

Specific heat, entropy, and magnetic susceptibility of liquid He³

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The spin contribution to the specific heat and entropy of liquid He³ is isolated by analyzing the experimental data. At high temperatures the spin entropy per particle approaches $S_0 \approx 0.972$, which is different from $\ln 2$. The constant S_0 does not depend on the density of the liquid. The nonspin contribution to the entropy is linear in the temperature. The temperature dependence of the pressure at a fixed liquid density exhibits clearly the spin contribution, which is found to be proportional to the logarithm of the temperature.

1. THE PHYSICAL PICTURE

1. In Ref. 1 Greywall reports the results of very accurate measurements of the constant-volume specific heat C_V of liquid He³ for temperatures T in the range from 0.005 to 2.5 °K and molar volumes in the range from 36.8 to 25.7 cm³/mole. The pressure at $T = 0$ was varied from 0 to 34 bar; the liquid density, from the equilibrium density n_0 to 1.4 n_0 . These are the first measurements of the C_V to be performed in such broad T and V ranges on the same apparatus. Earlier constant-pressure specific heat measurements were carried out by different authors in narrow temperature ranges, and are in poor agreement with each other. Reference 1 contains tables of C_V , entropy (S_V), pressure (P) and $\partial P/\partial T$ values for seven molar volumes of He³. Thompson *et al.*² have measured the magnetic susceptibility χ with a high degree of accuracy in roughly the same V and T regions. In the present paper we separate out the spin contribution to the fundamental thermodynamic characteristics of the liquid by analyzing and comparing the data reported in Refs. 1 and 2. We find universal and extremely simple temperature and He³-density dependence for C_V , S_V , P , and χ . These relations are found without the use of any model assumptions about the properties of He³. The paper is extremely close to experiment, and is meant for experimenters: to draw their attention to the study of the properties of He³ at high temperatures $T \approx 1$ °K, i.e., in the region where the Landau theory is no longer applicable, but the liquid is still cold.

2. Liquids, like gases, do not possess long-range order, and, as their fundamental characteristic, let us choose the momentum distribution function n_p of the particles. This function is isotropic and is, in the high- T limit, characterized by the thermal momentum $p_T^2 = 2mT$ (m is the mass of the atom) and low occupation numbers: $n_p \ll 1$. If we keep the density of the liquid constant and raise T , then there comes a time when the thermal momentum becomes smaller than the quantum momentum:

$$p_q = \frac{\pi}{a-D}, \quad T_\infty = \frac{p_q^2}{2m}, \quad p_q > p_T, \quad T_\infty > \frac{3}{2}T. \quad (1)$$

Here a is the interatomic distance and D is the diameter of an atom. The quantum momentum p_q is estimated on the basis of the uncertainty principle for the coordinate and momentum of the atom. It is important that, for a dense medium,

the coarse structure of n_p does not change when the temperature T is lowered further. The occupation numbers thus remain small, but there appears at a temperature $T < T_F$, where T_F is the degeneracy temperature, a small step against the background of a smooth momentum distribution n_p^R :

$$n_p = n_p^R + n_{00}\theta(p_F - p).$$

It is possible that there are several such steps and Fermi momenta p_F . It is, in our opinion, the smallness of n_p at all T that constitutes the important property distinguishing a dense isotropic condensed medium from a slightly nonideal gas. For a gas, $a \gg D$, and (1) is equivalent to the condition $T < \varepsilon_F$, where $\varepsilon_F = p_F^2/2m$. The real He³ is a dense liquid, and the Fermi momentum (the parameter of the ideal gas) is not a characteristic momentum for it. The conditions (1) are fulfilled for He³ at $T \lesssim 20$ °K. The degeneracy temperature T_F and the jump in the function n_p are small: $T_F \ll T_\infty$, $n_{00} \ll 1$. The smallness of n_{00} is a consequence of the high He³ density, since the characteristic momentum $p_q > p_F$ (even a weak inequality will do), and the number of particles responsible for the formation of the n_p jump is smaller than the total number of particles. This assertion is based on the Landau-Luttinger theorem³:

$$\int n_p d^3p = \int_0^{p_F} d^3p.$$

Since $n_p > n_p^R$ and $n_p \ll 1$, the following inequality is valid:

$$n_{00} < \int_0^{p_F} n_p d^3p / \int_0^{p_F} d^3p \ll 1.$$

The smallness of T_F is tightly bound with the smallness of n_{00} . Even a slight warming of the liquid leads to the disappearance of the weak singularity in n_p . The quantity n_{00} determines the weight of the Landau quasiparticles against the background of the total number of particles, and, as has been shown by Migdal,⁴ is the residue at the pole of the single-particle Green function:

$$G = G^R + n_{00}[\varepsilon - (p - p_F)v_F]^{-1}.$$

The strong pole singularity in G determines, even when the residue n_{00} is small, all the thermodynamic and kinetic properties of He³ at $T < T_F$, but becomes unimportant at $T > T_F$.

In the case of highly compressed He³ it is not T_F that serves as the lower temperature scale, but the temperature T_{cr} at which the liquid solidifies. As a result of the small mass of the He³ atom, there exists, for any density of the liquid, a region of intermediate T ($T_{cr}, T_F < T < T_\infty$) where universal dependences of the thermodynamic quantities on T are to be expected. Indeed, in the zeroth approximation $T_F, T_{cr} = 0$, $T_\infty = \infty$, and there is, in general, no energy scale. Therefore, the dimensional quantity T cannot enter into the expressions for the specific heat and entropy per particle: $C_V = 0$ and $S_V/R = S_0$. In the next approximations T can enter in these expressions in the combinations T_F/T and T/T_∞ :

$$S_V/R = S_0 + \gamma_0 T - T_0/T, \quad C_V/R = \gamma_0 T + T_0/T. \quad (2)$$

