusion coefficient is smaller than the expected value (Fig 7). We examine below in more detail the role the adsorbed layers might play in the spin diffusion experiment. These effects which were completely ignored by Rice are expected to be large at low temperatures where the monolayer susceptibility is very much greater than that of the liquid. There are three approaches all of which are derivatives of the two-fluid model. First we allow for the polarizing effect of the layers. Next we consider the delaying effect experienced by particles when they are adsorbed. Finally, we include the effects of surface diffusion.

The Two-Fluid Model

The idea that the system behaves as if two non-interacting 'fluids' is present has led to a reasonably self-consistent description of the net polarization of the film (Section 2). It is somewhat more difficult to justify this model when applied to transport experiments, but the picture preserves the essential physical feature, namely that those particles with higher susceptibility (the second-layer ones) are also the ones which travel farthest. We ignore motion in the adsorbed layers, treating the central liquid region as the only mobile part of the film. This may be conceptually correct because the dominant interaction is ferromagnetic exchange, so that it is immaterial whether one imagines one incident quasiparticle to be adsorbed and another randomly desorbed, or whether one particle remains in the layer and merely incoherently scatters the incident particle.

Since there are two non-interacting fluids (one in the Knudsen regime, the other in collisional regime)[47], we add the diffusing coefficients of each component (rather than adding scattering rates, which are proportional to D^{-1}). The total diffusion coefficient D will be given by

$$D = cD_k + (1 - c)D_L \tag{17}$$

$$\text{where} \quad c = f\chi_2 / (f\chi_2 + (1 - f)\chi_L) \tag{18}$$

and $f = e^{-d/\lambda}$ (λ being the mean free path of the total system and therefore equal to λ of bulk ^{3}He). The Knudsen term will be taken as the limiting expression given by Rice, namely

$$D_K = 1/3 \frac{(\nu + 1)}{(\nu - 1)} (1 + Z_o/4) V_F d_c \qquad (19)$$

where d_c is the controlling pore diameter. There is considerable evidence that a factor of two variation in pore-size is present in Vycor [48] and we take $d_c = 36$ Å, half of the volumetrically determined radius [16]. To relate to the experimental values, the scaling factor $F = \epsilon X$ has to be used and we take $F = 0.09$, the value used in the original work [23]. D_L, the bulk liquid diffusion coefficient, is ascribed to those particles colliding in the central region.

Fig 7 shows D calculated on this model and quite good agreement is obtained [49]. In calculating D_k we have used $1 + Z_o/4 = 0.26$, the value appropriate to 30 atm. liquid (this may be open to objection but the value for S. V. P. is not very different, 0.33 in fact). The specular reflection coefficient was assumed to be zero. Values of ν greater than zero would worsen agreement between experiment and model. Since number density is conserved in the central region we assume $V_F = 5.38 \times 10^3$ cm/sec [33]. The value of D_K is then 17×10^{-5} cm^2/sec. Sizeable contribution apparently comes from the few collisions that do occur in the central region at low temperatures and it may be that this relates to the fact that a single collision can scatter particles down a pore (with little subsequent probability of colliding) much more effectively than the Knudsen process.

New Model Allowing for Delaying Effects

The main objection to the previous model is that to get agreement, the value $d_c = 36$ Å was chosen (with however some justification [50]). The fact that the low temperature data are smaller than expected may be related to the presence of the slowly moving adsorbed layers [16]. In the absence of a microscopic theory (or the liklihood of one) we present a phenomenological model allowing for the delaying effect of the quasiparticle wavefunction when particles are adsorbed. We shall assume that the 'life-history' of a single quasi-particle, as it travels down a pore, can be replaced by an ensemble average of three non-interacting 'fluids', namely particles exchanged between the first layer: particles exchanged between the second layer: and particles colliding in the bulk region. The relative proportions of these 'fluids' will of course be highly temperature dependent. Because of the uncertainty in the value of the

scaling factor F (section 1) we shall allow F to vary within its range of experimental error and choose the valve shich gives the best agreement between model and experiment.

The main problem in any kinetic model of the film structure is that of quantifying the accommodation coefficient, the parameter which determines the fraction of particles desorbed from a layer with the characteristics of that layer. We assume on the basis of the discussion in (section 2) that this coefficient is $f = e^{-d/\lambda}$. In other words, the proportion of particles leaving a layer with the characteristics of that layer is equal to the number of similar particles arriving. Assimilation in the sense of this model is a 'quantum assimilation', the reasons for the different properties in each layer being quantum mechanical in origin.

The assumptions of the model

a) The number of particles incident on any surface $N = 1/4\ n\ V_F$

b) A fraction f N of these come from either 1st or 2nd layer without collision where $f = e^{-d/\lambda}$

c) gfN particles will penetrate into the 1st layer. g is treated as a variable parameter but is likely to be small for reasons given in d).

d) the surface density σ for any layer is related to the sticking time τ by

$\sigma = N\tau$: for the second layer

$$\frac{\tau_2}{(1-g)} = \frac{\sigma_2}{N} = \frac{10}{2 \times 10^{25}} \sim 5 \times 10^{-11} \text{ seconds};$$

for the 1st layer

$$\tau_1/g = \sigma_1/N \sim 10^{-10} \text{ seconds.}$$

NMR measurements [4] have shown that τ_c (for motion within the first layer) is $\sim 10^{-7}$ seconds. If the layer model is to be meaningful then $\tau_1 \gtrsim \tau_c$ (the inequality allowing for an interchange between 1st and 2nd layer without an incident quasiparticle from the liquid region). Hence $g << 1$.

e) the mean time $\bar{t}$ for a particle to pass a distance ℓ down a pore of diameter d is [51] given by

$$\bar{t} = (\ell^2 / 2dV_F + \ell^2 \tau / 2d^2), \qquad (20)$$

the first term allowing for the cosine-law of desorption then second for the delay which is related to the sticking time τ. The most general expression for diffusion in the regime $\lambda >> d$, including the effects of surface diffusion, is then [51]

$$D = \frac{1}{3} \frac{(d^2 + 3\tau D_s)}{(d/V_F + \tau)} \qquad (21)$$

where D_s is a surface diffusion term. In this first approximation we ignore the effects of surface diffusion in the second layer (setting D_s and $\tau = 0$) and take the second layer contribution D_2 to be given by equation (19) with $\nu = 0$, namely

$$D_2 = \frac{1}{3} (1 + Z_o/4)\, dV_F \qquad (22)$$

the Z_o term allowing for the fact that we have a quasiparticle system. The first layer contribution is given by [51]

$$D_1 = \frac{1}{3} d^2 \left[1 + \frac{3}{4} \frac{\tau}{\tau_c} \frac{r^2}{d^2}\right] / \left(\frac{d}{V_F} + \tau\right) \qquad (23)$$

