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Elementary Theory of Liquid Helium: Refinement of the Theory and Comparison with Feynman's Theory*

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It has been suggested that the excitations of liquid He^3 can be represented approximately as excitations of pairs of helium atoms acting as hindered plane rotators. For the low excitations N helium atoms may be considered as $N/2$ pairs; for the higher excitations the possibility of random pairing must be taken into account, a situation which is discussed in some detail. Because of fluctuations in the hindering potential, and because of interactions between localized excitations, the energy levels of the plane rotators are broadened into energy bands, which can give a good account of the specific-heat curve. The multiplicity of these levels is related on the one hand to the statistics and spin of He^3 atoms, and on the other to the vibrational modes of a quasi-lattice approximating the liquid, and is also concerned with the development of communal entropy in a quantum liquid. In He^4 the low-lying energy levels are excluded because of the spin and the statistics. Vibrations of single atoms, pair rotators, and double pairs, rotating or oscillating like meshed gears, have excitation energies close to that of a roton (the energies of the latter two types are estimated by comparison with He^3, allowing for the effect of the increased density on the hindering potential). These types of excitation are not all independent, however, and there is moderate difficulty in accounting for the multiplicity of the excitations as deduced empirically from the number of rotons appearing at different temperatures, which is obtained reasonably accurately from the specific heats. The picture presented here is compared with Feynman's theory; it concluded that there is good correspondence—even the difficulty concerning the multiplicity of the excitations being present in both cases. The relation of a broadened band of energy levels to the idea of a gas of excitations is considered, and it is concluded that such a gas should obey Fermi-Dirac statistics.

RECENTLY, we have developed the idea that the excitations (roton type) in liquid He^3 and He^4 can be treated as pairs of atoms acting as hindered plane rotators,[1,2] both the hindering potential and the circumstance that the rotator is effectively confined to a plane arising from the interaction of neighboring atoms. In this paper this idea will be reviewed and developed as to certain of its details, and an attempt will be made to correlate it with the theory of Feynman[3] and Feynman and Cohen.[4]

1. EXCITATIONS OF He^3

When exchange effects are important it is convenient, if possible, to consider the atoms in pairs, and it was suggested by Price, by Temperley, and by us[5] that N atoms of liquid He^3 be treated as $N/2$ pairs. Temperley's analysis of the specific heat, entropy, and paramagnetic susceptibility of He^3 indicated that these properties could be explained reasonably well if the pairs had a nondegenerate ground state, three excited states in the neighborhood of 0.4° above the ground state, and about eight excited states somewhere near 2.7° above the ground state.[6] Neglecting a Debye term (which Temperley may have overestimated[7] but which in any case is not important below 1°K), this leads to the following partition function for the N atoms forming $N/2$ pairs:

$$Z=(1+3e^{-0.4/T}+8e^{-2.7/T})^{N/2}. \tag{1.1}$$

Temperley pointed out that it can be merely an approximation to suppose that all the pairs have the same energy levels. In any case one cannot push the idea of separate energy levels too far, since there will always be transfers of energy from place to place in the liquid (compare de Boer[5]). These influences will result in broad bands of energy levels for the whole liquid, and the energy of a pair can be considered only as a rough mean. Temperley's set of energy levels give a sharp maximum in the specific heat curve around 0.15°K, which appears not to occur experimentally. Broadening of the energy band, especially if it means that the excitation energies range clear down to zero, should eliminate this maximum and make possible a better fit to the specific heat curve.

The effect of the broadening of the energy levels can be approximated by rewriting Temperley's partition function in the form

$$Z=\left(1+\int_0^\infty p_\epsilon e^{-\epsilon/kT}d\epsilon+\int_0^\infty p_\epsilon' e^{-\epsilon/kT}d\epsilon\right)^{N/2}, \tag{1.2}$$

ϵ/k being the energy in degrees. Here p_ϵ and p_ϵ' are the respective densities per unit energy range for the lowest excited levels and the next lowest excited levels. We

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[1] O. K. Rice, Phys. Rev. **98**, 847 (1955).

[2] O. K. Rice, Phys. Rev. **102**, 1416 (1956).

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

[4] R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).

[5] 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), Proc. Phys. Soc. (London) **A68**, 1136 (1955). See also J. de Boer and E. G. D. Cohen, Physica **21**, 79 (1955); J. de Boer, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), Vol. 2, Chap. 1.

[6] It is convenient to express the energy in degrees, the actual energies then being k times the values given per rotator or R times per pair-mole.

[7] O. K. Rice, *Conférence de Physique des Basses Températures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), p. 117 (Supplément au Bulletin de l'Institute International du Froid, 177, Boulevard Malesherbe, Paris 17^e).

TABLE I. Specific heats in calories per degree per mole.

T(°K)	1/10	1/5	1/3	1/2	1
C, calc., Eq. (1.6)	0.50	0.71	0.69	0.78	0.81
C, calc., Eq. (1.8)		0.67	0.68	0.80	0.85
C, expt.			0.71	0.78	1.03

have, of course,

$$\int_0^\infty p_\epsilon d\epsilon = 3, \tag{1.3}$$

with a similar expression for p_ϵ'. The validity of this procedure will be discussed in Sec. 4.

In order to calculate this partition function, we have represented p_ϵ and p_ϵ' by error functions:

$$\begin{aligned} p_\epsilon &= b\exp[-(\epsilon-\epsilon_0)^2/a^2k^2], && \epsilon\geq 0 \\ p_\epsilon &= 0, && \epsilon<0 \end{aligned} \tag{1.4}$$

and

$$\begin{aligned} p_\epsilon' &= b'\exp[-(\epsilon-\epsilon_0')^2/a'^2k^2], && \epsilon\geq 0 \\ p_\epsilon' &= 0, && \epsilon<0. \end{aligned} \tag{1.5}$$

The values ϵ_0/k and ϵ_0'/k, at which the energy-level densities are greatest, correspond roughly to the energies, 0.4° and 2.7°, of Temperley's levels, and the b's are found from the normalization condition. However, we have found it better to set

$$\int_0^\infty p_\epsilon' d\epsilon = 11. \tag{1.6}$$

Also we have chosen slightly different values of ϵ_0 and ϵ_0'. The parameters used are as follows:

$$\begin{aligned} \epsilon_0/k &= 0.48°, & \epsilon_0'/k &= 2.8°, \\ a &= 0.40°, & a' &= 1.333°. \end{aligned} \tag{1.7}$$

Values of the specific heat, C, given by these parameters are given in Table I (first row of calculated values) and compared to experimental values. The experimental values of the specific heat are taken from an empirical formula of Roberts and Sydoriak[8] (somewhat extrapolated at $T=\frac{1}{3}°$). It is seen that the agreement is very good except at 1°, and here higher energy levels are undoubtedly becoming of importance. Indeed one might expect them to have an effect at $T=\frac{1}{2}°$; at this temperature, however, enough of the pairs are excited into the energy levels centering around 2.8° so that they probably interfere with each other, and our partition function may give an overestimate for the specific heat; thus the good agreement may be in part due to compensating factors. (We shall see in Sec. 4 that excitations in the levels around 0.48° will not be expected to interfere with each other.)

