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Phenomenological Theory of the λ Transition in He^4†

K. C. LEE AND R. D. PUFF
University of Washington, Seattle, Washington
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It is shown that a certain set of phenomenological statements about fluctuations near the λ line yields a consistent picture of thermodynamic derivatives in the vicinity of this line. On the basis of this phenomenological description, we are able to predict properties near the λ line and compare these with experiments.

I. INTRODUCTION

THE singular behavior of the thermodynamic functions in the vicinity of the λ-transition line of liquid helium-4 has been observed frequently. Analysis of the experimental data usually employs the phenomenological relations of Pippard[1,2] and of Buckingham and Fairbank[3] (PBF relations), although the validity of these relations has sometimes been questioned.[4]

In this paper we present a certain set of phenomenological statements about fluctuations near the λ line. These statements are based on the results of a particular microscopic calculation. However, we shall bypass the microscopic theory, using its results as foundation for a phenomenological theory. Our results are in fact consistent with the PBF relations and we are able to understand the origin of the difficulties referred to above.

Section II deals with the basic approach and discussion of thermodynamic properties in terms of fluctuations. Section III is devoted to the assumptions. In Section IV we show that these assumptions are consistent with (and in fact require) the PBF relations. Section V treats the experimental data on a qualitative basis and demonstrates the experimental consistency of the PBF relations. Section VI contains a quantitative comparison of the theory with experiments. The comparison has been summarized in Tables I and II.

II. FORMULATION

The grand partition function Z can, of course, be used to calculate all the relevant thermodynamic derivatives. Alternatively, we may express the most useful second derivatives in terms of fluctuations in the grand canonical ensemble. In any dynamical approximation scheme, it is preferable to investigate the fluctuations since direct differentiation of an approximate $\ln Z$ is both difficult and very sensitive to the approximation method. This is particularly true when the thermodynamic derivatives are singular. It is considerably easier to isolate the source of the singularities and to construct a microscopic theory by investigating the fluctuations directly.

Three independent fluctuations of interest are

$$\frac{\Delta N^2}{N} \equiv \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} = \frac{1}{N\beta^2}\frac{\partial^2}{\partial\mu^2}\ln Z, \tag{1}$$

$$\frac{\Delta NE}{N} \equiv \frac{\langle NE\rangle - \langle N\rangle\langle E\rangle}{\langle N\rangle} = \frac{\mu}{N\beta^2}\frac{\partial^2}{\partial\mu^2}\ln Z - \frac{1}{N\beta}\frac{\partial^2}{\partial\mu\partial\beta}\ln Z + \frac{1}{N\beta^2}\frac{\partial}{\partial\mu}\ln Z, \tag{2}$$

$$\frac{\Delta E^2}{N} \equiv \frac{\langle E^2\rangle - \langle E\rangle^2}{\langle N\rangle} = \frac{\mu^2}{N\beta^2}\frac{\partial^2}{\partial\mu^2}\ln Z - \frac{2\mu}{N\beta}\frac{\partial^2}{\partial\mu\partial\beta}\ln Z + \frac{1}{N}\frac{\partial^2}{\partial\beta^2}\ln Z + \frac{2\mu}{N\beta^2}\frac{\partial}{\partial\mu}\ln Z, \tag{3}$$

where $\langle A\rangle$ denotes the grand canonical average $Z^{-1}\,\mathrm{Tr}e^{-\beta(H-\mu N)}A$, with chemical potential μ and inverse temperature $\beta = 1/kT$.

With the notation above, we have the isothermal compressibility

$$K_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T = \frac{k\beta^2}{N^2}TV\Delta N^2, \tag{4}$$

the bulk expansion coefficient at constant pressure

$$\alpha_P = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_P = -\frac{k\beta^2}{N^2}[N\Delta NE - W\Delta N^2], \tag{5}$$

the specific heat at constant pressure

$$C_P = T\frac{\partial S}{\partial T}\bigg|_P = \frac{k\beta^2}{N^2}[N^2\Delta E^2 - 2WN\Delta NE + W^2\Delta N^2], \tag{6}$$

and the specific heat at constant volume

$$C_V = T\frac{\partial S}{\partial T}\bigg|_V = \frac{k\beta^2}{N^2}\left[N^2\Delta E^2 - N^2\frac{(\Delta NE)^2}{\Delta N^2}\right], \tag{7}$$

where V is the total volume and W is the total enthalpy.

