where $\rho(\epsilon)\, d\epsilon$ is the number of *translational* states lying in the energy range between ϵ and $\epsilon + d\epsilon$. The factor of 2 in (9·17·1) accounts for the two possible spin states which exist for each translational state. Here the Fermi energy μ is to be determined by the condition (9·16·3), i.e.,

$$2 \int F(\epsilon)\rho(\epsilon)\, d\epsilon = 2 \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)}+1}\, \rho(\epsilon)\, d\epsilon = N \qquad (9\cdot 17\cdot 2)$$

Evaluation of integrals All these integrals are of the form

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\, d\epsilon \qquad (9\cdot 17\cdot 3)$$

where $F(\epsilon)$ is the Fermi function (9·16·4) and $\varphi(\epsilon)$ is some smoothly varying function of ϵ. The function $F(\epsilon)$ has the form shown in Fig. 9·16·1, i.e., it decreases quite abruptly from 1 to 0 within a narrow range of order kT about $\epsilon = \mu$, but is nearly constant everywhere else. This immediately suggests evaluating the integral (9·17·3) by an approximation procedure which exploits the fact that $F'(\epsilon) \equiv dF/d\epsilon = 0$ everywhere except in a range of order kT near $\epsilon = \mu$ where it becomes large and negative. Thus one is led to write the integral (9·17·3) in terms of F' by integrating by parts.

Let
$$\psi(\epsilon) \equiv \int_0^\epsilon \varphi(\epsilon')\, d\epsilon' \qquad (9\cdot 17\cdot 4)$$

Then
$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\, d\epsilon = [F(\epsilon)\psi(\epsilon)]_0^\infty - \int_0^\infty F'(\epsilon)\psi(\epsilon)\, d\epsilon$$

But the integrated term vanishes, since $F(\infty) = 0$, while $\psi(0) = 0$ by (9·17·4). Hence

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\, d\epsilon = -\int_0^\infty F'(\epsilon)\psi(\epsilon)\, d\epsilon \qquad (9\cdot 17\cdot 5)$$

Here one has the advantage that, by virtue of the behavior of $F'(\epsilon)$, only the relatively narrow range of order kT about $\epsilon = \mu$ contributes appreciably to the integral. But in this small region the relatively slowly varying function ψ can

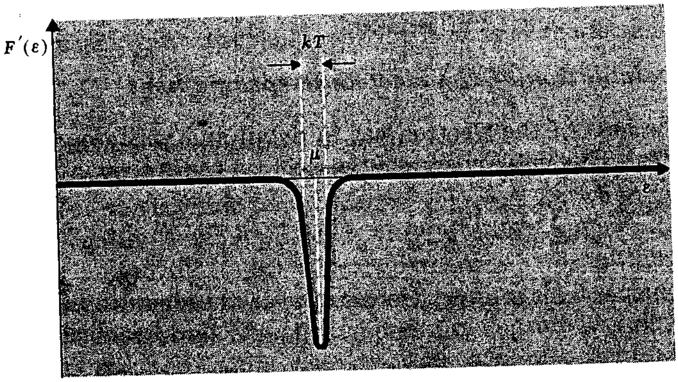

Fig. 9·17·1 The derivative $F'(\epsilon)$ of the Fermi function as a function of ϵ.

be expanded in a power series

$$\psi(\epsilon) = \psi(\mu) + \left[\frac{d\psi}{d\epsilon}\right]_\mu (\epsilon - \mu) + \frac{1}{2}\left[\frac{d^2\psi}{d\epsilon^2}\right]_\mu (\epsilon - \mu)^2 + \cdots = \sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi}{d\epsilon^m}\right]_\mu (\epsilon - \mu)^m$$

where the derivatives are evaluated for $\epsilon = \mu$. Hence (9·17·5) becomes

$$\int_0^\infty F\varphi\, d\epsilon = -\sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi}{d\epsilon^m}\right]_\mu \int_0^\infty F'(\epsilon)(\epsilon - \mu)^m\, d\epsilon \tag{9·17·6}$$

