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Interpretation of the Magnetic Behavior of Liquid Helium-3*

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Recent work indicates that the lining-up antiparallel of nuclear spins in liquid He^3 takes place at temperatures much lower than that which would be expected for an ideal Fermi-Dirac gas. This indicates that the energy gap between the state in which the spins are aligned and one in which they can orient themselves in a magnetic field is lower than in the ideal gas. A model is considered in which pairs of atoms rotate about each other, and it is shown that the energy gap will be less for rigid spheres than for point particles, which more resemble the ideal-gas case. The model based on rigid spheres gives a reasonably shaped curve for the temperature dependence of the magnetic susceptibility, but the energy gap is still too large. If the rotation is hindered the gap is lowered, and a rough estimate of the degree of hinderance of rotation in liquid He^3 could be made. However, it appears likely that cooperative phenomena involving all the atoms play a role; these are discussed and a comparison with He^4 is made.

FAIRBANK, Ard, and Walters[1] have recently measured the nuclear magnetic susceptibility of liquid He^3 below 1°K. At very low temperatures the nuclear spins of the He^3 tend to line up antiparallel and this causes the spin magnetic susceptibility to deviate from the classical $1/T$ law. Such a behavior would be expected of an ideal Fermi gas; indeed in an ideal Fermi gas of the same density and atomic mass as He^3 it should occur at a temperature ten times as high as that at which it is actually observed in liquid He^3. In solid He^3, where each atom is more nearly in its own cell and there is certainly much less exchange of atoms or sharing of volumes, it might be that this lining up of the spins would not occur.[2] Thus liquid He^3 represents an intermediate condition, as might, indeed, be expected.

Some idea of the mechanism by which such an intermediate situation may arise can be obtained by considering the energy level of a pair of atoms, treating them first as more or less hard spheres and then as point particles. The case of "hard" spheres is of course more like the situation which would actually occur in liquid He^3, and we shall attempt to set up a model which can be used as the basis for a semiquantitative description of the actual behavior of He^3.

Let us consider the motion of a pair of He^3 atoms situated in He^3 liquid. As an approximation we shall suppose that the center of gravity of this pair of atoms is fixed at the center of a cell in the liquid, and that they can rotate and vibrate like a diatomic molecule. Suppose the effective diameter of the atoms to be σ and their average distance from each other to be r_0. The effective range of radial motion in the liquid will then be approximately $2(r_0-\sigma)$, and these "vibrations" may be supposed to carry them between the relative distances σ and $2r_0-\sigma$.

The symmetry properties of the system are dependent upon the rotational state. If the rotational quantum number, j, is zero, then the nuclear spins must be paired antiparallel, and such a state will not contribute to the magnetic susceptibility. If $j=1$, then the spins are in the same direction, and this state can contribute to the magnetic susceptibility. The rotational energy of this state is given approximately by the usual formula,

$$\epsilon_j=j(j+1)h^2/8\pi^2\mu r_0^2, \tag{1}$$

where μ is the reduced mass of a pair of atoms (equal to one-half the atomic mass m). For the energy of excitation necessary to get the system in a state which can contribute to the magnetic susceptibility, we obtain

$$\epsilon_1-\epsilon_0=h^2/4\pi^2\mu r_0^2=h^2/2\pi^2 m r_0^2. \tag{2}$$

We wish to compare this situation with that which occurs when the atoms are considered as point particles. In doing this, we need to describe a system of point particles which is as nearly comparable to the pair of hard spheres as is possible. We are interested in the interaction of the two particles with each other, not with the other particles, and we shall consider a pair of point particles which can range over the whole volume occupied by the equivalent hard spheres, namely a volume of diameter $2r_0$. The two particles have independent energy levels. If both particles are in the lowest level, the spins are paired, and no contribution is made to the magnetic susceptibility, but if one of them is excited such a contribution is possible. The energy levels of the atoms are best found from the wave equation in spherical form, using the polar coordinates, r, θ, and ϕ. Just as with the hydrogen atom, θ and ϕ equations can be separated, and the r equation takes the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{l(l+1)}{r^2}R+\frac{8\pi^2 m}{h^2}(E-V)R=0. \tag{3}$$

Here l is the rotational quantum number, R is the radial part of the wave function, and V, the potential

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[1] Fairbank, Ard, and Walters, Phys. Rev. **95**, 566 (1954).

