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Volume Anomaly of Liquid He^3 Arising from Its Nuclear Spin System

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The anomalous volume expansion coefficient of liquid He^3 derived in a previous work through a discussion of its nuclear spin system will be shown to be describable quantitatively within the statistical thermodynamic formalism attached to its nuclear spin degrees of freedom. The theory predicts, through the large partial negative spin expansion coefficient, a volume minimum or a density maximum of saturated liquid He^3 subject to the volume behavior determined by its non-spin degrees of freedom. The temperature at which the density maximum should occur is higher than about 0.2°K. At this temperature, or very close to it, the negative spin expansion coefficient has a sharp minimum and the total liquid density is expected to have an inflection point in the density-temperature representative plane. Since the whole anomaly depends directly on the liquid compressibility, it should be most pronounced in the saturated liquid and should decrease under the application of external pressure.

1. INTRODUCTION

IN a previous work[1] devoted to the study of the various effects arising from the nuclear spin system of liquid He^3 on some of its thermal properties, we have been led to predict a partial density or volume anomaly. The discussion was, however, restricted for several reasons. One of these concerned the method of evaluating the partial spin volume $V_\sigma(T)$ and the somewhat arbitrary choice of the sign of this quantity. Also, the absence, at the time of our work, of liquid He^3 compressibility data allowed us to give only semiquantitative estimations of the actual magnitude of the partial spin volume and the associated partial spin expansion coefficient. Recent sound velocity measurements[2] in this Laboratory extended over a wide temperature interval do define the adiabatic compressibility values of liquid He^3, even at the lower temperatures where direct density measurements are not available, although preliminary expansion coefficient measurements[3] have been made at these low temperatures, $0.5 \leq T \lesssim 1.0$°K. In this latter range, however, the compressibility values depend on extrapolated values of the directly measured liquid densities.[4] Since the expected density anomaly is rather moderate, the smoothly extrapolated density values should yield fairly well approximated compressibility values, in view of the highly precise sound velocity data.[2] Inasmuch as the nuclear spin system appears to dominate the entropy and heat capacity of liquid He^3 at sufficiently low temperatures,[5] it seemed of interest to rediscuss the volume or density anomaly to be reasonably expected in a now experimentally accessible region, and to give the quantitative form of the theory outlined previously.[1] The theory could be further stabilized through the consideration of some recent nuclear paramagnetic susceptibility measurements[6] of compressed liquid He^3. The formalism of our theory is fully valid in the compressed liquid also, so that as soon as liquid compressibility and additional nuclear paramagnetic susceptibility values become available in the compressed liquid, new definite features of the phase diagram of liquid He^3 should appear, verifiable through experimentation. These features would correspond to the possible existence of two loci in the pressure-temperature or volume-temperature phase diagrams of this antisymmetric liquid. One of these is a locus of the points associated with the vanishing of the expansion coefficient of the liquid, that is the locus of density maxima or volume minima, a smooth line dividing the liquid region of the phase diagrams in two parts, associated, respectively, with the normal and abnormal, that is positive and negative, expansion coefficients of the liquid, on the high- and low-temperature side of the locus. The other locus is that of the inflection points of the liquid density or volume resulting from the vanishing of the second temperature derivative of the partial spin volume and its negative sign at low temperatures leading to the vanishing of the second temperature derivatives of the total liquid density or volume. We turn now to the description of the quantitative theory of the volume anomaly in liquid He^3, discussed briefly previously[1] in a more qualitative fashion.

2. THEORY OF THE VOLUME ANOMALY OF LIQUID He^3 ARISING FROM ITS NUCLEAR SPIN SYSTEM

The partial molar entropy of orientational spin disorder[5] in saturated liquid He^3 has been defined by

$$S_\sigma(T) = (R\ln 2)[\chi(T)/\chi_0(T)], \tag{1}$$

where $\chi(T)$ is the observed and hence actual nuclear paramagnetic susceptibility of saturated liquid He^3 at

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

[2] Lacquer, Sydoriak, and Roberts, *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, Ohio, 1958), p. 15.

