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# Nuclear Spin System of Liquid $He^3$

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The entropy and heat capacity of spin disorder in liquid $He^3$, obtained previously, define the partial thermodynamic potentials of the spin system. These in turn lead to the spin equation of state. The energy of spin excitation, quadratic in the liquid temperature at low temperatures, tends toward the limiting value of $\frac{1}{2}kT_0$, per spin, at high temperatures, $T_0$ being the empirical characteristic temperature of the spin system. The partial volume expansion coefficient of liquid $He^3$, arising from the spin excitations, is a linear function of the temperature at low temperatures and of considerable magnitude, which might make it accessible experimentally. The effect of the spin excitations on the vapor pressure of liquid $He^3$ might also be separable through a careful analysis of the data over a wide temperature interval.

## I. INTRODUCTION

THE explanation[1] of the behavior of the entropy of liquid $He^3$ at temperatures $T \gtrsim 0.25°K$, in terms of an entropy of spin disorder and nonspin entropy arising from the thermal excitations of the ordinary degrees of freedom of the liquid atoms, appears to be well substantiated through the recent analysis[2,3] of the pertinent data in liquid $He^3$. Particularly, at low temperatures, where the more conventional degrees of freedom are essentially frozen, the spin disorder is the dominant part of the total thermal disorder. These results suggest that a more complete discussion of the statistical thermodynamics of the spin system should be of interest for a derivation of some of the partial spin properties of liquid $He^3$ arising from it. It will thus be shown, with the use of a relatively mild assumption, that at low enough temperatures the expansion coefficient of liquid $He^3$ is determined essentially by its spin system. An additional partial physical property, accessible experimentally, has thus been added to the nuclear magnetic susceptibility, *viz.* the entropy and heat capacity of nuclear spin disorder, which tend to determine alone the thermal behavior of liquid $He^3$ at low temperatures. Furthermore, the effect of the nuclear system on the vapor pressure of liquid $He^3$ will be traced over a wide temperature interval. This effect might be demonstrated through a careful analysis of the vapor pressure data over a wide temperature interval.

The present considerations are all based on the previous evaluation of the entropy of orientational spin disorder and the associated heat capacity.[1] What was fundamentally involved there concerned the separation of the orientational spin disorder effects from other, possibly implicit, spin effects and, above all, from disorder of nonspin origin, connected with the thermal excitation of nonspin types of degrees of freedom. The various thermodynamic quantities derivable from the previously obtained entropy $S_\sigma$ and heat capacity $C_\sigma$ of spin disorder will be obtained here. Such a treatment of the partial properties of liquid $He^3$ seems to be well justified inasmuch as the explanation of the properties originating in the nonspin degrees of freedom presents serious difficulties if attempted to be based on general principles. This is well illustrated, indirectly, by the lack of a rigorous formalism to describe the properties of classical liquids. The partial properties of liquid $He^3$ associated with its spin system to be obtained here would, of course, appear automatically in the rigorous theory of this liquid.

## II. EQUATION OF STATE OF THE SPIN SYSTEM

Let $F(T,V)$ be the thermodynamic potential at constant volume or Helmholtz free energy of a system in equilibrium, occupying volume $V$ at temperature $T$:

$$F(T,V)=E(T,V)-TS(T,V), \qquad (1)$$

$E(T,V)$ being the total thermal energy and $S(T,V)$ the total entropy. Then, by definition, the equation of state of this system is

$$p(T,V)=-(\partial F/\partial V)_T, \qquad (2)$$

the pressure being expressed as a function of $V$ and $T$. Our present task is the derivation of that part $p_\sigma(T,V)$ of the pressure which is determined by the entropy of spin disorder[1] in liquid $He^3$,

$$S_\sigma(T,V)/R=(\ln 2)\chi(T,V)/\chi_0(T,V), \qquad (3)$$

$\chi$ and $\chi_0$ being the actual and the limiting Langevin nuclear magnetic susceptibilities of liquid $He^3$. The Helmholtz free energy of the spin system is

$$F_\sigma(T,V)=E_\sigma(T,V)-TS_\sigma(T,V), \qquad (4)$$

$E_\sigma(T,V)$ being the thermal energy of spin disorder. If $C_\sigma(T,V)$ is the heat capacity of spin disorder, we define $E_\sigma(T,V)$ by

$$\begin{aligned}E_\sigma(T,V)&=\int_0^T C_\sigma(T,V)dT\\&=\int_0^T T(dS_\sigma/dT)dT\\&=TS_\sigma(T,V)-\int_0^T S_\sigma(T,V)dT. \qquad (5)\end{aligned}$$

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[1] L. Goldstein, Phys. Rev. 96, 1455 (1954).
[2] T. R. Roberts and S. G. Sydoriak, Phys. Rev. 98, 1672 (1955).
[3] Abraham, Osborne, and Weinstock, Phys. Rev. 98, 551 (1955).

