where x^+ denotes $(\mathbf{x}, t+0^+)$. The effective field $A(x)$ generated by the external potential $U(x)$ is given by

$$A(x)=U(x)+\int d^3x''\, V(|\mathbf{x}-\mathbf{x}''|)\langle\rho(x'')\rangle. \quad \text{(A4)}$$

The reason for calling P the irreducible polarization part can be seen diagrammatically or from the equation for the change in the potential A generated by a change in the external potential,

$$\begin{aligned}\tilde{K}(x,x')&\\ &=\frac{\delta A(x)}{\delta U(x')}=\delta(x-x')+\int d^3x_1\, V(|x-x_1|)\tilde{S}(x_1,x')\\ &=\delta(x-x')+\int d^3x_1 d^4x_2\, V(|x-x_1|)\tilde{P}(x_1,x_2)\tilde{K}(x_2,x').\end{aligned}$$

Thus the quantity usually denoted as the inverse dielectric function is given by

$$K(k)=[1-V_kP(k)]^{-1}. \quad \text{(A5)}$$

The equation for the single-particle Green's function may be written as

$$\left(i\frac{\partial}{\partial t}+\frac{\nabla^2}{2m}-A(x)\right)G(x,x') - \int d^4x_1\, G(x,x_1)\Sigma(x_1,x')=\delta(x-x'), \quad \text{(A6)}$$

where the self-energy is

$$\begin{aligned}\Sigma(p)&=\int d^4(x-x')\, e^{-ip\cdot(x-x')}\tilde{\Sigma}(x,x')\\ &=+i\int\frac{d^4k}{(2\pi)^4}V_kG(p+k)\Gamma(p,k)K(k). \quad \text{(A7)}\end{aligned}$$

The vertex function is defined by the equation

$$\Gamma(p,k)=\int d^4(x-x')d^4(x-z) \times e^{-ip\cdot(x-x')-ik\cdot(x-z)}\frac{\delta\tilde{G}^{-1}(x,x')}{\delta A(z)}. \quad \text{(A8)}$$

We note from (A3) that the irreducible polarization part may be written as

$$P(k)=2i\int\frac{d^4p}{(2\pi)^4}G(p+k)G(p)\Gamma(p,k). \quad \text{(A9)}$$

The equation for $\tilde{S}(x,x')$ is obtained by calculating

$$\begin{aligned}\tilde{S}(x,x')&=\frac{\delta}{\delta U(x')}\sum_\sigma\langle\psi_\sigma^\dagger(x)\psi_\sigma(x)\rangle=-2i\frac{\delta}{\delta U(x')}\tilde{G}(x,x^+)\\ &=2i\int d^4x_1d^4x_2d^4x_3\,\tilde{G}(x,x_1)\frac{\delta\tilde{G}^{-1}(x_1,x_2)}{\delta A(x_3)}\\ &\qquad\times\tilde{G}(x_2,x^+)\frac{\delta A(x_3)}{\delta U(x')}, \quad \text{(A10)}\end{aligned}$$

where the factor of 2 arises from the sum over spins. Using (A5), (A8), and (A9), we may write the density autocorrelation function as

$$S(k)=P(k)/[1-V_kP(k)]. \quad \text{(A11)}$$

PHYSICAL REVIEW VOLUME 148, NUMBER 1 5 AUGUST 1966

Theory of Liquid Helium Three

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(Received 21 February 1966)

The present work contains a detailed study of two types of heat-capacity anomalies present in liquid He^3. One of these is the plateau formation at intermediate pressures, $p \lesssim 10$ atm. The other anomaly consists in the appearance of a flat constant-pressure heat-capacity maximum, followed by a shallow minimum, between the temperatures of 0.15 and 0.30°K, and the pressures of 10 and 30 atm, approximately. At somewhat higher pressures, over a small pressure range, only the heat-capacity maximum becomes observable. These heat-capacity anomalies originate with the competition of the thermal excitations of the spin and nonspin degrees of freedom, within the theoretical approach advanced here. The observation of the predicted low-amplitude heat-capacity extrema in compressed liquid He^3 may require heat-capacity measurements of increased accuracy, preferably at higher pressures. The problem of the heat-capacity behavior at low and very low temperatures has also been explored under a restrictive hypothesis. It will be assumed that the nature of the thermal excitations which appear in incontrovertible and independent heat-capacity data, available only at saturation and at temperatures above 0.2°K, persists on the spin and nonspin degrees of freedom down to the absolute zero. With the recently established universal character of the nuclear-paramagnetic-susceptibility ratio law of liquid He^3, down to 0.05°K, the stated assumption leads one to predict that the ratio of the total heat capacity to the temperature approaches parabolically in temperature its finite limit at the absolute zero. In the present theory, deviations from this behavior require a new paramagnetic-susceptibility law at the lowest temperatures.

1. INTRODUCTION

IN our initial approach[1] toward a theoretical formulation of the equilibrium thermal properties of liquid He^3, it was possible to prove that the observed peculiar shape of the saturated-liquid heat capacity as a function of the temperature had to arise with the competitive behavior of two component sets of degrees of freedom. One of these sets referred to the nuclear-spin

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

system; the He^3 atoms all carry on their nuclei an angular momentum of magnitude $(\hbar/2)$, and an elementary magnetic dipole moment whose magnitude is almost equal to that of a free neutron.[2] The formalism of the theory of the spin system led first to the recognition that the magnitude of the volume expansion coefficient of liquid He^3 should be exceptionally large at low temperatures[3] where the second set of degrees of freedom other than spin would be expected to be less effective. This latter system of nonspin degrees of freedom could not, as yet, be described satisfactorily. At the present time, its component thermal properties are obtained strictly empirically through subtraction of the theoretically evaluated properties of the spin system from the observed properties. The dominance of the spin system at the lower temperatures, however, allows one to describe semiquantitatively the thermal behavior of the liquid in terms of that of the spin system.[4] In particular, the characteristic thermal anomaly of liquid He^3, over the low-temperature region of its phase diagram, associated with entropy generation on isothermal compression, was shown to arise with the thermally anomalous spin system.[4] In spite of the strictly empirical and approximate treatment of the nonspin degrees of freedom, the over-all description of the equilibrium properties of liquid He^3 appears to be well established over the whole phase diagram, and rests on the competitive behavior of the two component systems of degrees of freedom.[5] There still remains, however, a largely unexplored thermal property in whose temperature variations this characteristic competition of the two subsystems of degrees of freedom should lead to new experimentally observable anomalies. This property is the heat capacity of the liquid throughout most of its phase diagram. While the pressure anomalies could be studied in detail, since they all occur at low temperatures,[4a] the temperature anomalies are controlled more severely by the competition of the two systems of degrees of freedom. The main object of the present paper is the problem of the temperature anomalies of the heat capacity. Within the framework of the present approach the existence of these anomalies will be directly proved through the approximate locations of the maxima and minima of the constant-pressure heat capacity of the liquid as a function of temperature when the liquid is compressed to pressures exceeding a certain minimum pressure, or $p\gtrsim 10$–12 atm. The extrema appear, however, to be relatively flat, and high-precision heat-capacity measurements seem necessary for their verification.

The program of the present paper is then as follows: First, various additional aspects of the physical arguments advanced earlier[1] on the form of the saturated-liquid heat capacity will be discussed. Then, heat-capacity data on the saturated liquid at $T\gtrsim 0.2°\mathrm{K}$ originating in three different laboratories[6–8] will be analyzed as a single set so as to derive from them an approximate formal expression for the nonspin heat capacity. A similar analysis in the compressed liquid is excluded, at the present time, because there are no data for high densities that are nearly as precise, or as closely spaced in temperature, as those of the Argonne group,[7] or even of the Los Alamos group,[6] for the saturated liquid. The formal representation of the derived saturated-liquid heat capacity will be studied at $T<0.2°\mathrm{K}$ down to the lowest temperatures on the assumption that no additional phenomena occur there. The temperature slope of the tangent of the heat capacity in the limit of the absolute zero turns out to be about the same as the one found earlier[4d] using a less elaborate approximation to the nonspin heat capacity. As shown earlier, on the basis of the spin heat capacity,[9] the commonly accepted heat capacity linear in the temperature is a mere myth, whose experimental proof will have to await the development of accurate heat-capacity measurement techniques in the limit of very low temperatures. Finally, the heat-capacity anomalies of the compressed liquid will be proved to occur at $T\gtrsim 0.10°\mathrm{K}$ and the above indicated pressures. In a relatively accessible temperature and pressure range, these anomalies cannot, probably, be stumbled upon and accurate heat-capacity measurements at close temperature intervals may be indispensable for the verification of their presence or absence.

2. QUANTITATIVE PROPERTIES OF THE SATURATED LIQUID He^3 HEAT CAPACITY

The first accurate heat-capacity measurements[6,7] on saturated liquid He^3 have disclosed at medium temperatures, $0.25\leq T\leq 0.75$–$0.80°\mathrm{K}$, a plateau-like behavior, that is a temperature interval over which this heat capacity $C_s(T)$ is of rather small variation. At the low-temperature end of this plateau T_i, the molar heat capacity $C_s(T_i)$ reaches a value of about $0.35R$, while at the high-temperature end T_f, the heat capacity $C_s(T_f)$ amounts to $0.45R$, approximately. For a ratio (T_f/T_i) of about 3, the relative heat-capacity increase $\{[C_s(T_f)-C_s(T_i)]/C_s(T_i)\}$ is about $\frac{1}{3}$. At the lower temperatures, C_s has to approach its final plunge toward its vanishing limit, by the Nernst theorem, on the assumption of no additional structure of this property at $T<T_i$. With this last extrapolated arc of the heat capacity $C_s(T)$, the latter exhibits a step-

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[2] H. L. Anderson and A. Novick, Phys. Rev. **73**, 919 (1948).

[3] L. Goldstein, Phys. Rev. **102**, 1205 (1956).

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[5] L. Goldstein, Phys. Rev. **133**, A52 (1964).

[6] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **93**, 1418 (1954); **98**, 1672 (1955).

[7] D. W. Osborne, B. M. Abraham, and B. Weinstock, Phys. Rev. **94**, 202 (1954); B. M. Abraham, D. W. Osborne, and B. Weinstock, *ibid.* **98**, 551 (1955).

[8] D. F. Brewer, J. G. Daunt, and A. K. Sreedhar, Phys. Rev. **115**, 836 (1959).

[9] L. Goldstein, Ann. Phys. (N.Y.) **14**, 77 (1961).

function-like character,

$$\begin{aligned} &dC_s/dT>0\,, \quad T<T_i\,, \\ &dC_s/dT\sim 0\,, \quad T_i<T<T_f\,, \\ &dC_s/dT\gg 0\,, \quad T>T_f\,. \end{aligned} \tag{1}$$

Since $C_s(T)\geq 0$, or positive semidefinite, its step-function-like shape represents a highly reduced degree of monotonic behavior. With the temperature derivative (dC_s/dT) exhibiting the temperature variations given by

$$d^2C_s/dT^2 \lesseqgtr 0\,, \quad \begin{matrix} T<T_i\,, \\ T>T_f\,, \end{matrix} \tag{2}$$

and with the expected continuity of $C_s(T)$ together with several of its temperature derivatives, one must have

$$d^2C_s/dT^2=0\,, \quad T_i<T<T_f\,, \tag{3}$$

at a point along its step or plateau. The almost nonmonotonic behavior of $C_s(T)$ suggests, through its plateau formation, that this behavior arises with some type of internal transformation whereby the class of thermal excitations of the system dominant at the low temperatures, $T<T_i$, are replaced by the class of thermal excitations dominant at the higher temperatures, $T>T_f$.

