THERMAL & STATISTICAL PHYSICS
SSP3133

STATISTICAL MECHANICS: STATISTICS FOR SMALL SYSTEMS

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  - Acknowledgement : PROFESSOR DR RAMLI ABU HASSAN

Probability : Mean value – single element system

Let P_s : probability the system in state S

f_s: function when the system in state S

$\bar{f} \approx$ mean value of f_s

Definition:

$$\bar{f} = \sum P_s f_s$$

Example 1:

1 coin: 2 states; H: head; T: tail

P_H: probability of landing heads is ½

P_T: probability of landing tail is ½

Let say f_S is the number of head showing.

Hence

$$f_S = 1 \text{ for H and } f_S = 0 \text{ for T.}$$

The mean value for f is

$$P_H f_H + P_T f_T = (1/2)(1) + (1/2)(0) = 1/2$$

- The average number of heads per coin showing is 1/2

Example 2: DICE

n: no of dot upward = f_S

if f_S = n, what is the mean value for the system?

$P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = 1/6 = P_S$

$$\bar{f} = \sum_S P_S f_S = \bar{f} = \sum_S P_S n = (1/6)(1) + (1/6)(2) + (1/6)(3) + (1/6)(4) + (1/6)(5) + (1/6)(6) = 3\tfrac{1}{2}$$

if $f_S = (n-1)^2$

$$\bar{f} = \sum_S P_S f_S = \bar{f} = \sum_S P_S (n-1)^2 = (1/6)(0) + (1/6)(1) + (1/6)(4) + (1/6)(9) + (1/6)(16) + (1/6)(25) = 9\frac{1}{6}$$

Note:

f, g : functions of the states of systems

c : constant

Then $\overline{(f+g)} = \bar{f} + \bar{g}$ and $\overline{cf} = c\,\bar{f}$

-few elements system

Let p = the probability the criterion is satisfied

q = the probability the criterion is **not** satisfied

Example:

i. criterion: a flipped coin lands head-up

$p = ½$ and $q = ½$

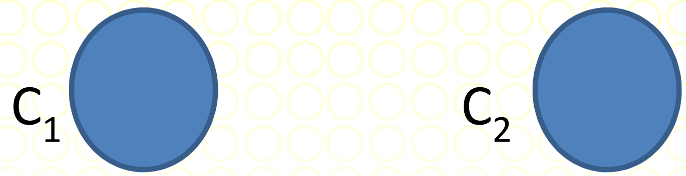
ii. criterion: a rolled dice lands with 2 dots up

$p = 1/6$ and $q = 5/6$

$$p + q = 1 \quad \text{or} \quad q = 1 - p$$

The probability the criterion is satisfied or not is always **one**

Example 3: 2 coins C_1 & C_2 (2 identical systems)



$p_1 + p_2 = 1$ and $p_2 + q_2 = 1$

For each element, the criterion IS or NOT satisfied is

$$(p_1 + p_2)(p_2 + q_2) = 1 \times 1 = 1^2 = 1$$
$$= p_1p_2 + p_1q_2 + q_1p_2 + q_1q_2$$

p_1p_2 – both elements satisfy the criterion

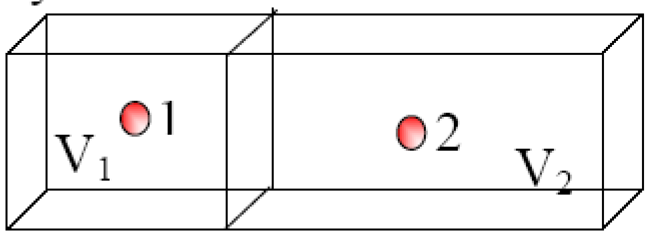
p_1q_2 – element 1 – satisfy the criterion
element 2 – not satisfy the criterion

