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On the Theory of Liquid He^3

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The difficulties raised by the elementary interpretation of the recently observed temperature variation of the nuclear paramagnetic susceptibility of liquid He^3 as an ideal antisymmetric fluid type of degeneration phenomenon are discussed. The susceptibility data are then shown to lead to a direct and rigorous evaluation of the entropy of spin disorder and the associated heat capacity. The observed enormous total entropy of liquid He^3 at low temperatures is thus explained to be overwhelmingly entropy of spin disorder. The spin heat capacity is about half of the observed total heat capacity at the lowest temperature of observations. It should tend to become the dominant part of the total liquid heat capacity below this temperature. The maximum of the spin heat capacity at low enough temperatures may become observable indirectly through the total heat capacity of the liquid.

1. INTRODUCTION

THE experimental results obtained recently on a number of fundamental properties of liquid He^3 appear to justify their discussion within the framework of the still fragmentary theory of this liquid. The present paper will be concerned mainly with the exploitation of the measurements[1,2] of the nuclear paramagnetic susceptibility of liquid He^3. It will thus be shown, seemingly on quite general grounds, that the susceptibility data supply, over the whole experimentally explored temperature interval, the number of He^3 atoms which are in doubly spin-degenerate levels and their complement, or the number of those which are aligned with their spin momenta antiparallel. These are thus in nondegenerate levels as a result of the effect of a spin ordering internal field, as intimated by the experimental workers.[2] On the basis of this result, the susceptibility data appear directly to determine the entropy of spin disorder and, through its temperature variation, the associated spin heat capacity of the liquid. The knowledge of these partial spin properties of the fluid could be evidently of importance insofar as their subtraction from the calorimetrically measured total entropy and heat capacity yields the "lattice" or "non-spin" entropy and heat capacity. The separate availability of these partial properties could be helpful in the investigations of the foundations of the theory of liquid He^3.

Before entering, however, into the main topic of this paper which we have just outlined, it seems necessary to discuss first the possible theoretical meanings of the susceptibility data, using here some of the results obtained previously by us[3] in the investigations of the magnetic properties of liquid He^3.

2. EXCHANGE ENERGY AND CHARACTERISTIC SPIN ORDERING TEMPERATURE IN LIQUID He^3

In our previous work[3] the exchange energy per liquid He^3 atom has been computed at the temperature of absolute zero and in the two limiting spin or magnetic configurations,

$$\mu_{\text{tot}}=\begin{cases} N\mu,\ (f) \\ 0,\ (a) \end{cases}$$

of total magnetic moment $N\mu$, N being the total number of atoms of the system and μ the measured He^3 nuclear magnetic moment, or vanishing moment. The former was called the ferromagnetic (f), the latter the antiferromagnetic configuration (a). The total energy of the latter configuration was proved to be lower than that of the former. This total energy was written to be

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[1] Fairbank, Ard, Dehmelt, Gordy, and Williams, Phys. Rev. 92, 208 (1953).

[2] Fairbank, Ard, and Walters, Post-deadline paper, Washington D. C. meeting of American Physical Society, April 29–May 1, 1954.

[3] L. Goldstein and M. Goldstein, Phys. Rev. 76, 464(A) (1949); J. Chem. Phys. 18, 538 (1950).

the algebraic sum of the kinetic, potential, and exchange energies, the latter being positive here for all physically plausible closest distances of approach of two He^3 atoms. The following admittedly crude approximations were involved in these calculations. The kinetic energy was taken to be that of a completely degenerate ideal antisymmetric fluid formed by the He^3 atoms with the known mass per atom and the extrapolated density of the liquid. In the calculation of the mean potential energy the ever-present spatial correlations between the liquid atoms have been neglected. This was equivalent to using the limiting large separation expression $n_0 dv(r)$ for the probability of finding an atom in the volume element dv, whose center is at a distance r from the origin atom, n_0 being the mean atomic concentration at the absolute zero. Finally, in the evaluation of the exchange energies, the close packing of the ideal antisymmetric collection of atoms in momentum space and the asymptotic free particle level density in this space proportional to the square of their linear momentum were used in conformity with the formalism of the ideal antisymmetric fluid model. It was thus proved that, within these limitations, the exchange energy per liquid He^3 atom in the antiferromagnetic configuration, the only one of interest to us here, was given by

