

Probability distributions

The probability of an event in a trial is:

$$\mathbb{P}(\text{event}) := \lim_{N \rightarrow \infty} \frac{n}{N}$$

given n occurrences in N trials.

For discrete probabilities:

$$\begin{aligned} \sum_{i=1}^q \mathbb{P}(i) &= 1 \\ \mathbb{P}(i \text{ or } j) &= \mathbb{P}(i) + \mathbb{P}(j) \\ \mathbb{P}(i \text{ and } j) &= \mathbb{P}(i)\mathbb{P}(j). \end{aligned}$$

Given continuous random variables:

$$\mathbb{P}([x, x + dx]) = P(x)dx$$

for P is the probability density function:

$$\int_{-\infty}^{\infty} P(x)dx = 1.$$

We define the **mean** and **variance** as:

$$\bar{x} = \sum_{i=1}^q x_i P_i \text{ or } \int_{-\infty}^{\infty} x P(x)dx$$

$$\begin{aligned} \overline{\Delta x^2} &= \sum_{i=1}^q (x_i - \bar{x})^2 P_i \\ &= \int_{-\infty}^{\infty} (x - \bar{x})^2 P(x)dx \\ &= \overline{x^2} - (\bar{x})^2. \end{aligned}$$

The **standard deviation** is the square root of the variance $(\overline{\Delta x^2})^{1/2}$ and:

$$\overline{f(x)} = \int_{-\infty}^{\infty} f(x)P(x)dx.$$

Binomial distribution

The probability of observing n events each with probability p in N trials is:

$$P_n = \binom{N}{n} p^n (1-p)^{N-n}$$

where $\binom{N}{n} = \frac{N!}{n!(N-n)!}$ with:

$$\bar{n} = Np \text{ and } \overline{\Delta n^2} = Np(1-p)$$

since we have that:

$$(a+b)^N = \sum_{n=0}^N \binom{N}{n} a^n b^{N-n}$$

$$\begin{aligned} f(\alpha) &= \sum_{n=0}^N \binom{N}{n} (p\alpha)^n (1-p)^{N-n} \\ &= (p\alpha + 1 - p)^N. \end{aligned}$$

Note that $\binom{N}{n}$ denotes ways to pick n items from N items. For large N :

$$\ln(N!) \approx N \ln(N) - N$$

known as **Stirling's approximation**.

We also define the **fractional deviation** as the deviation on the scale of the mean:

$$\frac{(\overline{\Delta x^2})^{1/2}}{\bar{x}} = \frac{1}{N^{1/2}}.$$

Taylor expansions

Let $s(n)$ be expanded at $n = a$:

$$\begin{aligned} s(n) &= s(a) + s'(a)(n-a) \\ &\quad + \frac{1}{2}s''(a)(n-a)^2 + \mathcal{O}[(n-a)^3]. \end{aligned}$$

Poisson distribution

Let $N \gg n$ and let p be the probability of an event in a trial. Assume that as $N \rightarrow \infty$, $p \rightarrow 0$. Under such conditions the binomial probability of observing n events in N trials is:

$$P_n \approx (\bar{n})^n \frac{\exp(-\bar{n})}{n!}$$

with mean and variance Np .

Gaussian distribution

Let N be very large. Then the binomial distribution becomes Gaussian:

$$P_n \approx \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(n-Np)^2}{2\sigma^2}\right)$$

via Stirling's approximation and Taylor expansions with variance $\sigma^2 = Np(1-p)$ and mean $\mu = Np$.

Microstates and macrostates

A **microstate** is a complete specification of **all degrees of freedoms** in a system, with respect to a microscopic model.

A **macrostate** is a limited description by the values of observables, like pressure.

We assume that the molecules are weakly interacting. (no interaction potentials)

Boltzmann law

Consider a **microcanonical ensemble** with **fixed** N and E . The Boltzmann law defines the entropy for isolated systems:

$$S(N, E, \{\alpha\}) := k_B \ln[\Omega(N, E, \{\alpha\})]$$

$$k_B = 1.381 \times 10^{-23} \text{ JK}^{-1}$$

where Ω is the corresponding number of microstates to a macrostate defined by a set of observables $\{\alpha\}$. The probability an isolated system with macrostate is:

$$\mathbb{P}(\alpha_i^*) = \frac{\Omega(\alpha_i^*)}{\Omega(\{\alpha\})}.$$

Maximum entropy is at the equilibrium state since it has the largest weight Ω . Hence an isolated system is most likely to be found at equilibrium.