[2] I. Pomeranchuk, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 919 (1950).

energy, has the form

$$\begin{aligned} V&=0 \quad \text{for } r<r_0\\ &=\infty \quad \text{for } r>r_0. \end{aligned} \tag{4}$$

Solutions of this equation for the region $r<r_0$ which have the proper behavior at $r=0$, are given[3] by the Bessel functions of order $l+\frac{1}{2}$. The first two solutions ($l=0$ and $l=1$) are

$$\begin{aligned} x^{-\frac{1}{2}}J_{\frac{1}{2}}(x)&=(2/\pi)^{\frac{1}{2}}x^{-1}\sin x,\\ x^{-\frac{1}{2}}J_{\frac{3}{2}}(x)&=(2/\pi)^{\frac{1}{2}}x^{-1}(x^{-1}\sin x-\cos x), \end{aligned} \tag{5}$$

where

$$x=(8\pi^2 mE/h^2)^{\frac{1}{2}}r. \tag{6}$$

Therefore the eigenvalues for $l=0$ are given by the positive roots of the equation

$$\sin x_0=0, \tag{7}$$

where x_0 is the value of x when $r=r_0$. The first of these is $x_0=\pi$, which gives

$$E_{01}=h^2/8mr_0^2. \tag{8}$$

The eigenvalues for $l=1$ are given by the positive roots of the equation

$$\tan x_0=x_0. \tag{9}$$

The first root of Eq. (9) is $x_0=4.493$ (see reference 2, p. 84). Thus the first eigenvalue for $l=1$ is

$$E_{11}=4.493^2h^2/8\pi^2mr_0^2. \tag{10}$$

This represents the lowest excited state. If one of the particles is in this state, the two particles can have the same spin and can contribute to the magnetic susceptibility. The excitation energy, therefore, is

$$E_{11}-E_{01}=[(4.493/\pi)^2-1]h^2/8mr_0^2. \tag{11}$$

Since $(4.493/\pi)^2-1\sim 1$, we see that

$$(E_{11}-E_{01})/(\epsilon_1-\epsilon_0)\sim\pi^2/4\sim 2.5. \tag{12}$$

Thus higher excitation for the point particles is required; therefore the magnetic susceptibility will fall below that anticipated from the Curie law at a higher temperature.

The difference between Eqs. (2) and (11) can be explained in a simple intuitive manner. In the case of the hard spheres, the small values of r are always excluded. This is true for both the lowest and next lowest energy level. In the case of the point particles, however, the small values of r are allowed for the lowest level, but for the next level, with $l=1$, they are effectively excluded by the rotational-potential term $l(l+1)/r^2$. This decrease in the free radial configuration space results in a relatively greater increase in the momentum, hence in the energy. It is important to point out that the effect of changing a pair of point particles to a pair of hard spheres is really to raise the lowest energy level more than the higher energy levels are raised. This may be a little difficult to see when one considers only the rotational energy, i.e., the energy connected with the angular momentum of the quantum state. It is evident, however, that the zero-point "vibrational" energy (i.e., that connected with the radial motion) is much higher for the hard spheres than for the point particles, and then it is seen that the smaller *difference* between the rotational states of the hard spheres merely means that the higher energy states are not raised as much above those of the point particles as is the case with the ground state.

We shall now calculate the magnetic susceptibility, using a model in which we suppose that N atoms can be considered as $N/2$ independent pairs of hard spheres. This, clearly, is not too realistic, especially because the pairs cannot be independent. We may hope, however, to make a calculation which can lay the groundwork for a semiquantitative understanding of the situation.