Then let $C_{s,i}(T)$ be the temperature rate of thermal excitations of the low-lying i states, and $C_{s,f}(T)$ that of the class of f states. At $T>0$, both of these rates are positive definite and it seems then justified to represent $C_s(T)$, the total heat capacity, through

$$C_s(T)=C_{s,i}(T)+C_{s,f}(T)\,. \tag{4}$$

A simple physical picture of the heat-capacity plateau may thus correspond to

$$C_{s,i}(T)>C_{s,f}(T)\,, \quad T<T_i\,, \tag{5a}$$

$$C_{s,i}(T)<C_{s,f}(T)\,, \quad T>T_f\,, \tag{5b}$$

with

$$\begin{gathered} C_{s,i}(T)=C_{s,f}(T)\,, \\ T_i<T=T_{if}<T_f\,, \end{gathered} \tag{6}$$

the two component heat capacities intersecting at T_{if}, a precise temperature of the plateau region. But in order for $C_s(T)$ to develop a plateau it seems necessary that

$$\langle C_{s,i}(T)\rangle_{(T_f-T_i)} \approx \langle C_{s,f}(T)\rangle_{(T_f-T_i)}\,, \tag{7}$$

or that the mean values of $C_{s,i}$ and $C_{s,f}$ over the approximate length of the plateau be about the same, which, with (1), requires, through (4), that

$$(dC_{s,i}/dT)+(dC_{s,f}/dT) \overset{\sim}{>} 0, \quad T_i<T<T_f\,. \tag{8}$$

With the condition (5b), the plateau formation is easily described in terms of $C_{s,i}$ and $C_{s,f}$, if

$$dC_{s,i}/dT<0\,, \quad T\gtrsim T_i\,, \tag{9}$$

i.e., if $C_{s,i}(T)$ becomes a decreasing function of T beyond the start of the plateau T_i.

The rough low-temperature extrapolation of the heat-capacity data[6] appears to justify, at these temperatures, the polynomial representations

$$C_{s,i}(T)=\sum_{\lambda=1} c_{i,\lambda}T^\lambda\,, \quad C_{s,f}(T)=\sum_{\lambda=1} c_{f,\lambda}T^\lambda\,, \quad T\ll T_i\,. \tag{10}$$

The condition (5a) then requires, with the positive component heat capacities,

$$c_{i,1}>c_{f,1}>0\,. \tag{11}$$

These considerations represent one possible way of analyzing the heat capacity of liquid He^3 observed with accuracy only at $T\gtrsim T_i$, and of describing it in terms of elements of a statistical thermodynamic formalism. Such a formal approach is less direct than the one advanced earlier[1,4] where a theory of the class of low-lying thermal excitations has been worked out at the start. This latter approach was motivated by the very large nuclear paramagnetic susceptibility of the saturated liquid when compared with that of the asymptotic ideal Fermi gas at the actual liquid density.[10] The susceptibility in the state specified by the macroscopic variables of state determines uniquely[1,11] the spin degeneracy of the liquid. This equilibrium spin degeneracy defines, in turn, the associated molar spin entropy in the state in question, through the Boltzmann theorem, as

$$S_\sigma(T,p)=(R\ln 2)(\chi(T,p)/\chi_0(T,p))\,, \tag{12}$$

R being the gas constant, with χ and χ_0 referring, respectively, to the actual susceptibility of the liquid and the susceptibility it would have if it were a classical ideal Curie-Langevin paramagnetic system. The above spin-entropy formula has been derived earlier[1,11] and its various aspects discussed on several occasions.[3–5] There is thus no need to expatiate upon it here. The very large values of $\chi(T,p)$ at the lower temperatures give rise to the very large dominant component spin entropy $S_\sigma(T,p)$, and the large temperature derivatives of (χ/χ_0) at these low temperatures yield a large component spin heat capacity

$$\begin{aligned} C_\sigma(T,p)&=T(\partial S_\sigma/\partial T)_p \\ &=(R\ln 2)T(\partial/\partial T)_p(\chi(T,p)/\chi_0(T,p))\,. \end{aligned} \tag{13}$$

It seems necessary at this stage to show briefly that the preceding approach through the formalism of the nuclear spin system is fully compatible with the requirement (1)–(8) imposed by the heuristic analysis of the observed total heat capacity $C_s(T)$ of the saturated liquid.

Susceptibility measurements[10,12] define, within experimental precision, spin-degeneracy temperatures $T_0(p)$, or briefly T_0, the latter in the saturated liquid, through a procedure of extrapolation of the susceptibility values

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[10] W. M. Fairbank, W. B. Ard, and G. K. Walters, Phys. Rev. **95**, 566 (1954).

[11] L. Goldstein, Ann. Phys. (N.Y.) **15**, 141 (1961).

[12] A. L. Thomson, H. Meyer, and E. D. Adams, Phys. Rev. **128**, 509 (1962).

down to the absolute zero. The calculated component spin heat capacity (13) turned out to be[1] over twice as large as the total heat capacity of the asymptotic ideal Fermi gas at the actual density of the liquid, in the limit of the lowest temperatures. Simultaneously, the component heat capacity arising with the nonspin degrees of freedom

$$C_{n\sigma}(T)=C_s(T)-C_\sigma(T)\,, \tag{14}$$

turns out to be less than one-half of the total heat capacity of the ideal asymptotic Fermi gas at these lowest temperatures. Here, the ratio

$$\lim_{T\text{ small}} C_\sigma(T)/C_{n\sigma}(\mathrm{i})\lesssim 5\,, \tag{15}$$

shows that these component heat capacities satisfy the inequality (5a) at the low temperatures.

At increasing temperatures, the liquid tends to become asymptotically an ideal paramagnet, or

$$\lim_{T\text{ large}} S_\sigma(T)\rightarrow R\ln 2\,,$$

or (16)

$$\lim_{T\text{ large}} \chi(T)/\chi_0(T)\rightarrow 1\,.$$

By (13),

$$\lim_{T\text{ large}} C_\sigma(T)\rightarrow 0\,, \tag{17}$$

and by (14),

$$\lim_{T\text{ large}} C_s(T)\rightarrow C_{n\sigma}(T)\,, \tag{18}$$

so that at these higher temperatures the requirement (5b) is again well satisfied by $C_\sigma(T)$ and $C_{n\sigma}(T)$. With the spin heat capacity having a maximum,[1]

$$\begin{gathered} dC_\sigma/dT=0\,,\quad d^2C_\sigma/dT^2<0\,,\\ T=T_\sigma\cong 0.43T_0\,, \end{gathered} \tag{19}$$

the large ratio (15) ensures, at $T<T_\sigma$,

$$dC_\sigma/dT>dC_{n\sigma}/dT>0\,. \tag{20}$$

Also, with decreasing $C_\sigma(T)$ at $T>T_\sigma$, the condition (8) for the near cancellation of these temperature derivatives is also well satisfied at $T>T_\sigma$, or the sum $[C_\sigma(T)+C_{n\sigma}(T)]$ corresponds to a plateau over some finite temperature interval beyond T_σ. The high-temperature behavior of $C_\sigma(T)$ can be shown[1] to ensure automatically the change in sign of the curvature of the saturated-liquid heat-capacity curve as a function of the temperature.

For a study of the temperature anomalies of the compressed liquid, it is both useful and convenient to obtain a formal though approximate representation of the component heat capacity $C_{n\sigma}(T)$, at saturation. This form of $C_{n\sigma}(T)$ together with the complete theoretical evaluation of $C_\sigma(T)$ yields a formal representation of the saturated-liquid heat capacity $C_s(T)$. This is given in the next section.

3. A FORMAL REPRESENTATION OF THE SATURATED-LIQUID HEAT CAPACITY

In our initial treatment of the spin system of the saturated liquid[1] we called attention to the possibility that the total heat capacity could be affected by the spin-heat-capacity anomaly, resulting in a maximum. The heat-capacity measurements between about 0.25 and 2.0°K by the Los Alamos[6] and Argonne[7] workers disclosed only a plateau formation. This plateau is also a consequence of the shape of the spin heat capacity in the present approach.

In previous work[1,3,4] on the various thermal properties of liquid He³, both saturated and compressed, we have refrained from a systematic quantitative analysis of the nonspin heat capacity. We have made use of the approximate and very simple linear nonspin heat capacity of Roberts and Sydoriak[6] obtained by them indirectly through their own nonspin entropy data $S_{n\sigma}(T)$. The approximate linearity in T of $C_{n\sigma}(T)$ suggested that one formally[4d] associate an apparent characteristic temperature to the nonspin degrees of freedom. In attempting to derive a more complete formal representation of the total saturated-liquid heat capacity, it seemed necessary to reanalyze the $C_{n\sigma}(T)$ heat capacity by making full use of all the available $C_s(T)$ data, including above all the Argonne[7] data, whose precision and close spacing would broaden the basis of the formal representation of $C_{n\sigma}(T)$. It was clear, however, at the start that no major over-all numerical modification would result thereby, and that the Roberts-Sydoriak $C_{n\sigma}(T)$ would still constitute an acceptable approximation. This is connected with the remarkable linearity of the nonspin entropy data. It is to be noted, though, that this linear nonspin entropy had a rather large negative intercept at the absolute zero. The attempt to describe formally a derived property, such as the entropy, rather than a directly measured one, that is a heat capacity, could not be considered satisfactory either.

In the present approach the spin heat capacity alone acquires a rigorous foundation of statistical thermodynamic character. The nonspin heat capacity appears to be representable, approximately, over the temperature range of the available data, in terms of formal elements resembling those of antisymmetric fluids. In this representation of $C_{n\sigma}(T)$ there appears a characteristic temperature $T_{0,n\sigma}$ which is about twice the Fermi temperature T_F of the asymptotic He³ Fermi gas at the liquid density, as noted already above. In terms of the formalism of the spin system,[1] the magnetic susceptibility is such that

$$\lim_{T\rightarrow 0^\circ\mathrm{K}} \chi(T)=\tfrac{3}{2}(N\mu^2/VkT_0)\,, \tag{21}$$

and

$$\lim_{T\rightarrow 0^\circ\mathrm{K}} C_\sigma(T)/R=(\tfrac{3}{2}\ln 2)(T/T_0)\,, \tag{22}$$

where $(N\mu^2/Vk)$ is the Curie constant for atoms of spin quantum number $\frac{1}{2}$, μ being the magnitude of their elementary magnetic dipole moment; N is Avogadro's number; V the molar volume of the fluid; and k Boltzmann's constant. The limit $\chi(T\rightarrow 0^\circ\mathrm{K})$ is a Pauli-type limit, since empirically, $T_0\neq T_F$, with T_F appearing strictly in the actual Pauli limit. At the saturated liquid He^3 density, T_F is about 5.0°K, and since T_0 is, approximately 0.43–0.45°K, one has (T_F/T_0) equal to about 10 or 11, and

$$\lim_{T\to 0^\circ\mathrm{K}} C_\sigma(T)/C_F(T)=\frac{\frac{3}{2}(\ln 2)/T_0}{(\pi^2/2T_F)} \simeq (2/\pi^2)(T_F/T_0) \approx 2. \tag{23}$$

Also, one obtains with $C_{n\sigma}$,[4d]

$$T_{0,n\sigma}\approx 10^\circ\mathrm{K}\,,$$

or,

$$T_{0,n\sigma}/T_F\sim 2\,,$$

the ratios indicated in the preceding section. These ratios are large, (T_F/T_0) being enormous, and suggest that starting with the ideal Fermi gas, having the actual density of the saturated liquid, as an initial zeroth approximation, a perturbation-theoretical type of approach toward a formal description of this liquid can hardly be expected to be satisfactory.

