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Thermal Excitations in Solid He^4

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The present paper is devoted to an extension of recent work on solid He^4 using a heuristic approach. The anomalous or negative isobaric expansion coefficients of the solid, in equilibrium with the anomalous liquid He^4II, will be re-evaluated in terms of the here derived approximate compressibilities of the solid based on sound velocity data. The entropy of solid He^4 will then be obtained in terms of the recent Los Alamos determinations of entropy changes on solidification and of two different sets of entropy values of the liquid along the melting line. The latter yield two distinct sets of solid entropy values. While numerically these are different, they appear to be much too large to be accommodated by simple phonon excitations of the solid at temperatures below $T_0(p_m)$, the temperature of the heat capacity anomaly of the liquid at the melting pressure line p_m. Below $T_0(p_m)$, both of these numerically different solid entropies exhibit temperature variations of such strength as to rule out their description in terms of simple phonon entropies. In addition, the two sets of solid entropies give rise to molar heat capacities of the order of the gas constant R, at the approaches of $T_0(p_m)$. The preceding thermal anomalies will be discussed from the viewpoint of the equilibrium between the fundamentally anomalous liqu'd and the solid. Analysis of the liquid entropy yields a new set of onset temperatures of the ordering process responsible for its peculiar transition phenomenon. The thermal anomalies, at or in the vicinity of the melting line, suggest peculiar dispersion and distribution properties of the frequency spectrum of solid He^4. Direct experimental investigations of the above apparent anomalies of the static thermal properties as well as of transport properties of this solid near the phase separation line seem to be of interest.

1. INTRODUCTION

IN recent work[1], we have been led to prove that solid He^4, in equilibrium with the thermally anomalous liquid He^4II, must have anomalous thermal properties over a finite domain of its thermodynamic state surface. The analysis leading to the above proof was based on the formalism of thermodynamics, and the hypothesis that the solid was less compressible than the liquid, whereby use was made of various experimental data referring to both liquid and solid He^4 along the phase separation line. The existence of the anomalous character of solid He^4 over finite intervals of the allowed range of variations of the primary variables of state, pressure, volume, and temperature, extends to this heavy isotope a similar state of affairs predicted earlier[2] to occur in the light isotope He^3. The thermal anomalies of solid He^3, in equilibrium with the thermally anomalous liquid He^3 along the phase separation line, have been verified indirectly by Sydoriak, Mills, and Grilly.[3] They showed that solid He^3 had negative isobaric volume expansion coefficients along the melting line from about 1.25° down to 0.4°K, the temperature range they have explored. This conclusion results from the assumed normal elastic properties of the dense phases of He^3, in analogy with the hypothesis used with He^4. However, direct determinations of the anomalous expansion coefficient of solid He^3 over even a limited region of its phase diagram are lacking at the present time.

A similar indirect verification of the predicted,[1] negative isobaric expansion coefficient of solid He^4 in equilibrium with the thermally anomalous liquid He^4II has also been performed recently by Grilly and Mills.[4] This verification has been made by these workers through their own experimental determinations of the various thermal properties of liquid and solid He^4 along the phase separation line over the temperature range extending from 1.30 to 2.0°K.

The anomalous expansion coefficient of solid He^4 is only one aspect of the thermal peculiarities of solid He^4. We have called attention earlier[1] to the rather remarkable temperature dependence of the entropy of solid He^4 along the melting line. In the present work, we should like to rediscuss briefly the anomalous isobaric expansion coefficients with the help of the here-obtained approximate compressibility coefficients of the solid. These have been obtained with the help of sound velocity data of Vignos and Fairbank,[5] with the limitations of simplifying assumptions on the elastic isotropy of the solid He^4 phases. The main object of the present work is, however, the investigation of the apparent entropy and heat capacity anomalies. The results obtained in the field of these problems appear to be, to a reasonable degree, independent of the simplifying assumptions which were needed to derive some of the bulk elastic properties of solid He^4.

As in our previous work, the approach in the present studies is of heuristic character, the methods of thermodynamics being used with certain elements of the statistical thermodynamic two-fluid model of liquid He^4II. Actually, the results obtained are again independent of the limitations inherent in the latter model.

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[1] L. Goldstein, Phys. Rev. Letters, **5**, 104 (1960); Phys. Rev. **122**, 726 (1961).

[2] L. Goldstein, Ann. Phys. (New York) **8**, 390 (1958); Phys. Rev. **112**, 1483 (1958).

[3] S. G. Sydoriak, R. L. Mills, and E. R. Grilly, Phys. Rev. Letters, **4**, 495 (1960); R. L. Mills, E. R. Grilly, and S. G. Sydoriak, Ann. Phys. (New York) **12**, 41 (1961).

[4] E. R. Grilly and R. L. Mills, Ann. Phys. (New York), 1962 (to be published).

[5] J. H. Vignos and H. A. Fairbank, Phys. Rev. Letters, **6**, 265 (1961).

The main limitations of the results could only arise from the exceptionally poor accuracy and precision of the various thermal properties of liquid and solid He^4 used in the thermodynamic relations. It is expected that the results derived here will be submitted to direct experimental verification.

2. VARIOUS ELASTIC PROPERTIES OF SOLID He^4

Before entering the main subjects of the present work, we should like to derive various approximate elastic properties of solid He^4 using recent sound velocity data.[5] These derived elastic properties will, in turn, enter into a re-evaluation of the anomalous isobaric expansion coefficients of the solid using the recent Los Alamos solid volume data.[4] The derivation of the approximate elastic properties is based on an assumption necessary, it seems, at the present time because of lack of sufficient data on the various directional and polarizational dependence of sound velocities in the crystalline solid He^4.

With the approximate elastic properties a more quantitative evaluation will be made of the mild anomaly of the melting pressure line, which was discussed by us earlier[1] in a qualitative way. Clearly, the limitations on the accuracy of the numerical results so obtained arising from the various assumptions will have to be kept in mind.

At the present time only compressional wave velocities of moderate frequency are available in solid He^4 at melting pressure and at pressures slightly higher.[5] These velocities have also been obtained in liquid He^4 at or near the melting line. The latter allow, of course, a straightforward calculation of the adiabatic compressibility coefficient of the liquid over the explored temperature range, with the help of the recent Los Alamos liquid He^4 volume data along the phase separation line. In solid He^4, however, it is necessary to assume that the velocity data refer to some type of directional average of the velocities of the compressional waves. This means that even on the working assumption of the fictitious solid of complete elastic isotropy, as a consequence of the possibly achieved collection of a fair number of randomly oriented crystals, one of the two elastic constants will have to be approximated in an independent way. Let then λ and μ be the adiabatic Lamé moduli,[6,7] or coefficients of the assumed elastically isotropic solid He^4. In such a solid, the longitudinal, l, or compressional, and the transverse, t, or shear, waves of small amplitude have the following velocities of propagation[6,7]:

$$\begin{aligned}[][v_l(p,T)]^2&=[\lambda(p,T)+2\mu(p,T)]/\rho(p,T),\\ [][v_t(p,T)]^2&=\mu(p,T)/\rho(p,T),\end{aligned} \tag{1}$$