We expect $\tau \gtrsim \tau_c \sim 10^{-7}$ secs, so that $\tau >> d/V_F$, giving $D_1 = \frac{1}{3} \frac{d^2}{\tau} + \frac{1}{4} \frac{r^2}{\tau_c}$ which is $<<$ D_2. Therefore spin diffusion is not important in the first layer ($D_1 = 0$).

f) The net diffusion coefficent is then given by

$$D = a_1 D_1 + a_2 D_2 + a_f D_f$$

where

$$a_1 = c_1 \chi_1 + O(g)$$

$$a_2 = f \chi_2 (c_2 + c_f) / \chi \qquad g \to 0 \qquad (24)$$

$$a_f = (1-f)(c_2 \chi_2 + c_f \chi_f) / \chi$$

with $a_1 + a_2 + a_f = 1$ (defining χ as in the two-fluid susceptibility model (section 2). In the expressions for a_i we have set $g = 0$ for simplicity so that the $a_1 D_1$ term is $<<$ the other terms and the sole function of the first layer is in the weighting of the overall expression by χ. Obviously g cannot be identically zero if the model is to be self consistent. One is considering (in principle) exchanges with the first layer. The definition of a_2 is straight-forward. The definition of a_f allows for particles leaving the second layer and diffusing in the central region, by bulk processes, and then returning to that layer. A further modification without this last term has also been

carried out but makes little difference to the final result. In both models we have assumed D_f equals the diffusion coefficient of bulk liquid ^{3}He. The curves show that good agreement is obtained with a scaling factor $\simeq$ 0.15, consistent with $\epsilon = .3$, $x \sim .5$ (fig 8). We note that a slight maximum is predicted around 0.07 K which is reproduced in the results. However, the value of D is also predicted to decrease at low T which does not appear to be consistent with the data. The same analysis could be carried out with non zero values of g, although on physical grounds one expects g to be small; this could however be important in that the main reason for the drop in D predicted is the rise in $c\chi_1$, in relation to the total χ, without a compensating term $a_1 D_1$.

Qualitative predictions, which might be used to test the above model experimentally are:-

(i) a drop in spin diffusion coefficient at lower temperatures.

(ii) a considerable increase in D if the first layer is replaced by ^{4}He, but with no significant drop appearing at lower temperatures. An increase might also be expected, of course, if the specular reflection coefficient increases, but comparisons between D and mass flow experiments should allow discrimination between these two possibilities; if ν changes, mass flow and D should be affected to the same extent; if the explanation above is correct, mass flow will not be significantly changed[52].

Spin Diffusion Allowing for Surface Diffusion

The previous analysis of the spin diffusion experiments ignored the possibility of quasiparticles diffusing in a two-dimensional sense within the second layer. While it is true of course that the quasiparticle concept is probably not valid in such situations it seems worthwhile for two reasons to examine the possibility phenomenologically. First, in gas experiments at high temperatures, it is usually the case that surface diffusion dominates Knudsen diffusion. Second, if we assume that the surface diffusion term, D_s, is similar to the bulk diffusion coefficient at $\sim$ 30 atm, then a large contribution will be expected at low temperatures. The effect of D_s will over-compensate for the drop due to the changing susceptibilities of the layers, causing D to eventually rise. Such an effect could be looked for experimentally.

The expression for D_2 is

$$D_2 = \frac{\left[1/3\ (1 + Z_o/4)\, V_F\, d + \left(\frac{V_F \tau}{d}\right) D_s\right]}{\left[1 + V_F \tau/d\right]} \qquad (25)$$

where $1 + Z_o/4 = .33$ at S.V.P. ($\tau = 5 \times 10^{-11}$ sec; $V_F = 5.38 \times 10^3$ cm/sec;

$d = 60\,\text{Å}$) and $D_s = D_{bulk}$ (30 atm)[53]. The total D is then given by equation 24. The resulting curve (fig 9) goes through a maximum at $\sim .07$ K (for reasons mentioned earlier) but instead of decreasing monatonically continues through a minimum at $\sim$ 10 - 15 mK and increases thereafter.

At very low temperatures equation (25) simplifies to

$$D = D_2 (c_2 + c_1) \chi_2 / \chi$$

where $\chi \simeq c_1 \chi_1$ and $\chi_2 = 2.95\, T$[8],

giving

$$D = aT + b/T \qquad (26)$$

with

$$a = 1/3\,(1 + Z_o/4)\, V_F d (c_2 + c_L)(\chi_2/\chi)/(1 + V_F \tau/d)$$

$$b = (V_F \tau/d)\, D_s\, (c_2 + c_L)\,(\chi_2/\chi)\,/\,(1 + V_F\,\tau/d)$$

A minimum is expected when $T = (b/a)^{\frac{1}{2}}$,

$$T_{min} = \left[\frac{3\,\tau\, Ds}{d^2(1+Z_o/4)}\right]^{1/2} \qquad (27)$$

Using $c_1 = 0.28$, $c_2 = 0.18$ and $c_L = 0.54$[16], $\tau = 3 \times 10^{-11}$ seconds from equation 3 and assuming that D_s is equal to the spin diffusion coefficient of bulk ^{3}He at ~30 atm, it is found that $T_{min} \simeq$ 10 mK. A smaller mean pore-diameter, or considerable number of smaller pores, will raise T_{min}. The behaviour predicted by equation (26) would of course be open to experimental study.

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27. In mass flow[22] and thermal conductivity [21] experiments X is defined,
somewhat differently, as an effective length (ℓ'/ℓ). X of reference 26
is then equal to $(\ell'/\ell)^2$ and the scaling factor taken to be $\epsilon(\ell'/\ell)^2$
compatible with reference 26. In the spin diffusion experiment[23] the
scaling factor us defined as X^2 (without the porosity factor) but chosen
by scaling the high temperature data.

28. The scaling factors in the thermal conductivity and spin diffusion experiments
are much smaller than in mass flow. There is good evidence that the latter
gives the true value, namely 0.03 (i) the mass flow values of scaling factor
(defined as $\epsilon(\ell/\ell)^2$) were checked by room temperature gas flow measurements
and are in agreement with values derived in reference 26 (John Butterworth
private communication). (ii) the scaling factors derived from liquid flow
in $\lambda \gg d$ and $\lambda \ll d$ regimes are compatible with each other and with the gas
flow measurements (if the gas accommodation coefficient is $\frac{1}{2}$). (iii) in
the mass flow experiment particles travel over macroscopic distances and
therefore sample the whole spectrum of bends, constrictions and blind holes.

29. In the thermal conductivity experiment, there is the possibility of thermal short circuits through the Vycor[21], and in the $\lambda \ll d$ regime thermal energy is passed on by collisions so that the particles themselves need to travel relatively small distances. If in the spin diffusion experiment the characteristic distance (which is related to the size of the field-gradient[16]) is comparable with d, then X will be closer to unity. Since D increases somewhat at lower temperatures, the scaling factor could even be regime-dependent.

30. Expressing τ^{-1} in Kelvins, we find that the rate of interaction is $\sim$1K, comparable with the value for bulk ^{3}He at S.V.P.[8].

