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Some Thermal Properties of Liquid Helium Three

Louis Goldstein
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

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The various anomalies exhibited by the thermal properties of liquid He^3 originate with its nuclear spin system according to the statistical thermodynamic formalism elaborated for the latter. This result of general character is verified directly through a quantitative evaluation of the volume expansion coefficient of the saturated liquid. The theory also yields the explanation of the observed pressure dependence of the temperature locus of its volume anomalies near saturation at moderate pressures. The quantitative extension of the theory into the regions of the compressed liquid and the solid will have to await the forthcoming of precise measurements of several thermal properties in these phases of He^3.

1. INTRODUCTION

In recent work[1] we have analyzed the thermal properties of the nuclear spin system in liquid He^3 on the basis of its statistical thermodynamics elaborated previously.[2] The anomaly of the volume expansion coefficient of the liquid could be shown to arise from the behavior of the spin system determined by the temperature and pressure dependence of the nuclear paramagnetic susceptibility of the liquid. In the present paper we propose to generalize quantitatively the theory[1–3] in deriving the total volume expansion coefficient of the liquid as well as some other properties closely connected with it in terms of empirically obtained properties required by the statistical thermodynamic character of the theory.

The formalism is based on the assumed additivity of the entropy of the nuclear spin system and the entropy associated with the degrees of freedom other than spin.[1,2] So far the main goal of the theory was a precise description of the partial properties of liquid He^3 arising from its nuclear spin system. In this the theory succeeded without involving any arbitrary parameters whatsoever. The generalization attempted in the present work, so as to include in the formalism the system of degrees of freedom other than spin, still succeeds essentially as long as one considers the liquid in equilibrium with its vapor, or under moderate external pressure, near saturation. However, some of the thermal properties of the compressed liquid established in this Laboratory by two groups of independent workers,[4] at or above 1.0°K, suggest already that in the compressed liquid as well as probably in the solid phase,[5] the nonspin degrees of freedom require, for their equation of state a parametric function $\epsilon_{n\sigma}(V,T)$ of the variables of state. This function is, of course, susceptible of evaluation through the formal description of some thermal properties of the liquid.

The statistical thermodynamic formalism used in connection with the nuclear spin system[1–3] leads in a fairly straightforward way to the derivation of the partial volume expansion coefficient of the nonspin degrees of freedom. This combined with that of the spin system yields the approximate total volume expansion coefficient of saturated liquid He^3 in fair agreement with preliminary data.[6] The problem in compressed liquid He^3 can only be discussed along semiquantitative lines, because accurate data on the nonspin degrees of freedom of compressed liquid or solid He^3 are not available at the present time. Results obtained near saturation condition and under moderate pressure appear to agree with the data.

2. THERMAL PROPERTIES OF LIQUID He^3

It has been established, experimentally, by Roberts and Sydoriak[7] that, to a fair degree of approximation, the partial heat capacity of the nonspin degrees of freedom in saturated liquid He^3 is linear in temperature over a fairly wide temperature interval. This interval is, however, reduced somewhat in transforming the saturated liquid heat capacity to the constant volume heat capacity at the volume of the saturated liquid at any precise temperature.[3] In this linear region it may be justified to write in a first approximation,

$$p_{n\sigma}(V,T)=\tfrac{2}{3}[E_{n\sigma}(V,T)/V], \tag{1}$$

that is to postulate the validity of the virial theorem. In (1), on account of the rather small variations of the liquid volume over the temperature interval of interest,

$$E_{n\sigma}(V,T)=\int_0^T C_{n\sigma}(V,T)dT. \tag{2}$$

In order to generalize somewhat the representation of the empirical results on the partial thermal properties of the nonspin degrees of freedom, it appears reasonable to rewrite the equation of state (1) in the less restricted form

$$p_{n\sigma}(V,T)=\tfrac{2}{3}\epsilon_{n\sigma}(V,T)E_{n\sigma}(V,T)/V, \tag{3}$$

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[1] L. Goldstein, Phys. Rev. **102**, 1205 (1956); **112**, 1483 (1958).

[2] L. Goldstein, Phys. Rev. **96**, 1455 (1954).

[3] L. Goldstein, Phys. Rev. **112**, 1463 (1958).

[4] R. H. Sherman and F. J. Edeskuty, Ann. Phys. (N.Y.) (to be published); E. R. Grilly and R. L. Mills, Ann Phys. (N.Y.) 8, 1 (1959).

[5] L. Goldstein, Ann. Phys. (N.Y.) 8, 390 (1959).

[6] R. D. Taylor and E. C. Kerr, Physica **24**, S133 (1958); Lee, Reppy, and Fairbank, Bull. Am. Phys. Soc. **3**, 329 (1958).

[7] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **98**, 1672 (1955); see also Abraham, Osborne, and Weinstock, Phys. Rev. **98**, 551 (1955).

in which the parametric function $\epsilon_{n\sigma}(V,T)$ is supposed to originate with the interactions existing within the system of nonspin degrees of freedom other than those which are taken into account through the empirical nonspin heat capacity and Eq. (2). Along the saturation line, and in the limited temperature interval of interest here the parameter $\epsilon_{n\sigma}$ appears to be close to its ideal limit of unity. However, as will be shown briefly below, in compressed liquid He^3 as well as in the solid phase, this parameter should take on values considerably lower than unity, judged from the standpoint of the theory valid in the saturated liquid.