The necessary fluctuations can all be obtained by a microscopic calculation of the thermodynamic Green's

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[1] A. B. Pippard, Phil. Mag. 1, 473 (1956).
[2] A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge University Press, New York, 1957), Chap. IX.
[3] M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 80.
[4] O. V. Lounasmaa, Phys. Rev. 130, 847 (1963).

function

$$L(12;1'2')\equiv -[\langle T\{\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')\}\rangle - \langle T\{\psi(1)\psi^\dagger(1')\}\rangle\langle T\{\psi(2)\psi^\dagger(2')\}\rangle], \quad (8)$$

where the indices refer to space-time variables, T is the Wick time-ordering symbol, and ψ is the usual field operator in the Heisenberg representation. We will not attempt to discuss the microscopic calculation here. The comparison with experimental data and the conclusions described below are based on several specific statements about the fluctuations which result from the microscopic calculation of L. For the purpose of this paper, we treat these statements as phenomenological assumptions, so that only thermodynamic manipulations are used to describe the results.

III. THE ASSUMPTIONS

We will suppose that the λ transition is characterized by the following conditions on the partition function Z:

(a) The first-order derivatives of $\ln Z$ are finite and continuous in the β, μ plane.

(b) The second-order derivatives of $\ln Z$ have singularities along a line in the β, μ plane (the λ line), the position of which is determined by an equation of the form

$$\Lambda(\beta,\mu)=0. \quad (9)$$

A position on this line will be denoted by the subscript λ [i.e., β_λ and μ_λ are values satisfying Eq. (9)]. These singularities appear in the fluctuations and are assumed to have the following nature:

$$\lim_{\beta,\mu\to\beta_\lambda,\mu_\lambda}\ \lim_{\substack{N,V\to\infty\\ N/V\to\mathrm{const}}}\left(\frac{\Delta N^2}{N},\ \frac{\Delta NE}{N},\ \frac{\Delta E^2}{N}\right)=\infty. \quad (10)$$

Before specifying the precise nature of these singularities, we may consider several possible relations among them in order to make contact with previous work.

(b′) Suppose that the conditions

$$\frac{\Delta E^2}{N}=r_\lambda\frac{\Delta NE}{N}=r_\lambda^2\frac{\Delta N^2}{N}\quad \text{as}\quad \beta,\mu\to\beta_\lambda,\mu_\lambda \quad (11)$$

and

$$\frac{d\mu_\lambda}{d\beta_\lambda}\equiv\lim_{\Lambda\to 0}-\frac{\partial\Lambda}{\partial\beta}\bigg|_\mu\bigg/\frac{\partial\Lambda}{\partial\mu}\bigg|_\beta=\frac{r_\lambda-\mu_\lambda}{\beta_\lambda} \quad (12)$$

are satisfied. Here, r_λ represents some finite function of β_λ and μ_λ. (a), (b), and (b′) form a set of phenomenological assumptions which can be shown to be essentially equivalent to those of Pippard[1,2] and of Buckingham and Fairbank.[3] Buckingham and Fairbank[3] derive a set of relations between the thermodynamic derivatives (the PBF relations [see Eqs. (19)–(21)] by assuming (a) together with a finite slope for the λ line in the P, T plane and the condition $C_P\to\infty$ less rapidly than $|T-T_\lambda|^{-1}$ as $T\to T_\lambda$. Their results also follow directly from (a), (b), and (b′).

However, we wish to establish (b′) by making a somewhat more detailed specification. Actually, in a microscopic theory, the fluctuation singularities are determined by the correlation function L. Any form of $L(\beta,\mu)$ which leads to a singular behavior such as that given by Eqs. (10) and (11) will also provide the specific form of Eq. (9). The phenomenological approach we plan to adopt here does not require a specific form for Eq. (9), but we should note that this form, as well as the particular singular behavior of the fluctuations, must emerge as integral properties of the function $L(\beta,\mu)$ translated into thermodynamic language. With this knowledge, one may then generate an equation such as (12) for the slope of the λ line.

