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Lambda Transformation of Liquid Helium Four

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It will be shown that the extrapolation of empirical logarithmic expressions of a group of thermal properties of liquid He⁴ at the approaches of the lambda transformation, implying their singular behavior, is without physical justification. These properties do not even start to become large until one invokes temperature separations from the lambda temperatures, the argument of the logarithmic expressions, which are very many orders of magnitude smaller than the root-mean-square temperature fluctuations of the liquid-He⁴ samples investigated. Consideration of temperature intervals smaller than the root-mean-square temperature fluctuations is excluded by statistical thermodynamics. On analyzing the lambda transformation at melting, first an exact thermodynamic relation will be proved through the geometrical properties of a class of isochores in the pressure-temperature diagram. Provided that the thermodynamic characteristics of the lambda transformation remain invariant all along the transformation locus, the thermodynamic relation proved at melting has the following corollaries: If the transformation volume line is not parabolic in temperature at the approaches of its end point at melting, singularities of a group of interrelated thermal properties must exist at the lambda transition. If this approach is parabolic, the existence of singularities neither is necessary nor can it be ruled out. In the latter case, new physical approaches would be needed for an unambiguous determination of the existence or absence of singularities of thermal properties at the lambda transformation.

1. INTRODUCTION

IN the course of recent work^{1,2} on solid He⁴ in equilibrium with the liquid phase, the anomalous lambda transformation of the latter was also discussed by us. The attempts at further clarifying the thermodynamic aspects of the liquid He⁴ II-He⁴ I transition were motivated, in connection with the problem of the liquid-solid equilibrium, by the fact that the transformation extends up to, and including, melting conditions. The solidification or melting process thus raises problems which refer to the equilibrium of both the normal and the anomalous liquid with the solid along the melting line. Similar problems of the dense phases in equilibrium with each other have been studied^{3,4} in connection with the solidification process of liquid He³, since the latter is thermally anomalous also over a wide temperature interval along the melting line. Prior to our work on the liquid-solid equilibrium of the two He isotopes, we had the opportunity⁵ of discussing the

unsatisfactory features of the variation of the liquid-He⁴ volume or density at saturation, around the He⁴ II-He⁴ I transformation temperature $T_{0,\text{sat}}$. It was thus realized that some type of volume anomaly is likely to occur somewhat beyond, if close to, the transformation temperature. The study of the temperature variation of the latent heat of vaporization⁵ similarly led to predict the occurrence of a sharp minimum of this property beyond $T_{0,\text{sat}}$, though close to it. This result was of strictly thermodynamic character and was derived from the temperature variation of the saturated liquid heat capacity. The anomaly of the latter was demonstrated with the highest temperature resolution so far, by Fairbank *et al.*,^{6,7} whereby it was implied that this property may be singular at $T_{0,\text{sat}}$, there being possibly an infinitely large heat capacity C_{sat} on extrapolation of a logarithmic fit to the heat capacity data over the range $10^{-2} \geq |T - T_{0,\text{sat}}| \geq 2 \cdot 10^{-6}$ °K. Prior to the saturated liquid heat capacity work,

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

² L. Goldstein, Phys. Rev. **128**, 1520 (1962).

³ L. Goldstein, Ann. Phys. (N. Y.) **16**, 205 (1961).

⁴ L. Goldstein and R. L. Mills, Phys. Rev. **128**, 2479 (1962).

⁵ L. Goldstein, Ann. Phys. (N. Y.) **2**, 177 (1957).

⁶ W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, in *Proceedings of the International Conference on Low-Temperature Physical Chemistry*, edited by J. E. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 50.

⁷ C. F. Kellers, Ph.D. dissertation, Duke University, 1960 (University Microfilms, Inc., Ann Arbor, Michigan, 1962) (unpublished).

the saturated liquid expansion coefficients $\alpha_{\text{sat}}(T)$ or $[V_{\text{sat}}^{-1}(dV_{\text{sat}}/dT)]$ were fitted⁸ with a function linear in $\ln(T_{0,\text{sat}}-T)$, at $10^{-3} \leq (T_{0,\text{sat}}-T) \leq 0.1^\circ\text{K}$. Additional work on the saturated liquid volumes, either indirect, as through refractive index⁹ and dielectric constant measurements,¹⁰ or direct volume measurements¹¹ on both sides of the transformation point, have confirmed the possibility of a logarithmic variation of the saturated liquid expansion coefficients, α_{sat} , over the range of $10^{-4} \leq |T - T_{0,\text{sat}}| \leq (5-6) \times 10^{-2}^\circ\text{K}$.

The nature of the conjectured volume anomaly⁵ on the saturated and compressed liquid was established experimentally as a minimum of the saturated liquid volume¹¹ or a minimum of the isochores¹² or of the isobars¹³ of the compressed liquid. The predicted shape⁵ of the latent heat of vaporization seems to be fully compatible with the behavior of the saturated liquid near the transformation temperature.

The object of the present work, within the formalism of thermodynamics, is an attempt at a qualitative approach to the problem of the existence or non-existence of the singularities implied by the data. It will thus be shown that the implication of the existence of a singularity of some property through the logarithmic term of an expression which describes the data, to some limited approximation, loses its physical basis as soon as the temperature fluctuations of the system imposed by statistical thermodynamics are taken into account. The extrapolation of the approximate logarithmic representation of the data beyond the experimental range thus appears physically unjustified, on the acceptance of the assumption of the validity of the analytical representation beyond its established range notwithstanding. The attempt at ascribing infinitely large values to some thermal properties at the He⁴ II-He⁴ I transition line, even though their apparent approach toward such values is extremely slow, and which also conflicts with statistical thermodynamics, meets with additional complications. Namely, the acceptance of the extrapolated singularities of certain thermal properties along the transformation line imposes very large values to other properties. These also seem to tend, apparently only very slowly, even logarithmically over finite ranges of the argument of the latter function, toward their finite, if very large, limits at the transition line.¹² Again, temperature fluctuations render physically meaningless the very extrapolation of the empirical fits so as to reach even a fraction of the implied finite but very large limits of

these nonsingular properties. Inasmuch as these regular properties escape observation of even fractional values of their limits at the transition line, the problem arises if the indicated extrapolations applied to the fits of the "singular" properties overshoots the correct, possibly very large, limits of these properties, as they would do it with the regular properties which are effectively finite at the transition. These extrapolations are extended into the range of the variables $(T_0 - T)$ or $(T - T_0)$, which range falls entirely within the range of the temperature fluctuations.

A possible experimental approach which may shed additional light on these problems will be seen to emerge from the present work. Provided that the thermodynamic characteristics of the liquid He⁴ II-He⁴ I transformation remain invariant along the transformation line, the melting condition included, a limiting property of this line derived geometrically, at melting, when combined with the experimental approach to be described, may yield qualitative justification for the existence or nonexistence of singular properties at the transformation line.

