

The slope of the Landau expression reaches the velocity of first sound at momentum p^* , where $p^*/\hbar = 2.16 \text{ \AA}^{-1}$. For $p > p^*$, the excitation spectrum continues to rise with slope equal to the sound velocity, rather than rising quadratically. This behavior might be expected, since for momenta greater than p^* , an excitation of momentum p^* plus a phonon of momentum $p - p^*$ have a smaller total energy than an excitation of momentum p whose energy is given by a continuation of the roton curve. The change in the appearance of the wavelength distribution of the scattered neutrons, mentioned in Sec. IV and shown in Fig. 5, occurs for momenta greater than p^* . We feel that for an unambiguous analysis of the processes taking place at higher momenta, an experiment using monoenergetic incident neutrons should be performed.

At higher temperatures, the excitation energy for a given momentum decreased, and a noticeable energy spread was observed. This indicates that the density of excitations is great enough at these temperatures that the effect of interactions between the excitations can no longer be neglected. In the roton region, the data may be represented by the Landau expression fitted at $T = 1.1^\circ\text{K}$, shifted downward by 0.22°K at $T = 1.60^\circ\text{K}$, and by 0.50°K at $T = 1.80^\circ\text{K}$.

The variation of the fitted values of Δ with T is given approximately by the empirical relation

$$\Delta/k = 8.68 - 0.0084T^7 \text{ }^\circ\text{K}, \quad (7)$$

where T is in $^\circ\text{K}$. This formula is suggested as a guide for interpolation between the measured values of the excitation energy at different temperatures; no particular theoretical significance is implied.

In the following paper,¹² a comparison is made between experimental determinations of the specific heat, entropy, second sound velocity, and normal fluid density of liquid helium, and values of these quantities calculated from the measured excitation spectrum.

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Excitations in Liquid Helium: Thermodynamic Calculations*

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The entropy, specific heat, normal fluid density, and velocity of second sound in liquid helium II have been calculated by applying statistical mechanics to the thermal excitations. The calculations were based on the energy-momentum relation obtained by neutron scattering measurements described by Yarnell, Arnold, Bendt, and Kerr, and were made on an IBM-704 electronic digital computer by numerical integrations over the observed excitation curve. A better approximation than Landau's has been obtained by extending Landau's theory to take account of the temperature dependence of the excitation curve. An expression of the form $E(p, T) = c - d(\rho_n/\rho)$ was used to interpolate the excitation energy between temperatures at which it was measured. Results between 0.2 and 1.8°K are not sensitive to the exact form of the interpolation expression. Agreement of the calculations with experimental measurements is as follows: entropy, $\pm 3\%$ in the temperature range 0.2 to 1.8°K ; specific heat, $\pm 4\%$ between 0.2 and 1.7°K ; second sound velocity, $\pm 4\%$ between 0.8 and 1.8°K , and $\pm 2\%$ between 1.0 and 1.7°K . The calculated normal fluid density ρ_n agrees with experimental values derived from second sound velocity and specific heat measurements within $\pm 8\%$ between 0.7 and 2.0°K , and within $\pm 5\%$ from 1.1 to 1.9°K . These values are, however, higher than those obtained from torsion pendulum measurements, which are 27% below the calculated value at 1.2°K . Also calculated as functions of temperature are the average effective mass (as defined by Landau) of excitations in four momentum intervals, and values of $-\kappa/\bar{B}$, the thermal conductivity κ divided by the average over momentum of the Khalatnikov nonequilibrium kinetic coefficient $-\bar{B}$, and η/\bar{C} , the viscosity η divided by the average value of the Khalatnikov coefficient \bar{C} .

I. INTRODUCTION

LANDAU¹ proposed that the thermodynamic properties of liquid helium II could be calculated by applying statistical mechanics to the ensemble of excita-

tions, which may be treated as a gas. In Landau's treatment, interactions between the excitations are neglected. Experimentally, the effect of interactions is shown by a dependence of the excitation energy on the temperature. It is possible to extend Landau's theory to take account of the temperature dependence of the excitations, and this is done in Sec. II below. The

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¹ L. Landau, *J. Phys. (U.S.S.R.)* **5**, 71 (1941); **11**, 91 (1947).

accuracy of calculations can be improved by numerically integrating the expressions for entropy and normal fluid density, rather than using analytic expressions in which the excitation curve has been approximated by a linear and a parabolic function. Since the whole excitation curve contributes to the integrals, the sharp distinction between phonons and rotons is lost. However, the linear portion of the curve at small momentum, and the minimum of the curve, make the largest contributions to the integrals, and we refer to these as the phonon and roton contributions respectively.

Our thermodynamic calculations have made no provision for the line width of the excitation curve, which was appreciable in the measurements made at 1.6 and 1.8°K. We have used the midpoint of the line as the energy level, and have made the calculations as if the line had zero width. We believe the width of the line is due to the uncertainty principle, applied to the short lifetime between collisions of the excitations.

It is well known that Bose statistics apply to phonons, which are quantized sound waves. The statistics obeyed by excitations having larger momenta has not been settled experimentally. Theoretical work by Feynman and Cohen² and by Brueckner and Sawada³ shows that the wave function which describes the excitations varies continuously with increasing momentum, implying that the statistics are the same for all excitations. Since the energy of the minimum of the excitation curve is at least three times as large as kT for temperatures $\leq 2^\circ\text{K}$, the statistics obeyed by rotons has little effect on the numerical results. We have, however, chosen to assume in the derivations that *all* excitations obey Bose statistics.

The vapor pressure, compressibility, and thermal coefficient of expansion also depend on integration of the excitation curve and its derivatives. However, to calculate these functions requires knowledge of the derivative $\partial E/\partial\rho$ of the excitation energy E with change of liquid helium density ρ . Neutron scattering measurements from liquid helium under pressure, which will provide this information, are being made by Henshaw.⁴ Results available at present are not complete, and functions which depend on $\partial E/\partial\rho$ have not been calculated.

II. THEORY OF ENTROPY AND SPECIFIC HEAT

In general, the thermodynamic properties of a simple system are functions of two independent variables, such as temperature T and volume V . In the case of liquid helium II, however, the excitation curve is known only for the liquid in equilibrium with the vapor pressure. Consequently, the theoretical treatment which follows will be limited to thermodynamic states along the saturated vapor-pressure curve, and the thermodynamic

properties will be considered functions of the single variable T . However, the density of liquid helium varies so little below 2.1°K that the calculated properties are practically identical with the constant-volume properties.