We may achieve a more complete phenomenological specification of the λ transition by making, instead of (b′), the following assumptions in addition to (a) and (b):

(c) $\Delta N^2/N$ has, in the limit N, $V\to\infty$ with N/V finite, an asymptotic isobaric expansion of the form

$$\frac{\Delta N^2}{N}\bigg|_{\mathrm{asym}}=\frac{a(P)}{N}+\frac{b(P)}{N}\log|T-T_\lambda|+O(|T-T_\lambda|). \quad (13)$$

We also assume the additional asymptotic forms

$$\frac{\Delta NE}{N}\bigg|_{\mathrm{asym}}=r\frac{\Delta N^2}{N}\bigg|_{\mathrm{asym}}+\frac{\Delta NE_R(P)}{N}+O(|T-T_\lambda|) \quad (14)$$

and

$$\frac{\Delta E^2}{N}\bigg|_{\mathrm{asym}}=r^2\frac{\Delta N^2}{N}\bigg|_{\mathrm{asym}}+\frac{\Delta E_R^2(P)}{N}+O(|T-T_\lambda|). \quad (15)$$

These are consistent with and, in fact, enforce the equality (11). It can also be seen that Eq. (12) follows from Eqs. (13)–(15) if we characterize the λ line by the familiar expression $\Lambda=[\Delta N^2(\beta,\mu)/V]^{-1}\to 0$ and demand that the quantities r, a/N, b/N, $\Delta NE_R/N$ and $\Delta E_R^2/N$ be finite along the λ line. In the following analysis, r appears only in the slope of the λ line in the P-T plane and can be determined experimentally. ΔNE_R and ΔE_R^2 represent remainders of the total fluctuations ΔNE and ΔE^2 after terms proportional to ΔN^2 are subtracted. Thus we have in effect the four constants a/N, b/N, $\Delta NE_R/N$, and $\Delta E_R^2/N$ to be evaluated on the λ line.

(d) We might expect these four constants to be different on the two sides of the λ line. However, it is a consequence of the microscopic theory, which we take here as a special further assumption, that only the constant a/N has different values on the two sides (we will call the two values a^{I}/N and a^{II}/N). A term containing the discontinuous parameter $a(P)$ *does* appear in both (14) and (15). However, it is present only in the term involving $\Delta N^2/N|_{\text{asym}}$. By writing (14) and (15) in the above form, we have only one discontinuous constant. It should be noted that Eq. (13) is of the logarithmic form used by Buckingham and Fairbank.[3] Thus, we expect both the familiar PBF relations and the logarithmic specific-heat singularity to remain unchanged. However, the continuity conditions on the constants will have additional important consequences.

IV. PBF AND EHRENFEST-LIKE RELATIONS

The assumption (a), which implies the continuity of $\langle N\rangle$ and $\langle E\rangle$ on the λ line, excludes the possibility of a first-order transition of the Ehrenfest type. This further implies continuity of the entropy S, the Gibb's free energy $\Phi=\mu\langle N\rangle$, and the enthalpy $W=\Phi+TS$. Therefore, all coefficients of the fluctuations in the expressions (4)–(7) are finite and continuous across the λ line.

The slope of the λ line in the P, T plane, $\sigma(T_\lambda)=dP_\lambda/dT_\lambda$, can be calculated from the assumption (c). Since

$$\sigma=\lim_{\Delta\to 0}\frac{\partial P}{\partial T}\bigg|_\Lambda =-\lim_{\Delta\to 0}\left(\frac{\partial\Lambda}{\partial T}\bigg|_\mu+\frac{\partial\Lambda}{\partial\mu}\bigg|_T\frac{\partial\mu}{\partial T}\bigg|_P\right)\bigg/\frac{\partial\Lambda}{\partial\mu}\bigg|_T\frac{\partial\mu}{\partial P}\bigg|_T,$$

we have

$$\sigma=-(1/T_\lambda V_\lambda)[Nr_\lambda-W_\lambda], \tag{16}$$

where we have used the thermodynamic relations

$$\frac{\partial\mu}{\partial T}\bigg|_P=-\frac{S}{N}\quad\text{and}\quad\frac{\partial P}{\partial\mu}\bigg|_T=\frac{N}{V}.$$

It is also useful to express the functions $\Delta NE_R(\beta_\lambda,\mu_\lambda)$ and $\Delta E_R{}^2(\beta_\lambda,\mu_\lambda)$ in terms of the familiar quantities $\alpha_0\equiv(1/V_\lambda)dV_\lambda/dT_\lambda$ and $C_0\equiv T_\lambda\, dS_\lambda/dT_\lambda$. Thus, we have

$$\alpha_0=-(k\beta_\lambda{}^2/\langle N\rangle_\lambda)\Delta NE_R(\beta_\lambda,\mu_\lambda) \tag{17}$$

and

$$C_0=2\alpha_0W_\lambda-\alpha_0T_\lambda V_\lambda\sigma+k\beta_\lambda{}^2\Delta E_R{}^2(\beta_\lambda,\mu_\lambda). \tag{18}$$

