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Thermal Excitations in Liquid He^3

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Using recently obtained data on various thermal properties of liquid He^3, the constant-volume heat capacity of the saturated liquid has been evaluated. This elementary heat capacity $C_v(T)$ was found to exhibit at least three inflection points over the temperature interval extending to the critical temperature. Of these, the one at the lowest temperature was shown to originate with the partial heat capacity of spin disorder. The inflection point at the approach of the critical temperature T_c is imposed by the thermodynamic result that $C_v(T)$ should reach its finite limit $C_v(T_c)$ from below with positively infinite first and second temperature derivatives. The laws governing the pressure dependence of the partial spin heat capacity over the liquid region of the He^3 phase diagram have been deduced. The remarkable pressure effects displayed by the spin system of liquid He^3 through its heat capacity may be expected to manifest themselves through the observable pressure dependence of the total liquid heat capacity at low enough temperatures where the spin heat capacity is dominant. A purely heuristic and indirect approach toward the problem of the existence of phonon type of partial excitations in liquid He^3 yields a negative answer, without, however, a definite exclusion of such symmetrical excitations in this antisymmetric liquid.

1. INTRODUCTION

THE fundamental problem raised by the application of the two kinds of statistics to the description of the thermal properties or the two liquid helium isotopes is, in principle, susceptible of solution. This requires first the determination of the characteristic energy spectrum of the N-atom system formed by these liquids, N being a number of the order of magnitude of Avogadro's number. With the available spectra, the canonical ensemble formalism, duly adapted to these quantum systems, should lead to a complete description of the equilibrium statistical thermodynamics of these systems. The difficulties of physical and analytical nature arising in the systematic attack on the problem of liquid helium appear to justify an indirect approach, grounded on the empirical knowledge of the various thermal properties of the liquid helium isotopes. Studies of these thermal properties within the framework of the formalism of statistical thermodynamics should lead to a description of these quantities which could be precise enough to reappear essentially unmodified in their formulation resulting from the more fundamental approach.

In the present paper we should like to give an account of an analysis of the thermal excitations in liquid He^3. The nature of these excitations has been studied on the basis of the simplest macroscopic conditions imposed on the liquid, that is under constant volume. Hence, the physically simplest heat capacity of the liquid, that is its constant-volume heat capacity, had to be obtained first, since this quantity is the temperature rate of variation of the sum total of all its internal thermal energy of excitation at a given temperature of the liquid. This constant-volume heat capacity may then be submitted to an analysis in terms of the excitations referring to various types of degrees of freedom of the liquid. In liquid He^3 the partial orientational spin excitations introduced previously[1] will appear to emerge clearly as the dominant thermal excitations at low temperatures. Other partial excitations failed to be describable, without considerable reserve, in terms of phonons. Several arguments of elementary physical character will be shown to deny the very existence of such partial symmetric excitations in liquid He^3. These same arguments used in connection with liquid He^4I cast doubt also on the unreserved validity of the assumption which allows phonon-type excitations to be effectively present in the high-temperature phase of liquid He^4.

In the course of the present work, a major effort was also made toward a complete clarification of the properties of the spin system in compressed liquid He^3, that is throughout the whole liquid region of its phase diagram. These investigations have disclosed a series of remarkable properties of the spin heat capacity of the liquid under external pressure. The experimental determination of the pressure dependence of total liquid heat capacity at low temperatures should lead to a clear recognition of the influence of the spin system on this and other thermal properties of liquid He^3 in this low-temperature range, where it becomes dominant.

2. VARIOUS TYPES OF HEAT CAPACITIES OF LIQUID He^3

The experimentally measured heat capacity of liquids refers, in general, to that of the saturated liquid. The same remark applies to other thermal properties such as the density, for instance, and the associated volume expansion coefficient. The saturated-liquid heat capacity is a fairly complex property, since a displacement along the saturation line in any one of the representative planes of the thermodynamic variables involves simultaneous changes in all the variables of state. The saturated-liquid heat capacity $C_s(T)$ is thus a function of three variables such as

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[1] L. Goldstein, Phys. Rev. 96, 1455 (1954); 102, 1205 (1956).

(p,V,T). The more elementary heat capacities such as the constant-pressure heat capacity C_p, or, above all, the constant-volume heat capacity C_v, are not expressed usually in terms of the more easily accessible $C_s(p,V,T)$. It seemed thus of interest, even necessary, to derive the expressions for C_p and C_v, and their ratio C_p/C_v or γ, in terms of C_s, and other properties of the saturated liquid, such as the density ρ, the associated expansion coefficient α_s, the velocity u of low-frequency sound waves in the saturated liquid, and the vapor pressure $p(T)$, all of which quantities are directly accessible to measurements.

One may start with the thermodynamic relations

$$c_p=c_s+T(\partial v/\partial T)_p(dp/dT), \tag{1}$$

$$c_v=c_s-T(\partial p/\partial T)_v(dv/dT), \tag{2}$$

where the c's are specific heats; v is the specific volume of the saturated liquid or ρ^{-1}. The partial derivatives are to be obtained with the help of the equation of state; the total derivatives are the slopes of the phase separation lines in the (p,T) and (v,T) thermodynamic planes, respectively. The derivative dp/dT is thus the slope of the vapor pressure line, while dv/dT is $\alpha_s v$. Equations (1) and (2), and the additional thermodynamic relation

$$c_p-c_v=T(\partial p/\partial T)_v(\partial v/\partial T)_p, \tag{3}$$

together with the equation of state, yield

$$\begin{aligned}\alpha_p&=v^{-1}(\partial v/\partial T)_p\\&=\alpha_s+\chi_T(dp/dT)\\&=\alpha_s+(\gamma/\rho u^2)(dp/dT),\end{aligned} \tag{4}$$

the normal expansion coefficient, under constant pressure, of the saturated liquid. The last of Eqs. (4) makes use of the expression of the velocity of small-amplitude sound waves in terms of the density and adiabatic compressibility χ_s or χ_T/γ, χ_T being the isothermal compressibility of the liquid. Combining the above equations, one obtains, after some algebra,

$$\begin{aligned}\gamma&=c_p/c_v\\&=[1+A(1+B^{-1})]/[1-A(1+B)],\end{aligned} \tag{5}$$

$$\begin{aligned}A&=(T\alpha_s/\rho c_s)(dp/dT),\\B&=(dp/dT)/(\rho u^2\alpha_s).\end{aligned} \tag{6}$$

Using again (1) and (2) with (4) and (5), one obtains

$$c_p=c_s/[1-A(1+B)], \tag{7}$$

$$c_v=c_s/[1+A(1+B^{-1})]. \tag{8}$$

The more elementary specific heats c_p and c_v, and their ratio γ, have now been expressed in terms of the properties, ρ, α_s, c_s, u, and dp/dT, all relative to the saturated liquid whose knowledge is necessary for its complete thermodynamic description. The specific heats c_p and c_v refer to the saturated liquid along isobars and isopycnals starting at the liquid saturation line and in its geometrical vicinity.

In He^3, densities of the saturated liquid and vapor,[2] vapor pressure,[3] heat capacity[4] C_s, and sound velocity[5] have all been measured over fairly wide temperature intervals. The thermodynamic relations (5), (7), and (8) yield with these data the heat-capacity ratio γ, and the elementary heat capacities C_p and C_v from about 0.5°K to temperatures close to the critical temperature, with a temperature gap to be discussed below.

The procedure followed in the evaluation of these quantities was to fit, by the method of least squares, the density $\rho(T)$, heat capacity $C_s(T)$, and sound velocity $u(T)$, by analytic expressions in the temperature T. These analytical fits reproduced with good approximations the observed data and, with the exception of the critical region, they have been used to extrapolate these properties somewhat outside the temperature range of the data. Actually, this type of extrapolation involved mainly the heat capacity C_s, which has only been measured with sufficient precision between about 0.4 and 2.0°K by the Los Alamos and Argonne workers.[4] Very recently these heat-capacity data have been extended[6] down to about 0.10°K. However, these results are somewhat of preliminary character and their full discussion could not be justified at the present time.

The observed liquid and vapor densities as analyzed by Kerr[2] clearly suggest that the rectilinear diameter law is fairly well obeyed by He^3. A new discussion of these data shows that the average densities of the liquid and vapor, $\frac{1}{2}[\rho_L(T)+\rho_{\text{vap}}(T)]$, were distributed around the mean of these with small standard deviation.[7] This mean value is the calculated critical density, which was found to be 0.04124 g/cc. The various types of least-square fits[8] of the density curves $\rho_L(T)$ and $\rho_{\text{vap}}(T)$, of the liquid and vapor, as a double-valued function of the temperature, along the lines suggested

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[2] E. C. Kerr, Phys. Rev. **96**, 551 (1954); Grilly, Hammel, and Sydoriak, Phys. Rev. **75**, 1103 (1949); W. E. Keller, Phys. Rev. **98**, 1571 (1954).

[3] Sydoriak, Grilly, and Hammel, Phys. Rev. **75**, 303 (1949); Abraham, Osborne, and Weinstock, Phys. Rev. **80**, 366 (1950); S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).

[4] G. de Vries and J. G. Daunt, Phys. Rev. **92**, 1572 (1953); **93**, 631 (1954); T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954); **98**, 1672 (1955); Osborne, Abraham, and Weinstock, Phys. Rev. **98**, 551 (1955).

[5] Laquer, Sydoriak, and Roberts, *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, Ohio, 1958), p. 15, and to be published. In a more restricted temperature range, similar measurements have also been reported by H. Flicker and K. R. Atkins, *Symposium on Liquid and Solid* He^3, (Ohio State University Press, Columbus, Ohio, 1958), p. 11.

[6] Brewer, Sreedhar, Kramers, and Daunt, Bull. Am. Phys. Soc. Ser. II, **3**, 133 (1958). We wish to thank here Dr. J. G. Daunt for communication of these results before publication.

[7] Dr. R. K. Zeigler of this Laboratory was kind enough to look into the statistical analysis of the density data.

[8] These types of least-square fits with double-valued functions have been studied by Mr. Paul E. Harper of this Laboratory. His cooperation was most appreciated.

by Kerr,[2] have all led to location of the critical temperature in the close vicinity of 3.4°K, with critical densities very near the above-mentioned value. The latter is practically the same as the one obtained by Kerr.[2] These studies all suggest that the saturated liquid and vapor density data were complete enough to enable one to obtain their satisfactory analytical approximate description, which in turn, yielded fairly good approximations of the liquid, or vapor, expansion coefficient α_s. The latter is anomalous at the approach of the critical point, where it becomes infinite.

The Los Alamos sound velocity data[5] extend over a wide temperature interval. However, the use of their analytical fit $u(T)$ to the close vicinity of the critical point, and to the critical point itself, is necessarily of unknown and somewhat questionable accuracy.

With the various limitations which are involved in the use of the data entering into the rigorous thermodynamic expressions (5), (7), and (8), whereby the temperature derivative (dp/dT) of the vapor-pressure curve is known with fair accuracy,[3] we are now prepared to discuss the calculated elementary heat capacities $C_p(T)$ and $C_v(T)$ and their ratio $\gamma(T)$.

The calculated molar heat capacities,[9] C_p/R, C_v/R, their ratio γ, as well as the graph of the analytical fit to the experimental molar saturated-liquid heat capacity C_s/R, are given in Fig. 1. Because of the extrapolated character of the C_s/R function beyond 2.0°K, this graph should be considered as divided essentially in two parts. The one extending up to 2.0°K represents a fairly well-established group of results. The region above 2.0°K is based on an analytical type of assumption on the functional behavior of C_s/R, and will have to be revised more or less depending on the degree of approximation achieved by the assumed shape of the extrapolated C_s/R function when compared with future data on this quantity.

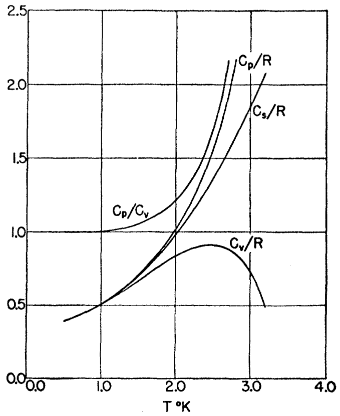

FIG. 1. Various molar heat capacities and the C_p/C_v ratio of liquid He³ *vs* the temperature. The portions of the curves above 2.0°K are based on extrapolations (see the text).

