

Lecture 13 - Partition function Z

What's Important:

- partition function
- fluctuations and specific heat
- work and Z
- entropy and Z

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Partition function

The sum over the Boltzmann factors $\exp(-\beta E_r)$ appears so frequently in statistical mechanics that it is given a special name, the partition function Z

$$Z = \sum_r e^{-\beta E_r} \quad (13.1)$$

This sum-over-states involves all accessible states r of the system. The partition function is useful for more than just notational convenience. Consider the mean energy, which we can write for discrete states as

$$\bar{E} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

But the numerator can also be expressed as

$$\sum_r E_r e^{-\beta E_r} = - \sum_r \frac{\partial}{\partial \beta} e^{-\beta E_r} = - \frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r} = - \frac{\partial}{\partial \beta} Z \quad (13.2)$$

Therefore, we can write the mean energy in the elegant form

$$\bar{E} = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta} \quad (13.3)$$

The partition function can also be used to determine the fluctuations in the energy. The mean squared deviation is

$$\overline{E^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2 \quad (13.4)$$

The mean energy has already been determined, so what we need next is to calculate the mean square of the energy, starting with the analog of Eq. (13.2)

$$\sum_r E_r^2 e^{-\beta E_r} = - \sum_r E_r \frac{\partial}{\partial \beta} e^{-\beta E_r} = (-1)^2 \frac{\partial}{\partial \beta} \sum_r \frac{\partial}{\partial \beta} e^{-\beta E_r} = \frac{\partial^2}{\partial \beta^2} Z$$

Like Eq. (13.1) then

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (13.5)$$

Substituting Eq. (13.5) and (13.3) into (13.4) gives:

$$\overline{E^2} = \overline{E}^2 - \overline{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{\partial \ln Z}{\partial \beta} \right)^2 \quad (13.6)$$

As cumbersome as this expression looks, it can be simplified. We work backwards from the second derivative of $\ln Z$:

$$\begin{aligned} \frac{\partial^2 \ln Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \frac{\partial \ln Z}{\partial \beta} \\ &= \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= \frac{\partial Z^{-1}}{\partial \beta} \cdot \frac{\partial Z}{\partial \beta} + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \\ &= -\frac{1}{Z^2} \cdot \frac{\partial Z}{\partial \beta} \cdot \frac{\partial Z}{\partial \beta} + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \\ &= -\frac{\partial \ln Z}{\partial \beta}^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \end{aligned}$$

This last line is just the right-hand side of Eq. (13.6), leaving us with

$$\overline{E^2} = \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (13.7)$$

Fluctuations and specific heat

Eq. (13.7) provides a compact derivation of the relationship between the specific heat of a system and the fluctuations in its energy. Start by breaking up the derivative and substituting Eq. (13.3):

$$\overline{E^2} = \frac{\partial}{\partial \beta} \frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \overline{E}$$

Now the heat capacity C_V is defined by

$$C_V = \frac{\partial \overline{E}}{\partial T} \quad (13.8)$$

To relate the derivative with respect to T to that with respect to β is simple

$$\begin{aligned} \frac{\partial \overline{E}}{\partial \beta} &= \frac{\partial T}{\partial \beta} \frac{\partial \overline{E}}{\partial T} = \frac{\partial (k_B \beta)^{-1}}{\partial \beta} \frac{\partial \overline{E}}{\partial T} \\ &= \frac{1}{k_B} (-1) \frac{1}{\beta^2} \frac{\partial \overline{E}}{\partial T} \\ &= -\frac{1}{k_B \beta^2} \frac{\partial \overline{E}}{\partial T} \end{aligned}$$

Inverting this expression (watch out for the T 's), and substituting into Eq. (13.8) gives

$$C_V = \frac{1}{k_B T^2} \overline{E^2}. \quad (13.9)$$

From a theoretical perspective, this equation permits the extraction of energy fluctuations from the specific heat.

Physically, it establishes that the faster the energy of a system increases with temperature, the greater are the fluctuations in its energy. That is, systems that require a lot of energy to increase their temperature (small specific heat) have small energy fluctuations.

Work and Z

Suppose now that there is a change in one or more of the external parameters h (for example, the volume) describing a system. For a given energy state E_r , the change associated with the change in h can be written as

$${}_h E_r = \frac{\partial E_r}{\partial h} dh$$

The work done **by** the system as a consequence of this shift is

$$- \frac{\partial E_r}{\partial h} dh$$

according to the sign convention in

$$d\bar{E} = dQ - dW.$$

Hence, the work done **by** the system as a consequence of all the shifts in energy states is

$$dW = \frac{\sum_r e^{-\beta E_r} - \frac{\partial E_r}{\partial h} dh}{\sum_r e^{-\beta E_r}} \quad (13.10)$$

The ensemble average is required because the system may roam between states. Now, the derivative of the Boltzmann factor can be written as

$$\frac{\partial}{\partial h} e^{-\beta E_r} = -\beta \frac{\partial E_r}{\partial h} e^{-\beta E_r}$$

Combining this with the definition of the partition function transforms (13.10) to

$$dW = \frac{\sum_r \frac{1}{\beta} \frac{\partial}{\partial h} e^{-\beta E_r} dh}{Z} = \frac{1}{\beta Z} \frac{\partial}{\partial h} Z dh = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h} dh$$

What good does this do us? In first year, work is equal to the product of a force acting through a distance. Here, dh is the generalized distance, so the generalized force must be

$$\phi = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h} \quad (13.11)$$

For example, if the variable h is the volume, then the pressure must be

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}.$$

Entropy and Z

To find the link between entropy and the partition function, we must determine how Z varies with both temperature (since it depends on T , whereas Ω depends on E) and mechanical characteristics h . With its dependence on T and h we write

$$d \ln Z = \frac{\partial \ln Z}{\partial h} dh + \frac{\partial \ln Z}{\partial \beta} d\beta \quad (13.12)$$

Now, $\ln Z / dh$ is just $\beta\phi$ (generalized force). The second term $\ln Z / d\beta$ is the (negative) of the mean energy:

$$\frac{\partial \ln Z}{\partial h} = \beta\phi \quad \frac{\partial \ln Z}{\partial \beta} = -\bar{E}$$

so Eq. (13.12) becomes

$$d \ln Z = \beta\phi dh - \bar{E} d\beta = \beta dW - \bar{E} d\beta$$

The last term can be rearranged using

$$d(\beta\bar{E}) = \bar{E} d\beta + \beta d\bar{E}$$

to read

$$d \ln Z = \beta dW + \beta d\bar{E} - d(\beta\bar{E})$$

or

$$d(\ln Z + \beta\bar{E}) = \beta(dW + d\bar{E}) = \beta dQ$$

Thus,

$$k_B d(\ln Z + \beta\bar{E}) = \frac{dQ}{T}. \quad (13.13)$$

Now, this expression looks like the expression for entropy, if we identify

$$S = k_B(\ln Z + \beta\bar{E}) \quad (13.14)$$

This can be reworked to give

$$TS = Tk_B \ln Z + \bar{E}$$

or

$$\bar{E} - TS = -Tk_B \ln Z = F \quad (13.15)$$

where F is the Helmholtz free energy.