5. Free energy minimisation

Mean and variance of energy fluctuations

Statistical Mechanics

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

$$P_i = \frac{1}{Z} \exp\left(-\beta E_i\right)$$

- Consider the mean energy

$$\overline{E} \equiv \sum_i E_i P_i = \frac{1}{Z} \sum_i E_i \exp(-\beta E_i)$$

$$= -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} \exp(-\beta E_i)$$

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

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

chain rule

$$\overline{E} = -\frac{dT}{d\beta} \frac{\partial \ln Z}{\partial T} = kT^2 \frac{\partial \ln Z}{\partial T}$$

Mean and variance of energy fluctuations

- Variance of the energy distribution $\overline{(\Delta E)^2} = \overline{(E - \overline{E})^2} = \overline{E^2} - \overline{E}^2$

- It turns out that this variance is related to the heat capacity C defined by

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

- Specifically, one can show (see notes)

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

- 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

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

- 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 $\bar{E}$.
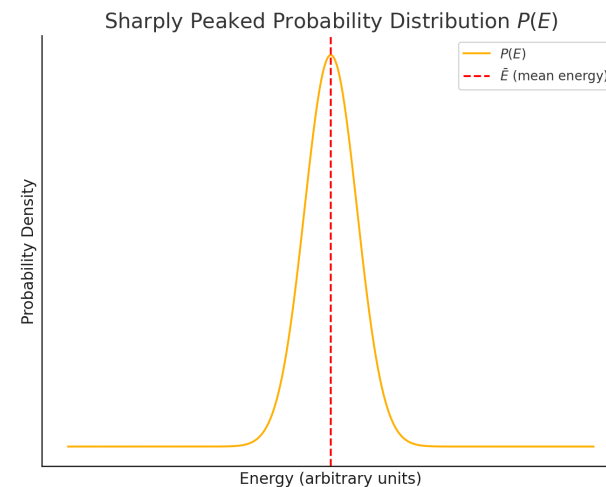
Energy distribution, entropy, and free energy

- 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 $\Omega(E)$

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

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

- 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 $\overline{E}$.

Sharply Peaked Probability Distribution $P(E)$

— $P(E)$
--- $\bar{E}$ (mean energy)

Probability Density

Energy (arbitrary units)

Energy distribution, entropy, and free energy

• Rearrange expression for $P(E)$

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

$$= \frac{1}{Z} \exp(-\beta(E - TS))$$

$$= \frac{1}{Z} \exp(-\beta F)$$

• 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

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

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

T ↑

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

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

- Note: In an isolated system, E = constant, therefore we just maximize the entropy to find the most likely macrostates. For a system in thermal contact with its environment, E is free to vary and we minimise the free energy.

- Energy entropy competition explains phenomena such as phase changes

Utility of partition function

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

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

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

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

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

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

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

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