We shall consider only the two energy levels, with $j=0$ and $j=1$ (assuming always that we are dealing with the lowest vibrational state). Let us suppose that the system is in a magnetic field H, and let the component of the magnetic spin moment of an He^3 atom be either M, if in the direction of the field (energy $=-MH$), or $-M$ if in the opposite direction. If the system is in the lower energy level ($j=0$) the resultant moment of a pair is zero. In the higher triplet energy level the component of the magnetic moment of a pair is $2M$, 0, or $-2M$. The Boltzmann factors for these energy levels ($j=1$) are, respectively, $\exp(-h^2/2\pi^2mr_0^2kT+2MH/kT)$, $\exp(-h^2/2\pi^2mr_0^2kT)$, and $\exp(-h^2/2\pi^2mr_0^2kT-2MH/kT)$, and the quantum weight of each of these states is $2j+1=3$. The total magnetic moment induced in N atoms or $N/2$ pairs will then be

$$\chi H=\frac{3(N/2)(2M)[\exp(-h^2/2\pi^2mr_0^2kT)][\exp(2MH/kT)-\exp(-2MH/kT)]}{1+9\exp(-h^2/2\pi^2mr_0^2kT)}, \tag{13}$$

where χ is the susceptibility of the N atoms. The factors arising from the magnetic energies are small if H is small, and are omitted from the partition function [denominator of Eq. (13)]. Assuming $2MH/kT\ll 1$ and expanding the corresponding exponentials in Eq. (13), we obtain

$$\chi=\frac{(12NM^2/kT)\exp(-h^2/2\pi^2mr_0^2kT)}{1+9\exp(-h^2/2\pi^2mr_0^2kT)}. \tag{14}$$

At very high temperatures this reduces to a Curie law of the form

$$\chi_0=12NM^2/10kT. \tag{15}$$

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[3] E. P. Adams, *Smithsonian Mathematical Formulae and Tables of Elliptic Functions* (Smithsonian Institution, Washington, D. C., 1922), pp. 202–203.

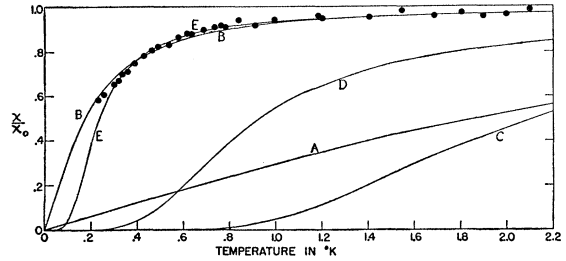

FIG. 1. Relative nuclear magnetic susceptibility as a function of temperature. Curve *A*, ideal Fermi-Dirac gas with density and atomic mass of He^3. Curve *B*, ideal Fermi-Dirac gas with adjusted parameter. Curve *C*, pair model, point particles. Curve *D*, pair model, hard spheres. Curve *E*, pair model, hard spheres with adjusted parameter. The experimental points and curves *A* and *B* are from the figure of Fairbank, Ard, and Walters,[1] an enlarged copy of which was kindly furnished by Professor Fairbank.

On the other hand, if the atoms were completely independent the limiting high-temperature form would be

$$\chi_0 = NM^2/kT. \tag{16}$$

The difference between Eqs. (15) and (16) is due to the use of only two rotational levels to obtain (15). It seems, therefore, reasonable to set as a rough approximation:

$$\chi/\chi_0 = 10 \exp(-h^2/2\pi^2 m r_0^2 kT) \times[1+9\exp(-h^2/2\pi^2 m r_0^2/kT]^{-1}. \tag{17}$$

We may first test the shape of this curve by giving mr_0^2 an arbitrary value so as to best fit the data. In Fig. 1, we show such a comparison with the experimental results, and also a curve for an ideal Fermi-Dirac gas with the constant similarly adjusted. It is seen that Eq. (17) gives a curve which is quite similar to that of the Fermi-Dirac gas except at very low temperatures, and that it fits the experimental data at least as well.