2. ISOBARS AND ISOCHOES OF LIQUID He⁴ IN ITS TRANSFORMATION REGION

The transformation line in the pressure-temperature, (p, T) , volume-temperature, (V, T) , and pressure-volume, (p, V) , thermodynamic diagrams are characterized by the following empirical inequalities:

$$-\infty < (dp_0(T)/dT) < 0; \quad \infty > (dV_0(T)/dT) \geq 0; \quad (1)$$

$$-\infty < dp_0(V)/dV < 0,$$

where the subscript "0" refers to the state variable at the transformation line, and the derivatives are total derivatives along this line. At the present time, there does not seem to be any experimental evidence for the occurrence of singular values of the above derivatives at any point of the transformation arcs, limited by the states $(p_{0,\text{sat}}, V_{0,\text{sat}}, T_{0,\text{sat}})$ and $(p_{0,M}, V_{0,M}, T_{0,M})$ at the saturation (subscript sat), and melting lines (subscript M). It must be noted here, however, that with

$$(d^2p_0/dT^2) < 0, \quad (d^2V_0/dT^2) > 0, \quad (2)$$

the decreasing negative derivatives (dp_0/dT) , with increasing temperatures, the largest negative value of this quantity at $p_{0,\text{sat}}$, or at low pressures near $p_{0,\text{sat}}$, has reached values obtained through the observation of flow processes¹⁴ which are numerically larger than those obtained through static equilibrium thermodynamic measurements.¹⁵ Inasmuch as it is unlikely that the single-valued thermodynamic functions relative to the transformation arcs, $p_0(T)$, $V_0(T)$, $V_0(p)$, have multivalued derivatives at any one of their points,

⁸ K. R. Atkins and M. H. Edwards, *Phys. Rev.* **97**, 1429 (1955).

⁹ M. H. Edwards, *Can. J. Phys.* **36**, 884 (1958).

¹⁰ C. E. Chase, E. Maxwell, and E. Millett, *Physica* **27**, 1129 (1961).

¹¹ E. C. Kerr and R. D. Taylor, *Ann. Phys. (N. Y.)* **26**, 292 (1964).

¹² O. V. Lounasmaa and L. Kaunisto, *Ann. Acad. Sci. Fennicae A VI*, No. 59 (1960).

¹³ E. R. Grilly and R. L. Mills, *Ann. Phys. (N. Y.)* **18**, 250 (1962).

¹⁴ W. E. Keller and E. F. Hammel, Jr., *Ann. Phys. (N. Y.)* **10**, 202 (1960).

¹⁵ W. H. Keesom, *Helium* (North-Holland Publishing Company, Amsterdam, 1942), pp. 186-254.

measurements yielding data converging toward a unique limit appear here to be highly desirable. Empirically,¹⁵ the transformation arcs $p_0(T)$, $V_0(T)$, and $p_0(V)$ appear to be of monotonic variation.¹⁶

We have to compare now the temperature variations of isochores $p(T, V)$ at the transition line $p_0(T)$ with that of the latter at their points of intersection, or in their neighborhood. According to thermodynamics,

$$\left(\frac{\partial p(T, V)}{\partial T}\right)_{V=V_0} = \left[\frac{dp_0(T)}{dT}\right] + \left[\frac{1}{V_0(T)}\chi_T(T_0, p_0)\right](dV_0/dT), \quad (3)$$

where $\chi_T(T_0, p_0)$, the isothermal compressibility at (p_0, V_0, T_0) , the state under consideration on the transition line, is positive as is the second term on the right-hand side, by the inequalities (1). Hence,

$$\left[\frac{\partial p(T, V)}{\partial T}\right]_{V=V_0} \geq (dp_0/dT), \quad (4)$$

or, in order for the anomalous isochore $p(T, V)$ of liquid He⁴ II, of negative temperature derivative, to cross the transition line, the inequality sign must prevail in (4), as shown previously.¹ If the temperature derivatives of the isochores are discontinuous at the transition line, then, necessarily, χ_T is also discontinuous, and (3) yields, at once, this discontinuity as

$$\Delta(\partial p/\partial T)_{V=V_0} = (\partial p_+/ \partial T)_{V_0} - (\partial p_- / \partial T)_{V_0} = [V_0(T)]^{-1}(dV_0/dT)\Delta(1/\chi_T), \quad (5)$$

one of the Ehrenfest-type relations.

If $(\partial p/\partial T)_V$ is continuous across the transition line, the existence of the locus $T_{\alpha, I}$ of the minimas of the isochores and isobars in the He⁴ I region imposes a change in the curvature of these characteristic lines of the state diagrams at $T < T_{\alpha, I}$. The isochores $p_-(T, V)$ being concave downward in the (p, T) plane, in the He⁴ II region, have to become concave upward in the He⁴ I region and the inflection points, if existed, are expected to form the locus of the transition points $p_0(T)$ or $V_0(T)$ for the isobars $V(T, p)$ in the (V, T) diagram. The isochores may, however, reach the transition line with finite second temperature derivatives, negative and positive, respectively, on the low- and high-temperature sides of the transition line. The functions $[\partial p(T, V)/\partial T]_V$, $(\partial V/\partial T)_p$, $(\partial p/\partial V)_T$, have then angular points on the transition lines, $p_0(T)$, $V_0(T)$, $p_0(V)$. This results in finite discontinuities of $(\partial^2 p/\partial T^2)_V$ at $p_0(T)$. Or, rewriting (3) as

$$dp_0/dT = (\partial p/\partial T)_{V=V_0} + (\partial p/\partial V)_{T=T_0}(dV_0/dT), \quad (6)$$

one obtains on the two sides of $p_0(T)$,

$$\begin{aligned} d^2 p_0/dT^2 &= (\partial^2 p_{\pm}/\partial T^2)_{V=V_0} + 2(\partial^2 p_{\pm}/\partial V\partial T)_{V_0, T_0}(dV_0/dT) \\ &\quad + (\partial p_{\pm}/\partial V)_{T=T_0}(d^2 V_0/dT^2) \\ &\quad + (\partial^2 p_{\pm}/\partial V^2)(dV_0/dT)^2, \quad (7) \end{aligned}$$

¹⁶ In Ref. 12, an approximate cubic expression in $(T_0, \text{sat} - T)$ is given for the transition arc $p_0(T)$ of the liquid density. This cubic has, however, an inflection point at about 1.87°K. Presum-

ably, the authors would not have considered this cubic satisfactory had they noticed its contortion.

$$\begin{aligned} \Delta(\partial^2 p/\partial T^2)_{V=V_0} &= - (dV_0/dT)[(dV_0/dT)\Delta(\partial^2 p/\partial V^2)_{T=T_0} \\ &\quad + 2\Delta(\partial^2 p/\partial V\partial T)_{V_0, T_0}]. \quad (8) \end{aligned}$$

According to the remarks made above, if it existed, the preceding discontinuity should be positive. The discontinuities of the other second partial derivatives are seen easily to be given by

$$\Delta(\partial^2 V/\partial T^2)_{p=p_0} = - (dp_0/dT)[(dp_0/dT)\Delta(\partial^2 V/\partial p^2)_{T=T_0} + 2\Delta(\partial^2 V/\partial p\partial T)_{p_0, T_0}], \quad (9)$$

and

$$\Delta(\partial^2 V/\partial p^2)_{T=T_0} = - (dT_0/dp)[\Delta(\partial^2 V/\partial T^2)_{p=p_0}(dT_0/dp) + 2\Delta(\partial^2 V/\partial T\partial p)_{T_0, p_0}], \quad (10)$$

where $T_0(p)$ is the inverse function of $p_0(T)$.