We shall extend Landau's theory¹ to the situation where the excitation energy E is a function of temperature as well as of momentum. The energy required to add to the system at temperature T one excitation of momentum p_j has been determined by the neutron scattering experiment, and will be denoted by $E_j(T)$. The total energy required to add a small number dn_j of excitations at each momentum p_j is thus

$$dU = \sum_j E_j(T) dn_j. \quad (1)$$

We assume that the energy required to produce an excitation thermally is identical with that required by neutron scattering. Then Eq. (1) is just the increase in internal energy U of the system associated with an increase in temperature from T to $T+dT$, provided each dn_j is the correct increase in the number of excitations for the system to remain in thermal equilibrium.⁵ Because of the dependence of E_j on temperature, Eq. (1) cannot be integrated to the familiar expression $U = \sum_j E_j n_j$. We must instead write

$$U = \sum_j \int_0^T E_j(T) \frac{dn_j}{dT} dT, \quad (2)$$

$$C_s = dU/dT = \sum_j E_j(T) \frac{dn_j}{dT}, \quad (3)$$

$$S = \int_0^T \frac{C_s}{T} dT = \sum_j \int_0^T \frac{E_j(T)}{T} \frac{dn_j}{dT} dT. \quad (4)$$

C_s is the specific heat along the saturated vapor-pressure curve, and S is the entropy.

In order to calculate values of the thermodynamic properties from these expressions, n_j must be known as a function of p_j and T . This can be found by a method similar to the usual microcanonical-ensemble treatment of a system of noninteracting particles.⁶ If we neglect the effect of interactions between excitations on the total wave function of the system (but not on the energy of the system), then the quantum state is specified by giving the number of excitations of each momentum p_j . Assuming Bose statistics to be applicable to excitations of all momenta, the total number of quantum states of the system corresponding to a dis-

⁵ Strictly speaking, Eq. (1) represents the heat flow dQ into the system, rather than the change in internal energy. However, in the first law of thermodynamics, $dU = dQ - pdV$, the pdV term for liquid helium II is less than 0.01% of dQ along the saturated vapor-pressure curve. Thus dQ is essentially equal to dU , and we have used the latter notation to facilitate comparison of Eqs. (2) and (7) below with the well-known corresponding expressions for the case E_j independent of T .

⁶ R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Chap. X.

² R. P. Feynman, Phys. Rev. **91**, 1291, 1301 (1953); **94**, 262 (1954); R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).

³ K. A. Brueckner and K. Sawada, Phys. Rev. **106**, 1128 (1957).

⁴ D. G. Henshaw, Phys. Rev. Letters **1**, 127 (1958).

tribution in which there are n_j excitations with momentum between p_j and $p_j + dp_j$ is given by the usual expression

$$\Omega = \prod_i \frac{(c_j + n_j - 1)!}{n_j! (c_j - 1)!} \approx \prod_i \frac{(c_j + n_j)!}{n_j! c_j!}, \quad (5)$$

where c_j is the number of individual excitation states with momentum between p_j and $p_j + dp_j$. The entropy S of the system is then

$$S = k \ln \Omega = k \sum_j \{ (c_j + n_j) \ln(c_j + n_j) - n_j \ln n_j - c_j \ln c_j \}, \quad (6)$$

where k is Boltzmann's constant, provided the values of the n_j are those for which Eq. (5) is a maximum subject to the restriction that the internal energy $U(n_1, n_2, \dots)$ be constant. This leads in the usual way to the conditions

$$\frac{\partial \ln \Omega}{\partial n_j} - \beta \frac{\partial U}{\partial n_j} = 0 \text{ for all } j. \quad (7)$$

$\beta = 1/kT$ is a Lagrangian multiplier. Because there is no requirement that the total number of excitations be constant, the other Lagrangian multiplier usually present is missing. From Eq. (1), $\partial U / \partial n_j = E_j(T)$, so that Eq. (7) leads to

$$n_j = c_j (e^{E_j(T)/kT} - 1)^{-1}. \quad (8)$$

which is the required functional expression for n_j .⁷

Using Eqs. (6) and (8), one obtains

$$S = k \sum_j \{ E_j(T) n_j / kT + c_j \ln(1 + n_j / c_j) \}. \quad (9)$$

This expression for the entropy, with n_j given by Eq. (8), is entirely equivalent to Eq. (4). However, for computational purposes Eq. (9) has the advantage that it requires knowledge only of $E_j(T)$, whereas direct use of Eq. (4) requires also knowledge of $dE_j(T)/dT$.

The sum in Eq. (9) can be changed to an integral. Letting c_j equal an element of volume in phase space,

$$c_j = 4\pi V p^2 dp / h^3, \quad (10)$$

the entropy per unit mass is given by

$$S = \frac{4\pi k}{\rho h^3} \int_0^\infty \left\{ \frac{E(p, T)/kT}{e^{E(p, T)/kT} - 1} - \ln(1 - e^{-E(p, T)/kT}) \right\} p^2 dp. \quad (11)$$

The usual Bose-Einstein condensation occurs only when

⁷ The form of this expression is of course familiar. However, its interpretation is somewhat different from the usual case in that U in Eq. (7) is given by Eq. (2) rather than by $U = \sum_j E_j n_j$. $E_j(T)$ is analogous to a chemical potential; it is the "free energy" required to add one additional excitation to the system at temperature T , rather than some sort of average energy per excitation, or the energy of an excitation at zero temperature. The derivation of Eq. (8) was included to emphasize this distinction, since it may not be generally appreciated; see G. S. Rushbrooke, *Trans. Faraday Soc.* **36**, 1055 (1940).

the number of particles is fixed. The linear dependence of energy on momentum in the phonon region assures that the integrand is well behaved where the momentum is small, and at large momenta $\exp[E(p, T)/kT]$ is always $\gg 1$.

The modification that we have made to Landau's treatment of liquid helium retains the assumption that the excitations are normal modes which can be identified and counted. The addition of a temperature-dependent excitation energy assumes a weak interaction between a particular excitation and all the others, which does not destroy the identity of the individual excitation. It is to be expected that as the temperature approaches the lambda point, the interactions become so strong that the description of the liquid in terms of elementary excitations (normal modes) breaks down. The line width is probably a useful indication of how valid the concept of individual excitations is at any given temperature. The equations derived above are expected to hold at temperatures at which the line width is small compared to the total energy of an excitation. Experimentally, for temperatures up to 1.8°K, the observed line width is less than one fourth of the total energy of an excitation, in the roton region.

III. EXPRESSIONS FOR NORMAL FLUID DENSITY, EFFECTIVE MASS, AND SECOND SOUND VELOCITY

Derivations of expressions for normal fluid density and second sound velocity are given by Landau,¹ and in a review article by Dingle.⁸ To derive the normal fluid density, it is assumed the excitations have a drift velocity \mathbf{v} relative to the superfluid, and that the equilibrium distribution Eq. (8) applies in a coordinate system moving with the excitations. The distribution function in a coordinate system in which the superfluid is at rest differs from Eq. (8) in that $E_j(T)$ is replaced with $E_j(T) - \mathbf{p}_j \cdot \mathbf{v}$, where \mathbf{p}_j is the vector momentum of an excitation. The definition of ρ_n is obtained by setting the resultant momentum of all the excitations equal to $\rho_n \mathbf{v}$. For small \mathbf{v} , that is, neglecting terms of order \mathbf{v}^2 and higher, the integration over the angle between \mathbf{p} and \mathbf{v} can be performed, to give

$$\rho_n = \frac{4\pi}{3kTh^3} \int_0^\infty \frac{e^{E(p, T)/kT} p^4 dp}{(e^{E(p, T)/kT} - 1)^2}. \quad (12)$$

The experimental excitation curve $E(p, T)$ was used in the numerical integration of Eq. (12) to calculate ρ_n at each temperature.