[3] R. D. Taylor and E. C. Kerr (to be published).

[4] E. C. Kerr, Phys. Rev. **96**, 551 (1954); Grilly, Hammel, and Sydoriak, Phys. Rev. **75**, 1103 (1949).

[5] L. Goldstein, Phys. Rev. **96**, 1455 (1954); see also *Symposium on Liquid and Solid* He^3 (Ohio State University Press, Columbus, Ohio, 1958), p. 57.

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

the temperature T, and $\chi_0(T)$ is the limiting Langevin susceptibility which the liquid would have at its actual density at T, if it were an ideal paramagnet. We have shown previously[1] that with the thermodynamics of the spin system being fully determined through the knowledge of its entropy, under saturation conditions, the equation of state of the spin system could be derived under the assumption that the partial volume derivative $(\partial S_\sigma/\partial V)_T$ was also available near the liquid-vapor saturation line. Using the approximate ideal Fermi gas formalism with the empirical susceptibility ratio function $\chi(T)/\chi_0(T)$, the resulting partial derivative $(\partial S_\sigma/\partial V)_T$ was positive as well as $p_\sigma(T,V)$, the partial spin pressure. Experimentally, however, this derivative was determined to have the negative sign, recently,[6] so that

$$p_\sigma(T,V)=\int_0^T(\partial S_\sigma/\partial V)_T dT<0. \tag{2}$$

If the numerical values of the derivatives were still given, to some degree of approximation, by the formalism of the ideal Fermi gas with the empirical apparent degeneration temperature, then, V being the liquid volume,

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

as shown previously. Here $E_\sigma(T)$ is the spin thermal excitation energy defined through the spin heat capacity temperature integral.[1]

The existence of such a negative spin pressure is in its effect similar to the application of an external pressure, tending to reduce the volume of the system through compression. The negative spin pressure may be said to correspond to the existence of an apparent attractive type of potential energy responsible for the negative pressure in question. Physically, this seems to correspond, at finite temperatures, to a decrease, from the state of absolute zero, of the apparent repulsion existing between parallel spin atoms, or the formation of a compensating negative potential type of energy with the ensuing negative spin pressure $p_\sigma(T,V)$. If we denote by p_σ', the apparent positive external pressure which could replace the effect of the negative $p_\sigma(T,V)$, then the existence of such an external pressure yields a relative volume decrease which may be written, approximately,

$$V_\sigma/V=-p_\sigma'(T)\kappa(T), \tag{4}$$

where $\kappa(T)$ is the compressibility of the liquid. This phenomenon resembles somewhat the phenomena of volume anomalies which are observed in ferromagnetic substances below their Curie point and whose theory was first discussed by Bauer.[7]

At the lower temperatures, the distinction between the various kinds of compressibilities may, of course, be omitted. Or, using Eq. (3) with p_σ' as defined above, one finds

$$V_\sigma(T)=-\tfrac{2}{3}E_\sigma(T)\kappa(T). \tag{5}$$

The definition of the partial spin volume V_σ through Eq. (4) is valid, provided that

$$|V_\sigma/V|\ll 1. \tag{6}$$

That the latter relation has to be fulfilled results from the fact that Eq. (4) is actually a differential type of relation, with V_σ standing for a small volume change δV_σ. Now, in Eq. (3) we know[1] that $E_\sigma(T)$ tends toward a finite value in the limit of high temperatures. In the approximate formalism discussed previously,[1] this limit is $\frac{1}{2}RT_0$ per mole, T_0 being the apparent-empirical degeneration temperature of the spin system.[1,5] But $\kappa(T)$, the compressibility of liquid He^3, is a fairly rapidly increasing function of the temperature, so that $V_\sigma(T)$ defined by Eq. (4) is a fairly rapidly decreasing function of the temperature, and Eq. (4) could thus lose its validity at higher temperatures if (6) were not satisfied. It is, however, possible to recast the above basic relation in a more rigorous form. Indeed, let