It is most interesting, however, to see what we obtain by setting m and r_0 equal to values expected from He^3. When this is done for the ideal Fermi-Dirac gas (using the known value of m and of the density) and for Eq. (17) (setting r_0 equal to the corresponding distance in He^4, 3.15A, known from x-ray data,[4] times the cube root of the ratio of the density[5] of He^4 to that[6] of He^3), it is seen (Fig. 1) that Eq. (17) with these parameters gives a curve which is better than that for the ideal Fermi-Dirac gas but which is still not very close to the experimental data.

A model using pairs of independent point particles, as in Eq. (11), gives a curve rather close to that for the ideal Fermi-Dirac gas. This is also shown in Fig. 1. Account has been taken of the difference in the possible spin states in this case, from those in the case of hard spheres, in drawing this curve.

The fact that Eq. (17), with the proper parameters inserted, gives a curve which is still not very close to the experimental data, indicates that the energy gap between the states with symmetrical and antisymmetrical orbital wave functions, given by Eq. (2), is still too high. The free rotation, therefore, still represents a situation in which it is too easy for the atoms to change places. If we assume that the rotation were forced to take place in a plane rather than taking place freely in space, this halves the energy gap, because the formula for the energy of a plane rotation depends on the rotational quantum as j^2 rather than as $j(j+1)$. This still does not suffice to bring the curve into coincidence with the experimental points.

If the rotation were hindered this would lower the energy gap still further. For example, a potential barrier at rotational angles of 0 and π would cause the first two wave functions to have forms of the type shown in Fig. 2. The symmetrical wave function acquires what amounts to a superimposed wavelength of half its original wavelength, which means that its energy is raised, and the energy gap is thus lowered. It is, in fact, well-known that the energy gap is roughly inversely proportional to the time required for a rotation to occur, so one could use the results on the magnetic susceptibility to make an estimate of the extent of the freedom of mutual rotation of atoms in He^3. The model, however, is probably not good enough for one to take such an estimate too seriously.

As a matter of fact, comparison with He^4 indicates that the situation must be more complicated than would be inferred from this simple picture. Direct calculation from Eq. (2) indicates that the energy gap, with the proper parameters for He^3 inserted, is about 4.5 calories per mole, or about 2.2 calories per mole of He^3 atoms. In order to fit the data on the magnetic susceptibility, the energy gap should be about $\frac{1}{4}$ of this, or 0.5 calorie per mole. This is a very small excitation energy; in He^4 the roton excitations involve approximately 2.5 calories per mole[7] of excited He^4 atoms. This difference

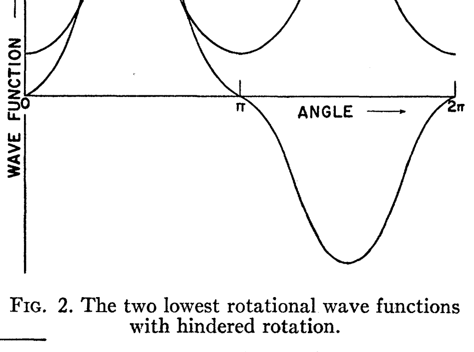

FIG. 2. The two lowest rotational wave functions with hindered rotation.

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[4] J. Reekie and T. S. Hutchison, Phys. Rev. **92**, 827 (1953).

[5] W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 207.

[6] E. C. Kerr, Phys. Rev. **96**, 551 (1954).

[7] See O. K. Rice, Phys. Rev. **96**, 1460 (1954).

may be, at least in part, connected with the fact that the quantum number j cannot have the value 1 in the rotation of a pair of He^4 atoms, on account of the statistics. Insofar as the pair approximation is good, then, the first excitation in He^4 must be to the next higher level, $j=2$. However, it is also probable that a cooperative interaction of all the atoms, peculiar to the Fermi-Dirac statistics, has something to do with the very low excitation energy in the case of He^3.

