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Comparison of the Energy Excitations in Liquid He^3 and He^4*

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In both He^3 and He^4 there are two types of excitation, a Debye type involving large numbers of molecules, and a localized type of excitation. The latter type is considered in this paper. In the case of He^3 the localized excitations of lowest energy can be discussed rather successfully by means of a pair-rotator model, with hindered rotation in a plane. The pair-rotator model breaks down in the case of the next higher group of excited levels; their energy is about right but there are more such levels than would be expected on the pair-rotator model. The reason for this is considered. In the case of He^4 the so-called roton excitations are of much higher energy than the excited levels in He^3, on account of the statistics and also on account of the effect of the higher density on the hindering of the rotation. These effects can be understood with the aid of the pair-rotator model. The model, itself, however, breaks down for these levels, and the nature of the break-down and the probable character of the rotons are discussed. The results are also of interest in connection with mixtures of He^3 and He^4. Some remarks are appended on the possibility of a λ transition in He^3.

SUFFICIENT is now known about the excitations in liquid He^3 and He^4 so that a comparison of the two cases should lead to new insights. In some respects they are quite similar. In each case the thermodynamic properties can be accounted for by assuming that there are two types of excitation; first, a Debye or phonon type involving simultaneous vibration of large numbers of atoms, and, secondly, a localized type of excitation involving only a small number of atoms (but in general at least two, and partaking of some of the character of a rotation—localized vibrational excitations would involve higher energies than need to be considered at low temperatures). It is the latter with which we wish to deal in this paper. The localized excitations in He^4 (rotons) involve much more energy than is the case with He^3. This difference is due principally to the difference in statistics, but, as we shall see, there is also an indirect effect arising from the difference in mass, which is sufficient to give He^3 a considerably higher zero-point energy than He^4 for any predetermined density and which consequently results in a much lower equilibrium value of the density for He^3.

Liquid He^3 has recently been treated with some success by means of what may be called a pair-rotator model,[1] in which N atoms are considered to form $N/2$ pairs which can undergo rotation, among other types of motion. If the pair-rotator model is to have validity, the cells in which the pairs are to rotate will be fixed by the surrounding molecules. Thus a molecule does not, at a particular instant, have a choice as to which other molecule it will pair with, but on the average is much more likely to exchange places with some one of its neighbors than with the others, this exchange being associated with a certain average energy [0.4° times the Boltzmann constant, according to Eq. (1)]. Although the pairing will change from moment to moment, this may be considered to be a part of the zero-point fluctuation and does not contribute to the entropy. If this were not the case, the pair-approximation would not give good results.

Temperley[1] has proposed a partition function for a pair whose logarithm is given by

$$\ln(1+3e^{-0.4/T}+8e^{-2.7/T}),$$

so that the partition function of He^3 *per atom* is given (after a Debye term is added) by

$$\ln(\text{p.f.})_{He^3}=\tfrac{1}{2}\ln(1+3e^{-0.4/T}+8e^{-2.7/T})+0.0108T^3. \quad (1)$$

The data on the nuclear paramagnetism, the specific heat, and the entropy can be reproduced by this partition function (and apparently only by one whose form is close to this). The weight, 3, of the energy level at $0.4k$ (about 0.8 cal per pair-mole) arises from the

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[1] P. J. Price, Phys. Rev. **97**, 259 (1955); O. K. Rice, Phys. Rev. **97**, 263 (1955); H. N. V. Temperley, Phys. Rev. **97**, 835 (1955); and (unpublished work).

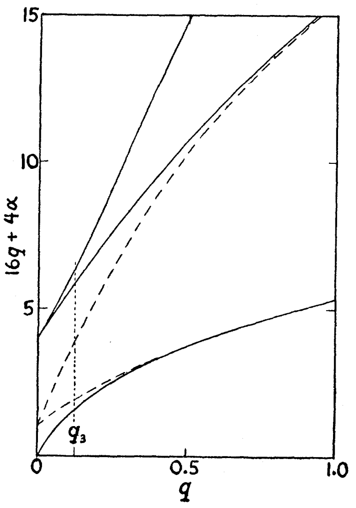

FIG. 1. The five lowest energy levels for the restricted rotator as functions of q. Solid curves, symmetrical rotational states; broken curves, antisymmetrical states. q_3 is the estimated value of q for He^3.

fact that this state is a triplet state with respect to the nuclear spin of He^3 (hence, also, it contributes to the paramagnetism). This state, then, has no spatial degeneracy.