In terms of the ideal antisymmetric formalism, it is possible to associate with the nonspin degrees of freedom, on the basis of their empirical heat capacity,[7]

$$C_{n\sigma,V}/R=aT,\quad a=0.426/°\mathrm{K}, \tag{4}$$

an apparent characteristic temperature given by

$$\begin{aligned} T_{0,n\sigma}&=\pi^2RT/2C_{n\sigma,V}\\ &=\pi^2/2a\\ &=11.6°\mathrm{K}. \end{aligned} \tag{5}$$

The coefficient a used here is somewhat smaller than the one given for the saturated liquid nonspin heat capacity. This reduction comes about through an approximate over-all linear fit of the constant volume nonspin heat capacity which falls below the saturated liquid nonspin heat capacity[3] beyond about 1.0°K. It should be noted that the empirically established[7] linearity of $C_{n\sigma,s}(T)$ involves a good deal of extrapolation, so that a certain amount of curvature of this partial heat capacity at the very low temperatures, this heat capacity being concave upward, cannot be ruled out at the present time. Such an upward concave extrapolation of $C_{n\sigma,s}$ was actually suggested by the workers of the Argonne Group.[7] The recent heat capacity measurements of the Ohio State University workers,[8] though extending in temperature well below that reached by the measurements of either the Los Alamos or Argonne workers,[7] cannot be used here for reasons which will be considered briefly below. Inasmuch as we shall essentially limit ourselves to temperatures less than about 1.5°K, the empirical relation (4), linear in temperature, is acceptable over this interval, in view of the smallness of the ratio $(T/T_{0,n\sigma})$, even at the upper end of the above temperature range.

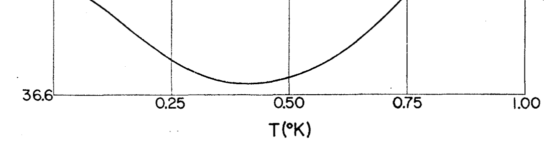

FIG. 1. Calculated molar volumes of liquid He^3 as a function of the temperature.

It should be noted that in dealing with the spin system[1] the parameter $\epsilon_\sigma(V,T)$ was found to be equal to (-1), corresponding to the situation whereby the virial theorem was there approximately verified to within the negative sign. The latter is a qualitative algebraic aspect of the fundamental anomaly of the spin system, which, however, seems to have a fairly clear physical interpretation.[5] In the system of the nonspin degrees of freedom of the compressed liquid, it will be shown below that the characteristic derivative

$$\begin{gathered}[dp_{n\sigma}/d(E_{n\sigma}/V)]_V=\tfrac{2}{3}\epsilon_{n\sigma}(V,T),\\ \epsilon_{n\sigma}(V,T)<1,\end{gathered} \tag{6}$$

is not ideal, the parameter $\epsilon_{n\sigma}$ falling below unity and depending in some way on the variables of state. The preceding result is imposed by the data in the compressed liquid, and, probably, also in the solid phase.[5]

Using the thermodynamic reasoning discussed previously in connection with the partial volume expansion coefficient of the spin system,[1] one finds for the partial volume expansion coefficient associated with the nonspin degrees of freedom

$$\alpha_{n\sigma,p}(V,T)=\tfrac{2}{3}(\kappa_T(V,T)/V)\epsilon_{n\sigma}(V,T)C_{n\sigma,V}(V,T), \tag{7}$$

where use was made of the equation of state (3) of the nonspin degrees of freedom. The total expansion coefficient of the liquid is then[1]

$$\begin{aligned}\alpha_p(V,T)&=\alpha_{n\sigma,p}(V,T)+\alpha_{\sigma,p}(V,T)\\ &=\tfrac{2}{3}(\kappa_T(V,T)/V)\\ &\quad\times[\epsilon_{n\sigma}(V,T)C_{n\sigma,V}(V,T)-C_{\sigma,V}(V,T)],\end{aligned} \tag{8}$$

where, as in (7), κ_T is the isothermal compressibility, which below about 1.0°K is the same practically as κ_S or κ_{sat}, the adiabatic compressibility or that along the saturation line, respectively. It should be remembered now that

$$C_{n\sigma,V}(V,T)=C_V(V,T)-C_{\sigma,V}(V,T), \tag{9}$$

where $C_V(V,T)$ is the observed total constant volume heat capacity, so that Eq. (8) is a statistical thermodynamic relation which correlates the following thermal properties of the liquid: α_p, κ_T, V, C_V, and $C_{\sigma,V}$, the latter being determined[2] through the empirical nuclear magnetic susceptibility ratio[9] $\chi(V,T)/\chi_0(V,T)$, χ_0 standing for the limiting Langevin susceptibility at the volume V and temperature T, which liquid He^3 would exhibit if it were an ideal nuclear paramegnetic system.