There is some overlapping of the different energy bands. The value of a' is such that about 14% of the integral, Eq. (1.6), is contributed beyond $|\epsilon-\epsilon_0|=\epsilon_0/2$. About 2.7% of it, or about 0.3 energy levels, is contributed from the region between $\epsilon=0$ and $\epsilon/k=1.0°$. In order to see the effect of this overlapping of the energy levels, we have also made a calculation in which we have replaced Eq. (1.6) by

$$\int_k^\infty p_\epsilon' d\epsilon = 11. \tag{1.8}$$

These calculated values are also given in Table I, and it is seen that the effect is relatively small.

The molal entropies at $T=0.5°$, given by use of Eqs. (1.6) and (1.8), respectively, are 1.49 and 1.44 entropy units, either of which is probably within a few hundredths of an entropy unit of the true value.[8] Thus the thermodynamic properties of He^3 below 1°K are well reproduced by Temperley's model with the broadened energy bands and slightly altered parameters.

The modified values of the parameters suggest that, for an approximate partition function, it would be better to replace Eq. (1.1) by

$$Z=(1+3e^{-0.48/T}+11e^{-2.8/T})^{N/2}. \tag{1.9}$$

In order to understand the approximate energy levels and multiplicities appearing in Eq. (1.9) on the basis of the hindered-plane-rotator model, we need to consider the spin multiplicity of pairs of He^3 atoms, the fact that He^3 obeys the Fermi statistics, and the nature of the energy levels of a plane rotator. These energy levels are shown as a function of the hindering potential in Fig. 1. The states which connect with the even rotational states at vanishing hindering potential are orbitally symmetric and hence spin singlets (solid lines in Fig. 1), and those connecting with the odd rotational states are orbitally antisymmetric and hence

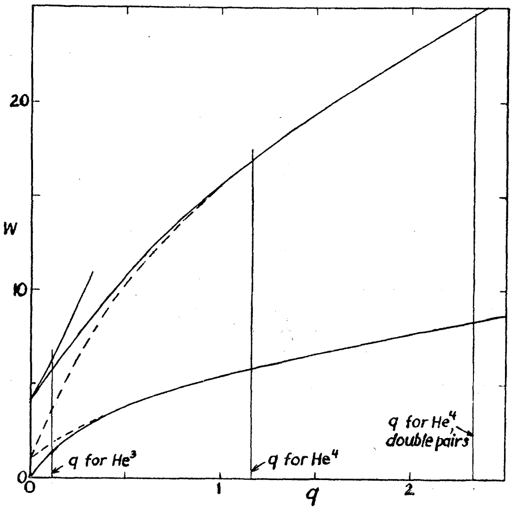

FIG. 1. Energy levels W of plane rotator in units $W_0=h^2/8\pi^2I$ (where I is moment of inertia of rotator) as functions of the hindering potential q in units $32W_0$.

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[8] T. R. Roberts and S. G. Sydoriak, Phys. Rev. 98, 1672 (1955).

spin triplets. If a hindering potential of 9.2 cal per pair-mole is chosen,[9] the excited states have energies equivalent, respectively, to 0.48° and 2.75°, in good agreement with Eq. (1.7), and are spin triplets. The triplet character would seem to be in accord with the multiplicity of the first excited state (without any spatial degeneracy, such as would occur if the pair were a space rather than a plane rotator) but the higher multiplicity of the second one needs further explanation, and a first attempt at this explanation has already been given.[1]

The difficulty is connected with the arbitrary procedure of dividing the N atoms into $N/2$ pairs. It has been pointed out that with this procedure the two lowest states of the plane rotator completely account for the spin degeneracy of the system. There is a fundamental difference between the first excited state and all the higher ones in that the former connects with one of the lowest vibrational states at the limit of high hindering potential, and hence in this limit has no excitation energy. With a hindering potential of 9.2 per pair-mole, the energy of the ground state (zero-point energy of the rotator) is about 1.8°, and the excitation to the next state, as noted, 0.48°; under these circumstances the motion of the pair is, indeed, rotational oscillation with occasional exchange of position, rather than nearly free rotation. When liquid He^3 as a whole is unexcited, half of the atoms have spin in one direction, half in the other. Each atom probably has on the average about four nearest neighbors, and its nearest neighbors will generally have opposite spin. This can presumably remain true, even if pairs of atoms are exchanging, since the spins of coupled atoms can turn over in pairs. It may be risky to attempt to elaborate such a roughly approximate description in too much detail, since we may well say more than the uncertainty principle allows; however, it is in the spirit of our approximation to say that if the small necessary excitation energy is available, the spin of one atom may be turned over, to give us an atom surrounded by four others of like spin. If it exchanges with one of them, the orbital state will be antisymmetric; this, of course, is why the excitation is necessary. Which of its four neighbors it will exchange with (and, thus, how much excitation energy will be required in any given case), may depend to some extent upon how easy the exchange will be; the hindering potential of 9.2 cal per pair-mole is only an average value, and will vary from one pair to another, so one might expect some preference for exchange with the neighbor for which the hindering potential happens to be smallest (incidentally, it is to be noticed that this requires the *highest* excitation energy). However, the average zero-point energy, around 2° for the hindered rotation, is only about half of the average zero-point energy per mole degree of freedom.[10] So the question as to which partner a given atom will take may well be determined by the accidental fluctuations associated with the zero-point energy. Since the atom has no choice as to the neighbor with which it is to pair, it is correct to consider a division of N atoms into $N/2$ arbitrary pairs.

