where \( \rho(\epsilon) \, d\epsilon \) is the number of translational states lying in the energy range between \( \epsilon \) 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 \( \mu \) is to be determined by the condition (9.16.3), i.e.,

\[
2 \int F(\epsilon) \rho(\epsilon) \, d\epsilon = 2 \int_{0}^{\infty} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \rho(\epsilon) \, d\epsilon = N \quad (9.17.2)
\]

**Evaluation of integrals** All these integrals are of the form

\[
\int_{0}^{\infty} F(\epsilon) \varphi(\epsilon) \, d\epsilon \quad (9.17.3)
\]

where \( F(\epsilon) \) is the Fermi function (9.16.4) and \( \varphi(\epsilon) \) is some smoothly varying function of \( \epsilon \). 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

\[
\psi(\epsilon) = \int_{0}^{\epsilon} \varphi(\epsilon') \, d\epsilon' \quad (9.17.4)
\]

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

\[
\int_{0}^{\infty} F(\epsilon) \varphi(\epsilon) \, d\epsilon = - \int_{0}^{\infty} F'(\epsilon)\psi(\epsilon) \, d\epsilon \quad (9.17.5)
\]

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 \( \psi \) can

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![Fig. 9.17.1](image-url)  
*Fig. 9.17.1 The derivative \( F'(\epsilon) \) of the Fermi function as a function of \( \epsilon \).*
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

\[ \int_0^\infty F(\epsilon) d\epsilon = - \sum_{m=0}^{\infty} \frac{1}{m!} \left[ \frac{d^m\psi}{d\epsilon^m} \right]_{\mu} \int_0^\infty F'(\epsilon) (\epsilon - \mu)^m d\epsilon \quad (9.17.6) \]

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 \( x = \beta(\epsilon - \mu) \) (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

\[ \int_0^\infty F'(\epsilon) (\epsilon - \mu)^m d\epsilon = -(kT)^m I_m \quad (9.17.8) \]

where

\[ I_m = \int_{-\infty}^{\infty} \frac{e^x}{(e^x + 1)^2} x^m dx \quad (9.17.9) \]

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

\[ I_m = 0 \quad \text{if } m \text{ is odd} \quad (9.17.10) \]

Also

\[ I_0 = \int_{-\infty}^{\infty} \frac{e^x}{(e^x + 1)^2} dx = -\left[ \frac{1}{e^x + 1} \right]_{-\infty}^{\infty} = 1 \quad (9.17.11) \]

By using (9.17.8), the relation (9.17.6) can then be written in the form

\[ \int_0^\infty F\varphi d\epsilon = \sum_{m=0}^{\infty} I_m \frac{(kT)^m}{m!} \left[ \frac{d^m\psi}{d\epsilon^m} \right]_{\mu} = \psi(\mu) + I_2 \frac{(kT)^2}{2} \left[ \frac{d^2\psi}{d\epsilon^2} \right]_{\mu} + \cdots \quad (9.17.12) \]

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

\[ \int_0^\mu F(\epsilon) \varphi(\epsilon) \, d\epsilon = \int_0^\mu \varphi(\epsilon) \, d\epsilon + \frac{\pi^2}{6} (kT)^2 \left[ \frac{d\varphi}{d\epsilon} \right]_\mu + \cdots \]  

(9.17.13)

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

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

(9.17.14)

Since for the present case, where \( kT/\mu \ll 1 \), the Fermi energy \( \mu \) differs only slightly from its value \( \mu_0 \) 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

\[ \frac{d}{d\epsilon} (\epsilon \rho) = \rho + \epsilon \rho', \quad \rho' = \frac{d\rho}{d\epsilon} \]

Eq. (9.17.14) becomes

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

(9.17.15)

Here we still need to know the change \( \mu - \mu_0 \) of the Fermi energy with temperature. Now \( \mu \) is determined by the condition (9.17.2) which becomes, by (9.17.13),

\[ 2 \int_0^\mu \rho(\epsilon) \, d\epsilon + \frac{\pi^2}{3} (kT)^2 \rho'(\mu) = N \]  

(9.17.16)

Here the derivative in the correction term can again be evaluated at \( \mu_0 \) 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 \( \mu_0 \) 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

\[ (\mu - \mu_0) = -\frac{\pi^2}{6} (kT)^2 \frac{\rho'(\mu_0)}{\rho(\mu_0)} \]  

(9.17.17)
Hence Eq. (9·17·15) becomes
\[ \bar{E} = \bar{E}_0 - \frac{\pi^2}{3} (kT)^2 \mu_0 \rho'(\mu_0) + \frac{\pi^2}{3} (kT)^2 \left[ \rho(\mu_0) + \mu_0 \rho'(\mu_0) \right] \]
or
\[ \bar{E} = \bar{E}_0 + \frac{\pi^2}{3} (kT)^2 \rho(\mu_0) \] (9·17·18)
since terms in ρ' cancel. The heat capacity (at constant volume) becomes then
\[ C_V = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3} k^2 \rho(\mu_0)T \] (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):
\[ \rho(\epsilon) \, d\epsilon = \frac{V}{(2\pi)^3} \left( \frac{4\pi \epsilon^2 \, d\epsilon}{d\epsilon} \right) = \frac{V}{4\pi^2} \frac{(2m)^{\frac{3}{2}}}{\hbar^2} \epsilon^{\frac{3}{2}} \, d\epsilon \] (9·17·20)
But
\[ \mu_0 = \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{\frac{1}{3}} \] by (9·16·10)

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

Equivalently this can be written in terms of N and μ₀ by eliminating the volume V between the last two equations. Thus one obtains
\[ \rho(\mu_0) = \left[ \frac{m}{2\pi^2 \hbar^2} (3\pi^2 N)^{\frac{1}{3}} \right] \left[ \frac{1}{\mu_0} \frac{\hbar^2}{2m} (3\pi^2 N)^{\frac{1}{3}} \right] = \frac{3}{4} \frac{N}{\mu_0} \] (9·17·22)

Hence (9·17·19) gives
\[ C_V = \frac{\pi^2}{2} \frac{k^2}{\mu_0} \frac{N}{T} = \frac{\pi^2}{2} kN \frac{kT}{\mu_0} \] (9·17·23)
or, per mole,
\[ c_V = \frac{3}{2} R \left( \frac{\pi^2}{3} \frac{kT}{\mu_0} \right) \] (9·17·24)

SUGGESTIONS FOR SUPPLEMENTARY READING


