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 \(\langle H \rangle\):

\[
\Delta E = \sqrt{\langle \left(H - \langle H\rangle\right)^2 \rangle} = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}
\]

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

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

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

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

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 \textit{thermodynamic limit}, in which \(N\rightarrow\infty\) and \(V\rightarrow\infty\) such that \(\frac{N}{V}\) remains constant.

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

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

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.

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\textbf{Contributors and Attributions}

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