In the case of the excitations near 2.8° the situation is quite different. In this case there is orbital excitation requiring cooperation of two adjacent atoms, and the way of pairing off is decided by that pair of atoms which has the orbital excitation, a choice being possible under these circumstances. If each atom has about four nearest neighbors there are approximately $4\times N/2$ possible pairs. Since the state is a triplet, this means an effective multiplicity of 6 per atom, or 12 per pair if we consider that there are $N/2$ pairs, assuming that all these excitations are independent of each other. The observed multiplicity, according to our estimate, is 11. Since an atom has a choice as to which neighbor it will pair with, the number of choices will be drastically reduced once a large fraction of the pairs is excited. This will not happen in the case of the lower excitation where there is an arbitrary or fixed division into $N/2$ pairs; in this case the separate excitations will be essentially independent of each other; this is important since a large fraction of them is already excited at 0.5°K. This situation is further discussed in Sec. 4.

The question arises as to whether there can be as many as $4\times N/2$ independent pairs, even when the density of excitations is low. This is a question which involves some rather fundamental considerations, and also has some applications to the case of He^4. If we were to suppose that the N helium atoms were fixed in a rigid lattice, there would be $3N$ normal modes of vibration. The normal modes could be thought of as derived through perturbations from the three vibrations of each of the N individual atoms moving in the surrounding potential-energy fields. The pair-rotators resemble somewhat partially developed normal modes of vibration, involving more than a single atom but not all the atoms. This description amounts to a way of setting up the individual degrees of freedom; singly excited rotational oscillators[11] can be thought of as derived by linear combination from excitations of individual atoms. The $3N$ first excitations of atomic oscillations thus cannot be independent of each other. Under ordinary circumstances one might question whether as many as two-thirds of the degrees of freedom could be assumed to be well described as rotational

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[9] This is based on a value of 3.57 A for the interatomic distance in He^3 (instead of 3.45 A as in reference 1); this new value is in turn based on the more recent value for He^4 of C. F. A. Beaumont and J. Reekie, Proc. Roy. Soc. London **A228**, 363 (1955).

[10] See F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1954), Vol. 2, Chap. B.

[11] When we refer to singly excited rotational oscillators, or to the first excited state, we are thinking of the states which connect to the first excited state at the pure vibration end of Fig. 1. The primarily spin-type of excitation (lowest broken curve of Fig. 1) can actually be thought of as part of the zero-point energy with respect to the excitations we are considering here and in the remainder of Sec. 1.

oscillations, especially since the singly-excited excitations of the phonon spectrum would also have to be derived from linear combinations of the $3N$ first excitations of the atoms.[12] Helium, however, has a density only about half as great as that of a close-packed structure. This will result in many extra excitations, though probably not of the rotational-oscillatory type. If a single helium atom among N atoms were excited, not only could any one of the N atoms be the one excited, in any one of three ways, but an atom would also have the choice of being either on a "lattice space" or a "vacancy." In fact there would be N vacancies for a given atom, but since the atoms are indistinguishable it would not matter which atom it was. So there would result a total of 6 possible excitations per atom. Actually the number of possible excitations might well exceed 6, since there might be more than N possible choices of "vacancies." Use of a vacancy would bring an atom close to more than four neighbors on the average, and would probably not lend itself well to cooperation of a pair to produce rotational oscillation, but an atom in this situation could contribute to the phonon excitations. In a liquid as dilute as He^3, it is perhaps not strange that there are something like 11/12 of 2 excitations per atom which have the low excitation energy characteristic of the hindered plane rotator.

It will be observed that the presence of vacancies is able to increase the number of excited states, but, of course, there is but one ground state, and the zero-point energy associated with it is probably an average of what might be expected for the zero-point energy of the various kinds of excitation, supposing them not to affect each other. Since the excitations which can be described as arising from rotational oscillations constitute a relatively small fraction of the total number, it is not surprising that the zero-point energy per degree of freedom is considerably greater than that expected for this particular type of excitation.

This discussion has an interesting relation to the concept of communal entropy. If all the degrees of freedom were in their first excited level, there would be more than 6 possible excitations per atom. For the number of distinguishable arrangements assuming N atoms and N vacancies, would be $(2N)!/(N!)^2$. This amounts to roughly four arrangements per atom, or 12 excitation states per atom, not counting spin states. This increase in the number of possible states is the beginning of the excitation of communal entropy. Communal entropy, like all other types of entropy, is completely frozen out[13] at 0°K; there is but one state which possesses the zero-point energy. Communal entropy can arise only when there is mixing of excited atoms. As long as there are only a few excitations, the fluctuations in position of the atoms, other than the excited ones, do not lead to any new states. Entropy of mixing between excited atoms and unexcited appears when there are only a few excited atoms, but communal entropy (which might be described as entropy of mixing with free space) can appear only when there are many excited atoms.

Although the presence of many excited atoms can give rise to extra distinguishable states, we shall, as noted above, find that the number of excitations which can be described in terms of the plane-rotator picture will not be raised correspondingly, since an atom cannot be a member of more than one pair at a time.

2. EXCITATIONS IN He^4

In the case of He^4 we have remarked[14] that around 1°K, where the roton density is low, the thermodynamic properties are consistent with the following equation for the number n of rotons per N atoms:

$$n=Nme^{-\epsilon/kT}. \tag{2.1}$$

Here ϵ is the energy of the excitations and m the multiplicity. Equation (2.1) is equivalent to the use of the partition function.

$$Z=(1+me^{-\epsilon/kT})^N, \tag{2.2}$$

which, since it is to be applied where the roton density is low, can be replaced by

$$Z=(1+2me^{-\epsilon/kT})^{N/2}, \tag{2.3}$$

which puts it on a basis comparable to our pair-rotator treatment of He^3. In either case the nth power term, with factor $e^{-n\epsilon/kT}$, represents an n-fold excitation, and the corresponding terms in Eqs. (2.2) and (2.3) are approximately equal as long as $N\gg n$. For the greatest term, n is given by Eq. (2.1).

