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Physics 114

Energy Fluctuations in the Canonical Ensemble

There is a simple relationship between the heat capacity of a system and the fluctuations of energy about the average in the canonical ensemble. To determine this relationship, we first examine the expectation values of the energy and the square of the energy:

$$\begin{aligned}\langle E\rangle &= \frac{1}{Z}\sum_j E_j e^{\frac{-E_j}{kT}} \\ \langle E^2\rangle &= \frac{1}{Z}\sum_j E_j^2 e^{\frac{-E_j}{kT}},\end{aligned}$$

where Z is the partition function, k is Boltzmann's constant, and T is the temperature. We now take a derivative:

$$\begin{aligned}\frac{\partial\langle E\rangle}{\partial T} &= \frac{1}{Z}\sum_j \frac{E_j^2}{kT^2} e^{\frac{-E_j}{kT}} + \left(\sum_j E_j e^{\frac{-E_j}{kT}}\right)\left(\frac{-1}{Z^2}\frac{\partial Z}{\partial T}\right) \\ &= \frac{1}{kT^2}\langle E^2\rangle - \langle E\rangle\frac{\partial \ln Z}{\partial T} = \frac{1}{kT^2}\left(\langle E^2\rangle - \langle E\rangle^2\right),\end{aligned}$$

where we have used Baierlein's eq. (5.16) for the last equality. Thus we have

$$\langle E^2\rangle - \langle E\rangle^2 = kT^2\frac{\partial\langle E\rangle}{\partial T} = kT^2 C_V. \tag{1}$$

Now we examine the standard deviation of the energy,

$$(\Delta E)^2 \equiv \langle (E - \langle E\rangle)^2\rangle,$$

and use the fact that the average of a sum is the sum of the averages to write

$$\begin{aligned}(\Delta E)^2 &= \langle E^2 - 2E\langle E\rangle + \langle E\rangle^2\rangle = \langle E^2\rangle - 2\langle E\langle E\rangle\rangle + \langle\langle E\rangle^2\rangle \\ &= \langle E^2\rangle - \langle E\rangle^2.\end{aligned}$$

But this is exactly what we found in eq. (1), and so we have

$$(\Delta E)^2 = kT^2 C_V. \tag{2}$$

Now we are in a position to determine how the relative energy fluctuations (defined as $\frac{\Delta E}{\langle E\rangle}$) scale with N, the number of particles in the system. We can rewrite the relative energy fluctuations as

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

Now, we know that both the heat capacity and the average energy are extensive quantities, which means that they vary directly with the size of the system. But since the size of the system varies directly with the number of particles, each must be directly proportional to N. This allows us to write

$$\frac{\Delta E}{\langle E\rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}, \tag{3}$$

which tells us that as the number of particles in the system increases, the size of the energy fluctuations in relation to the average energy is negligible.