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Statistical Mechanics

- Thermodynamics: studies systems considering only macroscopic parameters such as E, T, V, etc.

- Mechanics: predicts microscopic behavior by solving equations of motion. Impossible to solve for interacting systems with many bodies.

- Statistical Mechanics: combines thermo and mechanics and take advantage of large number of particles applying statistical methods

Elementary statistical concepts:

- Ensemble: very large number N of identically prepared systems.

- Probability of an event: number of systems in the ensemble for which the event has occurred, normalized by the number of systems N in the ensemble.

$$P_i = \frac{n_i}{N} \qquad \sum_{i=1}^{N} P_i = \sum_{i=1}^{N} \frac{n_i}{N} = \frac{N}{N} = 1$$

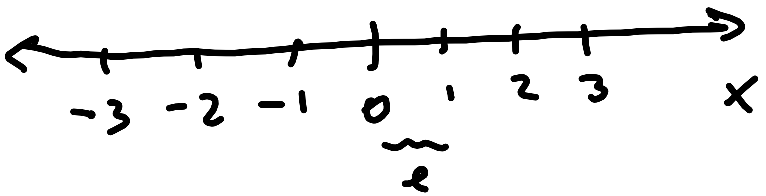
A probability distribution is always normalized to 1.

Probability Distributions

1_ Random Walk problem. (3D important for gases, proteins)

1D: two state system (important to study problems such as magnetism).

- a) where is the walker going to be after N steps?
- b) what is the probability of finding the walker a distance m from the start after N steps?



p : probability of 1 step to the right.

q : probability of 1 step to the left.

$q = 1 - p$ since $p + q = 1$

n_1 : # of steps to the right

n_2 : # " " " left

$N = n_1 + n_2$ total # of steps

$m = n_1 - n_2$ position after N steps.

$-N \le m \le N$

$m = n_1 - (N - n_1) =$

$= 2n_1 - N$

What is the probability of making n_1 steps to the right and n_2 to the left?

$$\frac{N!}{n_1!\,n_2!} p^{n_1} q^{n_2} = \frac{N!}{n_1!(N-n_1)!} p^{n_1} q^{N-n_1} = \binom{N}{n_1} p^{n_1} q^{N-n_1}$$

If $N=3$

n_1	n_2		
3	0	RRR	p^3
2	1	RRL RLR LRR	$p^2 q$
1	2	LLR LRL RLL	$p q^2$
0	3	LLL	q^3

$$W_N(n_1) = \frac{N!}{n_1!\,(N-n_1)!}\, p^{n_1} q^{N-n_1}$$

Probability of taking n_1 steps to the right after N steps.

if $p = q = \frac{1}{2}$ $\quad W_N(n_1) = \dfrac{\binom{N}{n_1}}{2^N}$

$\binom{N}{n_1}$ → # of events with n_1 steps to the right

2^N → all possible # of n_1 steps in N total # of steps.

$W_n(n_1)$ is called the binomial distribution.

P/ $\quad (p+q)^N = \sum_{n=0}^{N} \underbrace{\binom{N}{n} p^n q^{N-n}}_{W_N(n)}$

Let's connect $W_N(n_1)$ with $P_N(m)$ which is the probability of the walker being at a position m after N steps.

$$W_N(n_1) = \binom{N}{n_1} p^{n_1} q^{N-n_1} = \frac{N!}{n_1!\, n_2!} p^{n_1} q^{N-n_1} =$$

$m = n_1 - n_2$

$N = n_1 + n_2$

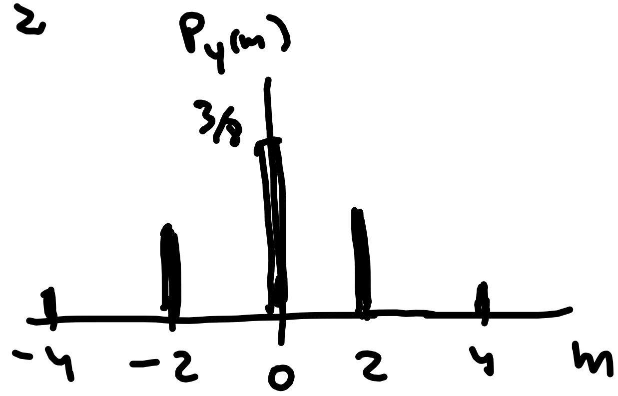
$$= \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}} q^{\frac{N-m}{2}} = P_N(m)$$