The situation may also arise with the equality sign in (4), or

$$dp_0/dT = (\partial p_- / \partial T)_{V_0} = (\partial p_+ / \partial T)_{V_0}. \quad (11)$$

The second derivatives of the isochores are thus continuous at the transition point, the second derivatives vanishing at the transition line, and $p_0(T)$ would be the locus of inflection points of the isochores. Inasmuch as dV_0/dT is finite at all points of $V_0(T)$, relations (1), the situation described by (11) requires by (3) that

$$\lim_{T \rightarrow T_0, p \rightarrow p_0} \chi_T(T, p) \rightarrow \infty, \quad (12)$$

or the isothermal compressibility must become singular at the transition line. Since, $(\partial p/\partial T)_V$ is finite by (1) or (11), the singularity of the isothermal compressibility is equivalent to that of the isobaric volume expansion coefficient $\alpha_p(T, p)$, or to that of the constant pressure-heat capacity as discussed further below. The condition (11) imposes a sharp minimum on the derivative $(\partial p/\partial T)_V$ at the transition line.

We turn now to the analysis of the experimental evidence on the temperature derivatives of the isochores and isobars in the transformation region.

Direct measurements of $(\partial p/\partial T)_V$ have been performed by Lounasmaa on both sides of the transition line, down to $|T - T_0(p)| \sim 10^{-3}$ °K in one set of experiments,¹² and to within 2×10^{-5} °K to $T_0(p)$ in a second independent experiment¹⁷ where only one single isochore was explored. Even though $(\partial p(T, V)/\partial T)_V$ is regular everywhere, it appeared that these partial derivatives could be approximately represented at the smallest values of $|T - T_0(p)|$, or between 10^{-1} and 2×10^{-3} (°K), and between about 10^{-2} and 2×10^{-5} (°K), in the second experiment,¹⁷ by an expression of the

¹⁷ O. V. Lounasmaa, Phys. Rev. **130**, 847 (1963).

type

$$(\partial p_{\pm}/\partial T)_V = A_{\pm} + B_{\pm} \ln |T - T_0(p)|, \quad (P)$$

where A_{\pm} and B_{\pm} are constants, A_{-} being negative, whose numerical values are between 2 and 8, the pressure being expressed in units of atmospheres. Clearly, these approximate expressions must break down at values of $|T - T_0(p)|$ below those explored experimentally, since $(\partial p_{\pm}/\partial T)_V$ is finite at $T_0(p)$.

An interesting feature of the $(\partial p/\partial T)_V$ measurements¹² at various volumes and down to $|T - T_0(p)| \geq 10^{-3}$ (°K) consists in that these derivatives, at the smallest values of $|T - T_0(p)|$ increased regularly as the volume of the explored isochore increased toward saturation volume. This variation of $(\partial p/\partial T)_V$, at $|T - T_0(p)| \geq 2 \times 10^{-3}$ °K, is opposite to the variation of the derivative (dp_0/dT) of the transition line itself. The latter is the smallest at saturation and increases with increasing pressure or decreasing volume along the transition. The recently observed trend of variation of $(\partial p/\partial T)_V$ in the neighborhood of the transition line¹² is fully in line with the original equation of state studies of Keesom¹⁵ on isochores. The more recent work of Lounasmaa,¹⁷ of increased accuracy at a molar volume close to that of one of the isochores in the earlier work,¹² and extending down to 2×10^{-5} °K in $|T - T_0(p)|$, appears to be in good agreement with the earlier work extending to $T_0(p) - T \simeq 2 \times 10^{-3}$ °K. The largest numerical values of $(\partial p/\partial T)_V$ at the smallest values of $|T - T_0(p)|$ are always three to ten times smaller than the values of dp_0/dT at $V = V_0$. In terms of the approximate logarithmic fits, like (P) above, the $(\partial p/\partial T)_V$ values reach those of (dp_0/dT) at values of $|T - T_0(p)|$, which are well below those used in macroscopic thermodynamics. For instance, if one assumes that the logarithmic representation of derivatives $(\partial p/\partial T)_V$ of the recently studied isochore by Lounasmaa¹⁷ may be extrapolated to $|T - T_0(p)| < 2 \times 10^{-5}$ °K, the latter difference being the limit of the experimental range, then the above representation yields a $(\partial p/\partial T)_V$ equal to (dp_0/dT) at $V = V_0$, at $T_0 - T \sim 10^{-23}$ °K. The value of $(\partial p_{-}/\partial T)_V$ at $(T_0 - T) \simeq 2 \times 10^{-5}$ °K being only -17 atm/°K, more than four times less than (dp_0/dT) which, at the volume of this isochore, is -76 atm/°K. As will be seen below, such small values of $(T_0 - T)$ are enormously smaller than the lower limits of the physically admissible values of this parameter allowed by the temperature fluctuations.

At the present time, the main result of $(\partial p/\partial T)_V$ measurements consists in that these derivatives are considerably smaller even at $|T - T_0| \simeq 10^{-5}$ °K than their finite limits they ought to reach at T_0 if the implications of the tentative interpretation of heat capacity^{6,7} and expansion coefficient measurements⁸⁻¹¹ were acceptable without qualification. The implied finite limits (dp_0/dT) of the derivatives $(\partial p/\partial T)_{V \rightarrow V_0}$ of isochores at the transformation line appear to be inaccessible experimentally in terms of the available

data on the latter.^{12,17} Within the explored range of $|T_0 - T|$, the $(\partial p/\partial T)_V$ values appear to be discontinuous in the sense that

$$\begin{aligned} & [\partial p_{+}(T_0 + \Delta T, V)/\partial T]_V \\ & > [\partial p_{-}(T_0 - \Delta T, V)/\partial T]_V \end{aligned} \quad (13)$$

or, at the same numerical values of the parameter $|T_0 - T|$, the derivative is larger in the He⁴ I region than it is in the He⁴ II region.^{12,17} If the preceding results were even qualitatively representative of the actual state of affairs at the transformation line or in its neighborhood, they would seriously conflict with the singular isothermal compressibility, expansion coefficient and constant pressure heat capacity at the transition line, implied by the interpretation based on the measurements of the two latter properties under saturation condition. It is hereby assumed tacitly that the thermodynamic characteristics of the transformation remain invariant as one moves away from saturation conditions along the transformation line.

We turn now to the discussion of the isobars $V(T, p)$ in the vicinity of the transformation line $V_0(T)$. Volume measurements along the saturation line and in the compressed liquid at the approaches of the melting line have been made recently in this laboratory.^{11,13} The compressed liquid isobars have been studied by Grilly and Mills¹³ under limited temperature resolution, and the isobaric expansion coefficients derived therefrom are very large at the transformation line. These expansion coefficients have been represented approximately as having a cusp at the transition temperature associated with large discontinuities of $(\partial^2 V/\partial T^2)_p$ at the transition line. The derived expansion coefficients reach values of about $(-0.16)/\text{°K}$ at the transformation line. This value is, numerically, larger by a factor of more than two than the saturated liquid-expansion coefficient derived by Kerr and Taylor¹⁴ from their saturated liquid volume measurements under increased temperature resolution and at $T_0 - T \simeq 10^{-4}$ °K. These authors fit their $(\ln V_{0,\text{sat}})$ values in terms of an expression depending as $\ln |T - T_0|^{T - T_0}$ on the temperature difference $|T - T_{0,\text{sat}}|$ at $|T - T_{0,\text{sat}}| \lesssim 3 \times 10^{-2}$ (°K). The expansion coefficient calculated therefrom thus depends linearly on $\ln |T - T_{0,\text{sat}}|$ in the neighborhood of $T_{0,\text{sat}}$. If this logarithmic fit is extrapolated into regions of $|T - T_0|$ well below those allowed by the temperature fluctuations, say down to $|T - T_0| \sim 10^{-15}$ (°K), even at such physically unjustified temperature differences, the expansion coefficient reaches a value of about $0.18/\text{°K}$ which is the value of the saturated liquid expansion coefficient α_s at about 4.6 °K, nowhere near the approaches of the critical temperature of about 5.2 °K.