$$\delta V_\sigma(T)/V=-\kappa(T)\delta p_\sigma'(T), \tag{7}$$

with

$$\delta p_\sigma'(T)\simeq\tfrac{2}{3}\delta E_\sigma(T)/V, \tag{8}$$

where at the lower temperatures the variation of the total volume V may be neglected. Then, the total molar spin volume is

$$\begin{aligned}V_\sigma(T)&=-\tfrac{2}{3}\int_0^T\kappa(T)\delta E_\sigma(T)\\&=-\tfrac{2}{3}\int_0^T\kappa(T)\left(\frac{dE_\sigma(T)}{dT}\right)dT\\&=-\tfrac{2}{3}\int_0^T\kappa(T)C_\sigma(T)dT,\end{aligned} \tag{9}$$

$C_\sigma(T)$ being the molar spin heat capacity of the saturated liquid. It is seen now that in order for $V_\sigma(T)$ to be small or moderate, it is necessary that $\kappa(T)$ should not increase too fast with temperature so as not to compensate for the slow decrease of the spin heat capacity $C_\sigma(T)$ with temperature. If $\kappa(T)$ is the adiabatic compressibility, then the integral relation (9) should remain valid up to the critical temperature T_c, since then over the whole temperature range $V_\sigma(T)$ will stay moderate.

From (9), we obtain

$$dV_\sigma/dT=-\tfrac{2}{3}\kappa(T)C_\sigma(T), \tag{10}$$

and the partial spin expansion coefficient is

$$\begin{aligned}\alpha_\sigma(T)&=V^{-1}(dV_\sigma/dT)\\&=-\tfrac{2}{3}V^{-1}\kappa(T)C_\sigma(T).\end{aligned} \tag{11}$$

It is seen that, as is the case with V_σ, the partial spin

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[7] E. Bauer, J. phys. radium **10**, 345 (1929); see also Pierre Weiss, *Le Magnetisme, Proceedings of the Solvay Congress* (Gautheir-Villars, Paris, 1932), pp. 325–345.

expansion coefficient α_σ is always negative. It vanishes, of course, at the absolute zero and since $\kappa(T)$ is expected to have only a moderate variation at the low temperatures, $T \lesssim 1.0°\mathrm{K}$, $\alpha_\sigma(T)$ will exhibit the characteristic temperature variations of $[-C_\sigma(T)]$. In particular, its minimum value will occur at about the position of the maximum of $C_\sigma(T)$. Indeed, (11) yields easily

$$d\alpha_\sigma/dT = -\alpha\alpha_\sigma - \tfrac{2}{3}V^{-1}C_\sigma(d\kappa/dT) - \tfrac{2}{3}V^{-1}\kappa(T)(dC_\sigma/dT). \quad (12)$$

Now $\alpha\alpha_\sigma$ is a rather small number, α being the total expansion coefficient; also $(d\kappa/dT)$ is expected to be quite small at low temperatures, where $\kappa(T)$ reduces essentially to its limiting value κ_0, the compressibility at the absolute zero. Hence, the right-hand side essentially vanishes close to the temperature at which dC_σ/dT vanishes. Hence, $\alpha_\sigma(T)$ has its minimum at a temperature close to the one at which $C_\sigma(T)$ is maximum. At this same temperature, $V_\sigma(T)$ has an inflection point, since from (10), d^2V_σ/dT^2 vanishes at about the same temperature where $\alpha_\sigma(T)$ is extremum. Let then T_σ be the temperature where V_σ has its inflection point. Then, at $T \leq T_\sigma$, where α_σ is a decreasing function of T, d^2V_σ/dT^2 is negative, and V_σ is thus concave downward in the (V_σ,T) plane, that is toward decreasing V_σ values. At temperatures $T \geq T_\sigma$, α_σ is an increasing function of T, d^2V_σ/dT^2 is positive, since dC_σ/dT is negative at these temperatures. Again, we have