Landau¹ has shown that ρ_n can be written as the product of the number of excitations N and the average effective mass \bar{m}^* of each excitation. It was in this way that Landau showed, in his 1941 paper, that the mass of a roton is given by μ , when the energy-momentum relation is given by $E = \Delta + p^2/2\mu$. In his 1947 paper, Landau

⁸ R. B. Dingle, *Suppl. Phil. Mag.* **1**, 111 (1952).

pointed out that for arbitrary dependence of the excitation energy on momentum, one can write $\rho_n = N \langle p^2 \rangle_n / 3kT$, where Boltzmann statistics were used. In an analogous manner, we can divide the integrand of Eq. (12) into the product of the number of excitations $n(p)$ and an "effective mass" $m^*(p)$. For $m^*(p)$ we obtain, using Bose statistics,

$$m^*(p) = \frac{p^2}{3kT} (1 - e^{-E(p,T)/kT})^{-1}. \quad (13)$$

It should perhaps be emphasized that m^* is the effective mass involved in bulk momentum transfer processes, and not a quantity which describes the momentum carried by a single excitation. It is associated with the drift velocity \mathbf{v} rather than with the total velocity of a single excitation.

The derivation of second sound velocity begins with an expression for conservation of energy in liquid helium II, valid for reversible processes,

$$\rho \frac{\partial S}{\partial t} + S \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho S \mathbf{v}_n) = 0, \quad (14)$$

where S is the entropy per unit mass, t is time, and \mathbf{v}_n is the velocity of the normal fluid component. First sound is a wave propagation in which $\partial S / \partial t$ is zero, and second sound is a wave propagation in which $\partial \rho / \partial t$ is zero. If the amplitude of the second sound wave is very small, so that S is nearly constant, and if the thermal coefficient of expansion is small enough that the coupling between first and second sound can be neglected, then the energy of a second sound wave can be derived, and is given by

$$\frac{TS^2}{2C_v} (\nabla \cdot \mathbf{x}_n)^2 + \frac{\rho_n}{2(\rho - \rho_n)} \mathbf{v}_n^2 = \text{constant}, \quad (15)$$

where \mathbf{x}_n is the local displacement of normal fluid from equilibrium. The first term is potential energy and the second term is kinetic energy. The velocity of propagation is then given by

$$v_2^2 = \left(\frac{\rho}{\rho_n} - 1 \right) \frac{TS^2}{C_v}. \quad (16)$$

A slightly different equation for the velocity of second sound,

$$v_2^2 = \frac{\rho}{\rho_n} \frac{TS^2}{C_v}, \quad (17)$$

has been given by Kramers, and by Ward and Wilks.⁹ To calculate second sound velocities, we have made the approximation that $C_v = C_s$, and put our calculated values of ρ_n , S , and C_s into both equations.

⁹ H. A. Kramers, *Physica* **18**, 653 (1952); J. C. Ward and J. Wilks, *Phil. Mag.* **42**, 314 (1951); **43**, 48 (1952).

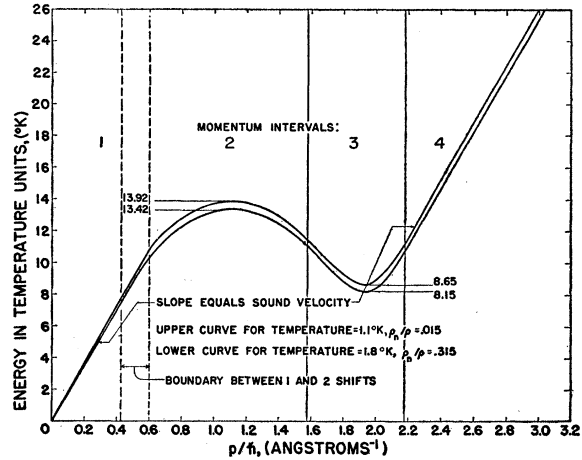


FIG. 1. The excitation curve at 1.1 and 1.8°K, and the momentum intervals.

IV. NUMERICAL METHODS

Equations (11) and (12) were integrated numerically with the aid of an IBM type 704 digital computer, at temperature intervals of 0.1°K between 0.2 and 2.1°K. The integrals were cut off at p/\hbar equal to 3.08 Å⁻¹, the contribution from higher values of p/\hbar being negligible. The momentum range was divided into four intervals, shown in Fig. 1, and the excitation energy curve was represented in each interval as follows:

Interval 1.—(Phonon region, covering values of p/\hbar from zero to the boundary of interval 2, designated p_1/\hbar . This boundary varied from 0.43 to 0.60 Å⁻¹, depending on temperature.) The energy in the phonon region was assumed to be given by $E = v_1 p$, where v_1 is the velocity of first sound. The measurements by Van Itterbeek, Forrez, and Teirlinck,¹⁰ extrapolated to 238 m/sec at zero temperature, were used for the sound velocity. The value of v_1 used at each temperature, and also p_1/\hbar , is given in Table I.

Interval 2.—(Region of the maximum in the excitation curve. Interval 2 extends from p_1/\hbar to 1.58 Å⁻¹.) Experimental data for the excitation energy were fitted with the inverted parabola $E/k = a - 11.5(p/\hbar - 1.113)^2$, where k is Boltzmann's constant. A complete curve for this interval was measured only at 1.1°K, for which temperature the value of a is 13.92°K. The values of a used at other temperatures are given in Table I. The value of p_1/\hbar at each temperature is the point of intersection of the linear relation used in interval 1 and the quadratic relation used in interval 2.

Interval 3.—(Region of the minimum in the excitation curve. Interval 3 extends from 1.58 to 2.18 Å⁻¹.) Smooth curves (not parabolas) were drawn by sight through the experimental measurements of excitation energy at two temperatures, 1.1 and 1.8°K, and the excitation energy was read from the curves at mo-

¹⁰ A. Van Itterbeek and G. Forrez, *Physica* **20**, 133 (1954); Van Itterbeek, Forrez, and Teirlinck, *Physica* **23**, 63, 905 (1957).

TABLE I. Various parameters used in the calculations.