To recapitulate, the isochores, although having always finite temperature derivatives, appear to have temperature coefficients at or near the transition line which are inaccessible to experimental control. To date, the experi-

mentally accessible limiting values are considerably lower than the approximate temperature derivatives (dp_0/dT) of the transition line $p_0(T)$ at the pertinent temperatures at which the isochores $p(T, V)$ reach this line. By (3), the limits (dp_0/dT) can only be reached, in general, if the isothermal compressibility were to become singular at the transition line. Actually, the approximate logarithmic representations of the $(\partial p/\partial T)_V$ data^{12,17} at the approaches of the transition can only yield values to the conditional limits equal to (dp_0/dT) provided one uses in the above fits values of $|T - T_0|$ such that

$$|T - T_0| \ll ((\Delta T^2)_{av})^{1/2}, \quad (14)$$

or values which are much smaller than the root-mean-square values of the temperature fluctuations of the systems investigated. Clearly, the logarithmic fits lose their meaning at the limit $T \rightarrow T_0$ as emphasized by Lounasmaa himself.^{12,17} Similarly, the tendency of the expansion coefficients toward their singular limits, implied in conjunction with the reaching by the coefficients $(\partial p/\partial T)_V$ their finite limits at the transition, is extremely slow. These thermal properties do not seem to justify any favorable conclusion as to their correct limits at the transition line.

We will return to the discussion of the isochores at the approaches of the transition line after an analysis of the behavior of the heat capacities near the transition line and a brief consideration of the temperature fluctuations.

3. HEAT CAPACITIES OF LIQUID He⁴ IN ITS TRANSFORMATION REGION

An important empirical result on the entropies $S_0(T, V)$ and $S_0(T, p)$ along the transformation line consists in the finite values of the total derivatives of these two entropy expressions:

$$dS_0(T, V)/dT = (\partial S/\partial T)_{V=V_0} + (\partial S/\partial V)_{T=T_0}(dV_0/dT), \quad (15)$$

or,

$$C_V(T_0, V_0) = C_0(T_0, V_0) - T_0(\partial p/\partial T)_{V=V_0}(dV_0/dT), \quad (16)$$

where C_V is the constant volume heat capacity at V_0 , C_0 is the heat capacity along the transformation line, or $T(dS_0/dT)$. Since $(\partial p/\partial T)_{V=V_0} < 0$, it is seen that

$$C_V(T_0, V_0) \geq C_0(T_0, V_0). \quad (17)$$

A possible case of (17) reducing to an equality will be considered further below.

With T and p , as independent variables, one obtains, similarly with (16),

$$C_p(T_0, p_0) = C_0(T_0, p_0) + T_0 V_0 \alpha_p(T_0, p_0)(dp_0/dT), \quad (18)$$

where $C_p(T_0, p_0)$ is the constant pressure heat capacity at the transition line $p_0(T)$, $C_0(T_0, p_0)$ stands for

$T_0(dS_0/dT)$, the heat capacity along the transition line, α_p is the isobaric expansion coefficient at the transition line, and (dp_0/dT) is the temperature derivative of $p_0(T)$. Since, $C_0(T_0, p_0)$ is finite together with (dp_0/dT) all along the transformation line, according to data available to date on these properties, it is seen that if $C_p(T, p_0)$ is singular, then so is $\alpha_p(T_0, p_0)$ and $\chi_T(T_0, p_0)$ in turn, and vice versa. These are the correlations between the possibly singular thermal properties on the transformation lines imposed by thermodynamics, and alluded to in the foregoing sections.

Let also $S_{\text{sat}}(T, V)$ and $S_{\text{sat}}(T, p)$ denote the entropy of the saturated liquid. One obtains with the former

$$dS_{\text{sat}}(T, V)/dT = (\partial S_{\text{sat}}/\partial T)_V + (\partial S_{\text{sat}}/\partial V)_T(dV_{\text{sat}}/dT), \quad (19)$$

or,

$$C_{\text{sat}}(T, V) = C_{V, \text{sat}}(T, V) + T(\partial p/\partial T)_{V, \text{sat}}(dV_{\text{sat}}/dT). \quad (20)$$

Here, $V_{\text{sat}}(T)$ is the saturated liquid volume in the (V, T) plane, and $(\partial p/\partial T)_{V, \text{sat}}$ is the partial temperature derivative of the liquid isochore $p(T, V_{\text{sat}})$ at its intersection with the saturation vapor pressure line $p_{\text{sat}}(T)$. We have seen that C_V is finite at the transition line, and at $(T_{0, \text{sat}}, V_{0, \text{sat}}, p_{0, \text{sat}})$ in particular. Hence, the saturated liquid heat capacity $C_{\text{sat}}(T, V)$ becomes singular if dV_{sat}/dT or α_{sat} , the expansion coefficient along the saturation line is singular at the transition point. It is to be noted that since $(\partial p/\partial T)_V < 0$, and $(dV_{\text{sat}}/dT) < 0$ around the transition temperature $T_{0, \text{sat}}$, $C_{\text{sat}} > C_{V, \text{sat}}$ in this region.

With $S_{\text{sat}}(T, p)$, one obtains again

$$C_{p, \text{sat}}(T, p) = C_{\text{sat}}(T, p) + TV_{\text{sat}}\alpha_p(T, p)(dp_{\text{sat}}/dT), \quad (21)$$

where (dp_{sat}/dT) is the temperature slope of the vapor pressure curve, $p_{\text{sat}}(T)$, $\alpha_p(T, p)$ is the isobaric expansion at saturation, that is, at the point where the isobar $V(T, p)$ reaches the saturation line. Since $\alpha_p < 0$ at $T_{\alpha, \text{II}} \leq T \leq T_{\alpha, \text{I}}$, and $(dp_{\text{sat}}/dT) > 0$, it is seen that $C_{p, \text{sat}} < C_{\text{sat}}$ over the temperature range $(T_{\alpha, \text{I}} - T_{\alpha, \text{II}})$.

It is seen easily that the Ehrenfest relations for ΔC_p or ΔC_V , across the transformation line, result at once from (16) and (17) as well as from (20) and (21) at saturation by writing these heat capacity relations above (+) and below (-) the transition line and subtracting.

At the saturation line and the transformation point, it is possible to eliminate $C_V(T, V)$ between (16) and (20), or to eliminate $C_p(T, p)$ between (18) and (21), yielding a connection between C_{sat} and C_0 , or

$$\begin{aligned} C_{\text{sat}}(T_{0, \text{sat}}; V_{0, \text{sat}}) - C_0(T_{0, \text{sat}}; V_{0, \text{sat}}) &= T_{0, \text{sat}}(\partial p/\partial T)_{V=V_{0, \text{sat}}}[dV_{\text{sat}}/dT - (dV_0/dT)] \\ &= T_{0, \text{sat}}V_{0, \text{sat}}\alpha_p(T_{0, \text{sat}}; p_{0, \text{sat}}) \\ &\quad \times [(dp_0/dT) - (dp_{\text{sat}}/dT)]. \quad (22) \end{aligned}$$

Since the expressions inside the square brackets are always negative, and since $(\partial p/\partial T)_{V=V_{0,\text{sat}}}$ as well as $\alpha_p(T_{0,\text{sat}}; p_{0,\text{sat}})$ are negative, one has necessarily

$$C_{\text{sat}}(T_{0,\text{sat}}; V_{0,\text{sat}}) > C_0(T_{0,\text{sat}}; V_{0,\text{sat}}). \quad (23)$$