At the low temperatures where the spin system plays a dominant role in determining the thermal properties of liquid He^3, we could broaden the foundation of our approach toward a theoretical formalism for liquid He^3. We could thus prove[5] that within the precision of the nuclear paramagnetic-susceptibility ratio data, down to 0.05°K, of the Duke University group,[12] the ratio formula (F being a characteristic function of the formalism, and α_{eff} an effective parameter of this formalism)[5]

$$\begin{gathered}\chi(T,p)/\chi_0(T,p)=-F'[\alpha_{\mathrm{eff}}(T,p)]/F[\alpha_{\mathrm{eff}}(T,p)]\,,\\ F'(x)=dF/dx;\quad \alpha_{\mathrm{eff}}(T,p)=f[\tau(p)]=f(T/T_0(p)),\end{gathered}\tag{24}$$

is universal. That is, all susceptibility ratios, in any state (p,V,T) of the liquid, are represented by a unique function of the reduced temperature $\tau(p)=T/T_0(p)$, where $T_0(p)$, or $T_0(V)$, is the empirical characteristic temperature of the spin system along the isobars p, or the isochores V. This result was implied already in the earlier work[1,4] on the spin system where the formalism of the ideal antisymmetric fluid was made use of for the description of the magnetic susceptibility of the liquid in terms of an empirically derived degeneracy temperature through the limit relation (21). With this result, which ensures the universal character of all the thermal properties of the spin system through that of (24), the component thermal properties of liquid He^3, throughout its phase diagram, become permanently determined through the Boltzmann theorem fixing the spin entropy. Hence, lower limits of the various thermal properties are available in the present approach. With the limit (21), denoted as χ_P, and the ideal classical Langevin-Brillouin limit

$$\chi_0(T)=N\mu^2/VkT\,,\tag{25}$$

one has, with (24), omitting the pressure parameter,

$$\chi(T)/\chi_P=\tfrac{2}{3}(T_0/T)(-F'(\alpha_{\mathrm{eff}})/F(\alpha_{\mathrm{eff}}))\tag{26}$$

and

$$\lim_{T\to 0^\circ\mathrm{K}} \chi(T)/\chi_P\to 1\,,\tag{27}$$

where use was made of the limiting low-temperature value[1] of $(-F'/F)$. A closer discussion of the details of the limit relation (27) showed[11] that when the reduced temperature $\tau=T/T_0$ reached a value of about 0.2, the limiting value of the ratio $\chi(T)/\chi_P$ has been reached from below to some approximation. The necessarily finite precision of the experimental measurements will tend to prevent the clear observation of the slow asymptotic approach of $[\chi(T)/\chi_P]$ toward its inaccessible limit of unity. The experimental determinations of the susceptibilities should be compatible with constant values of this property, essentially the limit (21), at $(T/T_0)\lesssim 0.2$. The data of the Duke University group tend to substantiate this result. Within the statistical thermodynamic formalism for the spin system, and with the experimental verification of the universal character of the susceptibility ratio law, Eqs. (24), the spin heat capacity, Eq. (13), a lower limit of the total heat capacity, is determined without ambiguity, and this over essentially the whole temperature and pressure range of existence of the liquid. However, in contrast with the susceptibility, the approach of the spin heat capacity toward its vanishing limit at the absolute zero is considerably slower. While this approach of $C_\sigma(T)$ toward its limit was also studied in detail,[11] these studies must be completed so as to extend them to the total heat capacity, $C_\sigma(T)+C_{n\sigma}(T)$. This raises the problem of finding an analytical if approximate representation of $C_{n\sigma}(T)$.

This latter problem will be considered here essentially from a heuristic viewpoint. The empirically derived temperature dependence of the nonspin heat capacity $C_{n\sigma}(T)$ will be accepted as a guide for its approximate analytical representation to be obtained by the method of least squares. As mentioned above, the heat-capacity measurements of three independent groups of workers[6–8] have been used over a temperature range where the data overlap. This range extends from 0.2 to 2.0°K, approximately, wherein the Los Alamos[6] and Argonne[7] data overlap between about 0.4 and 2.0°K, while the third data set[8] was used only between 0.2 and 0.7°K, even though this set extends to lower temperatures. Over this range of mutual overlap, the three independent sets of data are in satisfactory agreement, and they have been used as forming a single set.

The $C_\sigma(T)$ heat capacity obtained from the theory of the spin system yields on subtraction from the experimental heat capacities the experimental nonspin heat capacities $C_{n\sigma}(T)$. Since the $C_\sigma(T)$ or theoretical spin heat capacities are affected by experimental errors through the empirical characteristic temperature T_0 of the spin system, in attempting to represent $C_{n\sigma}(T)$ analytically, it seemed of interest to explore $C_{n\sigma}(T)$ for various likely values of T_0. We have taken the range of values of T_0 between 0.43 and 45°K, which range is compatible with the present experimental precision achieved in the highly indirect experimental determinations of T_0. The various $C_\sigma(T/T_0)$ heat capacities give rise to the corresponding $C_{n\sigma}$ heat capacities which are thus made to depend on T_0. It will be seen, however, that over the small range of T_0 values indicated above, the actual variations of $C_{n\sigma}$ are quite small.

While the theoretical $C_\sigma(T)$ is determined throughout the whole temperature range of the saturated liquid, the experimental $C_{n\sigma}$ values are given only between 0.2 and 2.0°K. Hence, any approximate analytical representation of $C_{n\sigma}$ is, strictly speaking, defined only over this temperature range. As a consequence, the representation of the total heat capacity $C_s(T)$ in terms of $C_\sigma(T)$ and $C_{n\sigma}(T)$ will also be restricted to that same interval. However, it was recognized in the earlier work[1,4] that the spin heat capacity became increasingly dominant at the lower temperatures. This suggested that an extrapolation of $C_{n\sigma}(T)$ to temperatures below those of the available $C_{n\sigma}$ data was justified in some restricted sense. Namely, if no major additional group of thermal excitations existed in liquid He^3, at the low temperatures, then the extrapolation of $C_{n\sigma}$ through its approximate analytical representation to temperatures outside the indicated range would be justified to a certain extent. If there existed an additional group of low-lying excitations which would affect $C_{n\sigma}(T)$ at $T \gtrsim 0.2$°K to a negligible degree only, then the above extrapolation procedure with the exact $C_\sigma(T)$ should yield a lower limit of the heat capacity at the lowest temperatures where the additional excitations would contribute to the total heat capacity. It may be noted here that the first display of the approximate linear nonspin entropy at $T \gtrsim 0.4$°K by the Los Alamos group[6] tended to exclude the collapsing of $C_{n\sigma}$ at the lower temperatures. The approximate representation of $C_s(T)$ is then (a_s being a constant characteristic of the saturated liquid)

$$C_s(T) = C_\sigma(T/T_0) + a_s T. \tag{28}$$

This representation displays the step-function behavior of the saturated-liquid heat capacity by construction, so to speak.

In combining the various sets of $C_s(T)$ data and obtaining a more complete $C_{n\sigma}(T)$, it seemed justified to analyze directly these nonspin-heat-capacity data, an approach which is far more satisfactory than the one followed by Roberts and Sydoriak.[6] We have attempted to fit the $C_{n\sigma}$ data through the method of least squares. In this connection it appears necessary to discuss now an asymptotic physical condition which may be invoked here to justify the least-squares polynomial fit as a function of T for $C_{n\sigma}$.

We saw previously[5] the accuracy with which the universal susceptibility ratio law describes the experimental susceptibility ratios. This ratio law is that associated with the antisymmetric-fluid formalism wherein the fundamental parameter values $T_0(p)$ are totally incompatible, both as far as their numerical values and as far as their pressure variations are concerned, with the limiting ideal Fermi degeneracy temperatures $T_F(p)$ at the actual densities of the liquid. The apparently well-grounded susceptibility-ratio law raises the possibility that the nonspin heat capacity $C_{n\sigma}$ might exhibit formally a temperature dependence resembling, to some extent, that of the asymptotic antisymmetric fluid. However, as is the case with the magnetic susceptibility, the effective degeneracy temperature of the nonspin degrees of freedom would have no close connection with the Fermi temperature of the ideal system having the actual density of liquid He^3. The asymptotic condition on the nonspin heat capacity may thus be formulated as follows: If at any temperature T it were possible to fully compensate in liquid He^3 for the nonideality arising with the interatomic couplings, then the formalism of the system so compensated must reduce to that of an ideal antisymmetric fluid at the actual density of the liquid. It is assumed that the compensation process is performed at constant density. Let $C_\sigma[T/T_0(p)]$ and $C_{n\sigma}[T/T_0'(\gamma)]$ be the spin and nonspin heat capacities of liquid He^3, γ standing for the coupling strength. Then,

$$\lim_{\gamma\to 0}\left[C_\sigma(T/T_0(\gamma)) + C_{n\sigma}(T/T_0'(\gamma))\right] = C_{\mathrm{id}}(T/T_F), \tag{29}$$

where $T_0'(\gamma)$ is a hypothetical characteristic temperature of the nonspin degrees of freedom of the liquid, and C_{id} is the ideal-antisymmetric-fluid heat capacity with the Fermi degeneracy temperature T_F of the noninteracting He^3 atoms at the concentration of the saturated liquid.

More generally, if $Q_\sigma[T/T_0(\gamma)]$ and $Q_{n\sigma}[T/T_0'(\gamma)]$ denote some thermal property associated, respectively, with the spin and nonspin systems, one should have, on the basis of the indicated asymptotic condition,

$$\lim_{\gamma\to 0}\left[Q_\sigma(T/T_0(\gamma)) + Q_{n\sigma}(T/T_0'(\gamma))\right] = Q_{\mathrm{id}}(T/T_F). \tag{30}$$

The assumption referring to the possibility of compensating for the interatomic couplings may be formulated according to

$$\lim_{\gamma\to 0} T_0(\gamma) = \lim_{\gamma\to 0} T_0'(\gamma) = T_F. \tag{31}$$

Over the interval $0.25 \leq T \lesssim 2.0$°K, the experimental nonspin heat capacity obtained according to the procedure (14) appeared to be linear in T, approximately. Additional powers of T would be mere corrective-type terms to account for the mild curvature compatible with the $C_{n\sigma}$ data. In attempting to fit these $C_{n\sigma}$ values with a polynomial in T, the condition (29) tends to impose a formal constraint upon the fit. Namely, at the low temperatures, $T \ll T_0'$, odd polynomials in T are more acceptable than even ones. Odd polynomials in T are equally more acceptable than general polynomials. Actually, $C_{n\sigma}$ representations through even polynomials are excluded on the basis of the asymptotic condition (29). It is to be remembered that $C_{\mathrm{id}}(T/T_F)$ is odd in (T/T_F). In the case of a general polynomial in

T, the coefficients of the even powers of T will have to vanish in the limit of vanishing coupling strength, $\gamma\rightarrow 0$. That is, if the $C_{n\sigma}$ data did require for their polynomial fit both odd and even powers of T, then if the asymptotic condition (29) were accepted, the coefficients of the odd and even powers of T would be of entirely different character. Or, explicitly, with

$$C_{n\sigma}(T)=\sum_{\lambda=1} c_\lambda(\gamma)T^\lambda, \quad \lambda=1, 2, \cdots, \tag{32}$$

one must have, by (29),

$$\begin{aligned} &\lim_{\gamma\rightarrow 0} c_\lambda(\gamma)\rightarrow \text{finite}, \quad \lambda \text{ odd},\\ &\lim_{\gamma\rightarrow 0} c_\lambda(\gamma)\rightarrow 0, \qquad \lambda \text{ even}. \end{aligned} \tag{33}$$

This essential differentiation between the behaviors of the two classes of coefficients of $C_{n\sigma}(T)$ would suggest a peculiarly complex physical situation as compared to the one where $C_{n\sigma}(T)$ would be describable, to some approximation, in terms of an odd polynomial in T, even without any sign requirement on the coefficients of such a polynomial.