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49. A similar analysis, applied to the thermal conductivity experiment in Vycor, gives a very good fit to the data up to 60 mk, where the 'shunt conductance' becomes sizeable. The same value of F was used (F = 0.09) and d_c was taken to be half the volumetric diameter (d_c = 30Å).

50. With a slightly reduced scaling factor it should be possible to use the same model with d_c = 70Å (instead of d_c = 36Å). If the scaling factor is chosen to give agreement at low temperatures, the data for 0.1K-0.2K would lie above the bulk liquid curve by an amount less than the experimental error (~80%).

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55. I am grateful to Miss Jane Thornton for her help in computation and graph-plotting.

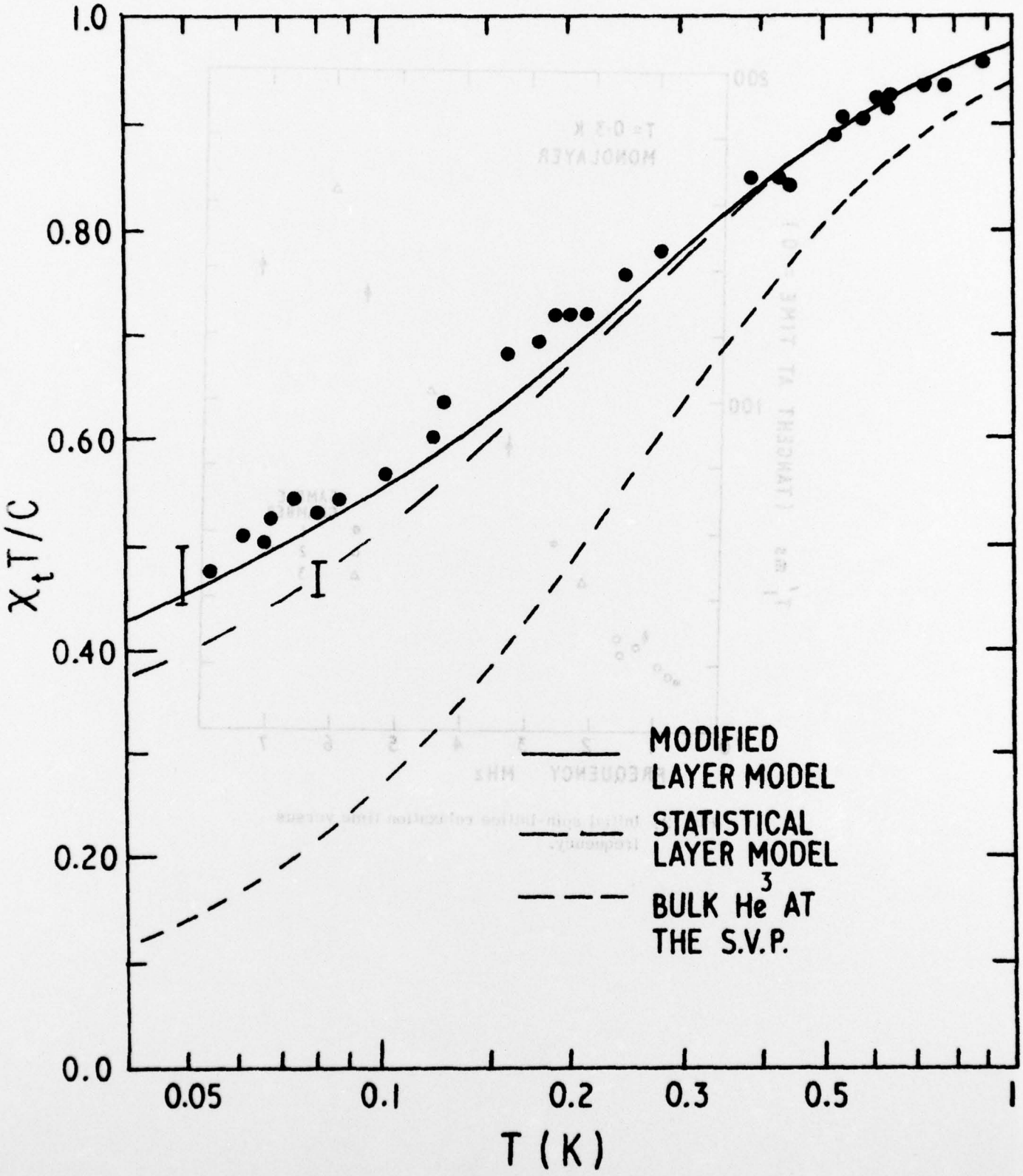


Fig. 1. Susceptibility of the saturated ^{3}He film[7]. The statistical layer model and the modified layer model refer to equations 1 and 4, respectively. (In the latter $f = e^{-d/\lambda}$ where $\lambda = 0.5/T^2$ in Å).

