7.6: Fluctuations

We will now calculate the fluctuations in the values of energy and the number of particles as given by the canonical and grand canonical ensembles. First consider N. From the definition, we have

$$\begin{aligned}\frac{1}{\beta}\frac{\partial Z}{\partial \mu} &= Z\langle N\rangle = Z\,\bar{N} \\ \frac{1}{\beta^2}\frac{\partial^2 Z}{\partial \mu^2} &= Z\langle N^2\rangle\end{aligned} \tag{7.6.1}$$

If we calculate $\bar{N}$ from the partition function as a function of β and μ, we can differentiate it with respect to μ to get

$$\frac{1}{\beta}\frac{\partial \bar{N}}{\partial \mu} = -\frac{1}{Z^2\beta^2}\left(\frac{\partial Z}{\partial \mu}\right)^2 + \frac{1}{\beta^2}\frac{\partial^2 Z}{\partial \mu^2} = \langle N^2\rangle - \langle N\rangle^2 = \Delta N^2 \tag{7.6.2}$$

The Gibbs free energy is given by $G = \mu\bar{N}$ and it also obeys

$$dG = -SdT + Vdp + \mu d\bar{N} \tag{7.6.3}$$

These follow from Equation 5.1.16 and Equation 5.1.10. Since T is fixed in the differentiations we are considering, this gives

$$\frac{\partial \mu}{\partial \bar{N}} = \frac{V}{\bar{N}}\frac{\partial p}{\partial \bar{N}} \tag{7.6.4}$$

The equation of state gives p as a function of the number density $\rho \equiv \frac{\bar{N}}{V}$, at fixed temperature. Thus

$$\frac{\partial p}{\partial \bar{N}} = \frac{1}{V}\frac{\partial p}{\partial \rho} \tag{7.6.5}$$

Using this in Equation 7.6.4, we get

$$\frac{1}{\beta}\frac{\partial \bar{N}}{\partial \mu} = \bar{N}\frac{kT}{\frac{\partial p}{\partial \rho}} \tag{7.6.6}$$

From Equation 7.6.2, we now see that the mean square fluctuation in the number is given by

$$\frac{\Delta N^2}{N^2} = \frac{1}{\bar{N}}\frac{kT}{\frac{\partial p}{\partial \rho}} \tag{7.6.7}$$

This goes to zero as $\bar{N}$ becomes large, in the thermodynamic limit. An exception could occur if $\left(\frac{\partial p}{\partial \rho}\right)$ becomes very small. This can happen at a second order phase transition point. The result is that fluctuations in numbers become very large at the transition. The theoretical treatment of such a situation needs more specialized techniques.

We now turn to energy fluctuations in the canonical ensemble. For this we consider N to be fixed and write

$$\begin{aligned}\frac{\partial U}{\partial \beta} &= \frac{\partial}{\partial \beta}\left[-\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta}\right] = \left[\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta}\right]^2 - \left[\frac{1}{Q_N}\frac{\partial^2 Q_N}{\partial \beta^2}\right] \\ &= \langle H\rangle^2 - \langle H^2\rangle \equiv -\Delta U^2\end{aligned} \tag{7.6.8}$$

The derivative of $U = \langle H\rangle$ with respect to $\bar{T}$ gives the specific heat, so we find

$$\Delta U^2 = kC_vT^2, \quad \frac{\Delta U^2}{U^2} = \frac{kC_vT^2}{U^2} \sim \frac{1}{N} \tag{7.6.9}$$

Once again, the fluctuations are small compared to the average value as N becomes large.