In the present work we will attempt to satisfy the condition (29) by fitting $C_{n\sigma}$ through a least-squares odd polynomial in T. In addition, other polynomial fits have also been obtained and compared with the odd-polynomial fit. These various least-squares fits have all been derived with the Moore-Zeigler computer program.[1] This program evaluates besides the coefficients of the assumed polynomial fit, the variance of the fit, that is, the mean-square error, mean over the data set, as well as the estimated root-mean-square (rms) errors $\langle\Delta c_\lambda{}^2\rangle^{1/2}$ of the coefficients c_λ of the fit. The program also yields the estimate of the averaged products of the errors Δc_λ and $\Delta c_\lambda'$, or $\langle\Delta c_\lambda \Delta c_\lambda'\rangle$, normalized with respect to their estimated rms error, or the covariances (λ,λ'). The matrix of the coefficients of the linear system of equations for the unknowns c_λ of the problem of least squares is also displayed by the program. Additional statistical characteristics associated with the least-squares fit are also included. However, the theory of least-squares fits does not directly provide any method for choosing the best fit amongst the various possible fits. The criteria for preferring one analytical expression to another are indirect and subjective. Some of these criteria are reviewed briefly by Moore and Zeigler.[13] One is evidently inclined to involve the estimated rms error over the data set, or ϵ_{rms}. Let thus N be the number of data points at the values x_i, ($i=1, 2, \cdots, N$) of the relevant independent variable x of the problem. Let $f(x_i)$, or f_i, be the value of the measured property $f(x)$ at x_i. If $\varphi(x)$ is the derived analytical least-squares fit of $f(x)$, the deviations at x_i are defined by

$$\begin{aligned} \Delta(x_i)&=f(x_i)-\varphi(x_i)\\ &=f_i-\varphi_i, \quad i=1, 2, \cdots, N, \end{aligned} \tag{34}$$

and,

$$\epsilon_{\text{rms}}=[\Sigma(\Delta(x_i))^2/(n-p)]^{1/2}, \tag{35}$$

where p is the number of independent parameters of $\varphi(x)$. If the latter is an mth degree polynomial in x, then

$$p\leq(m+1), \tag{36}$$

the lesser sign referring to the case where, by constraint, some powers of x have been excluded. Let then $\varphi_A(x)$ and $\varphi_B(x)$ be two least-squares fits to the data, and let $\epsilon_{\text{rms}}(A)$ and $\epsilon_{\text{rms}}(B)$ be the rms errors of φ_A and φ_B. One would, in general, prefer the fit with the smaller ϵ_{rms}, although if $|\epsilon_{\text{rms}}(A)-\epsilon_{\text{rms}}(B)|$ is moderate, the analytically simpler expression may be the first choice, unless the deviations $\Delta(x_i)$ have a less random distribution for the simpler fit than for the other. This then illustrates briefly some of the problems encountered in attempting to list by order of preference the various fits of the same type of the given set of data.

The rms errors of the parameters of the fits may not be directly useful for deciding between several least-squares fits. They may possibly contribute toward improving the list of preferential fits. The estimated rms errors of the individual coefficients c_λ of polynomial fits are of the type[13]

$$\delta c_{\lambda,\text{rms}}=\phi_{\lambda\lambda}(x_1,\cdots,x_N)\epsilon_{\text{rms}}, \tag{37}$$

where $\phi_{\lambda\lambda}$ is the λth diagonal element of the inverse matrix of the coefficients of the linear system of equations which determine the unknowns c_λ of the problem. In polynomial least-squares fits, large estimated $\delta c_{\lambda,\text{rms}}$ values of several of the coefficients, or of that of the dominant term, will tend to classify the fit as unsatisfactory, even though the ϵ_{rms} error of the fit itself and the distribution of the deviations $\Delta(x_i)$, Eq. (34), are acceptable.

We will consider now briefly the various polynomials which have been obtained here to represent approximately $C_{n\sigma}(T)$ of the saturated liquid over the indicated temperature interval. In particular, we will be concerned with the working form of $C_{n\sigma}(T)$ accepted here. This approximate $C_{n\sigma}$, although referring strictly to the saturated liquid, will be taken to represent an upper limit of the nonspin heat capacity of the compressed liquid. This has been amply justified earlier[4] on the basis of the normal pressure behavior of $C_{n\sigma}(T,p)$. This behavior is such that

$$(\partial C_{n\sigma}(T,p)/\partial p)_T<0, \quad T>0°\text{K},$$

or,

$$C_{n\sigma}(T, p=p_{\text{sat}})\geq C_{n\sigma}(T, p>p_{\text{sat}}). \tag{38}$$

The parameters of the accepted $C_{n\sigma}(T)$ polynomial

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[13] R. H. Moore and R. K. Zeigler, Los Alamos Report No. LA-2367, 1959 (Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C.).

fit are given in Table I. This is of the form

$$C_{n\sigma}(T,T_0)/R=\sum_{\lambda=0}^{2} c_{2\lambda+1}(T_0)T^{2\lambda+1}, \tag{39}$$

or an odd fifth-degree polynomial whose coefficients $c_{2\lambda+1}$ depend somewhat on T_0, as mentioned already. The rather small T_0 interval explored here appears, at the present time, to bracket the likely correct value of the saturated liquid T_0. However, if improved susceptibility data on the saturated liquid became available, they may yield a more accurate T_0 value which could fall outside the T_0 interval considered here. In this case, new $C_{n\sigma}(T)$ values will result and the procedure here followed will have to be repeated with the improved set of $C_{n\sigma}$ data.

Table I shows that the cubic and fifth-degree terms are correction terms whose importance increases, however, at increasing temperatures. The T^5 term has a positive coefficient, i.e., this fit does not reproduce the negative sign of the corresponding coefficient in the asymptotic low-temperature series representation of the ideal-antisymmetric-fluid total heat capacity. The inclusion of the T^3 and T^5 terms ensures the finite if small curvature of $C_{n\sigma}$ at increasing temperatures. Indeed, while at $T\lesssim 1.0$°K, $C_{n\sigma}(T)$ is concave downward, that is toward smaller $C_{n\sigma}$ values, at $T>1.0$°K, it has positive curvature. The dominance of the linear term in (39) is in accord with the qualitative results of the Argonne group[7] as well as with the approximate linear $C_{n\sigma}$ representation obtained indirectly by the Los Alamos group.[6] As shown also in Table I, the estimated rms relative errors of the coefficient $c_1(T_0)$, for the various T_0 values, amount to about 1%, while those of the much smaller $c_3(T_0)$ and $c_5(T_0)$ coefficients are about 10%. The over-all estimated rms errors ϵ_{rms} of the fits (39) are somewhat larger than $0.01R$ over the data set.

The least-squares fits of the type (39) can be further analyzed by lifting their constraint at the origin of the $(C_{n\sigma},T)$ plane, at the absolute zero. It is thus possible to verify if the polynomial without this constraint is compatible or close to the one derived with the constraint of vanishing at $T\rightarrow 0$°K. The elements $c_{2\lambda+1}{}^{(n)}$ of the no-constraint polynomials, similar to (39), are included in Table II. It is seen at once that the intercepts $c_0{}^{(n)}(T_0)$ have no numerical significance, their estimated relative rms errors being much too large. Simultaneously, it is seen that the other coefficients $c_{2\lambda+1}{}^{(n)}(T_0)$ of the no-constraint polynomials remain very close to the corresponding parameters of the constrained fits of Table I. However, the relative rms errors of the relevant no-constraint coefficients $c_1{}^{(n)}$, $c_3{}^{(n)}$, and $c_5{}^{(n)}$ have all increased over those of the fits with constraint (39). These relative errors of the coefficients $c^{(n)}(T_0)$ are, however, still acceptable. It is then most satisfactory to observe that the $C_{n\sigma}$ data do extrapolate to zero through the no-constraint fit

$$C_{n\sigma}(T,T_0)/R=c_0{}^{(n)}(T_0)+\sum_{\lambda=0}^{2} c_{2\lambda+1}{}^{(n)}(T_0)T^{2\lambda+1}, \tag{40}$$

with

$$c_0{}^{(n)}(T_0)\simeq 0.$$

TABLE I. The parameters and their relative estimated rms errors in the approximate molar nonspin heat-capacity polynomial fits of saturated liquid He^3, together with their estimated rms error, ϵ_{rms}.

T °K	c_1 (°K)$^{-1}$	$\delta c_1/c_1$ %	c_3 (°K)$^{-3}$	$(\delta c_3/c_3)$ %	c_5 (°K)$^{-5}$	$(\delta c_5/c_5)$ %	ϵ_{rms}/R
0.43	0.494	0.85	−0.0563	8.7	0.0139	8.6	0.0115
0.435	0.491	0.85	−0.0541	9.0	0.0135	8.8	0.0114
0.44	0.488	0.85	−0.0521	9.3	0.0131	9.0	0.0114
0.45	0.482	0.85	−0.0480	10.0	0.0123	9.5	0.0113

It is of importance to note here that the Moore-Zeigler[13] least-squares-fit program relies upon the numerical method of Harper[14] for the solution of the linear systems of equations which define the parameters of the fit. This method avoids the well-known difficulties[15] arising with the inversion of the matrix of coefficients of ill-conditioned linear systems. The solutions here obtained are of great numerical precision, compatible with the precision of the input data on $C_{n\sigma}(T)$.

Tables I and II show that the estimated rms errors are about the same for both fits (39) and (40), and amount to about $0.01R$. The constrained odd fifth-degree polynomial (39) appears to be stable when judged in terms of its behavior on relaxing the constraint at the absolute zero.

Various additional least-squares polynomials have also been obtained for $C_{n\sigma}$, and even though they are

TABLE II. Same as Table I with no constraint at the absolute zero.

T °K	$c_0{}^{(n)}$	$(\delta c_0{}^{(n)}/c_0{}^{(n)})$ %	$c_1{}^{(n)}$ (°K)$^{-1}$	$(\delta c_1{}^{(n)}/c_1{}^{(n)})$ %	$c_3{}^{(n)}$ (°K)$^{-3}$	$(\delta c_3{}^{(n)}/c_3{}^{(n)})$ %	$c_5{}^{(n)}$ (°K)$^{-5}$	$(\delta c_5{}^{(n)}/c_5{}^{(n)})$ %	ϵ_{rms}/R
0.43	0.00125	465	0.491	2.6	−0.0549	15.2	0.0136	12.4	0.0115
0.435	0.00016	3700	0.490	2.6	−0.0540	15.3	0.0134	12.5	0.0115
0.44	−0.0009	650	0.489	2.6	−0.0531	15.5	0.0133	12.6	0.0114
0.45	−0.0028	200	0.488	2.6	−0.0512	16.0	0.0129	13.0	0.0113

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[14] P. E. Harper, Los Alamos Scientific Laboratory Computer Program LA-LSS-FD 04, 1965 (unpublished).

[15] C. Lanczos, *Linear Differential Operators*, (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961), pp. 129–134.

not used in the present work it seems instructive to describe them briefly. For instance, the odd cubic fit, simpler than the odd fifth-degree fit (39), reduces practically to a linear fit because the negative coefficient $c_3(T_0)$ of the T^3 term is very small and of no numerical significance. Its estimated relative rms error is very large. On lifting the constraint at the origin, the no-constraint cubic fit acquires a large positive-nonspin heat-capacity intercept, amounting to more than $0.03R$. The linear term of this cubic fit is the dominant term, and the intercepts $c_0^{(n)}(T_0)$ and the now positive $c_3^{(n)}(T_0)$ coefficients have estimated relative errors of 16 and 22%, respectively. Hence, in contrast with the fits (39), the cubic fits fail to yield the correct extrapolation at $T \rightarrow 0°\text{K}$ on lifting the constraint. Furthermore, the no-constraint fits give rise to a relatively large variation of the dominant parameter $c_1(T_0)$, since $c_1^{(n)}(T_0)$ is about $0.9c_1(T_0)$. These odd cubic fits thus appear to be unstable. We may add here that the simplest linear fit to the $C_{n\sigma}$ data was found to be quite stable, but its ϵ_{rms} over the data set has become larger when compared with the rms errors of Tables I and II. Also, the linear fit has an unsatisfactory distribution of the deviations $\Delta(x_i)$, Eq. (34). It may, however, be considered as a first approximation toward a polynomial expression of $C_{n\sigma}(T)$, which is essentially identical with the one found by Roberts and Sydoriak[6] through their indirect approach.