These relations indeed hold for He³. Their accuracy rises with increasing T and as the density n increases. Figures 1 and 2 show plots, constructed from Greywall's data,¹ of $(S_V + C_V)/R$ and $C_V T/R$ as functions of T and T^2 respectively. Both functions are linear at high T . Unfortunately, Greywall stopped his measurements at $T = 2.5$ °K: it would have been interesting to determine the T 's up to which the asymptotic dependences (2) are valid. For an ideal crystal γ_0 and T_0 in (2) are exactly equal to zero, and the entropy is the sum of the spin and phonon contributions:

$$S_{cr}/R = \ln 2 - T_s^2/T^2 + T^3/\Theta^3.$$

Here Θ is the Debye temperature and T_s is of the order of the overlap integral for the wave functions of the atoms in neighboring lattice sites. For the liquid and the dense gas, in which the single-particle motion of the atoms is possible, nothing forbids the occurrence of the T_0/T and $\gamma_0 T$ terms in (2). There are also no limitations on the residual entropy S_0 in (2). This parameter for He³ differs appreciably from $\ln 2$, and is strikingly constant: as the density is raised from n_0 to $1.4n_0$, the quantity S_0 undergoes insignificant fluctuations in the interval from 0.964 to 0.972.

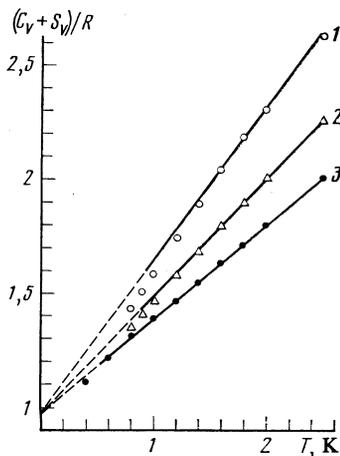


FIG. 1. Dependence on T of the quantity $(C_V + S_V)/R$ for different values of the molar volume V : 1) $V = 36.82$; 2) $V = 30.39$; 3) $V = 26.17$ cm³/mole. The straight lines are plots of functions of the type $(C_V + S_V)/R = S_0 + 2\gamma_0 T$.

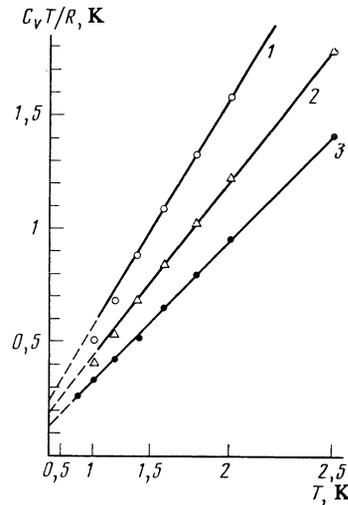


FIG. 2. Dependence on T^2 of the quantity $C_V T/R$ for different values of the molar volume V : 1) $V = 36.82$; 2) $V = 30.39$; 3) $V = 26.17$ cm³/mole. The straight lines are plots of functions of the type $C_V T/R = \gamma_0 T^2 + T_0$.

3. Laws of the type (2) should hold for any system with a nonzero single-particle density of states in the temperature region $T_l < T < T_u$, where T_l and T_u are respectively the lower and upper quantum scales. For the Landau theory $T_l = T_c$ and $T_u = T_F$, where T_c is the critical temperature of the transition of He³ into the superfluid state. In the case of liquid He⁴ the arguments adduced above are valid in the region $T_{cr}, T_\lambda < T < T_\infty$, where T_λ is the superfluid transition temperature. The analog of the n_p jump for He⁴ occurs in the ratio of the number of condensate particles to the total number of particles: $n_p = n_p^R + n_{00} \delta(\mathbf{p})$. The smallness of the number of condensate particles is also a consequence of the high density of the liquid. The quantity n_{00} is small, since the total number of "slow" atoms is small. In the case of He⁴, as in the case of He³, there exists a temperature region where C_V is proportional to T . Andreev⁵ has explained the linear dependence of C_V on T for He³, He⁴, and hydrogen by assuming that these liquids are close to their properties to glasses. Serving as the upper scale in Ref. 5 is the Debye phonon frequency ω_D , which is expressed, as in the case of solids, in terms of the sound velocity c and the density n : $\omega_D \sim cn^{1/3}$. Most of the time the atoms vibrate about the irregularly disposed equilibrium positions, and sometimes hop to neighboring vacant equilibrium sites. Andreev⁵ cited a rigorously defined type of single-particle motion, but actually based his analysis only on the fact that such a motion occurs. The assertions made in Ref. 5 have a general character, and are not connected with the assumption that there is short-range order in a liquid. An amorphous solid (glass) and a dense gas possess similar thermodynamic properties in the region of intermediate T . Indeed, if we reduce the atomic mass, the single-particle motion will destroy the short-range order, but the temperature interval $T_F < T < T_\infty$ will be preserved.

The analogy between a liquid and glass or a dense gas should not be carried too far. Thus, the large parameters ω_D and T_∞ are actually unobservable. In the case of solid He the

frequency ω_D is not just a quantity connected with the sound velocity and the density, but a parameter that can be found from specific-heat measurements. But in the case of liquid He^3 with density close to the equilibrium density n_0 there is no T region where we can observe even a trace of the phonon contribution to C_V . Furthermore, the correction to C_V , which is proportional to T^3 , has a negative sign, which is characteristic of a gas; the dominant term in C_V is $\propto T$; the next, $\propto -T^3$. The parameter T_∞ is also "bad" in the sense that it is too high. Furthermore, the density dependences of the quantity γ_0 in (2) and T_∞^{-1} do not duplicate each other. Apparently, the characteristic frequency $\omega_\perp = i_{c_\perp} k$ of the diffusion-induced transverse excitation serves as the large scale for semiquantum liquids. Tolochko and the present author show in Ref. 6 that such excitations should occur in liquid He^3 with $k \sim 1/a$. Notice also that in solids the transverse acoustic excitations have a lower ω_D than the longitudinal excitations, and it is precisely they which make the dominant contribution to the specific heat.

