



5. Free energy minimisation

Mean and variance of energy fluctuations



- Energy of a system connected to a heat bath exhibits thermal fluctuations (it is a free macroscopic variable) controlled by the Boltzmann distribution

$$P_i = \frac{1}{Z} \exp(-\beta E_i) \quad \beta = \frac{1}{kT}$$

- Consider the mean energy

$$\begin{aligned} \bar{E} &\equiv \sum_i E_i P_i = \frac{1}{Z} \sum_i E_i \exp(-\beta E_i) \\ &= -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} \exp(-\beta E_i) \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial \ln Z}{\partial \beta} \quad \begin{array}{l} \swarrow \text{chain rule} \\ \searrow \end{array} \\ \bar{E} &= -\frac{dT}{d\beta} \frac{\partial \ln Z}{\partial T} = kT^2 \frac{\partial \ln Z}{\partial T} \end{aligned}$$



Mean and variance of energy fluctuations

- Variance of the energy distribution $\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2$
- It turns out that this variance is related to the heat capacity C defined by

$$C \equiv \frac{\partial \bar{E}}{\partial T} = \frac{d\beta}{dT} \frac{\partial \bar{E}}{\partial \beta} = - \frac{1}{kT^2} \frac{\partial \bar{E}}{\partial \beta}$$

- Specifically, one can show (see notes)

$$C = \frac{1}{kT^2} \left[\overline{E^2} - \bar{E}^2 \right] = \frac{\overline{(\Delta E)^2}}{kT^2}$$

- The response of the energy to a change in temperature is related to the fluctuations of the energy at fixed T!

Mean and variance of energy fluctuations



- Since \bar{E} is proportional to N (extensive), so will be $C = \partial \bar{E} / \partial T$. Hence

$$\overline{(\Delta E)^2} \propto N \quad \text{and} \quad \frac{\left(\overline{(\Delta E)^2}\right)^{1/2}}{\bar{E}} \propto \frac{1}{\sqrt{N}}$$

- Although the energy is a free macroscopic variable, it takes on a sharply defined value \bar{E} .
- Consequently a large system in equilibrium with a heat bath should have essentially the same behavior as a large isolated system with fixed energy \bar{E} .

Energy distribution, entropy, and free energy



- For large N we expect many of the microstates to have the same energy.
- Rather than sum over all microstates, more convenient to sum over the possible values of the energy weighted by $\Omega(E)$

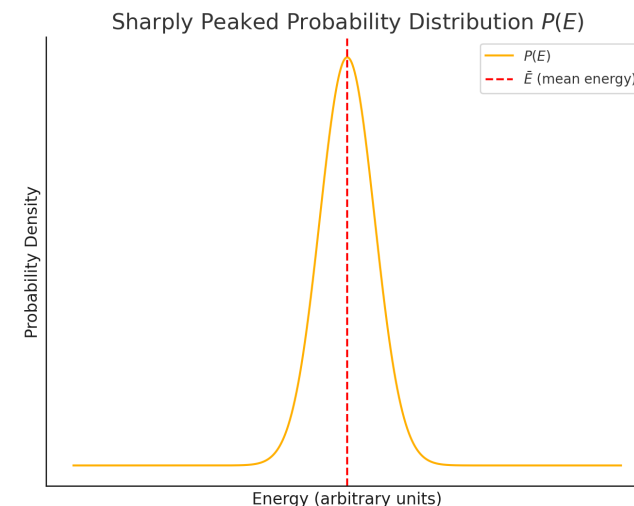
$$\bar{E} = \sum_E E p(E) = \frac{1}{Z} \sum_E \Omega(E) E \exp(-\beta E)$$

where $P(E) = \frac{1}{Z} \Omega(E) \exp(-\beta E)$

and $Z = \sum_E \Omega(E) \exp(-\beta E)$

- Often refer to $\Omega(E)$ as the **degeneracy** of energy E

- Since $E \sim N$, $\exp(-\beta E)$ is a sharply **decreasing** function of E .
- $\Omega(E)$ is exponentially large in N and is a sharply **increasing** function of E . The product is therefore a sharply peaked probability distribution around \bar{E} .



Energy distribution, entropy, and free energy



- Rearrange expression for $P(E)$ to absorb $\Omega(E)$ into the exponential.

$$\begin{aligned} P(E) &= \frac{1}{Z} \exp \left(-\beta \left(E - \frac{\ln \Omega(E)}{\beta} \right) \right) \\ &= \frac{1}{Z} \exp(-\beta(E - TS(E))) \\ &= \frac{1}{Z} \exp(-\beta F(E)) \end{aligned}$$

- Here $F(E) \equiv E - TS(E)$ is the (Helmholtz) free energy
- Peak of $P(E)$ occurs when the argument of the exponential is maximized.
- Thus, we see that the equilibrium value of the energy E is determined by **minimising the free energy**.
- *Key point 11: The equilibrium values of the macroscopic properties $E, \{\alpha\}$ of a system in equilibrium are such as to minimize the free energy $F(E, \{\alpha\}) \equiv E - TS(E, \{\alpha\})$*

Energy-entropy competition



Statistical Mechanics

$$F(E) = E - TS(E)$$

- Competition between energy and entropy, the arbiter of which is temperature.



