

FIGURE 3.2

Temperature dependence of the energy gap in the BCS theory. Strictly speaking, this universal curve holds only in a weak-coupling limit, but it is a good approximation in most cases.

### 3.6.3 Thermodynamic Quantities

With  $\Delta(T)$  determined, the temperature-dependent set of fermion excitation energies  $E_{\mathbf{k}} = [\xi_{\mathbf{k}}^2 + \Delta(T)^2]^{1/2}$  is fixed. These energies determine the quasi-particle occupation numbers  $f_{\mathbf{k}} = (1 + e^{\beta E_{\mathbf{k}}})^{-1}$ , which in turn determine the electronic entropy in the usual way for a fermion gas, namely,

$$S_{es} = -2k \sum_{\mathbf{k}} [(1 - f_{\mathbf{k}}) \ln (1 - f_{\mathbf{k}}) + f_{\mathbf{k}} \ln f_{\mathbf{k}}] \quad (3.55)$$

Given  $S_{es}(T)$ , the specific heat can be written as

$$C_{es} = T \frac{dS_{es}}{dT} = -\beta \frac{dS_{es}}{d\beta}$$

Using (3.55), we have

$$\begin{aligned} C_{es} &= 2\beta k \sum_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial \beta} \ln \frac{f_{\mathbf{k}}}{1 - f_{\mathbf{k}}} = -2\beta^2 k \sum_{\mathbf{k}} E_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial \beta} \\ &= -2\beta^2 k \sum_{\mathbf{k}} E_{\mathbf{k}} \frac{df_{\mathbf{k}}}{d(\beta E_{\mathbf{k}})} \left( E_{\mathbf{k}} + \beta \frac{dE_{\mathbf{k}}}{d\beta} \right) \\ &= 2\beta k \sum_{\mathbf{k}} -\frac{\partial f_{\mathbf{k}}}{\partial E_{\mathbf{k}}} \left( E_{\mathbf{k}}^2 + \frac{1}{2}\beta \frac{d\Delta^2}{d\beta} \right) \end{aligned} \quad (3.56)$$

$$\begin{aligned} \beta &= k_B T \\ \xi_{\vec{k}} &= E_{\vec{k}} - \mu \\ \mu &= \text{chemical potential} \end{aligned}$$

The first term is the usual one coming from the redistribution of quasi-particles among the various energy states as the temperature changes. The second term is more unusual and describes the effect of the temperature-dependent gap in changing the energy levels themselves.

Evidently, both terms in  $C_{es}$  will be exponentially small at  $T \ll T_c$ , where the minimum excitation energy  $\Delta$  is much greater than  $kT$ . This accounts for the exponential form (1.13) noted earlier. Another interesting limit is very near  $T_c$ .

Then, as  $\Delta(T) \rightarrow 0$ , one can replace  $E_{\mathbf{k}}$  by  $|\xi_{\mathbf{k}}|$  in (3.56). The first term then reduces to the usual normal-state electronic specific heat

$$C_{en} = \gamma T = \frac{2\pi^2}{3} N(0) k^2 T \quad (3.57)$$

which is continuous at  $T_c$ . The second term is finite below  $T_c$ , where  $d\Delta^2/dT$  is large, but it is zero above  $T_c$ , giving rise to a discontinuity  $\Delta C$  in the electronic specific heat at  $T_c$ . The size of the discontinuity is readily evaluated by changing the sum to an integral, as follows:

$$\begin{aligned} \Delta C &= (C_{es} - C_{en}) \Big|_{T_c} = N(0) k \beta^2 \left( \frac{d\Delta^2}{d\beta} \right) \int_{-\infty}^{\infty} \left( \frac{-\partial f}{\partial |\xi|} \right) d\xi \\ &= N(0) \left( \frac{-d\Delta^2}{dT} \right) \Big|_{T_c} \end{aligned} \quad (3.58)$$

where we have used the fact that  $\partial f / \partial |\xi| = \partial f / \partial \xi$  since  $\partial f / \partial \xi$  is an even function of  $\xi$ . Using the approximate form (3.54) for  $\Delta(T)$ , with  $\Delta(0) = 1.76 k T_c$ , we obtain  $\Delta C = 9.4 N(0) k^2 T_c$ . Comparing with (3.57), we find that the normalized magnitude of the discontinuity is

$$\frac{\Delta C}{C_{en}} = \frac{9.4}{2\pi^2/3} = 1.43 \quad (3.59)$$

The overall behavior of the electronic specific heat is sketched in Fig. 3.3*b*.

With  $C_{es}(T)$  determined numerically from (3.56), we can integrate it to find the change in internal energy  $U(T)$  as we decrease the temperature from  $T_c$ . At  $T_c$ , it must be the same as the normal value  $U_{en}(0) - \frac{1}{2} \gamma T_c^2$  since the specific heat remains finite there. Thus,

$$U_{es}(T) = U_{en}(0) + \frac{1}{2} \gamma T_c^2 - \int_T^{T_c} C_{es} dT \quad (3.60)$$