4. Andreev and Kosevich⁷ have investigated the kinetic phenomena in semiquantum liquids. In particular, for the thermal conductivity coefficient κ they obtain within the framework of the "glass" model the law $\kappa \propto T$, which, for He^4 , is obeyed in the T region where $C_V \propto T$. This law is characteristic of a cold gas as well, a fact which can be seen from the standard gas-kinetic relation⁸: $\kappa \sim C_V \bar{v} l$. For a cold gas $C_V \propto T$, and the mean free path l and the mean velocity \bar{v} of an atom do not depend on the temperature: $l \sim a$, $\bar{v} \sim p_q/m$. Entirely different extreme assumptions about the properties of the liquid lead to similar T dependences of the observed quantity. In such a situation it is useful, if we cannot elucidate, then at least to discover the empirical laws peculiar to semiquantum liquids. Liquid He^3 and He^4 can, on the basis of their properties, be placed not between glass and a dense gas, but alongside.

2. MAGNETIC SUSCEPTIBILITY

The experimental T dependence of χ is a universal one. The value of χ at $T = 0$ determines the temperature scale for χ at all T . In Ref. 2 the following empirical asymptotic laws are given for χ :

$$\Phi(\tau) = \tau(1 - \alpha\tau^2/2), \quad \tau \ll 1, \quad 1 - \Phi(\tau) = b\tau^{-2d}/2, \quad \tau \gg 1, \quad (3)$$

where $\Phi \equiv \chi T/c_k$, $\tau \equiv T/T_F$ (c_k is the Curie constant). As the density is varied, the parameter α in (3) varies nonmonotonically in the range from 1 to 1.1, while the quantities b and d vary monotonically: $0.77 < b < 1.45$; $0.91 < d < 1.43$. The following laws of variation are well obeyed in the entire regions of variation of T and n :

$$\begin{aligned} \Phi(\tau) &= \tau(1 + \tau^2)^{-1/2}, \quad T_F(n) = T_F(n_0)(n/n_0)^{\nu_F}; \\ T_F(n_0) &= 0.359^\circ\text{K}, \quad \nu_F = -1.93, \quad n/n_0 = V_0/V. \end{aligned} \quad (4)$$

To the equilibrium density n_0 corresponds the molar volume $V_0 = 36.84 \text{ cm}^3/\text{mole}$. The minimum value $T_F = 0.179^\circ\text{K}$ is attained on the liquid-crystal coexistence line. For the parameter Φ , which varies in the range from 0 to 1, the approximation (4) corresponds to the values $\alpha = b = d = 1$ in the

asymptotic formulas (3), and is accurate to within 2%. The expression (4) for Φ apparently does not contain any physics, and is also an analog of the empirical Curie-Weiss law, which is characteristic of a system of spins on a lattice: $\Phi_C = \tau/(\tau - 1)$. But the formula given in (4) for $T_F(n)$ is very exact and lays claim to the role of a physical law. The corresponding quantity for localized spins depends very strongly on the crystal density: $T_F \propto n^{-1.8}$. For a nearly ferromagnetic Fermi gas the dependence $T_F \propto (n_c - n)^{\nu_F}$, where n_c is the critical density, is to be expected. The majority of the observable quantities characterizing the thermodynamics of He^3 and its interaction with a long-wavelength external field also vary with the molar volume according to power laws. The determination of the T dependence of χ in a broad range of T is a difficult and an unsolved problem for He^3 . It is insensitive to the choice of a model. Thus, for an ideal gas $T_F = \frac{2}{3}\epsilon_F$ and the parameters in (3) are equal to: $d_0 = 0.75$; $\alpha_0 = 0.73$; $b_0 = 0.98$. Since d_0 , b_0 , and α_0 are close to the empirical values of d , b , and α , it is not surprising that, if we choose ϵ_F so as to obtain the correct value $\chi(0)$ of χ for $T \rightarrow 0$, then χ will be in good agreement with the ideal value χ_{id} at all T . Experimenters traditionally compare the measured χ with χ_{id} . Moriya gives in his review article⁹ extensive experimental data on the properties of nearly ferromagnetic metals. There exists a general empirical rule: if the magnetic susceptibility at $T = 0$ is high, then χ begins to obey the Curie law at very low T . This rule is applicable to liquid He^3 as well. The Curie law for χ is valid in the temperature region where the liquid is still cold. Below we shall use the expressions (4) without attempting to prove them.

Notice that the introduction of the designation T_F in (3) is not accidental. The parameter T_F , defined by the relation $\chi(0) = c_k/T_F$, is the degeneracy temperature for He^3 . This is almost obvious: since T_F determines the scale for χ , this same parameter should be the natural scale for all the spin characteristics of He^3 . Another definition of the degeneracy temperature is adopted in the literature: $\epsilon_F^* = p_F^2/2m^*$. The quantity ϵ_F^* is not directly observable, and is obtained from the gas parameters m^* and p_F . The scale ϵ_F^* is unnatural, being too large for He^3 . For He^3 all the low-temperature expansions are in powers of τ , while the high-temperature ones are in powers of τ^{-1} . Moreover, the actual expansions are in powers of the quantities $\Phi(\tau)$ and $\Phi(\tau)/\tau$.