High $T \rightarrow \infty$: F is dominated by $S \Rightarrow$ minimising F corresponds to maximizing S

Low $T \rightarrow 0$: F is dominated by $E \Rightarrow$ minimising F corresponds to minimizing E

- Note: In an isolated system, $E = \text{constant}$, therefore we just maximize the entropy to find the equilibrium state. For a system in thermal contact with its environment, E is free to vary and we must minimise the free energy instead.
- Energy entropy competition explains phenomena such as phase changes



Utility of partition function

- Recall $Z = \sum_E \Omega(E) \exp(-\beta E)$

- Summand is very sharply peaked at \bar{E} of width $N^{1/2}$ about the peak \Rightarrow

$$Z \approx \Omega(\bar{E}) \exp(-\beta \bar{E}) \times O(N^{1/2})$$

$$= \exp(-\beta F(\bar{E})) \times O(N^{1/2}) \quad \text{since } F(T) = F(\bar{E}) \text{ for a large system in equilibrium}$$

$$= \exp(-\beta F(T)) \times O(N^{1/2})$$

- Thus $\ln Z = -\beta F(T) + O(\ln N^{1/2})$

$$F(T) = \bar{E} - TS(T) = -kT \ln Z \quad \text{since } N \gg \ln N \text{ for a large system in equilibrium}$$

- Therefore, for a large system in thermal equilibrium, all the thermodynamic properties can be obtained from Z via the following formulae:

- Key point 12:* $F = -kT \ln Z, \quad \bar{E} = kT^2 \frac{\partial}{\partial T} \ln Z, \quad S = k \ln Z + \frac{\bar{E}}{T}$

Worked example



- A system has allowed energy $E_n = -R/n^2$ with $n = 1, 2, 3, \dots$ with $R = 13.6$ eV
- Suppose that for each energy E_n there are $2n^2$ different accessible microstates. (This is the case for a hydrogen atom.) Let $P(E_1)$ be the probability that the system has energy $E_1 = -R$ and $P(E_2)$ be the probability that $E_2 = -R/4$. Calculate the ratio $P(E_2)/P(E_1)$ for $T = 10^5$ K. Find the temperature at which $P(E_1) = P(E_2)$.

Solution

We have $P(E) = \frac{1}{Z} \Omega(E) e^{-\beta E}$ where $Z = \sum_i e^{-\beta E_i} = \sum_E \Omega(E) e^{-\beta E}$ and $\Omega(E_1) = 2$, $\Omega(E_2) = 8$

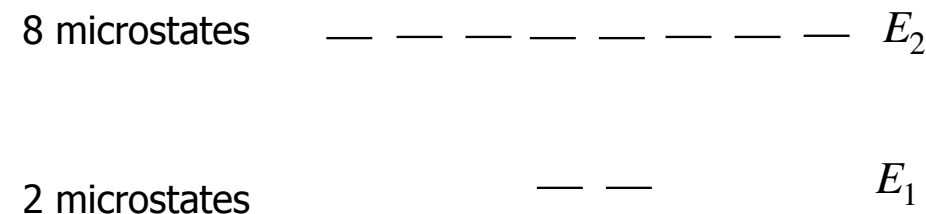
$$\frac{P(E_2)}{P(E_1)} = \frac{8}{2} e^{-\beta(E_2 - E_1)}. \text{ Sticking in the numbers given (convert to SI) yields } \frac{P(E_2)}{P(E_1)} \approx 1.2$$

For $P(E_2) = P(E_1)$ need $2e^{-\beta E_1} = 8e^{-\beta E_2}$

$$\beta(E_2 - E_1) = \ln 4$$

$$\Rightarrow T = \frac{E_2 - E_1}{k \ln 4}$$

$$\Rightarrow T = 8.6 \times 10^4 \text{ K}$$



Worked example



- A system has three microstates, a ground state with zero energy and two excited states with energy ϵ . The system is in equilibrium at temperature T . Find expressions for the partition function Z , the mean internal energy \bar{E} , the entropy S and the heat capacity C .
- Solution

$$Z = \sum_i e^{-\beta E_i} = \sum_E \Omega(E) e^{-\beta E}$$
$$= 1 + 2e^{-\beta\epsilon}$$
$$\ln Z = \ln(1 + 2e^{-\beta\epsilon})$$
$$\bar{E} = kT^2 \frac{\partial \ln Z}{\partial T} = \frac{kT^2}{1 + 2e^{-\beta\epsilon}} \times 2e^{-\beta\epsilon} \left(\frac{-\epsilon}{k} \right) \frac{(-1)}{T^2}$$
$$= \frac{2\epsilon e^{-\beta\epsilon}}{1 + 2e^{-\beta\epsilon}} = \frac{2\epsilon}{e^{\beta\epsilon} + 2}$$

$$S = \frac{\bar{E}}{T} + k \ln Z$$
$$= \frac{2\epsilon}{T(2 + e^{\beta\epsilon})} + k \ln(1 + 2e^{-\beta\epsilon})$$
$$C = \frac{\partial \bar{E}}{\partial T} = \frac{-2\epsilon}{[e^{\beta\epsilon} + 2]^2} e^{\beta\epsilon} \left(\frac{\epsilon}{k} \right) \frac{(-1)}{T^2}$$
$$= \frac{2\epsilon^2 e^{\beta\epsilon}}{kT^2 [e^{\beta\epsilon} + 2]^2}$$