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[8] Brewer, Sreedhar, Kramers, and Daunt, Phys. Rev. **110**, 282 (1958); Brewer, Daunt, and Sreedhar, Phys. Rev. **115**, 836 (1959). We wish to thank here the senior member of this group, Dr. J. G. Daunt, for communication of their latest stage experimental results before publication.

[9] W. M. Fairbank and G. K. Walters, *Proceedings of the Symposium on Liquid and Solid He*^{3} (Ohio State University Press, Columbus, 1958), p. 1 of the Supplement.

We have so far implied that $\epsilon_{n\sigma}(V,T)$ is equal to unity in the saturated liquid. Equation (8) shows that the anomaly of the saturated liquid expansion coefficient arises from the anomalous behavior of its spin system. With $\epsilon_{n\sigma} \leqq 1$, the expansion coefficient vanishes at the root T_α of the equation

$$\alpha_p(V,T_\alpha)=0;\quad \epsilon_{n\sigma}(V,T_\alpha)C_{n\sigma,V}(V,T_\alpha) = C_{\sigma,V}(V,T_\alpha). \quad (10)$$

At $T<T_\alpha$, the expansion coefficient is negative since

$$\epsilon_{n\sigma}C_{n\sigma,V}<C_{\sigma,V},\quad T<T_\alpha. \quad (11)$$

It may be appropriate now to comment on the abovementioned difficulty which arises when one attempts to use the more recent low-temperature total liquid He^3 heat capacity data[8] to derive with them, through (9), the $C_{n\sigma,V}$ values. Inasmuch as the susceptibility ratios[9] determine uniquely[2] the partial heat capacity of the spin system, the theory having no adjustable parameters in its formalism, the difficulty corresponds, at the present time, to a slight inconsistency between the saturated liquid heat capacity[8] and susceptibility ratio data.[9] Either the latter are somewhat high or the former somewhat low. This should be resolved by additional experimental work on these properties of liquid He^3 at temperatures below about 0.20–0.15°K. It hardly needs to be stressed that, however difficult, this lower temperature region in liquid He^3 constitutes a rather fertile experimental field. This not only from the point view of the above difficulty but, above all, because it seems to offer the possibility of verifying, or disproving, the present theory[1–3,5] of statistical thermodynamic character of the thermal properties of liquid and solid He^3.

Equation (8) shows that the expansion coefficient is expressed in terms of the empirical κ_T, $V(T)$, and, through (9), $C_V(V,T)$, in addition to the calculated $C_{\sigma,V}(V,T)$ values associated with the measured nuclear paramagnetic susceptibility ratios $\chi(V,T)/\chi_0(V,T)$. It is possible to reduce by one the number of the above empirical properties by calculating first $V(T)\alpha_p(V,T)$ or the derivative $(\partial V/\partial T)_p$,

$$\begin{aligned} V(T)\alpha_p(V,T) &= (\partial V/\partial T)_p \\ &= \tfrac{2}{3}\kappa_T(V,T)[\epsilon_{n\sigma}(V,T)C_{n\sigma,V}(V,T) - C_{\sigma,V}(V,T)], \end{aligned} \quad (8a)$$

and using the latter to obtain, by integration,

$$V(T)-V(0)=\int_0^T(\partial V/\partial T)_p dT, \quad (12)$$

which vanishes at a precise temperature T_δ, where $V(T_\delta)$ is equal to the volume of the liquid at the absolute zero $V(0)$. Using then the unique empirical volume $V(T_\delta)$ of Taylor and Kerr[6] we have obtained the liquid volume $V(T)$, whose graph is given in Fig. 1. T_δ is equal, to the approximation of the above numerical calculations, to about 0.764°K, provided that $\epsilon_{n\sigma}(V,T)$ is taken, along the saturation line, to be equal to its ideal value of unity. The molar liquid volume $V(T_\delta)$ or $V(0)$ is, approximately, 36.69$_3$ cc/mole. The calculated $V(T)$ values then lead finally to an evaluation of $\alpha_p(V,T)$, always on the assumption of the parameter $\epsilon_{n\sigma}$ to be unity. Figure 2 gives a graph of the expansion coefficient $\alpha_p(V,T)$, along isobars issuing at the saturation line.

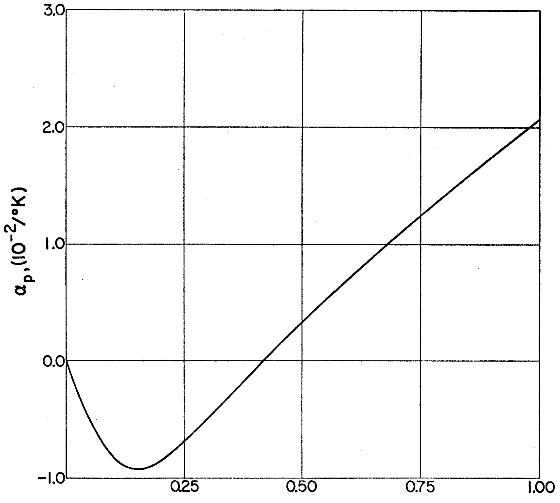

FIG. 2. The constant pressure volume expansion coefficient α_p, in units of 10^{-2}/°K, of saturated liquid He^3 as a function of the temperature.