The empirical results^{6,7} on C_{sat} appear to be approximately representable through

$$C_{\text{sat}} = A_{\text{sat}} + B_{\text{sat}} \ln |T - T_{0,\text{sat}}| + \begin{cases} D_{\text{sat}}, & T > T_{0,\text{sat}}, \\ 0, & T < T_{0,\text{sat}}, \end{cases} \quad (C)$$

$$10^{-6} \leq |T - T_0| \leq 10^{-2} \text{ (}^\circ\text{K)},$$

A_{sat} , B_{sat} , and D_{sat} being constants. It is of interest that a value of C_{sat} claimed to have been obtained⁷ at $T_0 - T = 2 \times 10^{-7}$ °K falls below the line (C) linear in $\ln(T_0 - T)$, although the relative error increases rapidly at $T_0 - T < 10^{-5}$ °K and reaches there ($\pm 10\%$) or more. Using the empirical fit to the C_{sat} data, as well as the thermodynamic connection between α_p and α_{sat} , together with available data on α_{sat} , V_{sat} , and (dp_{sat}/dT) , (21) yields for $C_{p,\text{sat}}$ an approximate relation similar to that of C_{sat} above, Eq. (C), with new constants A_p , B_p , and D_p .⁷ It should be noted that in deriving $C_{p,\text{sat}}$, it is assumed⁷ that the logarithmic fits to the α_{sat} data remain valid at $|T - T_0|$ values outside the range of measurements of α_{sat} . At $T = (T_{0,\text{sat}} - 10^{-6})$ °K, the calculated $C_{p,\text{sat}}$ is $10.7R$. Since, at these temperatures, γ_{sat} or $(C_{p,\text{sat}}/C_{V,\text{sat}})$ is unity for all practical purposes, this $C_{p,\text{sat}}$ at the indicated temperature is also $C_{V,\text{sat}}$. On the other hand, C_V is always finite at the transition line according to data available at the present time, as indicated above. Using Eq. (20), and the empirical^{12,18} $C_0(T_{0,\text{sat}}; V_{0,\text{sat}})$, the upper bound of $(\partial p/\partial T)_{V=V_{0,\text{sat}}}$ or (dp_0/dT) at the saturation line, as well as (dV_0/dT) at the same line, one finds the upper bound of $C_{V,\text{sat}}$ at $T_{0,\text{sat}}$ to be approximately

$$\lim \sup C_{V,\text{sat}}(T_{0,\text{sat}}; V_{0,\text{sat}}) \simeq 93R.$$

Other estimates range to up about twice this value.⁷

The question may be asked here, at what temperature very close to $(T_{0,\text{sat}})$ is the preceding approximate upper bound of $C_{V,\text{sat}}$ reached by $C_{p,\text{sat}}$ itself. Using the logarithmic fit derived for $C_{p,\text{sat}}$ from that of C_{sat} , Eq. (C) above, one finds that $C_{p,\text{sat}}$ would be equal to $(93R)$ at $(T_0 - T) \sim 10^{-64}$ (°K), a physically meaningless temperature difference resulting from the extrapolation of $C_{p,\text{sat}}$ into the above region of temperature differences. Clearly, on the assumption of the validity of this extrapolation, the $C_{p,\text{sat}}$ value is inaccessible as is the $C_{V,\text{sat}}$ value, and as was the case with the $(\partial p/\partial T)_V$ values at the transition line discussed above, all connected with the tacitly assumed singularity^{6,7} of C_p , χ_T , or α_p , at the transition line.

According to statistical thermodynamics,¹⁹ the root-

mean-square temperature fluctuations of a system, whether in contact with a heat reservoir of very large heat capacity or isolated, in the latter case any small volume element (ΔV) of the system is in contact with the rest of it of volume $(V - \Delta V)$, is given by

$$(\langle \Delta T^2 \rangle_{\text{av}})^{1/2} = [T/N^{1/2}(C_V/R)^{1/2}], \quad (24)$$

where C_V is the constant volume heat capacity of the system in question, N is Avogadro's number.²⁰ At $T_{0,\text{sat}}$ and with $C_V/R \sim 10$, which is already enormous, one finds

$$(\langle \Delta T^2 \rangle_{\text{av}})_{T_{0,\text{sat}}}^{1/2} \simeq 10^{-12} \text{ }^\circ\text{K},$$

and by taking the above indicated upper limit of $C_{V,\text{sat}}$ of $93R$, this is reduced only by about a factor of 3. Clearly, with such values of $(\langle \Delta T^2 \rangle_{\text{av}})^{1/2}$, if the empirical logarithmic fits did continue to have physical meaning outside the range of $|T - T_0|$ explored experimentally, statistical thermodynamics excludes $|T - T_0|$ values which fail to satisfy the inequality,

$$|T - T_0| \gg (\langle \Delta T^2 \rangle_{\text{av}})^{1/2}. \quad (25)$$

Only such values of the argument of the logarithm in Eq. (C), for instance, which are well outside the fluctuation range, are justified physically.

These limitations of strictly statistical thermodynamic character have been, apparently, completely neglected in the various works quoted above discussing singularities, where direct or indirect arguments have been advanced toward the likely occurrence of infinities of various thermal properties of liquid He⁴ at the transformation line. The considerations advanced here clearly emphasize the fundamental conceptual difficulties connected with attempts at using approximate empirical fits to data of some thermal properties of extremely slow temperature variation so as to extract with them indications favoring its possible singular behavior at some critical temperature or thermodynamic state. Not only is there a fundamental difficulty to justify through macroscopic thermodynamic measurements the extremely slow logarithmic approach toward a possible singularity of some property, but, as shown above, even finite, though possibly very large, values of certain correlated properties then appear to become inaccessible to measurements at even a fractional value of their very large limits at the critical state.

In view of these difficulties, which seem to exclude an unambiguous conclusion about the existence of singular thermal properties at the liquid He⁴ II-He⁴ I transformation line, it appears necessary to devise an

¹⁸ O. V. Lounasmaa, *Cryogenics* 1, 212 (1963).

¹⁹ G. L. de Haas-Lorentz, *Die Brownsche Bewegung* (Frederick Vieweg & Sohn, Braunschweig, Germany, 1913); cf. also, R. Fürth, *Schwankungserscheinungen in der Physik* (Frederick Vieweg & Sohn, Braunschweig, Germany, 1920).

²⁰ For a small isolated system of volume V , (24) underestimates the fluctuations in the sense that in this case one considers the subsystem of volume ΔV , and its constant-volume heat capacity will be smaller than that of the remainder of the system. To be sure, (ΔV) can be chosen to be, essentially, anywhere within V , subject to the requirement that it be large enough to be describable with the formalism of macroscopic thermodynamics.

approach to this problem where quantitative measurements may allow possibly a qualitative justification of the presence or absence of actual singularities of a group of thermal properties at the transition line. We should like to discuss such an approach in the next section under the assumption that the nature of the liquid-He⁴ transformation remains invariant all along the transformation line. If this assumption is omitted, then the approach to be studied would only yield information on the nature of this transformation at a single point of the transition line, namely, at melting.