3. ENTROPY, SPECIFIC HEAT, PRESSURE

1. In order to separate out the spin contributions to C_V and S_V , we, using the Greywall's data,¹ computed the C_V value from S_V . Since the nonspin contribution, which is nearly linear in the temperature, cancels out in the difference, the quantity $S_V - C_V$ depends only on the parameter τ . Figure 3 shows plots of $(S_V - C_V)T/RT_F$ as a function of T/T_F for three values of T_F . It can be seen that the parameter T_F indeed determines the scale for the spin contributions C_V^s and S_V^s . Therefore, there are grounds for the following separation of the contributions to C_V and S_V at $T \gg T_F$:

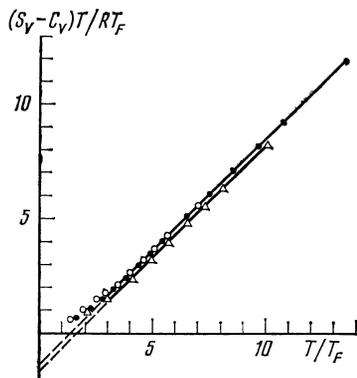


FIG. 3. Dependence on T/T_F of the quantity $(S_v - C_v)T/RT_F$ for three values of T_F : \circ) 0.359 °K; \triangle) 0.250 °K; \bullet) 0.185 °K. The straight lines are plots of functions of the type $(S_v - C_v)T/RT_F = S_0 T/T_F - 2T_0/T_F$.

$$S_v^\sigma/R = S_0 - T_0/T, \quad S_v^R/R = \gamma_0 T - \beta T^3/3, \quad S_v = S_v^R + S_v^\sigma; \\ C_v^\sigma/R = T_0/T, \quad C_v^R/R = \gamma_0 T - \beta T^3, \quad C_v = C_v^R + C_v^\sigma, \quad (5)$$

where C_v^R and S_v^R are the nonspin regular contributions. The correction βT^3 to C_v^R is very small at all $T < 2.5$ °K, and the parameter β is found inaccurately. But the sign of the correction $\propto T^3$ is definitely known. It is possible that it has the form $\beta T^3 \ln(T_\infty/T)$. On the other hand, the parameters γ_0 , T_0 , and S_0 in (5) can be very accurately determined, since we can find the derivatives of T_0 , S_0 and γ_0 with respect to the volume V of the system, using the identity $\partial P/\partial T = \partial S_v/\partial V$ and Greywall' experimental data¹ for the dependence of P and $\partial P/\partial T$ on T . Figure 4 shows the dependence of $T(\partial P/\partial T)$ on T^2 . The correction $1/12RT^4 \partial \beta/\partial V$ to the pressure is entirely insignificant, and there is no linear correction $\propto T \partial S_0/\partial V$, which implies almost exact constancy of the parameter S_0 ;

$$P(T) - P(0) = -P_0 \ln(T/T_F) + \delta T^2, \quad P_0 = (\partial T_0/\partial V)R, \\ (\partial P/\partial T)T = -P_0 + 2\delta T^2, \quad \delta = (\partial \gamma_0/\partial V)R. \quad (6)$$

The temperature T_{\min} at which the pressure P has its minimum can be readily found from (6): $T_2 = P_0/2\delta$. For $n = 1.4n_0$ this relation is accurate to within 1%.

In Table I we give the values of the parameters ∂_0 , P_0 , T_p , T_0/T_F , S_0 , T_F , and β for seven values of the molar volume of He³. Figure 5 shows the dependence of the spin pressure with the sign reversed on $\ln T$:

TABLE I. The principal thermodynamic characteristics of liquid He³.

$P(T=0.1 \text{ E})$ bar	$v, \text{ cm}^3/\text{ mole}$	$T_F, \text{ K}$	$\nu_0, \text{ K}^{-1}$	$\frac{m_0^*}{m}$	γ^σ	T_F	ΓT_F^3	$\frac{\Theta_C}{T_F}$	$\frac{T_0}{T_F}$	S_0	$P_0, \text{ bar}$	$\delta, \text{ bar/K}^2$	$T_p, \text{ K}$	$\beta \cdot 10^3, \text{ K}^{-3}$
0	36,82	0,359	0,350	0,352	0,858	1,70	1,28	0,692	0,964	0,701	0,561	0,468	3,54	
5	32,59	0,286	0,296	0,323	0,792	1,55	1,22	0,761	0,966	0,685	0,480	0,410	2,61	
10	30,39	0,250	0,265	0,303	0,765	1,47	1,10	0,772	0,972	0,852	0,474	0,392	1,35	
15	28,89	0,224	0,247	0,293	0,746	1,41	1,10	0,784	0,972	1,074	0,486	0,384	1,18	
20	27,70	0,207	0,233	0,284	0,744	1,37	1,15	0,763	0,971	1,339	0,504	0,380	1,08	
25	26,83	0,195	0,222	0,276	0,743	1,34	1,18	0,733	0,972	1,593	0,523	0,377	1,04	
30	26,17	0,185	0,213	0,270	0,751	1,32	1,21	0,697	0,972	1,837	0,542	0,374	1,02	

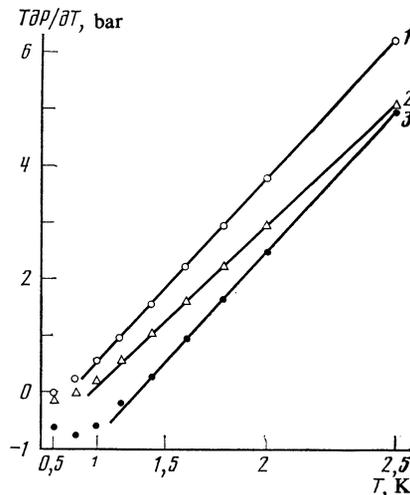


FIG. 4. Dependence on T^2 of the quantity $T\delta P/\delta T$ for the same molar-volume values given in Figs. 1 and 2. The straight lines are plots of functions of the type $T\delta P/\delta T = -P_0 + 2\delta T^2$.

$$P^\sigma(T) = P^\sigma(0) - P_0 \ln(T/T_F).$$

This law is obeyed at $T \approx 2$ °K to within 0.2%. On the other hand the law for C_v^σ is obeyed in the region $T > 2T_F$ to within 5%. The T dependence of $C_v^\sigma T/R$ at high densities $\approx 1.4n_0$ is nonmonotonic, and possesses a weak minimum.