$$E_{x,0} = -\tfrac{3}{2}\int_a^\infty \Phi(r) J_{\frac{3}{2}}{}^2(k_0 r)\frac{dr}{r}, \qquad (1)$$

where k_0, the length of the wave vector at the surface of the closely packed momentum sphere of radius p_0 associated with the antiferromagnetic configuration, is $p_0/\hbar$, $\hbar$ being Planck's constant divided by 2π; $\Phi(r)$ is the mutual potential energy of two stationary He atoms separated by a distance r; $J_{\frac{3}{2}}(y)$ is the Bessel function of order $\frac{3}{2}$; and a, a cutoff length which had to be introduced because of the diverging character of the integrand at close separations. Physically the cutoff length a is equivalent to the assumption that the probability of finding two He atoms at distances $r \leqslant a$ vanishes identically. The exchange energy (1) was evaluated numerically with both the so-called Slater-Kirkwood (S-K) and Margenau[4] (M) approximate potential energy expressions, $\phi_{\text{S-K}}$ and ϕ_{M}, for various values of the distance of closest approach a. The results appear in Figs. 1 and 2 of our previous work.[3] It seems of interest to give here a few E_x values of physical interest. These are included in Table I, in temperature units $E_x(a)/k$, k being Boltzmann's constant.

Table I. Approximate exchange energies per liquid He^3 atom, °K units, for two types of potential energies and various cutoff distances a, (A). The liquid is at the absolute zero temperature.

a A	$E_{x,\text{S-K}}(a)/k$ °K/atom	$E_{x,\text{M}}(a)/k$ °K/atom
2.4	0.72	1.62
2.5	1.03	1.68
2.6	1.12	1.59
2.7	1.07	1.42
2.8	0.98	1.23

A glance at Table I shows that for the physically plausible cut-off distances $a \sim 2.5$–2.6A, where the mutual potential energies become negative, or binding, the approximate antiparallel spin ordering energies or characteristic temperatures are of the order of magnitude of one °K. At the present time, one is apparently inclined to consider $\phi_{\text{S-K}}(r)$ as a closer approximation to the correct potential energy function than $\phi_{\text{M}}(r)$. At any rate, keeping in mind the approximations involved in the derivation of the spin orientation energy or characteristic temperature of about one °K, the latter cannot be interpreted in any other way than by associating it with an "antiferromagnetic" internal field energy per atom. In the present system of the coupled He^3 atoms this approximate spin ordering energy, resulting from the interaction of two atoms and the antisymmetric character of their wave function, might be envisaged as a quantity more closely connected to the fundamental properties of liquid He^3 than the degeneration temperature

$$T_0 = (\hbar^2/2mk)(3n_0/8\pi)^{\frac{2}{3}}, \qquad (2)$$

associated with a system of ideal antisymmetric He^3 atoms of actual or effective mass m and concentration n_0. The effective mass concept would, of course, be helpful for taking into account, in a rather indirect way, the atomic interactions.

In the evaluation of the energies of Table I, the limitations resulting from the plane wave character of the individual atomic wave functions should lead to an overestimation of these exchange energies. More localized wave functions which could be associated with liquid atoms are expected to yield lower exchange energies. It is unlikely that the assumption of the close packing of a momentum sphere, even though centered at the origin of the momentum space, is too far from the actual state of affairs in the liquid at the absolute zero and vanishing total spin momentum, particularly as far as the calculation of the exchange energy is concerned. The latter depends, indeed, only on the distance of two atoms in momentum space and not on their individual momenta. In estimating the effect of using the free particle level density in these calculations, one might be inclined to say that this results in overestimating the exchange energy at least in parts of the spectrum. This could, however, be compensated for by the contributions from other portions of the energy spectrum.