A rough estimate[14] of ϵ/k and m gave 10.1° and 9.3, respectively. A more accurate estimate can be made from specific heat data. To do this we must take account of the phonon excitations. Let $m_p d\epsilon$ be the number of phonon excitations per atom with energy between ϵ and $\epsilon+d\epsilon$. Then the complete partition function, including phonons and rotons, will be

$$Z=\left(1+\int_0^\infty m_p d\epsilon+me^{-\epsilon/kT}\right)^N. \tag{2.4}$$

The first term in the binomial expansion of 1 and $\int_0^\infty m_p d\epsilon+m\exp(-\epsilon/kT)$ gives the contribution of single excitations, the second term the contribution from cases where two energy levels are excited simultaneously (either two phonon levels, two roton levels, or both), etc. (compare Sec. 4). We may now write for the total entropy

$$\begin{aligned} S&=E/T+k\ln Z\\ &=kT\partial \ln Z/\partial T+k\ln Z. \end{aligned} \tag{2.5}$$

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[12] More highly excited phonon excitations are derived from multiple excitations in which more than one degree of freedom are excited; this will be discussed in more detail in the case of He^4.

[13] O. K. Rice, J. Chem. Phys. **6**, 476 (1938).

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

Here E is the total energy. Since both $\int_0^\infty m_p d\epsilon$ and $m\exp(-\epsilon/kT)$ will be small compared to 1 at low temperatures, we may expand the logarithms, obtaining

$$S = NkT\left[\partial\int_0^\infty m_p d\epsilon/\partial T + \partial(me^{-\epsilon/kT})/\partial T)\right] + Nk\left[\int_0^\infty m_p d\epsilon + me^{-\epsilon/kT}\right], \quad (2.6)$$

which means that in this approximation photon and roton energies and entropies are additive, and to obtain the roton entropy from the experimental results we can subtract the phonon entropy extrapolated as a Debye term from very low temperatures as though the rotons did not exist. $NkT\partial(me^{-\epsilon/kT})/\partial T$ is to be taken as the roton energy divided by T. If there is a range of roton energies, as is expected for the same reasons that the energy levels in He^3 were broadened, ϵ and m are average values, but

$$NkT\partial(me^{-\epsilon/kT})/\partial T = n\epsilon/T, \quad (2.7)$$

since $n\epsilon$ is the total roton energy, and, hence,

$$kT\partial \ln m/\partial T = \partial\epsilon/\partial T. \quad (2.8)$$

From Eqs. (2.6), (2.7), and (2.1) the roton part of the entropy is given by

$$S_r = nk(\epsilon/kT + 1). \quad (2.9)$$

It is better to use the roton specific heat C_r to calculate n, since the specific heat C is measured directly and the phonon part is a smaller fraction of the whole than is the case with the entropy. By differentiation of Eq. (2.9), and using

$$d\ln n/dT = \epsilon/kT^2, \quad (2.10)$$

which is obtained from Eqs. (2.1) and (2.7), we find

$$C_r = n(\epsilon^2/kT^2 + d\epsilon/dT). \quad (2.11)$$

This can also be interpreted as the result of the differentiation of the total roton energy $n\epsilon$ with respect to T.

We have obtained n and m from the data of Kramers, Wasscher, and Gorter.[15] The results are shown in Table II. We have given the values of ϵ/k and $d(\epsilon/k)/dT$ used to obtain n/N from Eq. (2.11) and m from Eq. (2.1); the final column gives values of ϵ/k calculated for the intervals from the values of n/N, using Eq. (2.10), in order to check the consistency of the calculation. The calculations are also reasonably consistent with Eq. (2.8). Some authors[16] have found values of the specific heat uniformly greater than those given by Kramers, Wasscher, and Gorter. A uniform change would not affect ϵ/k but would change m correspondingly. (See note at end.)

TABLE II. Number of rotons n per N atoms, multiplicity m, and excitation energy ϵ.[a]

T	C	C_r	ϵ/k	$d(\epsilon/k)/dT$	$100n/N$	m	ϵ/k, Eq. (2.10)
0.8	0.0222	0.0102	9.75	0.5	0.00328	6.4	
							9.85
1.1	0.191	0.160	9.90	0.5	0.0942	7.6	
							9.96
1.4	0.780	0.715	10.07	0.7	0.656	8.7	
							10.33
1.7	2.11	1.995	10.5	1.7	2.41	11.6	

[a] T and ϵ/k in °K; C and C_r in joules g^{-1} deg^{-1}.

We now wish to see how the experimental values of ϵ/k and m fit in with our ideas of what the excitations should be. In the first place we may note that He^4 has a zero-point energy which is estimated[10] to be in the neighborhood of 30 or 35 calories per mole or 10 to 12 per mole-degree-of-freedom. The first excitation should, then, be roughly 20 to 24 calories per mole-degree-of-freedom, or somewhat less than this if we allow for some anharmonicity. This corresponds to $\epsilon/k \sim 10°$, on the average, in excellent agreement with the experimental result.

Although oscillational rotations of pairs of atoms will not be independent of these vibrations, it will be desirable to estimate the energy expected to be associated with such excitations, in view of their low value in He^3. In the case of He^4 only symmetrical orbital states are possible, and we shall be interested in the first excited solid curve of Fig. 1. If one assumes the hindering potential to be the same as for He^3, and allows for the different mass, the ϵ/k for a hindered plane rotator would only be about 5°. However, the effect of the greater density of He^4 will be to raise this figure considerably. It is difficult to make an exact estimate of this effect, without knowing how much of the hindering potential in He^3 is due to penetration of the rotating pair into the repulsive part of the potential arising from the neighboring atoms and how much may arise from increased kinetic energy (zero-point energy) in the radial direction (i.e., perpendicular to the rotational motion) as the atoms go past each other. The hindering barrier is small enough in He^3 so that we can suppose that there is not too much penetration. The potential energy begins to go up when two atoms are about 2.9 A apart[17]; supposing that in He^3 the atoms of the rotating pair penetrate to within 2.8 A of their neighbors when the exchange occurs, we would suppose (multiplying this figure by the ratio of the cube root of the molecular density of He^3 to that of He^4) that the corresponding distance in He^4 would be 2.54 A. The potential energy at 2.54 A is about 39 calories per gram atom, or about 78 calories per pair mole, greater than it is at 2.8 A, so we might estimate the hindering potential to be around 85 calories per

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

[16] G. R. Hercus and J. Wilks, Phil. Mag. 46, 1163 (1954); Pearce, Markham, and Dillinger, National Science Foundation Conference on Low Temperature Physics and Chemistry, Baton Rouge, Louisiana (unpublished).

[17] J. L. Yntema and W. G. Schneider, J. Chem. Phys. 18, 646 (1950), Eq. (19).

pair mole.[18] This results in an excitation of about 12.8°, which is fairly close to the experimental results.

