Probability distributions

The probablity of an event in a trial is:

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

given n occurrences in N trials.
For discrete probabilities:

$$\sum_{i=1}^{q} \mathbb{P}(i) = 1$$

$$\mathbb{P}(i \text{ or } j) = \mathbb{P}(i) + \mathbb{P}(j)$$

$$\mathbb{P}(i \text{ and } j) = \mathbb{P}(i)\mathbb{P}(j).$$

Given continuous random variables:

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

for P is the probability density function:

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

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

$$\overline{x} = \sum_{i=1}^{q} x_i P_i \text{ or } \int_{-\infty}^{\infty} xP(x)\mathrm{d}x$$

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

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

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

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

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

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:

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

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 $N \to \infty$, $p \to 0$. Under such conditions the binomial probability of observing n events in N trials is:

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

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:

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

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

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 $\boldsymbol{H}$.

$$\{\uparrow\downarrow\uparrow\uparrow \ldots \downarrow\downarrow\uparrow\uparrow\}$$

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:

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

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

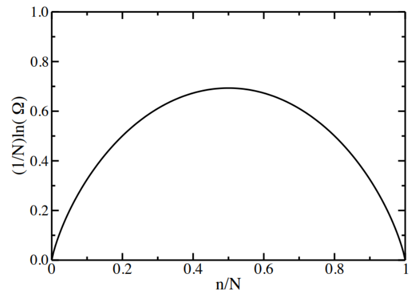
and the **weight** of this macrostate is:

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

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

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

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



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.

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

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:

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

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

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

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 $E_1 \to E_1 + \mathrm{d}E_1$ and $E_2 \to E_2 - \mathrm{d}E_1$:

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)\mathrm{d}E_1 = 0$$

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

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V$$
$$\implies \frac{\partial S_i}{\partial E_i} := \frac{1}{T_i}$$

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:

$$\mathrm{d}S = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathrm{d}E_1 > 0$$

where $T_1 > T_2$ implies negative $\mathrm{d}E_1$.

Boltzmann distribution

Consider a **canonical ensemble** with fixed particles N but changing energy E in thermal equilibrium 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:

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

and **heat capacity** is defined as:

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

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

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

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

and the probability of macrostate E is:

$$\begin{aligned}\mathbb{P}(E) &= \frac{1}{Z}\Omega(E)\exp(-\beta E)\\ &= \frac{1}{Z}\exp(-\beta F)\end{aligned}$$
$$Z = \sum_E \Omega(E)\exp(-\beta E)$$

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

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

$$\begin{aligned}Z &\approx \Omega(\overline{E})\exp\big(-\beta\overline{E}\big)\cdot\mathcal{O}[N^{1/2}]\\ &= \exp(-\beta F)\cdot\mathcal{O}[N^{1/2}]\end{aligned}$$

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

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

Weakly interacting constituents

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

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

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

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

The **probability** of particle 1 to exist at state j is given by:

$$\begin{aligned}\mathbb{P}(\epsilon_{j_1}) &= \sum_{i_2,\ldots,i_N}\frac{\exp\Big[-\beta(\epsilon_{j_1} + \epsilon_{i_2} + \ldots)\Big]}{Z}\\ &= \frac{\exp(-\beta\epsilon_{j_1})}{Z(1)}\end{aligned}$$

assuming particles can be distinguished.

Classical solids

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

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

with 6 degrees of freedom. Then:

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

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:

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

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:

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

with **characteristic temperature** T^*:

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

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

Ideal gases