$$d^2V_\sigma/dT^2 = -\tfrac{2}{3}\kappa(T)dC_\sigma/dT - \tfrac{2}{3}C_\sigma(T)d\kappa/dT, \quad (13)$$

resulting from (10); the first positive term on the right-hand side outweighs the second negative term which is proportional to the small $(d\kappa/dT)$. Hence, at $T > T_\sigma$, V_σ has to become concave upward in the (V_σ,T) plane. These results are fully displayed in Fig. 1 which is a graph of both $V_\sigma(T)$ and $\alpha_\sigma(T)$. It will be seen that $V_\sigma(T)$ decreases from zero at the absolute zero, parabolically in T at low enough temperatures as shown previously[1] as far as its T dependence was concerned. V_σ has an inflection point at about 0.2°K, beyond which it becomes concave upward.

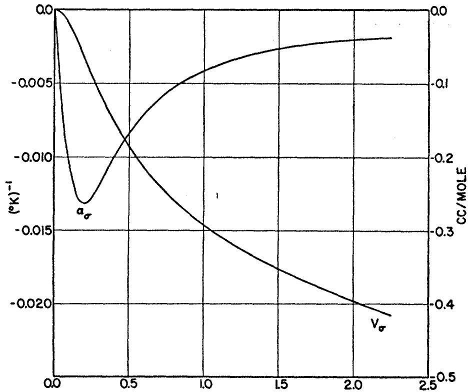

FIG. 1. The partial spin volume V_σ (cc/mole) and spin expansion coefficient $\alpha_\sigma(°\mathrm{K})^{-1}$, as a function of the temperature T(°K).

We wish to consider now briefly the thermodynamic aspects of the above results on the partial spin volume V_σ. We have proved rigorously[8] that at temperatures $T \leq T_\sigma$, T_σ being the temperature at which $C_\sigma(T)$ is maximum,[5] and near the saturation line,

$$[\partial C_\sigma(p,T)/\partial p]_T = -T(\partial^2 V_\sigma/\partial T^2)_p > 0, \quad T \leq T_\sigma, \quad (14)$$

or, in this range,

$$(\partial^2 V_\sigma/\partial T^2)_p < 0; \quad (15)$$

while

$$[\partial C_\sigma(p,T)/\partial p]_T = -T(\partial^2 V_\sigma/\partial T^2) < 0, \quad T > T_\sigma, \quad (16)$$

or, at these higher temperatures,

$$(\partial^2 V_\sigma/\partial T^2)_p > 0. \quad (17)$$

But these rigorous thermodynamic results are identical with those discussed above in connection with Eqs. (12) and (13), derived within the formalism of the theory of the spin system. The complete thermodynamic self-consistency of the theory of the partial spin volume $V_\sigma(T)$ is thus fully apparent through Eqs. (14)–(17).

What is there to be expected experimentally? Clearly, the present theory of the liquid He³ volume anomaly deals strictly with the spin system only. Hence, it cannot locate the actual position of the expected density maximum because the presumed positive or normal expansion coefficient determined by the normal degrees of freedom of the liquid is of unknown form, at the present time. Indeed, the total expansion coefficient is[8]