Temperature °K	Velocity of first sound, ^a v_1 m/sec	Liquid helium density, ^b ρ g/cc	p_1/\hbar Å ⁻¹	Interval 2, parameter a °K	Interval 4, parameter b °K
0.2	238.0	0.14550	0.60	13.94	28.38
0.3	238.0	0.14550	0.60	13.94	28.38
0.4	238.0	0.14550	0.60	13.94	28.38
0.5	238.0	0.14550	0.60	13.94	28.38
0.6	238.0	0.14550	0.60	13.94	28.38
0.7	237.9	0.14549	0.60	13.94	28.37
0.8	237.8	0.14549	0.60	13.94	28.35
0.9	237.7	0.14548	0.60	13.94	28.34
1.0	237.6	0.14547	0.60	13.93	28.31
1.1	237.3	0.14547	0.60	13.92	28.28
1.2	237.0	0.14547	0.60	13.90	28.24
1.3	236.6	0.14548	0.60	13.87	28.18
1.4	236.0	0.14550	0.60	13.81	28.11
1.5	235.2	0.14553	0.59	13.75	28.01
1.6	234.3	0.14557	0.58	13.67	27.90
1.7	233.0	0.14563	0.57	13.56	27.75
1.8	231.5	0.14572	0.56	13.42	27.56
1.9	229.5	0.14584	0.54	13.24	27.31
2.0	226.9	0.14599	0.51	13.01	27.00
2.1	222.2	0.14620	0.43	12.69	26.60

^a From reference 10.^b From reference 20.

mentum intervals of 0.02 Å⁻¹. These energies are given in Table II, and were stored in the memory of the computer. The computer calculated the energy at each momentum for temperature intervals of 0.1°K according to an interpolation formula described below.

Interval 4.—(Extends from 2.18 to 3.08 Å⁻¹.) The experimental excitation curve, within the accuracy of the neutron scattering measurements, is consistent with a linear relation having slope equal to v_1 . The excitation energy was fitted with the relation $E = v_1 p - b$, where values of v_1 and b are given in Table I.

A matter of some concern was the method to use in momentum intervals 2 and 3 for interpolation and extrapolation of the temperature dependence of the excitation energy, which was measured only in the region of the minimum, and only at three temperatures, 1.1, 1.6, and 1.8°K. In momentum intervals 1 and 4 the temperature dependence of the energy was taken to be the same as that of first sound velocity.

Experimental measurements of the energy of the minimum were fitted in the preceding paper¹¹ by the expression $\Delta(T)/k = 8.68 - 0.0084T^7$ °K, which passes through the best values measured at the three temperatures. It was realized that this relation is entirely empirical, and not necessarily exact, due to experimental uncertainties. After preliminary machine calculations were made, it was possible to evaluate various interpolation formulas, on the basis of agreement of the calculated entropy with values obtained from specific heat measurements, over the temperature range 0.2 to 2.1°K. The following interpolation formulas for the energy at

the minimum were tried:

$$\Delta(T)/k = 8.68 - 0.0084T^7 \text{ °K}, \quad (a)$$

$$\Delta(T)/k = 8.69 - 0.0155T^6 \text{ °K}, \quad (b)$$

$$\Delta(T)/k = 8.70 - 0.0289T^5 \text{ °K}, \quad (c)$$

$$\Delta(T)/k = 8.67 - 1.564(\rho_n/\rho) \text{ °K}, \quad (d)$$

$$\Delta(T)/k = 8.68 - 5.35 \times 10^{-22} N \text{ °K}, \quad (e)$$

$$\Delta(T)/k = 8.66 - 5.93 \times 10^{-22} N_{\text{heavy}} \text{ °K}, \quad (f)$$

where N is the total number of excitations per unit volume at temperature T , and N_{heavy} is the number of excitations in momentum intervals 2, 3, and 4 per unit volume. All the above equations agree with the neutron measurements at 1.1 and 1.8°K, but Eq. (c) gives an energy at 1.6°K which is low, outside the experimental error.

It was found that all the interpolation formulas gave agreement, within $\pm 5\%$, with experimental values of entropy between 0.2 and 1.8°K. The principal difference between the formulas was in extrapolating to higher temperatures, where *none* of the formulas gave good agreement. Equations (c) and (d) gave better agreement with entropy measurements than the other formulas. The excitation energy computed using Eq. (d) is in good agreement with neutron scattering measurements at 1.6°K. There are insufficient neutron scattering data to justify using an interpolation formula containing more than two terms, though obviously a better fit to entropy measurements above 1.8°K could be obtained.

For the results reported here, the computer calculated the excitation energy throughout interval 3, using an interpolation formula of the form $E(p, T) = c - d(\rho_n/\rho)$, and using the values given in Table II to compute the parameters c and d at each momentum. Parameters a and b in the energy expressions for intervals 2 and 4 were chosen to give the same values of the energy at

TABLE II. Values of $E(p, T)$ at 1.1 and 1.8°K for Interval 3 (roton minimum).

Momentum p/\hbar , Å ⁻¹	E/k at 1.1°K °K	E/k at 1.8°K °K	Momentum p/\hbar , Å ⁻¹	E/k at 1.1°K °K	E/k at 1.8°K °K
1.58	11.41	10.91	1.90	8.68	8.20
1.60	11.21	10.71	1.92	8.65	8.18
1.62	11.01	10.51	1.94	8.65	8.19
1.64	10.80	10.30	1.96	8.70	8.23
1.66	10.59	10.09	1.98	8.77	8.31
1.68	10.38	9.88	2.00	8.88	8.42
1.70	10.17	9.67	2.02	9.03	8.56
1.72	9.96	9.46	2.04	9.23	8.74
1.74	9.75	9.25	2.06	9.46	8.98
1.76	9.55	9.05	2.08	9.72	9.28
1.78	9.36	8.86	2.10	10.00	9.60
1.80	9.18	8.68	2.12	10.29	9.94
1.82	9.03	8.53	2.14	10.60	10.29
1.84	8.92	8.42	2.16	10.92	10.64
1.86	8.82	8.32	2.18	11.24	10.99
1.88	8.74	8.25			

¹¹ Yarnell, Arnold, Bendt, and Kerr, preceding paper [Phys. Rev. **113**, 1379 (1959)].

TABLE III. Calculated values for thermodynamic properties of liquid helium II.

