

## Exchange and Spectral Density in Two-Dimensional Helium-3: A $T_1$ Study

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$T_1$  measurements have been performed on the solid phase of helium-3 adsorbed on Grafoil. A theory has been developed to interpret these data on the basis of the hypothesis of a single correlation time for the exchange-induced spin motion. We infer that the relaxation is mediated by the internuclear dipolar interaction. We show how the  $T_1$ -minima data together with exact moment and hydrodynamic calculations may be used to approximate the spectral functions over their whole range. Thus we obtain numerical values for the exchange frequency for all regions of data. Our method is quite general and applicable to other systems.

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Exchange is one of those phenomena which are fundamentally quantum mechanical in origin. And one of the most striking manifestations of exchange is in helium-3<sup>1</sup> where in the solid phase there can be rapid atomic motion resulting in a diffusion coefficient more typical of a viscous fluid. In bulk solid helium-3 the dynamics of exchange have been studied by various techniques, principally that of nuclear magnetic resonance.<sup>2</sup>

Experiments on two-dimensional helium, submonolayer films of helium adsorbed on a substrate, have demonstrated an impressive phase diagram with solid, fluid, and mixed phases together with an assortment of transitions between them.<sup>3</sup> Characteristically, two-dimensional solid helium-3 exhibits exchange.<sup>4</sup>

We have performed an extensive series of NMR experiments on submonolayer films of helium-3 adsorbed on a substrate of exfoliated graphite known as Grafoil.<sup>5</sup> Previous measurements have been performed by Richards<sup>6</sup> mainly at a Larmor frequency of 1 MHz and by Satoh and Sugawara<sup>7</sup> at 10 MHz. In general these experiments and ours have tended to support the above-mentioned phase identifications. In this Letter we report on a study of exchange investigated through spin-lattice relaxation. Our measurements were performed over a range of frequencies between 1 and 10 MHz and at a temperature of 1.2 K, where the relaxation time was independent of temperature. Fractions  $x$  of a full monolayer between 0.7 and 1 were investigated. In these experiments the normal to the adsorption surface was perpendicular to the static magnetic field. Full experimental details will be published in a forthcoming paper.

The interpretation of spin-lattice relaxation measurements on adsorbed systems has in the past been somewhat problematic. In a  $T_1$  experiment, at the most elementary level, one wants simply to estimate the characteristic time for the motion of the spins. In bulk systems interpretation is relatively straightforward, being based upon reasonable beliefs about the origin of the fluctuating magnetic fields causing the relaxation, together with

assumptions about the form of the power spectrum of these fluctuations.

In adsorbed systems there are extra sources of magnetic fields from the substrate. Most surfaces will have some magnetic impurities. Furthermore, in exfoliated graphite there are demagnetizing fields arising from the substrate's anisotropic diamagnetism.<sup>8</sup> Two-dimensional systems have the further property that the conventional assumptions about the spectral density functions as made for bulk systems are often invalid.<sup>9</sup>

Notwithstanding these difficulties, however, there is one feature of spin-lattice relaxation measurements which has an unequivocal interpretation. That is the  $T_1$  minimum. Observation of a minimum in  $T_1$  as the motion varies monotonically indicates two things: First, that the characteristic time of the motion is of the order of the Larmor precession period, and second, that the value of  $T_1$  at the minimum is of the order of the Larmor frequency divided by the mean square value of the local relaxing fields. Thus from a set of  $T_1$  minima not only can one map out the speed of the motion, but also the mechanism for the relaxation may be inferred.

At the qualitative level and where  $T_1$  minima occur this is extremely helpful. But for a more detailed and quantitative characterization of the atomic behavior, and away from  $T_1$  minima, knowledge of the shape of the spectral density function is required.

We shall show in this communication how we have managed to overcome these problems so that the form of the exchange-modulated spectral density may be approximated and the frequency of exchange motion established over a wider range of solid densities than was heretofore possible.

The spin-lattice relaxation rate is given by the spectral density  $J(\omega)$  of local-field fluctuations at the Larmor frequency. For dipole-induced relaxation, the case of interest to us, there is, of course, also a double-frequency term. For the purposes of this discussion we shall ignore this term or, equivalently, regard it as subsumed into the

definition of  $J(\omega)$ .