$\rho(p,T)$ being the density of the solid in the state of pressure p, and temperature T. It should be remembered here that solid He^4 exists only as a consequence of the application of external pressure. Inasmuch as the longitudinal wave velocity data refer to a limited pressure interval along the melting pressure and above it, it will be shown briefly below that it is justified to omit the explicit pressure dependence[7] of the right-hand sides in Eqs. (1). In the liquid phase, the compressional wave velocities of small amplitude are given by

$$[v_L(p,T)]^2=\lambda_L(p,T)/\rho_L(p,T), \tag{2}$$

ρ_L being the density of the liquid, and λ_L its adiabatic elastic bulk modulus. In order to obtain the approximate moduli λ and μ of the solid, it is necessary, at the present time, to assume that the adiabatic modulus λ of the solid, in equilibrium with the liquid, is equal, in some approximation, to the bulk modulus λ_L of the liquid. This assumption, in the absence of sufficient data on the propagation of elastic waves in the solid, is probably equivalent to the use of a lower limit of λ. One would expect, in general,

$$\lambda_L(p,T)\neq\lambda(p,T). \tag{3}$$

The lack of desired precision to obtain, in the present attempt, the approximate elastic moduli of solid He^4, is compounded with the assumption of the fictitious solid of elastic isotropy. Such an elastically isotropic solid is then described in terms of two elastic moduli, the two Lamé moduli λ and μ. The connection between a linear combination of the two latter moduli of the solid and the adiabatic bulk modulus λ_L of the liquid, in equilibrium with each other, through

$$\lambda(p,T)+\tfrac{2}{3}\mu(p,T)>\lambda_L(p,T), \tag{4}$$

or

$$[\lambda_L(p,T)]^{-1}>[\lambda(p,T)+\tfrac{2}{3}\mu(p,T)]^{-1}, \tag{4a}$$

has been considered by us[1] in the limit of the heat capacity ratios γ_L, or $(C_{p,L}/C_{V,L})$, and γ_s or $(C_{s,p}/C_{s,V})$ being close to unity. In this case, $\gamma_L\sim\gamma_s\simeq1$, the inequality (4a) is equivalent to the one connecting the isothermal compressibility of the liquid, $\kappa_{T,L}(p,T)$, with that of the solid, $\kappa_T(p,T)$, the two phases being in equilibrium along the phase separation line, or to

$$\kappa_{T,L}(p,T)>\kappa_T(p,T). \tag{5}$$

In the assumed elastically isotropic solid, $\mu>0$. In connection with the relation (5) considered earlier[1] the volume decrease on solidification

$$\Delta V_m(T)=V_L(T)-V_s(T)>0, \tag{6}$$

V_L and V_s referring to molar volumes of the liquid and solid, has to be kept in mind.

In elastically isotropic materials, the Poisson ratio

$$\sigma=\lambda/2(\lambda+\mu)>0, \tag{7}$$

or the ratio of the transverse contraction to the longitudinal extension under longitudinal pull, appears to be positive.[6] Empirically,[5] in liquid He^{4}II and solid He^4,

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[6] A. E. H. Love, *Mathematical Theory of Elasticity* (reprint, Dover Publications, New York, 1944), pp. 293–309.

[7] L. Brillouin, *Les Tenseurs en Mécanique et en Elasticité* (reprint, Dover Publications, New York, 1946), pp. 212–349.

in equilibrium along the phase separation line, one has

$$[v_l(p,T)]^2 > [v_L(p,T)]^2, \tag{8}$$

or, with (1),

$$\lambda(p,T)+2\mu(p,T) > [\rho(p,T)/\rho_L(p,T)]\lambda_L(p,T). \tag{9}$$

Since the possibility of propagation of shear waves imposes, by (1), the relation

$$\mu(p,T) > 0, \tag{10}$$

one obtains with (4), through (5), and with γ values near unity,

$$\lambda(p,T) > \lambda_L(p,T) - \tfrac{2}{3}\mu(p,T),$$

or

$$\lambda+\mu > \lambda_L + \mu/3 > 0. \tag{11}$$

Combining this relation with the condition (7) on the Poisson ratio, one obtains

$$\lambda(p,T) > 0. \tag{12}$$

The latter inequality is thus compatible with the assumption stated above, or

$$\lambda(p,T) = \lambda_L(p,T), \tag{13}$$

which yields, with (1) and (2), the approximate shear modulus as

$$2\mu(p,T) = \rho(p,T)[v_l(p,T)]^2 - \rho_L(p,T)[v_L(p,T)]^2. \tag{14}$$

Also, through the definition of the adiabatic compressibility of the elastically isotropic solid,

$$\kappa(p,T) = [\lambda(p,T)+\tfrac{2}{3}\mu(p,T)]^{-1}, \tag{15}$$

one obtains, within the above limitations,

$$\kappa(p,T) = \tfrac{3}{2}\kappa_L(p,T)[1+(\rho v_l^2/2\rho_L v_L^2)]^{-1}, \tag{16}$$

while the approximate Poisson ratio becomes

$$\sigma = [1+(\rho v_l^2/\rho_L v_L^2)]^{-1}. \tag{17}$$

The approximate Lamé moduli of the solid in equilibrium with the liquid along the phase separation line as well as the approximate adiabatic compressibility coefficient of the solid $\kappa(p,T)$ have thus been expressed in terms of the experimentally measured densities, $\rho(T)$ and $\rho_L(T)$,[4] and longitudinal wave velocities v_l and v_L.[5] We should like to emphasize again the limitations of the preceding expressions of the elastic properties of the solid, limitations imposed by the lack of sufficient wave velocity data on the solid.

We give in Tables I, II, and III, the approximate adiabatic moduli λ and μ, the Poisson ratios σ of solid He^4, and the adiabatic compressibility of the liquid and solid, respectively. With the exception of κ_L, the adiabatic liquid compressibility, all of these are based on the approximate method of derivation outlined above. The Lamé moduli have values in the range of 100 to 260 atmospheres, which would thus justify the omission of their explicit pressure dependence at moderate excess pressures above the melting pressure. Within various limitations on the types of terms retained in the series representation of the elastic energy of deformation[7] the Lamé moduli may be written, in the present case,

$$\begin{aligned}\lambda(p_m+p,T) &\rightarrow \lambda(p_m,T)+p,\\ \mu(p_m+p,T) &\rightarrow \mu(p_m,T)-p.\end{aligned} \tag{18}$$

These modifications in the moduli predict the decrease of the longitudinal wave velocities in the solid on compression. By Eqs. (1), it is seen that the numerator of the longitudinal velocity expression decreases on compression, that is with increasing p, while its denominator, that is the density of the solid increases on compression, with the latter increase being rather small though. The behavior (18) of the moduli also yield a decrease of the compressibility on compression according to (15), as expected, of course. It is clear that in (18), the effect of the increased excess pressure p could also

TABLE I. Approximate Lamé moduli of solid He^4 along the phase separation line.

T (°K)	λ [a]	μ_H [b] (10^2 atm)	$\mu_{C,\mathrm{I}}$ [c]	$\mu_{C,\mathrm{II}}$ [c]
1.28–1.44	2.28–2.29	1.00		
1.44–1.76	2.29–2.36		1.38	1.62
1.80–1.92	2.58–2.62	1.00–0.90		

[a] This is the bulk modulus of the liquid.

[b] Hexagonal phase (H) at $T<1.44$°K; see reference 5.

[3] Cubic phase (C), with the two extreme values of the observed velocities (I) and (II); $1.44 \leqslant T \leqslant 1.76$°K. See references 5 and 8.

TABLE II. Approximate Poisson ratios of solid He^4 along the phase separation line.

