HOLE THEORY AND LIQUID He II.

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During recent years the theory of the liquid state has attracted considerable attention and several working models have been proposed to make it amenable to the methods of statistical mechanics. In the model discussed by Fürth (1941) the liquid is considered to be a continuum permeated with holes—the number of holes being equal to, or at any rate comparable to, the number of molecules. The radius of a hole is constantly changing and, in fact, a hole is characterised by four degrees of freedom, three corresponding to translation and the fourth corresponding to its radial oscillation. In the hole theory the atomic structure of the liquid has to be suppressed in order to provide a working model and because of this inherent weakness it can only be expected to give no better than order of magnitude comparison with experiment.

As the holes move in the material continuum much as the molecules do in the case of a gas, there is a formal similarity, clearly brought out and made use of by Fürth, between the hole theory and the kinetic theory of gases. Fürth has considered only the classical or the non-degenerate case. In this paper we extend it to the degenerate case and consider its possible application to liquid He II. The present paper is in the nature of a preliminary attempt and as such suffers from various limitations.

Let us consider a liquid continuum at temperature T and occupying a volume V. The number of wave functions for a hole corresponding to its kinetic energy lying between ϵ and $\epsilon+d\epsilon$, its radius between r and $r+dr$ and the conjugate momentum between p_r and p_r+dp_r is given by

$$a(\epsilon, p_r, r)d\epsilon\, dp_r dr = \frac{2\pi V(2m_1)^{3/2}\epsilon^{1/2}d\epsilon dp_r dr}{h^4}, \quad \ldots \quad (1)$$

where m_1 is the apparent mass of a hole corresponding to translatory motion and has the value

$$m_1 = \frac{2\pi}{3} r^3\rho, \quad \ldots \quad (2)$$

ρ being the density of the liquid. If $n(\epsilon, p_r, r)d\epsilon dp_r dr$ denotes the number of holes per unit volume having their kinetic energy lying between ϵ and $\epsilon+d\epsilon$, the radius between r and $r+dr$ and the conjugate momentum between p_r and p_r+dp_r then the distribution law is

$$n(\epsilon, p_r, r)\, d\epsilon\, dp_r dr = \frac{2\pi}{h^4} \frac{(2m_1)^{3/2}\epsilon^{1/2}\, d\epsilon\, dp_r dr}{\frac{1}{A}\,\mathrm{Exp.}\,[(w+\epsilon+p_r^2/2m_2)/kT]+\beta}, \quad \ldots \quad (3)$$

where w is the work done in forming a hole and is given by

$$w = 4\pi r^2\sigma + \frac{4\pi r^3}{3}(p-p_0),$$

σ being the surface tension of the liquid, p the external pressure, and p_0 the saturation vapour pressure of the liquid. m_2 denotes the apparent mass of the hole corresponding to radial oscillation and is given by

$$m_2 = 4\pi r^3\rho. \quad \ldots \quad (4)$$

As the holes presumably obey the Bose-Einstein statistics, we shall take $\beta = -1$. In this paper we shall consider the case of a liquid under its own vapour pressure, i.e. $p = p_0$, and hence

$$w = 4\pi r^2\sigma.$$

In the non-degenerate or classical case $A \ll 1$ and for degeneracy $A = 1$. In the degenerate case the number of holes, excluding those in the zero energy state, is given by

$$\frac{2\pi}{h^4}\int \frac{(2m_1)^{3/2}\epsilon^{1/2}d\epsilon\, dp_r dr}{\text{Exp.}\left[(w+\epsilon+p_r^2/2m_2)/kT\right]-1}, \quad .. \quad .. \quad .. \quad (5)$$

which we shall denote by n^*.

Integrating (5) with respect to p_r we have

$$n^* = \frac{4\pi^{3/2}}{h^4}\int (m_1)^{3/2}\epsilon^{1/2}d\epsilon\, dr \sum_{s=1}^{\infty}\left(\frac{m_2 kT}{s}\right)^{1/2} e^{-\frac{s(\epsilon+4\pi r^2\sigma)}{kT}},$$

and integrating further with respect to ϵ we have

$$n^* = 2\left(\frac{\pi kT}{h^2}\right)^2 \int m_1^{3/2} m_2^{1/2} \sum_{s=1}^{\infty} \frac{e^{-s4\pi r^2\sigma/kT}}{s^2}\, dr.$$