The expansion coefficient vanishes at about 0.417°K; its minimum is, at 0.150°K, where its value is −0.0092 /°K, approximately. By the Nernst theorem, α_p vanishes at the absolute zero and always with $\epsilon_{n\sigma}$ taken to be unity,

$$(\partial\alpha_p/\partial T)_p=-[\alpha_p(V,T)]^2+V^{-1}(\partial^2V/\partial T^2)_p, \quad (13)$$

or, with (8),

$$\begin{aligned} (\partial\alpha_p/\partial T)_p = &-[\alpha_p(V,T)]^2 \\ &+\tfrac{2}{3}V^{-1}\{(\partial\kappa_T/\partial T)_p[C_{n\sigma,V}-C_{\sigma,V}] \\ &+\kappa_T[(\partial C_{n\sigma,V}/\partial T)_p-(\partial C_{\sigma,V}/\partial T)_p]\}, \end{aligned} \quad (14)$$

and

$$\lim_{T\to 0}(\partial\alpha_p/\partial T)_p = \tfrac{2}{3}[\kappa_T(T=0)/V(0)][a-(\tfrac{3}{2}\ln 2)T_0^{-1}]; \quad (15)$$

or this limiting slope is a constant, a being the empirical constant included in (4), and T_0 in (15) is the characteristic temperature of the nuclear spin system, the limiting slope $(\partial C_{\sigma,V}/\partial T)_p$ having been given previously.[2] The result that α_p thus vanishes linearly in T, from negative values is a consequence of the linear vanishing of $C_{\sigma,V}(V,T)$ with T, which is the dominant property imposing the linearity in T of α_p, as predicted previously.[1] The latter limiting property is not affected by the precise shape and temperature variation of the nonspin heat capacity. If, in the future, accurate heat capacity measurements at the low temperatures, $T \lesssim 0.15$°K, would lead to an empirical $C_{n\sigma,V}$ different from the one used here, Eq. (4), the dominance of $C_{\sigma,V}$ at these low temperatures will insure the limiting linear variation of $\alpha_p(V,T)$ with temperature, at very low temperatures. Using the limiting value of the compressibility κ, estimated by Laquer, Sydoriak, and Roberts,[10] from their low-temperature sound velocity measurements, one obtains

$$\lim_{T\to 0}(\partial\alpha_{\sigma,p}/\partial T)_p = -0.126/(°\mathrm{K})^2;$$

$$\lim_{T\to 0}(\partial\alpha_{n\sigma,p}/\partial T)_p = 0.0232/(°\mathrm{K})^2, \tag{15a}$$

$$\lim_{T\to 0}(\partial\alpha_p/\partial T)_p = -0.103/(°\mathrm{K})^2.$$

Returning now to the total liquid volume $V(T)$, whose T^2 or parabolic approach toward $V(0)$ has been discussed previously,[1] its minimum is, of course, at the zero of α_p. The inflection point of $V(T)$ is at a temperature T_V, at which, by (13),

$$(\partial\alpha_p/\partial T)_p = -\alpha_p^2, \tag{16}$$

where the expansion coefficient still decreases. If T_β is the temperature of the minimum of α_p, then by (13) and (16),

$$T_V < T_\beta. \tag{17}$$

However, taking α_p to be about the same at T_V as it is at T_β, about $(-0.01/°\mathrm{K})$, an approximate value by excess, numerically, it is seen that the temperature slope of α_p at T_V is less, numerically, than $[-10^{-4}/(°\mathrm{K})^2]$, and the smallness of this suggests that an experimental differentiation between T_V and T_β could be difficult, or, that T_V and T_β should be rather close.

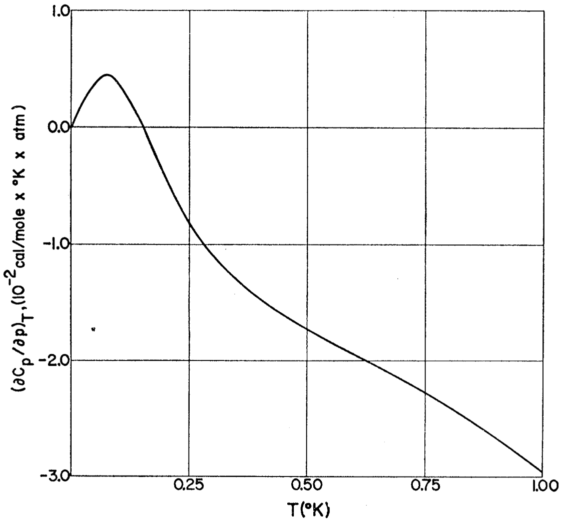

FIG. 3. The pressure slope $(\partial C_p/\partial p)_T$, in units of 10^{-2} cal/mole $\times$°K$\times$atmosphere, of the constant pressure heat capacity of liquid He^3, near saturation, as a function of the temperature.