4. THE LAMBDA TRANSFORMATION AT MELTING

Before entering the main topic of this section, it is necessary to discuss a restricted family of isochores of liquid He⁴ out to states of thermodynamic coordinates lying somewhat beyond the locus $T_{\alpha,I}$ where they become normal again. The region of the liquid-He⁴ phase diagram of particular interest to us has been specified previously.¹ The isochores of this region may be divided into several classes. For our problem, only those isochores which reach the transformation line and continue beyond it are of interest. This class has volumes in the interval

$$V_{0,M} \leq V \leq V_{0,sat}, \quad (26a)$$

where $V_{0,M}$ is the volume of the liquid at melting, and at the transformation line; that is, at the intersection of the liquid volume at melting, $V_M(T)$, and the volume transformation line $V_0(T)$. Actually, the subclass of isochores of volume somewhat below $V_{0,M}$ is also anomalous up to

$$V_{0,M} \leq V \leq V_{M,\alpha}, \quad (26b)$$

where $V_{M,\alpha}$ is the liquid volume at melting and at the end point of the locus $T_{\alpha,I}$. The families of isochores and isobars existing at temperatures $T \leq T_{\alpha,I}$ are all of particular interest, since they all display anomalies consisting in at least one extremum, not counting the one existing at the absolute zero. All isochores of volume

$$V_M(T=0) \leq V \leq V_{sat}(T=0), \quad (26c)$$

start at the absolute zero and increase first. Those of volume

$$V_M(T=0) \leq V \leq V(T_{M,min}), \quad (26d)$$

where $V(T_{M,m})$ is the liquid volume at melting and at the minimum of the melting pressure line,²¹ start at the absolute zero and increase with temperature until

²¹ The melting pressure anomaly of He⁴, discussed by us in Refs. 1 and 2, has been claimed to have been observed both indirectly, through the negative latent heat of melting, by J. Wiebes and H. C. Kramers, Phys. Letters 4, 298 (1963), and directly by C. Le Pair, K. W. Tacomis, R. De Bruyn Ouboter, and P. Das, Physica 29, 755 (1963). To our knowledge, an exhaustive experimental investigation of the melting pressure anomaly of He⁴ is, however, lacking at the present time. As pointed out further in the text, the result to be derived below is independent of the presence or absence of the melting line anomaly.

they reach the melting line. Here, these isochores develop a gap and leave the melting line at $p > p_{M,min}$, $p_{M,min}$ denoting the melting pressure minimum, and $T \geq T_{M,min}$. For our problem, these latter isochores which leave the melting line at $p \geq p_{M,m}$ and $T \geq T_{M,min}$ are of particular interest. Before studying these in some detail, we would like to digress briefly on some larger volume isochores.

The class of anomalous isochores contains two particular subclasses, the members of which have one or two common points with the vapor-pressure curve or the saturated-liquid volume curve at the lower temperatures. The isochoric arcs of one of these subclasses have volumes V such that

$$V_{sat}(T=0) \leq V \leq V_{sat,max}, \quad (27a)$$

$V_{sat,max}$ is the saturated liquid volume maximum at $T < T_{0,sat}$. These start out on the vapor pressure curve, leave the latter and return to it. The isochores of volume

$$V_{sat}(T=0) \geq V \geq V_{sat,min}, \quad (27b)$$

have only their end point on the vapor pressure line. These are limited arcs, over the low-temperature interval of interest here. The isochores of the subclass (27a) all leave the vapor-pressure curve with temperature derivatives

$$(\partial p / \partial T)_V = (dp_{sat} / dT) + (1 / V_{sat} \chi_T(T, p_{sat})) (dV_{sat} / dT), \quad (28)$$

and, since,

$$(dV_{sat} / dT) \geq 0, \quad 0 \leq T \leq T_{sat,max}, \quad (29)$$

$$(\partial p / \partial T)_V \geq (dp_{sat} / dT), \quad (30)$$

over the same temperature interval. The isochores of the volume interval (27a) start to increase first by (28) or (30); they develop their maximum at the locus $T_{\alpha,II}(p)$, and turn around to decrease and to reach the vapor-pressure line where

$$(\partial p / \partial T)_V < 0, \quad (30a)$$

since the second term on the right-hand side of (28) with $(dV_{sat} / dT) < 0$ will have to outweigh the first positive derivative (dp_{sat} / dT) of the vapor-pressure line. The isochoric arcs of the subclass (27a) become shorter as their volume parameter approaches $V_{sat,max}$ until the isochore of this latter volume reduces to a point to reemerge again from the vapor-pressure curve at $T > T_{sat,min}$ in the He⁴ I region, where it becomes normal together with this high-temperature extension of the subclass (27a), all starting out on the vapor pressure curve with the temperature slopes (28) or (30). It is seen at once that the end point of the locus $T_{\alpha,II}(p_{sat})$, where $(\partial p / \partial T)_V$ vanishes at the vapor pressure line, must occur at

$$T_{\alpha,II}(p_{sat}) > T_{sat}(V_{sat,max}), \quad (31)$$

where, by (28),

$$(d\hat{p}_{\text{sat}}/dT) = -(1/V_{\text{sat}}\chi_T(T, \hat{p}_{\text{sat}}))(dV_{\text{sat}}/dT), \quad (32)$$

which is only possible with $(d\hat{p}_{\text{sat}}/dT) > 0$ when $(dV_{\text{sat}}/dT) < 0$, or beyond the temperature of the saturated-liquid volume maximum; that is, beyond $T_{\text{sat}}(V_{\text{sat}, \text{max}})$. The opposite situation develops in the $\text{He}^4 \text{ I}$ region. Here, the temperature $T_{\alpha, \text{I}}(\hat{p}_{\text{sat}})$ of the locus of the minimas of the isochores or the minimas of the isobars must occur by (28) at a temperature where $(dV_{\text{sat}}/dT) < 0$; that is, where the saturated liquid volume still decreases before having thus reached its minimum of $V_{\text{sat}, \text{min}}$, or,

$$T_{\alpha, \text{I}}(\hat{p}_{\text{sat}}) < T_{\text{sat}}(V_{\text{sat}, \text{min}}). \quad (33)$$

We return now to the study of those isochores which start out at the melting line $\hat{p}_M(T)$ at $\hat{p}_M \geq \hat{p}_{M, \text{min}}$. These isochores are all decreasing functions of the temperature, and according to the relation (4) above, these isochores have finite first and second temperature derivatives with possible discontinuous variations of either one of these at the transformation line, as indicated by (5) and (8). This subclass of isochores of initial pressure

$$\hat{p}_{M, \text{min}} \leq \hat{p}_M \leq \hat{p}_M(T_{0, M}), \quad (34)$$

all reach the transition line. The arc of the melting line between the states, $(\hat{p}_{M, \text{min}}, V_{M, \text{min}}, T_{M, \text{min}})$ and $(\hat{p}_{0, M}, V_{0, M}, T_{0, M})$, is thus mapped point by point or state by state on to a segment of the transition line. The state $(\hat{p}_{0, M}, V_{0, M}, T_{0, M})$ is its own transformed point or map point; the melting line $\hat{p}_M(T)$ and the transition line $\hat{p}_0(T)$ intersect at this point.