But $\int_0^\infty F'(\epsilon)(\epsilon - \mu)^m\, d\epsilon = -\int_0^\infty \frac{\beta e^{\beta(\epsilon-\mu)}}{(e^{\beta(\epsilon-\mu)} + 1)^2} (\epsilon - \mu)^m\, d\epsilon$

$$= -\beta^{-m} \int_{-\beta\mu}^\infty \frac{e^x}{(e^x + 1)^2} x^m\, dx$$

where

$$x \equiv \beta(\epsilon - \mu) \tag{9·17·7}$$

Since the integrand has a sharp maximum for $\epsilon = \mu$, (i.e., for $x = 0$) and since $\beta\mu \gg 1$, the lower limit can be replaced by $-\infty$ with negligible error. Thus one can write

$$\int_0^\infty F'(\epsilon)(\epsilon - \mu)^m\, d\epsilon = -(kT)^m I_m \tag{9·17·8}$$

where

$$I_m \equiv \int_{-\infty}^\infty \frac{e^x}{(e^x + 1)^2} x^m\, dx \tag{9·17·9}$$

Note that

$$\frac{e^x}{(e^x + 1)^2} = \frac{1}{(e^x + 1)(e^{-x} + 1)}$$

is an even function of x. If m is odd, the integrand in (9·17·9) is then an odd function of x so that the integral vanishes; thus

$$I_m = 0 \qquad \text{if } m \text{ is odd} \tag{9·17·10}$$

Also

$$I_0 = \int_{-\infty}^\infty \frac{e^x}{(e^x + 1)^2}\, dx = -\left[\frac{1}{e^x + 1}\right]_{-\infty}^\infty = 1 \tag{9·17·11}$$

By using (9·17·8), the relation (9·17·6) can then be written in the form

$$\int_0^\infty F\varphi\, d\epsilon = \sum_{m=0}^{\infty} I_m \frac{(kT)^m}{m!}\left[\frac{d^m\psi}{d\epsilon^m}\right]_\mu = \psi(\mu) + I_2 \frac{(kT)^2}{2}\left[\frac{d^2\psi}{d\epsilon^2}\right]_\mu + \cdots \tag{9·17·12}$$

The integral I_2 can readily be evaluated (see Problems 9.26 and 9.27). One finds

$$I_2 = \frac{\pi^2}{3}$$

Hence (9 · 17 · 12) becomes

$$\blacktriangleright \qquad \int_0^\infty F(\epsilon)\varphi(\epsilon)\,d\epsilon = \int_0^\mu \varphi(\epsilon)\,d\epsilon + \frac{\pi^2}{6}(kT)^2\left[\frac{d\varphi}{d\epsilon}\right]_\mu + \cdots \qquad (9\cdot17\cdot13)$$

Here the first term on the right is just the result one would obtain for $T \to 0$ corresponding to Fig. 9 · 16 · 2. The second term represents a correction due to the finite width ($\approx kT$) of the region where F decreases from 1 to 0.

Calculation of the specific heat We now apply the general result (9 · 17 · 13) to the evaluation of the mean energy (9 · 17 · 1). Thus one obtains

$$\bar{E} = 2\int_0^\mu \epsilon\rho(\epsilon)\,d\epsilon + \frac{\pi^2}{3}(kT)^2\left[\frac{d}{d\epsilon}(\epsilon\rho)\right]_\mu \qquad (9\cdot17\cdot14)$$

Since for the present case, where $kT/\mu \ll 1$, the Fermi energy μ differs only slightly from its value μ_0 at $T = 0$, the derivative in the second small correction term in (9 · 17 · 14) can be evaluated at $\mu = \mu_0$ with negligible error. Furthermore one can write

$$2\int_0^\mu \epsilon\rho(\epsilon)\,d\epsilon = 2\int_0^{\mu_0} \epsilon\rho(\epsilon)\,d\epsilon + 2\int_{\mu_0}^\mu \epsilon\rho(\epsilon)\,d\epsilon = \bar{E}_0 + 2\mu_0\rho(\mu_0)(\mu - \mu_0)$$

since the first integral on the right is by (9 · 17 · 1) just the mean energy $\bar{E}_0$ at $T = 0$. Since

$$\frac{d}{d\epsilon}(\epsilon\rho) = \rho + \epsilon\rho', \qquad \rho' \equiv \frac{d\rho}{d\epsilon}$$