Let us consider the situation at 0°K, where presumably one-half the atoms have their spins in one direction and half have their spins in the opposite direction. Since the substance is in the liquid state and since the zero-point motion is considerable, it is hardly possible that the atoms have reached a state at 0°K in which no exchanges occur. Indeed, if they had, the spin-antiparallel alignment would have been destroyed. But if exchanges occur, we must assume that they take place between atoms which have mutually symmetrical spin functions (symmetrical exchanges) as well as between atoms which have antisymmetrical spin functions (antisymmetrical exchanges), and there must be some of each since half of the atoms have the same spin. However, if symmetrical exchanges were as frequent as antisymmetrical exchanges, there would be a considerable amount of localized angular momentum, which would force up the energy of the whole system. In order to avoid this situation, there will be some tendency for atoms in symmetrical spin states to stay as far away as possible from each other. This, however, raises the zero-point energy, so some compromise will have to be found. In any event, it is seen that the energy of the whole system is higher than it would be if the exchange problem were not involved,[8] (i.e., if there were no spin, and all exchanges were symmetrical as in He^4). Since the ground level of He^3 is thus raised, this may be another reason why excitation to a higher state should be lower in He^3 than in He^4. It may seem that the difference between 0.5 cal per mole and 2.5 cal per mole of excited atoms is large, but these energies are very small compared to the zero-point energy, so, taking account also of the effect mentioned in the preceding paragraph, the difference does not seem unreasonable.

In considering cooperative effects, there is a somewhat more specific point to which attention should be directed. The roton excitations in liquid He^4 apparently require the cooperation of a number of atoms, while in this paper, at least in the detailed calculations, we have considered interaction of pairs only.[9] It is of course possible that excitation in He^3 requires cooperation of several atoms, also. However, in the light of the lower density of He^3, and the presumed preliminary "excitation" even at absolute zero, described above, it may be that the consideration of pairs only is a better first approximation for finding the energy of excitation in this case than it would be in the case of He^4.

It is clear that the model used here can be made the basis of a theory of the specific heat of liquid He^3.

Note added in proof.—After submission of this paper I learned that P. J. Price[10] had already submitted a paper in which the same problem was treated by the same independent-pair model. The two papers appear to supplement each other; there is some difference in emphasis, for Price has stressed the possibility of finding a more reasonable model than the ideal-Fermi-gas model to account for the magnetic results, whereas I have particularly endeavored to find a semiquantitative explanation for the difference between the observed temperature parameter and that predicted from the ideal gas. Price has worked out the consequences of the model using the full set of energy levels; the fact that I find in better agreement with the experimental results by considering only the two lowest energy states may be a reflection of the hindered character of the rotation of a pair, the effect of the surrounding molecules being to bring the lowest levels closer together and effectively to isolate them from the others. Price mentions the possibility that long-range interactions will cause deviations from the calculated susceptibilities at very low temperatures; if these deviations are *not* too important, He^3 may possibly exhibit superfluidity at sufficiently low temperatures.[11]

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[8] In this connection, compare my earlier remarks, O. K. Rice, Phys. Rev. **93**, 1161 (1954), Sec. 4.

[9] I. Prigogine, J. Philippot, and co-workers [see I. Prigogine, Advances in Physics **3**, 131 (1954)] have obtained qualitative agreement with the properties of liquid He^4 considering only the interaction of pairs of atoms. However, there seems to be little doubt that the elementary excitations actually involve several atoms. Their results for a Fermi gas apparently do not coincide with those found here.

[10] P. J. Price, Phys. Rev. **97**, 259 (1955).

[11] O. K. Rice, Phys. Rev. **97**, 263 (1955).