Hence,

$$F_\sigma(T,V) = -\int_0^T S_\sigma(T,V)dT, \qquad (6)$$

and the equation of state of the spin system is, by (2),

$$p_\sigma(T,V) = \int_0^T (\partial S_\sigma/\partial V)_T dT, \qquad (7)$$

since $T$ and $V$ are taken to be independent.

Since $\chi(T,V)$ in (3) is an empirically determined function of its variables, it will be seen that with the definition (5) of $E_\sigma$, the equation of state (7) is quite general. In order to avoid the explicit use of the function $\chi(T,V)/\chi_0(T,V)$, which is available only in numerical form, it is convenient to use the approximation provided by the ideal antisymmetric fluid formalism for this susceptibility ratio, yielding[1]

$$S_\sigma(T,V)/R = (\ln 2)[-F'(\alpha)/F(\alpha)], \qquad (8)$$

$$F(\alpha) = [1/\Gamma(5/2)](T_0/T)^{\frac{3}{2}},$$
$$\alpha = \alpha(T,V), \quad F'(\alpha) = dF/d\alpha, \qquad (9)$$

$T_0$ being the apparent degeneration temperature of a fictitious ideal antisymmetric fluid whose paramagnetic susceptibility is identical with that of saturated liquid He$^3$. At the present time, the evaluation of the partial derivative $(\partial S_\sigma/\partial V)_T$ appearing in the equation of state (7) cannot be performed because the available data correspond to a line, of variable $T$ and $V$, on the susceptibility surface $\chi(T,V)$. We are thus compelled to use the apparent ideal antisymmetric fluid formalism for a derivation of $p_\sigma(T,V)$. It is thus clear that the $p_\sigma(T,V)$ values so obtained correspond to some approximation of the actual values of this quantity. A simple calculation yields

$$(\partial S_\sigma/\partial V)_T = \frac{R\ln 2}{V}\left[\frac{F''(\alpha)}{F'(\alpha)} - \frac{F'(\alpha)}{F(\alpha)}\right], \qquad (10)$$

since, if one uses (9) with $T_0$ expressed in terms of the total volume $V$, one has

$$(\partial\alpha/\partial V)_T = -V^{-1}[F(\alpha)/F'(\alpha)]; \quad F''(\alpha) = d^2F/d\alpha^2. \qquad (11)$$

With the expression for the spin heat capacity,[1] one obtains the equation of state of the spin system, to the approximation of this formalism, as

$$p_\sigma(T,V) = \tfrac{2}{3}\int_0^T [C_\sigma(T,V)/V]dT$$
$$= \tfrac{2}{3}E_\sigma(T,V)/V, \qquad (12)$$

showing that the virial theorem is valid here.

We give, in Fig. 1, the spin free energy $F_\sigma$ and the spin energy $E_\sigma$, in units of $RT_0$. At low temperatures, $T \ll T_0$, with $C_\sigma(T)$ given previously,[1] one obtains with the first of Eqs. (5),

$$\lim_{T\text{ small}} E_\sigma(T,V)/RT_0 = \tfrac{3}{4}(\ln 2)\tau^2(1 - \tfrac{1}{8}\pi^2\tau^2);$$
$$\tau = T/T_0, \qquad (13)$$

and, again with (5) and (6),

$$\lim_{T\text{ small}} F_\sigma(T,V)/RT_0 = -\tfrac{3}{4}(\ln 2)\tau^2\left(1 - \frac{1}{24}\pi^2\tau^2\right). \qquad (14)$$