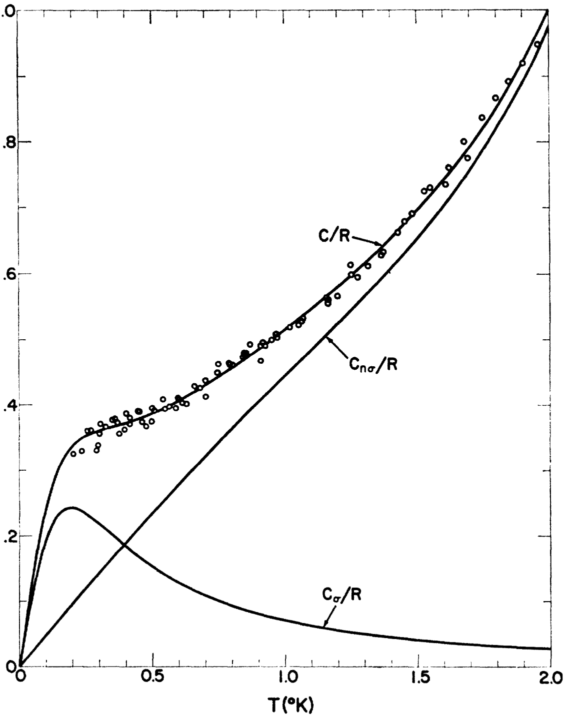

FIG. 1. The calculated spin, nonspin, and total-molar heat capacities of saturated liquid He^3, with the experimental data of three independent groups of workers; Refs. 6, 7, and 8.

The following types of least-squares polynomial fits of $C_{n\sigma}$ have also been obtained: even polynomials in T, both with the constraint on $C_{n\sigma}$ to vanish at the absolute zero and in the absence of this constraint. These fits are totally unacceptable because their rms errors are quite large, some ten times the ϵ_{rms} values of the fits (39). Furthermore, these fits are unstable, since on lifting the constraint at the origin they develop large positive intercepts, that is large $c_0^{(n)}$ values. Also the distributions of the deviations $\Delta(x_i)$ or $\Delta(T_i)$, Eq. (34), become practically regular.

Polynomial fits with all powers of T have also been studied, both with and without constraint at the origin. These types of fits turned out to be also unstable in the sense indicated above. In addition, the estimated relative errors of the coefficients $c_\lambda(T_0)$ and $c_\lambda^{(n)}(T_0)$, for $\lambda \geq 2$, were found to be large.

Inasmuch as these various least-squares fits are unique and the $C_{n\sigma}$ data are all available, a more detailed description of the discarded polynomials did not appear warranted. As mentioned, we will make use of the representation (39) of $C_{n\sigma}(T,T_0)$ throughout the rest of this work. In a first approximation, this same $C_{n\sigma}(T,T_0)$ will be taken to provide an approximate upper limit of the nonspin heat capacity in the compressed liquid of known $T_0(p) < T_0(p_{\text{sat}})$.

In the numerical evaluation of the total heat capacity of the saturated liquid, $C_s(T)/R$, in terms of (14), we have limited ourselves to the unique value of $T_0 = 0.45°\text{K}$, which is probably a good approximation to the correct T_0 of the saturated liquid. With (C_σ/R) having a solid theoretical basis,[1] the relation (14) achieves, within the stated limitations of the approach, with $C_{n\sigma}(T)$ given approximately by (39), an analytical representation of $C_s(T)$, the heat capacity of saturated liquid He^3. The validity of this representation is limited over the range 0.2–2.0°K, where $C_{n\sigma}$ is approximated by (39). The extrapolation of $C_{n\sigma}$ toward lower temperatures may well correspond to the actual nonspin heat capacity at $T < 0.2°\text{K}$ if no additional states of thermal excitations appeared at these lower temperatures in the nonspin system. If additional excitations existed whose contributions to $C_{n\sigma}$ at $T > 0.2°\text{K}$ were small and negligible, then the formal representation (14) of $C_s(T)$, with $C_{n\sigma}(T)$ given by (39), is only a lower-limit approximation to the total saturated-liquid heat capacity at these lower temperatures.

We give in Fig. 1 the theoretical spin heat-capacity curve with T_0 equal to 0.45°K, and the graph of the approximate $C_{n\sigma}(T)/R$ least-squares polynomial fit, Eq. (39), together with their resultant graph C/R, omitting the subscript s standing for saturation. The data points are also included. It is of interest to observe that the deviations

$$\Delta(T_i) = (C(T_i)/R)_{\text{exp}} - (C(T_i)/R)_{\text{calc.}} \tag{41}$$

have a fairly random distribution, with the exception, however, of the interval between 1.0 and 1.5°K, where the calculated total heat capacity appears to be larger than the measured values. However, the numerical values of the deviations $\Delta(T_i)$ over this reduced range reach 0.01 only occasionally, and such a deviation is entirely compatible with the experimental accuracy. The over-all rms error of the formal representation of the total heat capacity over the data set, or

$$\{\sum_{i=1}[\Delta(T_i)]^2/N\}^{1/2}=0.011\,, \tag{41a}$$

there being $N=86$ data points. It is clear that while the formal representation

$$C(T)/R=C_\sigma(T)/R+\sum_{\lambda=0}^{2}c_{2\lambda+1}(T_0)T^{2\lambda+1}\,, \tag{42}$$

of the total heat capacity appears to be satisfactory, the result obtained would gain in significance if it were still capable of describing the data over the low-temperature range $T<0.2$°K. At $T>2.0$°K, it is unclear, at the present time, if (42) will reproduce the data in a satisfactory way, even over some limited temperature range, because the rapid approach toward the critical region may increasingly affect the saturated-liquid heat capacity beyond the range of the data set.

Before turning to the problems of the heat capacity at low temperatures in the saturated liquid, and at finite temperatures in the compressed liquid, it appears interesting to consider more closely the anomalously shaped total heat capacity of Fig. 1, or Eq. (42). The latter formal representation accounts fairly well for the observed three characteristic regions of $C(T)$. The first of these is the rapidly increasing region at $T\lesssim 0.2$°K, with C/R reaching a value of about $\frac{1}{3}$ at 0.2°K. Between about 0.2 and 0.7°K, $C(T)$ increases by about 25% of its value at the beginning of this range, or by about $R/12$, the temperature increase being by a factor of 3.5. This is the plateau-like region of the heat capacity. Beyond this plateau, from about 0.7 to 2.0°K, or a temperature change by a factor close to 3, the heat capacity increases by a factor somewhat larger than 2. The saturated liquid heat capacity increases monotonically, in spite of the plateau, i.e.,

$$\begin{gathered}(d/dT)(C(T)/R)>0\,,\\ 0\leq T\leq 2.0°\mathrm{K}\,,\end{gathered} \tag{43}$$

throughout the indicated interval, subject to possible limitations in validity stated above at $T<0.2$°K. $C(T)$ is concave downward, according to the observations, up to about the end of the first quarter of the plateau. It has an inflection point in the middle of the plateau, viz.,

$$(d^2/dT^2)(C(T)/R)=0\,,\quad T\simeq 0.35°\mathrm{K}\,, \tag{44}$$

where its temperature derivative is given by

$$(d/dT)(C(T)/R)=0.115/(°\mathrm{K})\,,\quad T\simeq 0.35°\mathrm{K}\,, \tag{44a}$$

which derivative is some twenty times smaller than its value in the limit of the absolute zero, as shown in the next section.

4. BEHAVIOR OF THE SATURATED-LIQUID He³ HEAT CAPACITY AT LOW AND VERY LOW TEMPERATURES

While the formal representation (42) of the previous section describes in a satisfactory way the saturated-liquid heat-capacity data over the range 0.2–2.0°K, its intrinsic value must be qualified, as implied repeatedly above. This qualification refers to the fact that only the spin heat-capacity component of (42) possesses a solid-statistical-thermodynamic foundation. The heat capacity of the degrees of freedom other than spin has only an asymptotic basis, in the sense that this heat capacity must reduce to a component of the heat capacity of the limiting ideal antisymmetric fluid, on compensating for the interatomic couplings in coordinate space. Nevertheless, the formal representation (42) leads to definite physical predictions which can be submitted to experimental test. One of these predictions relative to the saturated liquid will be studied in the present section, while the remaining ones referring to the compressed liquid will be analyzed in the next section.

The representation (42) predicts a unique behavior of the saturated-liquid heat capacity at low temperatures and at the approaches of the absolute zero. As noted already, the use of (42) at $T<0.2$°K is based on the assumption that the two component heat capacities, $C_\sigma(T)$ and $C_{n\sigma}(T)$, exhaust the thermal excitations of the liquid at the low temperatures, as they appear to do at $T>0.2$°K, where their sum gives a satisfactory representation of the data available at the higher temperatures. If this assumption failed at the low and very low temperatures, then $C(T)$ given by (42) should be only a lower limit of the total heat capacity at $T<0.2$°K The above assumption will be used as a working hypothesis in what follows.

Part of the problem at hand has been discussed by us[9] in the course of the analysis of various thermal properties of liquid He³ arising with its nuclear spin system alone at the very low temperatures. These referred to the paramagnetic susceptibility $\chi(T)$ of the liquid and the spin heat capacity $C_\sigma(T)$ or the ratio $C_\sigma(T)/T$, to within a constant factor, as well as to the temperature derivative $(d/dT)C_\sigma(T)$, to within the same constant factor. The problem in the previous work, was considered along the following lines. Let the formulas describing the above properties be so normalized that they should all approach unity at $T\rightarrow 0$°K. One thus defines, as shown for the susceptibility by (26) and (27),

$$\chi(T/T_0)/\chi_P=\sigma_p(T/T_0)\,, \tag{45}$$

$$\frac{C_\sigma(T/T_0)/R}{\frac{3}{2}(\ln 2)(T/T_0)}=\sigma_c(T/T_0)\,, \tag{46}$$

and,

$$\frac{(d/dT)(C_\sigma(T/T_0)/R)}{\frac{3}{2}(\ln 2)T_0^{-1}}=\sigma_d(T/T_0). \tag{47}$$

The functions σ_p, σ_c, and σ_d have been given explicitly in the previous work.[9] These normalized properties are such that

$$\lim_{T\to 0^\circ\mathrm{K}}\left\{\begin{matrix}\sigma_p(T/T_0)\\ \sigma_c(T/T_0)\\ \sigma_d(T/T_0)\end{matrix}\right\}=1. \tag{48}$$

We have shown[9] that for identical values of the reduced temperature (T/T_0), one had

$$\sigma_p(T/T_0)>\sigma_c(T/T_0)>\sigma_d(T/T_0). \tag{49}$$

These inequalities state that, these normalized properties being decreasing functions of (T/T_0) or T, in order to reach a value of the normalized spin heat capacity which would differ from its asymptotic-inaccessible limit at the absolute zero by a quantity ϵ, the temperature $T_{\epsilon c}$, where σ_c takes on the value $(1-\epsilon)$ must be considerably lower than the temperature $T_{\epsilon p}$ at which the property σ_p reaches the value $(1-\epsilon)$. On the other hand, in order to observe the value $(1-\epsilon)$ of the normalized derivative σ_d, one must reach a temperature $T_{\epsilon d}$ such that $T_{\epsilon d}<T_{\epsilon c}$. Or, for identical values of σ_p, σ_c, and σ_d, the temperatures are such that

$$T_{\epsilon p}>T_{\epsilon c}>T_{\epsilon d}. \tag{50}$$

As noted already above, in connection with the limit (27), the formalism of the spin system predicts that if the susceptibility is measured down to a value of T/T_0 of 0.2 or 0.15, the asymptotic limit of this property at the absolute zero would be approached to a fair degree of approximation.[9] This result appears to be verified through the systematic susceptibility measurements of the Duke University group.[12] This verification consists in the practically constant value of the observed susceptibility over the whole liquid phase at temperatures already well above the lowest temperatures reached by these workers, that is at $T>0.05$°K.