One should probably also consider modes of excitation involving more than two atoms. We have previously discussed[2] the possibility of the rotation (or, rather the rotational oscillation, with rather infrequent exchange) of interlocking pairs, meshing like a pair of gears. With the same hindering potential, but now with twice the reduced mass, the value of q of Fig. 1 would be doubled; the excitation energy, again recalling the doubled reduced mass, turns out now to be reduced to about 9.4°. However, this much cooperation of several atoms would require an enchanced zero-point energy, which should presumably be added to the excitation; the exact amount is difficult to estimate, but there would seem to be no doubt that the result is as close as one might expect to the experimental result. This zero-point energy would go up rapidly as the number of atoms increased, and is presumably some indication of the difficulty of this type of cooperation; probably we do not need to consider more than two pairs of atoms in the case of He^4 or more than one in He^3. Possible rotations of more than two atoms have also been considered by de Boer,[5] but without allowing for the hindering potential.

We have pointed out that there are many ways in which two adjacent pairs of atoms can be selected,[2] but it now appears from the discussion in Sec. 1 that they are not independent of the single-atom vibrations, and so will not serve to explain the relatively large value of m. It is of interest, however, that we are not led to any low excitations, as we are in He^3, and that any way of estimating the energy gives a result fairly close to the observed value of ϵ/k.

We have pointed out in Sec. 1 that we might expect six or a few more lowest excitations per atom, so at first sight the value of $m\sim7.5$ seems quite reasonable. However, it must be noted that if there is a spread of excitation energies the effective value of m will be somewhat less than the actual number of excitations per atom. In the first place, the phonon excitations are included and, as will be seen in the following section, they may account for about one excitation per atom; secondly, the excitations having different energies will not be equally easily excited. If we assume that the number of energy levels $p_\epsilon d\epsilon$ in a range ϵ to $\epsilon+d\epsilon$, such that ϵ/k is near 10°, is given by an error function

$$p_\epsilon d\epsilon=b\exp[-(\epsilon-\epsilon_0)^2/a^2k^2]d\epsilon, \tag{2.12}$$

we can in this case, without appreciable error, carry the integration from $\epsilon-\epsilon_0=-\infty$ and write for the total number of levels

$$m_0=b\int_{-\infty}^{\infty}\exp[-(\epsilon-\epsilon_0)^2/a^2k^2]d(\epsilon-\epsilon_0). \tag{2.13}$$

The average value $\bar{\epsilon}$ of the energy of the rotons [which is the energy which appears (without the overrule) in Eqs. (2.1) to (2.11)] is given by

$$\begin{aligned}\bar{\epsilon}&=\int_{-\infty}^{\infty}\epsilon p_\epsilon e^{-\epsilon/kT}d(\epsilon-\epsilon_0)\Big/\int_{-\infty}^{\infty}p_\epsilon e^{-\epsilon/kT}d(\epsilon-\epsilon_0)\\&=\epsilon_0-a^2k/2T,\end{aligned} \tag{2.14}$$

and the partition function is given by

$$\begin{aligned}Z&=\left[1+\int_{-\infty}^{\infty}p_\epsilon e^{-\epsilon/kT}d(\epsilon-\epsilon_0)\right]^N\\&=(1+m_0e^{-\epsilon_0/kT}\exp(a^2/4T^2))^N\\&=(1+m_0\exp(-\bar{\epsilon}/kT)\exp(-a^2/4T^2))^N.\end{aligned} \tag{2.15}$$

Thus, by comparison with Eq. (2.2), we can write for the effective value of m

$$m=m_0\exp(-a^2/4T^2). \tag{2.16}$$

In view of the fairly small spread of the estimated energies of excitations of the roton type, it might be reasonable to suppose that a is as low as 1°. If this value of a be assumed, then we estimate the following values of m_0 from the values of m given in Table II:

T	0.8°	1.1°	1.4°	1.7°
m_0	9.5	9.4	9.9	12.7

The values of m_0 for the three lower temperatures are close to 9 or 10 and the number of required energy levels would go up to about 10 or 11 per atom if the phonon states were added. This is certainly somewhat higher than expected, but perhaps not out of reason.

The considerably higher calculated value of m_0 at 1.7° can be explained only as arising from interactions between rotons. Since there are actually only about 0.0241 roton per atom, it may seem that the interactions could not produce so much effect. But it must be remembered that the whole calculation is an approximation and that Eq. (2.2) or Eq. (2.4) will break down when there are interactions. We must, rather, consider directly the energy levels which go into the partition function. The increase in ϵ/k and in m_0 are associated with a greater density of the high energy levels of the whole system, which involve multiple excitation. Even with only 2% of the atoms excited,

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[18] This calculation is of course based on the assumption that the difference in density between He^3 and He^4 is to be ascribed to a difference in interatomic distance rather than an effective coordination number. If the latter were the case, a considerable increase in the hindering potential would still be expected, but it would be more difficult to make the calculation. If the number of nearest neighbors in He^4 is actually about four, as stated by Beaumont and Reekie,[9] it seems most likely that the number in He^3 will not be much less. D. G. Hurst and D. G. Henshaw [Phys. Rev. **91**, 1222 (1953); **100**, 994 (1955)], however, believe that there are a greater number of nearest neighbors at a greater average distance, and with a greater spread of distances; the over-all distribution is actually not too different according to the two sets of data. The value of the hindering potential obtained here is somewhat greater than a previous estimate,[2] but leads to an excitation energy only about 2° higher.

the excitations are not on the average far removed from each other, and if this approach causes the energy of excitations to be decreased, this will increase the density of high-energy excitations. Even double excitations of single atoms or single pairs may become of some importance, and in view of the anharmonicity of the vibrations may have some effect in increasing density of energy levels. To bring the magnitude of the effect into better perspective, we may note that if $100n/N$ were reduced to 2.36 the effect would disappear; there would be a concomitant reduction of C_r to 1.815 joules gram^{-1} degree^{-1}.

3. COMPARISON WITH FEYNMAN'S EXCITATIONS

Feynman[3] and Feynman and Cohen[4] have given a treatment of liquid helium starting from an entirely different point of view. Using a variation method they have constructed wave functions, for the liquid as a whole, whose energy is close to that of the rotons. This leads to the inference that the wave functions must be somewhat near the true ones, and it will be of considerable interest to compare the excitations of He^4 which we have described with those to be inferred from Feynman's wave function.