q_1p_2 – element 1 – not satisfy the criterion
element 2 – satisfy the criterion

q_1q_2 – both elements not satisfy the criterion

Example 4: BOX 1

system: a box with 2 air molecules inside



$V_1 + V_2 = V$ and $V_1 = V/3$

Criterion: all possible configurations

-The probability of either molecule in V_1,

$p_1 = 1/3$ & $p_2 = 1/3$

-The probability that each molecule is not in V_1,

$q_1 = 2/3$ & $q_2 = 2/3$

-the probability for all possible configuration

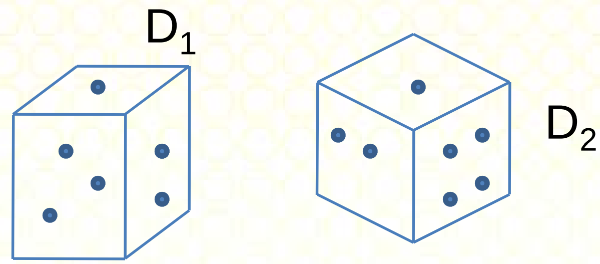
$$(p_1+q_1)(p_2+q_2) = 1x1 = 1^2 = 1$$
$$= p_1p_2 + p_1q_2 + q_1p_2 + q_1q_2$$

-both molecules in V_1: $p_1p_2 = (1/3)\ (1/3) = 1/9$

-mol.1 in V_1 & mol.2 in V_2: $p_1q_2 = (1/3)\ (2/3)$
$= 2/9$

-mol.1 in V_2 & mol.2 in V_1: $q_1p_2 = (2/3)\ (1/3)$
$= 2/9$

-both molecules in V_2: $q_1q_2 = (2/3)\ (2/3) = 4/9$



Example 5: 2 DICE

Criterion: one dot up for D_1 and D_2

Probability for one dot up: $p_1 = p_2 = 1/6$

Probability for NOT landing with one dot up: $q_1 = q_2 = 5/6$

$$(p_1 + p_2)(p_2 + q_2) = 1 \times 1 = 1^2 = 1 = p_1p_2 + p_1q_2 + q_1p_2 + q_1q_2$$

-one dot up for D_1 & D_2:	$p_1.p_2 = 1/36$
-one dot up for D_1 & not D_2 :	$p_1.q_2 = 5/36$
-one dot up for D_2 & not D_1:	$q_1.p_2 = 5/36$
- not D_1 & not D_2:	$q_1.q_2 = 25/36$

Identical Elements: with the same Probability

A: **For 2 identical elements**

$p_1 = p_2 = p \qquad q_1 = q_2 = q$

The possible configurations;

$$(p_1+q_1)(p_2+q_2) = (p + q)^2$$
$$= (p^2 + 2pq + q^2)$$

p^2: all satisfy the criterion
$2pq$: one satisfy – one does not
q^2: none satisfy the criterion

B: **For 3 identical elements** $(p_1+p_2)(p_2+q_2)(p_3+q_3) = (p + q)^3 = 1$

$$= (p^3 + 3p^2 q + 3q^2 p + q^3)$$

p^3: all satisfy the criterion
$3p^2q$: two satisfy – one does not
$3pq^2$: one satisfy – two do not
q^3: none satisfy the criterion

C: For N elements

$$(p_1+q_1)(p_2+q_2).....(p_N + q_N) = (p + q)^N$$

but

$$(p+q)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} p^n q^{(N-n)} = 1$$

Binomial Expansion

$P_N(n)$: the probability the system in state of n elements satisfy the criterion and N-n elements do not

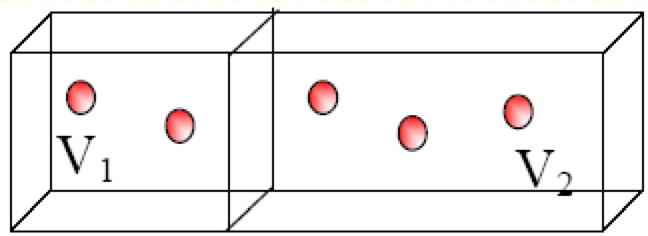
$$P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

$$\frac{N!}{n!(N-n)!}$$

Binomial Coefficient

-the number of different configurations of the individual elements, for which n satisfy the criterion and (N-n) do not

Example 6: BOX 2 – Consider 5 molecules in a box



$V_1 + V_2 = V$

$V_1 = (1/3)\ V$

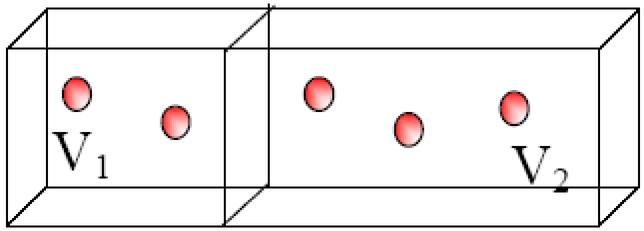
(i) find the prob. of 2 mol. in V_1 and 3 in V_2