Even though the directly evaluated exchange energies are relatively close to the experimentally found ordering energy[2] of about 0.45°K, the preceding studies do not explain why the experimentally established liquid He^3 paramagnetic susceptibility law should be so closely

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[4] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931); H. Margenau, Phys. Rev. **56**, 1000 (1939).

approximated by the Pauli susceptibility formula[5]

$$\chi_P(T) = (n\mu^2/kT)[-F'(\alpha)/F(\alpha)], \tag{3}$$

valid for an ideal antisymmetric gas of particles with spin $\hbar/2$, magnetic moment μ, concentration n, and degeneration temperature $T_0 = 0.45$°K. Here, for $\alpha > 1$,

$$\begin{aligned} F(\alpha) &= \sum_1^\infty (-)^{n-1} n^{-\frac{3}{2}} \exp(-n\alpha) = \tfrac{2}{3}(T_0/T); \\ F'(\alpha) &= dF/d\alpha, \end{aligned} \tag{4}$$

α being the negative Gibbs free energy per atom in units of kT. Clearly, it has not as yet been proved that the analytic form of the liquid He^3 susceptibility law is necessarily given by (3). The use of the "apparent" degeneration temperature of 0.45°K in connection with (3) tends to imply that this same temperature should appear in the expressions of the different thermal properties of the system, in accordance with its description as an ideal antisymmetric fluid of atoms of mass about ten times the atomic mass of He^3 and the actual density[6] of the liquid. These indeed yield with (2) a degeneration temperature of about 0.45°K. However, in the temperature interval explored so far, where $T \gtrsim 0.4$–0.5°K, the entropy and heat capacity data[7] in liquid He^3 rule out completely the possibility of accounting for them in terms of the ideal fluid formalism with a degeneration temperature of about 0.45°K.

It may be noted here that the degeneration temperature of about 5°K resulting from (2) where the liquid is pictured as a limiting ideal fluid leads to entropy values which appear to approximate crudely the measured entropies. This is however not the case with the heat capacities and the paramagnetic nuclear susceptibility.

We may thus conclude this section by saying that, at the present time, there is no unique and simple theoretical approach which accounts simultaneously for both the measured susceptibilities[1,2] and the entropies and heat capacities[7] of liquid He^3. However, the previously estimated[3] antiferromagnetic spin ordering energy of about 1.0°K, Table I, appears to be a fair approximation of the empirically obtained value of this energy derived from the susceptibility values.[2]

3. ENTROPY AND HEAT CAPACITY OF SPIN DISORDER IN LIQUID He^3

We shall now derive an entropy of spin disorder and the associated heat capacity which should be closely connected with the rigorous formulation of these thermal properties resulting from first principles within the framework of the correct theory of liquid He^3.

The liquid He^3 nuclear paramagnetic susceptibility measurements[1,2] over a wide temperature interval prove that at high temperatures the liquid tends to behave as an ideal paramagnetic system whose susceptibility obeys the Curie-Langevin law,[8] and at low temperatures its susceptibility is continuously reduced below the values predicted by the ideal limiting Langevin formula. The liquid ceases to be an ideal paramagnet as the temperature decreases and increasingly deviates from the ideal behavior as the low-temperature region is approached. An important feature of the empirical susceptibility law, over the temperature range explored so far, is its monotonic increase with decreasing temperatures.

In the present case of pure spin paramagnetism, the empirical susceptibility law can be explained on quite general grounds. Its results from the interplay of the disordering effects of thermal origin and the ordering effects due to both the application of a constant and uniform external magnetic field and the existence of an internal field, the latter tending to achieve antiparallel orientation of the nuclear spins.[3] Actually we are in presence of a "three-way" competition, insofar as the internal spin ordering phenomenon tends to oppose also the magnetization effect of the applied field. The existence of the internal field is of course a permanent and fundamental characteristic of the system. Let, then, $\nu(T)$ be the number, per unit volume, of those atoms or spin moments of the system at the finite temperature T which, as a result of thermal disorder, have escaped the orienting effect of the internal field. The magnetic moment $M(H,T)$ per unit volume induced in the system at temperature T, by application of the external uniform field of strength H, is given by the quantum-mechanical formula of Brillouin[9] for independent spins, or

$$\begin{aligned} M(H,T) &= \nu(T)\mu B_{\frac{1}{2}}(\mu H/kT) \\ &= \nu(T)\mu \tanh(\mu H/kT), \end{aligned} \tag{5}$$

for spin moments $\hbar/2$ and actual magnetic moments μ. In the paramagnetic range $\mu H \ll kT$ this yields the susceptibility

$$\begin{aligned} \chi(T) &= \lim_{\mu H \ll kT} M/H \\ &= \nu(T)\mu^2/kT. \end{aligned} \tag{6}$$

Hence, on the basis of the above reasoning,

$$\chi(T)/\chi_0(T) = \nu(T)/n, \tag{7}$$

where

$$\chi_0(T) = n\mu^2/kT \tag{8}$$

is the limiting Curie-Langevin susceptibility law, n being the atomic concentration in the system at temperature T. The ratio of the measured and ideal limiting susceptibilities, at the same temperature, is thus equal to the fraction of those atoms which, in absence of the external field, are in the double spin-degenerate levels

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[5] W. Pauli, Jr., Z. Physik. **41**, 81 (1927).

