Since free electrons are highly degenerate at ordinary temperatures, only those particles in states within a few kT of the Fermi level are excited and these only to a few kT above ε_F°.[24] As a result the internal energy of a free electron gas is only slightly more than that at absolute zero. On the basis of the *free electron model* presented in this section the free electron contribution to internal energy and specific heat are found to be (the development of this relationship is rather complicated, see Ref. 7)

$$\bar{u}_{el} = \frac{3}{5}\bar{R}\,\theta_F\left[1 + \frac{5}{12}\pi^2\left(\frac{T}{\theta_F}\right)^2\right] \qquad \bar{c}_{v,el} = \left(\frac{\partial \bar{u}_{el}}{\partial T}\right)_{\bar{v}} = \frac{\pi^2}{2}\bar{R}\left(\frac{T}{\theta_F}\right) \qquad \text{(IIID-21,22)}$$

Thus the free electron contribution to the specific heat is predicted to be linearly proportional to temperature and is quite small since $T \ll \theta_F$. Both of these general predictions are validated by experiment. However, the simple free electron model is apparently not sufficient to accurately predict the temperature coefficient in all metals. We will nevertheless employ these relationships in the following section to predict the total properties of solids.

III. THE PROPERTIES OF SOLIDS

We have developed the properties of photon, phonon and free electron gases. All three are present within a conducting solid. Though the photon gas is always present, we saw in Exer. 9 that its property contributions are negligible when compared to, even very low density, matter. Thus the properties of metallic conductors can be approximated as the sum of the phonon and free electron contributions

$$\bar{u}_{mtl} = \bar{u}_{phn} + \bar{u}_{el} \qquad \bar{c}_{v,mtl} = \bar{c}_{v,phn} + \bar{c}_{v,el} \qquad \text{(IIID-23a,b)}$$

The following problem illustrates the relative magnitudes of these contributions.

Example 10. Determine the phonon and free electron contribution to the zero point energy of copper ($\bar{u}^\circ_{phn} = 9/8\,\bar{R}\,\theta_D$, see footnote 18). In addition, determine the internal energy $(u - u^\circ)$ and specific heat contributions of these components at 100, 300, and 1000 K.

The phonon contributions can be determined using $\theta_D = 315$ K and eqns. IIID-13b and 15.

$$\bar{u}^\circ_{phn} = \frac{9}{8}\bar{R}\,\theta_D = \frac{9}{8}\cdot 8.314\ \text{J/(g mol K)}\cdot 315\ \text{K} = 2947\ \text{J/(g mol)}$$

With $x_D = \theta_D/T = 315\ \text{K}/100\ \text{K} = 3.15$, we find $D(3.15) = 0.268$. This gives

$$(\bar{u} - \bar{u}^\circ)(100\ \text{K})_{phn} = 3\,\bar{R}TD(x_D) = 3\cdot 8.314\ \text{J/(g mol K)}\cdot 100\ \text{K}\cdot 0.268 = 669\ \text{J/(g mol)}$$

and

$$\bar{c}_{v,phn}(100\ \text{K}) = 3\bar{R}\left[4D(x_D) - \frac{3x_D}{e^{x_D}-1}\right] = 3\cdot 8.314\ \text{J/(g mol K)}\left[4\cdot 0.268 - \frac{3\cdot 3.15}{(e^{3.15}-1)}\right] = 16.2\ \text{J/(gmol K)}$$

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[24] The Fermi level is depressed very slightly from its value at absolute zero

$$\varepsilon_F = \varepsilon_F^\circ\left[1 - \frac{\pi^2}{12}\left(\frac{T}{\theta_F}\right)^2\right]$$