$p = 1/3$ & $q = 2/3$

$N = 5,$ $n = 2$

$$P_5(2) = \frac{5!}{2!(5-2)!}\left(\frac{1}{3}\right)^2\left(\frac{2}{3}\right)^3 = 80/243$$

(ii) number of different possible arrangements for 2 mol in V_1 and 3 mol in V_2



$V_1 + V_2 = V$ $V_1 = (1/3)\,V$

$$\frac{N!}{n!(N-n)!} = 5!\,/\,(2!\,3!) = 10$$

State of a system relative to two different criteria;

-system of N elements in a state where;

n_1 elements satisfy 1st criterion

n_2 elements satisfy 2nd criterion

the probability $P_N(n_1,n_2)$

Note: an element's behaviour with respect to one of the criteria does not effect its behaviour with respect to the other ……`statistically independent criteria'

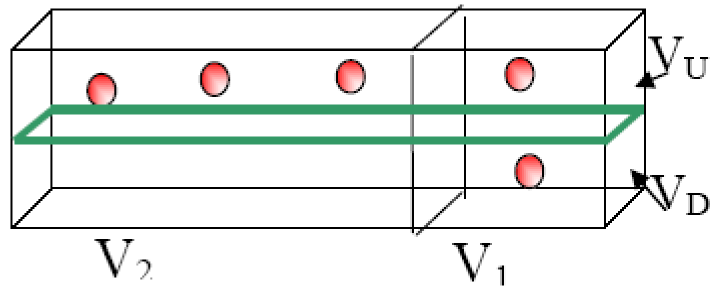
P_{ij}: the system in state i with respect to 1st criterion and also in state j with respect to the 2nd

$$P_{ij} = P_i \, . \, P_j$$

Or $$P_{ijk\ldots\ldots} = P_i \, . \, P_j . \, P_k, \ \ldots\ldots$$

Where i, j, k, ….

Example 7: BOX 3



System: 5 mol.

-find: the probability for 2 mol in V_1 and 4 mol in V_U

$V_U = V_D$

$N = 5; \quad n_i = 2; \quad n_j = 4$

$$P_5(2.4) = P_5(2).P_5(4) = \frac{N!}{n!(N-n)!} p_1^n q_1^{N-n} \cdot \frac{N!}{n!(N-n)!} p_2^n q_2^{N-n}$$

$$= \left(\frac{5!}{2!3!}\right)\left(\frac{1}{3}\right)^2\left(\frac{2}{3}\right)^3 * \left(\frac{5!}{4!1!}\right)\left(\frac{1}{2}\right)^4\left(\frac{1}{2}\right) = 0.051$$

Note: Binomial expansion – correct for any size

$$P_N(n) = \frac{N!}{n!\,(N-n)!} p^n q^{N-n}$$

But for large N, N! can be calculated using Stirling's formula

$$l(N!) \approx N \ln n - N + (\frac{1}{2}) \ln(2\pi N)$$

Probability Distribution of Discrete Random Variables

A probability distribution is listing of all the possible values that a random variable can take along with their probabilities.

Example: to find out the probability distribution for the number of heads on three tosses of a coin:

1 COIN;
3 tosses

First toss ……….T T T T H H H H
Second toss …….T T H H T T H H
Third toss ………. T H T H T H T H

Have a try first…..

Fill in the following table and compare your answers with that on the next page:

NO OF HEADS	FIRST THROW	SECOND THROW	THIRD THROW	MACRO STATE

NO OF HEADS	FIRST THROW	SECOND THROW	THIRD THROW		MACRO STATE
0	T	T	T	= 1	1
1	T	T	H		2
	T	H	T	= 3	
	H	T	T		
2	H	H	T		3
	H	T	H	= 3	
	T	H	H		
3	H	H	H	= 1	4
TOTAL			{1+3+3+1}		4 MACROSTATES

= 8
MICROSTATES

Hence the probability distribution is as follows:

No. of heads X	Probability P(X)	mean or expected value X.P(X)
0	1/8	0.000
1	3/8	0.375
2	3/8	0.750
3	1/8	0.375

Mean = E(X) = ∑X.P(X)

where E(X) = expected value,

X = an event,

P(X) = probability of the event

$$\Sigma X\, P(X) = 1.5$$

{0.0+0.375+0.75+0.375 = 1.5}

Binomial Distribution:

-discrete probability distributions

-Several characteristics underlie the use of the binomial distribution.