T (°K)	σ_H	$\sigma_{C,\mathrm{I}}$	$\sigma_{C,\mathrm{II}}$
1.28–1.44	0.35		
1.48–1.76		0.31	0.29
1.80–1.92	0.37		

TABLE III. Approximate adiabatic compressibility coefficients of liquid (L) and solid He^4(H,C) along the phase separation line.

T (°K)	κ_L	κ_H (10^{-3}/atm)	$\kappa_{C,\mathrm{I}}$	$\kappa_{C,\mathrm{II}}$
1.28	4.39	3.39		
1.32	4.38	|		
1.36	4.38	|		
1.40	4.37	↓		
1.44	4.37	3.38	3.12	2.97
1.48	4.36		|	|
1.52	4.35		|	|
1.56	4.34		|	|
1.60	4.33		|	|
1.64	4.31		|	|
1.68	4.29		|	|
1.72	4.27		↓	↓
1.76	4.24		3.05	2.90
1.80	3.87	3.15		
1.84	3.85	|		
1.88	3.84	↓		
1.92	3.82	3.11		

be described in terms of the associated volume decrease, so that in crossing from the larger volume cubic phase (C),[8] into the smaller volume hexagonal close-packed phase (H), the above type of modification of the moduli would be expected to exist in the normal, constant temperature-constant pressure first-order solid (C)-solid (H) phase transformation. The change in the moduli λ and μ could be defined with more precision if shear wave velocities were available, that is as long as the assumption of elastic isotropy is acceptable. If the Brillouin relations (18) were to describe, within limitations, the effect of an excess pressure on the Lamé moduli, this effect is more pronounced, by (18) and (1), on the velocities of shear waves than on those of the longitudinal waves. At the present time, experimental indications[5] would appear to be consistent with the relations (18).

It may be noted here that the liquid velocity data, at the melting line, appear to be incomplete in that they failed to exhibit the well-known cusp-like shape at the passing of the temperature of the heat capacity anomaly of the liquid. A more detailed investigation of the velocities in the liquid along the melting line and around the temperature of anomaly would be desirable. The same remark applies to the velocities in the solid or solids at and around their upper triple point.

In closing this section, we wish to re-emphasize the approximate character of the elastic properties of the solid derived above, and that the nature of the approximations achieved on these properties can not be assessed satisfactorily at the present time. As soon as shear wave velocities become available in solid He^4, elastic moduli of better approximation may be obtained, at least in the hexagonal solid with its ideal axial ratio. In the latter, as well known, the assumption of elastic isotropy may be expected to be better justified, in contrast with the body-centered cubic solid where elastic anisotropy predominates.[9] The elastic properties obtained thus for the cubic solid He^4 may be expected to be considerably poorer approximations to their actual values than those obtained for the hexagonal close-packed solid He^4.

3. THE ANOMALOUS MELTING LINE OF He^4 AT LOW TEMPERATURES

We have shown previously[1] that at temperatures where the thermal excitations of both liquid and solid He^4 would be expected to reduce to phonons of the Debye type the entropy of solid He^4, in equilibrium with liquid He^4 along the phase separation line, should be larger than that of the liquid. Or, with

$$\lim_{T\text{ small}} \Delta S_m(T)=S_{L,m}(T)-S_{s,m}(T)<0, \tag{19}$$

solidification is accompanied by entropy increase. This would be expected to originate with the excitation of acoustic phonons of all three directions of polarization in the solid continuum, in contrast with their excitation in the liquid phase where the transverse polarization phonons are absent. At low enough temperatures where the thermal excitations of both phases might be expected to be essentially of the continuum phonon type, the temperature derivative of the melting pressure $p_m(T)$ was shown[1] to be given by

$$\lim_{T\text{ small}} dp_m/dT=(4\pi^4/15)(T/\theta_L)^3(R/\Delta V_m)\times[1-(V_L/V_s)^{1/2}(\kappa_s/\kappa_L)^{3/2}\varphi(\sigma)], \tag{20}$$

where θ_L is the characteristic temperature of the liquid along the melting line, R is the gas constant, ΔV_m is the molar volume change on solidification (V_L-V_s), V_L and V_s being the molar volumes of the liquid and solid, κ_s and κ_L are the adiabatic compressibilities of the solid and liquid, and $\varphi(\sigma)$, a function of the Poisson ratio whose well-known form was given earlier.[1] With the Los Alamos volumes V_L and V_s,[4] and the Yale sound velocities,[5] one finds, using the Tables of the preceding section,

$$\Delta V_m \simeq 2\text{ cm}^3/\text{mole},\quad \varphi(\sigma)=10.6,\quad \theta_L=32.2°\text{K},$$

so that the value of the quantity inside the square brackets is (-6.55). To the approximation of the Tables given above, and on the assumption stated on the essentially continuum phonon type of thermal excitations in both phases, as well as the approximate temperature independence of the factors of T^3 in Eq. (20), probably well justified at low temperatures, one obtains, as predicted earlier,[1]

$$\lim_{T\text{ small}} dp_m/dT=-(4\pi^4/15)b(R/\Delta V_m)(T/\theta_L)^3, \tag{21}$$

where b is the numerical value of the quantity in the square brackets. If $p_{m,0}$ is the melting pressure in the limit of the absolute zero, one obtains with (21), on the assumption of θ_L being constant,

$$p_m(T)=p_{m,0}-(\pi^4/15)b(R\theta_L/\Delta V_m)(T/\theta_L)^4. \tag{22}$$

With the large value of θ_L of about 32°K, it is seen that the decrease of the melting pressure in the phonon range of the thermal excitations in both liquid and solid is quite small to be detected, let alone to be measured, without possibly considerable labor, at the present time. One has, indeed, with (22)

$$p_m(T=1.0°\text{K})-p_{m,0}=-0.052\text{ atm},$$

with ΔV_m taken to be 2 cm^3/mole. Since p_m around its minimum is about 25 atm, it is seen that the pressure increase over a reasonable temperature interval, say

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[8] The structure determinations by x-ray diffraction of the low-pressure solid He^4 have been completed recently by A. F. Schuch and R. L. Mills (to be published).

[9] A. F. Schuch, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957* (The University of Wisconsin Press, Madison, Wisconsin, 1958), p. 79, D. G. Henshaw, in the same Proceedings, p. 81.

TABLE IV. Approximate Debye characteristic temperatures of liquid (θ_L) and solid He^4(θ_H,θ_C), along the phase separation line.

T	θ_L	θ_H (°K)	$\theta_{C,\mathrm{I}}$	$\theta_{C,\mathrm{II}}$
1.28–1.44	32.2–32.3	23.7	···	···
1.44–1.76	32.3–32.6	···	27.6	29.9
1.76–1.92		22.3		

0.5°K, amounts only to about 0.2% of the total pressure, at most.

For later use, the approximate values of the Debye characteristic temperatures of the continuum solid have also been obtained in terms of the approximate numerical values of the Poisson ratios and the compressibilities, Tables II and III. The explicit expression of the solid characteristic temperatures have been given previously[1]; their approximate numerical values are included in Table IV

If the thermal excitations of both liquid and solid He^4 did reduce to phonons of the continuum type, and since the calculated characteristic temperatures of the solid may reasonably be expected to be fair approximations to their actual values at $T \lesssim 1.0$°K, with the derivative (dp_m/dt) becoming very small, the $p_m(T)$ curve tends to become a segment of straight line at $T<1.0$°K. This state of affairs would, however, be strictly of observational origin, and it can not represent an actual thermodynamically acceptable situation. It is, indeed, clear that the entropies of the liquid and solid phases, being continuous and differentiable functions of the variables of state, can become equal only at isolated values of the range of allowed variations of these variables.