In his earlier work Feynman wrote the wave function for the whole liquid (He^4) containing a single excitation in the form

$$\psi=\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\phi. \qquad (3.1)$$

Here $\mathbf{r}_i$ is the position vector for the ith atom, $\mathbf{k}$ the vector wave number determining the momentum and having the character of a quantum number, the sum is taken over all atoms and ϕ (a function of the distances between atoms, $\mathbf{r}_{ji}=\mathbf{r}_j-\mathbf{r}_i$) is the wave function of the ground state. The presence of ϕ prevents impossible overlapping of atoms. Feynman showed that with small $\mathbf{k}$ this would represent the phonon wave functions. This means that it would represent single excitations of the normal modes of vibration having long wavelengths. A double excitation of a given mode, for example, would be represented by a function like $\sum_i\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_i}e^{i\mathbf{k}\cdot\mathbf{r}_j}\phi$.

With large $\mathbf{k}$, a wave function like (3.1) would represent motion of a single atom (the summation merely symmetrizes the wave function and allows it to be any atom). With intermediate $\mathbf{k}$ several atoms may be involved; this type of excitation is a roton.

If the energy corresponding to one of these wave functions is evaluated by means of the integral expression $\int\psi^*H\psi d\tau/\int\psi^*\psi d\tau$, where H is the complete Hamiltonian for the whole liquid and $d\tau$ the corresponding volume element, it is found to be given by a curve of the form shown in Fig. 2. Up perhaps to the maximum the energy corresponds to a phonon excitation, while the rotons are represented by parts of the curve beyond the maximum and especially near the minimum.

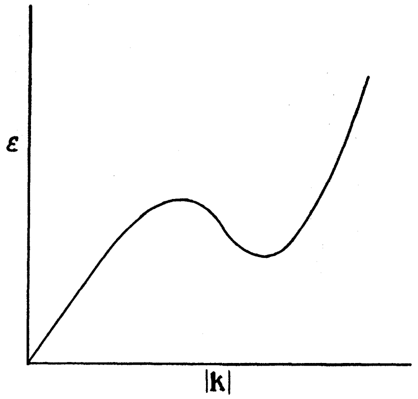

FIG. 2. Energy levels as a function of $|\mathbf{k}|$ according to Landau and Feynman.

Application of the momentum operator $-i\hbar\sum_i \text{grad}_i$ shows that the liquid as a whole has momentum, presumably with respect to the surroundings. This momentum is ascribed to the excitation. Only for small $\mathbf{k}$ is Eq. (3.1) an exact form; for larger $\mathbf{k}$ it is found that the current is not conserved. Feynman remarked that if this wave function were combined with one of the form $\sum_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}\phi$ to form a real wave function this conservation difficulty would be avoided. He rejected this solution because he felt that by collisions with phonons and with the wall the components would be separated, and since the sine and cosine functions would be equally good solutions further linear combination could again result in wave functions of the form (3.1). Therefore, he proposed the incorporation of a back flow, which could be represented approximately by a function of the form

$$\psi=\phi\sum_i\left[e^{i\mathbf{k}\cdot\mathbf{r}_i}\exp\left(i\sum_{j(j\neq i)}\frac{A\mathbf{k}\cdot\mathbf{r}_{ji}}{|\mathbf{r}_{ji}|^3}\right)\right], \qquad (3.2)$$

where $\mathbf{r}_{ji}=\mathbf{r}_j-\mathbf{r}_i$. This function had the double advantage of essentially eliminating the divergence of the current and of lowering the minimum in Fig. 2; A was determined so as to minimize the energy intergral for a given $\mathbf{k}$. The new function is still an eigenfunction of the momentum operator with the same eigenvalue as the unmodified function.

In spite of Feynman's arguments, it is our belief that the true eigenfunctions of H are not eigenfunctions of the momentum operator. An excited atom is affected by the field of its neighbors, and can exchange momentum with them. It can scarcely be expected to maintain a certain momentum in a certain direction. Therefore, it would appear that the complex wave functions should be combined to form real ones; instead of Eq. (3.2) we would have

$$\psi=\phi\sum_i\sin\left(\mathbf{k}\cdot\mathbf{r}_i+\sum_{j(j\neq i)}\frac{A\mathbf{k}\cdot\mathbf{r}_{ji}}{|\mathbf{r}_{ji}|^3}+\delta\right), \qquad (3.3)$$

where δ is a phase factor. This wave function retains the part which corresponds to the backflow, which seems to be necessary, even though the question of conservation of current no longer arises. It will give the same dependence of the energy integral on $\mathbf{k}$ as the function (3.2), and the density of energy levels will be the same. The wave function for that value k_m of $|\mathbf{k}|$ which corresponds to the minimum energy in the roton range will be an approximation to the true wave function for the lowest roton excitation. Although the ψ of Eqs. (3.3) for k_m is only an approximate wave function, its expansion in terms of the complete orthogonal set of true eigenfunctions will not be expected to involve the low-energy phonon wave functions to any appreciable degree; therefore, its energy integral will presumably give an upper limit to the energy of the lowest roton excitations. Since the inclusion of the backflow lowers the minimum roton energy considerably, it must contribute to the improvement of the wave function for k_m.

In addition to the effect on the energy, and quite apart from the conservation of current, there are some interesting physical reasons for inclusion of the backflow. London[19] pointed out that if a helium atom were entirely confined to the space between its neighbors the zero-point energy would be higher than it is. The lowering of the zero-point energy must imply some cooperation back flow, or "around flow," in the atoms surrounding any given atom even in the ground state, and it would be expected to be at least as important in an excited state. The optimum value k_m in the roton part of the excitation spectrum, as found by Feynman and Cohen, is close to 1.85 A^{-1}, corresponding closely to a wavelength of $2\pi/1.85 \sim 3.5$ A, which is somewhat larger than the expected mean free path for an atom completely confined by its neighbors, and this also indicates the desirability of taking the backflow into account.

The approximate wave functions of Eq. (3.3) depend upon pairs of atoms only through the factor ϕ, which merely prevents atoms from coming too close to each other, and in the backflow term, which is a kind of correction. Essentially they represent single-atom excitations, corresponding to the first excited vibrational state, which as we have seen, in Sec. 2, should require an excitation of about 10°. Feynman and Cohen have found that the best value of A at k_m gives an excitation of 11.5°. We have seen that the rotational oscillations which we have discussed are not independent of the single-atom vibrations, although their consideration gives valuable confirmation of the energy involved. The picture of Feynman, therefore, appears, upon analysis, to be reasonably consistent with the picture we have presented.