Characteristics of the Binomial Distribution:

1. The experiment consists of n identical trials.

2. Each trial has only one of the two possible mutually exclusive outcomes, success or a failure.

3. The probability of each outcome does not change from trial to trial, and

4. The trials are independent, thus we must sample with replacement.

Binomial Distribution: Fluctuations

Suppose the following binomial distribution;

- the probability of success: p
- the probability of failure: 1-p = q

the **mean** $\bar{n} = pN$

N : the number of elements per system

$\overline{\Delta n}$: average fluctuation of n about its mean value, $\bar{n}$

$$\overline{\Delta n} = \overline{(n - \bar{n})} = \bar{n} - \bar{n} = 0$$

-positive fluctuations cancel the negative one

the **standard deviation**

$$(standard\ deviation)^2 = \sigma^2 = \overline{(n - \bar{n})^2}$$

$$(standard\ deviatian) = \sigma = [\ \overline{(n-\overline{n})^2}\ ]^{1/2}$$

$$\sigma^2 = \overline{(n-\overline{n})^2} = \sum_n P_n (n-\overline{n})^2$$

$$= \sum_{n=0}^{N} \left(\frac{N!}{n!(N-n)!} p^n q^{N-n} \right) (n-\overline{n})^2$$

Solving----- $\sigma^2 = Npq$ or $\sigma = \sqrt{Npq}$

relative fluctuations $\frac{\sigma}{\overline{n}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{NP}} \propto \frac{1}{\sqrt{N}}$

Binomial Equation : able to identify three things;

- the number of trials
- the probability of a success on any one trial
- the number of successes desired

$$P_N(n) = \frac{N!}{n!\,(N-n)!}\,p^n\,q^{N-n}$$

Example 8: Binomial Distribution

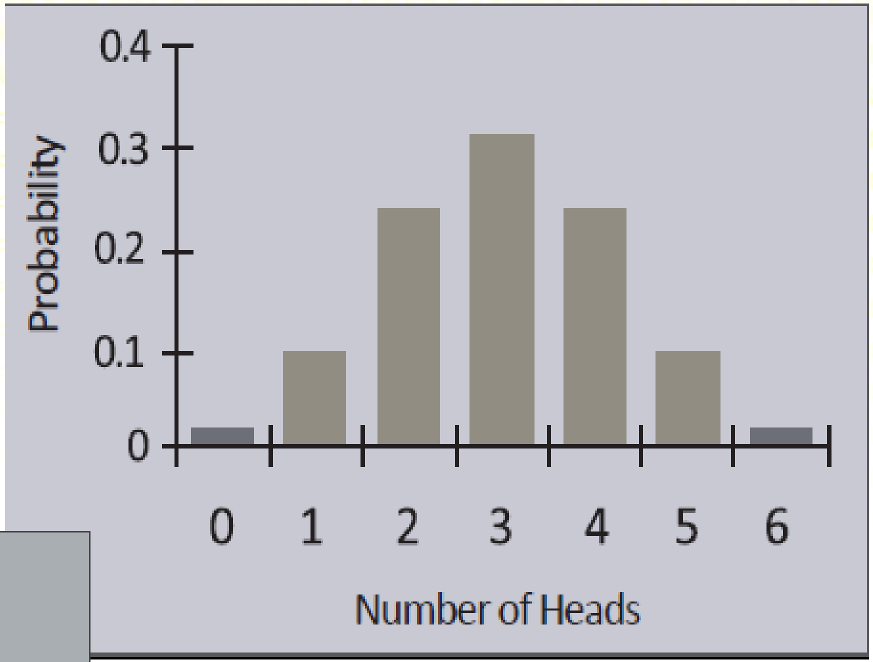
What is the probability of obtaining exactly 3 heads if a fair coin is flipped 6 times?

