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*

O. K. RICE
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina

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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).

molecules) and the state of the superfluid substrate does not depend on the position of the roton. At a sufficiently low temperature no account need be taken of more highly excited roton states of the same group of atoms; probably the only distinction between quantum states that needs to be considered resides in their nature and in the number of atoms involved. Thus there will be some multiplicity of the quantum state, and we shall as a first approximation consider it as a degenerate state of energy ϵ and multiplicity m. Furthermore, at the low temperatures considered, the rotons are independent of each other. We thus have two kinds of entities involved, namely, unexcited atoms and rotons, or groups of atoms in an excited energy level. It is seen that this enables us to give quite a literal interpretation of the two-fluid hypothesis if we say that the unexcited portion forms the superfluid, while the atoms in the rotons constitute the normal fluid. We consider helium II as a mixture of the two, and the number of different configurations of the system will depend upon the number of ways in which rotons and atoms can be arranged in order, provided that the density of rotons is small enough so that the question of overlapping does not arise. This results in an entropy of mixing given by

$$S_m = k \ln\left(\frac{(N-nq+n)!}{(N-nq)!n!}\right), \tag{1}$$

where N is the total number of atoms, including those in the rotons, n is the total number of rotons, and q is the average number of atoms in a roton. Since a roton has a degeneracy of m, the entropy of a roton is

$$S_r = k \ln m, \tag{2}$$

and its free energy (which can be taken as essentially the Gibbs free energy) is

$$G_r = \epsilon - kT \ln m. \tag{3}$$

If the free energy of the superfluid is taken as zero, the total free energy of the whole system is

$$G = nG_r - TS_m. \tag{4}$$

The equilibrium value of n is found by making G a minimum. Differentiating Eq. (4) with respect to n, using Eqs. (1) and (3), with the Stirling approximation, and setting the result equal to zero, we find

$$\epsilon - kT \ln m + (q-1)kT \ln(N-nq+n) - qkT \ln(N-nq) + kT \ln n = 0. \tag{5}$$

If the roton concentration is small, i.e., if n is very small compared to N, we obtain

$$n = Nme^{-\epsilon/kT}. \tag{6}$$

The roton part of the specific heat is given roughly (assuming ϵ is constant) by $\epsilon dn/dT$, hence we write

$$C = (Nm\epsilon^2/kT^2)e^{-\epsilon/kT}. \tag{7}$$

This form is of course very similar to that which is obtained in Landau's theory; the principal difference is that the factor in front of the exponential depends directly on m the multiplicity of the energy states of the roton, and there is no term which arises from the translational energy states of the roton, for the simple reason that we have assumed that the rotons have no translational energy.

The latter point is one that will stand some amplification. In Landau's theory, the velocity of the roton is not the material velocity of atoms exhibiting the excitation, but the velocity with which the excitation is passed on from point to point. The effective mass is, therefore, as we have noted, essentially a parameter which has to be chosen to give the proper entropy of the rotons, so that we have a factor of the right size to replace $Nm\epsilon^2/kT^2$ in Eq. (7) (or it may possibly be deduced from Feynman's theory). At least in the range of small density of rotons it is possible to make the thermodynamic consequences of the two theories coincide by the proper choice of the effective mass, on the one hand, or the multiplicity factor m, on the other. If the two theories turn out to be equivalent it will nevertheless be advantageous to have the value of m, which is more readily interpreted.

However, it is one of the properties of superfluid that it can flow freely around obstacles, and such obstacles should include particles of normal fluid. Thus there is certainly the possibility of bodily relative motion between the rotons and the superfluid. In this case, the total energy of the rotons would have the form $\epsilon + p^2/2\mu$, where p is the momentum and μ the effective mass. This is the same in form as the expression for the energy of rotons *first* suggested by Landau in 1941, though the significance of p is different. If this form of energy is used, and the rotons are assumed to be freely moving particles the value of μ required to give the proper entropy so as to obtain the observed specific heat of liquid helium is just of the order of magnitude expected for rotons of the size we have assumed. However, it is known that there is a critical velocity for thin films, in which the superfluid is moving and the normal fluid is stationary. This is[6] about 50 cm sec^{-1}, while the average thermal velocity of rotons consisting of 8 to 10 helium atoms, if behaving like an ideal gas at 1°K, would be at least 1000 cm sec^{-1}. Therefore it seems improbable that there can be development of an entropy of translation of the ideal gas type, and I believe that it is preferable to set up the expression for S_m in the form of Eq. (1). The actual bodily motion of rotons with respect to superfluid, though limited by the critical velocity, should be quite ample to account for second sound and the peculiar flow properties of liquid helium in the roton region. The whole development sug-