Temp. °K	Entropy S joules/mole-deg	Specific heat C_s joules/mole-deg	Normal fluid density ρ_n g/cm ³	ρ_n/ρ^a	Second sound velocity v_2 using Eq. (16) m/sec	Second sound velocity v_2 using Eq. (17) m/sec
0.2	2.22×10^{-4}	6.65×10^{-4}	2.85×10^{-8}	1.96×10^{-7}	137.4	137.4
0.3	7.49×10^{-4}	2.25×10^{-3}	1.44×10^{-7}	9.90×10^{-7}	137.4	137.4
0.4	1.78×10^{-3}	5.33×10^{-3}	4.59×10^{-7}	3.15×10^{-6}	136.9	136.9
0.5	3.47×10^{-3}	0.0105	1.33×10^{-6}	9.16×10^{-6}	125.0	125.0
0.6	6.12×10^{-3}	0.0199	5.96×10^{-6}	4.10×10^{-5}	83.2	83.2
0.7	0.0105	0.0407	3.11×10^{-5}	2.14×10^{-4}	47.2	47.2
0.8	0.0187	0.0906	1.27×10^{-4}	8.70×10^{-4}	29.9	29.9
0.9	0.0349	0.199	3.91×10^{-4}	2.69×10^{-3}	22.6	22.6
1.0	0.0654	0.404	9.74×10^{-4}	6.70×10^{-3}	19.8	19.9
1.1	0.119	0.749	2.07×10^{-3}	0.0142	18.9	19.1
1.2	0.205	1.28	3.91×10^{-3}	0.0268	18.9	19.2
1.3	0.336	2.05	6.72×10^{-3}	0.0462	19.2	19.7
1.4	0.526	3.11	0.0108	0.0745	19.7	20.4
1.5	0.785	4.52	0.0165	0.113	20.0	21.2
1.6	1.13	6.42	0.0241	0.166	20.1	22.0
1.7	1.59	8.82	0.0342	0.235	20.0	22.8
1.8	2.18	12.1	0.0473	0.325	19.2	23.4
1.9	2.95	16.3	0.0647	0.443	17.8	23.9
2.0	3.93	22.4	0.0874	0.599	15.2	24.0
2.1	5.26		0.120	0.818		

^a Values of liquid helium density ρ are given in Table I.

1.58 and 2.18 \AA^{-1} as were computed by interpolation. Values of ρ_n/ρ obtained from specific heat¹² and second sound velocity¹³ measurements were used. We claim no theoretical justification for the use of ρ_n/ρ in the interpolations. It should be noted, however, that the agreement of the calculated values of ρ_n using Eq. (12) with measured values would be approximately as good using any of the interpolation formulas given above.

An integration mesh was formed by dividing the four intervals respectively into 100, 50, 30, and 90 sub-intervals, except that 500 sub-intervals were used in interval 1 for temperatures $\leq 0.7^\circ\text{K}$. The integrals were evaluated using the five-interval quadrature formula,¹⁴

$$\int y dx = \sum_i \left\{ \frac{5g}{288} \sum_i c_i y_i \right\}, \quad (18)$$

where the y_i are equally spaced values of the integrand at the limits of sub-intervals of width g , and the weighting factors c_i have the values 19, 75, 50, 50, 75, and 19, respectively. The first summation is over j sets of five sub-intervals each, and the second summation is over the six values of y_i accompanying each set of sub-intervals. Errors in the numerical integration are of the order of 0.01% or less.

The specific heat was calculated by five-point numerical differentiation with respect to T of the results for entropy, using $C_s = T(dS/dT)_s$.¹⁵ The formula used

¹² Kramers, Wasscher, and Gorter, *Physica* **18**, 329 (1952); Wiebes, Niels-Hakkenberg, and Kramers, *Physica* **23**, 625 (1957).
¹³ R. D. Maurer and M. A. Herlin, *Phys. Rev.* **76**, 948 (1949); **81**, 444 (1951); de Klerk, Hudson, and Pellam, *Phys. Rev.* **93**, 28 (1954).

¹⁴ J. B. Scarborough, *Numerical Mathematical Analysis* (The John Hopkins Press, Baltimore, 1955), third edition, p. 131.

¹⁵ For $T \leq 0.6^\circ\text{K}$, C_s was calculated using Eqs. (3) and (8) with $dE_j(T)/dT$ set equal to zero.

was

$$C_s(T) = \frac{T}{1.2} \{ -S(T+0.2) + 8S(T+0.1) - 8S(T-0.1) + S(T-0.2) \}, \quad (19)$$

where T is in $^\circ\text{K}$. The error in differentiation was less than 0.1% for temperatures $\leq 1.8^\circ\text{K}$, and less than 1% at higher temperatures.

V. COMPARISON WITH CRYOGENIC MEASUREMENTS

The contributions of each of the four momentum intervals to the calculated entropy are shown as functions of temperature in Fig. 2. This figure shows that the division of the excitations into phonons (interval 1) and rotons (interval 3) is natural, as these two intervals

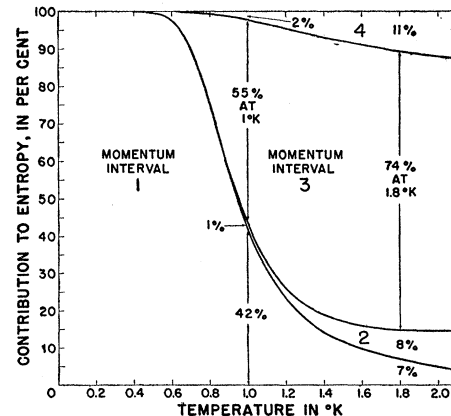


Fig. 2. Contributions of each of the four momentum intervals to the total entropy of liquid helium II, as functions of temperature.

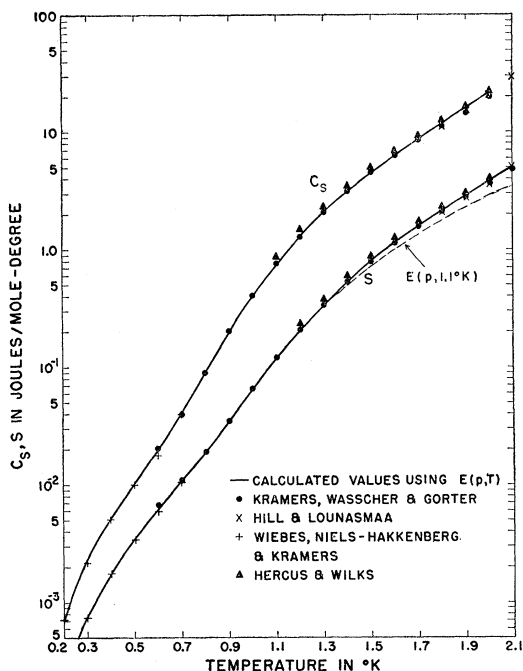


FIG. 3. Comparison of calculated and experimental values of entropy and specific heat of liquid helium II. The dashed line was calculated disregarding the temperature dependence of the excitation curve.

make the major contributions. This figure also shows that at temperatures above 0.6°K , the specific heat should no longer follow the T^3 law, which holds when only phonons are excited.

The results of calculations of entropy S and specific heat C_s are tabulated in Table III, and are also shown as solid lines in Fig. 3. Calorimetric measurements of these quantities are also shown in Fig. 3. Hill and Lounasmaa¹⁶ have stated that the measurements of Hercus and Wilks,¹⁷ which are about 10% higher than those of Kramers, Wasscher, and Gorter,¹² are probably in error.