2. The density dependence of the parameter γ_0 in (5) is a power-law one:

$$\gamma_0(n) = \gamma_0(n_0) (n/n_0)^{\nu_\gamma}, \quad (7)$$

$$\text{where } \nu_\gamma = -1.44, \quad \gamma_0(n_0) = 0.35 \text{ K}^{-1}$$

This law is obeyed in the broad interval from $n = n_0$ to $n = 1.84n_0$. The formula (7) agrees to within 4% with the experimental data obtained by Pandorf *et al.*¹⁰ for He³ and He⁴ and their solutions in the temperature range from 2 to 4.5 °K and molar-volume range from 20 to 23 cm³/mole. The values of the exponent ν_γ for He³ and He⁴ are almost equal, which again confirms the correctness of the separation of the spin contribution to C_v and S_v . The nonspin contribution $\gamma_0 T$ turned out to be insensitive to the type of particle statistics used. In Table I we also give values for the quantities m_0^* , which is the effective mass of the light quasiparticles:

$$m_0^* = \gamma_0 p_F^2 / \pi^2, \quad m_0^*(n) \approx m_0^*(n_0) (n/n_0)^{\nu^*}$$

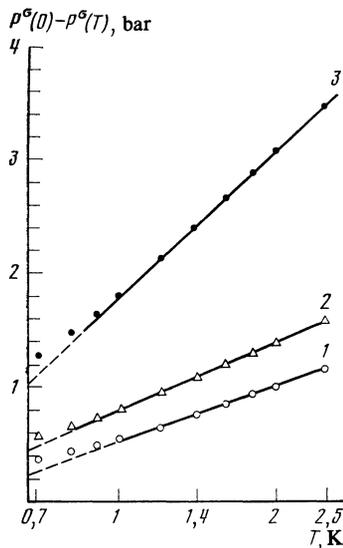


FIG. 5. Dependence on $\ln T$ of the quantity $P^\sigma(0) - P^\sigma(T)$ for the same molar volumes given in Figs. 1 and 2. The straight lines are plots of functions of the type $P^\sigma(0) - P^\sigma(T) = P_0 \ln(T/T_p)$.

Here $\nu^* = -0.773$ and $m_0^*(n_0) = 0.352m$. As shown in Ref. 6, the parameter m_0^* is an important characteristic of He^3 . The dispersion of the short-wave acoustic excitations is determined not by the value of the mass m^* of the heavy Landau quasiparticles, but by just the quantity m_0^* . Before the publication of Greywall's data¹ the parameter m_0^* was known very inaccurately.¹¹

3. The laws (5) and (6) hold in the high- T region where the dependence of the magnetic susceptibility χ on T is described by the Curie law to within fractions of one percent. But in the case of solid He^3 the approach of the spin entropy to the value $R \ln 2$ and that of χ to the Curie law occur in the same temperature range. The cause of this difference lies, apparently, in the fact that, while the spin entropy S_V^σ is a functional of $\chi(k)$, the long-wavelength limit $\chi(k=0)$ is measured in experiment. For localized spins χ does not depend on k , and the Curie law begins to hold, as the temperature is raised, for all the momenta simultaneously. But in the case of the liquid χ depends on the wave vector k , and the approach of the magnetic susceptibility to the Curie law occurs earlier for $k=0$ than for $k \sim 1/a$. The contribution of the momenta

$k \sim 1/a$ is, in our opinion, responsible, for the appearance of the slowly decreasing—with increasing T —term of the order of T_0/T in (5). In other words, in contrast to what obtains in a crystal, in a liquid there exists a nonzero probability of the atoms coming so close to each other that the exchange effects are not negligible at any temperature.

4. We can determine the spin entropy S_V^σ and the spin specific heat C_V^σ at all temperatures on the basis of the asymptotic dependences for S_V and C_V . To do this, we must, using Greywall's data,¹ subtract the value S_V^R from the total entropy and C_V^R from the total specific heat:

$$C_V^\sigma/R = C_V/R - \gamma_0 T + \beta T^3, \quad S_V^\sigma/R = S_V/R - \gamma_0 T + \beta T^3/3. \quad (8)$$

This operation is legitimate if the functions $S_V^R(T)$ and $C_V^R(T)$ are linear at all, and not just high, T . That this is in fact the case can be seen from Figs. 6 and 7, which depict the dependence of the quantities S_V^σ/R , $S_V^\sigma T_F/RT$, and $C_V^\sigma T_F/RT$ on T/T_F for three values of the parameter T_F . The parameter T_F alone determines the scale of C_V^σ and S_V^σ in the enormous interval $0.005 < T < 2.5$ °K. The spin specific heat and spin entropy are functions of the ratio T/T_F only. Notice that if we went from low to high T , it would be very difficult to separate the contributions to C_V and S_V , since at low temperatures $S_V^\sigma \gg S_V^R$ and $C_V^\sigma \gg C_V^R$. It turned out to be simpler to go down the temperature "scale" from the relation of high T , where $S_V^\sigma \approx S_V^R$ and $C_V^\sigma \approx C_V^R$, into the low- T region. The high accuracy of the measurements allowed Greywall to determine all the three coefficients in the low-temperature expansion of C_V :

$$C_V = \gamma T - \Gamma T^3 \ln(\Theta_c/T), \quad T \ll T_c. \quad (9)$$

In Table I we give the values of the dimensionless parameters ΓT_F^3 , Θ_c/T_F , and $\gamma^\sigma T_F$, where $\gamma^\sigma = \gamma - \gamma_0$. It can be seen that the parameter T_F is again the natural scale at low T : all the numbers in Table I are of the order of unity. Therefore, at low T

$$\frac{C_V^\sigma}{R} = \gamma^\sigma T - \Gamma T^3 \ln \frac{\Theta_c}{T}, \quad \frac{S_V^\sigma}{R} = \gamma^\sigma T - \frac{1}{3} T^3 \ln \frac{\Theta_s}{T}, \quad (10)$$

where

$$\Theta_s = \Theta_c e^{1/3}, \quad \frac{C_V^R}{R} = \frac{S_V^R}{R} = \gamma_0 T.$$

