

Appendix C extra - Partition function

This section introduces the partition function Z , a very useful tool for calculations in statistical mechanics. There is little new conceptual material here, although the partition function is used to obtain several important relations. Mathematical proofs in the textbook largely avoid invoking the partition function.

Partition function

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

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}} . \quad (\text{Cx4.1})$$

This sum-over-states involves all accessible states α 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

$$\bar{E} = \frac{\sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}}}{\sum_{\alpha} e^{-\beta E_{\alpha}}} .$$

The numerator of this expression can also be written as

$$\sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} = - \sum_{\alpha} \frac{\partial}{\partial \beta} e^{-\beta E_{\alpha}} = - \frac{\partial}{\partial \beta} \sum_{\alpha} e^{-\beta E_{\alpha}} = - \frac{\partial}{\partial \beta} Z . \quad (\text{Cx4.2})$$

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

$$\bar{E} = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta} . \quad (\text{Cx4.3})$$

Written in terms of Z , fluctuations in the energy have an equally compact form. The mean squared deviation of the energy is defined as

$$\overline{E^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2 . \quad (\text{Cx4.4})$$

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. (Cx4.2)

$$\sum_{\alpha} E_{\alpha}^2 e^{-\beta E_{\alpha}} = - \sum_{\alpha} E_{\alpha} \frac{\partial}{\partial \beta} e^{-\beta E_{\alpha}} = (-1)^2 \frac{\partial}{\partial \beta} \sum_{\alpha} \frac{\partial}{\partial \beta} e^{-\beta E_{\alpha}} = \frac{\partial^2}{\partial \beta^2} Z .$$

Similarly to Eq. (Cx4.3) then

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}. \quad (\text{Cx4.5})$$

Substituting Eq. (Cx4.5) and (Cx4.3) into (Cx4.4) gives:

$$\overline{E^2} = \overline{E^2} - \overline{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{\partial \ln Z}{\partial \beta}^2. \quad (\text{Cx4.6})$$

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. (Cx4.6), leaving us with

$$\overline{E^2} = \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (\text{Cx4.7})$$

Fluctuations and specific heat

Eq. (Cx4.7) 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. (Cx4.3):

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

Now the heat capacity C_v is defined by

$$C_v = \frac{\partial \overline{E}}{\partial T}. \quad (\text{Cx4.8})$$

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

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

Inverting this expression (watch out for the T 's), and substituting into Eq. (Cx4.8) gives

$$C_V = \frac{1}{k_B T^2} \overline{E^2}. \quad (\text{Cx4.9})$$

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 , the change associated with the change in h can be written as

$${}_h E_\alpha = \frac{\partial E_\alpha}{\partial h} dh.$$

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

$$-\frac{\partial E_\alpha}{\partial h} dh$$

according to the sign convention in the work-energy relation from thermodynamics

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

where Q is the heat absorbed by the system and d indicates an infinitesimal quantity. Hence, the work done **by** the system as a consequence of all the shifts in energy states is

$$dW = \frac{\sum_\alpha e^{-\beta E_\alpha} \left(-\frac{\partial E_\alpha}{\partial h} dh \right)}{\sum_\alpha e^{-\beta E_\alpha}}. \quad (\text{Cx4.10})$$

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

$$\frac{\partial}{\partial h} e^{-\beta E_\alpha} = -\beta \frac{\partial E_\alpha}{\partial h} e^{-\beta E_\alpha}.$$

Combining this with the definition of the partition function transforms (Cx4.10) to

$$dW = \frac{\frac{1}{\beta} \frac{\partial}{\partial h} e^{-\beta E_\alpha} dh}{Z} = \frac{1}{\beta Z} \frac{\partial}{\partial h} Z dh = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h} dh.$$

What good does this do us? In introductory physics courses, 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

$$\phi = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h}. \quad (\text{Cx4.11})$$

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 observables like h . With its dependence on T and h we write the change in $\ln Z$ as

$$d \ln Z = \frac{\partial \ln Z}{\partial h} dh + \frac{\partial \ln Z}{\partial \beta} d\beta. \quad (\text{Cx4.12})$$

Now, $\ln Z/dh$ is just $\beta\phi$ (generalized force from Eq. [Cx4.11]). 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. (Cx4.12) 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

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

With the replacement $\beta = (k_B T)^{-1}$, the last line becomes

$$k_B d(\ln Z + \beta\bar{E}) = \frac{dQ}{T}. \quad (\text{Cx4.13})$$

Now, this expression looks like the thermodynamic expression for entropy $dS = dQ/T$, if we identify

$$S = k_B(\ln Z + \beta\bar{E}). \quad (\text{Cx4.14})$$

This can be reworked to give

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

or

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

(Cx4.15)

where F is the Helmholtz free energy.