These quantities are both parabolic at small $\tau$ values. At high temperatures, we have obtained with a fair degree of approximation the limit of $E_\sigma/RT_0$, by integrating $C_\sigma(T)$ numerically up to $\tau$ equal to five and by using beyond this $\tau$ value the dominant term of the high-temperature expansion of $C_\sigma(T)$, i.e.,

$$\lim_{T\text{ large}} C_\sigma(T)/R = (\tfrac{3}{2}\ln 2)\lim_{\alpha\gg 1}\left[\frac{F''(\alpha)}{F'(\alpha)} - \frac{F'(\alpha)}{F(\alpha)}\right]$$
$$= [(\ln 2)/(2\pi)^{\frac{1}{2}}](1/\tau^{\frac{3}{2}}). \qquad (15)$$

This yielded

$$\lim_{T\to\infty} E_\sigma(T)/RT_0 = \tfrac{1}{2}. \qquad (16)$$

It was of course clear from the shape of $C_\sigma(T)$ curve given previously[1] that the total energy of spin disorder is finite in the limit $T\to\infty$. This energy is $(RT_0/2)$, per mole, and represents the additional energy expended in transforming the spin system from its configuration at the absolute zero, where all levels are doubly occupied, to the configuration in the limit of very high temperatures where all are singly occupied. This spin energy is automatically added to the energy of thermal excitation of the nonspin degrees of freedom.

One also finds in this limit,

$$\lim_{T\text{ large}} (F_\sigma/RT_0) = \tfrac{1}{2} - \tau\ln 2, \qquad (17)$$

showing that $F_\sigma$ becomes linear in $\tau$ at high tempera-

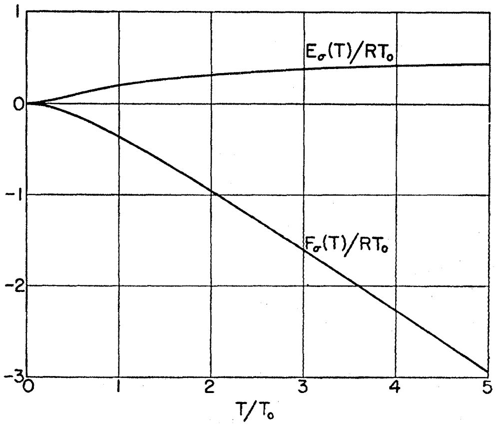

FIG. 1. Energy $E_\sigma$ and free energy $F_\sigma$ of spin excitation, in units of $RT_0$, *vs* the temperature ratio $T/T_0$.

tures, as expected from (4), since $E_\sigma$ and $S_\sigma$ tend toward constant limits.

The Gibbs free energy of the spin system is, with (4) and (12),

$$G_\sigma = (5/3)E_\sigma - TS_\sigma. \tag{18}$$

The limiting forms of this are

$$\lim_{T\text{ small}} (G_\sigma/RT_0) = -\tfrac{1}{4}(\ln 2)\tau^2[1+\tfrac{1}{8}\pi\tau^2], \tag{19}$$

and

$$\lim_{T\text{ large}} (G_\sigma/RT_0) = \tfrac{5}{6} - \tau \ln 2. \tag{20}$$

It will be observed that the Gibbs free energy of the spin system is always negative. This is in contrast with the behavior of the Gibbs free energy of the fictitious ideal antisymmetric fluid whose formalism describes, at $T \gtrsim 0.25°K$, the temperature variation of the nuclear magnetic susceptibility of liquid $He^3$. In other words, the statistical parameter $\alpha(T)$ or $(-G/RT)$ of the fictitious ideal antisymmetric fluid, whose magnetic susceptibility is the same as that of saturated liquid $He^3$, is completely different from the parameter $\alpha_\sigma(T)$ or $(-G_\sigma/RT)$ which is associated with the excitations of the spin system. While $\alpha_\sigma(T)$ is always positive, $\alpha(T)$ becomes negative at low temperatures. In addition, $\alpha_\sigma(T)$ is bounded over the whole temperature range, increasing from zero at the absolute zero, to (ln2) in the limit of high temperatures, while $\alpha(T)$ can take on any values between $(-\infty)$ and $(+\infty)$.

It should be noted here that $G_\sigma$ is associated with the spin excitations alone. Its temperature behavior is, at low temperatures, similar to that of the Gibbs free energy which one can associate with the thermal excitations of an ideal antisymmetric fluid, as was to be expected.