Substituting the expressions for m_1 and m_2 and integrating over r, we have finally

$$n^* = \frac{5}{\sqrt{6}}\,\frac{\pi}{128}\,\frac{\rho^2(kT)^{11/2}}{h^4\sigma^{7/2}}\,\xi(11/2). \quad .. \quad .. \quad .. \quad (6)$$

We shall speak of n^* as the number of energetic holes to distinguish them from holes in the zero energy state. The value of n^* decreases rapidly with temperature and, as n^* cannot exceed the number of molecules per unit volume of the liquid, the temperature T^* at which degeneracy sets in is given by

$$n^* = \frac{\rho}{m} = \frac{5}{\sqrt{6}}\cdot\frac{\pi}{128}\,\frac{\rho^2(kT)^{11/2}}{h^4\sigma^{7/2}}\,\xi(11/2),$$

$$\text{or } T^* = \left[\frac{\sqrt{6}}{5}\,\frac{128}{\pi}\,\frac{Nh^4\sigma^{7/2}}{M\rho k^{11/2}\xi(11/2)}\right]^{2/11}, \quad .. \quad .. \quad .. \quad (7)$$

where m is the mass of a molecule (not to be confused with the apparent mass of a hole). Above T^* the assembly of holes is non-degenerate whereas for temperatures lower than T^* it is in the degenerate state.

We shall now derive an expression for the energy E of the assembly. It is given by

$$E = \int\left(\epsilon+\frac{p_r^2}{2m_2}+w\right)n(\epsilon, p_r, r)\, d\epsilon\, dp_r\, dr. \quad .. \quad .. \quad .. \quad (8)$$

For the degenerate case it becomes

$$E = \frac{55}{\sqrt{6}}\,\frac{\pi\rho^2}{256}\,\frac{(kT)^{13/2}}{h^4\sigma^{7/2}}\,\xi(13/2) = \frac{11}{2}\,n^*kT\,\frac{\xi(13/2)}{\xi(11/2)}. \quad .. \quad .. \quad (9)$$

We may consider at this stage a tentative application of these results to liquid He II. In London's theory (1939) of liquid He II the atoms constitute the degenerate state, whereas here it is the holes which form the degenerate phase. London found that in the case of an ideal Bose-Einstein gas, i.e. particles having no size and no mutual forces, it is only the (temperature) derivative of the specific heat which is discontinuous at the λ-point and not the specific heat itself. In order to account for the large specific heat discontinuity of liquid helium observed at the λ-point, London had to assume the number of wave functions for a particle having its kinetic energy between ϵ and $\epsilon+d\epsilon$ to be nearly proportional to ϵ^4, whereas in the case of a particle moving in a field free

region this number varies as $\epsilon^{1/2}$. London suggested that the ϵ^4-law would presumably be the result of the interaction between the particles. In the hole model on the other hand the atomic forces enter (though crudely) into the theory through σ, the surface tension, and it is of interest to observe that the specific heat discontinuity follows from it immediately. (The essential reason for the existence of the discontinuity is that in the case of a hole, unlike the case of a particle, we have to deal with four degrees of freedom and not three.) The specific heat per unit mass of the liquid under its own vapour pressure is immediately obtained from (9) ignoring the negligible work done against the external pressure. We have

$$C_- = \frac{13}{2}\frac{55}{\sqrt{6}}\frac{\pi\rho^2 k}{256}\frac{(kT)^{11/2}}{h^4\sigma^{7/2}}\xi(13/2) = \frac{143}{4}n^* k\frac{\xi(13/2)}{\xi(11/2)}. \quad .. \quad .. \quad (10)$$

The minus suffix represents the degenerate case. It is interesting to note that the predicted variation of the specific heat is in agreement with the observed temperature-variation of the specific heat of He II. At the λ-point

$$C_- = \frac{13}{2}\frac{55}{\sqrt{6}}\frac{\pi\rho^2 k}{256}\frac{(kT^*)^{11/2}}{h^4\sigma^{7/2}}\xi(13/2) = \frac{143}{4}nk\frac{\xi(13/2)}{\xi(11/2)}. \quad .. \quad .. \quad (11)$$