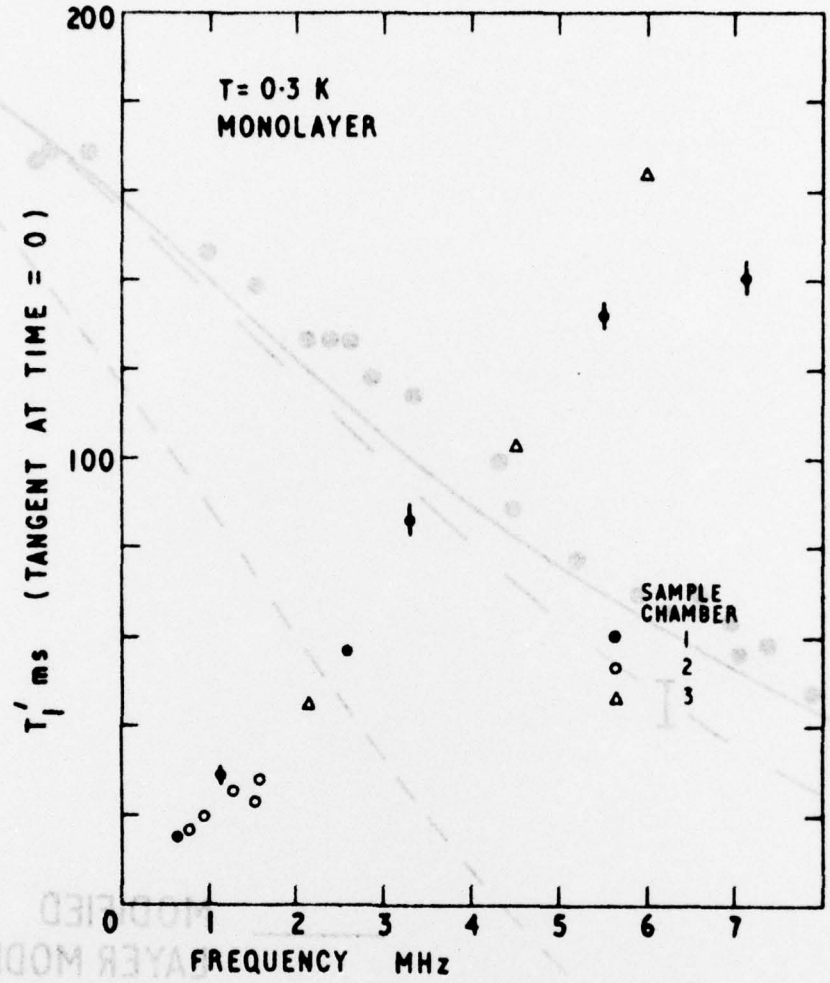
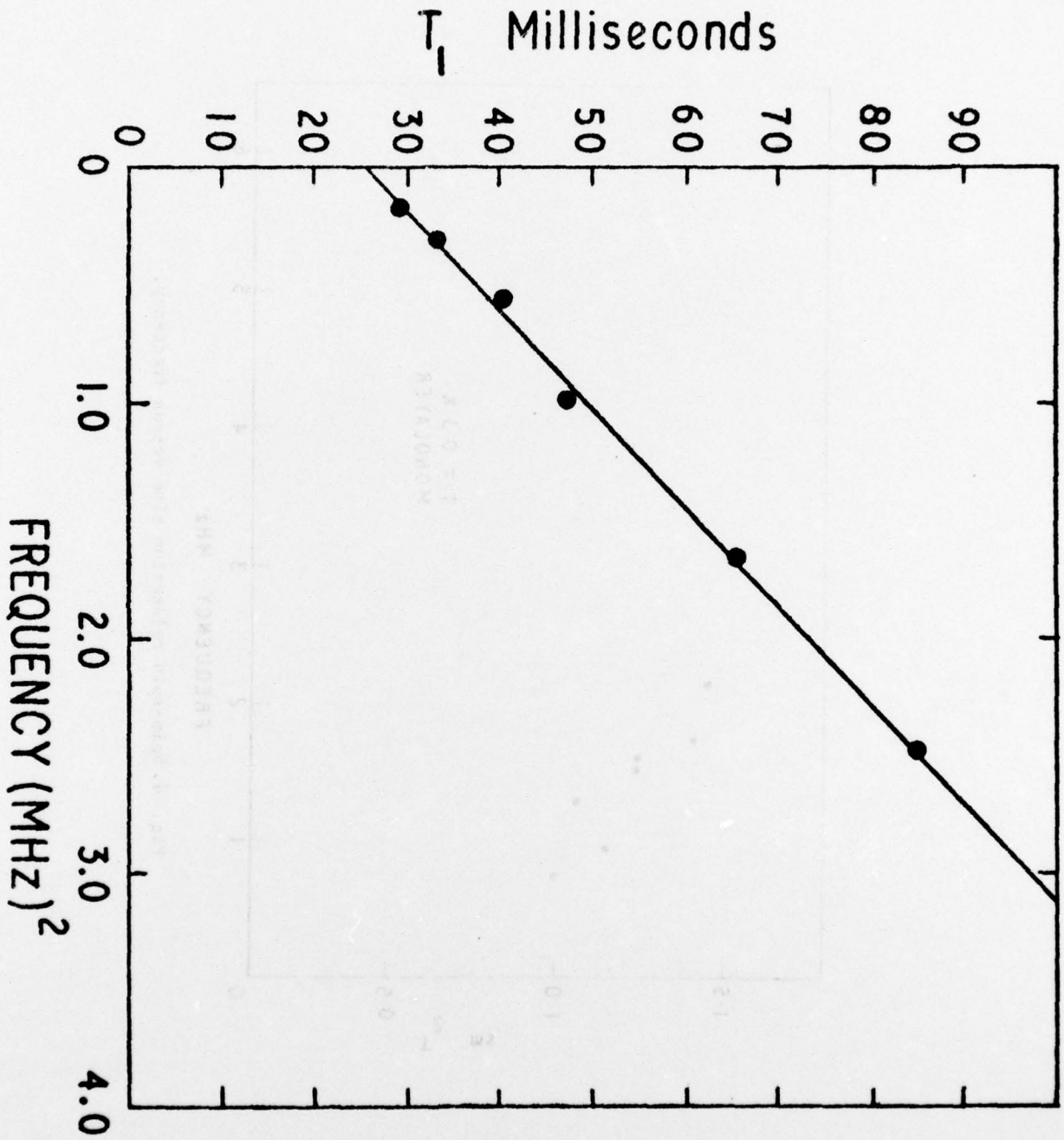


Fig. 2. Initial spin-lattice relaxation time versus frequency.

Fig. 3. T_1 plotted against (frequency)^2 for a saturated He^3 film (full-pores). The temperature was approximately 0.1 K. (reference 54).



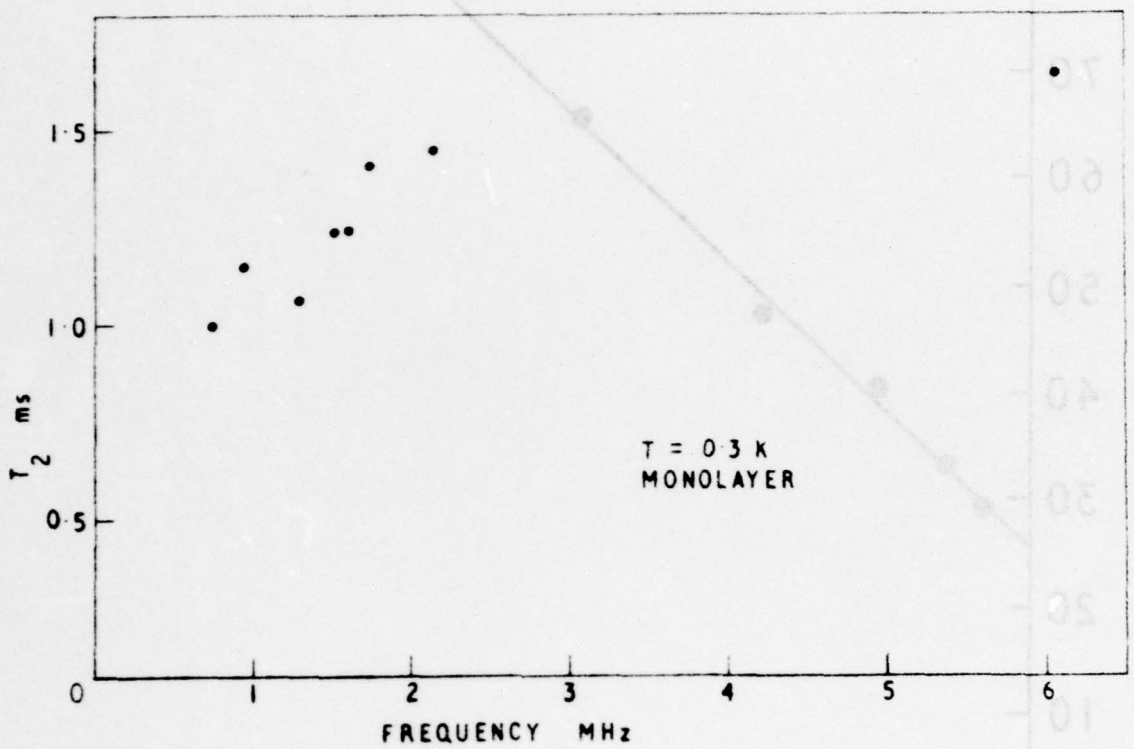


Fig. 4. Spin-spin relaxation time versus frequency.

