

## 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:

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

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

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

Given continuous random variables:

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

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  $\Omega$  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  $\Omega$ . 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:

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

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

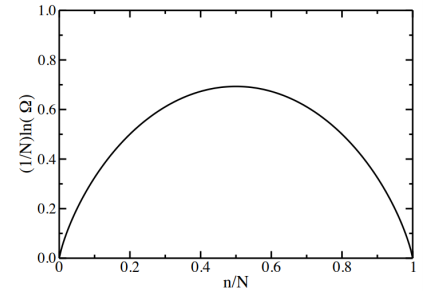
and the **weight** of this macrostate is:

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

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:

$$\begin{aligned}\Omega(N, E) &= \Omega(N_1, E_1)\Omega(N_2, E_2) \\ \implies S &= S_1 + S_2.\end{aligned}$$

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:

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

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