$$\alpha(T) = \alpha_\sigma(T) + \alpha_{n\sigma}(T), \quad (18)$$

and the vanishing of $\alpha(T)$ originates with the opposite signs of $\alpha_\sigma(T)$ (<0) and $\alpha_{n\sigma}(T)$ (>0). At any rate, below the temperature of the expected density maximum, $\alpha_{n\sigma}$ is numerically smaller than α_σ, and should continue to decrease smoothly toward zero from above, in the limit of the absolute zero. With $\alpha_{n\sigma}$ or $dV_{n\sigma}/dT$ being quite small, $d^2V_{n\sigma}/dT^2$, while positive is expected also to be quite small at low temperatures. Hence, the approach of the total liquid volume toward its limiting value at the absolute zero would be dominated by α_σ, $d\alpha_\sigma/dT$ or d^2V_σ/dT^2. The change of the latter from negative to positive values, as shown in Fig. 1, with its vanishing at the minimum of α_σ, cannot but impress itself on the temperature behavior of the total liquid volume. The latter has thus to exhibit an inflection point at some temperature lower than but close to the minimum of α_σ, where d^2V_σ/dT^2 has essentially its inflection point. Hence, beside the density maximum or volume minimum, saturated liquid He³ is expected to exhibit also an inflection point at a temperature somewhat below but close to that of $V_\sigma(T)$, at about 0.19°K. In other words, the saturated liquid density

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[8] L. Goldstein, preceding paper [Phys. Rev. 112, 1465 (1958)].

$\rho(T)$ is first concave upward in the (ρ,T) plane, has an inflection point close to T_σ, defined above, and then becomes concave downward beyond T_σ. Or, the molar volume $V(T)$ decreases first from its value at the absolute zero, being concave downward, because it is reasonable to expect that

$$\begin{aligned} &d^2V/dT^2 \simeq dV_\sigma/dT^2 < 0, && T<T_\sigma, \\ &d^2V/dT^2 \simeq d^2V_\sigma/dT^2 = 0, && T\simeq T_\sigma, \quad (19) \\ &d^2V/dT^2 = d^2V_\sigma/dT^2 + d^2V_{n\sigma}/dT^2 > 0, && T>T_\sigma, \end{aligned}$$

This is visible on Fig. 1, where it is sufficient to displace $V_\sigma(T)$ parallel to itself into the positive region of the (V,T) plane, so that $V(T)$ would approach from below a limiting volume line $V(T\rightarrow 0)$ parallel to the T axis, at about 37 cc/mole, the liquid volume at the absolute zero. That is, at very low temperatures where $\kappa(T)$ is essentially constant and equal to $\kappa(T\rightarrow 0)$ or $\kappa(0)$, one has

$$\begin{aligned} \lim_{T<T_\sigma} V(T) &= V_{n\sigma}(T\rightarrow 0) + V_\sigma(T) \\ &= V_{n\sigma}(T\rightarrow 0) - \tfrac{2}{3}\kappa(0)\int_0^T C_\sigma(T)dT \\ &= V_{n\sigma}(T\rightarrow 0) - (RT_0/2)[\kappa(0)](\ln 2)(T/T_0)^2 \\ &\qquad \times[1-\tfrac{1}{8}\pi^2(T/T_0)^2], \quad (20) \end{aligned}$$

where use has been made of the approximate analytical expression of $C_\sigma(T)$ given previously,[1,5] as well as of Eq. (9) above. To the above approximation, the approach of $V(T)$ toward its limit denoted by $V_{n\sigma}(T\rightarrow 0)$ at the absolute zero is thus parabolic in T and from below, as mentioned above in connection with Eq. (13). Or, since the density is (V referring to the molar volumes, and M being the molecular weight)

$$\begin{aligned} \lim_{T<T_\sigma} \rho(T) &= M\{V_{n\sigma}(T\rightarrow 0) - \tfrac{1}{2}RT_0[\kappa(0)](\ln 2)(T/T_0)^2 \\ &\qquad \times[1-\tfrac{1}{8}\pi^2(T/T_0)^2]\}^{-1}, \quad (21) \end{aligned}$$

one obtains, with

$$|dV_{n\sigma}/dT| \ll |dV_\sigma/dT|, \quad T<T_\sigma \quad (22)$$

the results:

$$\begin{aligned} \lim_{T<T_\sigma} d\rho/dT &= (\rho^2/M)R\kappa(0)(\ln 2)(T/T_0) \\ &\qquad \times[1-\tfrac{1}{4}\pi^2(T/T_0)^2] \quad (23) \end{aligned}$$

and

$$\begin{aligned} \lim_{T<T_\sigma} d^2\rho/dT^2 &= (2/M^2)\rho(d\rho/dT)^2 \\ &\quad + (\rho^2/M)R\kappa(0)(\ln 2)T_0^{-1}[1-\tfrac{3}{4}\pi^2(T/T_0)^2], \quad (24) \end{aligned}$$

showing that the density approaches its limit at the absolute zero from above, being concave upward at these low temperatures.

We are now prepared to extend the preceding discussion to the case of compressed liquid He^3. Since the compressibility of the liquid decreases with increasing pressure, while $C_\sigma(p,T)$ changes only by shifting its maximum toward lower temperatures,[8] it will be seen that $\alpha_\sigma(p,T)$ increases algebraically toward zero, with its minimum displaced simultaneously toward lower temperatures. This also means that the inflection point of $V_\sigma(p,T)$ is shifted toward lower temperatures, and with it the inflection point of $V(p,T)$, the total volume of the compressed liquid. This conclusion is, of course, subject to the condition mentioned above that $|d^2V_\sigma(p,T)/dT^2|$ remains large in comparison with $[d^2V_{n\sigma}(p,T)/dT^2]$ associated with the normal degrees of freedom. Hence, there is a locus of the inflection points in the phase diagrams of liquid He^3, which locus starting on the liquid-vapor phase separation line would be sloping toward lower temperatures. Examination of the experimental data[6] in the compressed liquid He^3 nuclear paramagnetic susceptibilities indicate that this locus would start at about 0.18–0.19°K on the liquid-vapor phase separation line, to end at about 0.05°K on the melting line.

The discussion of the locus of the liquid density maxima or volume minima is much less straightforward, since the above theory cannot locate these extrema, but explains only their origin through the interplay of the anomalous spin system and the expected normal behavior of the non-spin degrees of freedom. The locus in question is thus defined through the equation

$$\alpha(p,T)=0, \quad \text{or} \quad -\alpha_{n\sigma}(p,T)=\alpha_\sigma(p,T). \quad (25)$$

Let then T_μ be the temperature of the minimum of the saturated liquid volume or that of its density maximum. Consider the (V,T) phase diagram. In this plane, the locus can be a line of negative slope, that is a line reaching the melting line at a temperature higher than T_μ. Or, this line could, conceivably, be one of positive slope, ending on the melting line at a temperature lower than T_μ. If of the inequalities

$$|(\partial\alpha_{n\sigma}/\partial p)_T| > |(\partial\alpha_\sigma/\partial p)_T|, \quad |(\partial\alpha_{n\sigma}/\partial p)_T| < |(\partial\alpha_\sigma/\partial p)_T|, \quad (26)$$

the first prevails, whereby $\alpha_{n\sigma}(p,T)$ decreases with increasing pressure faster than $\alpha_\sigma(p,T)$ increases toward zero, then in the (V,T) plane, the locus of the maxima is expected to be directed toward increasing temperatures at increasing pressures. The opposite situation would develop with the second inequality in (26). At any rate, according to Eqs. (9) and (10), the partial spin volume $V_\sigma(p,T)$ and expansion coefficient $\alpha_\sigma(p,T)$, cannot but decrease in magnitude with increasing pressure as a result of the decreasing liquid compressibility values $\kappa(p,T)$ with increasing pressure. Hence, the application of external pressure will tend to decrease the sharpness of the density anomaly, which would be expected to be the most pronounced in the saturated liquid.

The location of the locus of the inflection points $T_\sigma(p)$ resulting from the minimum of the partial spin expansion coefficient allows one to give a qualitatively fairly complete picture of the pressure dependence of $C_p(p,T)$, the constant pressure heat capacity function of liquid He^3 over the whole liquid region of the phase diagram of this substance. This picture depends, indeed, uniquely on the locus of the inflection points of the liquid volume or density.