Fig. 5. T_2 against frequency for a full-pores He^3 sample at approximately 0.1 K. (reference 54).

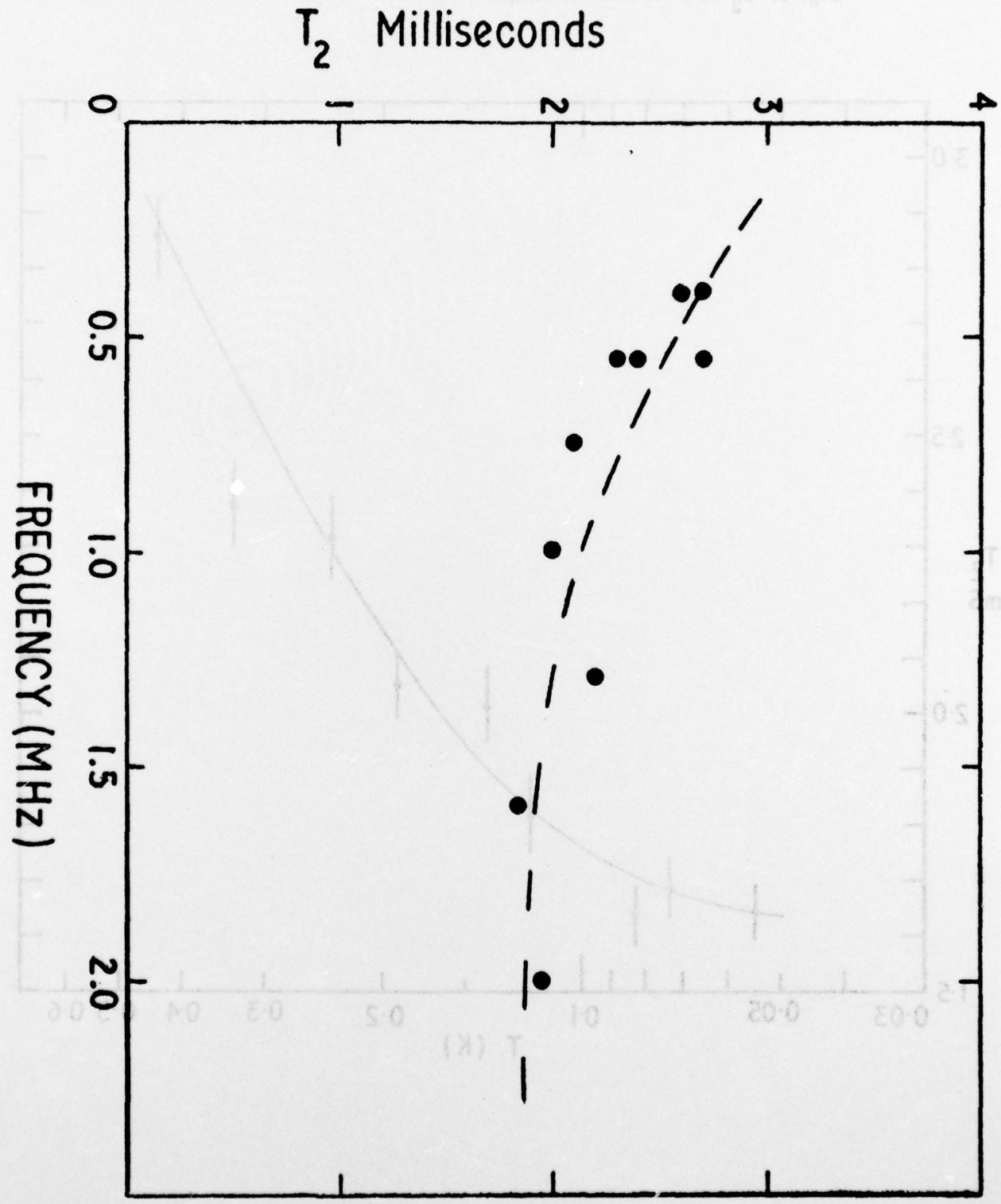


Fig. 6. T_2 as a function of temperature for a full-pores film (from reference 16).

