THE BEHAVIOR OF THERMODYNAMIC QUANTITIES NEAR THE λ-CURVE

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We show that the existing experiments on the thermodynamics of the λ-transition can be explained within the framework of a simple semi-phenomenological theory. This theory is based upon the fact that the slope of the λ-curve in the (μ, T) plane is large, and upon the assumption that C_p has a logarithmic singularity all along the λ-curve.

THE phenomenological considerations of Pippard [1] show that it follows, from the fact that the specific heat C_p becomes infinite on the λ-curve, that the compressibility $k_T = -V^{-1}(\partial V/\partial p)_T$ and the coefficient of thermal expansion $\alpha = V^{-1}(\partial V/\partial T)_p$ are infinite on the same curve, while C_V and $\beta = (\partial p/\partial T)_p$ show finite jumps (see also the review article by Buckingham and Fairbank [2]). The behavior of C_p and α has been studied experimentally in the neighborhood of the λ-point (the point where the λ-curve intersects the liquid-vapor curve). The data given in [2] are evidence of the fact that both these quantities have a logarithmic singularity in the transition point. Lounasmaa [3] has recently published the results of measurements of k_T and β in the vicinity of another point on the λ-curve: $T_\lambda = 2.023$°K, $V_\lambda = 24.2$ cm^3 mole^{-1}, $p_\lambda = 13.04$ atm. It turned out that β can well be represented by a linear function of $\ln|T - T_\lambda|$, while k_T does not show a logarithmic singularity, but only a small, finite jump. Lounasmaa's data are in direct contradiction to Pippard's theory.[1]

In the present paper we construct a semi-phenomenological theory of the λ-transition in He which is in agreement with the experimental data. The theory is based upon two facts:

1) the logarithmic behavior of C_p near the λ-curve,

2) the large value of the dimensionless quantity $(\partial\mu/\partial T)_\lambda$ (μ = chemical potential).

Strictly speaking, the logarithmic behavior of C_p is established near the λ-point; we shall, however, assume a similar behavior on the whole of the λ-curve.

The quantity $(\partial\mu/\partial T)_\lambda$ can be expressed in terms of quantities which are known experimentally, through the formula

$$(\partial\mu / \partial T)_\lambda = M\{-s + \rho^{-1}(\partial p / \partial T)_\lambda\}, \tag{1}$$

where M is the mass of a He atom, s the entropy per gram, and ρ the specific weight. The values of ρ and $(\partial p/\partial T)_\lambda$ can be taken from [2], and s from Mendelssohn's review article.[4] It turns out that $(\partial\mu/\partial T)_\lambda$ fluctuates between −20 and −45. This quantity is the large parameter of the problem and must be taken explicitly into account in the calculations.

Let the transition curve of the problem be given by the equation

$$\eta(\mu, T) = 0.$$

Let us introduce a quantity η as one of the new coordinates in the immediate vicinity of the transition curve. We shall assume that η has near any arbitrary point of the curve (μ_0, T_0) an expansion

$$\eta = a(\mu - \mu_0) + b(T - T_0),$$

$$b / a = -(\partial\mu / \partial T)_\lambda \gg 1. \tag{2}$$

We can introduce as another variable any coordinate which registers a point on the transition curve, for instance, the length of the curve l. The thermodynamical quantities have a singularity as $\eta \to 0$ for any value of l. We shall thus assume that C_p has a singularity of the form

$$C_p = A(l) \ln|\eta| + B(l). \tag{3}$$

From (3) we can establish the singular part of the potential $\Phi(T, p, N)$ and then also of $\Omega(T, V, \mu)$. Indeed, integrating (3) twice over T keeping p and N fixed, we get

$$\Phi \sim \eta^2 \ln|\eta|.$$

We find thus for $\Omega = -Vp(\mu, T)$ the expression

$$\Omega = D(l)\eta^2 \ln|\eta| + \Omega_{\mathrm{reg}}. \tag{4}$$

Using the experimental data for k_T and α[5] and for C_p[2] at the λ-point, we can easily estimate the derivatives of Ω_{reg}(He I):

$$(\Omega_{\mu T})_{reg} \sim (\Omega_{\mu\mu})_{reg} \approx -6\cdot 10^{36}\ \mathrm{erg}^{-1}\ \mathrm{cm}^{-3},\qquad (\Omega_{TT})_{reg} \approx -5\cdot 10^{38}\ \mathrm{erg}^{-1}\ \mathrm{cm}^{-3}. \tag{5}$$