[6] Grilly, Hammel, and Sydoriak, Phys. Rev. **75**, 1103 (1949); E. C. Kerr, Phys. Rev. **96**, (1954).

[7] G. deVries and J. G. Daunt, Phys. Rev. **92**, 1572 (1953); **93**, 631 (1954). T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954). Osborne, Abraham, and Weinstock, Phys. Rev. **94**, 202 (1954).

[8] P. Langevin, Ann. chim. et phys. **5**, 70 (1905).

[9] L. Brillouin, J. phys. et radium **8**, 74 (1927).

as stated by Fairbank and his collaborators on the basis of the ideal antisymmetric Fermi fluid type of degeneration mechanism. The preceding derivation of the ratio (7) is however quite general and independent of the particular mechanism responsible for the antiparallel alignment of the spins of the system.

It appears interesting to recall here the rigorous proof of the ratio (7) in the formalism of ideal antisymmetric fluids of atoms with spin $s\hbar$. Here one can start from first principles, as was first shown by Bloch[10] in the course of his discussion of the Pauli-formula (3). Let n_i be, at temperature T, the mean number of atoms in the state of kinetic energy ϵ_i, of spin degeneracy g, or $(2s+1)$. By definition,

$$n_i(T)=g[\exp(\alpha+\epsilon_i/kT)+1]^{-1}. \tag{9}$$

The probability of finding only one single atom in the group of g levels, or the g-fold level, is $n_i(T)$ times the probability that in this level group is empty. This latter probability is, by definition, $(1-n_i/g)$. Hence, the probability for having only a single atom of energy ϵ_i is

$$\sigma_i(T)=n_i(T)(1-n_i/g). \tag{10}$$

The total number of atoms in the system occupying singly the g-fold levels is thus

$$N_\sigma(T)=\sum_i \sigma_i(T), \tag{11}$$

the summation extending over the whole spectrum of the system. With the free particle continuous spectrum approximation $\epsilon(p)=p^2/2m$, p being their linear momentum and m their mass, and the associated level density $4\pi(V/h^3)p^2dp$ one finds in the whole system occupying volume V, using (9), (10), and (11),

$$N_\sigma(T)=4\pi g(V/h^3)\int_0^\infty \left\{p^2\left[\exp\left(\alpha+\frac{p^2}{2mkT}\right)\right]\Big/ \left[1+\exp\left(\alpha+\frac{p^2}{2mkT}\right)\right]^2\right\}dp, \tag{12}$$

which yields easily, when the denominator,

$$N_\sigma(T)=gV(2\pi mkT/h^2)^{\frac{3}{2}}\sum_{\lambda=1}^{\infty}(-)^{\lambda-1}\lambda^{-\frac{1}{2}}\exp(-\lambda\alpha), \tag{13}$$

is expanded. But from the definition of the parameter α, N being the total number of atoms of the system at temperature T, one has

$$\begin{aligned} N/V&=n\\ &=g(2\pi mkT/h^2)^{\frac{3}{2}}\sum_{\lambda=1}^{\infty}(-)^{\lambda-1}\lambda^{-\frac{3}{2}}\exp(-\lambda\alpha) \qquad (14)\\ &=g(2\pi mkT/h^2)^{\frac{3}{2}}F(\alpha). \end{aligned}$$

And finally, dividing (13) by (14), one obtains

$$\begin{aligned} \nu(T)/n&=\left[-\frac{1}{F(\alpha)}(dF/d\alpha)\right]\\ &=\chi_P(T)/\chi_0(T), \end{aligned} \tag{15}$$

using (3) and (8) for χ_P and $\chi_0(T)$, respectively. The general relation (7) is thus proved rigorously for ideal antisymmetric fluids.