The difficulty of observing the upswing of the melting line $p_m(T)$ at decreasing temperatures might possibly be overcome through the observation of the nonmonotonic character of the volume lines $V_L(T)$ and $V_s(T)$. The latter increase with decreasing temperatures, (4), down to $T \gtrsim 1.30$°K, the lowest temperature of the explored range. The volume lines could have maxima at the same temperature where $p_m(T)$ is minimum. These volume and pressure extremes are reasonably expected to occur at the temperature of intersection of the locus of vanishing isobaric expansion coefficients $\alpha_p(p,T)$ or of the vanishing derivatives $(\partial p/\partial T)_V$ of isochores of the liquid, that is $T_\alpha(p)_{\mathrm{II}}$ and the melting line $p_m(T)$. In the volume-temperature diagram, the maximum of $V_L(T)$ is at the foot of the locus of the vanishing partial derivatives $(\partial V_L/\partial T)_p$ at the $V_L(T)$ line. Inasmuch as dielectric constant measurements at radio frequencies are susceptible of great precision through frequency measurements, these could be used, indirectly, to locate the peak values of $V_L(T)$ and $V_s(T)$ as well as to verify the decrease of these volumes beyond their maximas. It is of interest to note here that the discussion given by us recently,[10] of the thermodynamic diagrams of He^3, seems to apply in the case of He^4 with even less restrictions, as a consequence of the practically verified existence of the locus $T_\alpha(p)_{\mathrm{II}}$.

4. THE ANOMALOUS ISOBARIC EXPANSION COEFFICIENT OF SOLID He^4 ALONG THE MELTING LINE

In our previous work, we have advanced various arguments of thermodynamic character which tended to indicate that the thermal anomalies of liquid He^{4}II may persist in the solid also, at least over a finite, though possibly small, pressure interval above the melting pressure. One could thus expect the isobaric volume expansion coefficient of the solid along the phase separation line to be negative over finite temperature intervals. This property could though be positive also, with numerical values less than the absolute value of the isobaric expansion coefficient of liquid He^{4}II in equilibrium with it. The anomalies expressed by the inequalities, the subscript s referring to the solid phase,

$$\begin{aligned}\alpha_{p,s}(T,p)=[V_s(T,p)]^{-1}(\partial V_s/\partial T)_p<0,\\ [\partial S_s(T,p)/\partial p]_T>0,\end{aligned} \tag{23}$$

could actually be verified by us[1] using the rigorous thermodynamic relation

$$\alpha_{p,m}(T,p)=[V_s(T,p)]^{-1}(dV_s/dT)+\kappa_{T,m}(T,p)(dp_m/dT), \tag{24}$$

where the subscript m refers to equilibrium conditions along the phase separation lines. A satisfactory evaluation of $\alpha_{p,m}$ of the solid was, however, prevented by the complete absence of solid compressibility values κ_T. Only approximate liquid compressibilities $\kappa_{T,L}$ were available. In terms of the relation (5), it is seen that the substitution of $\kappa_{T,L}$ for $\kappa_{T,m}$ in (24) yields an upper limit of $\alpha_{p,m}$, since both κ_T and dp_m/dT are positive quantities, the latter is positive over the explored temperature interval. Or,

$$\limsup \alpha_{p,m}=[V_s(T,p)]^{-1}(dV_s/dT)+\kappa_{T,L}(p_m)(dp_m/dT). \tag{25}$$

These upper limits of the solid isobaric expansion coefficients turned out to be negative at $T \lesssim 1.50$–1.55°K, and became positive above these temperatures up to about 1.65°K. Beyond the latter temperature even extrapolated liquid compressibilities $\kappa_{T,L}$ along the melting line became unavailable.

In their recent experimental work on liquid-solid equilibrium in He^4, Grilly and Mills have obtained isothermal compressibility values of liquid He^4 along the phase separation line. The latter more accurate and directly determined $\kappa_{T,L}$ values, as compared with the ones we were constrained to use, also yielded negative $\alpha_{p,m}$ values of the solid at low temperatures, in good agreement with our earlier findings.

It is possible now to achieve a possibly improved approximation to $\alpha_{p,m}$ than the one obtained through its

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[10] L. Goldstein, Ann. Phys. (New York) **16**, 205 (1961).

upper limit (25). Namely, the approximate solid compressibilities of Table III may now be used in (24), provided that these adiabatic compressibilities $\kappa(T,p)$ are not much smaller than the isothermal ones. Since,

$$\kappa_T(T,p)=\gamma(T,p)\kappa(T,p),\quad \gamma=C_p/C_V,$$

where the heat capacity ratio γ is necessarily larger or at least equal to unity, it is seen that in terms of the exact adiabatic compressibilities, one has

$$\lim\inf.\alpha_{p,m}(T,p)=V_s^{-1}(dV_s/dT)+\kappa(T,p)(dp_m/dT). \quad (26)$$

As will appear in the next section, the ratio γ, in the temperature range of interest here, appears to be close to unity, so that if accurate adiabatic solid compressibilities $\kappa(T,p)$ were available, the lower limit (26) may be a fairly good approximation to the actual values of $\alpha_{p,m}$. The assumption on the normal elastic properties expressed by Eq. (4a) has to be kept in mind in connection with the anomalous expansion coefficients under discussion.

Numerical evaluation of $\alpha_{p,m}$ with (26) and the necessarily approximate values of $\kappa(T,p)$ of Table III, again yields $\alpha_{p,m}$ values similar to those obtained earlier with the upper limits (25). The approximate lower limits of $\alpha_{p,m}$ became positive at $T\gtrsim 1.55$°K, where they stayed positive and became zero again at 1.70°K, beyond which they decreased again rapidly to reach large negative values at the approaches of $T_0(p_m)$, at 1.76°K. These approximate lower limit solid $\alpha_{p,m}$ values increase rapidly at $T>T_0(p_m)$ from large negative values close to the latter to become positive again at about 1.85–1.87°K. The existence of this latter anomalous region of $\alpha_{p,m}$ around $T_0(p_m)$ has been first suggested by Grilly and Mills[4] on the basis of their attempts at an approximate evaluation of the solid He^4 isobaric expansion coefficients along the melting line.

While this anomalous behavior of solid He^4 confirms and extends the anomalies found earlier, a direct experimental determination of the isobaric expansion coefficients of the solid seems to be necessary, in view of the absence of accurate solid isothermal compressibility values κ_T to be used in the rigorous formula (24). These experimental determinations of $\alpha_{p,m}$ would also help to clarify the existence of the normal or positive expansion coefficients over a limited temperature interval along the melting line.

5. THE EQUILIBRIUM BETWEEN THE ANOMALOUS LIQUID He^4II AND SOLID He^4

The main results of the preceding sections concern the likely naive phonon type of thermal excitations in both liquid and solid He^4 in equilibrium with each other at low enough temperatures. At higher temperatures, $T>1.0$°K, the anomalous, i.e., negative, isobaric expansion coefficient tends to rule out thermal excitations due to phonons of the continuum type as being of any quantitative significance. This conclusion is supported not only by the anomalous negative sign but also by the large numerical values of this thermal property. To be sure, we saw above that the expansion coefficient of the solid exhibited a normal or positive region over a short temperature interval, bracketed by the anomalous regions, with the one on the high-temperature side derived with only approximate values of the solid compressibility. This oscillatory behavior of the solid $\alpha_{p,m}$ is rather strange, and its direct experimental investigation over its normal and anomalous regions, according to the approximate calculations, is necessary and not without interest.

