The partition function and the calculation of various thermodynamic quantities

In our earlier article, we introduced the partition function. In this article, we will see that it is very useful. Recall that the partition function is given by

$$Z = \sum_i \exp(-E_i/kT) \tag{1}$$

If we introduce $\beta \equiv 1/kT$, we can express the partition function more succinctly as

$$Z = \sum_i \exp(-\beta E_i) \tag{2}$$

Then, what is the average energy of the system? As the Boltzmann factor is given by $\exp(-\beta E_i)$, we have

$$\langle E \rangle = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \tag{3}$$

The summation in the numerator may seem daunting. Nevertheless, notice that

$$-\frac{\partial Z}{\partial \beta} = \sum_i E_i \exp(-\beta E_i) \tag{4}$$

Thus, we see that

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \tag{5}$$

Therefore, once you know the partition function, calculating the average energy is very easy. In reality, the actual energy hardly deviates from the average energy, because we are dealing with a system with a huge number of particles. So, we can say $U = \langle E \rangle$.

What is the pressure in terms of the partition function? We know

$$P_i = -\frac{\partial E_i}{\partial V} \tag{6}$$

Thus,

$$P = \langle P \rangle = -\frac{\sum_i \frac{\partial E_i}{\partial V} \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \tag{7}$$

where we again used the fact that the pressure is just the average pressure.

Now notice that

$$\frac{\partial Z}{\partial V} = -\beta \sum_i \frac{\partial E_i}{\partial V} \exp(-\beta E_i) \tag{8}$$

Thus, we conclude

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} \tag{9}$$

Now, let's now consider the Helmholtz free energy. Using (5) and

$$S = -(\partial F/\partial T)_V \tag{10}$$

we get

$$\begin{aligned} F &= U - TS & (11) \\ &= -\frac{\partial \ln Z}{\partial \beta} - \beta \left(\frac{\partial F}{\partial \beta}\right)_V & (12) \end{aligned}$$

We also have

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{13}$$

It is easy to check that the following satisfies both (12) and (13) (**Problem 1.** Check this!)

$$F = -kT \ln Z \tag{14}$$

Thus, we expressed the Helmholtz Free energy in terms of the partition function.

In conclusion, you can calculate any thermodynamic quantities, once you obtain the partition function as a function of temperature and volume. You can calculate the energy by (5), the pressure by (9), the entropy by (10) and (14).

Problem 2. Express $\langle E^2 \rangle$ in terms of the partition function. Then, show

$$\langle (\Delta E)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2} \tag{15}$$

by using $\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$.

Problem 3. Suppose there are two possible states a boson called "A" can occupy: $E = 0$, $E = E_0$. If there are two As, what is the partition funtion? (Hint[1]) Repeat the calculation when the type of particle concerned is a fermion.

Summary

- The partition function is given by

$$Z = \sum_i \exp(-\beta E_i)$$

  where $\beta = 1/(kT)$

- Once we know the partition function, we can calculate various thermodynamics quantities. For example,

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$F = -kT \ln Z$$

[1] Recall they are indistinguishable.