Calculations of the entropy were also made in which the temperature dependence of the excitation curve was neglected. The excitation curve for 1.1°K was used for all temperatures, and $dE(p,T)/dT$ was set equal to zero. The values for entropy obtained in this way are shown as a dashed line in Fig. 3.

Figure 4 shows the deviation in percent of the calculated entropy from the calorimetric measurements of Wiebes, Niels-Hakkenberg, and Kramers,¹² at temperatures below 0.7°K , and from measurements of Kramers, Wasscher, and Gorter¹² at temperatures from 0.7 to 2.1°K . The calculated values agree with the measured values to within $\pm 3\%$ at all temperatures between 0.2 and 1.85°K .¹⁸ The deviation of the specific heat C_s

from measurements, not shown in Fig. 4, is $\pm 4\%$ between 0.2 and 1.7°K . If the numerical fit to the excitation curve used in the calculations was shifted to the limit of the experimental error quoted for the neutron scattering measurements in the preceding paper¹¹ ($\pm 0.1^\circ\text{K}$ energy equivalent in the minimum), the change in the calculated values of S and C_s would be about 5%. The deviation of the entropy curve calculated by neglecting the temperature dependence of the excitation curve is also shown in Fig. 4, and displays strikingly poorer agreement with calorimetric measurements above 1.3°K .

The entropy was also calculated using the excitation curve of Palevsky, Otnes, Larsson, Pauli, and Stedman¹⁹ in the region of the minimum (roton region). They state the temperature of the helium target for their measurements was 1.4 to 1.5°K . In order to obtain a complete excitation curve over the momentum range used in the calculations, we have used the velocity of first sound at 1.4°K for the slope in momentum intervals 1 and 4, and have matched the linear relation in interval 4, and our inverted parabola in interval 2, to join the Stockholm data smoothly. For the energy minimum between $1.72 \leq p/\hbar \leq 2.15 \text{ \AA}^{-1}$, we have used the parabola for which parameters are given by the authors. These parameters are $\Delta/k = 8.1^\circ\text{K}$, $p_0/\hbar = 1.90 \text{ \AA}^{-1}$, and $\mu = 0.16m(\text{He})$, [$m(\text{He})$ is the mass of a helium atom]. The calculated entropy obtained in this way is shown in Fig. 4, and lies 22% above the calorimetric

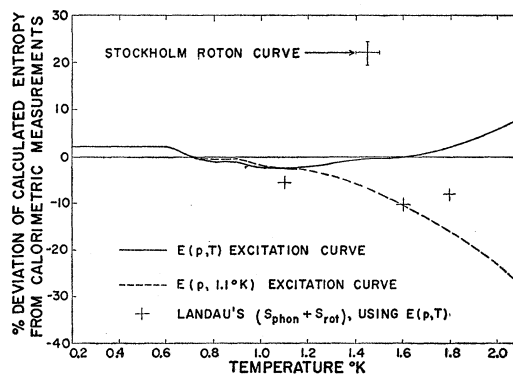


FIG. 4. Deviation of calculated entropies from measurements by Wiebes, Niels-Hakkenberg, and Kramers ($< 0.7^\circ\text{K}$), and from Kramers, Wasscher, and Gorter ($\geq 0.7^\circ\text{K}$). "Stockholm roton curve" is based on measurements by Palevsky, Otnes, Larsson, Pauli, and Stedman. ($S_{\text{phon}} + S_{\text{rot}}$) was calculated using Landau's equations based on an approximation of the excitation curve by two functions, one linear and one parabolic.

Wiebes, Niels-Hakkenberg, and Kramers, and from the fact that only the phonon region makes a contribution to the calculated entropy. Since the slope of the energy-momentum relation in interval 1 was determined from the sound velocity measurements, the 2% deviation below 0.6°K implies nothing about the accuracy of the neutron scattering measurements, but does indicate consistency between specific heat and sound velocity measurements, as pointed out by Wiebes, Niels-Hakkenberg, and Kramers.

¹⁹ Palevsky, Otnes, Larsson, Pauli, and Stedman, Phys. Rev. **108**, 1346 (1957); Palevsky, Otnes, and Larsson, Phys. Rev. **112**, 11 (1958).

¹⁶ R. W. Hill and O. V. Lounasmaa, Phil. Mag. **2**, 143 (1957).

¹⁷ G. R. Hercus and J. Wilks, Phil. Mag. **45**, 1163 (1954).

¹⁸ The straight-line portion below 0.6°K of the curve in Fig. 4 results from the T^3 dependence of the specific heat reported by

measurement. The reason the Stockholm data gives a higher value of entropy than the measurements reported in the preceding paper¹¹ is that their value of Δ/k for the roton minimum is 0.45°K lower than the value obtained by interpolation to 1.4°K of the Los Alamos measurements. The Stockholm data gives a value for the entropy in agreement with Kramers, Wasscher, and Gorter if calculations are made for 1.8°K .

Parabolic fits to the minimum in the excitation curve are reported in the preceding paper for each of the three temperatures at which the curve was measured. The parameters of the parabolas are: Δ/k equals 8.65°K (for $T=1.1$), 8.43°K (for $T=1.6$), and 8.15°K (for $T=1.8^\circ\text{K}$); p_0/\hbar equals 1.92 \AA^{-1} for all temperatures and $\mu=0.16m(\text{He})$ for all temperatures. We have used Landau's¹ formulas and calculated the contribution to S of phonons and rotons for the three temperatures. The values of $(S_{\text{phon}}+S_{\text{rot}})$ are plotted in Fig. 4, and lie below the calorimetric measurements, by 5 to 10%. This is expected, since the excitation curve in Landau's phonon and roton analysis lies above the observed curve in the region of the maximum, and also to the right of the minimum.

Values of the normal fluid density ρ_n calculated using Eq. (12) are given in Table III. These have been divided by experimental values²⁰ of ρ , given in Table I, and are plotted as a solid line in Fig. 5. Also included in Fig. 5 are values of ρ_n/ρ obtained from torsion pendulum measurements,²¹ and values calculated from Eq. (16)

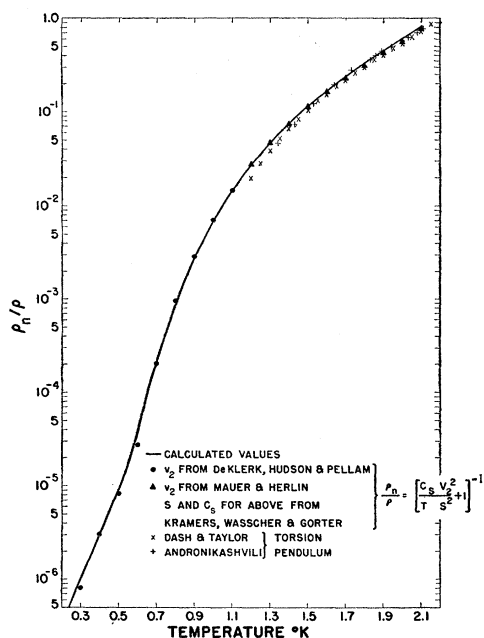


Fig. 5. Comparison of calculated and experimental values of ρ_n/ρ . Values of ρ are from reference 20.