These results have been obtained earlier,[1] at least in part, when we have also called attention to the possibility of a mild transformation like process in solid He^4 at or near the melting line.

The solidification process of liquid He^4 is different at low temperatures from what it is at higher temperatures, as indicated by the shape of the melting pressure line $p_m(T)$.[1] In terms of the two-fluid model of the liquid, we have shown[1] that the very strong temperature dependence of the liquid entropy, $S_{L,m}$, through that of the normal fluid fraction $(\rho_{n,m}/\rho_m)$, the ρ's referring to the densities, determines in a first approximation, the very strong temperature dependence of the temperature derivative dp_m/dT of the melting pressure. This leads in turn to the stronger temperature dependence of the melting line $p_m(T)$ at the approaches of $T_0(p_m)$, the temperature of the heat capacity anomaly of the liquid. This result appears to emphasize the expected dominance of the normal fluid atoms in the solidification process. The physical interpretation of this situation may be close to the one advanced earlier.[1] Namely, the solidification process, at temperatures $T>T_\alpha(p_m)_{\rm II}$, being accompanied by entropy loss of the liquid, the only atoms which can lose entropy are those which have entropy to begin with, that is the atoms belonging to the normal fluid fraction of the liquid, which, by definition, carry alone entropy.

The two-fluid model of liquid He^4II[11] seems to support the simple picture, according to which the normal fluid atoms $N_{L,n}(T,p)$ are distributed over a group of excited energy levels of the system as a whole, while the remaining $(N-N_{L,n})$ or $N_{L,0}(T,p)$ atoms, N being their total number, are still in a group of low-lying levels of essentially vanishing excitation energy.[11] If the $N_{L,0}$ atoms of the liquid played only a secondary role in the solidification process, such as changing necessarily their zero point motion and energy, then the normal atoms $N_{L,n}$, on losing part of their entropy, may still retain in the solid, in some limited sense, their inherently entropy carrying character.

It seems of interest to consider the following argument which tends to favor also the possibility of the normal fluid atoms to preserve on solidification, in some

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[11] L. Tisza, J. phys. radium (8) **1**, 164 350 (1940).

form, their normal character. Namely, the entropy change is, from thermodynamics,

$$\Delta S_m(T)=S_{L,m}(T)-S_{s,m}(T) \\ =(dp_m/dT)[V_{L,m}(T)-V_{s,m}(T)]. \quad (27)$$

The empirically determined melting pressure function $p_m(T)$, and its calculated temperature derivative were found to be very rapidly increasing functions of the temperature. But $S_{s,m}(T)$ is a linear combination of the very strongly temperature-dependent liquid entropy $S_{L,m}(T)$, and of the similar function $\Delta S_m(T)$. Hence, even though $S_{s,m}(T)$ can become numerically small, its temperature dependence must resemble that of $S_{L,m}(T)$ and $\Delta S_m(T)$ or (dp_m/dT). The temperature dependences of these functions, according to their experimentally determined values, are such as to eliminate naive or continuum phonon type of excitations as being of any significance in solid He^4 along the phase separation line, across from the thermally anomalous liquid He^{4}II, at higher temperatures.

The preceding argument leading to the anomalous temperature behavior of $S_{s,m}$ is strictly of heuristic and thermodynamic character. It does not involve any element of a tentative description of the liquid in terms of some model.

We would like to compare now the liquid entropy $S_{L,m}(T)$ with the entropy of the solid $S_{s,m}(T)$ over the temperature range of interest here. The solid entropies result from (27), with the empirical $S_{L,m}(T)$ values and the recently measured $\Delta S_m(T)$ values.[4] Inasmuch as there are two sets of liquid entropy values which are different enough to give rise to consideraly different solid entropies, the latter will have to be studied on the basis of both sets of $S_{L,m}(T)$ values, those of Keesom[12,13] and those of Lounasmaa.[14]

The solid entropies $S_{s,m}(T)$ with the Keesom $S_{L,m}$ values as well as the earlier set of ΔS_m values due to Swenson[15] have been given by us previously,[1] up to the temperature of the heat capacity anomaly of the liquid at $T_0(p_m)$. A recalculation of these with the more recent Grilly-Mills[4] ΔS_m values yields solid entropies in good agreement with those obtained previously. Above $T_0(p_m)$ the Keesom entropies are probably of lower accuracy, particularly near $T_0(p_m)$, since when they were evaluated the extension of the entropy anomaly because of the positive sign of $(\partial S_L/\partial p)_T$ up to the locus $T_\alpha(p)_{\mathrm{I}}>T_0(p)$, was unknown. Actually, these liquid entropy values yield with the Grilly-Mills ΔS_m values, at $T>1.80$°K, slightly decreasing solid entropies. One is inclined to attribute this behavior, which is rather difficult to contemplate, to the fairly large combined uncertainties in both $S_{L,m}(T)$ and $\Delta S_m(T)$. Between about 1.80 and 2.00°K, these entropies of the hexagonal solid seem to develop a plateau like region at about 0.20 to 0.25 R.

At all temperatures $T\gtrsim 1.30$°K, the solid entropy values are small differences of the liquid entropies $S_{L,m}$ and the entropy changes ΔS_m. This is particularly pronounced at the lower temperatures, where the accuracy of the $S_{s,m}$ values is likely to become quite poor. At the triple points T_t, liquid He^{4}II-hexagonal solid He^4-cubic solid He^4,[4,5] of about 1.44 and 1.76°K, the solid entropy has a discontinuous decrease given by

$$\Delta S_{\mathrm{tr}}(T_t)=S_{C,m}(T_t)-S_{H,m}(T_t), \quad (28)$$

the entropy difference of the two solid modifications. The numerical values of these transition entropies are quite small, and their determination at the upper triple point which seems to be close to[4] $T_0(p_m)$ could not be obtained as yet with satisfactory precision. The Los Alamos data bracket this entropy change approximately according to

$$0.03R\lesssim\Delta S_{\mathrm{tr}}(T_0)\lesssim 0.06R. \quad (29)$$

In terms of the larger liquid entropies of Keesom, the hexagonal solid entropy of about 0.14–0.11R at $T_0(p_m)$ would increase rapidly from this value to reach the large plateau-like value of about 0.20–0.25R at $T\gtrsim 1.80$°K.

