Low-Temperature Limit, $T \ll \theta_D$. At low temperatures the upper limit of the Debye integral approaches infinity. This definite integral can be evaluated in terms of the gamma and Riemann zeta functions, see Ref. 5. Its value is $\pi^4/15$. So, limit $x_D = \infty$, $D(x_D) = (3/x_D^3)(\pi^4/15)$.

Substituting into eqns. IIID-13, 15, and 16, we have

$$\bar{u}_{phn} = \frac{3\pi^4}{5}\bar{R}\left(\frac{T}{\theta_D}\right)^3 T \qquad \bar{c}_{v,phn} = \frac{12}{5}\pi^4\bar{R}\left(\frac{T}{\theta_D}\right)^3 \qquad \bar{s}_{phn} = \frac{4\pi^4}{5}\bar{R}\left(\frac{T}{\theta_D}\right)^3$$

High-Temperature Limit, $T \gg \theta_D$. At high temperatures the exponential can be expanded

$$e^x \simeq 1 + x \qquad x = \frac{h\nu}{kT} < x_D = \frac{h\nu_D}{kT} \gg 1$$

Then the integral becomes

$$D(x_D) \Rightarrow \frac{3}{x_D^3}\int_0^{x_D} \frac{x^3 dx}{(1 + x - 1)} = \frac{3}{x_D^3}\left(\frac{x_D^3}{3}\right) = 1$$

Substituting into eqns. IIID-15, 17, and 18, we have

$$\bar{u}_{phn} = 3\bar{R}T \qquad \bar{c}_{v,phn} = 3\bar{R}\left[4 - \frac{x_D}{(1 + x_D - 1)}\right] = 3\bar{R}$$

$$\bar{s}_{phn} = \bar{R}\left\{4 - 3\ln[1 - (1 - x_D)]\right\} = \bar{R}\left[4 - 3\ln\left(\frac{T}{\theta_D}\right)\right]$$

Exercise 14. A silicon rectifier is to be used at liquid hydrogen temperatures, 22 K. What would be the lattice contribution to $\bar{c}_v$ at that temperature?

II. THE PROPERTIES OF FREE ELECTRONS

The valence electrons of a metal are shared among a large number of nearest and next nearest neighbors of the densely packed metallic lattice, see Sect. II of Unit ICS. As a result these electrons can move about within the crystal participating in the conduction of electricity and heat (see Unit IIIE). Thus, free electrons can be realistically modeled as independent particles translating within their crystalline box.[18] Their energy levels and degeneracies are essentially those of the particle in a box, see Table IIIA-1. In Sect. IIIA of Unit IIIC, we treated the translation of molecular gases. The characteristic temperature for translation was found to be

$$\theta_{tr} = \frac{h^2}{8m^* V^{2/3} k}$$

[18]The potential portion of the internal energy corresponding to the repulsion between the negatively charged electrons and the positively charged lattice points is insignificant in comparison to the kinetic portion of the free electron energy in metallic conductors. Thus, free electrons in a metal can be treated as independent particles. This assumption tends to break down in semiconductors. Free electron-lattice point interactions, or scattering, is important to the determination of the magnitude of free electron transport. This topic is considered in Unit IIIE.