We have pointed out[2] that the weight of three is exactly what would be expected on the pair-rotator model if the pair-rotator acts as a hindered plane rotator. The lowest state of rotational oscillation is symmetrical in the space coordinates, hence antisymmetric in the spin coordinates and a singlet, while the next excited state is antisymmetrical in the space coordinates and hence a triplet. The normal twofold spatial degeneracy of the plane rotator (due to clockwise and counterclockwise rotation) is lifted in the hindered rotator. The existence of a hindering potential is of course to be ascribed to the interactions of neighboring molecules.

In treating the problem of hindered rotation it is commonly assumed that the potential energy is given as a function of the angle θ of rotation by an expression of the form[3] $V_0 - V_0 \cos 2\theta$, where V_0 is a constant parameter. This leads to the wave equation

$$d^2\psi/d\theta^2 + (8\pi^2\mu r_0^2/h^2)(W - V_0 + V_0 \cos 2\theta)\psi = 0, \quad (2)$$

where μ is the reduced mass, r_0 the interatomic distance for the rotator, and W is the value of the energy. This is Mathieu's equation, and can be written

$$d^2\psi/d\theta^2 + (4\alpha + 16q \cos 2\theta)\psi = 0, \quad (3)$$

where

$$\alpha = (2\pi^2\mu r_0^2/h^2)(W - V_0)$$

and

$$q = \pi^2\mu r_0^2 V_0/2h^2.$$

If V_0 is zero, Eq. (2) reduces to the equation for the plane rotator with energy levels given by

$$W = j^2h^2/8\pi^2\mu r_0^2, \quad (4)$$

where j is an integer. The quantity $16q+4\alpha$ is the energy expressed in terms of the unit $h^2/8\pi^2\mu r_0^2$. By finding the characteristic values of Mathieu's equation for periodic solutions, the allowed values of $16q+4\alpha$ can be determined[4] as functions of q. These values are shown in Fig. 1.

In attempting to apply these results to the pair-rotator model, we assume that r_0 is equal to the average interatomic distance in He^3, which we estimate[5] to be 3.46 A. Then $h^2/8\pi^2\mu r_0^2 = 2.68$ cal per pair-mole. However, according to Temperley's equation [Eq. (1)], which also agrees roughly with our own conclusions, the actual energy gap between the lowest singlet and the next triplet state is about 0.8 cal per pair-mole. Using the hindered plane-rotator model, we conclude from Fig. 1 that q must be about 0.145 ($V_0 = 6.2$ cal per pair-mole), as indicated on Fig. 1. With this value of q we see that there is a triplet level at an energy of roughly 7 cal per pair-mole above the ground state. This is close to the average energy of Temperley's suggested second group of excited energy levels, namely 5.4 cal per pair-mole. At first glance, however, the expected multiplicity is three, which contrasts with Temperley's multiplicity of eight. Temperley suggested that his eightfold level consisted of two triplets and two singlets. Exactly this composition is not required, however, and if the hindered pair-rotator picture has validity, it appears from Fig. 1 that the singlet states are rather high to be included.[6] On the other hand, it seems possible that some spatial degeneracy might appear in the higher energy levels. As mentioned above, the pair-rotator model implies that an atom pairs with a particular neighbor, determined by the instantaneous configuration of the system as a whole. It seems likely that this restriction would break down for excitations involving higher energies, so that an atom would select its partner at random regardless of the configuration, implying at least the possibility of several distinct, geometrically distinguishable states with comparable energy.[7] If there are not too many of these excitations they will not, furthermore, interfere with each other.

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[2] O. K. Rice, Phys. Rev. **97**, 1176 (1955).

[3] See L. Pauling, Phys. Rev. **36**, 430 (1930).

[4] S. Goldstein, Trans. Cambridge Phil. Soc. **23**, 303 (1927).

[5] This estimate is obtained from the average distance, 3.15 A, in He^4 [J. Reekie and T. S. Hutchison, Phys. Rev. **92**, 827 (1953)] and the cube root of the ratio of the density of He^4 [W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942), p. 207] to that of He^3 [E. C. Kerr, Phys. Rev. **96**, 551 (1954)].

[6] It should be stated that the term "degeneracy" should not be given too literal an interpretation. As Temperley quite explicitly mentions, it is not to be supposed that all the energy levels in a group coincide exactly. It is merely supposed that they constitute a fairly closely-spaced group, which can be considered as a group in which the degeneracy has been lifted by the perturbations only to a relatively small extent. The singlet states do appear too high to be included with the second triplet.

[7] This difference in the degeneracies of the various energy levels is discussed in an Addendum.