It is evident on the graph of γ that this ratio rises above unity, a little above 1.0°K. Actually, of course, γ is always larger than unity at finite temperatures, but its excess over unity is not accessible experimentally below some temperature. In liquid He³, this temperature appears to be about 1.0°K. The constant volume heat capacity $C_v(T)$ thus distinctly detaches itself from $C_s(T)$ or $C_p(T)$ at about 1.1–1.2°K, falling necessarily below the values of the latter. While below 1.0°K these heat capacities, being coincident practically, are all concave upward, that is

$$d^2C_j/dT^2>0, \quad (j=s,v,p), \quad T\lesssim 1.0°\text{K}, \tag{9}$$

two of them are such that

$$d^2C_p/dT^2>0, \quad d^2C_s/dT^2>0, \quad 0.5°\text{K}\leqslant T\leqslant T_c, \tag{10}$$

that is, these are concave upward over the indicated temperature interval, increasing monotonically toward infinity at T_c, together with the ratio γ.

Since this ratio γ is always larger than unity, we obtain with (5) or (6) a lower limit of the saturated-liquid specific heat c_s, by requiring the denominator of (5) to be positive. This lower bound of c_s, or $c_{s,\lambda}$, is such that

$$c_{s,\lambda}=(T\alpha_s/\rho)(dp/dT)+[T/(\rho u)^2](dp/dT)^2. \tag{11}$$

This lower bound of c_s may thus be said to be composed of two partial heat capacities, the first of which,

$$c_{s,\lambda}^{(1)}=(T\alpha_s/\rho)(dp/dT), \tag{12}$$

is connected with the expansion of the saturated liquid through its linear dependence on the expansion coefficient α_s, while the second term is independent of this expansion and is actually the constant-volume part of $c_{s,\lambda}$, or

$$c_{sv,\lambda}=[T/(\rho u)^2](dp/dT)^2. \tag{13}$$

As the temperature of the liquid increases toward the critical temperature T_c, the latter partial heat capacity tends toward a finite limit, so that

$$\lim_{T\to T_c} c_{s,\lambda}\geqslant (T/\rho)(dp/dT)\alpha_s, \tag{14}$$

and in the close vicinity of T_c, c_s itself tends to become identical with $c_{s,\lambda}^{(1)}$, becoming infinite at T_c with α_s.

The lower bound $c_{s,\lambda}$, by Eq. (8), depends on the sound velocity u, which quantity has to be extrapolated beyond about 3.20°K, if this lower bound is to be evaluated numerically. The study of $c_{s,\lambda}$ appeared to be instructive enough in the critical region, even though it could only be obtained with some approximation through the extrapolated sound-velocity values. Using one of the least-square fits of $u(T)$ and $\rho(T)$, whereby the latter density expression locates the critical point at somewhat below 3.40°K and the critical

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[9] Special thanks are due to Mrs. J. E. Powers for the major part of the numerical calculations. Mrs. B. Fagan and Miss D. Cooper have kindly cooperated through various numerical work, and Mrs. A. S. Luders and Mrs. B. M. Hindman through the drawing of the graphs.

TABLE I. Calculated sound velocities, expansion coefficients, and lower bounds of the component and total heat capacity in liquid He^3 in the critical region.

T (°K)	T/T_c	u (m/sec)	α_s $(°K)^{-1}$	$C_{sv,\lambda}/R$	$C_{s,\lambda}^{(1)}/R$	$C_{s,\lambda}/R$
3.20	0.9419	99.0	0.690	0.397	1.466	1.863
3.25	0.9566	94.73	0.850	0.508	1.970	2.478
3.30	0.9714	90.25	1.125	0.667	2.870	3.537
3.32	0.9772	88.36	1.306	0.754	3.477	4.231
3.34	0.9831	86.43	1.575	0.861	4.398	5.259
3.36	0.9890	84.48	2.043	0.998	6.020	7.018
3.38	0.9949	82.48	3.183	1.194	10.04	11.23
3.39	0.9978	81.47	5.444	1.344	18.03	19.37
3.395	0.9993	80.96	9.421	1.466	32.41	33.88
3.397	0.9999	80.76	27.74	1.563	98.32	99.88
3.3973	1.000	80.73	∞	1.615	∞	∞

density[10] at 0.04127 g/cc, which is almost identical with the mean value of $\frac{1}{2}[\rho_L(T)+\rho_{\mathrm{vap}}(T)]$ discussed above, we give in Table I the calculated values of u, α_s, $C_{sv,\lambda}/R$, $C_{s,\lambda}^{(1)}/R$, and the sum of these two partial lower bounds, $C_{s,\lambda}/R$, or the lower bound of C_s/R, in the vicinity of the critical point, that is between $0.94T_c$ and T_c. It will be seen that, compared with normal values of expansion coefficients, α_s is already enormous at $0.94T_c$.

Using the lower bound $c_{s,\lambda}$, Eq. (11), with Eq. (2), we obtain a lower bound of the constant-volume specific heat $c_{v,\lambda}$, given by

$$c_{v,\lambda}=[T/(\rho u)^2](dp/dT)^2 -(T\alpha_s/\rho)[(\partial p/\partial T)_v-(dp/dT)]. \quad (15)$$

In the vicinity of the critical point,

$$dp/dT \lesssim (\partial p/\partial T)_v, \quad (16)$$

and

$$\lim_{T\to T_c} c_{v,\lambda}=[T/(\rho u)^2](dp/dT)^2. \quad (17)$$

At the critical point itself, the difference $[(\partial p/\partial T)_v-(dp/dT)]$ vanishes rigorously, so that

$$c_v(T_c)=\{T_c/[\rho_c u(T_c)]^2\}[(dp/dT)_{T=T_c}]^2, \quad (18)$$

is the rigorous expression of the constant-volume specific heat at the critical point of any monatomic fluid. This formula was derived some time ago[11] along somewhat different lines.

As far as the heat capacity C_s is concerned, the development of its anomaly appears to be restricted to a temperature region of a few percent of T_c. Between about $0.94T_c$ and T_c, the partial lower bound $C_{sv,\lambda}/R$ increases by about a factor of four. The other lower bound $C_{s,\lambda}^{(1)}/R$, being linear in the expansion coefficient α_s, exhibits fully the expected anomaly at the approach of T_c. It should, of course, be remembered that the various thermal properties included in Table I are numerically only approximate; their temperature variation should, however, be qualitatively correct.

3. SOME QUALITATIVE FEATURES OF THE CONSTANT-VOLUME HEAT CAPACITY

We should like to discuss now some general characteristics of C_v. As noted above, Fig. 1 shows that in the interval $0.5°K \leqslant T \leqslant 1.1°K$, where the various heat capacities all coincide practically, the heat capacities are concave upward in the (C,T) representative plane. However, C_v has definitely an inflection point between about 1.5–1.6°K, with C_v becoming concave downward beyond this temperature.

Before discussing the temperature region $T>2.0°K$, where the calculated c_v values are based on extrapolated c_s values, as mentioned above, we should like to study the behavior of c_v at the approach of the critical temperature. We have seen above that the lower bound $c_{v,\lambda}$, Eq. (15), is the closer to the actual specific heat c_v, the nearer T is to T_c. One finds with Eqs. (15) and (17), with T near T_c,

$$\frac{dc_{v,\lambda}}{dT}=\frac{c_{v,\lambda}}{T}\left\{2T\alpha_s+1+2\frac{T}{u}\left|\frac{du}{dT}\right|+2T\frac{d\ln(dp/dT)}{dT}\right\} -\frac{T\alpha_s}{\rho}\left\{\left[\left(\frac{\partial p}{\partial T}\right)_v-\frac{dp}{dT}\right]\left[\alpha_s+\frac{d\ln\alpha_s}{dT}\right] +\frac{d}{dT}\left[\left(\frac{\partial p}{\partial T}\right)_v-\frac{dp}{dT}\right]\right\}. \quad (19)$$

On going over to the limit $T\to T_c$, one obtains

$$\lim_{T=T_c}\left(\frac{dc_{v,\lambda}}{dT}\right)=\lim_{T=T_c}\left(\frac{dc_v(T)}{dT}\right) =c_v(T_c)\left\{2\lim_{T=T_c}\alpha_s(T) +T_c^{-1}+2[u(T_c)]^{-1}\left|\frac{du}{dT}\right|_{T=T_c} +2\left[\frac{d\ln(dp/dT)}{dT}\right]_{T=T_c}\right\}, \quad (20)$$

because the second term with the curly brackets or the right-hand side of (19) vanishes rigorously, since the function $[(\partial p/\partial T)_v-(dp/dT)]$ vanishes together with all its temperature derivatives at T_c. Hence, (c_vT) approaches its finite limit $c_v(T_c)$ with a positive infinite temperature derivative, through the latter's linear dependence on $\alpha_s(T)$. One can now study d^2c_v/dT^2 near and at T_c through $d^2c_{v,\lambda}/dT^2$. One thus finds

$$\lim_{T\to T_c}\left(\frac{dc_v}{dT}\right)=\lim_{T\to T_c}\left(\frac{d^2c_v}{dT^2}\right)=+\infty, \quad (21)$$

or the constant-volume specific heat of monatomic liquids reaches its finite limit $c_v(T_c)$, Eq. (18), at the

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[10] The critical data are quite close to those estimated recently by V. Peshkov, J. Exptl. Theoret. Phys. (U.S.S.R.) 33, 833 (1957).

[11] Curtis, Boyd, and Palmer, J. Chem. Phys. 19, 801 (1951).

critical temperature with positive infinite first and second temperature derivatives, a rigorous thermodynamic result valid in all monatomic liquids. Its extension to molecular liquids will be considered briefly below.

Experimentally, as pointed out above, the second derivative d^2C_v/dT^2 vanishes at about 1.6°K. In approaching the critical point, we have just proved that this second derivative must become positive again. Hence, it must have at least one other zero between about 2.0°K and T_c, or C_v must have at least one additional inflection point in this higher temperature range. If the C_v curve calculated with the analytically extrapolated C_s values, exhibited in Fig. 1, could be taken at face value above 2.0°K, then the inflection point of C_v would appear between its apparent sharp maximum at about 2.4°K and a sharp minimum beyond 3.0°K. The latter would have to follow the maximum, assumed real for the moment, because the finite limit of c_v at T_c can only be reached from below, according to Eq. (21). We wish to emphasize again that, at the present time, the C_v curve of Fig. 1 has to be regarded with all due reserve beyond 2.0°K, on account of the extrapolated C_s values used in its calculation. However, the inflection point around 1.6°K is essentially an empirical result, and, furthermore, with the apparent maximum in C_v occurring by about 0.4–0.5°K beyond the experimentally established C_s values, this maximum could well be associated with the actual behavior of C_v. At any rate, it is seen that measurements of C_s are needed beyond 2.0°K in order to decide empirically whether the anomaly in C_v displayed by the apparent maximum at about 2.4–2.5°K is real or spurious, caused, in the latter case, by the failure of the analytical fit of $C_s(T)$ to represent an acceptable approximation of this heat capacity at $T > 2.0$°K.

It seems of interest to return again briefly to the consideration of the $C_{sv,\lambda}/R$ values included in Table I. Since this partial constant-volume heat capacity is also an approximate lower bound of the actual constant-volume heat capacity, by Eq. (15), it is seen that these lower bounds are fully compatible, as they should be, with the directly computed extrapolated C_v/R values, given in Fig. 1. In particular, the apparent sharp maximum of the latter heat capacity does not conflict with the approximate lower bound values of $C_{sv,\lambda}/R$, which are better approximations to C_v/R, the closer the temperature is to T_c. It is worth noting that the extrapolated C_v/R becomes equal to $C_{sv,\lambda}/R$ somewhat below 3.25°K, so that if the maximum of the former were real, its minimum would develop at about 3.0–3.25°K, beyond which it would increase smoothly toward its finite limit $C_v(T_c)$.

The present, essentially thermodynamic, discussion demonstrates that the elementary constant-volume heat capacity of liquid He^3 is not a monotonically increasing function of the temperature, and this may be one of the results of the present work. We have, so far, refrained from considering the low-temperature behavior of this heat capacity, which, of course, becomes identical with C_s and C_p at these low temperatures and to which we shall return in a moment. Clearly, the possible minimum of C_v at about 3.0–3.25°K is already a manifestation of the approaching critical region, which imposes the temperature behavior of C_v through Eq. (21). This latter result, of great generality, will now be extended to molecular liquids. In the latter, the limiting value $C_v(T_c)$, Eq. (18), is only a fraction of the total constant-volume heat capacity at T_c; another fraction of this property arises from the temperature rate of excitation of the internal energy levels of the molecules. Since the latter is hardly affected by the peculiar behavior of the liquid around the critical temperature, it will be realized that the development of the infinite slope of $C_v(T)$ as T_c is being approached is of purely intermolecular origin. This anomalous behavior is thus independent of the internal constitution of the molecules of the liquid, and the rigorous macroscopic thermodynamic results on the constant-volume heat capacity, Eq. (18), as a fraction of the total constant-volume heat capacity, and its anomalous temperature derivatives, Eq. (21), remain valid in all liquids at the critical temperature.