De Boer[5] has suggested that Feynman's excitations correspond only to the longitudinal or compressional type of normal vibration. Transverse vibrational modes, such as occur in solids, cannot occur in liquids on a large scale, but in the region of small wavelength they are replaced by rotations or rotational oscillations of small groups of atoms. It is our opinion that these are included in Feynman's excitations, since, as already noted, they appear not to be independent of the single-atom excitations. It is true that a term of the form $\sin(\mathbf{k}\cdot\mathbf{r}_i)$ such as arises as part of one of the exponentials in Eq. (3.1), has a series of parallel nodes. In a special case, for example, in which $k_y = k_z = 0$, we would have $\sin(k_x x_i)$, with nodal planes perpendicular to the x axis. Though the discussion given by Feynman (p. 267 of reference 3), by which he identified eigenfunctions of the form (3.1) with compressional waves, was not meant to apply to short wavelengths, this arrangement of nodes of the component sinusoidal functions, is still one that would be associated in a general way with compressional waves even when the wave length is short. But a linear combination of two wave functions, say one with $k_y = k_z = 0$ and the other with $k_x' = k_z' = 0$, and with $k_x = k_y'$ (so that they both correspond to the same energy), namely,

$$\sum_i e^{ik_x x_i} + \sum_i e^{ik_y' y_i},$$

would contain sinusoidal terms like $\sin(k_x x_i) + \sin(k_y' y_i)$ which would have two intersecting sets of nodal planes. This would correspond to a different, though not independent, type of vibration, certainly one involving some localized shear. It is more difficult to see what would happen with wave functions like (3.3), but qualitatively we would not expect the situation to be very different.

Since one apparently cannot, in any obvious way, call in the help of excitations which are not already included, the difficulty of finding enough excitations to account for the experimental results, noted at the end of Sec. 2, appears also in the Feynman's formulation. Feynman and Cohen noted this, remarking that the curvature around the minimum of their curve seemed to be too great. The energy, according to their curve, appears to rise sharply when $|\mathbf{k}|$ becomes greater than about 2.1 A^{-1}. Larger values of $|\mathbf{k}|$ presumably correspond to eigenfunctions which are related to higher excitations of the single-atom oscillators, and $|\mathbf{k}| = 2.1$, which corresponds to a wavelength of 3.0 A is a reasonable cutoff point. The classical range of motion for an oscillator with $h\nu/k = 10°$ in its first excited state and with a mass equal to that of He^4 would be about 3.8 A; but the backflow would increase the effective mass[20] and so decrease the range of motion. If we apply periodic boundary conditions to the wave functions at the edges of a cube with sides of length l, we find that the number of energy levels in a range between $|\mathbf{k}|$ and $|\mathbf{k}| + d|\mathbf{k}|$ (remembering that $|\mathbf{k}|$ is the magnitude of a vector

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[19] F. London, J. Phys. Chem. 43, 49 (1939).

[20] The backflow would *decrease* the *reduced* mass, but the coordinate to be used with the reduced mass is the relative position of the atom with respect to those taking part in the backflow, rather than its position in a fixed coordinate system.

and that the difference δk_x between consecutive allowed values of a component of $\mathbf{k}$ must obey the relation $l\delta k_x = 2\pi$) will be $4\pi l^3|\mathbf{k}|^2 d|\mathbf{k}|/(2\pi)^3$. The total number of atoms is l^3/v_0, where v_0 is the volume per atom (46 A^3). Thus, the number of states per atom up to $|\mathbf{k}| = 2.1$ A will be given by

$$(46/2\pi^2)\int_0^{2.1}|\mathbf{k}|^2 d|\mathbf{k}| = 7.2.$$

From this we must subtract the phonon states. One might reasonably assume that the phonon states extend up to the maximum in Fig. 2, which occurs at $|\mathbf{k}| = 1.3$, which would mean that the number of available states would be reduced to 5.5. If the curve should be flatter, so that the increase in energy occurred around $|\mathbf{k}| = 2.4$, and if the cutoff for the phonon states should be at $|\mathbf{k}| = 1.0$ instead of $|\mathbf{k}| = 1.3$, we would find about 10 available states.

The calculation of Feynman and Cohen apparently cannot say anything conclusive about the spread in energy, but the considerations of Sec. 2 make it appear that the spread of energies may be rather low. This might mean, for example, that the maximum in Fig. 2 should be lowered and pushed to the left. We may remark that the distribution of roton levels indicated by Fig. 2 would be rather different from that assumed in Sec. 2, since according to Fig. 2 we have many levels near the minimum, and a sharp cutoff there, as shown in Fig. 3. It seems quite possible that the theory of Feynman and Cohen has the levels too closely associated with the parameter k. However, it does seem that we can conclude from their work, not only that the minimum energy which they find is an upper bound for the lowest roton energy, but that there are at least as many states in the same general energy region as their distribution would suggest. This is true because the approximate wave functions of the form of (3.2) or (3.3) are all orthogonal to each other, if the function ϕ is made to conform to the periodic boundary conditions as well as the other parts of the function, so they can be used as a basis for expanding the true wave functions, and it seems unlikely that the perturbations will be large enough to throw the energies of the true wave functions entirely out of the region.

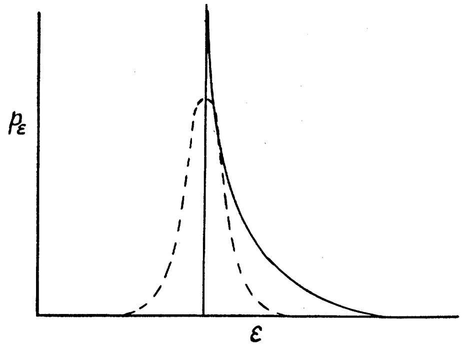

FIG. 3. Landau-Feynman energy distribution contrasted to error function.