Substituting Eqs. (13)–(18) into the expressions (4)–(7), we obtain the PBF relations

$$C_P=\sigma V_\lambda T_\lambda\alpha_P+C_0, \tag{19}$$

$$C_V(T_\lambda)=-\sigma V_\lambda T_\lambda\alpha_0+C_0, \tag{20}$$

$$\alpha_P=\sigma K_T+\alpha_0. \tag{21}$$

Ehrenfest-like relations can be derived from the above PBF relations, together with our special assumption (d) concerning the constants. Consider the quantities K_T, α_P, and C_P at two temperatures T^{I} and T^{II} equidistant from and on opposite sides of the λ line with $(T^{\mathrm{I}}-T_\lambda)/T_\lambda=(T_\lambda-T^{\mathrm{II}})/T_\lambda\ll 1$. We have immediately

$$\Delta K_T\equiv K_T(T^{\mathrm{I}})-K_T(T^{\mathrm{II}})\approx(k\beta_\lambda{}^2/N)(a^{\mathrm{I}}-a^{\mathrm{II}}),$$
$$\Delta\alpha_P\equiv\alpha_P(T^{\mathrm{I}})-\alpha_P(T^{\mathrm{II}})\approx(k\beta_\lambda{}^2/N)\sigma(a^{\mathrm{I}}-a^{\mathrm{II}}),$$
$$\Delta C_P\equiv C_P(T^{\mathrm{I}})-C_P(T^{\mathrm{II}})\approx(k\beta_\lambda{}^2/N)T_\lambda V_\lambda\sigma^2(a^{\mathrm{I}}-a^{\mathrm{II}}),$$

and therefore

$$\sigma=\lim_{|T_{\mathrm{I,II}}-T_\lambda|\to 0}\frac{\Delta\alpha_P}{\Delta K_T}=\lim_{|T_{\mathrm{I,II}}-T_\lambda|\to 0}\frac{\Delta C_P}{T_\lambda V_\lambda\Delta\alpha_P}. \tag{22}$$

V. QUALITATIVE ANALYSIS OF EXPERIMENTAL DATA

We may ask how small $|T-T_\lambda|/T_\lambda$ must be in order to compare the predictions of the PBF relations with experiment. Since these PBF relations have been derived from the asymptotic expansions (13)–(15), they should be valid whenever the linear variations $O(T-T_\lambda)$ in (13)–(15) are negligible compared with the first two terms. However, there has been some question as to the validity of both the asymptotic expansions and the PBF relations. In particular, we wish to understand the following three puzzling aspects of the experimental observations.

(1) In Lounasmaa's measurements[4] of

$$\beta_V=\partial P/\partial T|_V=\alpha_P/K_T$$

and K_T in the vicinity of a point on the λ line ($P_\lambda=13.04$ atm, $T_\lambda=2.023$°K), no sign of a logarithmic behavior in K_T close to T_λ was observed. Furthermore, a logarithmic fit for β_V in the temperature range 10^{-5}°K$\lesssim|T-T_\lambda|\lesssim 10^{-2}$°K was obtained, with a value $\beta_V=-18$ atm °K^{-1} at $|T-T_\lambda|=10^{-5}$ °K. Lounasmaa's empirical formulas read

$$K_T=0.0079-1.5|T-T_\lambda|\ \text{atm}^{-1},\quad T>T_\lambda$$
$$=0.0089+8.4|T-T_\lambda|\ \text{atm}^{-1},\quad T<T_\lambda \tag{23a}$$

and

$$\beta_V=3.5+3.4\log|T-T_\lambda|\ \text{atm°K}^{-1},\quad T>T_\lambda \tag{23b}$$
$$=-6.0+2.3\log|T-T_\lambda|\ \text{atm°K}^{-1},\quad T<T_\lambda$$

in this temperature range.

These results certainly seem to contradict the asymptotic expansion for K_T given by Eqs. (4) and (13) as well as the PBF relation (21). In fact, Eq. (21) implies

$$\beta_V(T_\lambda)=\sigma, \tag{24}$$

and the value of σ, by an independent measurement, is known to be about -76 atm°K^{-1} at $P=P_\lambda=13.04$ atm.

(2) Using the measured value[3,5] of C_P at the point $T-T_\lambda\approx 0.006$°K along the vapor-pressure curve[6] one

[5] We neglect the difference between the thermodynamic derivatives at constant pressure and the thermodynamic derivatives along the saturated vapor-pressure line.