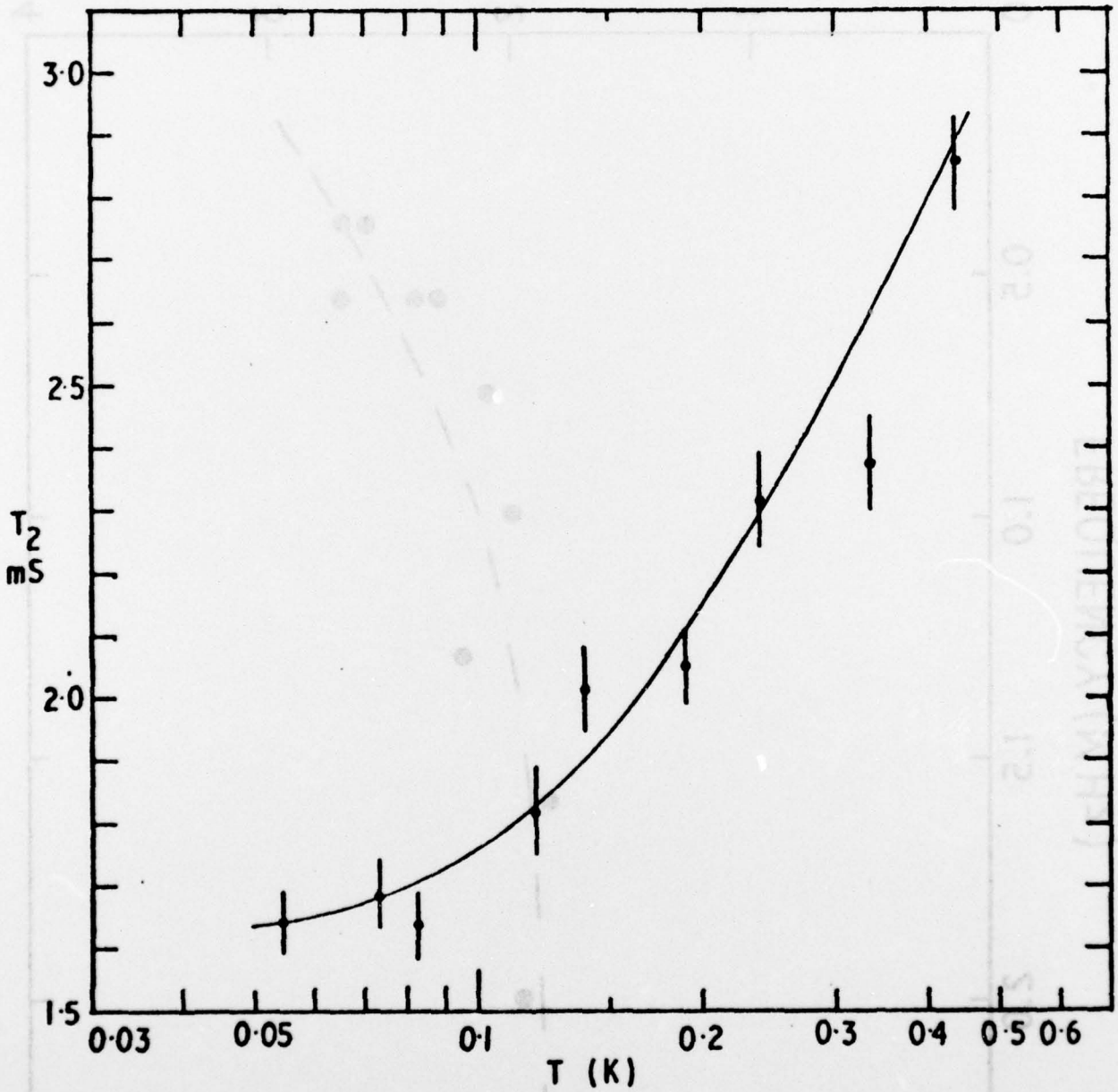


Fig. 7. The spin diffusion coefficient of liquid ^{3}He in Vycor[23] compared with (i) the theory of Rice[25] and (ii) a model allowing for surface polarization effects.

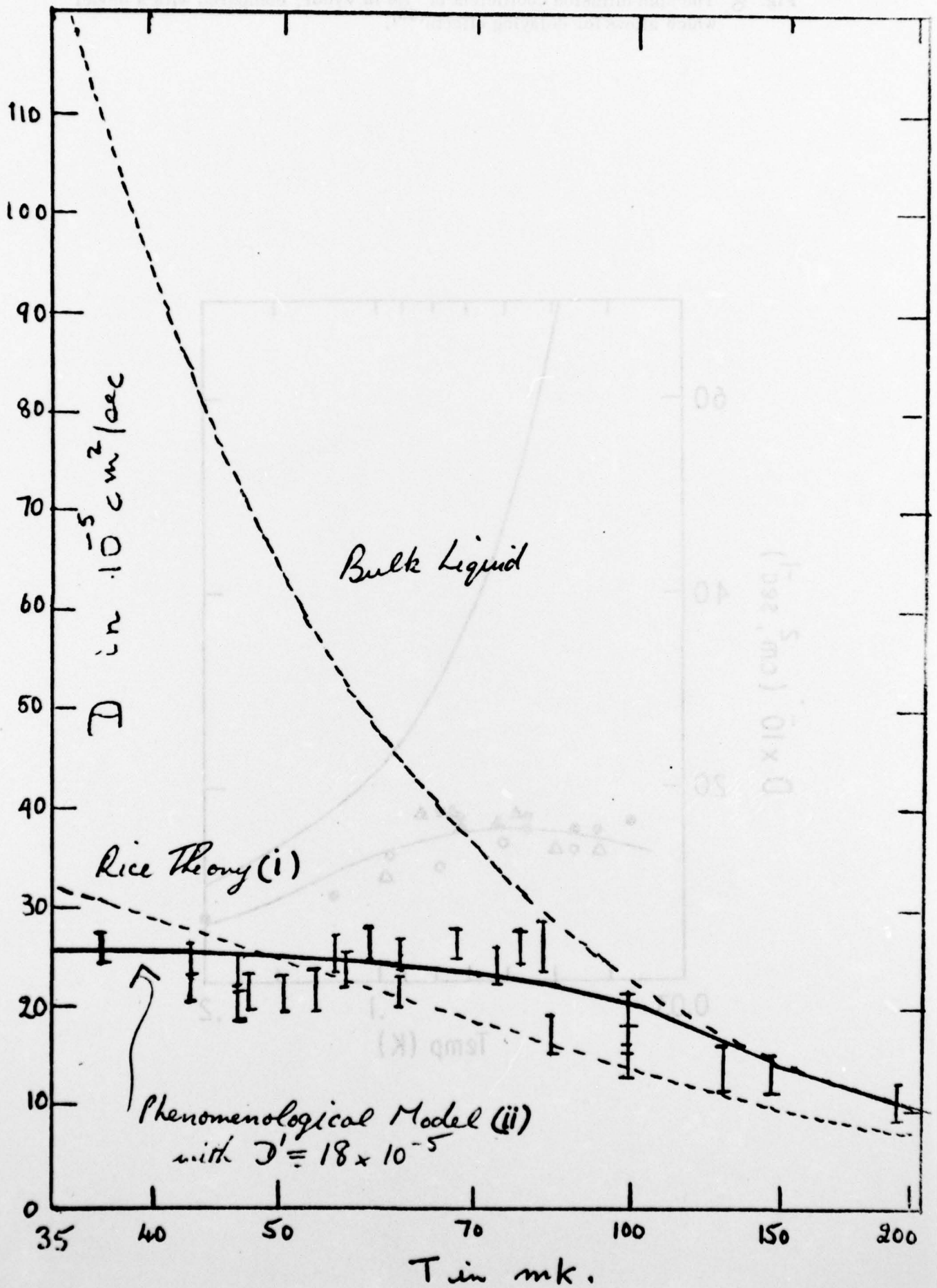


Fig. 8. The spin diffusion coefficient of ^{3}He in Vycor, compared with a model which allows for delaying effects[55].