4. GAS OF EXCITATIONS

In the original papers of Landau[21] the rotons were treated as a gas of excitations obeying the Bose-Einstein statistics. Feynman also followed this idea. If we think of localized excitations which are broadened into a band, there must be as many levels in the band as there were original localized levels. More than one localized level can be excited at the same time, and this would correspond to having an equal number of the levels in the band excited simultaneously. This assumes that if the liquid is excited in one particular way, it does not prevent it from being excited in some other way at the same time. The number of possible ways that a certain number of the levels of the bands can be excited, if it does not matter just which ones are excited, is just equal to the number of ways the localized excitations can be distributed among the possible positions in the liquid, *provided* that no level can be doubly excited. At least this proviso is necessary, unless we also suppose that two localized excitations can be exactly superimposed at the same place in the liquid—but this would amount to a higher excitation, and would not be included in the usual type of roton. Thus we would have something like the Pauli exclusion operating with respect to the placing of excitations in energy levels, so we conclude that the gas of excitations should obey the Fermi-Dirac statistics rather than the Bose-Einstein. It must be granted, however, that this distinction is somewhat academic in the case of He^4, for when the density of excitations became dense enough for any appreciable difference between the two statistics to become important, they would begin to affect each other, and this interaction between excitations would blur the effect of the statistics. Since the excitations may overlap, having one excitation may prevent development of a neighboring one—a kind of expanded exclusion principle.

One of the differences between He^3 and He^4 is that in the former this expanded exclusion principle does not operate with respect to the lower states (ground state and lowest triplet) of the pair model. If we consider just these lower excitations in He^3, there are, at any instant, exactly $\frac{1}{2}N$ possible positions for an excitation, and these excitations cannot overlap. It is not certain that they will not affect each other at all, but this would seem to be a reasonable approximation. The ground state gives one term in the partition function. There are $\frac{3}{2}N$ ways for a single excitation to occur, giving $\frac{3}{2}N$ terms in the partition function. There are $3^2(\frac{1}{2}N)(\frac{1}{2}N-1)/2$ terms in the partition function corresponding to double excitation, $3^3(\frac{1}{2}N)(\frac{1}{2}N-1)(\frac{1}{2}N-2)/3!$ terms corresponding to triple excitation, etc. It will be seen that with Eq. (1.3) these successive terms correspond exactly to those which occur in the binomial

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[21] L. D. Landau, J. Phys. U.S.S.R. 5, 71 (1941); 11, 91 (1947).

expansion of the $\frac{1}{2}N$ power of the first two terms in Eq. (1.2) namely, $(1+\int_0^\infty p_\epsilon e^{-\epsilon/kT}d\epsilon)^{N/2}$, the integration serving merely as an averaging device. Excitation to higher levels means, of course, additional terms in the system's partition function. For example, if there is one excitation to the higher triplet, this can occur in $11N/2$ different ways, and the contribution to the partition function in the light of Eq. (1.6) will be

$$\tfrac{1}{2}N\left(\int_0^\infty p_\epsilon' e^{-\epsilon/kT}d\epsilon\right)\left(1+\int_0^\infty p_\epsilon e^{-\epsilon/kT}d\epsilon\right)^{\frac{1}{2}N-1},$$

which would appear in the multinomial expansion of Eq. (1.2). However, if two of the higher levels were excited, these could occur in somewhat fewer than $11^2(\frac{1}{2}N)(\frac{1}{2}N-1)/2$ ways, because this would count cases in which two rotators had a common atom; the expanded exclusion principle begins to operate. These deviations would only become important, however, in the terms of the expansion involving high powers of $\int_0^\infty p_\epsilon' e^{-\epsilon/kT}d\epsilon$, and if the integral is not too large may be neglected.

I wish to thank Professor W. A. Bowers for a number of helpful discussions.

Note added in proof.—We have noted a statement by H. C. Kramers, in *Progress in Low Temperature Physics* (see reference 5), Vol. 2, p. 65, that the phonon specific heat of Kramers, Wasscher, and Gorter[15] is too large, though their total specific heats at 0.8°K and above are about right. Using the new phonon specific heat to obtain C_r changes Table II and the values of m_0 as follows:

T	ϵ/k	$100n/N$	m	m_0
0.8	9.39	0.0041	5.11	7.6
1.1	9.57	0.1030	6.19	7.6
1.4	9.88	0.683	7.94	9.0
1.7	10.4	2.44	11.1	12.1

The consistency with Eqs. (2.8) and (2.10) is improved, and the smaller value of m_0 almost removes the difficulty concerning the number of energy levels. At the lower temperatures $d(\epsilon/k)/dT$ is about 0.6, close to the value in Table II and that given by the Landau-Feynman theory.

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Radiation Effects in Shock-Wave Structure

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The equations for shock-wave structure, with the inclusion of radiation effects, are derived. These radiation effects are radiation pressure, radiation energy density, and radiative transfer of energy. Computations have been performed for a diffusion approximation of radiation flux and the neglect of radiation energy density and pressure. The results show that the over-all effect of radiation (under the aforementioned conditions) can be taken as a diminution of the Prandtl number, and that the shock width is larger than when viscosity and heat conduction alone are considered. The radiative contribution to the width of the shock is found to depend primarily on the ratio of the mean free path of radiation to that of the material particles. The proportionate increase in shock width is found to be a function of the Mach number and to increase with it.

Possible application of the above results to shock-wave propagation in a medium of low density is indicated.

1. INTRODUCTION

SACHS[1] has given the Rankine-Hugoniot conditions when the effects of radiation pressure and energy density are included with the hydrodynamics. Sachs examined only the end conditions of such a shock, and did not consider radiative transfer of energy. It is the object of this paper to give an analysis which includes the effects of such radiation terms on the detailed structure of a shock front. The analysis is by the Stokes-Navier equations with the gas possessing its usual viscosity and heat conductivity. The shock will be taken as plane, steady, nonrelativistic, with no superposed electric or magnetic fields.

Radiation pressure and energy density effects are important long before the shock is relativistic. For a shock propagating into air at standard conditions, a Mach number of 10^5 is needed before the shock may be considered relativistic, whereas radiation pressure becomes comparable to material gas pressure behind the shock at a Mach number of about 2×10^2. Again, radiative transport of energy may be important even though the other radiation terms are negligible. For air of atmospheric density, a temperature of a few million degrees must be reached before radiation pressure and energy density become important while radiative transport is significant even at much lower temperatures.

The significance of the results to shock propagation through rarefied atmospheres is also briefly considered.

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[1] R. G. Sachs, Phys. Rev. 69, 514 (1946).