[6] At this point there is a density minimum. Hence, $\alpha_p=0$, $C_P=C_V$. See, for example, E. C. Kerr and R. D. Taylor, Ann. Phys. (N. Y.) **26**, 292 (1964).

finds $C_V \approx C_P \approx 11$ J/g °K. However, using the measured values of C_0, α_0, and σ (see Sec. VI), we find from the PBF relation (20) the quantity[7]

$$C_V(T_\lambda) \approx 186 \text{ J/g °K}.$$

Without an essential singularity, this sharp rise in $C_V(T)$ (which is always less than C_P) is difficult to understand.

(3) On the other hand, the asymptotic behavior of the adiabatic sound velocity u predicted by the PBF relations is

$$\frac{1}{\rho u^2} = \frac{1}{\rho u_\lambda^2} - \frac{C_0^2}{\sigma^2 V_\lambda T_\lambda C_P} \tag{25}$$

with mass density ρ and

$$\rho u_\lambda^2 = \sigma^2 V_\lambda T_\lambda / (C_0 - \sigma \alpha_0 V_\lambda T_\lambda), \tag{26}$$

and the same values for C_0, α_0, and σ used in (2) above, when inserted in (25) and (26), seem to be in good agreement with the experimentally observed velocity.[3,8]

Thus (1) seems contradictory, (2) seems numerically difficult to understand, and (3) seems to be in agreement with the PBF relations. We will see that the PBF relations are, in fact, not contradicted by the experimental results (23). To understand this we may note the following inequalities:

$$|b/a^{\mathrm{I,II}}| \ll 1, \tag{27}$$

$$\left| \frac{N \Delta N E_R}{\sigma T_\lambda V_\lambda a^{\mathrm{I,II}}} - 1 \right| \ll 1$$

or

$$\left| \alpha_0 + \frac{\sigma(a^{\mathrm{I,II}}/N)}{kT_\lambda} \right| \ll \left| \frac{\sigma(a^{\mathrm{I,II}}/N)}{kT_\lambda} \right|, \tag{28}$$

$$\left| \frac{N^2 \Delta E_R^2 - 2W_\lambda N \Delta N E_R}{T_\lambda^2 V_\lambda^2 \sigma^2 a^{\mathrm{I,II}}} + 1 \right| \ll 1,$$

or

$$\left| C_0 + \sigma T_\lambda V_\lambda \left[\alpha_0 + \frac{\sigma(a^{\mathrm{I,II}}/N)}{kT_\lambda} \right] \right| \ll \left| \frac{V_\lambda \sigma^2 (a^{\mathrm{I,II}}/N)}{kN} \right|. \tag{29}$$

Although the exact values of these quantities are not necessary here (quantitative discussion is contained in Sec. VI), we may observe that b/a^{I} is roughly $-1/60$.[9]

The absence of the logarithmic dependence in (23a) within the temperature range $|T - T_\lambda| < 10^{-3}$°K, where the linear dependence becomes insignificant, can be understood by noting, from (27), that an accurate measurement simply requires very high resolution. The inequality (27) is consistent with the fact that no anomalous light scattering (critical opalescence) is observed in the λ transition. For example, a doubling of the density fluctuation from its normal value requires a temperature such that $T - T_\lambda \sim 10^{-60}$ °K!

On the other hand, the logarithmic behavior of C_P and α_P becomes apparent experimentally because of the inequalities (28) and (29). That is, the large constant parts cancel each other, leaving essentially only the logarithmic term. We will investigate the details of this cancelation in Sec. VI.

Furthermore the inequality (27) implies that ΔN^2 in the denominator of C_V [Eq. (7)] and

$$\beta_V = \frac{\alpha_P}{K_T} = \frac{1}{TV} \left[W - N \frac{\Delta N E}{\Delta N^2} \right] \tag{30}$$

has a "pseudo-asymptotic expansion" of the form

$$\frac{1}{\Delta N^2} \approx \frac{1}{a} \left[1 - \frac{b}{a} \log|T - T_\lambda| + O\left(\frac{b}{a} \log|T - T_\lambda| \right)^2 \right] \tag{31}$$

in the region

$$a \gg b \log|T - T_\lambda|. \tag{32}$$

When this expansion is used in Eqs. (7) and (30), both C_V and β_V can be shown to have logarithmic dependence for temperatures in the region given by (32). Of course, both $C_V(T_\lambda)$ and $\beta_V(T_\lambda)$ given by (20) and (24), respectively, can be obtained if the true asymptotic behavior $(\Delta N^2)^{-1} \to 0$ is used in (7) and (30). However, the true asymptotic region is experimentally unattainable, for the reasons discussed above.