$n_1 = \frac{N+m}{2}$

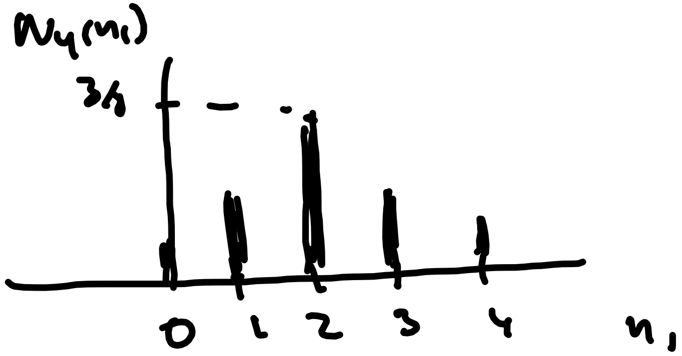
$n_2 = \frac{N-m}{2}$

I j $N = 4$ $p = q = \frac{1}{2}$

m	$P_N(m)$
0	3/8
± 2	1/4
± 4	1/16



n_1	$W_4(n_1)$
0	1/16
1	1/4
2	3/8
3	1/4
4	1/16



Calculation of mean values:

$$\bar{u} = \frac{\sum_{i=1}^{M} u_i P(u_i)}{\underbrace{\sum_{i=1}^{M} P(u_i)}_{1 \text{ (in general)}}} \equiv \langle u \rangle$$

u_i are discrete variables that take M possible values with probability $P(u_i)$

For our example $\bar{m} = 0$ and $\bar{n}_1 = 2$.

Moments of a distribution:

$$\overline{u^r} = \frac{\sum_{i=1}^{M} u_i^r P(u_i)}{\sum_{i=1}^{M} P(u_i)} \equiv \langle u^r \rangle$$

- The moments of the distribution if $r = 0, \ldots, \infty$ provide the complete distribution.
- A few moments allow to obtain a lot of information about the distribution. Particularly if N is large.

Moments about the mean or cumulants:

$$\overline{(\Delta u)^r} = \frac{\sum_{i=1}^{M} (u_i - \bar{u})^r P(u_i)}{\sum_{i=1}^{M} P(u_i)} = \langle u^r \rangle_c$$

if $r = 2$

$$\overline{(\Delta u)^2} = \overline{(u_i - \bar{u})^2} = \overline{u_i^2 - 2u_i\bar{u} + \bar{u}^2} = \langle u^2 \rangle - 2\langle u \rangle^2 + \langle u \rangle^2 = \langle u^2 \rangle - \langle u \rangle^2$$

The second cumulant is called the dispersion.

$$\overline{(\Delta u)^2} \equiv \langle u^2 \rangle_c = \langle u^2 \rangle - \langle u \rangle^2$$

If $r=1$ then $\langle u^1 \rangle_c = 0$!

Also $\left[\overline{(\Delta u)^2}\right]^{1/2} = \Delta^* u$ root-mean-square deviation.

- Cumulants are useful for diagramatic expansions.
- When N is very large only the average and the dispersion are finite with the other moments vanishing (we will see this later).

Properties of the binomial distribution:

• It is normalized:

$$\sum_{n_1=0}^{N} W_N(n_1) = \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} q^{N-n_1} = (\underbrace{p+q}_{1})^{N} = 1$$

• Average value of n_1 : $\langle n_1 \rangle$

$$\langle n_1 \rangle = \sum_{n_1=0}^{\infty} n_1 W_N(n_1) = \sum_{n_1=0}^{N} \binom{N}{n_1} n_1 p^{n_1} q^{N-n_1} =$$

Notice: $n_1 p^{n_1} = p \frac{d}{dp} p^{n_1}$

$$= p \frac{d}{dp} \sum_{n_1=0}^{N} \binom{N}{n_1} p^{n_1} p^{N-n_1} = p \frac{d}{dp} (p+q)^N = pN (\overbrace{p+q}^{1})^{N-1} = pN$$

$$\langle n_2 \rangle = \langle N - n_1 \rangle = N - \langle n_1 \rangle = N - Np = N(1-p) = Nq$$

$$\langle n_1^2 \rangle = \sum_{n=0}^{\infty} n_1^2 \, W_N(n_1) =$$

since $n_1^2 p_1^{n_1} = \left(p \frac{d}{dp}\right)^2 p^{n_1}$

$$= \left(p \frac{d}{dp}\right)^2 (p+q)^N =$$

$$= (pN)^2 + Npq$$

Then

$$\overline{(\Delta n_1)^2} = \langle n_1^2 \rangle - \langle n_1 \rangle^2 = (pN)^2 + Npq - (Np)^2 = Npq$$

and $\Delta^* n_1 = \sqrt{Npq}$

Distribution width:

$$\frac{\Delta^* n_1}{\langle n_1 \rangle} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{p}}\,\frac{1}{\sqrt{N}} \qquad \frac{1}{\sqrt{N}} \text{ if } p = q = \frac{1}{2}$$