Statistical mechanics 1

#### 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:

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

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

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:

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

since we have that:

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

$$f(\alpha) = \sum_{n=0}^{N} {N \choose n} (p\alpha)^n (1-p)^{N-n}$$
$$= (p\alpha + 1 - p)^N.$$

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:

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

# Taylor expansions

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

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

## 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 nevents 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.

Given N molecules with total energy E the **Boltzmann law** defines entropy:

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

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

where  $\Omega$  is the number of corresponding microstates to a macrostate N, E with a set of observables  $\alpha$ .

i.e. for any macrostate there correspond many microstates. If one molecule has  $k \propto V$  microstates in volume V then N molecules have  $k^N \propto V^N$  in V.

#### 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 ground state  $\epsilon_{\downarrow} = -mH$ .

Since we can write the total energy E as:

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

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

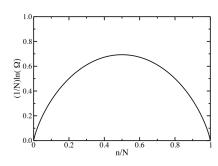
and the  $\mathbf{weight}$  of this macrostate is:

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

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

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

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



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 of n in the left, from the center of our array.

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

The weight of macrostate  $n_L$  now is:

$$\Omega(N, E=0)$$