In attempting to complete the graph of the $C_v(T)$ function toward the absolute zero, one is led to a heat capacity which becomes concave downward in the (C_v,T) plane, as indicated by Roberts and Sydoriak[4] on the $C_s(T)$ function. With this extended graph one obtains the qualitative temperature dependence of $C_v(T)$, dC_v/dT, and d^2C_v/dT^2, over almost the whole temperature interval from the absolute zero to the critical temperature T_c. At the present time, the behavior of $C_v(T)$ is uncertain between about 2.3 to 3.2°K, as discussed above. It seemed, nevertheless, instructive to give in Table II the qualitative behavior of d^2C_v/dT^2. Of the various temperature regions limited by the zeros of this second temperature derivative, the one close to T_c is similar in all liquids, as discussed above. Disregarding the latter region, Table II and Fig. 1 disclose the multiple alternations of the sign of the curvature of $C_v(T)$. These alternations suggest, perhaps, the complexity in the thermal excitations of liquid He^3, whereby various types of excitations could

TABLE II. Qualitative behavior of the second temperature derivative d^2C_v/dT^2 of the constant-volume heat capacity of liquid He^3.

Approximate temperature or interval (°K)	Sign or value of d^2C_v/dT^2
(0–0.4)	(−)
(0.5)–(1.5–1.6)	(+)
$1.6<T$	(−)
$0.95\,T_c-T_c$	(+)
T_c	$(+\infty)$

possibly cooperate in the sense that they become individually dominant in the various temperature intervals. That at the lower temperatures this is effectively the case will be demonstrated in the next section.

4. ANALYSIS OF THE CONSTANT-VOLUME HEAT CAPACITY OF LIQUID He^3 IN TERMS OF ELEMENTARY THERMAL EXCITATIONS

4.1 Temperature Region Affected by the Heat Capacity of Spin Disorder

One of the main purposes of the present work consists in an attempt at a possible decomposition of the constant-volume heat capacity of liquid He^3 into its more elementary components. Such an analysis should enable one to recognize, possibly, whether the thermal excitations of the liquid could be described approximately in terms of known excitations and whether certain types of excitations could, to some reasonable extent, be shown to be more likely absent than present in this liquid.

As mentioned in Sec. 1, the fundamental approach to the problem of liquid He^3 is to follow the systematic investigation of the N-atom system, interacting according to a poorly known interaction law, of which even the pairwise interaction part is known incompletely, at best, at the present time. The solution of the characteristic-value problem associated with such a collection of N interacting atoms, subject to antisymmetric statistics, yielding its energy spectrum, is needed, in principle, for the rigorous statistical-mechanical description of such a system. The magnitude of the difficulties encountered in such a direct approach to the theory of liquid He^3 appears to be considerable. This state of affairs tends to justify, it seems to us, the use of indirect methods which should, nevertheless, yield the description of certain properties of the system in a manner not too different from that resulting eventually from the fundamental approach.

In this sense, the asymptotic limiting ideal Fermi-gas model of liquid He^3, associated with the switching off of the interatomic couplings, while at the same time keeping the density at its value prior to the switching off process, was of some limited use. This model applied[12] thus to the liquid phase required the smooth variation of its various thermal properties as a function of the variables of state. In addition, the model was capable of giving, at lower temperatures, $T \lesssim 2.0°\mathrm{K}$, the order of magnitude of the entropy of the system. An improvement of the model through introduction into its formalism of the approximate pair potential energies of the He^3 atoms was again capable of yielding, to some degree of approximation, the binding energy of the system in the ground state and the exchange energy, using plane de Broglie waves for the individual wave functions of the atoms.[13] This has led, to within the approximations of the calculations, to the exclusion of the ferromagnetic behavior at the absolute zero, and to the definition of a characteristic energy $|\epsilon_0|$ or temperature $|\epsilon_0|/k$, k being Boltzmann's constant, of the order of magnitude of 1.0°K, which could be expected to play a role in the nuclear paramagnetic behavior of the liquid.[1] The ferromagnetic ground state being excluded, the system was capable of reaching its ground state with vanishing total spin moment. Clearly, for this state to be reached the system has to develop a kind of an internal field, the energy of which, per atom, appeared to be well approximated by the absolute value $|\epsilon_0|$ of the exchange energy in this spin configuration.[1] Empirically,[14] T_0, the characteristic temperature $|\epsilon_0|/k$, appears to be close to 0.5°K. Hence, at $T>T_0$, the nuclear paramagnetic susceptibility of liquid He^3, $\chi(T)$, a smooth, continuous, and monotonic function of T, would be expected to be less than but also close to that of an ideal paramagnet, whose susceptibility $\chi_0(T)$ is that given by the law of Langevin.[15] At $T<T_0$, the susceptibility $\chi(T)$ should fall below its ideal limiting Langevin value, at the same temperature and density, and should approach smoothly and asymptotically a finite limit, its maximum value, accessible only at the absolute zero. We have shown[1] that, under conditions which could be well specified, the molar entropy of orientational spin disorder was given, for liquid He^3 whose atoms have spin $\hbar/2$, by

$$S_\sigma(T)/R=(\ln 2)[\chi(T)/\chi_0(T)], \tag{22}$$

and, under the conditions stated, valid apparently in the case of saturated liquid He^3, since

$$\chi(T)/\chi_0(T) \leqslant 1, \tag{23}$$

the full spin entropy of $R\ln 2$ can only be reached by the system asymptotically from below, when its susceptibility $\chi(T)$ approaches the Langevin-Brillouin limit[16] $\chi_0(T)$. Stated in other words, when a system of atoms or molecules of spin $s\hbar$, and given magnetic moment, exhibits the limiting Langevin-Brillouin susceptibility law, then its entropy of orientational spin disorder is complete, that is it is equal to $R\ln(2s+1)$, per mole of the system. Or, vice versa, if a paramagnetic system has achieved the orientational spin entropy of $R\ln(2s+1)$, then, *ipso facto*, its paramagnetic susceptibility must be given by the limiting Langevin-Brillouin law. Or, as pointed out and discussed in detail previously,[1,17] the ratio of the actual susceptibility $\chi(T)$ of the system of N_0 atoms, to the limiting susceptibility $\chi_0(T)$ of the same system, at the same temperature and density, is

$$\chi(T)/\chi_0(T)=N(T)/N_0, \tag{24}$$

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[12] L. Goldstein (unpublished calculations).

[13] L. Goldstein and M. Goldstein, J. Chem. Phys. **18**, 538 (1950).

[14] Fairbank, Ard, and Walters, Phys. Rev. **95**, 566 (1954).

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

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

[17] L. Goldstein, *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, Ohio, 1958), p. 57.

the fraction of those atoms $N(T)/N_0$ of the system which are available for magnetization by a small, external, uniform magnetic field, in presence of which the $N(T)$ atoms distribute themselves over the available magnetic spin sublevels of the atoms according to the Boltzmann distribution. If there are $(2s+1)$ such levels, that is if the degree of spin degeneracy is $(2s+1)$, then by Boltzmann's entropy theorem the partial orientational spin entropy per "available" atom is $\ln(2s+1)$, or (N_0 being Avogadro's number) per mole, $[\chi(T)/\chi_0(T)]R\ln(2s+1)$. For s equal to $\frac{1}{2}$, this reduces to (22). The component entropy $S_\sigma(T)$ defines the whole thermodynamics of the spin system arising from the orientational or directional behavior of the atomic or molecular spins of the collection of atoms or molecules exhibiting the above-stated magnetic susceptibility behavior.

By the smooth, continuous, and monotonic character of the susceptibility function $\chi(T)$ of liquid He^3 throughout the whole temperature interval $0.1 \leqslant T \leqslant T_c$, as established experimentally,[14,18] the development of the partial spin entropy (22) from its vanishing value, by the Nernst law, to its maximum limit of $R\ln 2$ per mole of liquid He^3, is accompanied, according to thermodynamics, by the development of a partial heat capacity of spin disorder, through

$$\begin{aligned} C_\sigma(T)/R &= T[d(S_\sigma/R)/dT] \\ &= (\ln 2)T(d/dT)[\chi(T)/\chi_0(T)]. \qquad (25) \end{aligned}$$

The entropy of spin disorder expressed by Eq. (22) can be proved rigorously within the formalism of the ideal Fermi gas of atoms of spin $\hbar/2$. We have given[1,17] a series of arguments of precise physical significance which showed that, under the conditions specified, the spin entropy expression (22) could be considered to be valid in a system like liquid He^3. Using for $\chi(T)$ the experimentally determined susceptibility values,[14] it was shown[1] that the partial entropy of spin disorder S_σ tended to become the dominant part of the total entropy of liquid He^3 below about 0.8–1.0°K. The heat capacity of spin disorder C_σ was expected to become the dominant part of the total heat capacity of the liquid at still lower temperatures. In particular, a sharp decrease of this total heat capacity could not occur before the characteristic anomaly of the partial spin heat capacity,[1] through its peculiar maximum, was reached from the high-temperature side. At very low temperatures, the empirical values of the susceptibility, which, of course, are a complete representation of all possible interactions within the liquid yielding the observed $\chi(T)$ values, suggested that $C_\sigma(T)$ should vanish, asymptotically, linearly with the temperature. This asymptotic linear region of C_σ could only be reached at $T < 0.05$°K.

The thermodynamically evaluated constant-volume heat capacity of liquid He^3 was decomposed into two parts, the constant-volume spin heat capacity and its complement, the nonspin heat capacity at constant volume. Inasmuch as the decomposition of the total heat capacity of the saturated liquid

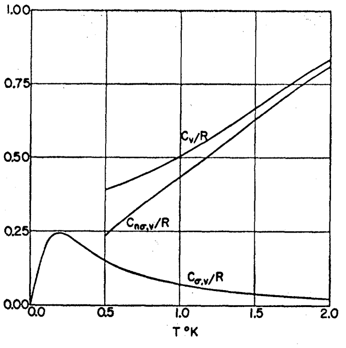

FIG. 2. Analysis of the constant volume molar heat capacity of liquid He^3 in terms of the constant-volume spin and nonspin heat capacities.

$$C_s = C_{\sigma,s} + C_{n\sigma,s}, \qquad (26)$$

is justified on the basis of the decomposition of the entropy of the saturated liquid, we may also write

$$C_v = C_{\sigma,v} + C_{n\sigma,v}, \qquad (27)$$

and using Eq. (8) so as to connect the molar heat capacities, one obtains

$$C_{\sigma,v}/R = (C_{\sigma,s}/R)[1 + A(1+B^{-1})]^{-1}, \qquad (28)$$

with A and B defined by Eq. (6). The calculated heat capacities C_v/R, $C_{\sigma,v}/R$, and $C_{n\sigma,v}/R$ are given in Fig. 2. Of these, C_v/R and $C_{n\sigma,v}/R$ are only available above 0.5°K, as the various heat capacities of Fig. 1.

Figure 2 shows that the partial heat-capacity curves $C_{\sigma,v}$ and $C_{n\sigma,v}$ intersect at about 0.35–0.40°K, below which temperature $C_{\sigma,v}$ becomes the dominant part of the total heat capacity. The apparently roughly linear character of $C_{n\sigma,v}(T)$ at low temperatures resembles of course the similar behavior of $C_{n\sigma,s}$. The approximate linearity of the latter partial nonspin heat capacity in the temperature interval 0.4–2.0°K has been pointed out by Roberts and Sydoriak.[4] To the approximation of our calculations, the degrees of freedom of liquid He^3 responsible for the constant-volume nonspin heat capacity of the saturated liquid yield an approximately vanishing curvature for this $C_{n\sigma,v}(T)$ function, that is a constant positive temperature rate of increase $(d/dT)(C_{n\sigma,v}/R)$ of about 0.4/°K below about 1.0°K. We give in Table III the calculated C_σ/R values of the saturated liquid, omitting the subscripts, whose accuracy is determined essentially by the empirical susceptibility values, together with its approximate first and second temperature derivatives, $(d/dT)(C_\sigma/R)$ and $(d^2/dT^2)(C_\sigma/R)$. Since, below about 1.0°K, C_σ and $C_{\sigma,v}$ are identical for all practical purposes, the heat capacity $C_{\sigma,v}/R$ and its derivatives are replaced by C_σ/R and its derivatives, Table III being limited between the absolute zero and 0.55°K. The graph of the partial molar spin heat capacity C_σ/R has been

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[18] G. K. Walters and W. M. Fairbank, Phys. Rev. **103**, 262 (1956); and *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, Ohio, 1958), p. 1 of the Supplement.