The susceptibility measurements define through (7) the number of liquid He^3 atoms which have "freed" themselves from the spin orienting internal field and became thus, as far as their spins are concerned, independent. If the volume of the liquid is V, the total number of these spin-free or spin-disordered atoms is

$$N_\sigma(T)=\nu(T)V, \tag{16}$$

and the total number of their spin configurations is, g or $(2s+1)$ being equal to 2 for spins $\frac{1}{2}$,

$$P_\sigma(T)=2^{N_\sigma(T)}. \tag{17}$$

By Boltzmann's theorem, they contribute to the total entropy of the liquid the entropy of spin disorder

$$S_\sigma(T)=N_\sigma(T)k\ln 2, \tag{18}$$

or, per mole of the liquid, N being Avogadro's number,

$$\begin{aligned} S_\sigma(T)&=(N_\sigma/N)R\ln 2\\ &=[\chi(T)/\chi_0(T)]R\ln 2, \end{aligned} \tag{19}$$

R being the gas constant, and where use has been made of (7). For our evaluation of the entropy of spin-disorder only the experimental values of $\chi(T)/\chi_0(T)$ are needed. The analytical form of the latter ratio and the knowledge of the detailed mechanism explaining the empirical susceptibility law are not needed at all, provided, of course, that this empirical susceptibility law belongs to that very wide class of susceptibilities for which the reasoning leading to (7) is valid.[11]

To the spin entropy (19) there is associated a heat capacity of spin disorder

$$\begin{aligned} C_\sigma(T)&=T(dS_\sigma/dT)\\ &=RT(\ln 2)(d/dT)[\chi(T)/\chi_0(T)], \end{aligned} \tag{20}$$

where, of course, the temperature derivative can be evaluated directly with the empirical ratio $\chi(T)/\chi_0(T)$. The knowledge of the latter determines thus also the heat capacity of spin disorder in liquid He^3 in as absolute a way as it determines the spin entropy.

At the present time, and for reasons of simplifying the above calculations of entropy and heat capacity of spin disorder, it is convenient to adopt for $\chi(T)/\chi_0(T)$ the expression resulting from (3), that is Eq. (15),

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[10] F. Bloch, Z. Physik **53**, 216 (1929).

[11] That the susceptibility measurements should lead to the entropy of spin disorder in liquid He^3 has been suggested independently by Drs. T. R. Roberts and S. G. Sydoriak of this laboratory before the recent results of Fairbank and his group (reference 2) became available.

which is claimed[2] by the experimental workers to constitute a fair analytical approximation to the measured values of this ratio, with an "apparent" degeneration temperature T_0 of 0.45°K. Hence, the spin entropy (19) becomes with (15),

$$S_\sigma(T)/R = [-F'(\alpha)/F(\alpha)](\ln 2). \tag{21}$$

We want to emphasize, however, that the use of the preceding analytical approximation of the spin entropy in liquid He^3 cannot and need not be, at the present time, interpreted as being equivalent to an acceptance of the elementary statistical gas degeneration mechanism on which it is based. The various difficulties raised by such an interpretation have been discussed in the preceding section.

The limiting values of S_σ, at both ends of the temperature interval, are:

$$\lim_{T \text{ large}} S_\sigma/R = (\ln 2) \lim_{\alpha \gg 1}[-F'(\alpha)/F(\alpha)] = \ln 2, \tag{22}$$

if the definition (4) of $F(\alpha)$ is used. Up to terms in $(1/\alpha^2)$, or $(T/T_0)^2$, one has

$$\begin{aligned}\lim_{T \text{ small}} S_\sigma/R &= (\ln 2) \lim_{\alpha \ll 0}[-F'(\alpha)/F(\alpha)] \\ &= (\tfrac{3}{2}\ln 2)\frac{1}{(-\alpha)}\left[1-\frac{\pi^2}{6\alpha^2}\right] \\ &= (\tfrac{3}{2}\ln 2)(T/T_0)\left[1-\frac{\pi^2}{12}(T/T_0)^2\right].\end{aligned} \tag{23}$$

The low-temperature expansion of $F(\alpha)$,

$$\underset{\alpha \ll 0}{F(\alpha)} = \frac{1}{\Gamma(5/2)}(-\alpha)^{\frac{3}{2}}\left[1+\frac{\pi^2}{8\alpha^2}\right], \tag{24}$$

has been used in deriving (23). The analytical approximation (21) of S_σ predicts thus the linear vanishing of the spin entropy with temperature.