Another aspect of the preceding situation is associated with the pressure variation of the constant pressure heat capacity at a constant temperature, according to the thermodynamic relation

$$(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p. \tag{18}$$

One obtains here, in terms of $\alpha_p(V,T)$ given by (8),

$$(\partial C_p/\partial p)_T = -\tfrac{2}{3}T\{(\partial\kappa_T/\partial T)_p[\epsilon_{n\sigma}C_{n\sigma,V} - C_{\sigma,V}] + \kappa_T[(\partial/\partial T)_p(\epsilon_{n\sigma}C_{n\sigma,V} - C_{\sigma,V})]\}, \tag{19}$$

This shows that at low temperatures the heat capacity first increases with pressure as a consequence of the dominance of the spin heat capacity through its temperature derivative in the second term on the right-hand side of (19), and as predicted on the basis of the behavior of the spin system at low temperatures.[3,5] The pressure slope vanishes, as we just saw, at T_V, the inflection point of the liquid volume, to become negative at $T > T_V$. We give in Fig. 3, the graph of $(\partial C_p/\partial p)_T$ at the saturation line. It vanishes at the absolute zero and at T_V, and has one maximum at about 0.076°K where its value is, approximately, 0.00443 (cal/mole$\times$°K$\times$atmos). The value of $(\partial C_p/\partial p)_T$ at T_β, is, with (13), (16), and (18),

$$(\partial C_p/\partial p)_{T_\beta} = -V(T_\beta)T_\beta[\alpha_p(T_\beta)]^2. \tag{20}$$

This is negative because of (17). However, with $V(T_\beta)$ equal to about 37 cc/mole, $T_\beta \sim 0.15$°K, and α_p being about $(-0.01/°\mathrm{K})$, it is seen that, in units of (cal/mole $\times$°K$\times$atmos), the slope at T_β is about -1.3×10^{-5}, which is a rather small slope. This again shows that T_β, though larger than T_V, should be quite close to it, the slope at T_V being zero by definition. The numerical calculations of the quantities $(\partial V/\partial T)_p$, $\alpha_p(V,T)$, and $(\partial C_p/\partial p)_T$ according to the relations given above yield T_V and T_β, for $\epsilon_{n\sigma}$ being equal to unity, as being essentially coincident at 0.15°K, as mentioned already.

In connection with the numerical evaluations of $V(T)$, α_p and $(\partial C_p/\partial p)_T$, it is well to keep in mind that the errors affecting the various empirical quantities entering into these calculations are cumulative, and tend to limit necessarily the numerical precision with which the above properties are obtainable. The same limitations apply to the temperatures T_V or T_β, T_α, at which α_p vanishes an T_δ. At the present time, it, would seem justified to state that at or above T_α, the volume $V(T)$ as well as the expansion coefficient α_p appear to agree fairly well with the experimental values of preliminary character of Taylor and Kerr.[6]

In the calculations of the above properties the parameter $\epsilon_{n\sigma}$ was taken to be unity. If accurate values of α_p were available, Eq. (8) would allow the determination of $\epsilon_{n\sigma}(V,T)$, in terms of the other properties entering into Eq. (8). At the present time, however, it

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[10] Laquer, Sydoriak, and Roberts, Phys. Rev. **113**, 417 (1959).

TABLE I. Approximate values of the characteristic temperatures T_V, T_β, T_α, T_δ, and of the minimas $\alpha_p(T_\beta)$ at various values of the constant parameter $\epsilon_{n\sigma}$.

$\epsilon_{n\sigma}$	T_V (°K))	$T\beta$ (°K)	$T\alpha$ (°K)	$T\delta$ (°K)	$\alpha_p(T\beta)$ $(°\mathrm{K})^{-1}$
1.0	0.150	0.150	0.417	0.764	−0.00917
0.95	0.151	0.151	0.429	0.792	−0.00934
0.90	0.153	0.153	0.442	0.822	−0.00951
0.85	0.155	0.155	0.457	0.854	−0.00968
0.80	0.156	0.157	0.472	0.890	−0.00985
0.75	0.158	0.159	0.488	0.928	−0.0100

is not possible to obtain actually the parameter $\epsilon_{n\sigma}(V,T)$ along the saturation line. It seemed, nevertheless, instructive to obtain approximately and indirectly the effect of several constant values of $\epsilon_{n\sigma}$ on the temperatures, T_V, T_β, T_α, the zero of α_p, and T_δ, the zero of the volume variation $[V(T)-V(0)]$. We give in Table I these various temperatures as well as the values of α_p at their minimas.

The influence of a constant $\epsilon_{n\sigma}$ on the various characteristic temperatures and the minimum of α_p can be easily understood by noting that T_α is the temperature of intersection of the increasing $\epsilon_{n\sigma}C_{n\sigma,V}$ function and the decreasing branch of the spin heat capacity $C_{\sigma,V}$, Eqs. (8) and (10). Hence with decreasing $\epsilon_{n\sigma}$ the product $\epsilon_{n\sigma}C_{n\sigma,V}$ is depressed, causing the zero $T_\alpha(\epsilon_{n\sigma})$ to shift toward higher temperatures. Also, the limiting very low-temperature negative slope $(\partial\alpha_p/\partial T)_{T\to 0}$ decreases with decreasing $\epsilon_{n\sigma}$, causing a more rapid fall of α_p with temperature toward a decreasing minimum $\alpha_p(T_\beta)$. The increased negative loop of α_p, causes the volume change $[V(T)-V(0)]$, Eq. (12), to become more negative and shifts thus its zero T_δ toward higher temperatures.