TABLE III. The molar spin heat capacity C_σ/R and its approximate first and second temperature derivatives.

T (°K)	C_σ/R	$(d/dT)(C_\sigma/R)$ $(°\text{K})^{-1}$	$(d^2/dT^2)(C_\sigma/R)$ $(°\text{K})^{-2}$
0.0	0.0	2.31	0.00
0.05	0.112	1.95	−10.8
0.10	0.195	1.23	−14.7
0.15	0.235	0.477	−12.3
0.20	0.243	−0.007	−7.21
0.25	0.234	−0.244	−3.28
0.30	0.219	−0.335	−1.08
0.35	0.201	−0.352	0.00
0.40	0.183	−0.335	0.42
0.45	0.167	−0.310	0.56
0.50	0.152	−0.279	0.62
0.55	0.139	−0.248	0.60

given previously in terms of the dimensionless variable T/T_0, T_0 being the empirical apparent degeneration temperature which seems to enter into the approximate analytical representation of the susceptibility data[14] of saturated liquid He^3.

Table III shows that the minimum value of $(d/dT)\times(C_\sigma/R)$ is reached at about 0.35°K, where its value is close to −0.35/°K. If, at this temperature, the extrapolated temperature derivative of the linear $C_{n\sigma}/R$ is still about 0.4/°K, then at about this temperature the total liquid He^3 heat capacity has an inflection point, since $(d^2/dT^2)(C_\sigma/R)$ vanishes there. The tangent of the total heat-capacity curve at this temperature has an almost zero or very small positive slope. In other words, the existence and location of the first, low-temperature, inflection point of the total heat capacity of liquid He^3 is well accounted for, as intimated previously,[7,17] through the opposing trends of temperature variation of the component spin and nonspin heat capacities. At very low temperatures, the increasing total heat capacity $C(T)$ has to have negative second temperature derivatives, since it is concave downward toward the temperature axis. Beyond the inflection point, about 0.35–0.40°K, the total heat capacity becomes concave upward, that is toward increasing $C(T)$ values.

These results distinctly show the role played by the partial spin heat capacity in the behavior of the total heat capacity at the low temperatures. We have called attention previously[1] to the possibility that the peculiar maximum of the spin heat capacity might become observable indirectly through the total heat capacity of the liquid, which, of course, is alone observable. It is now clearly demonstrated that the existence of this maximum is responsible for the slowing down of the temperature rate of decrease of the total heat capacity. Furthermore, we are now in a position to appreciate fully that the downward trend of the total heat capacity could not start at temperatures above 0.35–0.38°K. Indeed, as the negative slope dC_σ/dT increases toward zero below that temperature, the decreasing trend of the nonspin heat capacity ceases to be cancelled or compensated by the increasing trend of C_σ with decreasing temperatures. That is, the total heat capacity will start decreasing slowly below about 0.35–0.38°K, down to about 0.2°K, where the maximum of C_σ is located. On the low-temperature side of this maximum of C_σ, the positive slopes dC_σ/dT and $dC_{n\sigma}/dT$ become additive. As a result, an accelerated downward trend of the total heat capacity can only occur below the temperature of the maximum of $C_\sigma(T)$. This appears to be in agreement with the still preliminary experimental results of the Ohio State University group.[6]

Since the real and accelerated downward trend of temperature variation of $C(T)$ starts only at about 0.19–0.20°K, one would expect the total heat capacity to exhibit a finite curvature through its $C_\sigma(T)$ component down to rather low temperatures, that is low in comparison with 0.20°K. This state of affairs is rather well illustrated by Table III. It is seen there that the asymptotically linear region of $C_\sigma(T)$ has not been reached yet at 0.10°K. Had one assumed that C_σ/R is essentially linear in T below 0.10°K, then the slope of this linear extrapolation, wrongly interpreted as the slope of $C_\sigma(T)/R$ at the absolute zero, would have been about 1.95/°K, or lower by about 0.35/°K than its correct limit of about 2.30/°K, that is by some 18% of this apparent slope of 1.95/°K. It will be seen that $(d/dT)(C_\sigma/R)$ is, at 0.025°K, approximately, about 2.24/°K, or, still, by some 3% lower than the correct limit. Clearly, the preceding numerical values of $C_\sigma(T)$, or those of its temperature derivatives, are completely tied to the empirical values of the nuclear paramagnetic susceptibilities of the liquid. Should these be revised to some extent, then the above numerical values of the spin heat capacity and its temperature derivatives will have to be modified accordingly. The theory[1] of the properties of the nuclear spin system of liquid He^3 has no adjustable constant or constants whatsoever in its formalism, so that the numerical values of some of these properties such as the spin entropy and spin heat capacity are defined solely by the nuclear paramagnetic susceptibility function $\chi(T)$, or the susceptibility ratio $\chi(T)/\chi_0(T)$.

4.2 Nuclear Spin System of Compressed Liquid He^3

The partial spin heat capacity has to play a role in the determination of the total heat capaacity of liquid He^3 under pressure as well as in the solid phase, at low enough temperatures, provided that the application of external pressure does not lead to an anomaly in the nuclear paramagnetic susceptibility as a function of the temperature. Experimentally,[18] the spin disorder increases with increasing pressure p, because the susceptibility function $\chi(p,T)$ or the susceptibility ratio $\chi(p,T)/\chi_0(p,T)$ is such that

$$\chi(p,T)/\chi_0(p,T)>\chi(T)/\chi_0(T), \tag{29}$$

where the right-hand side corresponds to the ratio of the saturated liquid at the same temperature. The susceptibility $\chi_0(p,T)$ is the limiting Langevin-Brillouin ideal susceptibility associated with the density or atomic concentration achieved by the isothermal compression $(p_s,T)\rightarrow(p,T)$, p_s being the saturated vapor pressure at T. The theory of the partial spin entropy[1] is based strictly on the Boltzmann entropy theorem and should thus be fully valid in liquid He³ under pressure or in solid He³ provided that the conditions specified for the behavior of the paramagnetic susceptibility[1] are fulfilled. Hence,

$$S_\sigma(p,T)/R=(\ln 2)[\chi(p,T)/\chi_0(p,T)], \qquad (30)$$

and, the empirical observations then require, according to (29), that

$$S_\sigma(p,T)>S_\sigma(T), \qquad (31)$$

$S_\sigma(T)$ denoting the spin entropy of the saturated liquid. Since, furthermore, the total entropy of the liquid is

$$S(p,T)=S_\sigma(p,T)+S_{n\sigma}(p,T), \qquad (32)$$

and that since $S_{n\sigma}(p,T)\geqslant 0$, one sees that

$$\begin{aligned} S_\sigma(p,T)&=(R\ln 2)[\chi(p,T)/\chi_0(p,T)]\\ &\leqslant S(p,T), \end{aligned} \qquad (33)$$

or the partial spin entropy can never become larger than the total entropy. If at some low temperature $\chi(p,T)$ near the melting line is considerably larger than $\chi(T)$ associated with the saturated liquid at the same temperature T, still $\chi(p,T)\leqslant\chi_0(p,T)$, since this susceptibility cannot become larger, paramagnetism being permanently assumed, then the ideal limiting susceptibility $\chi_0(p,T)$ at this same temperature and pressure. If the latter value is reached, then $S_\sigma(p,T)$ must be equal to its upper limit of $R\ln 2$ per mole, as discussed above, and the total entropy of the liquid $S(p,T)$, at the pressure p and temperature T, must satisfy the inequality (33). By Eq. (29), the spin heat capacity is now such that its peak value is now displaced to temperatures lower than where it occurs in the saturated liquid. However, again, the peak value of this partial heat capacity $C_\sigma(p,T)$ cannot exceed $0.24R$, per mole, as it appears clearly on the invariant representation of $C_\sigma(T)/R$ given previously.[1] It is assumed here that the susceptibility of the compressed liquid is still describable analytically, to some degree of approximation, as appears to be the case with $\chi(T)$, the susceptibility of the saturated liquid. The analytical description depends on one empirical parameter $T_0(p)<T_0$, T_0 referring to the saturated liquid.

There is here an aspect of the spin heat capacity which is worth considering. Namely, it may possibly occur that at low temperatures and under pressure, the spin and nonspin heat capacities would behave in sufficiently different ways so that the spin heat capacity anomaly through its maximum would become much more pronounced, with respect to the nonspin heat capacity, than in the saturated liquid. In the latter, it is seen on Fig. 2 and Fig. 1, the spin heat capacity is responsible for the plateau of the total heat capacity below about 1.0°K, and also for its sharp drop at the low temperature end of this plateau, at about 0.2°K. In the compressed liquid as well as in the solid phase, provided that the susceptibility functions of these modifications of the fluid satisfy the conditions specified above, at low enough temperatures, the partial spin heat capacity peak might become observable on the total heat capacity as a well-defined hump preceding its sharp drop on the low-temperature side of the anomaly.

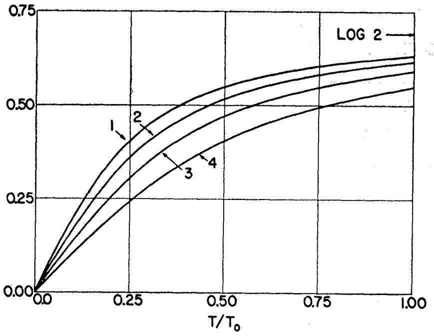

FIG. 3. The molar spin entropy of staturated liquid He³, $S_\sigma(T)/R$, curve 4, *vs* the ratio (T/T_0), T_0 being the empirical apparent degeneration temperature, and the $S_\sigma(p,T)/R$ curves of compressed liquid He³, curves 1, 2, and 3, *vs* the $T/T_0(p)$ ratio. $T_0(p)$ values associated with these curves are, respectively, $T_0/2$, $3T_0/5$, and $3T_0/4$. The abscissas correspond to the same T with the appropriate $T/T_0(p)$ values.

On the assumption that the observed nuclear paramagnetic susceptibility $\chi(p,T)$ or the susceptibility ratio $\chi(p,T)/\chi_0(p,T)$ is such that one still has approximately[1]

$$\begin{gathered} \chi(p,T)/\chi_0(p,T)=-F'[\alpha(p,T)]/F[\alpha(p,T)], \qquad (34)\\ F'(\alpha)=dF/d\alpha, \end{gathered}$$

where $F(\alpha)$ is the function defined in the formalism of an ideal Fermi gas, one has

$$S_\sigma(p,T)/R=(\ln 2)(-F'/F). \qquad (35)$$

The right-hand side can be represented by an asymptotic type of series in terms of the ratio $T/T_0(p)$ at $T<T_0(p)$. At $T\geqslant T_0(p)$, the series representation is convergent throughout the interval $(T_0(p),\infty)$. Now the ratio $-F'(\alpha)/F(\alpha)$ is a decreasing function of the parameter $T_0(p)$, and, hence, if $T_0(p)$ is such that $dT_0(p)/dp<0$, then

$$dS_\sigma(p,T)/dp=(dS_\sigma/dT_0)(dT_0/dp)>0, \qquad (36)$$

as required by (29) and (31), which qualitatively express the observations.[18] This state of affairs is illustrated in Fig. 3, where we give four entropy curves, $S_\sigma(T/T_0)$ and $S_\sigma(T/T_0(p))$, with $T_0(p)$ taken to be $(\frac{3}{4}T_0)$, $(\frac{3}{5}T_0)$, and $(T_0/2)$, associated with the compressed liquid. These $T_0(p)$ values have been chosen arbitrarily, inasmuch as, at the present time, the $T_0(p)$ function is not known. In Fig. 3, an upward displacement along a line $T=\text{const}$ corresponds to an isothermal compression. A displacement along an $S_\sigma=\text{const}$ line toward the left corresponds to a transformation at constant spin entropy. Since the isothermal compression yields, by (36), an increase in the spin entropy, a compression at constant spin entropy is seen to lead to cooling.