The asymptotic relation between the adiabatic sound velocity and the specific heat at constant pressure given by (25) and (26) does not depend on the inequalities (27)–(29) for its validity. That is, we obtain (25) and (26) from the PBF relations (19) and (21) directly by the use of the thermodynamic formulas $1/\rho u^2 = K_S = K_T C_V/C_P$ and $C_V = C_P - TV\alpha_P^2/K_T$.

The experimental estimate of u_λ in (26) is obtained by an extrapolation of the measured u curve plotted against C_P.[8] Since C_P has an essential singularity, the extrapolation of the experimental curve of u and the asymptotic value of u_λ (when $C_P \to \infty$), should agree.

Thus, the observed behavior of K_T, β_V, C_V, C_P, and α_P in the experimentally accessible temperature region can be understood from the inequalities (27)–(29), while the sound-velocity formulas (25) and (26) are generally correct in both the experimental region and in the true asymptotic limit.

[7] The Fairbank and Buckingham estimate (Ref. 3) is ≈370 J/g °K. The precise number is not important at this point. The predicted value $C_V(T_\lambda)$ is clearly much larger than the 11 J/g °K quoted for $T = T_\lambda + 6\text{–}8 \times 10^{-3}$ °K.

[8] I. Rudnick and K. A. Shapiro, Phys. Rev. Letters **15**, 386 (1965).

[9] This fact was pointed out by C. E. Chase, E. Maxwell, and W. E. Millet, Physica **27**, 1129 (1961). Their estimate of a^{I}/b is -68.

VI. QUANTITATIVE COMPARISON WITH EXPERIMENT

If we use the isobaric asymptotic expansions (13)–(15), we find from (4)–(6) the asymptotic forms

$$K_T=K_1^{\mathrm{I,II}}+K_2\log|T-T_\lambda|+O(|T-T_\lambda|),\quad(33)$$

$$\alpha_P=\alpha_1^{\mathrm{I,II}}+\alpha_2\log|T-T_\lambda|+O(|T-T_\lambda|),\quad(34)$$

$$C_P=C_1^{\mathrm{I,II}}+C_2\log|T-T_\lambda|+O(|T-T_\lambda|),\quad(35)$$

where the superscripts I and II refer to $T>T_\lambda$ and $T<T_\lambda$, respectively, and

$$K_1^{\mathrm{I,II}}=(k\beta_\lambda^2/N^2)T_\lambda V_\lambda a^{\mathrm{I,II}},\qquad K_2=(k\beta_\lambda^2/N^2)T_\lambda V_\lambda b,\quad(36)$$

$$\alpha_1^{\mathrm{I,II}}=\alpha_0+(k\beta_\lambda^2/N^2)T_\lambda V_\lambda \sigma a^{\mathrm{I,II}},\qquad \alpha_2=(k\beta_\lambda^2/N^2)T_\lambda V_\lambda\sigma b,\quad(37)$$

$$C_1^{\mathrm{I,II}}=C_0+\sigma T_\lambda V_\lambda\alpha_1^{\mathrm{I,II}},\quad C_2=\sigma T_\lambda V_\lambda \alpha_2.\quad(38)$$

The inequalities (28) and (29), in terms of the parameters defined by (37) and (38), are $|\alpha_1^{\mathrm{I,II}}|\ll|\alpha_2|\times|a^{\mathrm{I,II}}/b|$ and $|C_1^{\mathrm{I,II}}|\ll C_2|a^{\mathrm{I,II}}/b|$, respectively. Our analysis of the experimental data shows that these inequalities are indeed satisfied and that their validity leads to the observed logarithmic behavior of α_P and C_P. In addition to the ordinary thermodynamic variables on the λ line, we have the five parameters α_0 [related to ΔNE_R by Eq. (17)], C_0 [related to ΔE_R^2 by Eq. (18)], $a^{\mathrm{I,II}}$, and b. Each of these is a function of pressure P_λ. Again, we emphasize that (33)–(35) are supposed to be valid for any pressure P_λ and for any temperature closer to the λ line than $|T-T_\lambda|\sim10^{-3}$ °K. The equations can be used to obtain forms for $C_V=C_P-TV\alpha_P^2/K_T$ and $\beta_V=\alpha_P/K_T$ which are also valid in this region.