Two-state model magnets

Consider an array of N magnetic dipoles and total energy E that is subject to a magnetic field \mathbf{H} .

$$\{\uparrow\downarrow\uparrow\uparrow \dots \downarrow\downarrow\uparrow\uparrow\}$$

Define n to be the number of dipoles with energy $\epsilon_{\uparrow} = +mH$ (excited state) and the remaining in $\epsilon_{\downarrow} = -mH$ (ground state).

Since we can write the total energy E as:

$$mH(n - (N - n)) = E$$

$$\therefore n = \frac{1}{2} \left(N + \frac{E}{mH} \right)$$

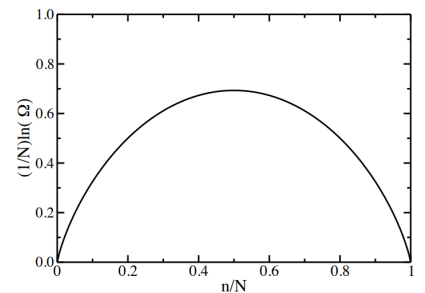
and the **weight** of this macrostate is:

$$\Omega(N, E, n) = \binom{N}{n}.$$

If $N \gg 1$ we use Stirling's approximation and define $x = n/N$:

$$\Omega(N, E, n) \approx \exp[Ns(x)]$$

$$s(x) = -(1-x) \ln(1-x) - x \ln x.$$



For in the $s(x)$ plot above our end points are computed via limits.

Now let the number of excited dipoles be $n = N/2$ and denote n_L as the number excited dipoles in the left.

$$\underbrace{\{\dots \uparrow\downarrow\uparrow \dots\}}_{n_L} | \dots \downarrow\downarrow\uparrow \dots \}$$

The weight of macrostate n_L now is:

$$\Omega(N, E=0, n_L) = \binom{N/2}{n_L} \binom{N/2}{n - n_L}$$

which under large N becomes:

$$\frac{1}{N} \ln[\Omega(N, 0, n_L)] \approx s(y)$$

for $y = n_L/(N/2)$. If $N \rightarrow \infty$:

$$\Omega(N, 0, n_L) = \begin{cases} 0 & y \neq 0.5 \\ 2^N & y = 0.5 \end{cases}$$

or that $n_L = N/4$ exactly for large N .

Entropy

Entropy is a **measure of disorder** in a system. For subsystems in equilibrium:

$$\Omega(N, E) = \Omega(N_1, E_1)\Omega(N_2, E_2) \\ \implies S = S_1 + S_2.$$

If $E_1 \rightarrow E_1 + dE_1$ and $E_2 \rightarrow E_2 - dE_1$:

$$dS = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 = 0$$

since overall we have an isolated system. i.e. objects in thermal equilibrium have the same temperature:

$$dE = TdS - PdV \\ \implies \frac{\partial S_i}{\partial E_i} := \frac{1}{T_i}$$

since fixed number of particles N in an isolated system implies a fixed volume V .

i.e. temperature is the **ratio of change** of S and E of a system! If there exists a temperature gradient:

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 > 0$$

where $T_1 > T_2$ implies negative dE_1 .

Boltzmann distribution

Consider a **canonical ensemble** with fixed particles N but **changing energy E** in thermal equilibrium *with heat reservoir* at temperature T .

Then the probability of **an** energy state E_i for this canonical ensemble is:

$$\mathbb{P}(E_i) = \frac{1}{Z} \exp(-\beta E_i) \\ Z = \sum_j \exp(-\beta E_j) \text{ and } \beta = \frac{1}{k_B T}.$$

Partition function Z is the sum of **all** microstates E_i of the ensemble.

Free energy minimisation

The **mean energy** is computed as:

$$\bar{E} = \sum_i E_i \mathbb{P}(E_i) \\ = -\frac{1}{Z} \sum_i \left(\frac{\partial}{\partial \beta} \exp(-\beta E_i) \right) \\ = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \\ = k_B T^2 \frac{\partial \ln Z}{\partial T}$$

and **heat capacity** is defined as:

$$C := \frac{\partial \bar{E}}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial \bar{E}}{\partial \beta} \\ = \frac{(\Delta E)^2}{k_B T^2}$$

since $(\Delta E)^2 = \bar{E}^2 - \bar{E}^2$.