Since $\hat{p}_M(T)$ and $\hat{p}_0(T)$ intersect, the isochoric arcs $\hat{p}_-(T, V)$ in the $\text{He}^4 \text{ II}$ region have temperature and pressure lengths $(T_0 - T_M)$, $(\hat{p}_M - \hat{p}_0)$, which decrease as $\hat{p}_M(T)$ approaches $\hat{p}_{0, M}$ or $\hat{p}_M(T_{0, M})$, the intersection of $\hat{p}_M(T)$ and $\hat{p}_0(T)$. Since, in the affine (\hat{p}, T) plane, no length of arc or that of a straight line segment can be defined, any use of such lengths will be understood to refer to the temperature and pressure differences of the end points of these segments. The isochoric arcs of decreasing volume have thus decreasing lengths in the $\text{He}^4 \text{ II}$ region, and in the limit $\hat{p}_M \rightarrow \hat{p}_{0, M}$, $T_M \rightarrow T_{0, M}$, $V_M - V_{0, M}$, the isochoric arc $\hat{p}_-(T, V)$ reduces to a point. The derivatives of these arcs at the transition line are such that

$$(\partial \hat{p}_- / \partial T)_{V \rightarrow V_0} < 0, \quad (35)$$

and, also, we saw above, the condition (4)

$$(\partial \hat{p}_- / \partial T)_{V \rightarrow V_0} \geq (d\hat{p}_0 / dT),$$

must be satisfied and is rewritten here for convenience. As the starting point $\hat{p}_M(T)$ of the arcs $\hat{p}_-(T, V)$ approaches $\hat{p}_M(T_0)$, these arcs tend to get closer to their chords, the temperature slopes of which also approach the temperature derivatives of the isochores

at $\hat{p}_0(T)$. Since the derivative function $\hat{p}_{T-}'(T, V)$ or $(\partial \hat{p}_-(T, V) / \partial T)$ at $\hat{p}_0(T)$ is regular and well behaved, it is seen that even though the isochoric arc $\hat{p}_-(T, V)$ at $T < T_{0, M}$ reduces to a point at $(\hat{p}_{0, M}, T_{0, M})$: the derivative function there becomes identical to the temperature derivative of the limiting vanishing chord of $\hat{p}_-(T, V)$; that is, to the temperature slope of the tangent to the transition line $\hat{p}_0(T)$ at its intersection with the melting line. We have thus obtained a strictly geometrical proof of the relation

$$\lim_{T_M \rightarrow T_{0, M}, V_M \rightarrow V_{0, M}} (\partial \hat{p}_-(T, V) / \partial T)_V = \lim_{T \rightarrow T_{0, M}} (d\hat{p}_0 / dT), \quad (36)$$

which states that the limiting value of the partial temperature derivatives of the isochores $\hat{p}_-(T, V)$ on the low-temperature side of the transition line, subject to the conditions (35) and (4) above, must be identical to the temperature slope of the tangent to the transition line $\hat{p}_0(T)$ at its intersection with the melting line. But, according to the thermodynamic relation (3) rewritten here for $\hat{p}_-(T, V)$,

$$[\partial \hat{p}_-(T, V) / \partial T]_{V \rightarrow V_0} = (d\hat{p}_0 / dT) + [1/V_0(T)\chi_{T-}(T_0, \hat{p}_0)](dV_0 / dT), \quad (3a)$$

the geometrical result (36) requires that

$$\lim_{T \rightarrow T_{0, M}, V_0 \rightarrow V_{0, M}, \hat{p}_0 \rightarrow \hat{p}_{0, M}} [V_0\chi_{T-}(\hat{p}_0, T_0)]^{-1} \times (dV_0 / dT) \equiv 0. \quad (37)$$

Clearly, the vanishing of this product in the state $(\hat{p}_{0, M}, V_{0, M}, T_{0, M})$ will occur if either one of the following three situations is realized:

$$\begin{aligned} \lim_{T_0 \rightarrow T_{0, M}, \hat{p}_0 \rightarrow \hat{p}_{0, M}} \chi_{T-}(T, \hat{p}) &\rightarrow \infty, \\ \lim_{T_0 \rightarrow T_{0, M}, V_0 \rightarrow V_{0, M}} (dV_0 / dT) &\neq 0, \end{aligned} \quad (38a)$$

or, in the same limits,

$$\lim \chi_{T-}(T, \hat{p}) \rightarrow \text{finite}, \quad \lim (dV_0 / dT) \rightarrow 0, \quad (38b)$$

or, again in the same limits,

$$\lim \chi_{T-} \rightarrow \infty, \quad \lim (dV_0 / dT) \rightarrow 0. \quad (38c)$$

If, and only if, the thermodynamic characteristics of the liquid- He^4 transformation process at melting are identical with those of all the other points of the transformation arcs $\hat{p}_0(T)$ or $V_0(T)$, that is, if the limit points $(\hat{p}_{0, M}, V_{0, M}, T_{0, M})$, $(\hat{p}_{0, \text{sat}}, V_{0, \text{sat}}, T_{0, \text{sat}})$ belong to the set of transformation points, then (38a) has the following interpretation: If the finite temperature slope of (dV_0 / dT) at the melting line is established experimentally, then this result on the measurement of a finite property at a single point of the volume transition line confirms the occurrence of singularities of the isothermal compressibility χ_{T-} , the isobaric volume expansion coefficient α_{p-} , and the constant pressure heat capacity C_{p-} by (18) on the $\text{He}^4 \text{ II}$ side of the transition.

If $V_0(T)$ has a parabolic approach toward its end

point at the melting volume line $V_M(T)$ of the liquid, with the vertex at $(V_{0,M}, T_{0,M})$, that is, ρ being a constant, if

$$\lim_{T \rightarrow T_{0,M}} V_0(T) = V_{0,M}(T_{M,0}) + \rho(T - T_{M,0})^2 + \dots, \quad (39)$$

then the requirement on the existence of singularities of χ_{T-} , α_{p-} , C_{p-} at the transition line may be disposed of completely. The behavior (39) of $V_0(T)$ near the melting line is fully compatible with finite values of the indicated group of three thermal properties at the transition line, situation (38b). However, the behavior (39) does not rule out the occurrence of these singularities at the transformation line by (38c). Hence, if (39) describes correctly the behavior of $V_0(T)$ near $T_{0,M}$ within the framework of thermodynamics, a new experimental approach has to be devised toward the problem of deciding whether all properties are finite, situation (38b), or whether some of them are singular on the He⁴ II side of the transition, situation (38c). It should be noted here that the explicit use above of the melting pressure minimum was strictly for convenience of the geometrical proof of (36). This proof is valid whether $p_{M,\min}$ actually exists or not.

It seems not without interest to appraise the possible situation, (38b), in the light of the measured isothermal compressibilities^{12,13,17} as well as the inaccessibility of finite but very large values of this possibly singular property as a consequence of the limitations resulting from temperature fluctuations discussed in the foregoing sections. Before so doing, however, we would like to consider briefly some consequences of the parabolic limiting behavior (39) of $V_0(T)$ near $T_{0,M}$.

Let $S_M(T, V)$ be the entropy of the liquid at melting, and $S_0(T, V)$ the entropy along the transition line. These yield, at once,

$$C_M(T, V) = C_V(T, V) + T(\partial p / \partial T)_{V=V_M} (dV_M / dT), \quad (40)$$

where C_V is the constant volume heat capacity at melting, and

$$C_0(T, V) = C_V(T, V) + T(\partial p / \partial T)_{V=V_0} (dV_0 / dT), \quad (41)$$

where C_V is the constant volume heat capacity at the transition line. At melting, or $(T_{0,M}, V_{0,M})$, the latter reduces, by (39), to

$$\lim_{T \rightarrow T_{0,M}, V \rightarrow V_{0,M}} C_0(T, V) = C_{V-}(T_{0,M}, V_{0,M}), \quad (42)$$

$(\partial p / \partial T)_{V=V_{0,M}}$ being the finite derivative (dp_0 / dT) in this state by (36). We have alluded to this relation (42) in the foregoing section in connection with (17).