In compressed liquid He^3, or in solid He^3, the partial nonspin heat capacities are not available at the present time, above all at the lower temperatures where their values are critical in connection with the predicted[3,5] anomalous pressure behavior of the spin heat capacities $C_\sigma(p,T)$. The quantitative evaluation of the expansion coefficient $\alpha_p(V,T)$ of the compressed liquid cannot thus be made at the present time. Beside the absence of the total heat capacities $C_p(p,T)$, and with them the nonspin heat capacities $C_{n\sigma,p}(p,T)$, there is another circumstance tending to prevent a straightforward discussion of $\alpha_p(V,T)$ for the liquid under pressure or the solid phase. Namely, new and more accurate experimental values of the nuclear paramagnetic susceptibilities and susceptibility ratios would be important for a verification of the rule deduced recently[5] on the pressure effect of these properties. In spite of these obstacles which prevent one from obtaining the compressed liquid or solid He^3 expansion coefficients along isobars of the phase diagram, the formalism established[1,2,5] and used above was already sufficient to yield an explanation of the anomalous temperature variation of the pressure derivatives $(\partial C_p/\partial p)_T$ near the saturation line. In addition, we are also in measure to advance an explanation of another property of liquid He^3 reaching into the compressed liquid phase region near saturation conditions, using the above formalism. This concerns the locus of the zero of the expansion coefficient $T_\alpha(p)$.

According to Eq. (8), the zero T_α of $\alpha_p(V,T)$ associated with the saturated liquid is that temperature at which the positive or normal nonspin expansion coefficient is equal, numerically, to the anomalous spin expansion coefficient, or T_α is the root of

$$\alpha_{n\sigma,p}(V,T_\alpha)+\alpha_{\sigma,p}(V,T_\alpha)=0, \tag{21}$$

as pointed out already previously[1,2] and discussed above. Equation (8) also allows one to obtain qualitatively the pressure dependence of $T_\alpha(p)$ near the saturation line. At T_α, where α_p vanishes, we have by (13), (18), and (19),

$$\begin{aligned}\lim_{T\to T_\alpha}&(\partial^2V/\partial T^2)_p\\ &=\tfrac{2}{3}R\kappa_T(T_\alpha)\{(\partial/\partial T)_p[\epsilon_{n\sigma}(C_{n\sigma,V}/R)]\\ &\qquad\qquad-(\partial/\partial T)_p(C_{\sigma,V}/R)\} \qquad (22)\\ &=-T_\alpha^{-1}(\partial C_p/\partial p)_{T_\alpha}\\ &=-T_\alpha^{-1}[(\partial C_{n\sigma,p}/\partial p)_{T_\alpha}+(\partial C_{\sigma,p}/\partial p)_{T_\alpha}].\end{aligned}$$

On assuming, without thereby reducing greatly the generality of the result to be obtained, that $\epsilon_{n\sigma}$ varies only slowly with temperature near T_α in comparison with $C_{n\sigma,V}$, one has, by (4),

$$\epsilon_{no}(\partial/\partial T)_p(C_{n\sigma,V}/R)=a\epsilon_{n\sigma};\qquad (\partial/\partial T)_p(C_{\sigma,V}/R)=b(T), \tag{23}$$

where the temperature derivative of the spin heat capacity has been studied previously.[2,3] At T_α equal to about 0.42°K, one has[3]

$$a=0.426/(°\mathrm{K}),\quad b(T_\alpha)=-0.32/(°\mathrm{K}), \tag{23a}$$

or

$$(\partial C_{n\sigma,p}/\partial p)_{T_\alpha}<0,\quad (\partial C_{\sigma,p}/\partial p)_{T_\alpha}<0, \tag{23b}$$

a result conform to the previous discussion[3] of the formalism. But according to (23a) and (22),

$$|(\partial C_{n\sigma,p}/\partial p)_{T_\alpha}|>|(\partial C_{\sigma,p}/\partial p)_{T_\alpha}|, \tag{24}$$

or the nonspin heat capacity is depressed more by external pressure than the spin heat capacity, at the saturation line and at T_α. Also, omitting the subscripts p or V above, at the low temperatures in question, and provided that

$$\epsilon_{n\sigma}\gtrsim b/a,\quad (b/a\simeq 0.75), \tag{25}$$

the temperature of intersection of $\epsilon_{n\sigma}C_{n\sigma}$ and C_σ, $T_\alpha(p+\delta p)$, at the pressure δp above the saturation pressure, is seen to be shifted toward a temperature higher than $T_\alpha(p)$, as a result of the larger depression of $\epsilon_{n\sigma}C_{n\sigma}$ compared with that of C_σ. Hence,

$$\begin{aligned} T_\alpha(p+\delta p)-T_\alpha(p)&>0,\\ (\partial T_\alpha/\partial p)_{T_\alpha}&>0,\end{aligned} \tag{26}$$

that is the locus of the zeros $T_\alpha(p)$, in the (T,p) plane must increase with increasing pressure in the vicinity of the saturation line. This is the explanation of the observed pressure dependence[4] of the locus $T_\alpha(p)$ at small external pressures, near the saturation line.