In the limit of low temperatures, $T\ll T_0$, the functions $\sigma(T/T_0)$ have asymptotic expansions.[9] Here we will limit ourselves to the discussion of $C(T)/RT$ and $(d/dT)[C(T)/R]$. One has then with the asymptotic expansion[9] of C_σ/RT, and using (42) for $C(T)$,

$$\lim_{T\ll T_0}[C(T)/RT]=(\tfrac{3}{2}(\ln 2)/T_0)\times[1-\sum_{\lambda=1}(2\lambda+1)p_{2\lambda}(T/T_0)^{2\lambda}]+\sum_{\lambda=0}^{2}c_{2\lambda+1}(T_0)T^{2\lambda}, \tag{51}$$

where the coefficients $c_{2\lambda+1}(T_0)$ are given in Table I, while the $p_{2\lambda}$ coefficients have been tabulated previously[9] up to p_{12}, or up to λ equal to 6. One has, similarly,

$$\lim_{T\ll T_0}(d/dT)[C(T)/R]=(\tfrac{3}{2}(\ln 2)/T_0)\times[1-\sum_{\lambda=1}(2\lambda+1)^2p_{2\lambda}(T/T_0)^{2\lambda}]+\sum_{\lambda=0}^{2}(2\lambda+1)c_{2\lambda+1}(T_0)T^{2\lambda}. \tag{52}$$

It is thus seen that on the basis of the formal representation (42), both $C(T)/RT$ and $(d/dT)[C(T)/R]$ approach parabolically their finite limit at the absolute zero. Their osculating parabolas, with their common vertex at the absolute zero are, respectively,

$$\lim_{T\to 0^\circ\mathrm{K}}C(T)/RT=[(\tfrac{3}{2}(\ln 2)/T_0)+c_1(T_0)]-[(\tfrac{9}{2}(\ln 2)p_2/T_0^3)+c_3(T_0)]T^2, \tag{53}$$

and

$$\lim_{T\to 0^\circ\mathrm{K}}(d/dT)(C(T)/R)=[(\tfrac{3}{2}(\ln 2)/T_0)+c_1(T_0)]-3[(\tfrac{5}{2}(\ln 2)p_2/T_0^3)+c_3(T_0)]T^2,$$
$$p_2=\pi^2/12=0.8225. \tag{54}$$

The common vertex value of these two properties is thus

$$\lim_{T=0^\circ\mathrm{K}}(C(T)/RT)=\lim_{T=0^\circ\mathrm{K}}(d/dT)(C(T)/R)=(\tfrac{3}{2}(\ln 2)/T_0)+c_1(T_0). \tag{55}$$

We give in Fig. 2 the graphs of $C(T)/RT$ and $(d/dT)[C(T)/R]$ at the lowest temperatures, for two values of T_0, which may bracket the actual T_0 value of saturated liquid He^3, as mentioned already. It is to be noted that the asymptotic series representation of $C_\sigma(T/T_0)$ tends to break down at rather small values of T/T_0, so that the calculated curves refer to exact

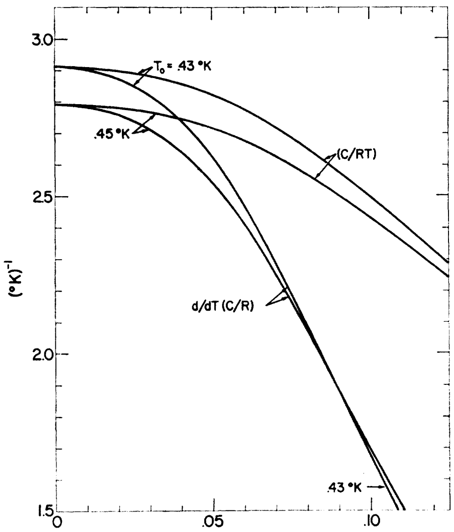

FIG. 2. The theoretical (C/RT) ratios and derivatives $d(C/R)/dT$ in saturated liquid He^3 for two approximate T_0 values.

values of both C_σ and (dC_σ/dT) and not to those resulting with the asymptotic series representations.

It is seen, and this was already exhibited in part in the analysis of the spin system,[9] that with a characteristic temperature of the spin system as low as 0.45°K, the appearance of a finite heat capacity arc which might be taken to coincide approximately with the tangent to the heat capacity curve at the absolute zero is confined to temperatures $T \lesssim 0.02$°K if judged in terms of the ratio $C(T)/RT$. In terms of the much more stringent criterium expressed by the behavior of $(d/dT)[C(T)/R]$, the so-called "heat capacity linear in T" tends to recede toward much lower temperatures of questionable accessibility.

The vertices of the osculating parabolas (54) and (55), the temperature slopes of the tangent to the heat capacity at the absolute zero, are likely to be included between the limits given in Fig. 2, or

$$\begin{aligned} 2.79/(°\mathrm{K}) \leq [C(T)/RT]_{T=0°\mathrm{K}} \\ = (d/dT)[C(T)/R]_{T=0°\mathrm{K}} \leq 2.91/(°\mathrm{K}). \quad (56) \end{aligned}$$

At the present time, it seems doubtful if heat-capacity measurements could distinguish between the two limits (56) of the likely location of the correct vertex of the osculating parabolas associated with the heat capacity. However, at temperatures $T > 0.05$°K, the accuracy of $C(T)/RT$ or of $(d/dT)[C(T)/R]$ measurements may reach a level where at least the correct trend of temperature variation of these quantities becomes experimentally accessible and a comparison with the calculated trends reaches some degree of justification.

It is to be noted that the lower limit of the vertex at 2.79/°K is very close to the one resulting with the indirect approximate linear fit of $C_{n\sigma}(T)$ of the Los Alamos group,[6] when completed by the limit of $[C_\sigma(T/T_0)/RT]$ or $[\frac{3}{2}(\ln 2)/T_0]$, with T_0 taken to be 0.45°K, approximately. It is seen that if one expressed formally the limiting value of $[C(T)/RT]_{T=0°\mathrm{K}}$ in terms of the ideal antisymmetric formula, one would find with the limits (56), the characteristic temperatures 1.70 and 1.77°K, respectively. The formal apparent characteristic temperature resulting with the linear terms of $C_{n\sigma}(T,T_0)/R$ turns out to be about 10°K, as indicated already above.

5. HEAT-CAPACITY ANOMALIES OF COMPRESSED LIQUID He^3

In our initial approach[1] to the heat capacity problems of liquid He^3 we have called attention to the possibility for the spin heat-capacity peak to become observable on the total heat capacity, which, of course, is the only directly measurable heat capacity. Inasmuch as in our approach the nonspin heat capacity $C_{n\sigma}(T,T_0)$ is described only semiphenomenologically, we have refrained, in earlier work, from confronting the theoretical C_σ's with the empirical $C_{n\sigma}$'s because of the scarcity of incontrovertible independent heat-capacity data in compressed liquid He^3. Scarcity of such data still persists but the availability of better founded $T_0(p)$ values for the spin system which satisfy the character of universality of the susceptibility ratio law[5] appears to justify the analysis and the almost quantitative prediction of the main anomalies of the compressed-liquid heat capacity occurring at relatively low but accessible temperatures.

The universal character of the susceptibility ratio law[5] ensures the universal character of the spin entropy $S_\sigma[T/T_0(p)]$ and that of the properties originating with S_σ. Or, in terms of the reduced temperature $T/T_0(p)$, part of the total heat capacity of liquid He^3 is also a universal function of this coordinate. If this type of behavior extended also to the nonspin heat capacity $C_{n\sigma}[T,T_0(p)]$, then the total heat capacity $C[T,T_0(p)]$ represented as a function of the reduced temperature would be also of universal character. That is, the $C[T/T_0(p)]$ curve would be similar to the total heat capacity curve of Fig. 1, or the total heat capacity of liquid He^3, at all pressures, would be a permanently increasing function of the temperature, with a characteristic plateau originating with the interplay of the spin degrees of freedom and the degrees of freedom other than spin. This is, however, not the case, because the thermal properties of the degrees of freedom other than spin seem to have no direct and strong dependence on the characteristic temperature $T_0(p)$ of the spin system. The total heat capacity of liquid He^3 is not an invariant under the transformation induced by compression, even though its component heat capacity $C_\sigma[T/T_0(p)]$ is such an invariant function.

This lack of formal pressure invariance of the total heat capacity $C(T,p)$ arises from the contrasting pressure variations of C_σ and $C_{n\sigma}$, at least over a finite but important temperature range. Over this range, one has

$$[\partial C_\sigma(T/T_0(p))/\partial p]_T \geq 0, \quad T \text{ low}, \quad (57)$$

and we rewrite the relation already referred to above,

$$(\partial C_{n\sigma}(T,p)/\partial p)_T \leq 0, \quad \text{all } T, \quad (38)$$

where the equal signs refer to the absolute zero for both C_σ and $C_{n\sigma}$, and for C_σ the equal sign also refers to a locus of points of the phase diagram, at nonzero temperatures, as shown earlier in a detailed analysis of the spin heat capacity.[4a] Beyond this locus, one must have,

$$\left[\frac{\partial C_\sigma(T/T_0(p))}{\partial p}\right]_T < 0, \quad T \text{ high}, \quad (58)$$

or a normal pressure behavior like that of $C_{n\sigma}$.

It is convenient now to refer to the graphs of the two component heat capacities of Fig. 1 for a visualization of the pressure effect on C_σ and $C_{n\sigma}$. We have shown earlier[4a] that on compression the spin-heat-capacity peak is shifted toward lower temperatures. The spin-heat-capacity arc on the low-temperature side of the peak is thus lifted from its initial pressure, while the higher temperature arc is depressed. It is instructive and useful to consider additional aspects of the relations (57) and (58). One has, denoting by

$\tau(p)$ the reduced temperature $T/T_0(p)$,

$$\begin{aligned}(\partial/\partial p)_T C_\sigma(\tau_p) &= (dC_\sigma/d\tau)(\partial\tau/\partial p)_T \\ &= |(\partial\tau/\partial p)_T|\,(dC_\sigma/d\tau),\end{aligned} \tag{59}$$

since

$$(\partial\tau/\partial p)_T = -(\tau(p)/T_0(p))(dT_0(p)/dp) \geq 0. \tag{60}$$

Hence, by (59), the infinitesimal transformation associated with the isothermal compression $(T,p) \rightarrow (T,\, p+\delta p)$, causes the representative point of $C_\sigma(\tau)$ to slide upward or downward on the invariant universal graph of $C_\sigma(\tau)$, with

$$(dC_\sigma/d\tau) \gtrless 0, \quad \text{according as} \quad \tau \lessgtr \tau_\sigma, \tag{61}$$

where τ_σ is the reduced temperature of the spin-heat-capacity peak $C_{\sigma M}$. The maximum of C_σ is a fixed point of the transformation induced by isothermal compression of the liquid. Indeed, by (59),

$$\begin{gathered}(dC_\sigma/d\tau) = 0, \quad \tau = \tau_\sigma, \quad C_\sigma = C_{\sigma M}, \\ (\partial/\partial p)_T C_\sigma(\tau(p) = \tau_\sigma(p)) = 0.\end{gathered} \tag{62}$$

In the $(C_\sigma(T/T_0(p)),T)$ representative diagram, the spin-heat-capacity peak has only its temperature coordinate shifted toward lower values on isothermal compression. That is,

$$\begin{gathered}C_\sigma(T_\sigma(p)) \equiv C_\sigma(T_\sigma(p+\delta p)), \\ \lim_{\delta p\ \text{small}} T_\sigma(p+\delta p) = T_\sigma(p) + (dT_\sigma/dp)_p \delta p + \cdots \\ < T_\sigma(p),\end{gathered} \tag{63}$$

because, γ being a characteristic numerical constant of the spin system,

$$\begin{gathered}T_\sigma(p) = \gamma T_0(p), \\ dT_\sigma/dp = \gamma(dT_0/dp) < 0, \quad \gamma \simeq 0.43.\end{gathered} \tag{64}$$

In the (C_σ,T) plane, isothermal compression of the liquid causes the spin heat-capacity peak to shift along the line

$$\begin{aligned}C_\sigma &= C_{\sigma M}(T_\sigma) \\ &= 0.24R,\end{aligned} \tag{65}$$

parallel to the temperature axis, as implied by (62).