The smaller liquid entropy values of Lounasmaa lead to a numerically less anomalous situation, above all at $T>T_0(p_m)$. The entropy of the solid along the melting line, $S_{C,m}(T)$, that is the cubic solid entropy, increases very rapidly with temperature to reach a value of about 0.10–0.11R at the triple point $T_0(p_m)$. To illustrate this rapid increase, it will suffice to consider the ratio

$$S_{C,m}(1.68°\mathrm{K})/S_{C,m}(1.76°)\simeq 0.5.$$

It should be noted that the ratio of these cubic solid entropies resulting from the Keesom liquid entropies is also about 0.5 at these two temperatures. The approximate entropy values at $T_0(p_m)$, taken to be the temperature of the upper triple point, are now, in the hexagonal solid, as a consequence of the uncertainties in $\Delta S_{\mathrm{tr}}(T_0)$ given above, such that

$$0.07R\gtrsim S_{H,m}(T_0)\gtrsim 0.044R. \quad (30)$$

Beyond $T_0(p_m)$, as was the case with the solid entropies $S_{H,m}$ obtained with the Keesom entropies, these smaller solid entropies resulting with the Lounasmaa liquid entropies, have a decreasing trend which is now more marked because of their lower values. These smaller $S_{H,m}$ entropies are now entirely within the range of simple phonon entropies, in terms of the approximate characteristic temperatures θ_H given in Table IV. It should be noted here that the possibly larger value of 0.07R of $S_{H,m}(T_0)$ could not be easily reconciled with continuum phonon excitations alone. At the present time, the $S_H(T)$ values along the cubic-hexagonal phase transition line are not available.

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[12] W. H. Keesom and Miss A. P. Keesom, Physica, **3**, 105 (1936).

[13] W. H. Keesom, *Helium* (North-Holland Publishing Company, Amsterdam, 1942), pp. 226–247.

[14] O. V. Lounasmaa, Cryogenics **1**, 212 (1961).

[15] C. A. Swenson, Phys. Rev. **79**, 626 (1950); **86**, 870 (1952); **89**, 538 (1953).

On the basis of the preceding two sets of entropy values of solid He^4 along the melting line, one is in presence of two possible situations (A) and (B). In case (A), resulting from the larger Keesom liquid entropies, the solid entropy curve $S_{s,m}(T)$ is similar to that of the liquid. That is $S_{s,m}(T)$, or $S_{C,m}(T)$, at $T>1.44$°K, increases very rapidly through $T_0(p_m)$, and after its discontinuous decrease there, continues to increase as $S_{H,m}(T)$, reaching a plateau-like region. If we denote by τ a finite though small temperature interval beyond $T_0(p_m)$, one has, in the liquid phase,

$$\lim_{T\gtrsim T_0+\tau} S_{L,m}(T)=S_{0,L}(T)+s_{L,m}(T);\quad s_{L,m}<S_0,L, \qquad (31)$$

where $S_{0,L}$ is the entropy at the start of the plateau-like region. This entropy might possibly be connected with the reaching of complete disorder within the liquid, in the sense that the characteristic distribution of its atoms over the group of excited energy levels and the group of low-lying levels or the ground level of vanishing excitation, has ceased to exist. In terms of the two-fluid model, the peculiar static thermal properties of liquid He^{4}II might possibly originate with the circumstance that the major part of the thermal excitations consists in the lifting of atoms from the group $N_{L,0}(T,p)$ into the group of excited atoms $N_{L,n}(T,p)$, with the additional thermal excitations of the latter group being of the order of a correction, or very small in comparison with the former. With,

$$N_{L,n}(T,p)+N_{L,0}(T,p)=\text{const}, \qquad (32)$$

one has

$$0=[\partial(N_{L,n}+N_{L,0})/\partial T]_p\delta T+[\partial(N_{L,n}+N_{L,0})/\partial p]_T\delta p,$$

or, for arbitrary δT and δp,

$$\begin{aligned}[][\partial N_{L,n}(T,p)/\partial T]_p&=-[\partial N_{L,0}(T,p)/\partial T]_p,\\ [\partial N_{L,n}(T,p)/\partial p]_T&=-[\partial N_{L,0}(T,p)/\partial p]_T.\end{aligned} \qquad (33)$$

Since on thermal excitation, that is on temperature increase, $N_{L,n}$ increases, one must have

$$[\partial N_{L,n}(T,p)/\partial T]_p>0. \qquad (34)$$

If, in some approximation

$$S_L(T,p)\simeq\sigma_{\mathrm{Pl}}N_{L,n}(T,p), \qquad (35)$$

the entropy of the liquid is a measure of the number of normal atoms, an assumption which seems to be fairly well supported by the data on the entropy, as recognized by Tisza,[11] then (34) is simply a statement equivalent to the requirement of the positive definite character of the constant pressure heat capacity. The anomalous or negative expansion coefficient imposes the positive sign on the partial derivative

$$[\partial N_{L,n}(T,p)/\partial p]_T>0 \qquad (36)$$

through that of the entropy. The latter inequality ceases to be valid, in terms of the approximate entropy representation (35), at $T<T_\alpha(p)_{\mathrm{II}}$.

Actually, the proportionality constant σ_{Pl} in (35) depends to some extent on T and p, but this dependence is very mild indeed in comparison with the dependence of $N_{L,n}(T,p)$ on these variables of state. The entropy expenditure per normal atom σ_{Pl} may be written as

$$\sigma_{\mathrm{Pl}}=(S_{0,L}/N), \qquad (35a)$$

so that $S_{0,L}$, the entropy at the start of the plateau-like region, is achieved on exhausting the low-lying levels of the system by lifting all the atoms into the group of normal atoms. In Eq. (31), the additional small entropy term $s(T,p)$ may be associated with the more routine type of thermal excitations, of possibly translational or of similar origin. Inasmuch as beyond the temperature $(T_0+\tau)$, assumed to define the start of the entropy branch of strongly reduced temperature rate of increase, the plateau-like branch, σ_{Pl} becomes there essentially constant, the decreased temperature and pressure dependence of the liquid entropy reduces to that of $s(T,p)$.

The preceding tentative modification of the approximate two-fluid picture of liquid He^{4}II accounts for the extension of the anomalous static thermal properties beyond the locus $T_0(p)$ of the temperatures of the heat capacity anomaly, although it goes beyond the locus $T_\alpha(p)_{\mathrm{I}}$. The return to normalcy there could originate with the $s(T,p)$ term, which could be included in (35), and whose negative pressure derivative would compensate the pressure derivative of $N_{L,n}(T,p)$ at $T\gtrless T_\alpha(p)_{\mathrm{I}}$.

It seems of interest to further digress here on the behavior of the entropy of the liquid. The empirical results[13,14] seem to indicate, as is necessary, that

$$[\partial s(T,p)/\partial p]_T<0, \qquad (37)$$

and as would be expected from this normal component of the entropy. The preceding relation manifests itself through the loss of sharpness of the entropy plateau formation with decreasing pressure. As $s(T,p)$ increases with decreasing pressure, it becomes a larger fraction of $S_{0,L}(T,p)$ in the representation (31) extended to a state (T,p) of the liquid, and the plateau-like behavior so sharp along the melting line, disappears essentially at the liquid-vapor phase separation line, to become recognizable mostly by a sharp bend of the entropy curve. This tendency to form a plateau-like region is connected with the change in sign of the curvature of the entropy $S_L(T,p)$ on the two sides of the temperature of the heat capacity anomaly of the liquid. Or,

$$d^2S_L/dT^2>0,\ T<T_0;\quad d^2S_L/dT^2<0,\ T>T_0, \qquad (38)$$

since the inequality

$$dS_L/dT=C_L/T>0, \qquad (39)$$

requiring the liquid heat capacity to be positive even along the melting line, is probably always satisfied here. The entropy $S_L(T,p)$ is thus concave upward at $T<T_0$,

and concave downward at $T > T_0$, in the (S_L, T) representation. With

$$dC_L/dT = (C_L/T) + T(d^2S_L/dT^2), \tag{40}$$

it is seen that if the heat capacity had a cusp at T_0, then, omitting the subscript L,

$$\begin{aligned} dC_-/dT &= (C_-/T) + T(d^2S_-/dT^2) > 0, \quad T \leq T_0 \\ dC_+/dT &= C_+/T + T(d^2S_+/dT^2) < 0, \quad T \leq T_0 \end{aligned} \tag{41}$$

and, the discontinuity of its temperature derivative, is

$$\begin{aligned} \Delta(dC/dT)_{T_0} &= (dC_+/dT)_{T_0} - (dC_-/dT)_{T_0} \\ &= T_0[(d^2S_+/dT^2)_{T_0} - (d^2S_-/dT^2)_{T_0}] \\ &< 0. \end{aligned} \tag{42}$$