The spectral density may be expressed as the Fourier transform of the autocorrelation function of the local-field fluctuations,  $G(t)$ . The expression for  $G(t)$  is given by an equation of the form

$$G(t) = \text{Tr}\{H_d(t)H_d(0)\},$$

where  $H_d$  is the internuclear dipolar Hamiltonian and the time evolution is generated by an exchange Hamiltonian. For Heisenberg nearest-neighbor pair exchange or for the more recently proposed three-particle exchange, the Hamiltonian<sup>10</sup> is linear in a parameter  $J$ , the exchange frequency, which reflects the rapidity of the motion. The important point is that there is a characteristic time or, equivalently, a frequency that "scales" the motion. Clearly  $J$  does just that. It follows that the autocorrelation function will depend on  $t$  and  $J$  only through the product  $Jt$ .

We therefore express  $G(t)$  as the product of its initial value  $G(0)$  and a shape function  $S(Jt)$ . The spectral density then has the form

$$J(\omega) = [G(0)/J]K(\omega/J), \quad (1)$$

where  $K$ , the reduced spectral function is the Fourier transform of the shape function  $S$ . This implies a general expression for  $T_1$  which means that both  $J/T_1$  and  $\omega/T_1$  are functions simply of  $\omega/J$ .

It is convenient to consider the phenomenon of the  $T_1$  minimum from this point of view.  $\omega/T_1$  will have a maximum for some particular value of  $\omega/J$ , say  $\omega/J = C$ . The magnitude of  $C$  depends purely on the shape of the function  $K(\omega/J)$ . We are thus in a position to make two general conclusions about minima in the spin-lattice relaxation time: (1) A minimum in  $T_1$  at Larmor frequency  $\omega$  is seen when  $J$  has value

$$J = \omega(\text{min})/C.$$

(2) The value of  $T_1$  at the minimum is given by

$$\omega(\text{min})/T_1 = G(0)CK(C).$$

And since  $CK(C)$  is a constant it follows that  $T_1$  is proportional to the Larmor frequency at the minimum.

The factor  $G(0)$  is essentially the second moment of the cw resonance line. So while observation of a  $T_1$  minimum gives the order of magnitude for the motion frequency  $J$ , from a set of minima the local fields can be estimated; the relaxation mechanism may be established. This last result is of particular importance in the NMR of adsorbed systems since, as stated, in such cases there can be spurious sources of local fields, each providing a relaxation channel.

In Fig. 1 we have plotted our experimental  $T_1$  minimum values against Larmor frequency and the linearity is clearly exhibited.  $T_1$  is multiplied by  $\omega^3$  to eliminate the intrinsic density dependence of  $G(0)$ . From the slope of the line we are able to conclude that the relaxation is indeed mediated by the internuclear dipolar interaction.

The experimental measurements of  $T_1$  as a function of frequency reflect the form of the spectral density or, equivalently, the reduced spectral function  $K(\omega/J)$ . From Eq. (1) it follows that a plot of  $J/T_1$  against  $\omega/J$  will yield the shape of the function  $K$ . However, this is not possible since  $J$  is as yet undetermined. But  $J$  is proportional to frequency at the  $T_1$  minima. Thus the shape of the reduced spectral function will be indicated on a plot of  $\omega(\text{min})/T_1$  against  $\omega/\omega(\text{min})$ . In other words, when plotted in this way the experimental data should fall on a single curve. Such a graph is shown in Fig. 2. This shows data for those coverages where a  $T_1$  minimum has been observed at some frequency. It appears that the points do fall on a common curve. This supports the hypothesis that for the range of film densities considered the temporal behavior is determined by a single characteristic time.

One also observes that unlike in bulk systems, here there is a continuing increase of the spectral density at low frequencies, a special feature of few-dimensional systems.

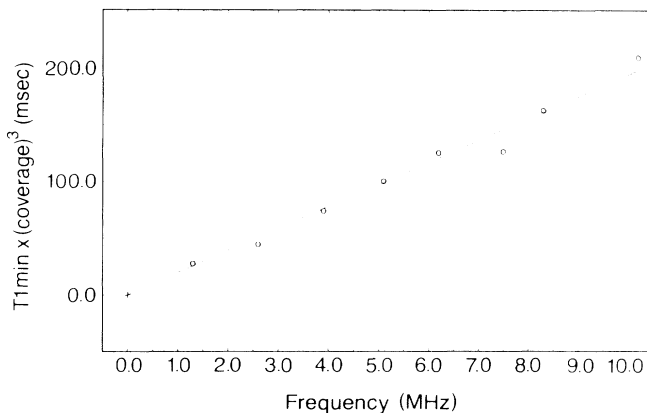


FIG. 1.  $T_1$ -minima data against Larmor frequency.