In contrast, on isothermal compression, the regular behavior of $C_{n\sigma}(T,T_0)$, with its expected dominant term linear in T as in the saturated liquid at low and medium temperatures, would consist in a rotation of $C_{n\sigma}$ around the origin of the $(C_{n\sigma},T)$ plane toward smaller values of $C_{n\sigma}$, that is toward the temperature axis. With the pressure increase of the spin heat capacity at $T < T_\sigma(p)$, and the simultaneous, if smaller, pressure decrease of $C_{n\sigma}$ throughout the whole temperature interval, by (38), C_σ becomes increasingly larger than $C_{n\sigma}$ at $T < T_\sigma(p)$. This then should allow the spin heat capacity to impress its anomaly, that is its peak, upon the resultant total heat capacity $C(T,p)$, under sufficient compression. Indeed, with the formal representation (14), or of the type (42), using straight temperature derivatives instead of partial derivatives, the pressure parameter being kept constant, one obtains the locations $T_M(p)$ and $T_\mu(p)$ of the total constant-pressure heat-capacity maxima and minima as the roots of

$$(d/dT)C_\sigma(T/T_0(p)) = -(d/dT)C_{n\sigma}(T,T_0(p)). \tag{66}$$

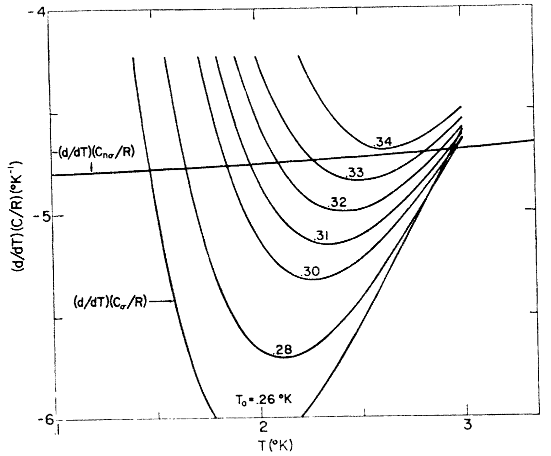

FIG. 3. The existence of the heat-capacity extrema in compressed liquid He^3. The approximate temperatures of the heat-capacity maxima and minima, over a limited pressure range, are those of the points of intersection of the two component temperature derivative curves.

In the absence of an exact explicit analytical expression for C_σ, the roots of (66) can be obtained numerically or graphically. We give in Fig. 3 the graphs of both sides of Eq. (66), under the already mentioned restrictive assumption that $C_{n\sigma}(T,T_0,p)$ is equal approximately, at all pressures p, to the saturated liquid nonspin heat capacity, denoted as $C_{n\sigma}$ in Fig. 3. The pressure decrease, Eq. (38), of $C_{n\sigma}(T,p)$ is thus neglected here, but correct account is taken of the pressure variations of C_σ, Eq. (59), through the empirically determined $T_0(p)$ function of the spin system.[12] The pressure range covered in Fig. 3 extends from about 11 atm

$$[T_0(p \simeq 11 \text{ atm}) \sim 0.34°\text{K}]$$

up to the pressure of the isobar tangent to the melting-pressure line at its minimum, or somewhat below 30 atm, where $T_0(p)$ is close to 0.26°K.

Before discussing the solutions of Eq. (66), at the various pressures, we have to consider the temperature derivatives of $C_\sigma[T/T_0(p)]$. In addition to the characteristic features of C_σ, given by (62)–(65), we have to note that $C_\sigma(\tau(p))$ has an inflection point at $\tau_{\sigma\varphi}$, or

$$\begin{gathered}(d^2/d\tau^2)C_\sigma(\tau) = 0, \quad \tau_{\sigma\varphi} \simeq 0.76; \\ C_\sigma(\tau_{\sigma\varphi}) = 0.203R; \quad (d/d\tau)C_\sigma(\tau = \tau_{\sigma\varphi}) = -0.16R.\end{gathered} \tag{67}$$

In analogy with (64),

$$\begin{aligned}T_{\sigma\varphi}(p) &= \tau_{\sigma\varphi}(p)T_0(p) \\ &= 0.76T_0(p),\end{aligned} \tag{68}$$

and with $[dT_0(p)/dp] < 0$, on compression, beside $T_\sigma(p)$, the inflection point of C_σ at $T_{\sigma\varphi}(p)$ is also shifted toward lower temperatures. Simultaneously, under pressure increase, the minima of $(d/dT)C_\sigma[T/T_0(p)]$, given by (67), are shifted toward larger negative values, since

$$(d/dT)C_\sigma(T/T_0(p))_{T_{\sigma\varphi}} = -0.16R/T_0(p). \tag{69}$$

The family of the spin-heat-capacity temperature-derivative curves of Fig. 3 display the characteristic behavior of $(d/dT)C_\sigma[T/T_0(p)]$ as a function of both temperature and pressure.

With the lower limit $(-)(d/dT)(C_{n\sigma}/R)$, and the two intersections of its graph with the temperature-derivative curves of the spin heat capacities, $(d/dT)(C_\sigma/R)$, in Fig. 3, the existence of two solutions $T_M(p)$ and $T_\mu(p)$ is proved rigorously for pressures p such that $T_0(p) \lesssim 0.34°\mathrm{K}$ and $T_0(p) \gtrsim 0.26°\mathrm{K}$, or $11 \leq p \lesssim 30$ atm approximately. It should be noted here that if $C_{n\sigma}(T,p)$ and $(-)(d/dT)C_{n\sigma}(T,p)$ were known at all pressures, the main difference with Fig. 3, representing the two sides of Eq. (66) would consist in displacing slowly upward the almost linear $(-)(d/dT)(C_{n\sigma}/R)$ parallel to itself. As a consequence, the relevant pressure interval might start at a pressure somewhat below 10 atm, and the lower temperatures $T_M(p)$ of the heat-capacity maxima would be shifted toward smaller values, while those of the minima $T_\mu(p)$ would be increased somewhat, with respect to the temperatures given in Fig. 3 through the intersections. This, however, could in no way affect the existence of these heat-capacity extrema over the indicated pressure interval.

This result accounts at once for the absence of any heat-capacity peak of the saturated liquid, that is for its monotonically increasing character with temperature throughout the explored temperature range, 0.2–2.0°K. It is to be noted that by (68) and (69),

$$\begin{gathered} T_{\sigma\varphi}(p_{\mathrm{sat}}) \simeq 0.33-0.34°\mathrm{K}, \\ (d/dT)(C_\sigma(T,p_{\mathrm{sat}})/R)_{T_{\sigma\varphi}} \simeq (-0.37)-(-0.35)/°\mathrm{K}, \end{gathered} \tag{70}$$

so that the curve of the temperature derivative of the saturated-liquid spin heat capacity is situated well above that of $(-)(d/dT)[C_{n\sigma}(T,p_{\mathrm{sat}})/R]$, this latter being almost equal to $-c_1(T_0)$, or about $(-0.48)/°\mathrm{K}$ at 0.1°K, and $(-0.47)/°\mathrm{K}$ at about 0.3°K, with T_0 taken to be 0.45°K, approximately. The latter derivative is seen to conform to the one indicated above for $(d/dT)[C(T)/R]$ at its inflection point of 0.35°K; see (44a).

It is thus fully justified to write

$$dC_\sigma/dT > (-)dC_{n\sigma}/dT, \quad p_{\mathrm{sat}} \leq p \lesssim p_i, \tag{71}$$

or there is a pressure interval, (p_{sat}, p_i), in the region of lower pressures, at which the total constant-pressure heat capacity of liquid He³ is of monotonic temperature variation, increasing always with the temperature. The approximate upper limit p_i of this interval appears to be around 10 atm. Actually, the pressure p_i is that pressure at which Eq. (66) has two coincident solutions, or when $(d/dT)C_\sigma[T/T_0(p_i)]$ and $(-)(d/dT)C_{n\sigma}(T,p_i)$ have a single point of contact. At $p > p_i$, Eq. (66) has two real temperature roots up to $p \simeq 30$ atm. It is seen at once, as stated already, that the smaller temperature root $T_M(p)$ gives the temperature of the constant-pressure heat-capacity maximum, and the larger root $T_\mu(p)$ that of the minimum. There is thus a unique temperature $T_\varphi(p)$, located between $T_M(p)$ and $T_\mu(p)$, where the heat capacity, as a function of the temperature, changes the sign of its curvature, from negative to positive, or $T_\varphi(p)$ is the inflection point of the heat capacity. This temperature $T_\varphi(p)$ is, of course, different from the inflection point $T_{\sigma\varphi}(p)$ of the spin heat capacity, although it is likely to be close to it.

We have thus obtained the following results. Over the phase diagram of liquid He³, and specifically over the pressure interval extending from saturation condition up to the pressure $p_{m\mu}$, which is the pressure of the isobar tangent to the anomalous melting pressure line of He³ at its minimum, the heat capacity of liquid He³ exhibits two distinct types of anomalous behavior. At low pressures, between saturation and some intermediate pressure p_i, estimated to be around 10 atm, the anomaly of the total heat capacity is similar to that of the saturated liquid with its characteristic flat plateau-like region discussed above. Over this same lower pressure range, and throughout the explored temperature interval, the heat capacity is a monotonically increasing function of the temperature.

At higher pressures, one has

$$\begin{gathered} (d/dT)C(T,p)\begin{pmatrix} > \\ = \\ < \end{pmatrix}0, \quad T\begin{pmatrix} < \\ = \\ > \end{pmatrix}T_M(p), \\ (d/dT)C(T,p)\begin{pmatrix} < \\ = \\ > \end{pmatrix}0, \quad T\begin{pmatrix} < \\ = \\ > \end{pmatrix}T_\mu(p), \\ p_i \leq p \leq p_{m\mu}. \end{gathered} \tag{72}$$

This proves that in contrast with the nuclear-paramagnetic-susceptibility ratio law and with the formula for the spin heat-capacity component, the total heat capacity is no universal function of its independent variables. While the solutions of Eq. (66), represented approximately through Fig. 3, prove the existence of the heat-capacity extrema over the pressure interval indicated by (72), the extent or amplitude of these extrema cannot be given at the present time. However, estimates based on the use of the upper limits of $C_{n\sigma}(T,T_0,p)$, that is $C_{n\sigma}(T,T_0,p_{\mathrm{sat}})$, indicate that the maxima at $T_M(p)$ may be expected to be quite flat, and the minima at $T_\mu(p)$ quite shallow. The experimental determination of these anomalies may thus require heat-capacity measurements of increased accuracy. It is equally clear, on the basis of Fig. 3, that the observations of the heat-capacity extrema may be facilitated at the higher pressures, where the interval $(T_\mu - T_M)$ is larger. As seen in Fig. 3 in terms of the lower limit on the saturated-liquid negative derivative $(-)(d/dT)C_{n\sigma}$, the maxima at higher pressure should appear around 0.15–0.20°K, and the minima around 0.30°K.

We saw above that p_i is that pressure for which Eq.

