Within the constraints imposed by the high-temperature limit, we can use these results to investigate the distribution of the particles over the rotational levels.

Exercise 7. Determine the proportion of oxygen molecules at room temperature that are in the first, second, tenth, and one hundredth rotational level.

The answer to Exer. 7 demonstrates that linear molecules are distributed broadly over the rotational levels at elevated temperatures. It also shows that there is a level of maximum occupation. This level can be determined by differentiating the rotational distribution function.

Example 8. Derive an expression for the level index of the most heavily occupied rotational level in the high temperature limit.

The level of greatest occupancy is defined by the condition, $d\rho_r(\ell)/d\ell = 0$. Then since

$$\frac{d\rho_r(\ell)}{d\ell} = \frac{d}{d\ell}\left[\frac{\theta_r}{T}(2\ell+1)e^{\ell(\ell+1)(-\theta_r/T)}\right] = \frac{\theta_r}{T}\left[2 - \frac{\theta_r}{T}(2\ell+1)^2\right]e^{\ell(\ell+1)(-\theta_r/T)}$$

Setting this derivative equal to zero and simplifying we obtain: $(-2T/\theta_r + 4\ell^2 + 4\ell + 1) = 0$. Or using the quadratic formula and eliminating the root corresponding to negative values of ℓ,

$$\ell_{max} = \left(\frac{T}{2\theta_r}\right)^{\frac{1}{2}} - \frac{1}{2}$$

Recognize that this expression will not yield an integer value for ℓ_{max}. We have used a continuous representation of ℓ. The result should be interpreted as the nearest whole number.

Exercise 8. Use the formula developed in Exmp. 8 to determine the rotational level of highest occupancy in oxygen at room temperature.

Consideration of linear rotators is simplified by the fact that they have a single appreciable moment ($I_x = I_y = I$, $I_z = 0$). Nonlinear molecules (polyatomic molecules whose atoms do not form a line) have three appreciable, potentially distinct moments. As a result nonlinear polyatomic molecules have three rotational temperatures, $\theta_{r,x}$, $\theta_{r,y}$ and $\theta_{r,z}$. (Frequently two have the same value.) The solution of the Schroedinger equation and the evaluation of the partition function series is complicated by the presence of three rotational modes. Fortunately, there are no nonlinear molecules with even a single rotational temperature large enough that its gaseous states are not within the high temperature limit $T \gg \theta_{r,x}, \theta_{r,y}, \theta_{r,z}$. Thus we need consider the *rotational partition function for nonlinear molecules* only in this limit.

Ans. 6. Following the same procedure as that of Exmp. 6, we find at the normal boiling point of helium [$p = 1.013 \cdot 10^5 N/m^2$, $T = 4.22$ K, $M = 4.003$ kg/(kg mol)] that $n_j/g_j|_{max} = 0.134$. This certainly does not satisfy the indistinguishable limit. To establish a boundary, we arbitrarily set $n_j/g_j|_{max} = 10^{-2}$ and solve for $T_{lim} = 11.9$ K. Thus helium gas at atmospheric pressure satisfies the indistinguishable limit above about 12 K.