$$= k \sum_{i=1}^{l} \Big[n_i \ln\Big(\frac{g_i + n_i}{n_i}\Big) + g_i \ln\Big(\frac{g_i + n_i}{g_i}\Big)\Big]$$

$$= k \sum_{i=1}^{l} \Big[n_i \ln\Big(\frac{g_i}{n_i} + 1\Big) + g_i \ln\Big(1 + \frac{n_i}{g_i}\Big)\Big]$$

Exercise 7. For Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distributions, we have

$$\frac{g_i}{n_i} = \mathrm{e}^{(\alpha+\beta E_i)} + J$$

where

$$J = \begin{cases} \ \ 0 & \text{for Maxwell-Boltzmann distribution} \\ \ \ 1 & \text{for Fermi-Dirac distribution} \\ -1 & \text{for Bose-Einstein distribution} \end{cases}$$

Find out values of the constants α and β.

Solution: Since the values of α and β do not depend on the distribution, we consider the simple case of Maxwell-Boltzmann distribution, so that

$$n_i = g_i \ \mathrm{e}^{-\alpha} \ \mathrm{e}^{-\beta E_i} \tag{6.30}$$

Average energy of particles in an ideal gas is

$$\bar{E} = \frac{E}{N} = \frac{\sum_{i=1}^{l} n_i E_i}{\sum_{i=1}^{l} n_i}$$

Using equation (6.30), we have

$$\bar{E} = \frac{\sum_{i=1}^{l} E_i g_i \ \mathrm{e}^{-\alpha} \ \mathrm{e}^{-\beta E_i}}{\sum_{i=1}^{l} g_i \ \mathrm{e}^{-\alpha} \ \mathrm{e}^{-\beta E_i}} = \frac{\sum_{i=1}^{l} E_i g_i \ \mathrm{e}^{-\beta E_i}}{\sum_{i=1}^{l} g_i \ \mathrm{e}^{-\beta E_i}}$$

When energy levels are closely packed, we can consider it as a continuum. Then, E_i is replaced by E, g_i by $g(E)$, and summation over the energy states by the integration over the energy. Thus, we have

$$\bar{E} = \frac{\int E g(E) \ \mathrm{e}^{-\beta E} \mathrm{d}E}{\int g(E) \ \mathrm{e}^{-\beta E} \mathrm{d}E}$$

For the particles with no spin, we have (see appendix)

$$g(E) \ \mathrm{d}E = 2\pi V \Big(\frac{2 \ m}{h^2}\Big)^{3/2} E^{1/2} \ \mathrm{d}E$$

(ii) Fermi-Dirac distribution

(iii) Bose-Einstein distribution

(iv) Condition for application of Maxwell-Boltzmann distribution

Using Stirling formula, we have

$$\ln W = N \ln N - N + \sum_{i=1}^{l} (n_i \ln g_i - n_i \ln n_i + n_i)$$

$$= N \ln N - \sum_{i=1}^{l} n_i \ln \left(\frac{n_i}{g_i}\right) \tag{7.16}$$

and for the maximum value of W, we have

$$n_i = g_i \, \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} \mathrm{e}^{-E/kT} \tag{7.17}$$

Using equation (7.17) in (7.16), we have

$$\ln W = N \ln N - \sum_{i=1}^{l} n_i \left(\ln N + \ln\Big[\frac{1}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\Big] - \frac{E}{kT}\right)$$

$$= N \ln N - N \ln N - N \ln\Big[\frac{1}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\Big] + \frac{EN}{kT}$$

$$= N \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{EN}{kT}$$

Using $E = 3kT/2$, we have

$$\ln W = N \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} N \tag{7.18}$$

Thus, the entropy (equation 7.18) is

$$S = kN \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} kN \tag{7.19}$$

3.4 Gibbs paradox

In order to check the additive property of entropy of the gas, let us increase each of the volume V and number of particles N of the gas by a common factor p, then the entropy S' of the new system (using equation 7.19) is

$$S' = kpN \ln\Big[pV\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} kpN$$

$$= p\left(kN \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} kN\right) + pNk \ln(p) \tag{7.20}$$

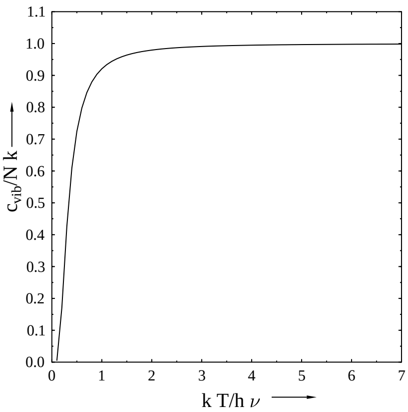

Figure 3: Variation of (c_{vib}/Nk) versus $kT/h\nu$.

rotational level with the quantum number J is $(2J+1)$. The rotational partition function is

$$Z_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)\ \exp\Big[-\sigma_r J(J+1)\Big]$$

where $\sigma_r = B/kT$.

(i) At low temperatures ($kT << B$, *i.e.*, $\sigma_r >> 1$), we have

$$Z_{\text{rot}} = 1 + \sum_{J=1}^{\infty}(2J+1)\ \exp\Big[-\sigma_r J(J+1)\Big]$$

(a) The Helmholtz free energy is

$$F_{\text{rot}} = -NkT\ \ln Z_{\text{rot}} = -NkT\ \ln[1 + \sum_{J=1}^{\infty}(2J+1)\ \exp\{-\sigma_r J(J+1)\}]$$

$$= -NkT\sum_{J=1}^{\infty}(2J+1)\ \exp[-\sigma_r J(J+1)]$$

where we used the expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3}\dots$$

and neglected the quadratic and higher order terms.

(b) Entropy S_{rot} of the gas is

$$S_{\text{rot}} = -\frac{\partial F_{\text{rot}}}{\partial T} = Nk\sum_{J=1}^{\infty}(2J+1)\ \exp[-\sigma_r J(J+1)]$$