It seems probable from the case of He^4 (see Reekie and Hutchison[5]), that each atom has on the average four nearest neighbors with which it could pair. Such a pair, however, would involve two atoms. Therefore, the effect of random pairing would be to introduce a degeneracy of 4/2 per atom into the corresponding term of the partition function, or a degeneracy of 4 per pair. Taking into account the fact that we are dealing with a triplet state, the total possible degeneracy becomes 12, whereas the observed degeneracy is about 8. It appears, thus, that the random-pairing degeneracy is not fully developed, but the order of magnitude observed appears to be about right. With this amendment, the hindered pair-rotator model seems not to do badly in the case of He^3. It is not to be denied that, in spite of this apparent success, it is a highly idealized model, and must be accepted with some reserve. Indeed, we have already mentioned certain effects which may result from interactions between the pair-rotators, or from cooperative effects involving all the atoms.[1] However, the usefulness of the hindered plane pair-rotator in the case of He^3 tempts us to accept it tentatively as an aid in the comparison of He^3 with He^4.

Since He^4 obeys the Bose-Einstein statistics and has no spin, we need to consider only symmetrical, singlet states, represented by the solid curves in Fig. 1. Since the interatomic distance is so much less in He^4 we may expect the potential barrier against free rotation of a pair to be much greater than in He^3. Just how much greater is of course difficult to say. If we suppose q to be 0.5 for He^4, then we see from Fig. 1 that the energy gap between the ground state and the next singlet state is something like 17 cal per pair-mole, since the value of $h^2/8\pi^2\mu r_0^2$ for He^4 is 2.45, taking[5] r_0 as 3.15; if q should be 1.0, then the energy gap would be about 25 cal per pair-mole. These energies are just of the order of magnitude of the excitation for rotons. (Only the order of magnitude and the fact that this level is higher than the second group of excitations for He^3 can be of importance—in view of the complications to be considered the rather close agreement with the roton excitation energy must be a coincidence.) An important difference between He^3 and He^4 lies in the degeneracy of the excited state. The degeneracy in He^4 is much greater, despite the fact that a singlet rather than a triplet state is involved. We have estimated[8] from specific heat data that the degeneracy is about 9; this however, is based on atoms, not pairs of atoms, and the pair model would require that the degeneracy of pairs be 18.

In estimating the degeneracy, we assumed that rotons were groups of atoms which formed an ideal solution with the single atoms of superfluid. This, of course, is an approximation at best, but it means essentially that the groups of atoms can be definitely located with relation to the single atoms of the superfluid. This localization might be to some extent blurred by the zero-point motion. This would mean that the entropy of mixing was overestimated; if it had to be lowered, it would have to be compensated by increasing the estimate of the degeneracy. However, it seems probable that *groups* of atoms can be better localized among the other atoms than these atoms can be localized with respect to each other.

The high degeneracy probably arises from the fact that a number of atoms (perhaps six or eight) seem to be involved in the roton excitations. With the large amount of energy required it appears likely that a pair would have reached, so to speak, its "dissociation energy," it being held in its cell essentially only by the repulsion of the surrounding atoms. In other words, the individuality of the pairs would break down, and we could expect some cooperative effects in which a number of atoms are involved; coordinated rotations of several neighboring pairs could conceivably effect a lowering of the hindering potential, and such coordinated rotations could occur in a variety of ways. Of course considerable lowering of the effective hindering potential would be required in order for the total excitation of a whole group of six or eight atoms to be no higher, or only a little higher, than that expected for a pair. It is also possible that rotations of the group of atoms as a whole might contribute to the degeneracy. This possibility was mentioned by Feynman,[9] who, however, carefully refrained from any categorical statement that the roton excitations were necessarily of this nature.

We think that there may be some experimental evidence that the roton excitations are more likely to involve mutual rotations of individual pairs than rotation of the whole group. If rotation of the whole group is involved it is not clear that the spacing of the atoms within the group should be much affected; so it is not too easy to see why the rotons are denser than the residual fluid, i.e., the superfluid, as they presumably are, in view of the negative coefficient of expansion of helium II. If, however, the individual excited atoms move more freely through longer distances (i.e., have greater "mean free paths," as would be expected from individual or pairwise excitation) than the atoms of superfluid, then, as we have remarked before,[8] the excited energy levels should depend less strongly on interatomic distances than is the case in the ground state. This permits the roton atoms to lower their potential energy by decreasing their average interatomic distance. This may, in fact, be one of the ways that cooperative effects in the excitation can lower the total energy, and so make such excitations more probable, though this effect is undoubtedly small.