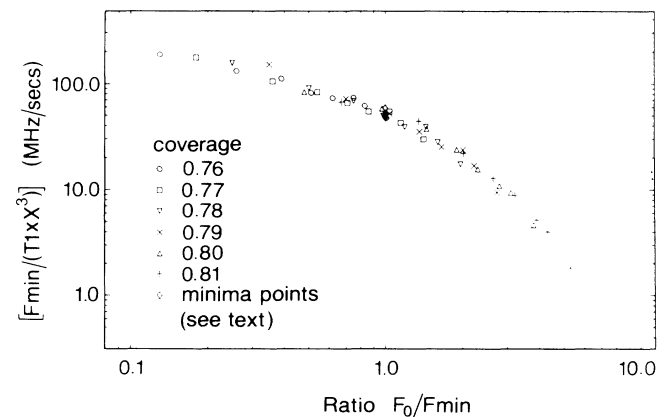


FIG. 2. Universal plot of  $T_1$  data.

It is clear that in the vicinity of the  $T_1$  minima NMR is a powerful spectroscopic probe of microscopic dynamics: The temporal features of the atomic motion may be mapped out through observation of minima at successive Larmor frequencies. The analysis is very general, being independent of the precise features of the spectral density function. But correspondingly, the conclusions are only qualitative in that the constant  $C$  remains undetermined. To find an actual value for  $J$  at a minimum, the shape of the spectral density must be known. And if the shape were known then the atomic motion could be analyzed— $J$  could be found—in regions away from  $T_1$  minima, where  $\omega/J$  is too large or too small.

In general it is impossible to calculate exactly the form of the spectral density function and some sort of approximation procedure must be used. For a 2D system such a procedure for  $G(t)$  must respect both short- and long-time behavior. A moment-type calculation gives the short-time expansion and hydrodynamic arguments based on the solving of a diffusion equation give a long-time asymptotic expansion. These short- and long-time descriptions relate to the high- and low-frequency descriptions of the spectral density. Approximation of  $G(t)$  or  $J(\omega)$  over its entire range thus corresponds to interpolation between the calculated small- and large-argument behavior. But such interpolation is, of course, not unique. In particular, different expressions could, while reflecting correctly the low- and high-frequency forms for  $J(\omega)$ , give midrange values that differ somewhat. We have overcome this problem in the following way.

Our method is to supplement the theoretical information calculated at the ends of the range with reliable experimental information on the value of  $K$  at an intermediate point. This is obtained from the  $T_1$ -minima experimental data; from the slope of the graph of  $T_1$  against frequency the intermediate value  $CK(C)$  is given.

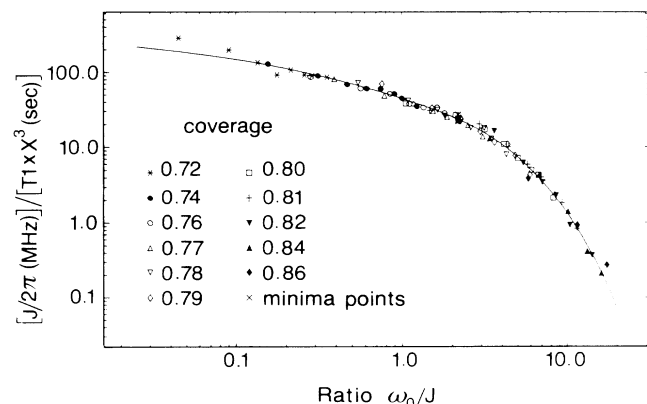


FIG. 3. Reduced plot of all  $T_1$  data and approximation curve.

We have then a procedure for approximating  $J(\omega)$  over the complete range of interest: (1) From the long- and short-time approximations to  $G(t)$ , construct an interpolation expression with some remaining variable parameter(s). (2) Take the Fourier transform of this expression to give the spectral density function  $J(\omega)$ . (3) From this  $J(\omega)$  find the slope of the  $T_1$ -minimum versus frequency line [a function of the adjustable parameter(s)]. (4) Choose the parameter(s) to give the experimentally observed slope. In this way one is able confidently to make a good approximation to the spectral density function over its entire range. And of course the constant  $C$  relating  $J$  to the frequency of the minimum will be determined. The details of these calculations will be discussed in a future publication. A summary is presented here.

