

The Entropy of Liquid He³†

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The vapor pressure of liquid He³, as measured by Abraham, Osborne, and Weinstock, is found to fit the following equation:

$$\log_{10}(P_{\text{mm}}/T^{5/2}) = 2.3126 - 1.1561/T - 0.25254T - 0.00667T^2 + 0.05266T^3 - 0.01210T^4,$$

up to 2.5°K. The entropy curve of the liquid derived from this equation goes smoothly to zero at 0°K, and in fact lies very close to the theoretical curve for a Fermi-Dirac smoothed potential liquid below 1°K. Hence the vapor pressure data furnish no evidence for the existence of a transition below 1°K.

IN a recent paper,¹ Abraham, Osborne, and Weinstock reported very accurate measurements of the vapor pressure of pure liquid He³ down to 1.025°K on the Kistemaker scale. They represent their data by the following equation, valid up to the critical point,

$$\log_{10}p_{\text{mm}} = -0.97796/T + 2.5 \log_{10}T + 0.000302T^3 + 1.91594. \quad (1)$$

Equation (1), when extrapolated down to the absolute zero, leads to a residual entropy of 0.21R with the nuclear spin contribution of $R \ln 2$ neglected, or 0.91R with the spin. This led Abraham *et al.* to suggest that there exists a phase transition or specific heat anomaly in liquid He³ below 1°K, which removes the residual entropy. Similar views were expressed by Singwi,² who suggested that near 1°K the Fermi-Dirac nature of the liquid entropy is replaced by a Debye T^3 -law with $\theta_D \sim 4^\circ\text{K}$, in "a sort of λ -transition."

It shall be shown that it is possible to represent the vapor pressure data of Abraham *et al.* by a smooth function which has the right vapor pressure constant including the nuclear spin, fits the data about as well as (1) from 1 to 2.5°K and leads to a vanishing entropy at 0°K.

The Gibbs potential for a nonideal gas is, up to the second power of the second virial coefficient with higher virial coefficients neglected,

$$G_{\text{nonideal}}(T, p) = G_{\text{ideal}}(T, p) + Bp - (Bp)^2/2RT,$$

where, for a gas of molecular weight 3.0162 and spin $\frac{1}{2}$,

$$G_{\text{ideal}}(T, p) = RT[\ln p_{\text{mm}}/T^{5/2} - \frac{3}{2} \ln 3.0162 - \ln 2 - 2.976] \\ = RT[2.3026 \log_{10} p_{\text{mm}}/T^{5/2} - 5.325].$$

Hence,

$$G_{\text{nonideal}}(T, p) = RT[2.3026 \log_{10} p_{\text{mm}}/T^{5/2} - 5.325] \\ + Bp - (Bp)^2/2RT, \quad (2)$$

which along the vapor pressure curve is equal to the Gibbs potential of the liquid

$$G_{\text{liq}}(T) = G_{\text{nonideal}}[T, p(T)]. \quad (3)$$

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¹ Abraham, Osborne, and Weinstock, *Phys. Rev.* **80**, 366 (1950).

² K. S. Singwi, *Phys. Rev.* **87**, 540 (1952).

The liquid entropy is expressed by

$$S_{\text{liq}}(T) = -(\partial G/\partial T)_p = -dG_{\text{liq}}/dT + V_{\text{liq}}dp/dT, \quad (4)$$

where V_{liq} is the molar volume of the liquid. At the absolute zero S_{liq} should, by Nernst's theorem, be equal to zero. Since near the absolute zero the terms $(d/dT)[Bp - (Bp)^2/2RT]$ and $V_{\text{liq}}dp/dT$ converge rapidly to zero (possibly even with a horizontal tangent), we have, for sufficiently small temperatures,

$$S_{\text{liq}}(T \rightarrow 0) = -(dG_{\text{liq}}/dT)_{T \rightarrow 0} = 0,$$

which means simply that the expression

$$[2.3026 \log_{10}(p_{\text{mm}}/T^{5/2}) - 5.325],$$

written in the form of a power series in T , should not contain a constant term nor terms involving lower powers than T^{-1} .

