4.5: Energy Fluctuations in the Canonical Ensemble

In the canonical ensemble, the total energy is not conserved. ($H(x) \neq \text{const}$). What are the fluctuations in the energy? The energy fluctuations are given by the root mean square deviation of the Hamiltonian from its average $\langle H \rangle$:

$$\Delta E = \sqrt{\langle (H - \langle H \rangle)^2 \rangle} = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$$

$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q(N, V, T)$

$\langle H^2 \rangle = \frac{1}{Q} C_N \int dx H^2(x) e^{-\beta H(x)}$ }}

$= \frac{1}{Q} C_N \int dx \frac{\partial^2}{\partial \beta^2} e^{-\beta H(x)}$

$= \frac{1}{Q} \frac{\partial^2}{\partial \beta^2} Q$

$= \frac{\partial^2}{\partial \beta^2} \ln Q + \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta} \right)^2$

$= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right]^2$

$= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[\frac{\partial}{\partial \beta} \ln Q \right]^2$

Therefore

$$\langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Q$$

But

$$\frac{\partial^2}{\partial \beta^2} \ln Q = kT^2 C_V$$

Thus,

$$\Delta E = \sqrt{kT^2 C_V}$$

Therefore, the relative energy fluctuation $\frac{\Delta E}{E}$ is given by

$$\frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{E}$$

Now consider what happens when the system is taken to be very large. In fact, we will define a formal limit called the **thermodynamic limit**, in which $N \longrightarrow \infty$ and $V \longrightarrow \infty$ such that $\frac{N}{V}$ remains constant.

Since C_V and E are both extensive variables, $C_V \sim N$ and $E \sim N$,

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \longrightarrow 0 \quad as \quad N \rightarrow \infty$$

But $\frac{\Delta E}{E}$ would be exactly 0 in the microcanonical ensemble. Thus, in the thermodynamic limit, the canonical and microcanonical ensembles are equivalent, since the energy fluctuations become vanishingly small.