The heat capacity cusp requires

$$(d^2S_+/dT^2)_{T_0} < -(C_+/T_0^2), \tag{43}$$

or the second temperature derivative jumps discontinuously from the positive value of $(d^2S_-/dT^2)_{T_0}$ to the negative value of $(d^2S_+/dT^2)_{T_0}$. The second of the relations (42) is equivalent to

$$\begin{aligned} \Delta(d^2S/dT^2)_{T_0} &= (d^2S_+/dT^2) - (d^2S_-/dT^2) \\ &< 0, \end{aligned} \tag{42a}$$

with this negative discontinuity being finite. It is seen at once that this discontinuity tends toward $(-\infty)$, if the heat capacity tended toward infinity at T_0, on either side or both sides of it.

Beyond T_0, the second derivative will have to increase rapidly to insure the observed tendency of the entropy to become flat, with the formation first of a minimum of C_+, beyond which

$$dC_+/dT = (C_+/T) - T|d^2S_+/dT^2| > 0, \quad T \geq T_0 + \tau; \tag{44}$$

the heat capacity increases, even though the entropy is concave downward with a small enough numerical value of d^2S_+/dT^2.

The plateau-like region of the entropy would thus start at $T > T_0$, where d^2S_+/dT^2 is much larger algebraically than at T_0, or much smaller numerically. The entropy $S_L(T,p)$ would thus be continuous with its first temperature derivative at T_0, with a break of the latter at this temperature, on the assumption of the existence of a cusp in the heat capacity. In addition, $S_L(T,p)$ would exhibit a step-function-like behavior, as a consequence of its very rapid temperature increase on both sides of T_0. It is the start of the upper step which we have attempted to connect with the component entropy $S_{0,L}$ introduced through Eq. (31), with $(T_0 + \tau)$ being the starting temperature of the upper step. At the present time, a precise determination of τ and $S_{0,L}$ would be a rather difficult task, although both of them could be bracketed. The preceding discussion seems to describe qualitatively the liquid He^4 entropy data[13,14] over a fairly wide temperature range which includes the temperatures of the heat capacity anomaly $T_0(p)$.

In terms of the tentative interpretation here advanced, the physical meaning of the shape of the entropy curves would require that the temperatures $T_0(p)$ do not correspond to the ending there of the peculiar disordering process responsible for the anomalies of the derivative properties, such as heat capacity and expansion coefficient or the associated entropy increase on isothermal compression. The temperature which would represent the end of this process appears to be beyond $T_0(p)$, at the starting temperature of the upper step branch of the entropy curves. This raises, of course, the problem of the connection between the temperature at which the static equilibrium properties become anomalous or $T_\alpha(p)_\mathrm{I}$, the knee-point temperatures $[T_0(p) + \tau]$ of the entropy curves, and $T_0(p)$, that of the heat-capacity anomaly, which was claimed to coincide with the start of the anomalous energy and momentum transport phenomena. The discussion of this problem, however, is outside the subject matter of the present paper.

With the Lounasmaa liquid entropies along the phase separation line, the rapid temperature increase of the solid entropy in the cubic phase is still preserved, this was referred to, above, as case (B). But this behavior stops at the upper triple point, yielding a one-sided anomaly limited to temperatures $T \leq T_0(p_m)$. As emphasized already, the entropy values of this cubic solid He^4 at the approaches of $T_0(p_m)$ appear to be too large to be accommodated by Debye phonon excitations alone. It should also be noted here, that this one-sided anomaly of the entropy of the cubic solid leaves out of account the negative isobaric expansion coefficient of the hexagonal solid along the melting line at temperatures below that of the lower triple point at 1.44°K, approximately, as well as the possible negative expansion coefficient of this solid at pressures above but close to the melting pressure.

The analysis of the entropy anomalies of both cases (A) and (B) would be incomplete without studying the heat capacities they give rise to. The very strong temperature increase of the solid entropy along the melting line leads, in both cases, to a similar increase in the heat capacity at the approach of $T_0(p_m)$. In case (A), one finds that the molar heat capacity of the cubic solid, $C_{C,m}(T)$ reaches values of several R in the vicinity of $T_0(p_m)$. In case (B), a value of about $1.5R$ is reached somewhat below $T_0(p_m)$. These enormous heat capacity values result directly from the two sets of liquid entropy data, $S_{L,m}(T)$, and the entropy change data $\Delta S_m(T)$, using various numerical procedures, the analytical form of these entropies being unknown. While the various types of approximations yield different numerical values of these heat capacities, they never fail to lead to very large values, of the order of one or several R, in the neighborhood of $T_0(p_m)$. On the high-temperature side of $T_0(p_m)$, actually at $T \geq 1.80$°K, one observes the rapid fall of the heat capacities originating with the case (A) entropies. In this case, as we saw above, the anomalous behavior of the solid should extend to both the cubic and hexagonal solids at $T \leq T_0(p_m)$. Actually, satisfactory solid heat capacities could not be obtained from the entropies because of lack of precision in their temperature variations at $T > T_0(p_m)$, as mentioned already. The large decrease of the heat capacity of the hexagonal solid can, however, be demonstrated by simply using the liquid entropies beyond $T_0(p_m)$. The liquid heat capacities are, indeed, upper limits of the hexagonal solid heat capacities, according to the Keesom liquid entropies[12] and the entropy change data of Grilly and Mills.[5] With,

$$\begin{aligned} C_{H,m} &= T(dS_{H,m}/dT) \\ &= T[(dS_{L,m}/dT) - (d\Delta S_m/dT)], \end{aligned} \tag{45}$$

and, the empirical result,[5] expressed by

$$(d\Delta S_m/dT) > 0, \quad T > T_0(p_m)$$

it is seen that beyond $T_0(p_m)$,

$$T(dS_{L,m}/dT) = C_{L,m}(T) > C_{H,m}(T). \tag{46}$$

The heat capacity anomaly would be restricted in case (B), to $T \leq T_0(p_m)$, in line with the one-sided entropy anomaly of the cubic solid. It should be noted though, that in the absence of the entropy values of the hexagonal solid at $T < T_0(p_m)$, the one-sided character of the thermal anomaly of the solid limited strictly to the cubic phase has not been demonstrated.