The total entropy of the liquid is given by Eq. (32). In considering now the total entropy changes on isothermal compression, it will be seen that with

$$[\partial S(p,T)/\partial p]_T=[\partial S_\sigma(p,T)/\partial p]_T + [\partial S_{n\sigma}(p,T)/\partial p]_T, \qquad (37)$$

the entropy anomaly arising from the spin entropy, according to (36), could be enhanced, decreased or fully compensated by the abnormal, $(\partial S_{n\sigma}/\partial p)_T>0$, or normal, $(\partial S_{n\sigma}/\partial p)_T<0$, behavior of the nonspin entropy, over part or the whole of the available pressure interval. At the present time, the pressure dependence of $S_{n\sigma}(p,T)$ is unknown. At low temperatures and over some pressure interval the spin entropy with its pressure anomaly could become dominant.

A direct thermodynamic consequence of (36) is, in virtue of

$$[\partial S(p,T)/\partial p]_T=-(\partial V/\partial T)p, \qquad (38)$$

the relation

$$V^{-1}(\partial V/\partial T)_p=V^{-1}(\partial V_\sigma/\partial T)_p+V^{-1}(\partial V_{n\sigma}/\partial T)_p, \qquad (39)$$

where, approximately, we have introduced the partial volumes V_σ and $V_{n\sigma}$ and, through them, the partial expansion coefficients α_σ and $\alpha_{n\sigma}$, of the spin system and the normal degrees of freedom, respectively. Equation (39) may now be written as a relation between the expansion coefficients at constant pressure,

$$\alpha_p(T)=\alpha_{\sigma p}(T)+\alpha_{n\sigma,\,p}(T), \qquad (40)$$

showing that the total expansion coefficient could become anomalous through $\alpha_{\sigma,\,p}(T)$. Depending, however, on the temperature and pressure, the negative spin expansion coefficient $\alpha_{\sigma,\,p}(T)$ could be reduced or eliminated through the normal behavior of $\alpha_{n\sigma,\,p}(T)$.[19]

On the basis of the assumption stated above on the sole use of a unique parameter $T_0(p)$, defined by the susceptibility measurements, in the approximate analytical description of $\chi(p,T)$ and $S_\sigma(p,T)$, we are now fully prepared to map the liquid region of the phase diagram of He^3 in the (p,T) plane onto the (S_σ,T) plane. This mapping is, of course, closely related to the mapping of the phase diagram on to the $(\chi(p,T),T)$ plane. It should be remembered, however, that the existence of a particular analytical approximation to $\chi(p,T)/\chi_0(p,T)$ is not needed at all. We have emphasized this important point previously,[1] in connection with the discussion of the saturated liquid. Indeed, once the susceptibility ratio has been obtained empirically, the definition of $S_\sigma(p,T)$ through Eq. (33) is complete. The assumption expressed by (34) is of purely auxiliary character, and is made for analytical convenience.

The region of the (S_σ,T) plane is limited on the side of the low S_σ-values by the $S_\sigma(p_s(T),T)$ curve associated with the spin entropy of the saturated liquid, $p_s(T)$ denoting the saturated vapor pressure. For instance, the $S_\sigma(T)/R$ curve of Fig. 3 is this saturated liquid spin entropy curve. The liquid region of the (S_σ,T) plane is thus limited by $S_\sigma(T)/R$ and the asymptote at S_σ/R equal to ln2, parallel to the T axis. In order to map now the liquid phase region of the (p,T) plane of He^3, we have to make two possible assumptions concerning the shape of the melting line $p_M(T)$.

We shall consider first the case where $p_M(T)$ is normal or it is a monotonically increasing function of T, from its lowest value $p_M(0)$, at the absolute zero, upward, this value $p_M(0)$ being necessarily reached with a vanishing slope. The melting line in question has thus a minimum at the absolute zero. In order to facilitate the mapping process, it is convenient to divide the liquid phase region of the (p,T) diagram into three parts, by the two isobars $p=p_c$, that is the critical isobar parallel to the T axis and passing through the end point of the vapor pressure line at T_c, and by the isobar $p=p_M(0)$, tangent to the melting line at the absolute zero. The three regions of the (p,T) diagram we shall map successively are, symbolically,

$$0\leqslant p\leqslant p_c;\quad p_c\leqslant p\leqslant p_M(0);\quad p\geqslant p_M(0). \qquad (41)$$

The isobar $p=\text{const}$ with $p<p_c$, in the (p,T) plane, intersects the vapor pressure line at a temperature $T<T_c$, and, hence, this isobar extending from the absolute zero up to the temperature T is a finite segment. The associated susceptibility ratio $\chi(p,T)/\chi_0(p,T)$ will also be a finite arc, extending from the origin of the $((\chi/\chi_0),T)$ plane up to a point where this arc intersects the susceptibility ratio curve associated with the saturated liquid, which we denote by $\chi(T)/\chi_0(T)$. Hence, $S_\sigma(p,T)/R$ reduces also to a finite arc, starting at the origin of the $(S_\sigma/R,T)$ plane, increasing first faster than the $S_\sigma(T)/R$ of the saturated liquid, then slower, to curve around and intersect $S_\sigma(T)/R$ with a slope necessarily smaller than the slope of the latter at the common temperature T. That is, all isobaric spin entropy curves at $p<p_c$ are such that

$$S_\sigma(p,T)\geqslant S_\sigma(T),\quad p\leqslant p_c, \qquad (42)$$

and, at the vapor pressure curve $p=p_s(T)$,

$$S_\sigma(p,T)=S_\sigma(T);\quad [\partial S_\sigma(p,T)/\partial T]_p<dS_\sigma/dT; \qquad (43)$$

the derivative on the right-hand side of the inequality in (43) is taken along the spin entropy curve of the

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[19] In our direct treatment of the spin system, in the second paper of reference 1, prior to the experimental work on the pressure effects on the susceptibility ratio, reference 17, a positive V_σ was used together with a positive dV_σ/dT, associated with the saturated liquid. With the recent Los Alamos data, reference 5, on the compressibility, a more complete quantitative study of the volume anomaly of the spin system became possible.

saturated liquid. Hence, the smooth and monotonic $S_\sigma(p,T)$ curve starts out at the absolute zero with a slope larger than $S_\sigma(T)$, to end at $S_\sigma(T)$ with a slope smaller than the latter, at their temperature of intersection.

As p increases toward p_c, the isobaric $S_\sigma(p,T)$ curves tend to intersect the $S_\sigma(T)$ curve at increasingly higher temperatures. Actually, the highest temperature of intersection, that is T_c, is so high that, for all practical purposes, at pressures higher than one-half to three-fourths atmospheric pressure, these $S_\sigma(p,T)$ curves are similar to $S_\sigma(T)$, and they intersect only very close to their would-be common asymptote at $R\ln2$. Clearly, $S_\sigma(T)$ itself is of finite length since its end point is at T_c.

At pressures in the region $p_c \leqslant p \leqslant p_M(0)$, the $S_\sigma(p,T)$ curves again start at the origin, their slopes at the origin increase with p, and they are, in principle, of infinite length, in constrast with the $S_\sigma(p,T)$ and $S_\sigma(T)$ curves, $p<p_c$, which are all of finite length. These high-pressure $S_\sigma(p,T)$ curves have $R\ln2$ as a true asymptote. The $S_\sigma(p,T)$ curves of Fig. 3 are typical representatives of these fully developed spin entropy curves. The $S_\sigma(T)$ curves of this graph, the lowest one, would in principle stop at T_c, which is however so larger in comparison to T_0 ($\sim$0.45°K) that this curve would be extremely close to the asymptote at temperatures well below T_c already.

Finally, we have to consider the pressure region $p \geqslant p_M(0)$. This region is, of course, limited in the (p,T) plane by the melting line $p_M(T)$. Since, experimentally, increasing pressures yield increased susceptibility ratios in the liquid phase, it will be seen that the $S_\sigma(p_M(T),T)$ curve will be located always higher than all the other isobaric spin entropy curves $S_\sigma(p,T)$. Actually, $S_\sigma(T)$ and $S_\sigma(p_M(T),T)$ both start at the origin, and at all T, $S_\sigma(p_M(T),T)$ is larger than $S_\sigma(T)$, both tending asymptotically toward $R\ln2$. Remember, however, what was said above about the finite length of $S_\sigma(T)$. The area of the (S_σ,T) plane included between these two spin entropy curves is associated with the liquid phase region of the (p,T) diagram mapped on to the spin entropy-temperature plane. Neither of these two limiting spin entropy curves belong to the family of the isobaric spin entropy curves. The latter fill up the region limited by the $S_\sigma(T)$ and $S_\sigma(p_M(T),T)$ curves. The mapping is now complete, but we have to consider now in some more detail the pressure region $p \geqslant p_M(0)$. Any isobar of this liquid region of the (p,T) diagram starts at some finite temperature T of the melting line and extends, in principle, toward infinity or the high-temperature side. Clearly then the associated $S_\sigma(p(T),T)$ curves start now at some finite temperature on the $S_\sigma(p_M(T),T)$ line, increase with increasing T, but stay permanently below the preceding limiting spin entropy curve, and tend asymptotically, at high temperatures, toward $R\ln2$, per mole. That is, while the $S_\sigma(p,T)$ curves at $p \leqslant p_c$ were finite arcs limited on the high-temperature side by the $S_\sigma(T)$ curve, in this high-pressure region $p>p_M(0)$, the $S_\sigma(p,T)$ curves, though extending toward infinitely high temperatures, are limited on the low-temperature side by the $S_\sigma(p_M(T),T)$ curve. Since they are always below the latter, it is seen that

$$[\partial S_\sigma(p,T)/\partial T]_p < dS_\sigma(p_M(T),T)/dT, \qquad p \geqslant p_M(0). \tag{44}$$

We have to turn now to the discussion of the mapping on the assumption[20] of a possibly anomalous melting line $p_M(T)$, which has a minimum $p_M(T_{\min})$ at some finite temperature $T_{\min}$. Clearly the mapping just performed at pressures $p \leqslant p_M(0)$ remains unchanged provided that the limiting isobar $p=p_M(T_{\min})$ replaces the isobar $p=p_M(0)$ of the normal case. The isobar $p=p_M(T_{\min})$ in the (p,T) plane is tangent to the anomalous melting line at its minimum at $T_{\min}$. Along this isobar we obtain the last normal $S_\sigma(p,T)$ curve of the new set. This curve is normal because it starts at the absolute zero, increases monotonically, to tend toward the asymptote ($R\ln2$) in the limit of high temperatures. Actually, $T_{\min}$ might be already high enough at this $p_M(T_{\min})$ pressure.

Let us turn now the the portion of the spin entropy curve associated with the anomalous arc of the melting line between the absolute zero and $T_{\min}$. All points of this branch of the melting line are at a higher pressure than the isobar $p=p(T_{\min})$, with the exception of their point of contact at $T_{\min}$. In addition, this branch of the melting line has at least two extrema, a maximum at the absolute zero and the minimum at $T_{\min}$. Hence, this branch has at least one inflection point. The spin entropy curve associated with this branch of the melting line has to start at the origin, to increase over and above the $S_\sigma(p(T_{\min}),T)$ curve, and then it will have to turn around to develop a contact point with the latter isobaric spin entropy at $T_{\min}$. Beyond $T_{\min}$, $S_\sigma(p_M(T),T)$ increases again over and above $S_\sigma(p(T_{\min}),T)$, to tend finally, at high temperatures toward the asymptote of $R\ln2$. Along the melting line then, one has

$$dS_\sigma(p_M(T),T)/dT = [dS_\sigma(p_M,T)/dp](dp/dT) \geqslant 0, \qquad T \leqslant T_{\min}. \tag{45}$$

Below $T_{\min}$, p decreases along the melting line, or $dp/dT \leqslant 0$, and $dS_\sigma/dp<0$, hence the inequality (45). Above $T_{\min}$, (45) is again valid automatically, since there $dp/dT>0$, and the positive pressure derivative of the spin entropy is likely to be valid along the melting line as it is valid below it, according to the observations. It is thus seen that as a consequence of the anomalous melting line, the associated limiting $S_\sigma(p_M(T),T)$ entropy curve is somewhat contorted. Now, the

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[20] I. Promeranchuk, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 919 (1950); Osborne, Abraham, and Weinstock, Phys. Rev. **85**, 158 (1952).

isobars of the phase diagram in the pressure interval $(p_M(0), p(T_{\min}))$ intersect the melting line at two points of temperature $T_1 < T_{\min}$ and $T_2 > T_{\min}$, respectively. The isobaric spin entropy curves associated with one of these isobars in the above pressure interval, start at the origin and are included between the two entropy curves $S_\sigma(p(T_{\min}),T)$ and $S_\sigma(p_M(T),T)$. These two curves form two loops, intersecting at the origin and forming a contact at $T_{\min}$, and intersecting again in the limit of high temperatures asymptotically at $R\ln 2$. It will be seen that, below $T_{\min}$,

$$[\partial S_\sigma(p(T),T)/\partial T]_p > dS_\sigma(p_M(T),T)/dT, \quad p_M(0) \geqslant p \geqslant p_{\min};\quad 0 \leqslant T \leqslant T_{\min}, \tag{46}$$

and, above $T_{\min}$,

$$[\partial S_\sigma(p,T)/\partial T]_p < dS_\sigma(p_M,T)/dT, \quad p \geqslant p_{\min},\quad T \geqslant T_{\min}. \tag{47}$$

This completes the mapping of the isobars and of the phase separation lines of the (p,T) diagram of liquid He^3 on to the (S_σ,T) plane. It should be noted though, that, so far, there is no direct empirical evidence favoring the existence of an anomalous branch of the melting line of He^3.