From this and the entropy (3.55) we may then compute the free energy

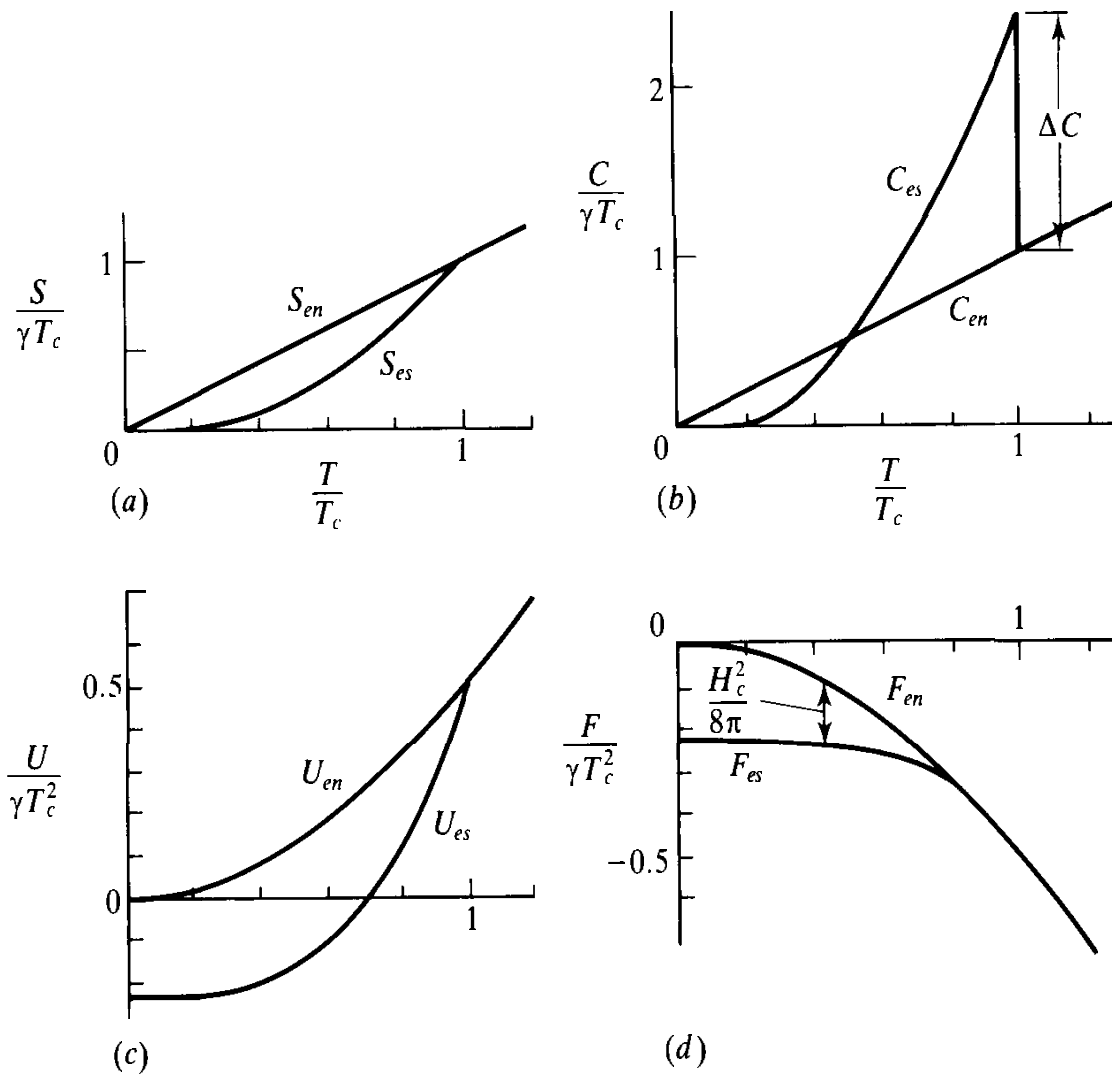
$$F_{es}(T) = U_{es}(T) - T S_{es}(T) \quad (3.61)$$

Assuming that the effect of the superconducting transition on the lattice free energy can be neglected, the thermodynamic critical field is then determined through the relation

$$\frac{H_c^2(T)}{8\pi} = F_{en}(T) - F_{es}(T) \quad (3.62)$$

where  $F_{en}(T) = U_{en}(0) - \frac{1}{2} \gamma T^2$ . These various thermodynamic quantities are plotted in Fig. 3.3. A useful numerical tabulation has been given by Mühlischlegel.<sup>19</sup>

<sup>19</sup>B. Mühlischlegel, *Z. Phys.* **155**, 313 (1959).



**FIGURE 3.3**

Comparison of thermodynamic quantities in superconducting and normal states.  $U_{en}(0)$  is chosen as the zero of ordinates in (c) and (d). Because the transition is of second order, the quantities  $S$ ,  $U$ , and  $F$  are continuous at  $T_c$ . Moreover, the slope of  $F_{es}$  joins continuously to that of  $F_{en}$  at  $T_c$ , since  $\partial F/\partial T = -S$ .

Since the critical-field curve  $H_c(T)$  can be measured with greater accuracy than can typical thermodynamic quantities, it is of some importance to note that one can be derived from the other by rigorous thermodynamic computations, starting from (3.62). For example, the approximate parabolic temperature dependence of  $H_c$  quoted in (1.2) is inconsistent with an exponential variation of  $C_{es}$ , such as that quoted in (1.13), but it is consistent with a  $T^3$  variation. Precise measurements of the deviation of  $H_c(T)$  from the parabolic approximation have been used by Mapother<sup>20</sup> to test the BCS predictions of thermodynamic properties.

<sup>20</sup>D. E. Mapother, *Phys. Rev.* **126**, 2021 (1962).