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[6] K. R. Atkins, Advances in Phys. **1**, 169 (1952), see p. 189. It is true that the critical velocity increases as the film becomes thinner, so some question may exist regarding the upper limit.

gests that quite a literal interpretation of the two-fluid hypothesis may have considerable validity.

We shall now use Eq. (7) to determine ϵ/k and m. Using the specific heat data of Kramers, Wasscher, and Gorter[7] between 1.0° and 1.5°K and allowing for the phonon contribution by subtracting 0.0235 T^3 joule g^{-1} deg^{-1}, we obtain

$$\epsilon/k = 10.1°\text{K}, \quad m = 9.3.$$

The value of ϵ is of course approximately the same as the value of the energy increment obtained in Landau's theory. The value of m is rough since it depends fairly strongly on ϵ/k. Feynman[1] has suggested that the average roton might consist of six helium atoms involved in some kind of cooperative motion. If there were a range of about nine or ten in the number of helium atoms involved, this would account for the value of m. This might indicate that actually, on the average, eight or ten helium atoms are involved in a roton.

In making these calculations we have assumed that the roton concentration is small. It is somewhat tempting to suppose, however, that Eqs. (1) through (5) could be used at much higher concentrations (i.e., higher temperatures) provided ϵ and m could be evaluated as functions of T. As T increases, higher-energy levels must become accessible, so the value of ϵ (which is essentially an average value) and m must both increase. It may be possible to make a rough interpolation, since the values are known at the λ point, where the liquid is almost pure normal fluid. If there is actually an average of eight atoms per roton, the value of ϵ/k corresponds to an energy of about 2.5 calories per mole of helium in rotons, which is not far from the energy of liquid helium at the λ point, namely, 3.0 calories per mole, so that relatively little change is found in the average energy of superfluid over this range of temperatures. Still using eight atoms per roton, we find a change in entropy from about $(R/8)\ln 9.3 = 0.55$ to about 1.6 eu (entropy units) per gram atom, corresponding to about a 1.7-fold increase in the number of available energy levels for each atom, or about a 70-fold increase per roton of eight atoms. This seems to be a rather large change and means that as the roton concentration increases and some of them coalesce, there is a disproportionate increase in the number of energy levels, which certainly in large measure compensates for the decrease in entropy of mixing which occurs when concentration of rotons increases. This is, presumably, what causes the continued increase in specific heat up to the λ point. Looked at from the point of view of the energy levels of the whole system, we may say that there are many low-energy levels (case of few rotons) because these are localized and can be located in different regions of the fluid (entropy of mixing); on the other hand, the density of high-energy levels (case of many rotons) receives a contribution because the presence of some freely moving atoms makes it easier for other atoms to move freely also, when the rotons coalesce, and there may be highly excited energy levels in which the energy *per atom* is even lower than it is in isolated rotons.

The value of ϵ is comparable to the heat of vaporization of liquid helium, and one might intuitively expect that a single atom could be excited to a number of energy levels with energy appreciably less than the energy necessary to separate it from the liquid altogether. However, the result seems to be that this cannot occur in the case of helium. By the time the liquid gets to the λ point, it may be that individual atoms can move through the liquid fairly readily without each one having enough energy to evaporate, as we suggested in a previous paper.[8]

If this picture of liquid helium has any element of truth, it will be clear that entropy of mixing of superfluid and normal fluid must play an important role in determining the properties of the liquid, and that we were, therefore, correct in taking it into account in our discussion of the thermodynamics of liquid helium,[9] though some of the details may need to be changed (see Appendix). The present picture also is in accord with the ideas which we have discussed recently in considering the λ transition,[8] in that a separation of superfluid and normal fluid is visualized. The point of view taken here is that which is appropriate for a dilute solution of normal fluid in superfluid, whereas in discussing the λ point it is necessary to consider the reverse case.