In order to find out the magnitude of the specific heat discontinuity at the λ-point, we must determine the specific heat for the non-degenerate case and evaluate its limiting value at $A = 1$. From (3) and (8) we have, after integrating with respect to the variables ϵ, p_r and r

$$n = \frac{5}{\sqrt{6}}\frac{\pi}{128}\frac{\rho^2(kT)^{11/2}}{h^4\sigma^{7/2}}\sum_{s=1}^{\infty} A^s/s^{11/2},$$

$$E = \frac{55}{\sqrt{6}}\frac{\pi}{256}\frac{\rho^2(kT)^{13/2}}{\sigma^{7/2}}\sum_{s=1}^{\infty} A^s/s^{13/2}, \quad .. \quad .. \quad .. \quad (12)$$

where n is the number of holes and E the energy, both referring to unit volume of the assembly. Defining a dimensionless parameter A_0 by the relation

$$A_0 = n\frac{\sqrt{6}}{5}\frac{128}{\pi}\frac{h^4\sigma^{7/2}}{\rho^2(kT)^{11/2}} = \sum_{s=1}^{\infty} A^s/s^{11/2}, \quad .. \quad .. \quad .. \quad (13)$$

we have, after inverting the series (13),

$$A = A_0 - \frac{A_0^2}{2^{11/2}} - \left(\frac{1}{3^{11/2}} - \frac{1}{4^5}\right)A_0^3 - \cdots \quad .. \quad .. \quad (14)$$

Substituting this value of A in (12) we obtain

$$E = \frac{11}{2}nkT\left[1 - \frac{A_0}{2^{13/2}} - A_0^2\left(\frac{2}{3^{13/2}} - \frac{1}{2^{11}}\right) - \cdots\right], \quad .. \quad .. \quad (15)$$

and hence for the specific heat in the non-degenerate state we have

$$C_+ = \frac{11}{2}nk\left[1 + \frac{9}{2}\frac{A_0}{2^{13/2}} + 10A_0^2\left(\frac{2}{3^{13/2}} - \frac{1}{2^{11}}\right) + \cdots\right]. \quad .. \quad .. \quad (16)$$

Approaching the λ-point from the non-degenerate side we obtain for the specific heat at the λ-point

$$C_+ = \frac{11}{2}nk\left[1 + \frac{9}{2}\frac{A_0}{2^{13/2}} + 10A_0^2\left(\frac{2}{3^{13/2}} - \frac{1}{2^{11}}\right) + \cdots\right],$$

$$= \frac{11}{2}nk\left[1 + \frac{9}{2}\frac{\xi(11/2)}{2^{13/2}} + 10\left(\frac{2}{3^{13/2}} - \frac{1}{2^{11}}\right)(\xi(11/2))^2 + \cdots\right], \quad .. \quad (17)$$

and hence we obtain for the discontinuity for the specific heat at the λ-point the expression

$$C_- - C_+ = \frac{11}{2} nk\left[\frac{13}{2}\frac{\xi(13/2)}{\xi(11/2)} - \left\{1+\frac{9}{2}\frac{\xi(11/2)}{2^{13/2}}+10\left(\frac{2}{3^{13/2}}-\frac{1}{2^{11}}\right)(\xi(11/2))^2+\ldots\right\}\right], \quad (18)$$

where at the λ-point the concentration of the holes is of course given by

$$n = n^* = \frac{5}{\sqrt{6}}\frac{\pi}{128}\frac{\rho^2(kT)^{11/2}}{h^4\sigma^{7/2}}\xi(11/2).$$

Assuming that the number of holes is equal to the number of atoms in the liquid we obtain

$$C_- - C_+ = \frac{11}{2}\frac{R}{M}\left[\frac{13}{2}\frac{\xi(13/2)}{\xi(11/2)} - \left\{1+\frac{9}{2}\frac{\xi(11/2)}{2^{13/2}}+10\left(\frac{2}{3^{13/2}}-\frac{1}{2^{11}}\right)(\xi(11/2))^2+\ldots\right\}\right],$$

$$\text{or } C_- - C_+ \sim 14{\cdot}6 \text{ Cal.} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (19)$$

This may be compared with the observed discontinuity which somewhat exceeds 5 calories per gram. It is satisfactory that the theoretical discontinuity is larger than the observed one.

It may be remarked that the temperature of the λ-point as given by the theoretical expression is (taking $\sigma = 0{\cdot}32$ and $\rho = 0{\cdot}146$) 12·9 which is about five times larger than the observed value but considering the uncertainty in the value of σ and the crude nature of the theory the agreement is not unreasonable.

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