Here Ω is taken per unit volume and the temperature is measured in energy units. The fact that $(\Omega_{\mu\mu})_{reg}$ and $(\Omega_{\mu T})_{reg}$ are small compared with $(\Omega_{TT})_{reg}$ is a consequence of the fact that the compressibility of the liquid is small.

Differentiating (4) we find

$$\Omega_{\mu\mu} = Da^2 \ln|\eta| + (\Omega_{\mu\mu})_{reg}, \tag{6}$$

$$\Omega_{\mu T} = Dab \ln|\eta| + (\Omega_{\mu T})_{reg}, \tag{7}$$

$$\Omega_{TT} = Db^2 \ln|\eta| + (\Omega_{TT})_{reg}. \tag{8}$$

The coefficients of $\ln|\eta|$ in (6), (7), and (8) differ in the λ-point by a factor 45. The ratio of the regular parts in (6) and (7) is equal to ≈ 1 [cf. (5)]. The singular part of $\Omega_{\mu\mu}$ will therefore be small in the temperature range where the singular and the regular parts of $\Omega_{\mu T}$ are of the same order of magnitude. Because $\ln|\eta|$ increases slowly, the region where the singular part of $\Omega_{\mu\mu}$ is significant will be practically inaccessible:

$$\ln(|T - T_\lambda| / T_\lambda) \sim -10.$$

We now find the thermodynamic quantities:

$$k_T = -n^{-2}\Omega_{\mu\mu}, \tag{9}$$

$$\beta = \beta_{reg} - n\Omega_{\mu\mu}^{-1} Dab \ln|\eta|, \tag{10}$$

$$C_V = -T\Omega_{TT} + T\Omega_{\mu T} / \Omega_{\mu\mu} = (C_V)_{reg} - TDb^2 \ln|\eta| [1 - Da^2 \ln|\eta| / \Omega_{\mu\mu}]. \tag{11}$$

We have already explained that $Da^2 \ln|\eta| \ll \Omega_{\mu\mu}$. One checks easily that the singular parts of C_p and C_V are the same while the regular parts differ by a relatively small quantity $\sim(\Omega_{\mu T}/\Omega_{TT})_{reg}$.

We note that if we had started from the logarithmic behavior of C_V we would have obtained for $F(T, V, N)$ a singularity of the form

$$F \sim -\eta^2 \ln|\eta|,$$

which at first sight leads to an instability of the system: $(\partial p/\partial V)_T > 0$. Of course, there is in actual fact no instability because the singularity in C_V is only apparent, and in the immediate vicinity of the λ-curve C_V tends to a finite limit.

We have shown that k_T shows a finite jump, while β and C_V behave as linear functions of $\ln|T - T_\lambda|$; this agrees qualitatively with Lounasmaa's experiments[3] (for a quantitative agreement one would have to measure the specific heat).

The theory admits a quantitative check at the λ-point. To do this we compare the magnitude of the quantity b/a found from the slope of the λ-curve with the same quantity found from the ratio of the coefficients of $\ln|T - T_\lambda|$ of α[4] and of C_p.[2] These quantities turn out to be equal to 45 and 30, respectively. It follows experimentally that k_T tends to different limits as $T \to T_\lambda \pm 0$. The coefficients of $\ln|\eta|$ in β are thus also different below and above the λ-curve (cf. [3]). The corresponding coefficients in C_p are the same.

It seems remarkable that $(\partial\mu/\partial T)_\lambda$ is large. For a perfect gas $(\partial\mu/\partial T)_\lambda = 0$. One usually assumes that the interaction in He is relatively weak. The large value of $(\partial\mu/\partial T)_\lambda$ indicates, apparently, that perturbation theory is inapplicable even for relatively small values of the coupling constant.

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