The spin heat capacity $C_\sigma(T)$, Eq. (20), becomes, within the same formalism,

$$\begin{aligned}C_\sigma(T)/R &= (\ln 2)T\left[\left(\frac{F'(\alpha)}{F(\alpha)}\right)^2 - \frac{F''(\alpha)}{F(\alpha)}\right]\left(\frac{d\alpha}{dT}\right) \\ &= (\tfrac{3}{2}\ln 2)\left[\frac{F''(\alpha)}{F'(\alpha)} - \frac{F'(\alpha)}{F(\alpha)}\right],\end{aligned} \tag{25}$$

since from (4),

$$T(d\alpha/dT) = -\tfrac{3}{2}(F(\alpha)/F'(\alpha)). \tag{26}$$

In the high and low temperature limits, one obtains

$$\lim_{T \text{ large}} C_\sigma/R = 0, \tag{27}$$

since

$$\lim_{\alpha \gg 1}[F''(\alpha)/F'(\alpha)] \to -1, \quad \lim_{\alpha \gg 1}[-F'(\alpha)/F(\alpha)] \to 1.$$

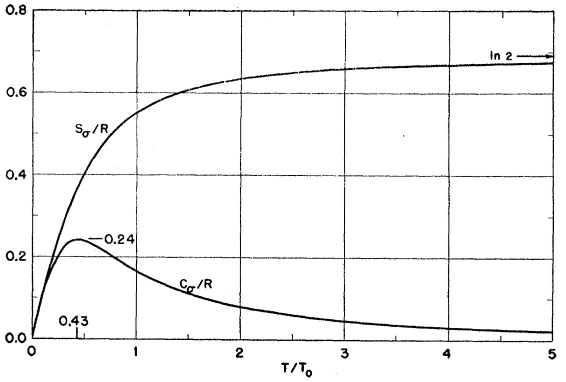

FIG. 1. Molar spin entropy S_σ/R and spin heat capacity C_σ/R in liquid He^3 as a function of the temperature ratio T/T_0, T_0 being a characteristic temperature of spin orientation of about 0.45°K, according to the nuclear paramagnetic susceptibility data (reference 2).

Also, up to terms in $(1/\alpha^2)$, or $(T/T_0)^2$,

$$\begin{aligned}\lim_{T \text{ small}} C_\sigma/R &= (\tfrac{3}{2}\ln 2)\frac{1}{(-\alpha)}\left(1-\frac{\pi^2}{3\alpha^2}\right) \\ &= (\tfrac{3}{2}\ln 2)(T/T_0)[1-\tfrac{1}{4}\pi^2(T/T_0)^2].\end{aligned} \tag{28}$$

C_σ vanishes thus at both ends of the temperature interval. Since it is always positive, $S_\sigma(T)$ being a monotonically increasing function of T, it has at least one maximum. The position of this maximum is at $\alpha = -1.90$, $T/T_0 = 0.43$, and the peak value of C_σ/R is 0.24.

It is interesting to note here, in passing, that the very low-temperature spin entropy and spin heat capacity of the ideal antisymmetric fluid, up to terms linear in T, are only relatively small fractions of the total entropy and heat capacity. The ratios S_σ/S_{tot} and C_σ/C_{tot} equal $3\ln 2/\pi^2$ or 0.21. The spin portions of these quantities amount only to 21 percent of the totals at these low temperatures.

By using the Tables[12] of the function $F(\alpha)$ and its derivatives at $T/T_0 \leqslant 2$, $\alpha \leqslant 1.23$, and the expansion (4) at $T/T_0 > 2$, the analytical approximations (21) and (25) of the spin entropy S_σ/R and spin heat capacity C_σ/R have been evaluated[13] in the range $0 \leqslant T/T_0 \leqslant 5$, $-20 \leqslant \alpha \leqslant 2.7$. They are given in Fig. 1.

As mentioned in the Introduction, the knowledge of the spin entropy and the associated heat capacity allows one, after subtracting them from the measured total liquid He^3 entropy and heat capacity, to obtain the nonspin or lattice portions of these thermal properties. Using the entropy and heat capacity data of the

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[12] J. McDougall and E. C. Stoner, Trans. Roy. Soc. (London) **A237**, 67 (1938).