The observed pressure increase the locus $T_\alpha(p)$ is connected with the larger reduction through pressure displayed by the nonspin expansion coefficient $\alpha_{n\sigma}$ compared with the pressure increase of the negative spin expansion coefficient α_σ. This comes about physically through the circumstance that at $T\geqslant T_\alpha$, $T_\alpha \simeq 0.42$°K, the spin system has already reached a degree of disorder which is not far from being complete, the spin entropy being at that temperature some 80% of its limiting value of $(R\ln 2)$ per mole. Hence $(\partial S_\sigma/\partial p)_T$, whose numerical value is also $|(\partial V/\partial T)_p|$, or $V|\alpha_\sigma|$, must be rather moderate or small. In contrast with this, the normal system of the nonspin degrees of freedom is not subject to pressure limitations of their normal decreasing entropy on compression at temperatures of the order of T_α, and its response to the application of external pressure may reasonably be expected to be always larger than that of the spin system. While the proof (26) of the increasing pressure slope of $T_\alpha(p)$ is valid only near the saturation line, the preceding considerations on the larger pressure response of the nonspin degrees of freedom as compared with the spin system tend to suggest the monotonically increasing character of $T_\alpha(p)$ up to the melting line and beyond, in the solid phase also, which may reasonably be expected to be also anomalous.[5]

The lower limit of $\epsilon_{n\sigma}$ in (25) defines the upper limit of $T_\alpha(p_s)$ at the saturation line through

$$\begin{aligned}\epsilon_{n\sigma}&\geqslant b(T_\alpha)/a\\ &=a^{-1}(\partial/\partial T)_p(C_{\sigma,V}(T_\alpha)/R),\end{aligned} \tag{27}$$

or, the allowed limits of $T_\alpha(p_s)$ are

$$1\geqslant \epsilon_{n\sigma}\geqslant b(T_\alpha)/a,\quad 0.42°\mathrm{K}\lesssim T_\alpha(p_s)\leqslant 0.49°\mathrm{K}, \tag{27a}$$

where the range of $T_\alpha(p_s)$ is included in Table I. As mentioned already, the preceding discussion assumed, for simplicity, that $\epsilon_{n\sigma}$ was a constant practically. The calculations of α_p with the various $\epsilon_{n\sigma}$ values indicate that at temperatures $T>T_\alpha$, the value of $\epsilon_{n\sigma}$ must be closer to unity than to its lower limit so as to reproduce the observed expansion coefficients.[6] At the lower temperatures, however, the smaller $\epsilon_{n\sigma}$ values still appear to lead to α_p values which could well correspond to their actual values not yet available at the present time.

At higher pressures, $T_\alpha(p)$ increases to reach a value of about 1.26°K at the melting line at a pressure of about 47.3 atmospheres, according to independent measurements of two Los Alamos groups of workers.[4] However, the entropy changes on compression at all temperatures below those of the locus $T_\alpha(p)$, starting from saturation condition and up to the melting line appear to be rather small. This occurs because of the opposite signs of these changes, positive or anomalous in the spin system and negative or normal in the system of nonspin degrees of freedom. Inasmuch as at about 1.25°K, the nuclear spin system has practically reached its asymptotic entropy limit in the saturated liquid,[2] and, *a fortiori*, in the compressed liquid,[3] at these higher temperatures only the nonspin degrees of freedom can exhibit some slight entropy decrease. This suggests that the partial nonspin heat capacity should also decrease only moderately from its value in the saturated liquid. In order now for the theory of the volume anomaly in the saturated liquid to stay valid in the compressed liquid, as well as probably in the solid also,[5] it is necessary that the parameter $\epsilon_{n\sigma}(V,T)$, the derivative, to within the factor $\frac{3}{2}$, of the pressure associated with the thermal excitations with respect to the energy density of the latter, should take on rather moderate values. This will insure the reduction of the product $\epsilon_{n\sigma}C_{n\sigma}$ so that it will equal the rather small values of the spin heat capacity[2,3] $C_{\sigma,V}$ at temperatures increasing up to about 1.25°K or beyond, in the solid phase also.[5] At the higher pressures, along isobars, the total heat capacity $(C_{n\sigma,p}+C_{\sigma,p})$ should exhibit long plateaus at a heat capacity level only slightly higher, by about $(0.05–0.07)R$, than the peak value of the spin heat capacity[2,3] of about $0.24R$. This means that while the increasing $C_{n\sigma}$ partial nonspin heat capacity branch and the decreasing partial spin heat capacity branch C_σ, at the higher pressures, may become equal at temperatures still not much higher than $T_\alpha(p_s)$, the product $\epsilon_{n\sigma}C_{n\sigma}$ will equal C_σ only at the higher temperatures associated with the locus $T_\alpha(p)$.