²⁰ E. C. Kerr, J. Chem. Phys. **26**, 511 (1957); K. R. Atkins and M. H. Edwards, Phys. Rev. **97**, 1429 (1955).

²¹ E. L. Andronikashvili, J. Exptl. Theoret. Phys. U.S.S.R. **18**, 424 (1948); J. G. Dash and R. D. Taylor, Phys. Rev. **105**, 7 (1957).

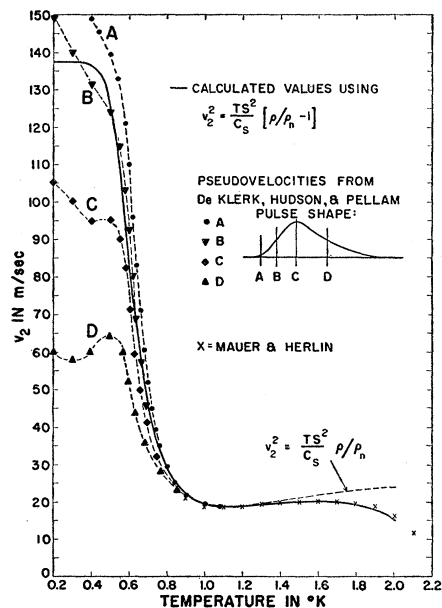


Fig. 6. Comparison of calculated and experimental values of second sound velocity. Curves A, B, C, D show dispersion of heat pulses at low temperatures.

using specific heat and entropy data from Kramers, Wasscher, and Gorter, and from Wiebes, Niels-Hakkenberg, and Kramers,¹² and second sound velocity data from Mauer and Herlin, and from de Klerk, Hudson, and Pellam.¹³ The agreement between the calculations and the values of ρ_n/ρ obtained from second sound measurements is within $\pm 8\%$ over the temperature range 0.7 to 2.0°K , and is within $\pm 5\%$ between 1.1 and 1.9°K . The torsion pendulum measurements of ρ_n/ρ are systematically lower than the values obtained from second sound velocity measurements, the difference increasing toward the low-temperature limit of the torsion pendulum measurements. At 1.2°K the discrepancy is 27%.²²

The velocity of second sound was computed by substituting calculated values of S , C_s , and ρ_n into Eq. (16). The results are tabulated in Table III, and are plotted as a solid line in Fig. 6. The calculations agree with measurements of de Klerk, Hudson, and Pellam, and of Mauer and Herlin¹³ to within $\pm 4\%$ over the temperature range from 0.8 to 1.8°K , and within $\pm 2\%$ between 1.0 and 1.7°K . Below 0.7°K , the mean free path of excitations is comparable to the dimensions of the apparatus which was used to measure second sound velocity. At these low temperatures, the second sound heat pulses undergo dispersion in transmission, and curve A in Fig. 6 represents the velocity of the leading edge of the pulse, as reported by de Klerk, Hudson, and

²² The quantity ρ_n/ρ was used to interpolate the excitation curve between temperatures at which the excitation energy was measured, but since measurements were made at 1.1°K , any reasonable interpolation to 1.2°K would still yield calculated values of ρ_n/ρ in disagreement with torsion pendulum measurements.

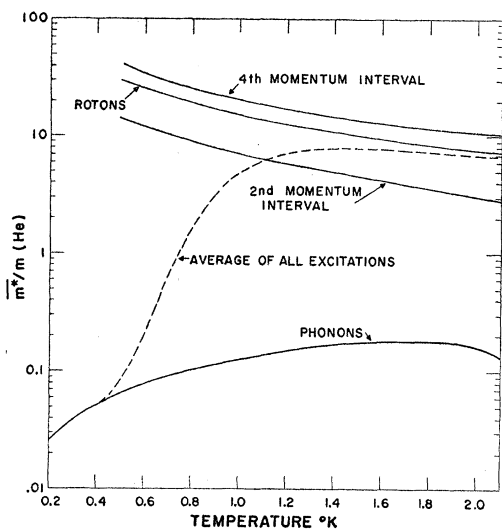


FIG. 7. Average values, for each momentum interval, of the effective mass of the excitations, as defined by Landau. The quantity $m(\text{He})$ is the mass of a He^4 atom. The average value for all the excitations is also shown.

Pellam. Curve *B* is the velocity of the point of steepest rise on the leading side of the pulse, curve *C* is the velocity of the highest point of the pulse, and curve *D* is the velocity of the point of steepest descent on the back side of the pulse. Curve *A* approaches the velocity of first sound at zero temperature, and is apparently due to phonons which make very few collisions between the radiator and the detector. The calculated curve, which agrees pretty well with curve *B*, approaches Landau's value of $v_2 = v_1/\sqrt{3}$ at zero temperature.

Calculations were also made using Eq. (17), and the results are tabulated in Table III, and plotted as a dashed line in Fig. 6. The calculated values are higher than experimental measurements above 1.3°K.

VI. EFFECTIVE MASS OF THE EXCITATIONS AND KHALATNIKOV COEFFICIENTS

The effective mass m^* of the excitations as defined by Landau is discussed in Sec. III. We have calculated weighted averages,

$$\bar{m}^* = \frac{\int n(p)m^*(p)dp}{\int n(p)dp}, \quad (20)$$

for each momentum interval, and the results are shown in Fig. 7. The curves for intervals 1 and 3 have been labeled "phonons" and "rotons" respectively. The decrease in \bar{m}^* for phonons above 1.8°K does not have any fundamental significance; it is due to the peculiarity of the calculation, in which p_1/\hbar , the boundary between intervals 1 and 2, shifts from 0.56 \AA^{-1} at 1.8°K, to 0.43 \AA^{-1} at 2.1°K. Figure 7 shows that all of the excitations, other than phonons, may be considered "heavy," and that the average effective mass of rotons varies

from about 40 to 500 times the average effective mass of phonons.

When the distribution $n(\mathbf{p}, \mathbf{r})$ of excitations in liquid helium deviates from the equilibrium distribution, here designated $n_0(p)$, then $n(\mathbf{p}, \mathbf{r})$ can be obtained by solving an equation of continuity in position and momentum space.²³ Khalatnikov has studied the case where the spacial derivatives of quantities defining the state of the system are small. He obtains an expression²⁴ for the deviation from equilibrium $n(\mathbf{p}, \mathbf{r}) - n_0(p)$ which contains three coefficients, *A*, *B*, and *C*, whose values are determined by the nature of the interactions between excitations. In general, *A*, *B*, and *C* are functions both of momentum and temperature. The nonequilibrium properties of the excitation gas, such as the viscosity η of the normal fluid, the thermal conductivity κ , and four coefficients of second viscosity, depend on *A*, *B*, and *C*. Theoretical expressions for the coefficients of second viscosity, as well as for Khalatnikov's coefficient *A*, all depend on knowledge of $\partial E(p, T)/\partial p$, for which there are insufficient experimental data to make calculations.