The nature of the roton excitations and the smaller volume of rotons as compared to superfluid are, of course, intimately connected with the behavior of He^4

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

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

at elevated pressures. It is found that the specific heat at constant volume increases with increasing pressure.[10] This means greater ease of excitation, hence relative lowering of the energy of excitation. What we really should conclude is that the rotons are less affected by pressure than the superfluid. In the superfluid the zero-point energy is raised by pressure more than the energy of the rotons is raised, since the energy levels of rotons depend less strongly on the density, as noted in the preceding paragraph. Of course, the potential barrier to rotation should increase with increasing density, and if the hindered rotator model (and this may apply not only to a pair-rotator model but to any model involving rotation of groups of atoms as a whole) had not broken down in the case of He^4, we should expect enhanced pressure to have the opposite effect (i.e., more effect on the roton energy than on the zero-point energy). But if what happens involves "dissociation by rotation" of the pair-rotator, then the observed effect is easily understood if the zero-point energy of the superfluid is raised more than the dissociation energy. In the light of these remarks, a study of the effect of pressure on the thermodynamic properties of He^3 would be extremely interesting.

If a roton is a group of atoms having excitations internal to the group and having a number of energy levels (the excitation energy is, of course, an average only, and we may expect in actuality a range of energies, as with He^3), it should behave rather similarly to a classical liquid. Liquid He^3 is certainly sufficiently highly excited around 1°K to behave like a classical liquid. There is, therefore, some basis for the belief that rotons and He^3 would mix and to a reasonable approximation form an ideal solution, even at this low a temperature. The deviation of He^3-He^4 mixtures from ideality, according to Taconis' hypothesis,[11] arises in large part from insolubility of He^3 in superfluid He^4, which may be caused by effects on the zero-point energy.[12] We have recently shown[13] that Taconis' hypothesis, together with the assumed ideality of a mixture of He^3 and excited He^4 and the perhaps somewhat questionable assumption that the average number of atoms involved in a roton is not affected by the presence of He^3, gives a reasonably good account of the experiment of Sommers, Keller, and Dash[14] on the heat and entropy of mixing at 1°K.

The picture of liquid He^3 and He^4, which emerges from the present considerations, requires some modifications in the suggestion which we have previously made[12] concerning the apparent lack of a λ transition in He^3. We had proposed earlier[15] that the λ transition in He^4 is connected with the appearance of clusters of superfluid. In the later work we considered a possible mechanism for the formation of such clusters, and pointed out that the formation of clusters of appreciable numbers of atoms of superfluid might be expected to result, in He^4, in a lowering of the zero-point energy. We explained the lack of such clusters in He^3 on the grounds that an He^3 atom would always have some neighbors in a spin state such that their relative angular momentum could not be zero, at least if there was any exchange at all. However, the pair-rotator model represents a situation in which the lowest energy of a pair is attained, there being no exchange involving separate pairs. If this picture is correct, it is quite possible that clusters of "superfluid" He^3 (i.e., liquid He^3 without excitations) might appear as the temperature was lowered; in this case, also, there might be an energetic advantage in clusters of appreciable magnitude. This might then result in a λ transition in He^3 at sufficiently low temperatures. On the other hand, since the formation of large clusters of He^3 with all pairs of atoms in their lowest states of restricted rotation would require some special arrangement of atoms in order to keep the atoms of a pair which had a mutually symmetrical spin wave function relatively far away from each other,[1] this might *not* be energetically favorable. The situation in this case does not seem to be nearly as clear cut as with He^4. Temperley[1] has suggested that the alignment of spins may involve a Curie-type transition, but without suggesting clusters and without using the word "superfluid."

In conclusion, we think it may be said that despite the fact that it represents a highly idealized picture, the hindered plane pair-rotator model seems to be surprisingly successful in facilitating the discussion of the properties of He^3, with due regard for its limitations, and it appears also to give a semiquantitative understanding of the differences between He^3 and He^4. The differences, of course, arise principally from the much higher excitations required in He^4, a property which is to be traced to the fact that He^4 lacks antisymmetrical states. The differences are, however, enhanced by the resistance to relative motion of the atoms caused by the smaller interatomic distance in He^4. It is very interesting that it appears to be possible to treat the lowest excited energy level of He^3 very well by means of the pair-rotator model with hindered rotation, but that this model appears to begin to break down for the next series of excited states. In He^4, on account of the considerable hindrance to rotation, the lowest excited states have a higher energy even than the second set of excited states in He^3, and for them the pair-rotator model breaks down even more completely. The nature of these excited states can, however, be tentatively inferred, and in making this inference the model is of considerable assistance.