The partial thermodynamic properties of the spin system resemble those associated with two nondegenerate internal energy levels of a system of atoms or molecules.[4] In the latter system, a fraction of the available thermal excitation energy is used up in lifting some of the atoms from the lower to the upper internal level. Since a given amount of energy defined by the separation $\Delta E$ of the two internal levels is needed in this process, the partial heat capacity associated with these levels has to vanish at both ends of the temperature interval assuring thus its temperature integral to be finite and equal to $\Delta E$, per atom, over the whole interval. Geometrically, this partial heat capacity has to have at least one maximum, and this is similar to the behavior of $C_\sigma(T)$ as shown previously.[1] In the spin system, the apparent energy difference of the two spin configurations, one at the absolute zero and the other in the limit of high temperatures, amounts, to the approximation of (16), to $\frac{1}{2}kT_0$, per spin, in terms of the characteristic temperature $T_0$. While instructive, the similarity with the system with the internal levels is only superficial. The spin system is, both physically and formally, vastly different from that of the system of atoms with the two internal energy levels.

## III. SOME PARTIAL PROPERTIES OF LIQUID $He^3$ ORIGINATING WITH ITS SPIN SYSTEM

The physical meaning of the increasing spin excitations with temperature, in liquid $He^3$, was shown[1] to correspond to the gradual freeing of the spins from the powerful internal field tending to increase spin order. We may thus look upon the pressure $p_\sigma$ in agreement with the definition (7) as a manifestation of the spin excitations competing with the internal field. Its development is accompanied by a volume increase $V_\sigma$ of the system, such that the relative volume change is, to a first approximation,

$$V_\sigma/V = p_\sigma(T)\kappa(T), \tag{21}$$

$V$ being the total volume at $T$ and $\kappa(T)$ the compressibility of the liquid. The volume $V_\sigma$ is, of course, included in any volume measurement and cannot be separated experimentally from the total liquid volume. It is of interest, however, to estimate the magnitude of the small volume $V_\sigma$, by giving its lower limit. This can be obtained at once, by using in (21) the compressibility of liquid $He^4$, $\kappa_4(T)$, instead of $\kappa(T)$. Since one should have $\kappa(T) \geqslant \kappa_4(T)$, then, with (12), one obtains

$$V_\sigma(T) \geqslant \tfrac{2}{3}E_\sigma(T)\kappa_4(T). \tag{22}$$

At 1.2°K, with the compressibility $\kappa_4$ being about[5] $1.24 \times 10^{-8}$ cgs unit, $V_\sigma$ becomes about 0.11 cc/mole, which is only some 0.3% of the total volume[6] of 36.9 cc/mole.

While the spin volume increase $V_\sigma$ is small and cannot be observed directly, it has a possibly observable effect on the expansion coefficient of liquid $He^3$ at low enough temperatures. Indeed, let us define the partial spin expansion coefficient by

$$\begin{aligned}\alpha_\sigma(T) &= V^{-1}(dV_\sigma/dT)\\ &= \frac{2}{3V}[\kappa(T)(dE_\sigma/dT) + E_\sigma(d\kappa/dT)].\end{aligned} \tag{23}$$

It will be observed that the two terms in the bracket are different functions of the temperature. At low temperatures, $\kappa(T)$ will be close to $\kappa_0$, the compressibility at the absolute zero, while $dE_\sigma/dT$ or $C_\sigma$, the spin heat capacity, is linear in $T$. The second term with $E_\sigma(T)$ varies at least as $T^2$, even if $d\kappa/dT$ were assumed to be a constant, a rather extreme assumption. One would expect $d\kappa/dT$ to increase at least linearly with the temperature. The leading term of the partial expansion coefficient is thus linear in $T$ at low enough tempera-

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[4] W. Schottky, Physik. Z. **23**, 448 (1922).

[5] K. R. Atkins and C. E. Chase, Proc. Phys. Soc. (London) **A64**, 826 (1951).

[6] E. C. Kerr, Phys. Rev. **96**, 551 (1954).