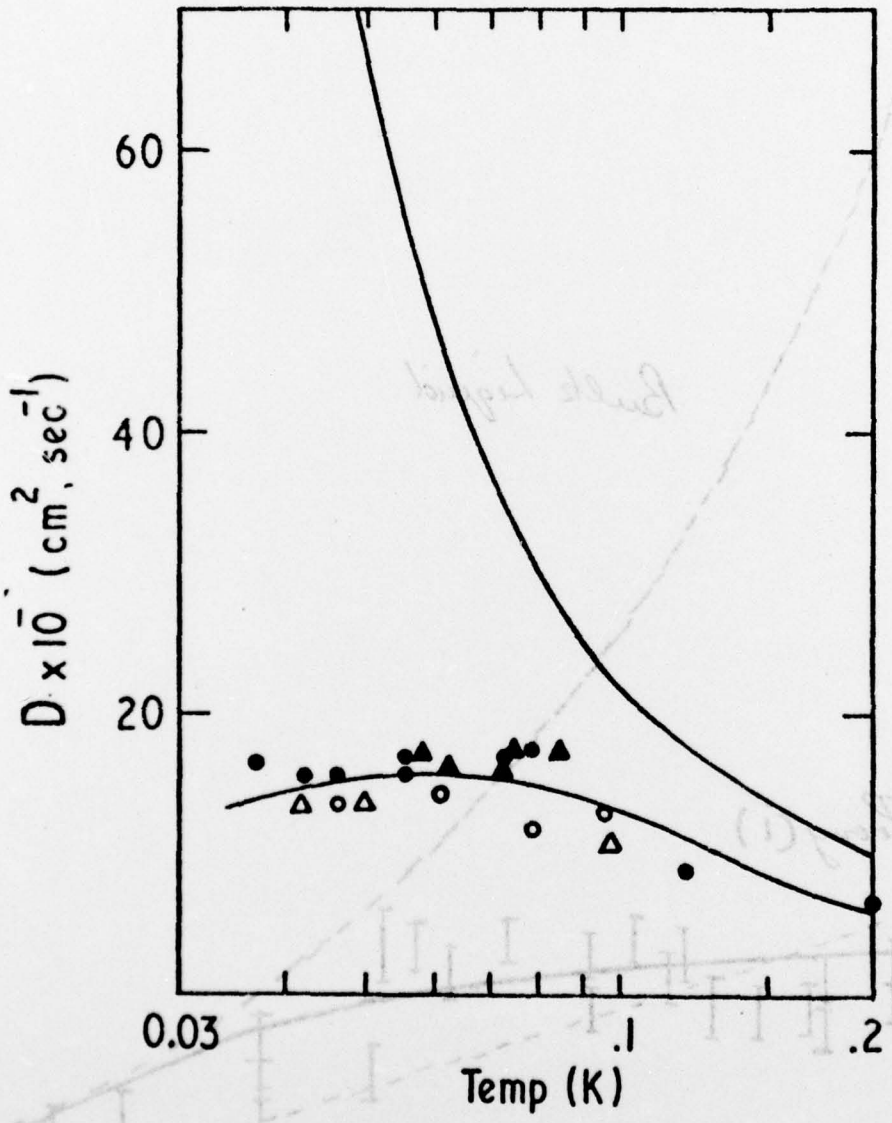
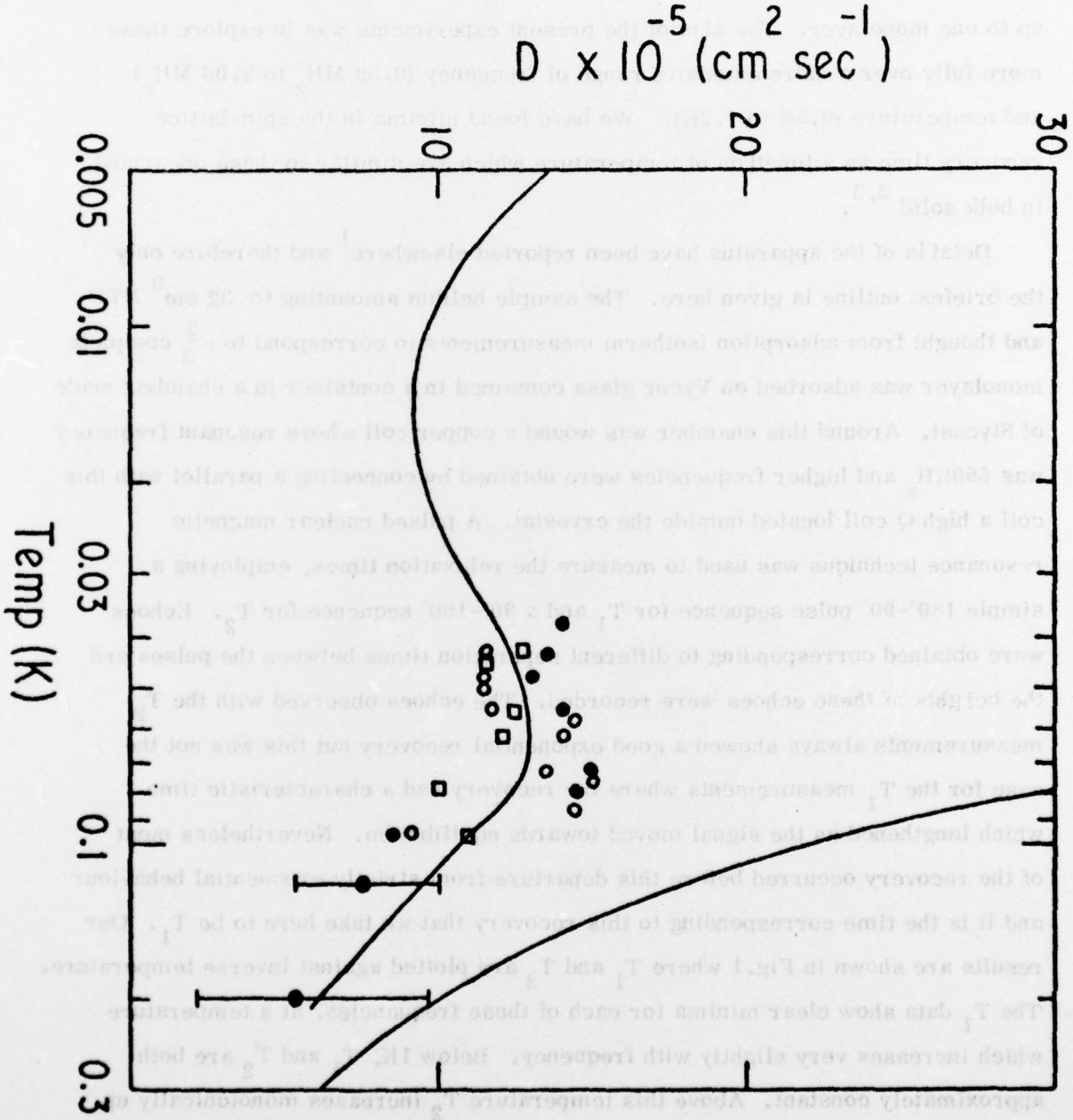


Fig. 9. The spin diffusion coefficient of ^{3}He in Vycor, compared with a model allowing for surface diffusion[55].



III. Minima in Spin-Lattice Times in Adsorbed Helium

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In previous papers[1] we have described several measurements of the spin-lattice (T_1) and spin-spin (T_2) relaxation times of ^{3}He films adsorbed on Vycor porous glass within the temperature range $0.3 < T < 1.5$K, at various coverages up to one monolayer. The aim of the present experiments was to explore these more fully over a more extensive range of frequency (0.59 MH_z to 2.06 MH_z) and temperature (0.3K to 4.2K). We have found minima in the spin-lattice recovery time as a function of temperature which are similar to those occurring in bulk solid[2,3].