It is worth noting finally that the region of the (S_σ,T) plane limited by the $S_\sigma(p_M(T),T)$ curve, the S_σ axis, and the horizontal asymptote $(R\ln 2)$, is to be associated with the spin entropy of the solid phase of He^3, under the same conditions as those satisfied by the nuclear paramagnetic susceptibility of the liquid phase. Data available so far on the solid[18] seem to fall in this region of the (S_σ,T) plane. It is, however, not entirely clear if the set of susceptibility ratios given for the solid phase correspond to an isobar or not.

4.3 Partial Heat Capacity of Spin Disorder of Compressed Liquid He^3

The results obtained in the preceding section on the entropy of spin disorder of compressed liquid He^3 can now be further exploited to derive from them the constant-pressure heat capacities of spin disorder.

To this effect, consider the family of spin entropy curves of Fig. 3. These are obtained from the assumed invariant analytic approximation based on the formalism of ideal Fermi gases given previously,[1] by a change of the abscissa scale. The lowest member of the group of spin entropy curves is the $S_\sigma(T)$ curve of the saturated liquid, the upper three curves correspond to the apparent degeneration temperatures $T_0(p)$ of $(3T_0/4)$, $(3T_0/5)$ and $(T_0/2)$, respectively. T_0 is the apparent degeneration temperature of the saturated liquid, equal to about 0.45°K. The experimental results[18] on the nuclear paramagnetic susceptibilities of compressed liquid He^3 seem to indicate that the isobaric ratios $\chi(p,T)/\chi_0(p,T)$ can indeed be derived from either of them by a change in the abscissa scale. This means that the constant pressure parameter p associated with a given curve of the family appears to affect the shape of the ratio curves through a temperature parameter $T_0(p)$, so that these susceptibility ratios appear to admit a universal expression in terms of the dimensionless variable $T/T_0(p)$. Since, at the present time, a proof of this invariant character of $S_\sigma(p,T)$ is not available, we shall have to assume, for analytical simplicity, that $S_\sigma(p,T)$ is a universal function $S(T/T_0(p))$, with $T_0(p)$ derivable approximately from the empirical χ/χ_0 ratios; the $T_0(p)$ curve in the (p,T) diagram is effectively an auxiliary critical line, starting at about 0.45°K on the vapor pressure line and increasing, with a negative slope, up to the melting line.

The heat capacity of spin disorder is, rigorously,

$$C_\sigma(p,T) = T(\partial S_\sigma(p,T)/\partial T)_p, \tag{48}$$

so that with

$$S_\sigma(p,T) = S_\sigma(T/T_0(p)), \tag{49}$$

one must also have

$$C_\sigma(p,T) = C_\sigma(T/T_0(p)), \tag{50}$$

or the constant-pressure spin heat capacity is also a universal function of $T/T_0(p)$ if $S_\sigma(p,T)$ is such a function. If the approximate analytic description of $S_\sigma(T/T_0(p))$ is taken to be the one resulting from the formalism of ideal Fermi fluids, with the empirical $T_0(p)$ function, one has with (34), as shown previously,[1]

$$C_\sigma(p,T)/R = (\tfrac{3}{2}\ln 2)\left(\frac{F''(\alpha)}{F'(\alpha)} - \frac{F'(\alpha)}{F(\alpha)}\right),$$
$$F(\alpha) = F[\alpha(p,T)] = F[\alpha(T/T_0(p))], \tag{51}$$
$$F'(\alpha) = dF/d\alpha,\quad F''(\alpha) = d^2F/d\alpha^2.$$

Before turning now to the numerical evaluations of the $C_\sigma(p,T)/R$ functions, with the help of (51), it seems of of interest to refer again to the $S_\sigma(p,T)$ curves of Fig. 3. Consider a pair of these curves, one of the pair being the $S_\sigma(T)$ curve associated with the saturated liquid, and which limits, as discussed above, the liquid phase region of the (S_σ,T) plane on the high-temperature side. Let T be some low temperature and imagine that we construct the tangents at the temperature T to $S_\sigma(T)$ and to $S_\sigma(p,T)$, located above $S_\sigma(T)$. It is then evident that at these low temperatures,

$$[\partial S_\sigma(p,T)/\partial T]_p > dS_\sigma(T)/dT. \tag{52}$$

As the temperature increases, it will be seen that $S_\sigma(p,T)$ tends to reach the asymptote $(R\ln 2)$ faster than $S_\sigma(T)$, and, beyond some temperature $T_x(p)$, $S_\sigma(p,T)$ becomes less steep than $S_\sigma(T)$, or

$$[\partial S_\sigma(p,T)/\partial T]_p < dS_\sigma(T)/dT,\quad T > T_x(p). \tag{53}$$

Now the curves of the $S_\sigma(p,T)$ family are all monotonically increasing functions of T, having a finite slope at the origin. The slopes $(\partial S_\sigma/\partial T)_p$ are monotonically decreasing functions of T, since $(\partial^2 S_\sigma/\partial T^2)_p$ is always negative, the $S_\sigma(p,T)$ curves being always concave downward in the (S_σ,T) plane. The derivatives decrease thus from

$$[\partial S_\sigma(p,T)/\partial T]_{p,\,T=0} \quad \text{to} \quad [\partial S_\sigma(p,T)/\partial T]_{p,\,T\ \text{large}},$$

the latter limit being zero since the asymptote $S_\sigma(p,T\rightarrow\infty)$ or $R\ln 2$ is independent of T. It should be noted that while $S_\sigma(T)$ has an end point at T_c, and does not belong to the set of isobaric spin entropy functions $S_\sigma(p,T)$, its end point is of such high temperature, as pointed out above, that, practically, $S_\sigma(T)$ would have reached its asymptote well below T_c. Hence, by (52) and (53), the derivative functions $(\partial S_\sigma/\partial T)$ intersect in the $(\partial S_\sigma/\partial T,T)$ plane at one and only one point. The intersections of the $[\partial S_\sigma(p,T)/\partial T]_p$ curves with the (dS_σ/dT) curve of the saturated liquid occur at the temperatures $T_x(p)$. It is easy to see that $T_x(p)$ is a decreasing function of the pressure p; that is, the higher the value of the pressure p, the lower is the temperature $T_x(p)$ at which $(\partial S_\sigma/\partial T)_p$ intersects and falls below dS_σ/dT. Similarly, any two of the derivative functions $[\partial S_\sigma(p_i,T)/\partial T]_{pi}$ and $[\partial S_\sigma(p_k,T)/\partial T]_{pk}$, intersect at a single point whose temperature is $T_x(p_i,p_k)$. Again, the larger the pressure difference (p_k-p_i), the lower is the value of $T_x(p_i,p_k)$.

Multiplying both sides of the inequalities (52) and (53) by T, we obtain

$$\begin{aligned} &C_\sigma(p,T)>C_\sigma(T), \quad T<T_x(p),\\ &C_\sigma(p,T)<C_\sigma(T), \quad T>T_x(p). \end{aligned} \tag{54}$$

The spin heat capacities vanish, of course, at the absolute zero; they also vanish at high temperatures where the spin entropy becomes equal to its constant asymptotic limit. Since they are defined as $T[\partial S_\sigma(p,T)/\partial T]_p$, or a product of T and the just-discussed monotonically decreasing functions $(\partial S_\sigma/dT)_p$, they can have only one maximum. As shown above, the spin entropy curves as well as the spin heat capacity curves appear to have an invariant representation. With the analytical approximation based on the formalism of ideal Fermi gases for the susceptibility ratio $\chi(p,T)/\chi_0(p,T)$, we have given previously[1] the $C_\sigma(T/T_0)$ curve of the saturated liquid. We now give in Fig. 4, on the basis of the same approximation, the $C_\sigma(p,T)$ or $C_\sigma(T/T_0(p))$ curves obtained by a simple change of of the abscissa scale. These C_σ curves of Fig. 4 are associated, respectively, with the S_σ curves of Fig. 3. They, of course, show their intersection points with each other. The intersections with the $C_\sigma(T)$ curve of the saturated liquid occur at the temperatures $T_x(p_i)$, and with each other, at the temperatures $T_x(p_i,p_k)$. These temperatures of intersection are of course the same as those at which the spin entropy temperature derivative functions dS_σ/dT, $(dS_\sigma/\partial T)_{Pi}$, $(\partial S_\sigma/\partial T)_{Pk}$ intersect.

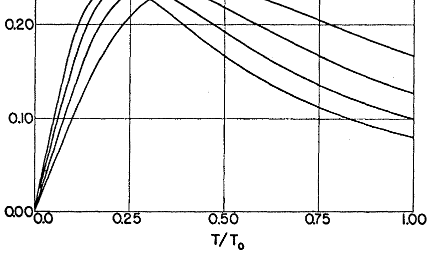

FIG. 4. The molar heat capacity of spin disorder $C_\sigma(T)/R$, of saturated liquid He^3, curve 4 *vs* (T/T_0), and of $C_\sigma(p,T)/R$, of compressed liquid He^3 *vs* $T/T_0(p)$, curves 1, 2, and 3. The $T_0(p)$ values of the latter are the same as those of the corresponding entropy curves of Fig. 3. The abscissas correspond always to the same T values, with the appropriate (T/T_0) ratios.

In virtue of the fact that the C_σ's are invariant functions of $T/T_0(p)$, their maxima occur always at[1]

$$T_{\max}(p)=0.43T_0(p), \tag{55a}$$

and their values at the maximum are identical and equal[1] to about $0.24R$,

$$\begin{aligned} C_\sigma(T_{\max}(p_s))=C_\sigma(T_{\max}(p_i))&=C_\sigma(T_{\max}(p_k))\\ &=\cdots=0.24R. \end{aligned} \tag{55b}$$

At the present time the experimental data[18] are not complete enough to derive from them the $T_0(p)$ function, besides the result stated above in connection with Eq. (36), that $dT_0(p)/dp<0$.

For a clearer understanding and more thorough appreciation of the origin of the $C_\sigma(p,T)$ curves of Fig. 4, and, with it, of the thermal properties of the spin system, it seems advisable to study the (C_σ,T,p) space to which the spin heat capacity sample curves of Fig. 4 belong. Consider a rectangular coordinate system of these three variables, and let the (C_σ,T) and (C_σ,p) planes be vertical, and the (p,T) plane horizontal. We assume that a positive rotation, through $\pi/2$, around the C_σ axis brings the p axis in coincidence with the T axis. In the physically meaningful octant of this coordinate system,

$$\Sigma\ (C_\sigma,p,T)=0, \tag{56}$$

the spin heat capacity surface, is limited at the low pressures, starting at the origin, by a curved surface

$$\Sigma_l(C_\sigma,p,T)=0, \tag{57a}$$

perpendicular to the (p,T) plane, whose intersection with this plane is the vapor pressure line $p(T)$, or the liquid-vapor phase separation line. The $\Sigma(C_\sigma,p,T)$ surface intersects the vertical curved surface Σ_l in the $C_\sigma(p_s,T)$ heat capacity curve associated with the saturated liquid, whose perpendicular projection on the (C_σ,T) coordinate plane is the $C_\sigma(T)$ curve.