Consider the (p,T) phase diagram of He^3. In this plane, the locus of the points $T_\sigma(p)$ starts at about 0.18–0.19°K on the liquid-vapor phase separation line, at a very low pressure, and decreases with increasing pressure, to reach the melting line at about 0.05°K, as discussed above. Draw two lines parallel to the pressure axis through the two limiting points of the locus $T_\sigma(p)$, extending between the two phase separation lines. These two constant temperature lines together with the locus $T_\sigma(p)$ define three regions of the (p,T) plane. At $T \lesssim T_\sigma(P)$, where $T_\sigma(P)$ is the melting line endpoint of $T_\sigma(p)$, that is about 0.05°K, we have at all points of this region

$$(\partial^2 V/\partial T^2)_p < 0, \tag{27}$$

and, hence, by the thermodynamic relation

$$[\partial C_p(p,T)/\partial p]_T = -T(\partial^2 V/\partial T^2)_p, \tag{28}$$

$C_p(p,T)$ will increase from its value on the saturation line at a chosen T value, monotonically, until the melting line is reached, where this constant temperature heat capacity arc stops in the $(C_p(p,T),p)$ representative plane.

In the region between the two constant temperature lines, $T_\sigma(P) < T < T_\sigma(p)$, starting at the saturation line, the constant temperature heat capacity arcs start to increase with pressure first until the locus $T_\sigma(p)$ is reached; they then have to turn around, since on the high pressure side of the locus, $(\partial^2 V/\partial T^2)_p$ is positive at all points of the phase diagram, and by (28), $C_p(p,T)$, at the chosen constant T, cannot but increase there with increasing pressure, until the melting line is reached, where again this finite constant temperature heat capacity arc ends, exhibiting thus a maximum.

Finally, at $T > T_\sigma(p)$, that is $T \gtrsim 0.18$–0.20°K, the finite constant temperature heat capacity arcs always decrease throughout the whole pressure interval available at the chosen T between the liquid-vapor line and the melting line.

A comparison of these heat capacity behaviors of liquid He^3 with application of external pressure with our recent studies[8] on the spin heat capacities in compressed liquid He^3, shows the complete parallelism between the pressure effects on the spin heat capacity and the total liquid heat capacity. This parallelism comes about through the fact pointed out previously[1,5,8] that as far as the liquid heat capacity is concerned, this quantity is dominated by the spin heat capacity below the temperature of the maximum of the latter, that is below T_σ. At $T < T_\sigma$, the qualitative pressure dependence of the total liquid heat capacity has to be essentially that of C_σ. Above T_σ, the derivatives $(\partial^2 V_\sigma/\partial T^2)_p$ and $(\partial^2 V_{n\sigma}/\partial T^2)_p$ are both of the same sign, they are both positive, and this explains the similar pressure dependences of C_σ and $(C_\sigma + C_{n\sigma})$ or the total liquid heat capacity over the whole liquid region of the He^3 phase diagram.

The preceding result on the pressure effect of the liquid He^3 heat capacity was obtained independently by Hammel[9] on the assumption of the existence of the volume minima. This assumption then leads, through the Nernst theorem, to the existence of inflection points on the low-temperature side of the minima, since the expansion coefficients have to vanish again at the absolute zero. However, the thermodynamic formalism cannot explain the origin of the volume anomalies. We have shown in this paper, in agreement with our previous semiquantitative description[1] of the partial spin volume and expansion coefficient, that these anomalies arise from the peculiar thermal properties of the nuclear spin system of liquid He^3, tending to oppose the normal behavior determined by the degrees of freedom other than spin. These results also suggest that solid He^3 might also exhibit properties in which the nuclear spin system could play a major role.

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[9] Hammel, Sherman, and Edeskuty (to be published).