Details of the apparatus have been reported elsewhere[1] and therefore only the briefest outline is given here. The sample helium amounting to 32 cm^3 NTP and thought from adsorption isotherm measurements to correspond to $\sim\frac{2}{3}$ complete monolayer was adsorbed on Vycor glass contained in a container in a chamber made of Stycast. Around this chamber was wound a copper coil whose resonant frequency was 590KH_z and higher frequencies were obtained by connecting a parallel with this coil a high Q coil located outside the cryostat. A pulsed nuclear magnetic resonance technique was used to measure the relaxation times, employing a simple 180°-90° pulse sequence for T_1 and a 90°-180° sequence for T_2. Echoes were obtained corresponding to different separation times between the pulses and the heights of these echoes were recorded. The echoes observed with the T_2 measurements always showed a good exponential recovery but this was not the case for the T_1 measurements where the recovery had a characteristic time which lengthened as the signal moved towards equilibrium. Nevertheless most of the recovery occurred before this departure from strictly exponential behaviour and it is the time corresponding to this recovery that we take here to be T_1. Our results are shown in Fig.1 where T_1 and T_2 are plotted against inverse temperature. The T_1 data show clear minima for each of these frequencies, at a temperature which increases very slightly with frequency. Below 1K, T_1 and T_2 are both approximately constant. Above this temperature T_2 increases monotonically up to 4.2K, and throughout the whole temperature range T_2 is approximately an order of magnitude smaller than T_1. A feature of the T_1 data is that they increase with frequency over the whole temperature range, while the T_2 data show no measurable dependence on frequency.

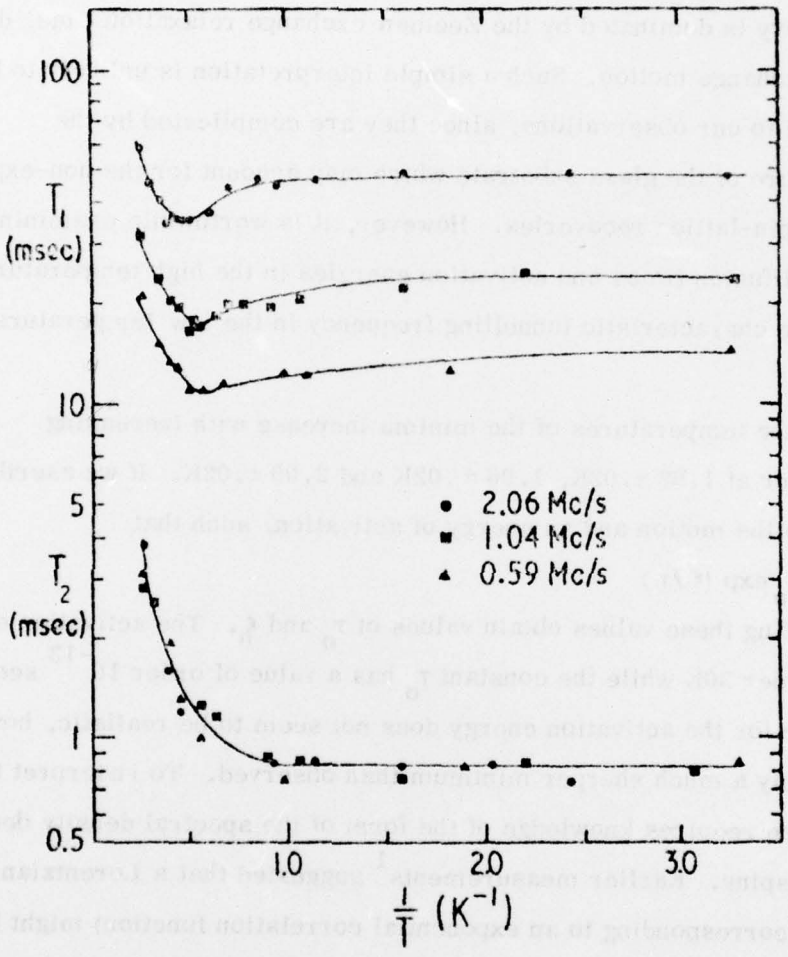

100
10
5
1
0.5
T_1 (msec)
T_2 (msec)
2.06 Mc/s
1.04 Mc/s
0.59 Mc/s
1.0
2.0
3.0
$\frac{1}{T}$ (K^{-1})

Figure 1

There is a broad similarity between the data presented here and those[2,3] for bulk solid ^{3}He. In the latter case, the high temperature region corresponds to direct relaxation of the Zeeman energy to the lattice and the minimum in T_1, which is a standard feature of BPP theory, occurs where the diffusion time is around ω_o^{-1} where ω_o is the Larmor frequency. In the low temperature plateau region, the recovery is dominated by the Zeeman-exchange relaxation time, due to tunnelling or exchange motion. Such a simple interpretation is unlikely to be directly applicable to our observations, since they are complicated by the heterogeneous nature of the glass substrate which may account for the non-exponential character of the spin-lattice recoveries. However, it is worthwhile examining the implications for diffusion times and activation energies in the high temperature region, and for the characteristic tunnelling frequency in the low temperature region.

We note that the temperatures of the minima increase with increasing frequency and occur at 1.92 ±.02K, 1.96 ±.02K and 2.00 ±.02K. If we ascribe a diffusive time to the motion and an energy of activation, such that

$$\tau = \tau_o \exp(\epsilon/\tau)$$

then we can by fitting these values obtain values of τ_o and ϵ_0. The activation energy would appear to be of order 30K while the constant τ_o has a value of order 10^{-13} secs. Such a large value for the activation energy does not seem to be realistic, however, since it would imply a much sharper minimum than observed. To interpret the plateau region, one requires knowledge of the form of the spectral density describing the motion of the spins. Earlier measurements[1] suggested that a Lorentzian spectral density (corresponding to an exponential correlation function) might be the most appropriate, and certainly the comparatively small variation of T_1 with frequency is in accord with this. An analysis of these data is currently being made assuming various spectral densities but an estimate for the time characterising the proposed tunnelling motion can be found from the relationship

$$\tau_{tun} \sim 1/T_2 \overline{\Delta\omega^2}$$

which holds for a Lorentzian spectral density in the region where

$$\omega\tau_{tun} >> 1. \overline{\Delta\omega^2}$$

is the second moment of the resonance line, and can be calculated if the relative positions of neighbouring spins are known. One extreme for $\overline{\Delta\omega^2}$ would occur if

the spins were uniformly distributed which for our adsorbate would produce a value of $\sim 10^{8} sec^{-2}$. Another extreme would be tight packing of the atoms into islands composed of a triangular lattice such that the atoms were at the spacing of the minimum of their van der Waals potential. This would produce a value for $\Delta \omega^2$ of $\sim 5 \times 10^{8}$ sec^{-2}. Thus τ_{tun} would be expected to lie within the range 10^{-6} to 10^{-5} secs. Further measurements should elucidate this picture and in particular experiments are planned for several different coverages of adsorbate.

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