The $\Sigma(C_\sigma,p,T)$ surface is limited on the high-pressure side by a curved surface

$$\Sigma_h(C_\sigma,p,T)=0, \tag{57b}$$

perpendicular to the (p,T) plane, intersecting the latter in the melting line $p_M(T)$. The intersection of the $\Sigma(C_\sigma,p,T)$ surface with the Σ_h surface is the $C_\sigma(p_M(T),T)$ line, which projected on the (C_σ,T) plane yields the limiting curve of the spin heat capacities associated with liquid He^3 along the melting line, as $C_\sigma(T)$ is the other limiting spin heat capacity curve of saturated liquid He^3. The Σ surface starts on the p axis, slopes sharply upward, and develops a continuous ridge-like line of constant altitude, that is of constant C_σ, equal to $0.24R$, given by (55b). This ridge is the locus of contacts of the $C_\sigma=0.24R$ plane, perpendicular on the C_σ axis, and the Σ surface. It will be seen, again by Eq. (55), that this ridge-like line of the Σ surface starts at the limiting Σ_l surface, Eq. (57a), at low pressures, at a temperature of about $0.43T_0$ or with T_0 equal, in the saturated liquid, to about 0.45°K, at about 0.194°K. It then curves toward lower temperatures on the Σ surface to come to a stop on the high-pressure side of Σ, that is on the Σ_h surface, Eq. (57). In our Fig. 4, we have taken $(T_0/2)$ for the apparent degeneration temperature of the limiting high-pressure $C_\sigma(p,T)$ curve, along the melting line, with T_0 standing for the apparent degeneration temperature of the saturated liquid. Since the p axis belongs to the Σ surface, as mentioned above, this Σ surface starts on this line, slopes upward fast at the low temperatures toward the ridge, and then downward gently, on the high-temperature side of the ridge, reaching only asymptotically, in the limit of high temperatures, the (p,T) plane. The low-temperature slopes of the Σ surface become steeper as one approaches the higher pressure regions, showing that the Σ surface slopes upward in pressure on the low-temperature side of the ridge. The opposite behavior is realized on the high-temperature side of the ridge, where the Σ surface slopes downward both in temperature and pressure.

Consider now a series of planes perpendicular to the p axis, intersecting the Σ surface along the $C_\sigma(p,T)$ lines. The lower the pressure, the higher is the temperature at which the planes $p=\text{const}$ intersect the ridge. In other words the maxima of the $C_\sigma(p,T)$ lines, all of the same value or height, are displaced toward lower temperatures as the pressure p increases. The perpendicular projections of these intersections on the (C_σ,T) plane are the various $C_\sigma(T/T_0(p))$ curves of the Fig. 4. It is realized now that the $C_\sigma(p,T)$ curves never intersect in the (C_σ,p,T) space, because they are located on parallel planes. Only their projections on the (C_σ,T) plane intersect.

We are ready now to discuss the variation of $C_\sigma(p,T)$, at a constant T, as a function of the pressure p. For this, it appears convenient to consider three temperature regions:

$$T\geqslant T_0(p_l);\quad T_0(p_h)\leqslant T\leqslant T_0(p_l);\quad T\leqslant T_0(p_h). \tag{58}$$

$T_0(p_l)$ is the highest temperature of the ridge of the Σ surface, associated with the saturation vapor pressure, and $T_0(p_h)$ is the lowest temperature of the ridge, associated with the melting line, as discussed above. Let the three planes be perpendicular on the T axis at $T=T_1$, $T=T_2$ and $T=T_3$, respectively, with $T_1>T_0(p_l)$, $T_0(p_h)<T_2<T_0(p_l)$, and $T_3<T_0(p_h)$. The T_1 plane intersects the Σ surface on the high-temperature side of the ridge, so that the curve of intersection $C_0(p,T)$ falls uniformly with increasing pressure. Hence,

$$[\partial C_\sigma(p,T)/\partial p]_T<0,\quad T>T_0(p_l). \tag{59a}$$

The trace of this plane on the (C_σ,T) plane is a straight line to the right of the last maximum associated with $C_\sigma(T)$ or $C_\sigma(T/T_0)$ in Fig. 4. An isothermal compression starting from the saturated vapor pressure, or the condition of the saturated liquid represented by the curve No. 4, $C_0(T/T_0)$, is this downward directed straight line, perpendicular to the T axis or the (T/T_0) axis. Clearly, as evident on Fig. 4, C_σ decreases with increasing pressure, the curves 3, 2, and 1, of increased p values, are intersected successively.

Let now the plane $T=T_2$ intersect the Σ surface, between the two end points of the ridge. Starting from the Σ_l surface, or a point of $C_\sigma(T)$ at T_2, it is seen that the curve of intersection first increases toward higher values than $C_\sigma(T_2)$, as the curve approaches the ridge, or

$$[\partial C_\sigma(p,T)/\partial p]_T>0,\quad p<p(C_{\sigma,\max},T), \tag{59b}$$

on the low-pressure side of the ridge, the right-hand side of the second inequality being that pressure at which, for the chosen T value, C_σ has its ridge value, that is its maximum. At the ridge,

$$[\partial C_\sigma(p,T)/\partial p]_T=0,\quad p=p(C_{\sigma,\max},T), \tag{59c}$$

since C_σ is maximum there. On the high-pressure side of the ridge, the curve of intersection decreases monotonically, since the high pressure-high temperature (that is $T>T_{\text{ridge}}$) side of the Σ surface is sloping downward both along increasing temperature and pressure lines, as pointed out above. Hence, one has here

$$\begin{gathered}[\partial C_\sigma(p,T)/\partial p]_T<0,\quad p>p(C_{\sigma,\max},T),\\ T_0(p_h)\leqslant T\leqslant T_0(p_l).\end{gathered} \tag{59d}$$

Finally, in third or lowest temperature interval, the behavior of $C_\sigma(p,T)$ is such that

$$[\partial C_\sigma(p,T)/\partial p]_T>0,\quad 0<T<T_0(p_h), \tag{59e}$$

as the discussion of the $T=T_3$ planes intersection with the Σ surface of known shape on the low temperature side of the ridge, described above, would show. This state of affairs is again clearly visible on Fig. 4, where at temperatures lower than the maximum of curve 1, the assumed limiting curve, an isothermal compression follows a straight line, perpendicular on the T or (T/T_0) axis, upward, showing a monotonic increase of $C_\sigma(p,T)$ with p, as expressed by (59e).

Finally, it may be shown easily that as a result of the properties expressed by (43), (44), and (46), the partial spin heat capacities at constant pressure are lower by a finite amount than the $C_\sigma(T)$ values *along* the vapor pressure line, at the same temperature. At the melting line, in the abnormal case, they are lower than *along* the melting line, and higher than *along* the latter line in the normal region of this line, always at the same temperature. These differences in the spin heat capacities are actually discontinuities.

We have seen above, Eq. (36), that

$$(\partial S_\sigma/\partial p)_T = -(\partial V_\sigma/\partial T)_p > 0, \quad 0 < T < \infty. \tag{60}$$

Since

$$\lim_{T\to 0}\,(\partial S_\sigma/\partial p)_T = 0, \quad \lim_{T\text{ large}}\,(\partial S_\sigma/\partial p)_T = 0, \tag{61}$$

it is seen that $(\partial V_\sigma/\partial T)_p$, being always negative, vanishes also at these two limits. Hence, it has at least one minimum. Now, at $0 > T > T_0(p_h)$, by (59c), $C_\sigma(p,T)$ is a monotonically increasing function of the pressure, at all pressures in the liquid region of the phase diagram. According to thermodynamics, one has

$$[\partial C_\sigma(p,T)/\partial p]_T = -T(\partial^2 V_\sigma/\partial T^2)_p. \tag{62}$$

Hence, in this low-temperature range, both $(\partial V_\sigma/\partial T)_p$ and $(\partial^2 V_\sigma/\partial T^2)_p$ are negative, or $V_\sigma(p,T)$ is a decreasing function of the temperature, being also concave downward there. Specifically, $C_\sigma(T)$ associated with the saturated liquid is such that the preceding relation (62) is satisfied by it over the whole low-temperature side of its maximum, but $(\partial C_\sigma/\partial p)_T$ vanishes at the temperature of the maximum, to become negative on the high-temperature side of the maximum, as discussed above. At the position of the maximum of $C_\sigma(T)$, $(\partial^2 V_\sigma/\partial T^2)_p$ vanishes, or $V_\sigma(p,T)$ has an inflection point at this temperature, $(\partial V_\sigma/\partial T)_p$ having a minimum there. Also, $V_\sigma(p,T)$ becomes concave upward at temperatures higher than the one at the maximum of $C_\sigma(T)$. These various thermodynamic conditions imposed upon V_σ would allow, on the basis of the previous discussion[19] of the nuclear spin system of liquid He^3, a more complete study of the volume anomaly arising from the spin system. This problem, however, falls outside the scope of the present work and its consideration will have to be reserved for subsequent work.*

We should like, at this point, to close the present discussion of the remarkable properties of the spin entropy and spin heat capacity, and to return to a further analysis of the saturated liquid He^3 constant volume heat capacity.

4.4 On the Partial Constant Volume Heat Capacity of Liquid He^3 Associated with Its Normal Degrees of Freedom

We have pointed out above that the $C_{n\sigma,\mathrm{V}}$ heat capacity appears to be a roughly linear function of the temperature, in a limited temperature interval,

$$\begin{gathered} C_{n\sigma,\mathrm{V}}/R \simeq \gamma T, \\ 0.40/°\mathrm{K} \leqslant \gamma \lesssim 0.44/°\mathrm{K}, \\ 0.4\text{–}0.5°\mathrm{K} \leqslant T \leqslant 1.5\text{–}1.7°\mathrm{K}. \end{gathered} \tag{63}$$

The physical significance of the approximately linear region of $C_{n\sigma,\mathrm{V}}$ might be connected with the following state of affairs. Inasmuch as we are dealing with bound atoms, it might be justified to some extent to associate $\frac{1}{2}kT$ for the thermal energy of excitation per translational and potential degree of freedom. Then N_0 being the total number of atoms of the system and ν the effective number of excited degrees of freedom, $\nu \leqslant 6$, one may write

$$\begin{aligned} N_0 k\gamma T &= (\nu/2)N(T)k, \\ N(T)/N_0 &= (2\gamma/\nu)T, \end{aligned} \tag{64}$$

giving the fraction of atoms $[N(T)/N_0]$ which are thermally excited below about 1.5–1.7°K. The remaining atoms are in the ground-state configuration of the system. Clearly, this is a rather extreme interpretation whereby it is assumed that the atoms of the liquid are capable of taking on the full classical thermal excitation energy of $\frac{1}{2}kT$ per effective degree of freedom. If some of these cannot be fully excited, ν would decrease accordingly. This semiclassical picture is intended only to visualize the characteristic degeneracy in liquid He^3 exhibited through its $C_{n\sigma,\mathrm{V}}$ partial heat capacity. Here, the lack of thermal excitations as compared with the full equipartition is tentatively described as a kind of division of the normal degrees of freedom into those fully excited and those which are in their fundamental state. As a result, the thermal energy of these normal degrees of freedom is

$$E_{n\sigma}(T) = \tfrac{1}{2}\nu N(T)kT, \tag{65}$$

and the temperature rate of the thermal excitations is composed of two terms, assuming for simplicity that ν is practically independent of T,

$$\begin{aligned} C_{n\sigma,\mathrm{V}} &= (dE_{n\sigma}/dT)_\mathrm{V} \\ &= \nu k[T(dN(T)/dT) + N(T)], \end{aligned} \tag{66}$$

which exhibits the qualitative constant-volume heat-capacity behavior of degenerate systems, whereby the thermal excitations result in removing atoms from the ground state and in increasing the thermal energy of the already excited atoms. This semiqualitative description of the thermal excitations of the normal degrees of freedom tends to enhance the autonomy of the two component systems of degrees of freedom, those associated with the spin system and those belonging to the former class of degrees of freedom. This autonomy is particularly emphasized at the low temperatures, where the spin entropy tends to become dominant together with the thermal energy of the system in

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* L. Goldstein, accompanying paper, Phys. Rev. **112**, 1483 (1958).

comparison with the corresponding properties localized on the collection of the normal degrees of freedom.

4.5 Further Analysis of the Liquid He^3 Constant-Volume Heat Capacity in Terms of Elementary Equations

This section will be devoted to the examination of the possible existence in liquid He^3 of partial phonon type of thermal excitations and their contribution to the constant volume heat capacity. Clearly, a rigorous solution to the problem of existence of phonon type of excitations can only be based on an approach governed by first principles. The problem in question may, perhaps, be restated as follows: let liquid He^3, a collection of bound atoms subject to the Pauli principle, be in its ground state; are there excited states in the spectrum of this system describable in terms of phonons which obey Bose statistics?