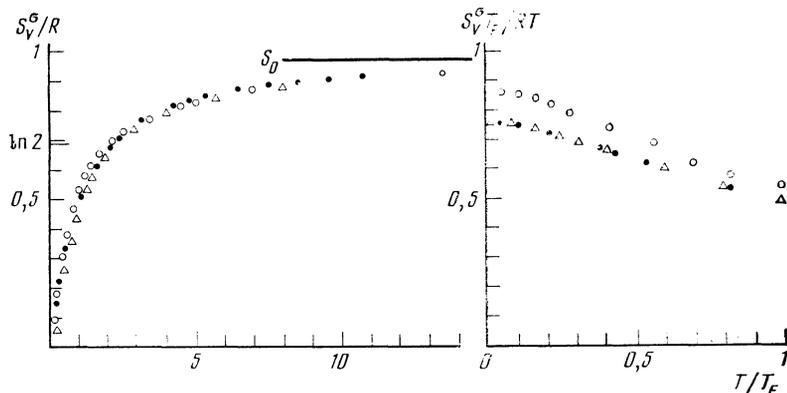


FIG. 6. Dependence on T/T_F of S_V^σ/R and $S_V^\sigma T_F/RT$ for the same T_F values given in Fig. 3.

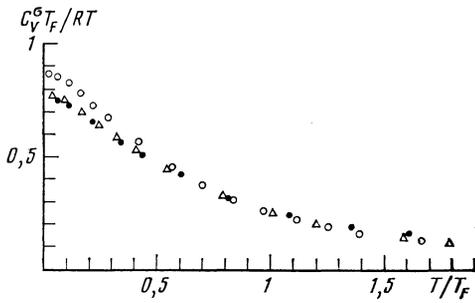


FIG. 7. Dependence on T/T_F of $C_V^\sigma T_F/RT$ for the same T_F values given in Fig. 3.

In experiment the parameter Γ varies in the range from 36.8 to 225 K^{-3} . The density dependence of Γ has the form

$$\Gamma(n) = \Gamma(n_0) (n/n_0)^{\nu_1}, \quad \Gamma(n_0) = 36.8 \text{ K}^{-3}, \quad \nu_1 = 5.02.$$

It is characteristic that the asymptotic dependences (10) hold right up to high $T \approx \Theta_C/2$ (Θ_C varies, as n is increased, from 0.46 to 0.22 $^\circ\text{K}$), i.e., the expressions (10) are valid in the region where $\ln(\Theta_C/T) \approx 1$. Greywall was the first to point out this important circumstance. The existence of the correction $T^3 \ln T$ to C_V was predicted by Éliashberg,¹² and Brinkman and Engelsberg¹³ have given an estimate for the region of applicability of the law (10) for He^3 : $T < 0.025 \text{ }^\circ\text{K}$. It is usually difficult to detect a logarithmic law, and here we must think of how to get rid of it. Indeed, the value of Θ_C in (10) is of the normal—for He^3 —order of magnitude of T_F : the ratio Θ_C/T_F (Table I) varies from 1.1 to 1.28. It is not possible to find the parameter Θ_C within the framework of the low-temperature Fermi-liquid expansions, since it cannot be expressed in terms of the characteristics of the liquid at the Fermi surface. Let us try to find the relation between the spin contributions, C_V^σ and S_V^σ , and the magnetic susceptibility χ constructively without the use of model assumptions, trusting, of course, that such a relation exists.

4. EMPIRICAL RELATIONS FOR C_V^σ , S_V^σ , AND χ

Let us first of all write down the asymptotic expressions for S^σ and $\Phi = \chi T/c_k$, replacing all numbers of the order of unity simply by unity:

$$\begin{aligned} S_V^\sigma/R &= 1 - 1/\tau, \quad \Phi = 1 - 1/\tau^2, \quad \tau \gg 1, \\ S_V^\sigma/R &= \tau - \tau^3 \ln(1/\tau^2), \quad \Phi = \tau(1 - \tau^2), \quad \tau \ll 1. \end{aligned} \quad (11)$$

In (11) the substitution $\tau \rightarrow \Phi(\tau)$ suggests itself, after which the low-temperature expansions have meaning at $\tau \gg 1$ as well and the high-temperature expansions have meaning at $\tau \ll 1$:

$$\begin{aligned} S_V^\sigma/R &= \Phi - \Phi^2/\tau, \quad \tau \gg 1, \\ S_V^\sigma/R &= \Phi - \Phi^3 \ln(1/\Phi^2), \quad \tau \ll 1. \end{aligned} \quad (12)$$

Therefore, we can endeavor to seek the relation between S_V^σ and Φ in the form of an expansion of S_V^σ in powers of Φ and Φ/τ . This expansion should contain $(\Phi/\tau)^n$ terms, since the

asymptotic form of S_V^σ contains a T_0/T term, which we cannot obtain if we have only powers of Φ :

$$\frac{S_V^\sigma}{R} = \kappa \Phi - \frac{\lambda}{3} \Phi^3 \ln \frac{\Phi_s^2}{\Phi^2} + \lambda_1 \Phi^5 + \dots - \frac{\tau_0}{\tau} \Phi^2 + \frac{\tau_2^2}{\tau^2} \Phi^3 + \dots \quad (13)$$

Two of the coefficients in (13) are known: $\lambda = \Gamma T_F^3/2$ and $\tau_0 = T_0/T_F$. There is hope that the series (13) converges, since even the first approximation $S_V^\sigma = \kappa \Phi$, with $\kappa = S_0$, reproduces the experimental S_V^σ curve in the region $T < T_F$ to within 25%, and possesses the correct asymptotic form in the region $T > T_F$. We can truncate the series (13), but it is better to approximate it by the functions

$$\frac{S_V^\sigma}{R} = \kappa \frac{\tau}{\tau_1} \ln \left(1 + \Phi \frac{\tau_1}{\tau} \right) - \frac{\lambda}{3} \Phi^3 \ln \left(\rho_s^2 + \frac{\Phi_s^2}{\Phi^2} \right). \quad (14)$$