Eq. (9 · 17 · 14) becomes

$$\bar{E} = \bar{E}_0 + 2\mu_0\rho(\mu_0)(\mu - \mu_0) + \frac{\pi^2}{3}(kT)^2[\rho(\mu_0) + \mu_0\rho'(\mu_0)] \qquad (9\cdot17\cdot15)$$

Here we still need to know the change $(\mu - \mu_0)$ of the Fermi energy with temperature. Now μ is determined by the condition (9 · 17 · 2) which becomes, by (9 · 17 · 13),

$$2\int_0^\mu \rho(\epsilon)\,d\epsilon + \frac{\pi^2}{3}(kT)^2\rho'(\mu) = N \qquad (9\cdot17\cdot16)$$

Here the derivative in the correction term can again be evaluated at μ_0 with negligible error, while

$$2\int_0^\mu \rho(\epsilon)\,d\epsilon = 2\int_0^{\mu_0} \rho(\epsilon)\,d\epsilon + 2\int_{\mu_0}^\mu \rho(\epsilon)\,d\epsilon = N + 2\rho(\mu_0)(\mu - \mu_0)$$

since the first integral on the right side is just the condition (9 · 17 · 2) which determined μ_0 at $T = 0$. Thus (9 · 17 · 16) becomes

$$2\rho(\mu_0)(\mu - \mu_0) + \frac{\pi^2}{3}(kT)^2\rho'(\mu_0) = 0$$

or

$$(\mu - \mu_0) = -\frac{\pi^2}{6}(kT)^2\frac{\rho'(\mu_0)}{\rho(\mu_0)} \qquad (9\cdot17\cdot17)$$

Hence Eq. (9·17·15) becomes

$$\bar{E} = \bar{E}_0 - \frac{\pi^2}{3}(kT)^2\mu_0\rho'(\mu_0) + \frac{\pi^2}{3}(kT)^2[\rho(\mu_0) + \mu_0\rho'(\mu_0)]$$

or

$$\bar{E} = \bar{E}_0 + \frac{\pi^2}{3}(kT)^2\rho(\mu_0) \tag{9·17·18}$$

since terms in ρ' cancel. The heat capacity (at constant volume) becomes then

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3}k^2\rho(\mu_0)T \tag{9·17·19}$$

This agrees with the simple order of magnitude calculation of Eq. (9·16·15).

The density of states ρ can be written explicitly for the free-electron gas by (9·9·19):

$$\rho(\epsilon)\,d\epsilon = \frac{V}{(2\pi)^3}\left(4\pi\kappa^2\frac{d\kappa}{d\epsilon}\,d\epsilon\right) = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\epsilon^{1/2}\,d\epsilon \tag{9·17·20}$$

But

$$\mu_0 = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3} \qquad \text{by (9·16·10)}$$

Hence

$$\rho(\mu_0) = V\frac{m}{2\pi^2\hbar^2}\left(3\pi^2\frac{N}{V}\right)^{1/3} \tag{9·17·21}$$

Equivalently this can be written in terms of N and μ_0 by eliminating the volume V between the last two equations. Thus one obtains

$$\rho(\mu_0) = \left[\frac{m}{2\pi^2\hbar^2}(3\pi^2N)^{1/3}\right]\left[\frac{1}{\mu_0}\frac{\hbar^2}{2m}(3\pi^2N)^{2/3}\right] = \frac{3}{4}\frac{N}{\mu_0} \tag{9·17·22}$$

Hence (9·17·19) gives

$$C_V = \frac{\pi^2}{2}k^2\frac{N}{\mu_0}T = \frac{\pi^2}{2}kN\frac{kT}{\mu_0} \tag{9·17·23}$$

or, per mole,

$$c_V = \frac{3}{2}R\left(\frac{\pi^2}{3}\frac{kT}{\mu_0}\right) \tag{9·17·24}$$

SUGGESTIONS FOR SUPPLEMENTARY READING

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