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[10] See W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942), p. 219.

[11] Taconis, Beenakker, Nier, and Aldrich, Phys. Rev. **75**, 1966 (1949).

[12] O. K. Rice, Phys. Rev. **93**, 1161 (1954), Sec. 4.

[13] O. K. Rice, Phys. Rev. **96**, 1464 (1954).

[14] Sommers, Keller, and Dash, Phys. Rev. **92**, 1345 (1953).

[15] O. K. Rice, Phys. Rev. **76**, 1701 (1949).

ADDENDUM: DISCUSSION OF THE DEGENERACY OF THE ENERGY LEVELS IN He^3

Referring to Fig. 1, it is seen that in the case of $V_0=0$, i.e., pure rotation, the lowest energy level is single and symmetrical in the rotational coordinates, while all the other levels are double. As V_0 increases, and we approach the condition of pure oscillation, each level is double, there being one symmetrical singlet state and one antisymmetrical triplet state. One of these states connects with the rotational level just above that with which the other connects. The multiplicity of the energy levels is most readily understood by considering the case of V_0 large. Let us consider all the energy levels which can arise from the lowest pair of symmetrical and antisymmetrical states, that is, from the lowest vibrational state with V_0 large. If V_0 is large we can consider that each particular position A in space has a wave function ψ_A (excluding spin). Taking a particular pair of atoms, if atom 1 is at position A and atom 2 at position B the wave function is $\psi_A(1)\psi_B(2)$, while if they have changed position the wave function is $\psi_B(1)\psi_A(2)$. Of course, the wave function must be properly symmetrized; the two energy levels, lowest solid and lowest broken line in Fig. 1 correspond to $\psi_A(1)\psi_B(2)+\psi_B(1)\psi_A(2)$ and $\psi_A(1)\psi_B(2)-\psi_B(1)\psi_A(2)$, respectively, provided ψ_A and ψ_B are the lowest wave functions for their particular positions, and therefore identical except that one is centered at A and the other at B.

Now consider the whole assembly of N atoms, each having the wave function corresponding to the lowest energy state. Each of these N wave functions, ψ_A, ψ_B, ψ_C, $\cdots$, has a particular spin function, either α, corresponding to spin in one direction, or β, corresponding to spin in the other direction, associated with it. Since there are two spin possibilities for each atom, there are altogether 2^N possibilities. Since these wave functions contain both spatial coordinates and spin, each must be made antisymmetrical to exchange of atoms. There will be 2^N independent wave functions built up from the set of lowest wave functions, ψ_A, ψ_B, ψ_C, $\cdots$, and the spin functions. These, of course, do not all have to have the same energy.

We turn now to the case of $N/2$ pair-rotators, rotating in a plane. Each one of these pairs can have a singlet and a triplet state built up out of the proper combination of, e.g., ψ_A and ψ_B, and the spin functions. Thus each pair has four states; altogether the $N/2$ pairs will have $4^{N/2}=2^N$ states. Thus the hindered-plane-rotator model, when its two lowest energy levels are considered, gives exactly the correct number of states built up from the lowest eigenfunctions of individual atoms; and presumably it is the only rotator model which will do this. Further, it can give some idea of what the energies involved are.

A higher oscillational level of the hindered rotator with large V_0 corresponds to higher individual energy levels, with wave function ϕ, let us say. If an atom has wave function ϕ it must, if the pair rotator model is reasonably correct, have one nearest neighbor with a similar function. If there are two atoms among the N atoms which have a wave function ϕ, and if each atom in the system has on the average four nearest neighbors, then there are $2N$ distinct ways in which two of the N functions, ψ_A, ψ_B, ψ_C, $\cdots$, can be replaced by ϕ's. Once this replacement is made, then the possible number of states, including spin, can be found just as before. However, it is seen that it is not sufficient to say that any one of $N/2$ pairs can have its wave functions replaced by ϕ's. This gives only one-fourth the total number of possibilities. We thus see how it comes about that the hindered-plane-rotator model can give a reasonable account of the energies of the three lowest sets of energy levels in He^3, and how it can give the correct multiplicity for the lowest and next lowest set of levels, yet may be expected to break down in giving the multiplicity for the third set of levels. Of course, strictly speaking, this means that the partition function no longer has the form given by Eq. (1), but if not too many ψ's are replaced by ϕ's this should not cause serious error.