In attempting to analyze the constant-volume heat capacity of liquid He^3 in terms of a component phonon type of heat capacity, one should endeavor to justify that compressional waves of small amplitude in this liquid may indeed be considered to be quantized. That is, that their mean free path should be at least equal to, or larger than, a fair fraction of their wavelength, over the whole allowed spectrum.[21] For more simplicity, we will assume that no transverse elastic waves are propagated in liquid He^3. The problem is now to compare the mean free path of the small-amplitude compressional waves with their wavelength in as wide a region of their spectrum as possible. No measurements have as yet been made on the absorption of either low- or high-frequency ultrasonic waves in liquid He^3. In the absence of any data it would seem justified to estimate the mean free path of these waves with the help of the absorption laws derived on the basis of the classical dissipation processes arising from internal friction and heat conduction, first considered by Stokes and Kirchhoff, respectively.[22] In so doing, however, the limitations inherent in these arguments will have to be kept in mind.

The absorption coefficients of compressional waves arising from viscous dissipation and heat conduction are given, respectively, by[22]

$$\alpha_\eta = (8\pi^2/3)(\eta/\rho u\lambda^2),$$
$$\alpha_K = 2\pi^2[K(\gamma-1)/c_p\rho u\lambda^2], \qquad (67)$$

where η and K are the coefficients of viscosity and heat conductivity, and λ is the wavelength of the sound waves, the other symbols have been used already. The quantization of waves of wavelength λ may be said to be justified if

$$\alpha_\eta\lambda \lesssim \tfrac{1}{2}, \quad \alpha_K\lambda \lesssim \tfrac{1}{2}, \quad (\alpha_\eta+\alpha_K)\lambda \lesssim 1. \qquad (68)$$

Defining the critical wavelengths

$$\lambda_\eta = (8\pi^2/3)(\eta/\rho u), \quad \lambda_K = 2\pi^2 K(\gamma-1)/c_p\rho u, \qquad (69)$$

the conditions (68) become

$$\lambda \gtrsim (\lambda_\eta + \lambda_K), \qquad (70)$$

or only waves of wavelength larger than $(\lambda_\eta+\lambda_K)$ will have mean free paths longer than their wavelength, that is the length of their wave train will be at least one wavelength. If the classical absorption processes were operative throughout the whole compressional frequency spectrum of the liquid, then (70) states that only frequencies.

$$\nu \leqslant \nu_{\mathrm{crit}} = (\rho u^2/2\pi^2)[\tfrac{4}{3}\eta + (K(\gamma-1)/c_p)]^{-1} \qquad (71)$$

can be propagated and, also quantized. The portion of the spectrum

$$\nu_{\mathrm{crit}} \leqslant \nu \leqslant \nu_{\mathrm{max}} \qquad (72)$$

cannot be propagated. The maximum frequency ν_{max} of the compressional waves which can be propagated, in a structure of identical atoms separated by a given distance d, is defined by the minimum wavelength of the spectrum λ_{min} as

$$2d = \lambda_{\mathrm{min}}; \quad \nu_{\mathrm{max}} = u/2d = k\Theta/h, \qquad (73)$$

where u is the appropriate velocity of these waves and Θ the Debye longitudinal characteristic temperature associated with the structure. It should be remembered though that the very concept of structure in liquids, above all at increasingly high temperatures, is an uneasy one, at best. Hence, a clear-cut definition of λ_{min} or ν_{max} does not really exist in liquids at higher temperatures, even though a numerical definition is possible with the help of some average interatomic separation d_{Av}.

The assumed extension of the validity of the classical absorption laws of compressional waves over the whole frequency spectrum of the liquid is based on the additional hypothesis that the viscosity coefficient η and heat conductivity coefficient K remain independent of the frequency. Clearly, this hypothesis appears, at first sight, to be a highly fragile one, and its possible invalidity could remove, at high frequencies, practically all physical significance attached to the classical absorption laws. However, at the present time, there is good experimental evidence in liquid He^{4}I for justification of the validity of the classical absorption laws up to a frequency of 1.5×10^7 cycles per second.

First of all, the essentially static viscosity measurements[23] yield values of the viscosity coefficient which are in complete agreement with those resulting from measurements with a quartz cylinder performing

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[21] A number of authors have used, in a purely *ad hoc* manner, the partial phonon constant-volume heat capacity in liquid He^3 without any attempt at justifying it. See, for example, K. S. Singwi, Phys. Rev. **87**, 540 (1952) and, more recently, Flicker and Atkins, reference 5.

[22] See, for instance, Lord Rayleigh, *The Theory of Sound* (Dover Publications, Inc., New York, 1945), Vol. 2, pp. 312–322.

[23] R. D. Taylor and J. G. Dash, Phys. Rev. **106**, 398 (1957).

torsional oscillations[24] at a frequency of about 3×10^4 cycles/sec. It is of great interest that these measurements agree also in the liquid He^{4}II range. In liquid He^{4}I, the kinetic relation connecting the coefficient of heat conductivity K with the viscosity coefficient η and the constant volume specific heat c_v,

$$K = ac_v\eta, \tag{74}$$

is fairly well verified,[23,25] with the numerical coefficient a having an average value, over the explored temperature interval, which is in fair agreement with the limiting gas-kinetic value of $\frac{5}{2}$ of Maxwell. In liquid He^3, the c_v values obtained by us have been used to verify again with a fair degree of approximation the kinetic relation (74) with the recently measured viscosity coefficients[23] and heat conductivity coefficient values.[25] This state of affairs tends to suggest that in liquid He^3 also, the frequency range over which the transport coefficients remain independent of the frequency of the sound waves is as large as in liquid He^{4}I. In the latter liquid, there is, finally, indirect experimental evidence, through the measured absorption coefficient of sound waves[26] of 1.5×10^7 cycles/sec frequency, for the complete validity of the use of the static transport coefficients at this high frequency. This is a rather important argument in the present discussion of the possible division of the thermal excitations in liquid He^3 into phonon and other types of components. Indeed, this appears to prove that in liquid He^{4}I, and, indirectly, in liquid He^3 also, that the classical sound absorption laws remain valid in the frequency range extending from zero up to 1.5×10^7 cycles/sec, a rather wide spectrum, and offers a rather solid basis for their assumed validity at even higher frequencies. To be sure, the use of the classical absorption laws at frequencies higher than 1.5×10^7 cycles/sec rests, at the present time, on an extrapolation.

The calculated critical wavelengths λ_η and λ_K and their sum $(\lambda_\eta+\lambda_K)$, in liquid He^3, are given in Table IV. They have been obtained in the temperature range 1.0–3.0°K, using smoothed values of η and K, as well as the γ and c_p values calculated above. Since the calculated minimum wavelengths, using the average interatomic separations in liquid He^3, amount, by (73), to about 10 A, Table IV shows that as the temperature increases, on the basis of the stated assumptions, the soundwave spectrum which can be propagated in the liquid becomes narrower. It will also be seen that the allowed shortest-wavelength limit of the spectrum increases rapidly toward very large wavelengths, that is very large in comparison with the structural limit of about 10 A. On the basis of these results, the validity of the assumption of a complete elastic frequency spectrum excited according to the Planck-Debye distribution and its use as a partial thermal excitation spectrum becomes questionable, to say the least. However, as pointed out at the start of the discussion of this problem, the above arguments and results tending to withdraw all physical significance of the phonon excitations and their contribution to the constant volume heat capacity of liquid He^3 are not absolute enough to allow a definite exclusion of phonon participation in the thermal excitations of this liquid.

TABLE IV. Approximate classical short-wavelength limits of the allowed spectrum of the longitudinal elastic waves in liquid He^3.

T (°K)	λ_η[a]	λ_K (angstrom units)	$(\lambda_\eta+\lambda_K)$
1.0	51.9	0.76	53
1.5	52.0	5.30	57
2.0	54.2	18.1	72
2.5	68.2	52.2	140
3.0	137.0	199.0	336

[a] The kinetic relation (74) has been used in this calculation with the smoothed data of reference 25 extrapolated to 3.0°K.

It seems of interest to invoke here a somewhat different type of semiquantitative but fairly general argument tending to oppose also the justification of phonon types of thermal excitations in liquid He^3 as well as in liquid He^{4}I. The directly computed apparent characteristic temperatures Θ in liquid He^3 between 0.5 and 3.2°K are 13.8 and 6.8°K, respectively. In liquid He^{4}I, the Θ values at 2.2 and 5.0°K are, respectively, 18.3 and 9.2°K, approximately. Over these temperature intervals, the Θ values decrease by a factor of about two. This emphasizes the instability of the structures to which one attempts to assign, in a highly *ad hoc* manner, phonon types of excitations. This instability manifests itself more strongly through the increasingly large values of the volume expansion coefficients at rising liquid temperatures. Both expansion coefficients, $\alpha_s(T)$ and $\alpha_p(T)$, tend smoothly toward infinity as $T \rightarrow T_c$, $\alpha_p(T)$ increasing faster than $\alpha_s(T)$ by Eq. (4). Now if the whole or part of the large expansion coefficient were attributed to the anharmonic terms in the expression of the elastic energy of the liquid, then it seems inescapable that the very large values of the expansion coefficient would, at high liquid temperatures, tend to deny the dominance of the harmonic term in the elastic energy expression when compared with anharmonic ones. It would then follow that the very concept of harmonic oscillations has to lose its sharpness and with it a good deal of its significance, at these high temperatures. This argument based on the instability of the liquid structure at increasingly high temperatures, though not completely quantitative, seems to be of some potency in attributing only arithmetic significance to the phonon type of partial constant-volume heat capacity both in liquid He^3 and in liquid He^{4}I.

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[24] B. Welber and S. L. Quimby, Phys. Rev. **107**, 645 (1957).

[25] Lee, Donnelly, and Fairbank, Bull. Am. Phys. Soc. Ser. II, **1**, 64 (1957); and H. A. Fairbank and D. M. Lee, *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, 1958), p. 26. See also, L. J. Challis and J. Wilks, *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, 1958), p. 38.

[26] J. R. Pellam and C. F. Squire, Phys. Rev. **72**, 1245 (1947).

5. CONCLUDING REMARKS

On the basis of the results obtained in the present work, it appears justified to state that the thermodynamic derivation of the constant volume heat capacity $C_v(T)$ of saturated liquid He^3, from the various data accumulated recently on its thermal properties, had led us to recognize the existence of at least three inflection points of this elementary heat capacity. The data available at the present time were not sufficient to obtain precise values of $C_v(T)$ beyond 2.0°K. The $C_v(T)$ values given above at temperatures higher than 2.0°K are based on analytically extrapolated, approximate $C_s(T)$ or saturated-liquid heat capacity values. These extrapolations may become worse at increasingly high temperatures. In particular, the fairly sharp maximum of $C_v(T)$ at about 2.4°K could be spurious, to some extent. Of the three definitely established inflection points of $C_v(T)$, the first at about 0.35–0.40°K coincides with the location of the inflection point of the component heat capacity of spin disorder, $C_\sigma(T)$. The inflection point occurring at the highest temperature receives a thermodynamic explanation, through an investigation of the behavior of $C_v(T)$ at the approach of the critical temperature T_c. It is thus shown that $C_v(T)$ reaches its finite limit $C_v(T_c)$, at T_c, with positively infinite first and second temperature derivatives.

Besides the elementary partial heat capacity of spin disorder, the thermal excitations of the more conventional degrees of freedom of the liquid appear to correspond to those of a degenerate system whereby the number of frozen degrees of freedom is smoothly decreased with rising temperatures. This qualitative picture seems to remain valid approximately up to temperatures close to, or even higher than, that of the middle inflection point of $C_v(T)$.

It is felt that definite progress could be achieved in the understanding of the entropy and heat capacity of the spin system throughout the liquid region of the phase diagram of this substance. The $C_\sigma(p,T)$ spin heat capacity exhibits, as a function of the external pressure p, a series of remarkable properties, in various precisely defined temperature intervals. This behavior should manifest itself through the pressure dependence of the total observable heat capacity of compressed liquid He^3, at the lower temperatures. On the basis of the rather meager data on the thermal properties of solid He^3, it would appear that in this phase too, the spin system becomes dominant at low temperatures, through its entropy and heat capacity. The description of the thermal properties of the normal degrees of freedom in this antisymmetric solid appears to be a most interesting and challenging problem.

Finally, various arguments, of qualitative or semiquantitative character, have been advanced, all tending to exclude partial phonon type of thermal excitations in liquid He^3, as well as in liquid He^4I. These arguments cannot yield, however, the rigorous solution to the problem of whether or not this antisymmetric collection of bound atoms can possess a group of partial elementary excitations subject to symmetrical statistics.