[13] I wish to thank here Mr. Max Goldstein and Miss M. L. Johnson for these calculations, and Mrs. L. E. Moss for the preparation of the graph. The low-temperature, $T/T_0 \leqslant 2$, susceptibilities have been used already in Table I of our previous work, reference 3.

three independent groups of workers referred to above,[7] a somewhat cursory comparison has been made between their data and the spin entropy and heat capacity obtained in the present work. This comparison shows that at temperatures $1.0 \leqslant T \leqslant 1.5$°K, a very large portion of the enormous liquid He^3 entropy is spin entropy, while below 1°K the entropy tends to become overwhelmingly spin entropy. This result is of interest insofar as it indicates that at low temperatures most of the "nonspin" degrees of freedom of liquid He^3 are already frozen, as one would expect them to be. As far as the heat capacity is concerned, it is found that at 0.4°K, about 40 percent of it is of spin origin and C_σ tends to become its dominant part at $T \leqslant 0.4$–0.3°K. The characteristic peak of the spin heat capacity might be detectable in its effect on the total heat capacity at temperatures lower than those reached so far. The qualitative shape of the spin heat capacity curve is, of course, of permanent significance and is not connected with the analytical approximations used in the computation of the C_σ curve of Fig. 1.

It is expected that the experimental workers in the field of entropy and heat capacity investigations of liquid He^3 might analyze, in greater detail, their own respective data with the help of the practically absolute spin entropies and spin heat capacities obtained above. These experimental data appear, at the present time, to be still somewhat of preliminary character.

In conclusion we may thus say that a rigorous explanation has been given here for the origin of the very large liquid He^3 entropy at low temperatures. This is based on a rigorous evaluation of the partial entropy and heat capacity of spin disorder using the experimentally measured nuclear paramagnetic susceptibilities. It may be expected that the peculiar maximum of the spin heat capacity becomes observable indirectly on the total liquid heat capacity at low enough temperatures.

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Statistical Mechanics of Helium II near 1°K*

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It now seems probable that the roton excitations in helium II can be considered to be cooperative motions of small groups of atoms, the group as a whole being in an excited quantum state. This leads to a very literal interpretation of the two-fluid hypothesis, and suggests that the entropy of mixing of rotons and the unexcited atoms be calculated on the basis of the lattice theory of liquids. From this the thermodynamic properties of liquid helium are deduced, and the degeneracy of the roton energy level (giving the intrinsic entropy of the rotons) is obtained from the observed specific heat. The change in the thermodynamic properties of normal fluid (rotons) between 0°K and the λ point is discussed. Finally the peculiar properties of the coefficient of thermal expansion are considered in the light of the two-fluid hypothesis.

THE nature of the roton excitations in liquid helium II has recently been discussed by Feynman[1] who concluded that they involve cooperative motions, perhaps rotations, of a small number of atoms. Somewhat similar ideas, though differing in detail, had previously been advanced by Toda[2] and Matsubara.[3]

In considering the statistical behavior of the rotons it has generally been assumed that they can be treated as though they were a Bose-Einstein gas of particles of some particular effective mass. This was done originally by Landau,[4] and the thermodynamics of such a system has recently been considered in some detail by Goldstein[5] who has discussed some of the difficulties which arise. Landau's treatment is based upon the idea that the excitations arise from interactions of waves, which can be represented as excitons or considered as wave packets. The excitons are assumed to have a certain effective mass and to obey Bose-Einstein statistics. These assumptions serve to determine the entropy contributed by the excitons, but the effective mass must be taken as a parameter, and it is difficult to interpret.

Since the roton interactions are apparently localized over a region containing only a few atoms, it would seem reasonable to explore some other type of approximation, such as the lattice theory of liquids. Indeed, the lattice theory of liquids would seem to be peculiarly adapted to treatment of the rotons in the region around 1°K where the rotons are few in number. For in this temperature region the roton, according to the picture which has been developing, represents a small group of atoms in a single quantum state (though the energy may be broadened by interaction with the neighboring

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[1] R. P. Feynman, Phys. Rev. **94**, 262 (1954).

[2] M. Toda, Progr. Theoret. Phys. (Japan) **6**, 458 (1951).

[3] T. Matsubara, Progr. Theoret. Phys. (Japan) **6**, 714 (1951).

[4] L. D. Landau, J. Phys. (U.S.S.R.) **5**, 71 (1941); **8**, 1 (1944); **11**, 91 (1947); see R. B. Dingle, Advances in Phys. **1**, 111 (1952).

[5] L. Goldstein, Phys. Rev. **89**, 597 (1953).