If we restrict our attention to the point where P_λ equals the vapor pressure ($T_\lambda=T_0$), we may find experimental values for our parameters. α_0 has been measured directly,[10] $C_1^{\mathrm{I,II}}$ and C_2 are known from very accurate C_P measurements along the vapor-pressure curve.[3] C_0 has not been measured directly, but can be estimated from the slope of the family of entropy curves at different pressures. From the data of Lounasmaa and Kojo,[11] we obtain an estimate $C_0\approx4.85$ J/g °K. We will use this value, recognizing that slightly different choices are possible. Other necessary numerical values along the vapor pressure curve at T_0 are[10]

$$T_0=2.117\text{°K},\quad \sigma=-97.805\ \text{atm/°K},$$
$$P_0=0.050\ \text{atm},\quad \alpha_0=1.227\text{°K}^{-1},\quad(39)$$
$$\rho_0=0.1461\ \text{g/cm}^3,$$

while the specific-heat data of Buckingham and Fairbank give

$$C_1^{\mathrm{I}}=-0.65\ \text{J/g °K},$$
$$C_1^{\mathrm{II}}=\ 4.55\ \text{J/g °K},\quad(40)$$
$$C_2=-3.00\ \text{J/g °K}.$$

Equation (38), together with the choice for C_0 described above and the experimental values (40), yields

$$a^{\mathrm{I}}/N=7.95\times10^{-2},$$
$$a^{\mathrm{II}}/N=8.21\times10^{-2},\quad(41)$$
$$b/N=-1.36\times10^{-3}.$$

The quantities $\alpha_1^{\mathrm{I,II}}$ and α_2 have been measured directly.[6,9] In addition, measurement of the adiabatic sound velocity[8] provides an experimental value for u_λ^2 and for C_0/σ if we use the theoretical results in (25) and (26). In Table I we compare the theoretical estimates of these five quantities with the experimentally determined values. We have also included the theoretical values for the compressibility, although no direct experimental data for this quantity along the vapor-pressure curve are available.

In obtaining theoretical expressions for β_V and C_V, we must use the "pseudo-asymptotic" expansion, recognizing that the experimentally available temperature region will always be such that $(b/a)\log|T-T_\lambda|\ll1$. In this region the expansion (31), together with Eqs. (33)–(35) and the thermodynamic identities, leads to the following expressions:

$$\beta_V=\beta_1^{\mathrm{I,II}}+\beta_2^{\mathrm{I,II}}\log|T-T_\lambda|+O[((b/a)\log|T-T_\lambda|)^2],\quad(42)$$

$$C_V=\bar{C}_1^{\mathrm{I,II}}+\bar{C}_2^{\mathrm{I,II}}\log|T-T_\lambda|+O[((b/a)\log|T-T_\lambda|)^2],\quad(43)$$

for $(a/b)\log|T-T_\lambda|\ll1$ and $|T-T_\lambda|<10^{-3}$ °K. The constants are given by

$$\beta_1^{\mathrm{I,II}}=\alpha_1^{\mathrm{I,II}}/K_1^{\mathrm{I,II}},\quad(44)$$
$$\beta_2^{\mathrm{I,II}}=\alpha_2/K_1^{\mathrm{I,II}}-K_2\alpha_1^{\mathrm{I,II}}/(K_1^{\mathrm{I,II}})^2,$$

$$\bar{C}_1^{\mathrm{I,II}}=C_1^{\mathrm{I,II}}-T_\lambda V_\lambda(\alpha_1^{\mathrm{I,II}})^2/K_1^{\mathrm{I,II}},\quad(45)$$
$$\bar{C}_2^{\mathrm{I,II}}=C_2[1-\alpha_1^{\mathrm{I,II}}K_2/\alpha_2K_1^{\mathrm{I,II}}]^2.$$

Therefore, we can calculate theoretical values for the

TABLE. I. Comparison of experimental and theoretical parameters along the vapor-pressure curve.

	Unit	Theoret.	Eq. No.
$\bar{C}_1^{\mathrm{I}}$	J/g°K	−0.81	(45)
$\bar{C}_1^{\mathrm{II}}$	J/g°K	4.55	(45)
$\bar{C}_2^{\mathrm{I}}$	J/g°K	−3.18	(45)
$\bar{C}_2^{\mathrm{II}}$	J/g°K	−3.00	(45)
β_1^{I}	atm/°K	2.2	(44)
β_1^{II}	atm/°K	4.0×10^{-2}	(44)
β_2^{I}	atm/°K	1.7	(44)
β_2^{II}	atm/°K	1.6	(44)

[10] O. V. Lounasmaa and L. Kannisto, in *Proceedings of the International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1961), p. 535.