The approximation (14) can be justified, but we propose to treat the expression (14) as an empirical expression. Since the function Φ coincides exactly with $\tau/(1 + \tau^2)^{1/2}$, (4), we can simplify the formula (14) greatly and find the parameters κ , τ_1 , ρ_s^2 , Φ_s , and λ from the asymptotic forms of S_V^σ for $T > T_F$ and $T < T_F$, knowing the quantities γ^σ , Φ_s , Γ , and T_0, S_0 :

$$\begin{aligned} S_0 &= \kappa - \frac{\lambda}{3} \ln(\rho_s^2 + \Phi_s^2), \quad \ln \frac{\Phi_s}{T_F \Phi_s} = \frac{3\kappa}{4\lambda(1 + \tau_1)}, \\ \gamma^\sigma T_F &= \frac{\kappa}{\tau_1} \ln(1 + \tau_1), \quad \lambda = \frac{\Gamma T_F^3}{2}, \quad \frac{T_0}{T_F} = \frac{\kappa \tau_1}{2}. \end{aligned}$$

The dependence (14) agrees with experiment to within 2%. The formula (14) is not improved in accuracy if we do not use the empirical expression (4) for Φ , but substitute in it the experimental values of Φ . As was to be expected, the parameters τ_1 , κ , λ , Φ_s , ρ_s^2 (Table II) depend weakly on the molar volume. By making the same approximations, we can obtain the expression for the spin specific heat C_V^σ/R :

$$\begin{aligned} \frac{C_V^\sigma}{R} &= \kappa \tau \frac{\partial}{\partial \tau} \left\{ \frac{\tau}{\tau_1} \ln \left(1 + \Phi \frac{\tau_1}{\tau} \right) \right\} \\ &\quad - \lambda \Phi^2 \frac{\partial \Phi}{\partial \tau} \tau \ln \left(\rho_c^2 + \frac{\Phi_c^2}{\Phi^2} \right), \end{aligned} \quad (15)$$

where $\Phi_s \equiv \Phi_c e^{1/2}$ and $\rho_s^2 = 1.086 \rho_c^2$. The dependence (15) agrees with the identity $C = \tau \partial S / \partial \tau$, since the following relation holds to within 1% in the entire interval $0 < \Phi < 1$:

$$\int_0^\Phi \Phi_1^2 \ln \left(\rho_c^2 + \frac{\Phi_c^2}{\Phi_1^2} \right) d\Phi_1 = \frac{\Phi^3}{3} \ln \left(\rho_s^2 + \frac{\Phi_s^2}{\Phi^2} \right). \quad (16)$$

If we set $\Phi = \tau(1 + \tau^2)^{1/2}$, then $\tau \partial \Phi / \partial \tau = \Phi(1 - \Phi^2)$, and we have for the total specific heat $C_V = C_V^\sigma + C_V^R$ from (15) the expression

$$\begin{aligned} \frac{C_V}{R} &= \kappa \frac{\tau}{\tau_1} \ln \left(1 + \Phi \frac{\tau_1}{\tau} \right) - \frac{\kappa \Phi^3}{1 + \Phi \tau_1 / \tau} \\ &\quad - \lambda \Phi^3 (1 - \Phi^2) \ln \left(\rho_c^2 + \frac{\Phi_c^2}{\Phi^2} \right) + \gamma_0 T - \beta T^3. \end{aligned} \quad (17)$$

In Table II we also give the values of ρ_c^2 and Φ_c . The empirical formula (17) is less accurate than (14), it being accurate to

TABLE II. Parameters of the empirical functions $S_V^\nu(T)$ and $C_V^\nu(T)$ (the formulas (14) and (17)).

V , cm ³ /mole	λ	κ	τ_1	Φ_S	Φ_C	ρ_S^2	ρ_C^2
36,82	0,851	1,268	1,092	1,047	0,750	1,824	1,680
32,59	0,775	1,220	1,247	1,007	0,721	1,659	1,528
30,39	0,735	1,193	1,295	0,903	0,647	1,649	1,518
28,89	0,705	1,176	1,334	0,898	0,643	1,576	1,451
27,70	0,685	1,163	1,312	0,925	0,663	1,462	1,346
26,83	0,670	1,153	1,272	0,933	0,668	1,378	1,269
26,17	0,659	1,147	1,215	0,937	0,671	1,340	1,234

within 5%, which is admissible, since the approximation (4) is for Φ , while (15) contains the τ derivative of Φ . The maximum deviation of the dependence (17) from the experimental curve occurs in the region $T \approx 1$ K, where we can roughly use for C_V^ν the asymptotic formula $C_V^\nu = RT_0/T$. But in the region of the C_V^ν maximum, which occurs at $\tau \approx 1$, the error introduced by the use of (17) is the same as the error made when the formula is used in the region $T < T_F$, this error being 1%. We do not overrate the good agreement of the empirical dependence (14) and (17) with experiment, but the fact that the series expansions of C_V^ν and S_V^ν in powers of Φ and Φ/τ converge is extremely important for the choice of a realistic model for He³. Regardless of whether we assume existence or absence of short-range order in liquid He³, there comes a point in the theory of He³ gas and He³ glass when we introduce the scale T_F on the basis of the experimental data. After this, the auxiliary parameters of the type m^* , p_F , and ϵ_F^* no longer enter into the relations connecting the observable quantities, and remain numbers of the order of unity. All the theories are then alike. We can, on the basis of dimensional considerations, simply set $S_V^\nu = \Phi$, and it will be in quite good agreement with experiment.