Finally, as a sort of addendum, we should like to make a few remarks concerning the peculiar behavior of the coefficient of expansion of helium II. Atkins and Edwards[10] have recently found that there is a slight expansion with increasing temperature in the phonon range, as might be expected, followed by the well-known rather considerable contraction between 1°K and the λ point. On the basis of the two-fluid hypothesis this is formally accounted for by saying that normal fluid has a slightly smaller volume than superfluid.[11] In order to understand this further we have to inquire why the thermal plus zero-point energy of normal fluid changes less rapidly with the density than is the case with

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[7] Kramers, Wasscher, and Gorter, Physica **18**, 329 (1952).

[8] O. K. Rice, Phys. Rev. **93**, 1161 (1954). The results of this paper, however, do not depend upon the detailed nature of the excitations.

[9] O. K. Rice, Phys. Rev. **76**, 1701 (1949). Indeed the existence of entropy of mixing was already implicit in Landau's original treatment, and Landau noted [L. D. Landau, Phys. Rev. **75**, 884 (1949)] that his theory was different from that of L. Tisza [Phys. Rev. **72**, 838 (1947)] in that it did not make the entropy proportional to the density of normal fluid.

[10] K. R. Atkins and M. H. Edwards, Phys. Rev. **93**, 1416 (1954).

[11] We have already (reference 9) treated the dependence of the λ temperature on pressure from this point of view. This calculation indicates that the partial volume of each of the two fluids may itself vary somewhat with circumstances.

superfluid.[12] The ground state energy (aside from the background of potential energy) is zero-point energy only, which depends upon the free range of motion of an atom hemmed in between other atoms. But a free range of motion, depending on the space between atoms, is very strongly dependent on density. An excited energy level probably involves motions of atoms through larger distances, and these distances will probably depend less strongly on density. Thus such an energy level itself does not depend so strongly on density, and that part of the helium where such an energy is excited settles down to a smaller interatomic distance, since this results, especially in liquid helium, in a lowering of the potential energy. Thus the negative coefficient of thermal expansion seems reasonable enough.

APPENDIX

It seems desirable to set forth the expressions for the partial molecular entropies, $\bar{s}_n$ and $\bar{s}_s$, for normal and superfluid, respectively, which are obtained from the theory here developed for the dilute roton region. $\bar{s}_n$ can be obtained by differentiating the entropy $S=S_m+nS_r$ with respect to n, holding $N-nq$, the number of superfluid atoms, constant, and then dividing by q, the number of atoms in a roton. This gives, if $n/N\ll 1$,

$$\bar{s}_n=(k/q)[\ln(N/n)+\ln m]. \tag{8}$$

The molecular entropy is given, at mole fractions x_n and x_s by

$$s=x_n\bar{s}_n+x_s\bar{s}_s=(qn/N)\bar{s}_n+[(N-qn)/N]\bar{s}_s. \tag{9}$$

Using Eq. (7), and neglecting the phonon contribution, we also have

$$\begin{aligned} s&=\int_0^T (C/NT)dT \\ &=\int_0^T (m\epsilon^2/kT^3)e^{-\epsilon/kT}dT \\ &=mke^{-\epsilon/kT}(1+\epsilon/kT). \end{aligned} \tag{10}$$

From Eqs. (6), (8), (9), and (10), and noting that qn/N is small, we obtain

$$\begin{aligned} \bar{s}_s&=mke^{-\epsilon/kT} \\ &=s/(1+\epsilon/kT). \end{aligned} \tag{11}$$

When it was assumed that s had the form,

$$s=s_\lambda(T/T_\lambda)^r,$$

where s_λ and T_λ denote values at the λ point and r is a constant, we found,[13] under the further assumption that there is no *enthalpy* of mixing of normal and superfluid but only *entropy* of mixing, that

$$\bar{s}_s=s/(1+r);$$

this is quite analogous to Eq. (11), only the dimensionless quantity ϵ/kT being replaced by its near equivalent, r.

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[12] The rate of increase of this energy with decreasing volume represents a pressure which pushes outward, and which is balanced by the pressure due to the potential energy.

[13] O. K. Rice, Phys. Rev. **78**, 182 (1950).