The expression,

$$\log_{10}(p_{\text{mm}}/T^{5/2}) = 2.3126 - 1.1561/T - 0.25254T \\ - 0.00667T^2 + 0.05266T^3 - 0.01210T^4, \quad (5)$$

has been found to satisfy the above requirement and to fit the experimental vapor pressure data very well for the range up to 2.5°K. Table I gives a comparison of (1), (5) and the experimental data. Above 2.5°K higher powers are necessary. However, there, deviations resulting from the higher virial coefficients would have to be considered because of the nearness of the critical point (3.35°K).

Substituting (5) in (2) and (4), we have

$$S_{\text{liq}} = R[1.1630T + 0.04608T^2 - 0.4850T^3 + 0.1393T^4] \\ - d/dT[Bp - (Bp)^2/2RT] + V_{\text{liq}}dp/dT, \quad (6)$$

whereas (1) would lead to³

$$S_{\text{liq}}^{\text{AOW}} = R[0.9134 - 0.002782T^3] \\ - d/dT[Bp - (Bp)^2/2RT] + V_{\text{liq}}dp/dT. \quad (7)$$

A comparison of (6) and (7) is given in Fig. 1. For V_{liq} the measurements of Grilly, Hammel, and Sydorik⁴

³ Actually the entropy values computed by Abraham *et al.* deviates above 1°K from our values recalculated on the above basis by a small but not identifiable correction. This, however, does not essentially change their general results.

⁴ Grilly, Hammel, and Sydorik, *Phys. Rev.* **75**, 1103 (1949).

have been used, and for B the computed values of deBoer, Kranendonk, and Compaan.⁵

The entropy of an ideal Fermi-Dirac gas with spin $\frac{1}{2}$, molecular weight 3.0162 and molar volume 38 cm³ is included in Fig. 1 as $S^{F.D.}$. It can be seen that for low temperatures S_{liq} is linear with temperature with slope $1.17R$. This is very close to the value $S^{F.D.}(T \rightarrow 0) = 1.01RT$. This strongly suggests that liquid He³ can roughly be considered as a degenerate Fermi-Dirac gas confined in the molar volume V_{liq} (this is equivalent to representing the liquid by the smoothed potential model), with other excitations (Debye waves as well as other interactions) entering at higher temperatures. Lifshitz⁶ by a similar argument obtained $S_{liq} = 0.76RT - 0.068RT^3$ as a crude estimate.

TABLE I. The vapor pressure of liquid He³ between 1.025 and 2.517°K. p : experimental data of Abraham, Osborne, and Weinstock. p_1 : vapor pressure from Eq. (5) proposed here; p_2 : vapor pressure from Eq. (1), proposed by Abraham, Osborne, and Weinstock. Up to and including 2.382°K the difference between the two interpolation formulas is nowhere greater than 0.4 percent.

$T(^{\circ}K)^a$	$p(\text{mm})$	$p_1(\text{mm})$	$p_2(\text{mm})$	$p-p_1(\text{mm})$	$p-p_2(\text{mm})$
1.025	9.71	9.75	9.75	-0.04	-0.04
1.026	9.81	9.80	9.79	+0.01	+0.02
1.038	10.41	10.35	10.34	+0.06	+0.07
1.042	10.46	10.54	10.53	-0.08	-0.07
1.058	11.29	11.32	11.30	-0.03	-0.01
1.121	14.74	14.75	14.72	-0.01	+0.02
1.182	18.79	18.69	18.65	+0.10	+0.14
1.183	18.68	18.76	18.72	-0.08	-0.04
1.298	28.00	27.98	27.95	+0.02	+0.05
1.363	34.16	34.33	34.31	-0.17	-0.15
1.513	52.59	52.45	52.51	+0.14	+0.08
1.644	72.78	72.70	72.81	+0.08	-0.03
1.785	99.65	99.69	99.74	-0.04	-0.09
1.935	135.0	134.92	134.72	+0.1	+0.3
2.046	165.1	165.65	165.12	-0.6	± 0.0
2.162	201.1	202.13	201.74	-1.0	-0.6
2.257	234.2	234.34	234.39	-1.1	-0.2
2.382	282.7	283.39	283.02	-0.7	-0.3
2.517	342.4	340.14	343.32	+2.3	-0.9

^a On Kistemaker's scale.