For every macrostate E there corresponds $\Omega(E)$ microstates:

$$\bar{E} = \sum_E \left(\Omega(E) \cdot E \right) \left[\frac{1}{Z} \exp(-\beta E) \right]$$

and the probability of macrostate E is:

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

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

where $F = E - TS$. **Free energy F** is **minimised** by the equilibrium state \bar{E} .

If N_1 is very large, $\mathbb{P}(\bar{E}) \rightarrow 1$ and:

$$Z \approx \Omega(\bar{E}) \exp(-\beta \bar{E}) \cdot \mathcal{O}[N^{1/2}] \\ = \exp(-\beta F) \cdot \mathcal{O}[N^{1/2}]$$

for here $F = \bar{E} - TS(T)$. Importantly:

$$F(T) = -k_B T \ln Z \\ \bar{E}(T) = k_B T^2 \frac{\partial \ln Z}{\partial T} \\ S(T) = k_B \ln Z + \frac{\bar{E}(T)}{T}.$$

Weakly interacting constituents

Consider a system of N particles. In the absence of interaction potentials given a microstate r with total energy E_r :

$$E_r = \epsilon_{i_1} + \dots + \epsilon_{i_N}$$

for ϵ_{i_j} is the j^{th} particle in the i^{th} state and has the following partition function:

$$Z = [Z(1)]^N \\ Z(1) = \sum_i \exp(-\beta \epsilon_i)$$

where this is a sum of all energy states of particles. The **probability** of particle 1 to exist at the state j is given by:

$$\mathbb{P}(\epsilon_{j_1}) = \sum_{i_2, \dots, i_N} \frac{\exp[-\beta(\epsilon_{j_1} + \epsilon_{i_2} + \dots)]}{Z} \\ = \frac{\exp(-\beta \epsilon_{j_1})}{Z(1)}$$

assuming particles can be distinguished.

If a_i, b_j, \dots are the states of different types of energy contributions then:

$$E_{ij\dots} = E_{a_i} + E_{b_j} + \dots \\ Z = \sum_{i,j,\dots} \exp[-\beta E_{ij\dots}] \\ = Z_a \times Z_b \times \dots$$

Classical solids

A classical $3d$ solid with N particles has spring oscillators which connects every particle. Every oscillator has energy:

$$\epsilon = \frac{1}{2} k x^2 + \frac{1}{2} m v^2$$

with 6 degrees of freedom. Then:

$$\bar{E} = 3Nk_B T$$

and is known as the Dulong–Petit law.

Einstein's model of solids

Consider a system of N particles which are weakly interacting. If every particle is modelled after the **same** $3d$ quantum oscillator with frequency ω then:

$$Z = [Z_{1d}(1)]^{3N} \\ Z_{1d}(1) = \sum_{n=0}^{\infty} \exp(-\beta \epsilon_n) \\ = \frac{\exp(-\frac{x}{2})}{1 - \exp(-x)}$$

where ϵ_n is the one dimensional harmonic oscillator at the n^{th} energy state:

$$\epsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega$$

and $x = \beta \hbar \omega$. We have also used:

$$\sum_{n=0}^{\infty} a^n = \frac{1}{1-a} \text{ where } |a| < 1.$$

Then the system the following properties:

$$\bar{E} = 3N\bar{\epsilon} = 3N \cdot -\frac{\partial}{\partial \beta} \ln [Z_{1d}(1)] \\ = 3N\hbar\omega \left[\frac{\exp(-x)}{1 - \exp(-x)} + \frac{1}{2} \right] \\ C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \left(\frac{\partial x}{\partial T} \right)_\omega \left(\frac{\partial \bar{E}}{\partial x} \right)_\omega \\ = 3Nk_B \frac{x^2 \exp(x)}{(\exp(x) - 1)^2} \\ S_{vib} = 3Nk_B \left[\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right]$$

with **characteristic temperature T^*** :

$$T^* = \frac{\hbar \omega}{k_B}$$

and is weakly interacting when $T \gg T^*$.

Ideal gases