It seemed instructive at this stage to obtain a precise idea of the numerical values of $\epsilon(V,T)$ in a classical liquid. In view of the fact that abundant data on the thermal properties exist primarily in water whose volume anomaly at about 4°C is similar qualitatively to that of liquid He^3, we have obtained, with Eq. (8), the values of $\epsilon(V,T)$ of saturated liquid water, through the thermodynamic relation,

$$\epsilon(V,T)=\tfrac{3}{2}(\partial V/\partial T)_p[\kappa_T(V,T)C_V(V,T)]^{-1}, \tag{28}$$

over a range of temperatures.[11] Using the data compiled for water[12] we give in Table II the saturated liquid water $\epsilon(V,T)$ values. At the temperatures of this table, but in compressed water, up to pressures of about 250

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[11] Thanks are due Mrs. J. E. Powers for the majority of the numerical work, as well as Miss D. L. Cooper and Miss B. A. Moore for various calculations, and Mrs. B. M. Hindman for the drawing of the graphs.

[12] N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1953), second edition.

TABLE II. Calculated values of the parameter $\epsilon(V,T)$ in saturated liquid water.

t (°C)	$\epsilon(V,T)$	t (°C)	$\epsilon(V,T)$
0.0	−0.024	80	0.54
10	+0.075	100	0.63
20	0.16	150	0.78
30	0.24	200	0.83
50	0.38		

atmospheres, the values of $\epsilon(V,T)$ remain practically constant at a fixed temperature.

The parameter ϵ is $\frac{3}{2}$ times the parameter $\gamma(V,T)$ used in the discussion of the equation of state of solids.[13] Because of the volume anomaly of saturated or moderately compressed water, it is seen that $\epsilon(V,T)$ is negative below the temperature of the volume minimum, it vanishes at the latter, becomes positive and increases monotonically at increasing temperatures. The ϵ values of Table II are only illustrative of those which may occur in liquids. The molecular character of water has also to be kept in mind.

The small or moderate $\epsilon_{n\sigma}$ values imposed by the data[4] on the locus $T_\alpha(p)$ in compressed liquid He³ suggest, as do the ϵ values of Table II, the complexity of the formalism correlating the pressure and the energy density of the thermal excitations in these systems.

It is easy to show with Eqs. (8) and (28), that in saturated liquid He³, the total parameter $\epsilon_{\text{sat}}(V,T)$ is

$$\epsilon_{\text{sat}}(V,T)=\frac{\epsilon_{n\sigma}(V,T)C_{n\sigma,V}(V,T)-C_{\sigma,V}(V,T)}{C_{n\sigma,V}(V,T)+C_{\sigma,V}(V,T)}, \quad (29)$$

and with $\epsilon_{n\sigma}$ taken to be approximately equal to its limiting ideal value of unity, one obtains, with[2]

$$\lim_{T\to 0} C_{\sigma,V}=2.31RT,$$

and with the empirical $C_{n\sigma,V}$, Eq. (4),

$$\lim_{T\to 0}\epsilon_{\text{sat}}(V,T)=-0.69, \quad \lim_{T\text{ large}}\epsilon_{\text{sat}}(V,T)=1.$$

This range of values of ϵ_{sat} displays the pathological behavior of saturated liquid He³.

It seems appropriate finally to comment qualitatively on the volume anomaly along lines emphasized previously.[1] This anomaly may be understood in the following way: at the absolute zero the vanishing total spin angular momentum of liquid He³ imposes therein a fairly rigid spatial order, with a very large atomic volume as a result of the tendency of the parallel spin atoms to be separated by the largest distances compatible with the minimum of the total energy. As the temperature of the liquid increases, the rapid temperature rate of increase of the spin disorder allows a contraction to set in because of the possibility of parallel spin atoms to approach each other in coordinate space as a result of their increasing separation in momentum space. This contraction phenomenon, though small as far as the total volume change is concerned, continues up to the temperature $T_\alpha(p_s)$ at which the degree of spin disorder is fairly complete[2] and beyond which the ever present normal temperature rate of volume increase originating with the nonspin degrees of freedom overtakes the anomalous volume contraction arising from the behavior of the spin system.

In concluding then, it appears justified to say that the approximate evaluation of the total volume expansion coefficient of saturated liquid He³ performed in this work lends support to the statistical thermodynamics formalism of the thermal properties of this liquid elaborated previously.[1–3,5] The theory should thus be also successful to account for the temperature variation of the constant pressure heat capacity pressure slopes $(\partial C_p/\partial p)_T$ near saturation condition, as a consequence of the thermodynamic correlation of these properties. In addition, the theory offers a fairly rigorous explanation of the pressure dependence of the locus $T_\alpha(p)$ of the vanishing expansion coefficients, near saturation condition or under very moderate external pressures. The verification of the theory in the liquid subject to increasingly larger external pressure, and probably also in the solid phase,[5] will have to await the forthcoming of various data of sufficient accuracy in these high-pressure regions of the phase diagram of He³.

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[13] M. E. Grüneisen, *Proceedings of the Solvay Conference*, held in 1913 (Gauthier-Villars, Paris, 1921), pp. 243–280.