It is clear from Fig. 1 that, in order that liquid He³ conform to Nernst's theorem, it is *not* necessary to assume a discontinuity at low temperatures in either the entropy curve or the specific heat curve, but that the entropy of liquid He³ may be perfectly smooth and continuous. The deviation from the $S^{F.D.}$ curve is probably not only due to the Debye specific heat contribution but also to inadequacies of the present interpretation which by necessity could not take proper account of the contributions of the higher virial coefficients of the vapor in the calculation of G_{liq} along the vapor pressure curve.

The change in curvature of S_{liq} might indicate that there is a flat minimum in the specific heat curve $C_p = T(\partial S/\partial T)_p = T[dS/dT + (\partial V/\partial T)_p(dp/dT)]$,

⁵ deBoer, van Kranendonk, and Compaan, *Physica* **16**, 545 (1950).

⁶ E. M. Lifshitz, *J. Exptl. Theor. Phys. (U.S.S.R.)* **21**, 659 (1951).

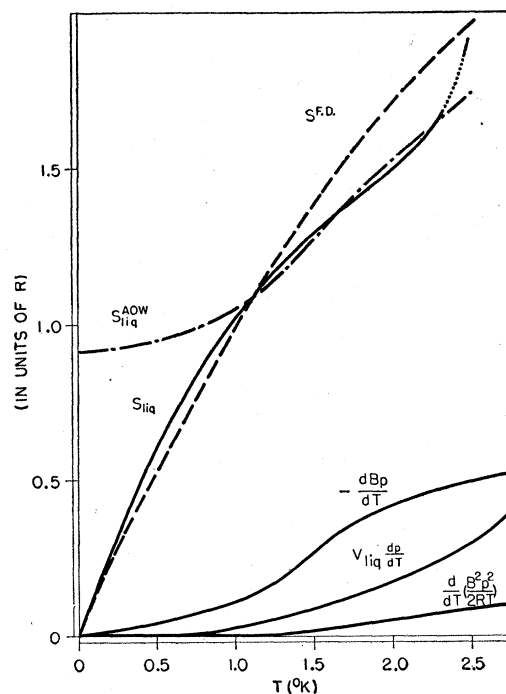


FIG. 1. Entropy of liquid He³. The solid line (S_{liq}) represents Eq. (6), derived from the vapor pressure equation proposed here. S_{liq}^{AOW} represents Eq. (7), derived from the formula of Abraham *et al.* $S^{F.D.}$ is the entropy of a Fermi-Dirac smoothed potential model liquid included for comparison. The various correction terms employed in Eqs. (6) and (7) are plotted in the lower part of the drawing.

since $(\partial V/\partial T)_p$ is negligible up to 1.5°K. Such a defect was first discussed by Simon in connection with Miller's interpretation⁷ of the crude vapor pressure measurements by Sydoriak, Grilly, and Hammel.⁸ From S_{liq} as given in Fig. 1 one would estimate the trough to be near 1.5°K. However, its existence can in no way be considered as ascertained, since its magnitude is within the estimated error. It is perhaps worth mentioning that a similar change of curvature at a somewhat higher temperature ($\sim 2^{\circ}K$) is obtained for $S^{F.D.}$, if the variation in the molar volume⁴ with rising temperatures is being taken into account.

The above discussion does of course not exclude the possibility of a transition in liquid He³, but it shows that the present vapor pressure data do not give any support for the assumption of such a transition. Direct measurements of the specific heat of liquid He³ and of the vapor pressure just below 1°K would be most significant.

Pomeranchuk⁹ argued that the melting pressure curve for solid He³ must have a negative slope if there is appreciable nuclear spin alignment in the liquid but not in the solid, that is, if $S_{solid} > S_{liq}$, since he expects

⁷ A. R. Miller, *Nature* **163**, 283 (1949).

⁸ Sydoriak, Grilly, and Hammel, *Phys. Rev.* **75**, 303 (1949).

⁹ I. Pomeranchuk, *J. Exptl. Theor. Phys. U.S.S.R.* **20**, 919 (1950).

ordering of the spins resulting from magnetic spin interaction alone to occur at about 10^{-7} degree K. However measurements by Weinstock, Abraham, and Osborne¹⁰ give a positive slope of the melting pressure curve down to 0.5°K .

