IIIC-A, eqn IIIC-A1. The only necessary modification is multiplication by a factor of two to account for the fact that free electrons may have either spin up or spin down.[19]

$$g_{el}(\varepsilon) = 4\pi V\left(\frac{2\ m^*_{el}}{h^2}\right)^{3/2} \varepsilon^{\frac{1}{2}} \qquad \text{(IIID-18)}$$

The introduction to the unit, specifically Exer. 1, demonstrated that free electrons in a metal do not satisfy the Boltzmann limit. Therefore, before we develop their property contributions, we must evaluate the unknown Lagrange multiplier α applicable to free electrons. In the preceding section we found that α equals zero for systems in which the particles are massless. This conclusion was reached by exploiting the fact that massless particles need not be conserved. However, free electrons are not massless; they must be conserved. Thus, we cannot use the same technique with free electrons.

Recall that the Boltzmann limit is prescribed by the condition $(g_j/n_j)_{max} \Rightarrow e^{\alpha} >> 1$. The fact that free electrons do not even come close to satisfying the Boltzmann limit restricts the possible values of α substantially, viz., $0 < e^{\alpha} \sim 1$. That is, α is restricted to at most small positive, zero, or negative values. As we noted at the beginning of this unit, approach to the limit is promoted by high temperatures. So we expect α to be a function of temperature such that it becomes increasingly negative as temperature decreases. With the aid of this perception we introduce the definition[20]

$$\alpha \equiv -\frac{\varepsilon_F}{kT} \qquad \text{(IIID-19)}$$

ε_F has units of energy and is called the *Fermi level* (or *Fermi energy*).[21] With this definition, the Fermi distribution function becomes

$$F(\varepsilon) = \frac{n^{FD}(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad \text{(IIIB-14)}$$

[19]In addition to translation, the electrons undergo rotation about their own axes. Because of their charge, this motion gives rise to a magnetic moment which acts up or down according to the direction of rotation. In the absence of an external field, the energy associated with this motion is constant, so it is neglected. The degeneracy, however, is multiplied by a factor of two due to the up or down orientation of the spin vector.

[20]This definition introduces no new assumptions as long as we do not prescribe that ε_F is a constant. The significance of the definition is that by separating the anticipated approximate relationship of α with temperature, we may expect ε_F to be, at best, only weakly dependent on T.

[21]ε_F is the chemical potential (μ) or Gibbs function per particle discussed in Unit VID. For a formal identification of α, see Ref. 7.

Ans. 14. For silicon θ_D = 658 K. Thus x_D = 658 K/22 K = 29.9. The low-temperature approximation is applicable

$$\bar{c}_{v,phn} = \frac{12}{5}\pi^4 \frac{8.314\ \text{J/(g mol K)}}{(29.9)^3} = 7.27 \cdot 10^{-2}\ \text{J/(g mol K)}$$