We have studied, in some detail, the liquid heat capacities based on the Keesom entropies in connection with the more elementary heat capacities, of constant pressure, $C_{p,m}^{(L)}$, and constant volume $C_{V,m}^{(L)}$, along the melting line. It may not be entirely redundant to give here the rigorous thermodynamic formulas, which were derived very briefly some time ago in connection with the liquid-vapor equilibrium,[16] and which connect now the elementary heat capacities with those along the melting line $C_{L,m}$. One has here

$$\begin{aligned} C_{p,m}^{(L)} &= C_{L,m}[1 - P(1+Q)]^{-1}, \\ C_{V,m}^{(L)} &= C_{L,m}[1 + P(1+Q^{-1})]^{-1}, \end{aligned} \tag{47}$$

where

$$\begin{aligned} P &= T(dV_{L,m}/dT)(dp_m/dT)/C_{L,m}, \\ Q &= V_{L,m}\kappa_L(dp_m/dT)/(dV_{L,m}/dT). \end{aligned} \tag{47a}$$

All properties on the right-hand sides of (47) refer to properties along the melting line, $V_{L,m}$ and $C_{L,m}$ being molar volumes and molar heat capacities, κ_L stands for the adiabatic compressibility of the liquid along the melting line. The preceding formulas also give, of course, the elementary heat capacities $C_{p,m}^{(s)}$, $C_{V,m}^{(s)}$ of the solid along the melting line, provided that $C_{s,m}$ and $V_{s,m}$ be used with the solid adiabatic compressibility κ, on the right-hand sides of (47) and (47a).

The calculations indicated that while

$$(C_{p,m}^{(L)}/C_{V,m}^{(L)})$$

or $\gamma_{L,m}$ increased slowly along the melting line, its value in the vicinity of $T_0(p_m)$ reached values of about 1.15–1.20, approximately. A similar calculation performed for the cubic solid, in case (A), and within the limitations of the assumed elastically isotropic cubic solid He^4 adiabatic compressibilities of Table III, yielded, approximately, values of $(C_{p,m}^{(s)}/C_{V,m}^{(s)})$ or $\gamma_{s,m}$ which were only slightly larger than unity close to $T_0(p_m)$. This then appeared to justify, to some degree, the use of the approximate adiabatic compressibilities of the solid phases instead of the isothermal ones in the evaluation of their approximate isobaric expansion coefficients in Sec. 4 above. The limitations inherent in the assumption of elastic isotropy of the cubic solid has been emphasized there.

Returning to the solid heat capacities arrived at in the present work, it is of importance to note here that solid He^4 heat capacity measurements by Keesom and Miss Keesom,[12] at pressures $p \gtrsim 42$ atmospheres, or fairly well above melting pressure, did not disclose any heat capacity anomaly over the explored temperature range, $1.25 \leqslant T \leqslant 2.0$°K, beside the observation that the temperature dependence of these measured heat capacities was greater than the T^3 dependence.

Another series of solid He^4 constant volume heat capacity measurements at pressures $p \gtrsim 31$ atmospheres,[17] between about 0.5 and 1.5°K exhibited normal volume dependence over the explored temperature and volume ranges. These results tend to limit the anomalous entropy and heat capacity regions discussed in the present work to a fairly narrow pressure interval above melting pressure. The limited temperature range of the largest volume heat capacity measurements should be noted here. The temperature dependence of these heat capacities was reduced to a $(T/\theta)^3$ dependence, by assigning to the characteristic temperature of the solid a fairly strong temperature variation with a peculiar maximum at about 0.7–0.9°K.

We have often referred, in the present work, to the limiting Debye continuum type of phonon system. Isobaric expansion coefficients, entropies and heat capacities resulting from various indirect data on liquid and solid He^4 have been compared with corresponding properties originating with the simplest continuum type of phonon excitations. This seems to be justified at the present stage of the scarcity of data on solid He^4, in the pressure and temperature intervals where anomalies might occur. The complete breakdown of the limiting simplest model of phonon excitations clearly emerged here at the approaches of $T_0(p_m)$. The phonon system associated with the discrete lattice motions,[18] including

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[16] L. Goldstein, Phys. Rev. **112**, 1465 (1958).

[17] J. Wilks, *Proceedings of the International Conference on Low-Temperature Physics* (Oxford University Press, New York, 1951), p. 33; F. J. Webb, K. R. Wilkinson, and J. Wilks, Proc. Roy. Soc. (London), **A214**, 546 (1952).

[18] For the most recent reviews of the status of the theory, compare M. Blackman, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII/1, pp. 325–382, and G. Leibfried, in the same volume, pp. 104–324.

the low-frequency, or acoustical, and high-frequency, or optical branches of characteristic vibrations with their respective groups of polarization directions is, necessarily, the only realistic method of description of thermal excitations in crystalline solids, like solid He^4. The practical usefulness of this method of approach necessitates various experimental data. These may comprise the empirical determination of the dispersion laws of the characteristic vibration spectrum of the solid $\nu_\alpha(\mathbf{k})$, $\mathbf{k}$ being the propagation vector of the vibration of frequency ν, along a direction specified by α. The derivation of the associated spectral distribution function $\rho(\nu)$ of the characteristic frequencies, which defines through the Planck thermal distribution of the vibrations the total excitation energy and the corresponding constant volume heat capacity, raises in turn a problem whose solution is again approximate, of semiempirical character, at least at a certain stage of the corresponding knowledge of the empirical $\nu(\mathbf{k})$ function. The approximate heat capacities resulting from the theory lead to temperature variations different from the limiting continuum model T^3 law. These originate with the temperature dependence of the characteristic temperature which in some cases become quite strong.[18] If confirmed, the peculiarities in $\nu(\mathbf{k})$ and $\rho(\nu)$ must be ultimately responsible for the entropy and heat capacity anomalies of solid He^4 at, or near, the melting line and near $T_0(p_m)$. The problem of the negative isobaric expansion coefficients of the solid, both hexagonal and cubic, at $T \lesssim 1.50$–1.55°K is probably another aspect of the apparent thermal anomalies of the solid He^4 phases.

We would like to conclude by stating that while the above-mentioned solid He^4 heat capacity measurements favor a fairly normal behavior of this solid over the explored temperature and pressure ranges, additional experimental work on heat capacities and isobaric expansion coefficients would be of great interest over a region of the phase diagram around the melting pressure line. These should clarify the presence or absence of the various anomalies which present data, however indirect, seem to favor. In view of the possible connection between heat capacities and heat conductivity coefficients, experiments on the latter, in the relevant pressure and temperature intervals, would be also desirable.

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Decay of an Electric Current in a Superconductor*

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A theory of the decay of an electric current in a superconductor is presented. The calculations have been done using a model within the BCS theory of superconductivity, ignoring magnetic effects. The decay of current, from a specially chosen initial state, is found both for low temperatures and for temperatures near the critical temperature. The persistence of currents remains unexplained. The related problem of thermal conductivity is re-examined in an Appendix.

1. INTRODUCTION

The Bardeen-Cooper-Schrieffer[1] (BCS) theory of superconductivity has been quite successful in explaining the thermodynamic features and the Meissner Effect. There has, however, been no quantitative verification of the transport properties of superconductors. For example, Bardeen-Rickayzen-Tewordt[2] (BRT) applied the theory to the case of thermal conductivity of superconductors but their results were in disagreement with experiment. The basic question of electric conductivity has found no satisfactory answer.

The main purpose of this paper is a study of how an electric current decays in a BCS superconductor. The calculation is based on a simple model in which the interaction between quasi-particles can be neglected without error.

Bogoliubov[3] has observed that a state of the electron gas which results from the BCS ground state by a small displacement in momentum space, is stable, or

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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[2] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).

[3] N. N. Bogoliubov, Nuovo cimento **7**, 794 (1958).