The structure or density of solid He^3 is not yet known. It is quite possible that solid He^3 is different from other solids regarding the alignment of the nuclear spin. Solid He^3 might be so very loosely packed that, for similar reasons as in the liquid state, a spin alignment occurs in the solid state at a much higher temperature than assumed by Pomeranchuk, and that, at a finite temperature, $S_{\text{solid}} < R \ln 2$.

Another possibility would be that, as liquid He^3 is compressed towards the solidification line, it may gradually or discontinuously be squeezed into a structure almost as localized as in the solid state, and lose

¹⁰ Weinstock, Abraham, and Osborne, Phys. Rev. **85**, 158 (1952).

the characteristics of a smoothed potential liquid. In this case the spins would become disorganized under compression *before* solidification. This would mean that the thermal expansion coefficient of the liquid under sufficient pressure would become negative, since $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$.

Weinstock, Abraham, and Osborne¹¹ proposed to extrapolate the vapor pressure data in such a way as to give $S_{\text{liq}} > R \ln 2$, $T \geq 0.5^\circ\text{K}$. In view of our interpretation ($S_{\text{liq}} \rightarrow 0$ when $T \rightarrow 0$), this possibility is in no way demanded by the experimental data and appears to us less likely than either of the two alternatives mentioned above.

An experiment to decide directly the degree of nuclear spin alignment in liquid as well as in solid He^3 by measuring the intensity of the nuclear resonance adsorption is being conducted at this University.

¹¹ Weinstock, Abraham, and Osborne, Phys. Rev. **89**, 787 (1953).

Bohm's Interpretation of the Quantum Theory in Terms of "Hidden" Variables

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An analysis of Bohm's theory, emphasizing the role of probability in it, is presented.

IN two recent articles¹ David Bohm has suggested a "deterministic" interpretation of quantum mechanics based on the introduction of "hidden" variables. It is the purpose of this note to analyze his interpretation and especially the role of probability in it, by examining the complete mathematical formulation of the theory. We are led to the conclusion that if Eq. (10) below must be postulated, then the suggested interpretation is not an ordinary statistical mechanics of a deterministic theory, which is the kind of interpretation many physicists have hoped for and which some have thought this to be. On the other hand, if Eq. (10) can be deduced from the other postulates of the theory, as Bohm attempts to prove in his latest¹ paper, then the theory is essentially an ordinary statistical mechanics of a deterministic theory.

I. DETERMINISTIC MECHANICS OF A SINGLE PARTICLE

In order to present our analysis, we shall first give a precise formulation of Bohm's theory for a single particle in an external potential $V(x)$. Bohm postulates that the particle of mass m has a position $x(t)$ at time t , and thus also a velocity $\dot{x}(t)$. These quantities $x(t)$ and

$\dot{x}(t)$ are the so-called "hidden" variables. In addition to $x(t)$ and $\dot{x}(t)$, there is a "quantum mechanical field" $P(x, t)$. The quantities $P(x, t)$ and $x(t)$ satisfy the following equations:

$$\dot{P} + \nabla \cdot (m^{-1} P \nabla S) = 0, \quad (1)$$

$$\dot{S} + \frac{1}{2m} (\nabla S)^2 + V(x) - \frac{\hbar^2}{2m} \frac{\nabla^2 P}{P} = 0, \quad (2)$$

$$\dot{x} = \nabla S / m. \quad (3)$$

In these equations $S(x, t)$ is a modified Hamilton-Jacobi function which is not assigned a physical interpretation,² and \hbar is Planck's constant.

The above equations must be supplemented by the following initial conditions in order to determine a unique solution:³

$$P(x, 0) = P_0(x), \quad (4)$$

$$S(x, 0) = S_0(x), \quad (5)$$

$$x(0) = x_0. \quad (6)$$

² An alternative formulation, not employing S , is possible but does not alter the main discussion to be given below.

³ It is interesting to notice that the function $S_0(x)$ must be given for all x in order to determine a single trajectory. In contradistinction to this, in classical mechanics a trajectory is uniquely

¹ David Bohm, Phys. Rev. **85**, 166, 180 (1952); **89**, 458 (1953).