6.3: Ideal Gas

Recall the canonical partition function expression for the ideal gas:

$$Q(N,V,T) = \frac{1}{N!}\left[\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]^N$$

Define the thermal wavelength $\lambda(\beta)$ as

$$\lambda(\beta) = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

which has a quantum mechanical meaning as the width of the free particle distribution function. Here it serves as a useful parameter, since the canonical partition can be expressed as

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

The grand canonical partition function follows directly from $Q(N,V,T)$:

$$\mathcal{Z}(\zeta,V,T) = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{V\zeta}{\lambda^3}\right)^N = e^{V\zeta/\lambda^3}$$

Thus, the free energy is

$$\frac{PV}{kT} = \ln\mathcal{Z} = \frac{V\zeta}{\lambda^3}$$

In order to obtain the equation of state, we first compute the average particle number $\langle N\rangle$

$$\langle N\rangle = \zeta\frac{\partial}{\partial\zeta}\ln\mathcal{Z} = \frac{V\zeta}{\lambda^3}$$

Thus, eliminating ζ in favor of $\langle N\rangle$ in the equation of state gives

$$PV = \langle N\rangle kT$$

as expected. Similarly, the average energy is given by

$$E = -\left(\frac{\partial\ln\mathcal{Z}}{\partial\beta}\right)_{\zeta V} = \frac{3V\zeta}{\lambda^4}\frac{\partial\lambda}{\partial\beta} = \frac{3}{2}\langle N\rangle kT$$

where the fugacity has been eliminated in favor of the average particle number. Finally, the entropy

$$S(\mu,V,T) = k\ln\mathcal{Z}(\mu,V,T) - k\beta\left(\frac{\partial\ln\mathcal{Z}(\mu,V,T)}{\partial\beta}\right)_{\mu,V} = \frac{5}{2}\langle N\rangle k + \langle N\rangle k\ln\left[\frac{V\lambda^3}{\langle N\rangle}\right]$$

which is the Sackur-Tetrode equation derived in the context of the canonical and microcanonical ensembles.