(66) has the double root

$$T_M(p_i)=T_\mu(p_i). \tag{73}$$

As the pressure increases beyond p_i, one has

$$(dT_M(p)/dp)<0, \quad (dT_\mu(p)/dp)>0, \quad p>p_i, \tag{73a}$$

where the second inequality may be valid over only a limited temperature range. There is thus a locus of the heat-capacity extrema $T_{M\mu}(p)$. As defined somewhat more closely below, the locus $T_M(p)$ of the maxima starts out at the melting pressure line, on the low-temperature side of its minimum, to slope downward with a negative pressure derivative toward increasing temperatures. The locus develops a pressure minimum at the pressure p_i, to increase first beyond p_i. This first increasing arc is the locus of the heat-capacity minima. While this arc must also meet the melting line, it is undetermined as yet whether $T_\mu(p)$ is monotonic or not between p_i and the melting line.

We have to consider now the behavior of the heat capacity in the region of the phase diagram of somewhat difficult accessibility, that is at $p>p_{m\mu}\simeq 29$ atm, and $T\lesssim T_{m\mu}\sim 0.32$–$0.33$°K, where $T_{m\mu}$ stands for the temperature of the melting-pressure minimum. As pointed out to us by our colleague, Dr. R. L. Mills, in this region of the phase diagram, as a consequence of the actual isolation of the liquid sample because of the formation of solid He^3 in the channel leading to the sample, constant-pressure heat-capacity measurements are excluded. However, the constant-volume heat capacities in the above region of the phase diagram are quite close to constant-pressure heat capacities. The low-temperature branch of these constant-volume heat capacities extends between the absolute zero and the melting line at $T\lesssim 0.30$°K, as do the liquid isochores. Considering again Eq. (66) and its graphical representation in Fig. 3, it is seen that as the liquid volume decreases below its maximum at the melting line,[16] the spin-heat-capacity temperature derivatives $(d/dT)(C_\sigma)$ end on the melting line at decreasing temperatures, i.e., their increasing branch soon stops below the $(-)(d/dT)(C_{n\sigma})$ curve, and above all below the compressed-liquid negative nonspin-heat-capacity temperature derivatives. Hence, at $T<0.30$°K, only $T_M(p)$ or $T_M(V)$ will occur, and Eq. (66) will have only one solution, at $V<V_{mM}$, the latter volume being the maximum liquid volume at melting[16] near the melting pressure minimum $p_{m\mu}$ and its temperature $T_{m\mu}$. The anomalies of the constant-volume heat capacities of $V<V_{mM}$, and at $T<T_{m\mu}$, reduce to a single maximum, which should be observable before these finite-arc heat capacities terminate at the melting volume line $V_m(T)$.

If the isochoric arcs at $V<V_{mM}$, $T<T_{m\mu}$, become shorter, ending on the melting volume line at $T\lesssim 0.12$–0.15°K, then it is expected that Eq. (66), referring now to the constant-volume heat-capacity temperature derivatives, loses its meaning since it can have no solution, because the spin-heat-capacity temperature derivatives at smaller volume will end at their decreasing branch at values of $(d/dT)C_\sigma[T/T_0(V)]$ which are larger than the corresponding nonspin-heat-capacity negative derivatives $(-)(d/dT)C_{n\sigma}(T,p)$. Along these short isochoric arcs terminating on the melting volume line of the liquid, the heat capacities become monotonically increasing functions of the temperature. There must exist an isochore of volume, say, V_c such that the heat capacity $C(T,\, V=V_c)$ develops its maximum just at the melting line. The corresponding melting pressure p_{mc} and temperature T_{mc} is the starting point of the locus loop $T_M(p)$ alluded to above. There is a corresponding end point of the $T_\mu(p)$ branch of the locus of heat-capacity extrema ending on the melting line, possibly near $p_{m\mu}$, as mentioned above.

In order to complete the study of the compressed liquid-He^3 heat capacities, it is necessary to consider their likely behavior in the limit of very low temperatures. This can be done, in some approximation, on the plausible assumption that the nonspin heat capacity $C_{n\sigma}(T,p)$ is formally similar to $C_{n\sigma}(T,T_0,p_{\text{sat}})$, with the condition (38) of normal pressure behavior of these nonspin heat capacities. Since the pressure effect of $C_\sigma[T/T_0(p)]$ is anomalous at low temperatures, $T<T_\sigma(p)$, by (57), it is seen that the ratio

$$\begin{gathered} C_\sigma(T/T_0(p))/C_{n\sigma}(T,T_0,p)>5, \\ T\rightarrow 0\text{°K}, \quad p>p_{\text{sat}}, \end{gathered} \tag{74}$$

this ratio being somewhat less than five at saturation, as noted in (15). As the pressure increases, the ratio $C_\sigma/C_{n\sigma}$ increases fairly rapidly. This then allows one to define at low temperatures, in the compressed liquid, approximate lower and upper limits of the total heat capacity. These are, respectively,

$$\begin{aligned} &C_l(T,p>p_{\text{sat}})=C_\sigma(T/T_0(p)), \quad T\ll T_0(p), \\ &C_u(T,p>p_{\text{sat}})=C_\sigma(T/T_0(p))+C_{n\sigma}(T,T_0), \\ &\qquad\qquad\qquad\qquad\qquad\qquad T\ll T_0(p), \end{aligned} \tag{75}$$

where $C_{n\sigma}(T,T_0)$ is the approximate nonspin heat capacity of the saturated liquid studied in Sec. 3.

It appears instructive to discuss the explicit very low temperature formulas of the preceding two limits of $C(T,p)$. We will limit ourselves here to the consideration of the osculating parabolas of the $[C(T,p)/T]$ ratios associated with the limits (75). Using (53) one obtains, with $T_0(p)$ in place of T_0 [the latter referring in (53) to the spin system of the saturated liquid],

$$\begin{aligned} C_l(T,p)/RT=&(\tfrac{3}{2}(\ln 2)/T_0(p)) \\ &-\left[\frac{3\pi^2}{8}(\ln 2)/(T_0(p))^3\right]T^2, \quad T\rightarrow 0, \end{aligned} \tag{76}$$

$$C_u(T,p)/RT=C_l(T,p)/RT+c_1(T_0), \quad T\rightarrow 0,$$

since $c_3(T_0)$ appearing in the coefficient of the T^2 term of $[C_{n\sigma}(T,T_0,p)/RT]$ in (75) is completely negligible in comparison with the corresponding coefficient in $\{C_\sigma[T/T_0(p)]/RT\}$ included in (76). Using the ap-

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[16] L. Goldstein and R. L. Mills, Phys. Rev. **128**, 2479 (1962).

TABLE III. Approximate elements of the limiting molar-heat-capacity–temperature ratios, $C(T,p)/RT$, of compressed liquid He^3 at very low temperatures.

p (atm)	$T_0(p)$ °K	$[\frac{3}{2}(\ln 2)/T_0(p)]^a$ $(°K)^{-1}$	$[(\frac{3}{2}(\ln 2)/T_0(p))+c_1(T_0)]^{b,c}$ $(°K)^{-1}$	$(3\pi^2/8)\ln 2/[T_0(p)]^3$ $(°K)^{-3}$
10	0.348	2.99	3.48	60.9
15	0.318	3.27	3.76	79.8
20	0.294	3.54	4.03	101
25	0.274	3.79	4.28	125
30	0.258	4.03	4.52	149

[a] Lower limits.
[b] Upper limits.
[c] $c_1(T_0)$ is the average of the c_1 values of Table I.

proximate Duke University $T_0(p)$ data,[12] together with an average of the $c_1(T_0)$ values of Table I, we give in Table III the approximate lower limits of the $[C(T,p)/RT]$ parabola vertices, their upper limits, and the coefficient of the T^2 term, at several pressures. It is to be remembered here that the graphs of the limit vertices have been given previously by the Duke University group[12] using their own $T_0(p)$ data and the early $C_{n\sigma}$ fit.

It will be seen that the limiting value of the ratio $C_\sigma/C_{n\sigma}$ or $C_\sigma/c_1(T_0)T$ increases by a factor somewhat less than 2 from saturation to about 30 atm, or from less than 5 to about 8. At the higher pressures and at the very low temperatures, the nonspin heat capacity tends to become a mere correction to the spin heat capacity. The latter property results from the universal susceptibility ratio law[5] of liquid He^3 through the Boltzmann theorem,[1] Eq. (12). This ratio law has been verified experimentally down to the temperature of about 0.05°K. Unless the susceptibility ratio below this temperature exhibits an entirely new behavior, the essentially parabolic approach of $C(T,p)/RT$ or of $C_\sigma[T/T_0(p)]/RT$, approximately, toward its finite limit at the absolute zero is a direct consequence of the ratio law assumed to be valid at $T<0.05$°K, outside the temperature range where it has been verified experimentally.

An additional qualification of the parabolic behavior of $C(T,p)/RT$ may arise from the inadequate formal description of the nonspin heat capacity $C_{n\sigma}(T,p)$. In our derivation of the approximate analytical fit of $C_{n\sigma}(T,T_0,p_{\text{sat}})$, Eq. (39), we have used the asymptotic no-coupling limit of the nonspin heat capacity together with stability considerations on the behavior of $C_{n\sigma}$ at $T\rightarrow 0$°K, as imposed by the Nernst theorem: viz., $C_{n\sigma}$ had to be a positive semidefinite quantity. If these requirements on $C_{n\sigma}$ are set aside, which would be rather arbitrary, and polynomial fits to the saturated-liquid nonspin-heat-capacity data are accepted which include even powers of T, then, as was done by ourselves and stated, in Sec. 3, at low temperatures, $C_{n\sigma}$ may have a term in T^2. However, as is apparent in Tables I and II, as well as in the results obtained in all types of polynomial fits to the $(C_{n\sigma}/R)$ data at saturation, the negative coefficients of the T^2 terms, together with the coefficients of any powers of T, were always less than unity. Now in the (C/RT) ratio, the parabolic term of (76) may be written as $\{(-)[3\pi^2(\ln 2)/8]/[T_0(p)]^2\}[T/T_0(p)]T$, and with the numerical values of the coefficients of Table III, it is seen that only at $T/T_0(p)<10^{-2}$ will this term become as small as the one resulting from the T^2 term of the $C_{n\sigma}$ fits. But $T_0(p)/100$ is a temperature of a few millidegrees, so that only at temperatures in the millidegree range would the linear term of the hypothetical $C_{n\sigma}/RT$ ratio become noticeable. Hence, unless either in saturated or compressed liquid He^3 the nonspin heat capacity is of entirely different structure from the one imposed by, and derived approximately with, the saturated-liquid $C_{n\sigma}$ data at $T\gtrsim 0.2$°K, the experimentally founded paramagnetic susceptibilities throughout the liquid phase diagram, and down to 0.05°K, with their presently justified extrapolations below this temperature, require the ratios $C(T,p)/T$ to approach parabolically in T their finite vertices at the absolute zero.

A sensible comparison of these results with liquid He^3 heat-capacity data, at saturation and under compression, will be justified if and when incontrovertible heat-capacity data at $T<0.2$°K and at very low temperatures become available from several entirely independent groups of workers. At the present time the long series of technical problems arising in low- and very-low-temperature liquid-He^3 heat-capacity measurements has not appeared to have been tackled in any systematic and consistent way. It is, however, reasonable to expect that independent compressed-liquid-He^3 accurate heat-capacity measurements at $T\gtrsim 0.10$–0.15°K may soon verify the presence of the low-amplitude extrema predicted here. Independent susceptibility measurements by several groups at $T<0.05$°K, where the difficult problem of the transfer of accurate amounts of heat to small liquid-He^3 samples does not arise, may contribute equally to the determination of the temperature behavior of the liquid heat capacity at the lowest temperatures, according to the theoretical approach discussed above.

ACKNOWLEDGMENTS

I wish to thank Mrs. J. E. Powers for her extensive computer work on the least-squares fits. K. R. Crandall has cooperated through several calculations. We have also benefited from several discussions on problems of the theory of least squares with Dr. R. K. Zeigler, Dr. P. E. Harper, and Dr. R. H. Moore.