Statistical Mechanics: Lecture 5

Energy in Canonical Ensemble

In canonical ensemble, the energy of the system is not constant, as it constantly exchanges energy with the heat-bath. However, we can always calculate the average energy. Average energy, like the average of any quantity, can be written as

$$\begin{aligned}\langle E\rangle &= \frac{1}{\Delta}\int E(p,q)\rho(p,q)dpdq \\ &= \frac{1}{\Delta}\frac{1}{Z}\int Ee^{-E/kT}dpdq \qquad (1)\end{aligned}$$

From now now, we will use $\beta = 1/kT$, for brevity.

$$\langle E\rangle = \frac{1}{\Delta}\frac{1}{Z}\int Ee^{-\beta E}dpdq \qquad (2)$$

Derivative of $e^{-\beta E}$ with respect to β will pull down $-E$. Using this, we can rewrite the above equation as

$$\begin{aligned}\langle E\rangle &= \frac{1}{\Delta}\frac{1}{Z}\int -\frac{\partial}{\partial\beta}e^{-\beta E}dpdq \\ &= \frac{1}{Z}\left(-\frac{\partial}{\partial\beta}\right)\frac{1}{\Delta}\int e^{-\beta E}dpdq \\ &= \frac{1}{Z}\left(-\frac{\partial}{\partial\beta}\right)Z\end{aligned} \tag{3}$$

Thus we see that the average energy of the system is very simply related to the partition function:

$$\boxed{\langle E\rangle = -\frac{\partial \log Z}{\partial\beta}} \tag{4}$$

Energy fluctuations

Since energy of a system is not constant in canonical ensemble, apart from calculating its average, we will also be interested in knowing how much the energy deviates from its average value. A good measure of it is the energy *fluctuation*, defined as

$$\Delta E \equiv \sqrt{\langle (E - \langle E\rangle)^2\rangle}, \tag{5}$$

where the angular brackets denote thermal average or ensemble average. This expression can be simplified as follows

$$\begin{aligned}\Delta E =& \sqrt{\langle (E - \langle E\rangle)^2\rangle} \\ =& \sqrt{\langle (E^2 - 2E\langle E\rangle + \langle E\rangle^2)\rangle} \\ =& \sqrt{\langle E^2\rangle - 2\langle E\rangle\langle E\rangle + \langle E\rangle^2} \\ =& \sqrt{\langle E^2\rangle - \langle E\rangle^2} \end{aligned} \tag{6}$$

Square of energy fluctuation can be writte, for canonical ensemble, as

$$\begin{aligned}(\Delta E)^2 =& \langle E^2\rangle - \langle E\rangle^2 \\ =& \frac{1}{\Delta}\frac{1}{Z}\int E^2 e^{-\beta E} dp\, dq - \left(-\frac{\partial \log Z}{\partial\beta}\right)^2 \\ =& \frac{1}{\Delta}\frac{1}{Z}\int \left(\frac{\partial^2}{\partial\beta^2}\right) e^{-\beta E} dp\, dq - \left(\frac{\partial \log Z}{\partial\beta}\right)^2 \\ =& \frac{1}{Z}\left(\frac{\partial^2}{\partial\beta^2}\right)\frac{1}{\Delta}\int e^{-\beta E} dp\, dq - \left(\frac{\partial \log Z}{\partial\beta}\right)^2 \\ =& \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial\beta^2}\right) - \left(\frac{\partial \log Z}{\partial\beta}\right)^2 \\ =& \frac{\partial^2 \log Z}{\partial\beta^2} \end{aligned} \tag{7}$$

The last step can be verified by working backwards and obtaining the last but one step. Energy fluctuation also depends quite simply on the partition function. The above result can be manipulated to obtain some useful relations

$$
\begin{aligned}
(\Delta E)^2 &= \frac{\partial^2 \log Z}{\partial \beta^2} \\
&= -\frac{\partial}{\partial \beta}\left(-\frac{\partial \log Z}{\partial \beta}\right) \\
&= -\frac{\partial}{\partial \beta}\langle E\rangle \\
&= -\frac{\partial T}{\partial \beta}\frac{\partial}{\partial T}\langle E\rangle \\
&= \frac{1}{k\beta^2}\frac{\partial}{\partial T}\langle E\rangle
\end{aligned} \tag{8}
$$

But, $\frac{\partial\langle E\rangle}{\partial T}$ is the specific heat of the system. The above equation thus becomes

$$
\boxed{(\Delta E)^2 = kT^2 C_v}, \tag{9}
$$

where C_v is the specific heat of the system, at constant volume. Thus, we see that energy fluctuations are intimately related to the specific heat of the system.

Relation between canonical and micro-canonical ensembles

Microcanonical and canonical ensemble describe physically different scenarios. One with energy fixed, and the other with energy constantly exchanged with a heat-bath. One might wonder how different the results obtained from the two would be. Also, one would like to understand how crucial is the choice of the ensemble, to study the properties of a system, because for a given system, it may not always be possible to estimate if considering the system to isolated is a good approximation or not.

We know that the average energy of a gas is proportional to the number of particles, $\langle E\rangle \propto N$. So should be the specific heat, because specfic heat is just $\frac{\partial\langle E\rangle}{\partial T}$. So, $C_v \propto N$. So energy fluctuations should be proportional to $\sqrt{N}$

$$\begin{aligned}\Delta E &\propto \sqrt{C_v} \\ &\propto \sqrt{N} \qquad (10)\end{aligned}$$

Magnitude of fluctuation can be correctly estimated by the quantity $\Delta E/\langle E\rangle$:

$$\begin{aligned}\frac{\Delta E}{\langle E\rangle} &\propto \frac{\sqrt{C_v}}{\langle E\rangle}\\ &\propto \frac{\sqrt{N}}{N}\\ &\propto \frac{1}{\sqrt{N}}\end{aligned} \tag{11}$$

It is clear than in the thermodynamic limit, the fluctutation would become zero

$$\lim_{N\to\infty}\frac{\Delta E}{\langle E\rangle} \propto \lim_{N\to\infty}\frac{1}{\sqrt{N}} = 0 \tag{12}$$

So, in the limit of number of particles being very large, the fluctions are negligible, and the energy remains practically constant. If the energy is alsmost constant, one can also safely use microcanonical ensemble to describe the system. So we conclude that the in the thermodynamic limit ($N \to \infty$), canonical and microcanonical ensembles should give similar results.