Also, (40) and (41) lead, with (36), to

$$C_M(T_{0,M}, V_{0,M}) = C_0(T_{0,M}, V_{0,M}) + T_{0,M} (dp_0 / dT) (dV_M / dT), \quad (43)$$

which connects the heat capacity along the melting line C_M with that along the transition line C_0 , in the

state $(p_{0,M}, V_{0,M}, T_{0,M})$, the derivatives (dp_0 / dT) and (dV_M / dT) both referring to this state. It is seen that C_0 being finite, C_M will be singular if (dV_M / dT) is singular. Notice that second term on the right-hand side of (43) is positive since both (dp_0 / dT) and (dV_M / dT) are negative in the state in question.

In returning now to the possible situation described by (38b) with (39), it is appropriate to consider the inequality (33). It should be recalled here that, empirically,¹¹ the minimum of the saturated liquid volume occurs at about $[T_{0,\text{sat}} + (0.006)^\circ\text{K}]$. By (33), the locus $T_{\alpha,1}$ must thus meet the saturation line at $T_{0,\text{sat}} < T < (T_{0,\text{sat}} + 0.006^\circ\text{K})$. The saturation vapor pressure²² at $T_{\text{sat},\min}$ is higher by about 60×10^{-3} mm Hg, at 0°C , than at $T_{0,\text{sat}}$. The saturation vapor pressure at $T_{\alpha,1}(p_{\text{sat}})$ will also be closer to $p_{0,\text{sat}}$ than the just indicated pressure difference. If, as implied on the basis of physically unjustifiable extrapolation,⁸⁻¹¹ $(\partial V_- / \partial T)_p$ did become $(-\infty)$ at the transition line, this quantity will have to increase from $(-\infty)$ to zero over a temperature interval less than 6×10^{-3} °K. On the other hand, at increasing pressures, the temperature interval $[T_{\alpha,1}(p) - T_0(p)]$ over which the isobar $V(T, p)$ has to recover from its singularity to reach zero, increases considerably. The temperature interval of recovery from the implied singularity to its zero of $(\partial V / \partial T)_p$ increases from saturation to melting¹³ by a factor of about 15.

We saw above that if χ_T were singular at the transformation line, as a consequence of the implied singularity of the isobaric expansion coefficient, so that the partial temperature derivatives $(\partial p / \partial T)_V$ would reduce to the total derivatives (dp_0 / dT) of the transformation line, at the same temperature, then this derivative reaches its lowest value of about (-100) to (-90) (atm/°K), at saturation. This derivative has to increase to zero at the average rate of 1.7×10^4 atm/(°K)². On the other hand, at increasing pressures, (dp_0 / dT) decreases numerically, or increases algebraically, while at the same time the recovery interval to reach zero increases rapidly, as mentioned. Geometrically, the recovery process of $(\partial V / \partial T)_p$ or $(\partial p / \partial T)_V$ from their anomalies at the transition line is queer, to say the least.

The preceding discussion did not advance any argument for or against the possible situation described by (38b). It is, however, remarkable that the experimentally determined $(\partial p / \partial T)_V$ values at the approaches of the saturation line exhibit an apparently more normal behavior.^{12,17} These measured partial derivatives of isochores are the smallest numerically at the largest liquid volumes near saturation, and they increase numerically at decreasing liquid volumes. Here the numerically smaller $(\partial p / \partial T)_V$ values near the transition line also have a smaller temperature interval $[T_{\alpha,1}(p) - T_0(p)]$ to reach their zero and their

²² Natl. Bur. of Std, (U. S.) Monograph 10 (1960).

normal region, while the numerically larger $(\partial p/\partial T)_V$ values at decreasing liquid volumes have also a larger recovery interval $[T_{\alpha, I}(p) - T_0(p)]$, a geometrically more satisfactory behavior. It is of interest that this trend of variation of $(\partial p/\partial T)_V$ at the approaches of the transformation line has been first exhibited in the early experimental studies¹⁵ of the diagrams of state of liquid He⁴. Again, the preceding discussion does not yield any definite argument in favor of the inequality,

$$\lim_{T \rightarrow T_0, p \rightarrow p_0} (\partial p_-/\partial T)_V > (dp_0/dT),$$

which then would be equivalent to the existence of finite, though possibly large, values of the isothermal compressibilities at the transformation line. The latter, in turn, would impose, by (38), the parabolic approach (39) of $V_0(T)$ toward $V_0(T_{0, M})$. The finite compressibilities would be equivalent to the absence of the implied singularities of the expansion coefficients α_{sat} , α_p , and α_M , this latter referring to the coefficient along the melting line, and of the heat capacities C_{sat} , C_p , and C_M at the transition. It seems, however, that the peculiar geometrical situation with respect to the derivatives, (dp_0/dT) , $(\partial p_-/\partial T)_V$, and the temperature intervals $(T_{\alpha, I} - T_0)$, will have to be kept in mind until it is explained satisfactorily.²³

²³ It is of some interest to call attention here to the following situation: In the highly increased temperature resolution experiments of Refs. 6 and 7, the largest saturated liquid-He⁴ heat capacity claimed to have been measured, at 2×10^{-6} °K below $T_{0, \text{sat}}$, was $10.47R \pm (10\%)$. This heat capacity is actually smaller than the largest measured saturated liquid-He⁴ heat capacity at $T_{0, \text{sat}}$, reported graphically in Ref. 15. The latter is given as $11.75R$, which is outside the estimated 10% precision claimed in Ref. 7. The estimated precision of this largest measured heat capacity is, however, not available to us.

The following remarks should round out the discussion of the isochores leaving the melting line $p_M(T)$, at $T_M \geq T_{0, M}$. It will be seen that if $(\partial p/\partial T)_V$ were discontinuous across the transition line, then at melting $p_+(T, V_{0, M})$ would leave $p_M(T)$ with a derivative such that

$$(\partial p_+/\partial T)_{V_{0, M}} > (dp_0/dT), \quad T = T_{0, M},$$

and, in addition, $(\partial^2 p_+/\partial T^2)_{V_{0, M}} > 0$, in contrast with $(d^2 p_0/dT^2)$, which is negative at all points of $p_0(T)$. If this partial derivative were continuous along $p_0(T)$, then $p_+(T, V_{0, M})$ must have a common tangent with $p_0(T)$ at $T_{0, M}$, while $(\partial^2 p_+/\partial T^2)_{V_{0, M}}$ would be positive, in contrast with $(d^2 p_0/dT^2)$; the two curves $p_0(T)$ and $p_+(T, V)$ would thus have a first-order contact at the melting line. The class of isochores of volume $V_M < V_{0, M}$ all start out on the melting line $p_M(T)$ with negative first- but positive second-partial temperature derivatives as they approach their minimas on $T_{\alpha, I}(p)$. Finally, the last member of this class of volume $V_M(T_{\alpha, I})$ leaves the melting line with vanishing temperature derivative, having its minimum on the melting line at $T_{\alpha, I}(p_M)$, to increase beyond as a normal isochore. All isochores of volume $V_M < V_{0, M}(T_{\alpha, I})$ are normal.

In concluding, it seems justified to emphasize the approach outlined above toward obtaining new, possibly decisive, information on the thermodynamic features of the transformation phenomenon of liquid He⁴. Accurate experimental determinations of a branch of the volume transition line $V_0(T)$ at its approaches of the liquid volume at melting, as well as its temperature derivatives, appear to be of great thermodynamic significance.