6.4: Particle Number Fluctuations

In the grand canonical ensemble, the particle number N is not constant. It is, therefore, instructive to calculate the fluctuation in this quantity. As usual, this is defined to be

$$\Delta N = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}$$

Note that

$$\begin{aligned} \zeta \frac{\partial}{\partial \zeta} \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T) &= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N^2 \zeta^N Q(N, V, T) - \frac{1}{\mathcal{Z}^2} \left[\sum_{N=0}^{\infty} N \zeta^N Q(N, V, T) \right]^2 \\ &= \langle N^2 \rangle - \langle N \rangle^2 \end{aligned}$$

Thus,

$$\begin{aligned} (\Delta N)^2 &= \zeta \frac{\partial}{\partial \zeta} \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T) \\ &= (KT^2) \frac{\partial^2}{\partial \mu^2} \ln \mathcal{Z}(\mu, V, T) \\ &= kTV \frac{\partial^2 P}{\partial \mu^2} \end{aligned}$$

In order to calculate this derivative, it is useful to introduce the Helmholtz free energy per particle defined as follows:

$$a(v, T) = \frac{1}{N} A(N, V, T)$$

where $v = \frac{V}{N} = \frac{1}{\rho}$ is the volume per particle. The chemical potential is defined by

$$\begin{aligned} \mu &= \frac{\partial A}{\partial N} \\ &= a(v, T) + N \frac{\partial a}{\partial v} \frac{\partial v}{\partial N} \\ &= a(v, T) - v \frac{\partial a}{\partial v} \end{aligned}$$

Similarly, the pressure is given by

$$P = -\frac{\partial A}{\partial V} = -N \frac{\partial a}{\partial v} \frac{\partial v}{\partial V} = -\frac{\partial a}{\partial v}$$

Also,

$$\frac{\partial \mu}{\partial v} = -v \frac{\partial^2 a}{\partial v^2}$$

Therefore,

$$\begin{aligned} \frac{\partial P}{\partial \mu} &= \frac{\partial P}{\partial v} \frac{\partial v}{\partial \mu} \\ &= \frac{\partial^2 a}{\partial v^2} \left[v \frac{\partial^2 a}{\partial v^2} \right]^{-1} \\ &= \frac{1}{v} \end{aligned}$$

and

$$\begin{aligned}\frac{\partial^2 P}{\partial \mu^2} &= \frac{\partial}{\partial v}\frac{\partial P}{\partial \mu}\frac{\partial v}{\partial \mu} \\ &= \frac{1}{v^2}\left[v\frac{\partial^2 a}{\partial v^2}\right]^{-1} \\ &= -\frac{1}{v^3 \partial P/\partial v}\end{aligned}$$

But recall the definition of the **isothermal compressibility**:

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{v\partial p/\partial v}$$

Thus,

$$\frac{\partial^2 P}{\partial \mu^2} = \frac{1}{v^2}\kappa_T$$

and

$$\Delta N = \sqrt{\frac{\langle N\rangle kT\kappa_T}{v}}$$

and the relative fluctuation is given by

$$\frac{\Delta N}{N} = \frac{1}{\langle N\rangle}\sqrt{\frac{\langle N\rangle kT\kappa_T}{v}} \sim \frac{1}{\sqrt{\langle N\rangle}} \rightarrow 0 \;\; as\langle N\rangle \rightarrow \infty$$

Therefore, in the thermodynamic limit, the particle number fluctuations vanish, and the grand canonical ensemble is equivalent to the canonical ensemble.