Khalatnikov gives the following expression for viscosity:

$$\eta = \frac{4\pi}{15kTh^3} \int_0^\infty C(p, T)n_0(p)[n_0(p)+1] \frac{\partial E}{\partial p} p^4 dp, \quad (21)$$

where *E* is the excitation energy; and for thermal

TABLE IV. Calculated values of Khalatnikov coefficients. η is viscosity and κ is thermal conductivity of liquid helium II.^a

Temp. °K	η/\bar{C} poise/sec	$-\kappa/\bar{B}$ joules/ deg-cm-sec ²	$\bar{C} = \eta/(\eta/\bar{C})$ seconds	$-\bar{B} = \kappa/(-\kappa/\bar{B})$ seconds
0.2	3.23			
0.3	1.63×10			
0.4	5.16×10	2.53×10^9		
0.5	1.29×10^2	1.17×10^{11}		
0.6	3.18×10^2	7.53×10^{11}		
0.7	9.60×10^2	1.77×10^{12}		
0.8	3.19×10^3	3.25×10^{12}	2.51×10^{-8}	2.25×10^{-7}
0.9	9.60×10^3	5.75×10^{12}	4.38×10^{-9}	2.63×10^{-8}
1.0	2.48×10^4	1.01×10^{13}	1.19×10^{-9}	5.80×10^{-9}
1.1	5.53×10^4	1.71×10^{13}	4.07×10^{-10}	1.76×10^{-9}
1.2	1.10×10^5	2.78×10^{13}	1.64×10^{-10}	6.13×10^{-10}
1.3	2.01×10^5	4.31×10^{13}	7.46×10^{-11}	2.55×10^{-10}
1.4	3.41×10^5	6.43×10^{13}	3.93×10^{-11}	1.21×10^{-10}
1.5	5.45×10^5	9.20×10^{13}	2.31×10^{-11}	
1.6	8.37×10^5	1.28×10^{14}	1.46×10^{-11}	
1.7	1.25×10^6	1.72×10^{14}	9.76×10^{-12}	
1.8	1.80×10^6	2.27×10^{14}	7.06×10^{-12}	
1.9	2.58×10^6	2.94×10^{14}	5.27×10^{-12}	
2.0	3.65×10^6	3.76×10^{14}	4.19×10^{-12}	
2.1	5.26×10^6	4.83×10^{14}	3.40×10^{-12}	

^a Values of η and κ are from smooth curves drawn through measurements by Zino'eva and by Heikkila and Hollis-Hallett (reference 25).

²³ I. M. Khalatnikov, Uspekhi Fiz. Nauk 59, 673 (1956) (translation by M. G. Priestley), Eq. (12.1).

²⁴ I. M. Khalatnikov, reference 23, Eq. (13.9).

conductivity:

$$\kappa = \frac{4\pi}{3kT^2h^3} \int_0^\infty B(p,T)n_0(p)[n_0(p)+1] \times \frac{\partial E}{\partial p} \left(\frac{pST}{\rho_n} - E \frac{\partial E}{\partial p} \right) p^2 dp. \quad (22)$$

The thermal conductivity κ is that which exists when there is no temperature-induced flow of normal fluid or superfluid. κ is obtained from measurements of the attenuation of second sound. The amount of heat transported by thermal conductivity (for a given temperature gradient) is only 10^{-6} or 10^{-7} as large as by convection of the normal fluid component.

We have calculated the integrals Eqs. (21) and (22), without the factors $C(p,T)$ and $B(p,T)$, and the results are given in Table IV. By comparing calculations with smooth curves drawn through measurements of η and κ by Zinov'eva and by Heikkila and Hollis-Hallet,²⁵ we obtain average values \bar{C} and \bar{B} (a negative number) for the Khalatnikov coefficients, averaged over all momenta. $-\bar{B}$ and \bar{C} are given in Table IV and plotted in Fig. 8. According to Khalatnikov, these coefficients, which have units of seconds, are proportional to the average time between collisions of "heavy" excitations.²⁶ If the velocity and the cross sections of the excitations are not strongly temperature dependent, then we would expect the curves for $-\bar{B}$ and \bar{C} to be similar to a plot of $1/N_{\text{heavy}}$, the reciprocal of the number of "heavy" excitations. The quantity $1/N_{\text{heavy}}$, and also $1/N$, the reciprocal of the total number of excitations, are plotted in Fig. 8 for comparison. The order of magnitude of the calculated coefficients seems to be correct to represent collision times.

²⁵ K. N. Zinov'eva, J. Exptl. Theoret. Phys. **31**, 31 (1956) [translation: Soviet Phys. JETP **4**, 36 (1957)]; W. J. Heikkila and A. C. Hollis-Hallet, Can. J. Phys. **33**, 420 (1955).

²⁶ I. M. Khalatnikov, reference 23, see discussion of Eqs. (14.2) to (14.6).

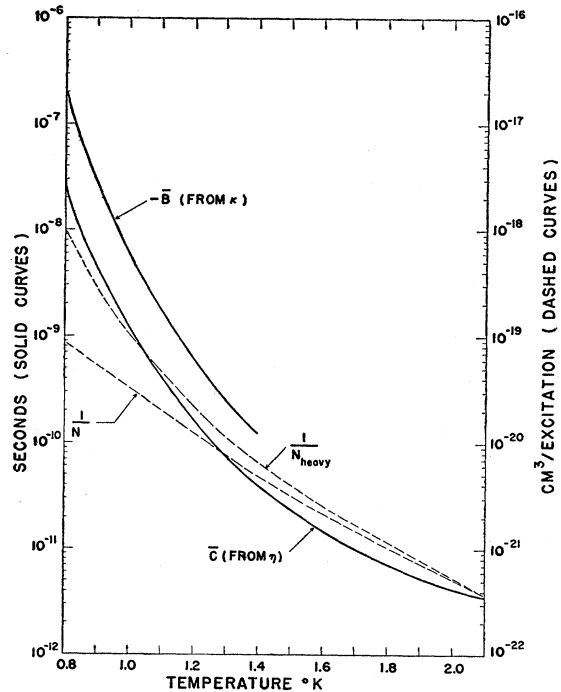


FIG. 8. Average values of the Khalatnikov nonequilibrium kinetic coefficients $-B$ and C , as well as the reciprocal $1/N_{\text{heavy}}$ of the number of "heavy" excitations, and the reciprocal $1/N$ of the total number of excitations.

The average Khalatnikov coefficients are included in this paper because they can be calculated from the measured excitation curve, and because it is hoped that they may prove useful in evaluating the validity of Khalatnikov's theory.

ACKNOWLEDGMENTS

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