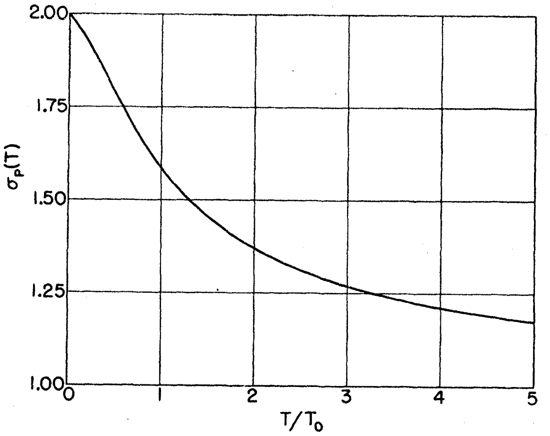

FIG. 2. The spin factor $\sigma_p$ of the liquid He$^3$ vapor pressure *vs* the temperature ratio $T/T_0$.

tures. The expansion coefficient determined by the other degrees of freedom is not expected to have such a linear dependence on the temperature, at such low temperatures. However, such a linear dependence cannot be ruled out completely at the present time, because of the anomalous nonspin heat capacity; the correct shape of the latter is still unknown at low temperatures. We obtain, with (23),

$$\lim_{T\ \text{small}} \alpha_\sigma(T) \simeq \frac{2}{3V}\kappa(T)C_\sigma(T) = \frac{\ln 2}{V}\kappa(T)R(T/T_0), \qquad (24)$$

where we have used the low-temperature limit[1] of $C_\sigma(T)$. A lower limit of the right-hand side results by using there $\kappa_4(T)$ instead of the presently unknown liquid He$^3$ compressibility $\kappa(T)$. With $\kappa_4$ equal to 1.24 $\times 10^{-8}$ cgs unit, as above, $V$ about 37 cc/mole, and $T_0$ equal to 0.45°K, one finds

$$\lim_{T\ \text{small}} \alpha_\sigma(T) \geqslant 0.043T/°\text{K}. \qquad (25)$$

At $T$ equal to 0.2°K, this yields a partial expansion coefficient of at least 0.0086/°K, which is quite large.

The experimental verification of the linear relation (25) might be of interest. If positive, the results would tend to justify the views on spin disorder as being the dominant thermal excitation in liquid He$^3$ at low temperatures.

We should like finally to discuss the effect of the nuclear spin system on the vapor pressure of liquid He$^3$. This appears to be the only liquid where this effect could be traced over a relatively wide temperature interval. We may write the vapor pressure equation in the form

$$p(T) = [(2\pi M)^{3/2}R^{5/2}/N^4h^3]T^{5/2}\exp(G_{n\sigma}/RT) \times \exp[\ln 2 + (G_\sigma/RT)], \qquad (26)$$

where the nuclear spin degeneracy factor $(2s+1)$ or 2, in the vapor phase, is included in the last factor through (exp ln2). All corrections of various origin, both in the liquid and the vapor phase, are assumed to be included in $G_{n\sigma}$. The factor in front of $T^{5/2}$ is the vapor pressure constant for vanishing spin, with $M$ being the atomic mass, and $N$ Avogadro's number. We may thus write the following for the specific spin factor of the vapor pressure:

$$\sigma_p(T) = \exp[\ln 2 + (G_\sigma/RT)]. \qquad (27)$$

According to (19), at low temperatures where the Gibbs free energy $G_\sigma$ vanishes with $T$ as $T^2$, the spin factor $\sigma_p(T)$ tends toward 2, arising entirely from the vapor phase. As the temperature increases, the spin excitations tend to balance the factor due to the vapor phase, and $G_\sigma/RT$, according to (20), tends asymptotically, rather slowly because of the $(1/T)$ term, toward $(-\ln 2)$, compensating fully the vapor phase factor. We give in Fig. 2, the spin factor $\sigma_p(T)$, as a function of the ratio $T/T_0=\tau$, up to $\tau$ equal to five.

In normal liquids whose atoms have a nuclear spin and which exist only at temperatures high enough so that $\sigma_p(T)$ is there equal to unity over the whole temperature range, it is fully justified to leave the spin degeneracy factor out of account in the vapor pressure constant. The latter factor is fully compensated for by the complete spin excitation of the liquid atoms. In liquid He$^3$, however, the $\sigma_p(T)$ factor remains large, that is, considerably larger than unity out to high temperatures because of the very slow convergence of $G_\sigma/RT$ toward $(-\ln 2)$ in (27). This is illustrated in Fig. 2. Hence, as far as the contribution of the liquid spin system to the vapor pressure is concerned, a unique situation appears to exist in liquid He$^3$. A careful analysis of the liquid He$^3$ vapor pressure data over a wide temperature interval might disclose the spin factor $\sigma_p(T)$. An empirical separation of this spin factor from the other pressure factors appears to be of interest in yielding additional information on the role played by the nuclear spin system in the macroscopic thermal properties of liquid He$^3$.