The predictions of the various models of He³ differ appreciably only in the expressions they yield for the corrections to C_V^ν and S_V^ν . There has not in the history of He³ been a single paper in which the experimental value of the parameter T_F is obtained from first principles, but there are a few different models that lead to the relation $S_V/R = \kappa\Phi$, with $\kappa \approx 1$ (Goldstein,¹⁴ Castaing¹⁵). The Landau theory¹⁶ gives a relation between the parameters T_F and γ :

$$T_F \gamma = \pi^2 (1 + F_0^a) / 3, \quad S_V/R = \gamma T, \quad \Phi = T/T_F \quad \text{for} \quad T \rightarrow 0$$

(F_0^a is the fundamental harmonic of the spin-dependent quasiparticle scattering amplitude). In experiment the quantity γT_F varies in the range from 0.98 to 0.79 as the He³ density is increased. Since $\pi^2/3$ is a large number, but $\pi^2 (1 + F_0^a) / 3 \approx 1$, the almost exact constancy of $F_0^a \approx -0.75$ is only a reflection of the fact that there is no scale other than T_F for He³ in the region $T < T_F$, and the model of He³ within the framework of which a close value of F_0^a is obtained is not confirmed as a realistic model.

5. DISCUSSION

1. As the density increases, the spin effects weaken in solid He³, but become stronger in liquid He³. This can be seen from a comparison of the quantities P_0 and δ (see Table

I). The spin pressure increases in absolute value as the molar volume V decreases. But the nonspin pressure, which is $\propto \delta T^2$, depends weakly on V , since the exponent V_γ (6), (7) is close to unity. If indeed there is short-range order in liquid He³, and the atoms are most of the time spatially separated, then the Pauli principle should very quickly be "switched off" as the density increases. What we see indicates the opposite: as the density increases, liquid He³ does not move closer in its properties to solid He³, but rather moves away from it. If now we remember that the residual entropy per atom S_0 does not tend to the value $\ln 2$, then it becomes clear that the simplest short-range order—one atom at one site of an irregular lattice—is not realized in He³. If, on the other hand, we assume that the number of He atoms is smaller than the number of sites, then the "extraneous" entropy $S_0 - \ln 2$ can be interpreted as the entropy of the vacancies. But for the constancy of S_0 to be explainable, the vacancy density must not depend on the density of the liquid, which, in our opinion, is impossible. An additional disorder can be introduced in another way: we can allow two atoms with opposite spins to occupy the same site.

We must have experimental data for He³ and He⁴ and their solutions in the regions of high T and n and in the region close to the melting curve if we are to understand which variant has been "chosen" by nature. We can, for example, measure the pressure $P(V, T)$ (and it can be measured very accurately); the entropy $S_V(T)$ can then be found by integrating the identity $\partial P / \partial T = \partial S_V / \partial V$. The constant of integration is found from the value $R \ln 2 = S_{cr}$ for solid He³ at the point $T_{\min} = 0.32$ °K where the melting curve has its minimum. Notice that in Ref. 1 the quantities S and P are found through integration of the specific heat over V and T . A high accuracy is not required in the determination of S_V ; the important thing is for the temperature scale not to vary with T and n . We can then separate the contributions to the S_V and C_V for He³ and He⁴ according to how they depend on V and T . We could not find in the literature data for the entropy of He⁴ at high $T \sim 2 - 10$ °K. It is important to know whether the S_V for He⁴ contains, besides the term linear in T , a constant of the type S_0 . The most extensive information about the properties of He³ and He⁴ would be provided by $C_V(T)$ curves determined with the same apparatus in the broad temperature range $T < 10$ °K and broad density range $n_0 < n < 2n_0$. It is possible that, near the melting curve, the $C_V(T)$ curve for He³ has a weak minimum at $T_{\min}^2 \sim T_0 / \gamma_0$, (5). It can be seen from Greywall's data¹ that, for $n \approx 1.4n_0$, this dependence has a broad plateau in the region

$T > T_F$; this is a result of the competition, as T increases, between the increasing quantity $\gamma_0 T$ and the decreasing quantity T_0/T . It will be interesting to know whether there is in the V - T phase diagram for He^3 and He^4 a region where the parameter β , (5), has the opposite sign, which would be an indication of the existence of weakly-damped phonons with frequencies $\gtrsim T$. It is also important to determine the He^3 density at which the power-law dependence of γ_0 and T_F on the density breaks down. The experimental determination of the parameter T_0 at high n and T would enable us to find the quantity T_F as well, since the ratio T_0/T_F (see Table I) depends weakly on the molar volume. We can, by taking into account the fact that the parameter T_F is the scale for χ , (3), obtain information about χ in the region of high T where the magnetic susceptibility is small and it is difficult to measure it. The extrapolation of the dependences for C_V and S_V from the region of high T and n into the region of low T would enable us to predict the properties of supercooled liquid He^3 .

The majority of experimenters traditionally work with helium at constant pressure. But physically, data obtained at constant volume of the liquid are more informative. The dependence of $A(V_0, T)$ on T for the observable quantity A , determined at a single value of the molar volume V_0 , is already useful. But one $A(P_0, T)$ curve is almost useless, since at high T the density of helium is strongly dependent on T , and it is necessary to have a series of curves $A(P_i, T)$ in order to go over to the function $A(V, T)$. Greywall's work¹ is a rare exception: he measured what can be analyzed and computed. Notice that we lose the accuracy of the experimental data when we go over from the variables P, T to V, T since there is some indeterminacy in the dependence of P on V . The principal physical parameter of helium is its density (the molar volume); as for the pressure P it is a secondary quantity. It is not accidental that the above-presented density dependences of the thermodynamic quantities of He^3 are so simple.

In conclusion, it is a pleasure to thank A. F. Andreev, D. N. Khmel'nitskiĭ, and G. M. Éliashberg for discussions and L. A. Tolochko for his help in the investigation.

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