The full expression for the dipole-mediated spin-lattice relaxation time was used, including the double-frequency term. Long- and short-time expansions were calculated as in Ref. 9 and these were used together with the  $T_1$ -minima data extracted from Fig. 1.

We had then complete expressions for the spectral densities and thus an expression for  $T_1$ . The constant  $C$  relating the frequency of the minima to the value of  $J$  was then found to be  $\omega(\text{min})/J = 2.19 \pm 0.01$ .

Having established this relation we were able to obtain an actual value for  $J$  from each observed  $T_1$  minimum. We were then in a position to replot the data of the universal curve in Fig. 2 now using the more meaningful  $\omega/J$  for the abscissa. This is shown in Fig. 3. The solid curve shows the behavior predicted by our approximated spectral densities. Note that there was only one truly adjustable factor, obtained from the slope of the data on  $T_1$  minima versus frequency. The shape of the curve is

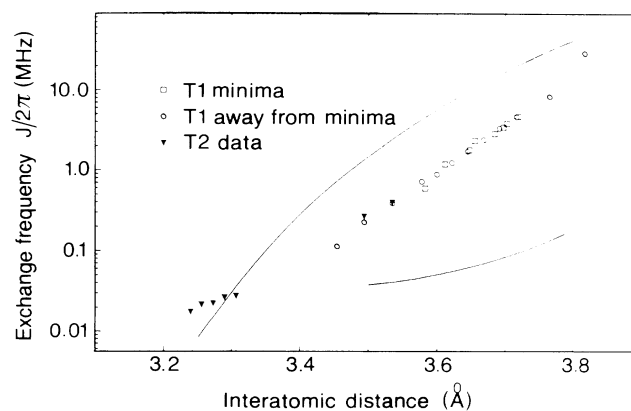


FIG. 4. Exchange frequency as a function of interatomic distance for helium-3 adsorbed on Grafoil. Lower solid curve is theoretical calculation of Cowan *et al.* (Ref. 4). Upper solid curve is calculation of Roger (Ref. 10). For this upper curve only the slope should be considered; the absolute value is undetermined.

determined entirely from the short- and long-time calculations. The fit is most satisfying.

Also on this graph we have plotted the data obtained away from the minima. In these cases  $J$  is initially unknown. Trial values of  $J$  were varied to give the best fit of the points to the existing curve.

Finally, in Fig. 4 we show the obtained values of  $J$  as a function of interatomic spacing  $d$ . At densities corresponding to  $d$  less than about  $3.45 \text{ \AA}$  there are other contributions to  $T_1$  so that the above analysis does not apply. For interest, in this region we have indicated values of  $J$  obtained from  $T_2$  measurements and analyzed according to the same spectral density functions.

For comparison the two solid curves indicate theoretical calculations of  $J$  by Cowan *et al.*<sup>4</sup> for Heisenberg two-particle exchange and by Roger<sup>10</sup> for three-particle exchange.

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<sup>1</sup>A. Landesman, *Ann. Phys. (Paris)* **8**, 53 (1973).

<sup>2</sup>M. G. Richards, *Adv. Magn. Reson.* **5**, 305 (1971).

<sup>3</sup>M. Bretz, J. G. Dash, D. C. Hickernel, E. O. McLean, and O. E. Vilches, *Phys. Rev. A* **8**, 1589 (1973).

<sup>4</sup>B. P. Cowan, M. G. Richards, A. L. Thomson, and W. J. Mullin, *Phys. Rev. Lett.* **38**, 165 (1977).

<sup>5</sup>Grafoil is the trade mark of a product marketed by Union Carbide.

<sup>6</sup>M. G. Richards, in *Phase Transitions in Surface Films*, edited by J. G. Dash and J. Ruvalds, NATO Advanced Study Institute, Series B, Vol. 51 (Plenum, New York, 1980).

<sup>7</sup>K. Satoh and T. Sugawara, *J. Low Temp. Phys.* **38**, 37 (1980).

<sup>8</sup>D. C. Hickernel, D. L. Husa, J. G. Daunt, and J. E. Piott, *J. Low Temp. Phys.* **15**, 29 (1974).

<sup>9</sup>B. P. Cowan, *J. Phys. C* **13**, 4575 (1980).

<sup>10</sup>M. Roger, *Phys. Rev. B* **30**, 6432 (1984).