[11] O. V. Lounasmaa and E. Kojo, Physica 36, 3 (1959).

parameters appearing in (42) and (43) in the case where P_λ is the vapor pressure. Although no experimental verification is possible, we have entered the calculated parameters in Table II. In order to test these results, we need direct experimental data for K_T, C_V, and β_V along the vapor-pressure curve.

In order to analyze Lounasmaa's data, we should note that the constant-volume expansions of the fluctuations have the same form as the isobaric expansions (13)–(15). This follows from the fact that the form of Λ [Eq. (9)] provided by the microscopic theory yields a constant-volume expansion identical in form to (13). Alternatively, our entire analysis, with its emphasis on specific assumptions about the fluctuations, could have been translated to the V, T plane. Of course, the constants a and b will be different. Specifically the five constants α_0, C_0, $a^{\mathrm{I,II}}$, and b are functions of V_λ.

If the linear dependence of K_T is neglected ($|T-T_\lambda| \lesssim 10^{-3}$ °K), Eqs. (36), (37), and (44) imply

$$\beta_1^{\mathrm{I,II}}=\sigma+\alpha_0/K_1^{\mathrm{I,II}}. \tag{46}$$

Using Lounasmaa's values[4] at $P_\lambda=13.05$ atm [see Eqs. (23a) and (23b)], we find

$$\sigma=-81\ \mathrm{atm/°K}, \qquad \alpha_0=0.67\ \mathrm{°K^{-1}}. \tag{47}$$

These should be compared with the directly measured values[10]

$$\sigma=-72.88\ \mathrm{atm/°K}, \qquad \alpha_0=0.533\ \mathrm{°K^{-1}}. \tag{48}$$

Since no other logarithmically dependent quantities are measured around this point, we cannot make a similar analysis of $\beta_2^{\mathrm{I,II}}$. We should emphasize that the theoretical estimates in Tables I and II, as well as the results in Eq. (47), are not very precise. The numbers given have been calculated using (39), and there is a large cancelation in expressions like (37).

VII. CONCLUSION

We have shown that a certain set of phenomenological statements about fluctuations near the λ line yields a consistent picture of thermodynamic derivatives in the vicinity of this line. These statements appear to follow from a particular microscopic theory. However, the complete theory is not necessary for an understanding of the implications, and the microscopic analysis leading to the fluctuation statements will be discussed in a separate paper. We should emphasize that this analysis does not enable us to calculate the five parameters $a^{\mathrm{I,II}}$, b, ΔNE_R, and ΔE_R^2 explicitly. However, the form of the fluctuations, with the appearance of the above parameters, can be obtained by a particular approximation scheme for the thermodynamic Green's functions. Since the primary purpose of this paper is to examine the implications of this scheme's fluctuation statements, we have chosen to treat such statements as phenomenological assumptions. Having made these assumptions, we carry out a purely thermodynamic analysis which leads to the familiar PBF relations and to a set of Ehrenfest-like relations.

The five unknown parameters are determined by using appropriate experimental results. There then remain several additional quantities, determined by the same parameters, which we have calculated and compared with experiment (Table I). Direct experimental determination of quantities like K_T and C_V along the vapor-pressure curve would make additional comparison (with Table II) possible.

TABLE II. Calculated values of the parameters appearing in C_V and β_V for the pseudo-asymptotic temperature range along the vapor-pressure curve.

	Unit	Theoret.	Eq. No.	Expt.	Ref.
α_1^{I}	°K^{-1}	36×10^{-3}	(37)	49×10^{-3}, 38×10^{-3}	a
α_1^{II}	°K^{-1}	0.5×10^{-3}	(37)	1×10^{-3}, 2.47×10^{-3}	a
α_2	°K^{-1}	20×10^{-3}	(37)	21×10^{-3}, 16×10^{-3}	a
C_0/σ	J/g atm	-4.96×10^{-2}	(25)	-4.88×10^{-2}	b
u_λ^2	m^2/sec^2	5.39×10^4	(26)	4.76×10^4	b
K_1^{I}	atm^{-1}	1.2×10^{-2}	(36)		
K_1^{II}	atm^{-1}	1.3×10^{-2}	(36)		
K_2	atm^{-1}	-2.1×10^{-4}	(36)		

[a] References 6 and 9.
[b] Reference 8.