free electrons. Therefore, we set out the result in terms of the particle's parameters.

$$g_{tr}(\varepsilon) = \frac{\pi}{4}\frac{\varepsilon^{1/2}}{(k\,\theta_{tr})^{3/2}} = 4\pi V\left(\frac{2m^*}{h^2}\right)^{3/2}\varepsilon^{1/2} \qquad \text{(IIIC-A1)}$$

This unit is devoted to the determination of the properties of indistinguishable particles in their Boltzmann limit. Therefore, it would be imprudent to apply these methods without testing to see that the limit, $n_j \ll g_j$, is satisfied.

Exercise A3. Show that the states of the first (or ground) level have the highest occupancy.

Exer. A3 shows that it is not necessary to investigate the entire level index series, since $n_j/g_j|_{max} = n_1/g_1$. A further simplification can be achieved when we recognize that the values of θ_{tr} (see Sect. IIIA) are many orders of magnitude smaller than the value of any individual characteristic temperature of an internal mode, $\theta_p \gg \theta_{tr}$ (see Sects. IIIB, C, and D). Therefore, the translational mode is excited at far lower temperatures than any of the internal modes. In the following example we exploit this fact to reduce the indistinguishable limit test to a function of the translational mode alone.

Example A2. Under the assumption that the translational mode is fully excited, $T \gg \theta_{tr}$, study the effect of the internal modes on the prediction of n_1/g_1.

We can write for the separate translational and internal modes: $g_1 = g_{tr,1}g_{in,1}$, $\varepsilon_1 = \varepsilon_{tr,1} + \varepsilon_{in,1}$, and $Z = Z_{tr}Z_{in}$. Then assuming that the limit is satisfied we can write

$$\frac{n_1}{g_1} = \frac{N\,e^{-\varepsilon_1/kT}}{Z} = N\left(\frac{e^{-\varepsilon_{tr,1}/kT}}{Z_{tr}}\right)\left(\frac{e^{-\varepsilon_{in,1}/kT}}{Z_{in}}\right)$$

Consider an expansion of the reciprocal of the internal mode term.

$$\left(\frac{Z_{in}}{e^{-\varepsilon_{in,1}/kT}}\right) = \left[\left(g_1\,e^{-\varepsilon_1/kT} + g_2\,e^{-\varepsilon_2/kT} + g_3\,e^{-\varepsilon_3/kT} + \cdots\right)e^{\varepsilon_1/kT}\right]_{in}$$

$$= g_1 + g_2\,e^{-(\varepsilon_2-\varepsilon_1)/kT} + g_3\,e^{-(\varepsilon_3-\varepsilon_1)/kT}$$

Then when we recognize that the internal mode is, at least, much less excited than translational mode, we expect $(Z\,e^{\varepsilon_1/kT})_{in} \simeq g_{in,1}$. Thus

$$\frac{n_1}{g_1} = \frac{n_1}{g_{tr,1}\,g_{in,1}} \le \frac{N\,e^{-\varepsilon_{tr,1}/kT}}{Z_{tr}\,g_{in,1}}$$

Finally, the translational mode is assumed to be fully excited; so $T \gg \theta_{tr} = (\varepsilon_{tr,1}/3k)$. Thus the limit test simplifies to

$$\frac{n_{tr,1}}{g_{tr,1}} \le \frac{N}{Z_{tr}} \ll 1$$