Answer: N = 6, n = 3, p = q = 0.5

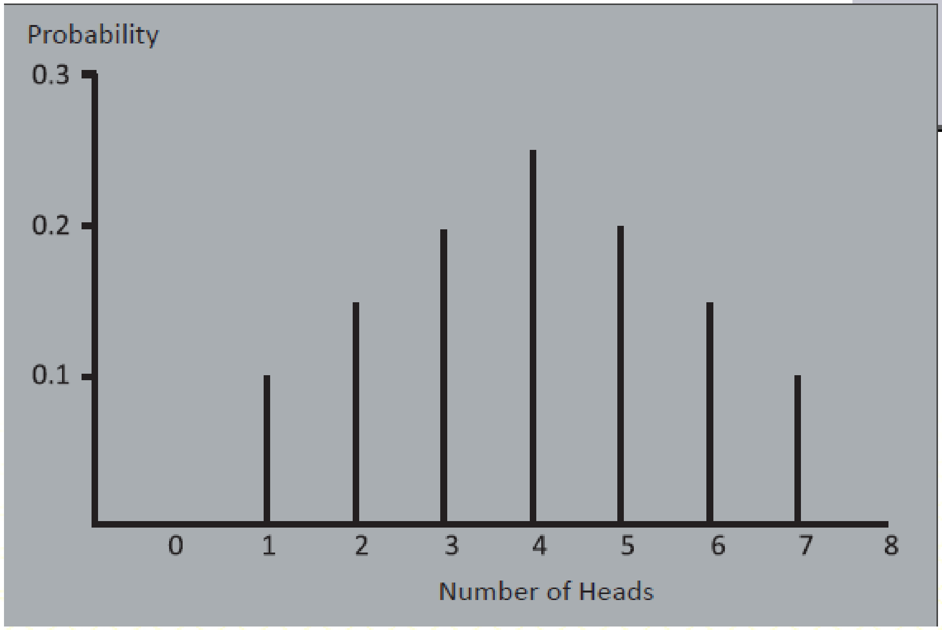
$$P(3) = \frac{6!}{3!\,(6-3)!} 0.5^3 1 - 0.5^{6-3}$$
$$= \frac{6\,x5x4x3x2}{(3x2)(3x2)} (0.125)(0.125) = 0.3125$$

Binomial distributions

p = 0.5



or



Properties of Binomial Distribution

Mean	**np**
Variance	**npq**
Standard deviation	**$(npq)^{1/2}$**

Binomial Distribution: Fluctuations

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$$\sigma^2 = \overline{(n-\overline{n})^2} = \sum_n P_n (n-\overline{n})^2$$

$$= \sum_{n=0}^{N} \left(\frac{N!}{n!(N-n)!} p^n q^{N-n} \right) (n-\overline{n})^2$$

solving----- $\sigma^2 = Npq$ or $\sigma = \sqrt{Npq}$

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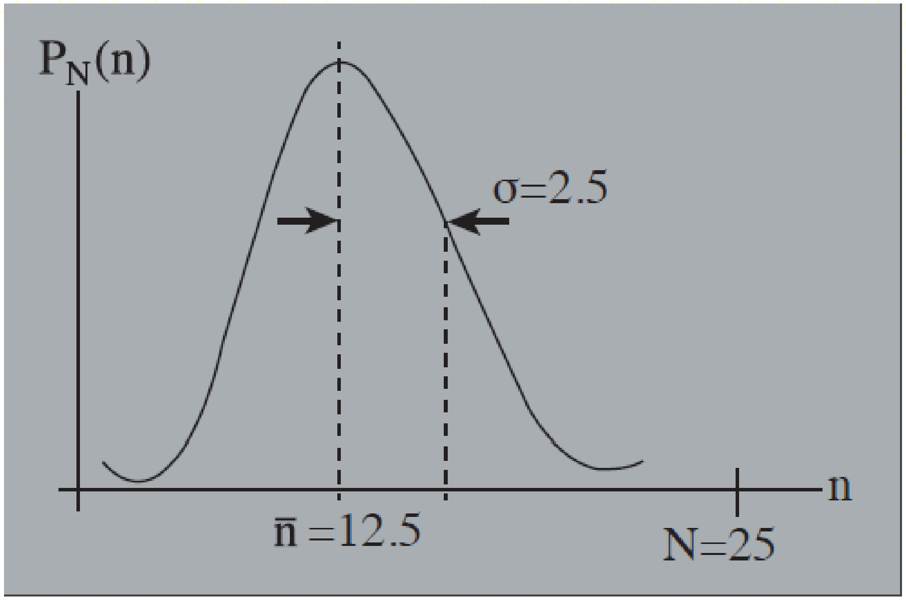
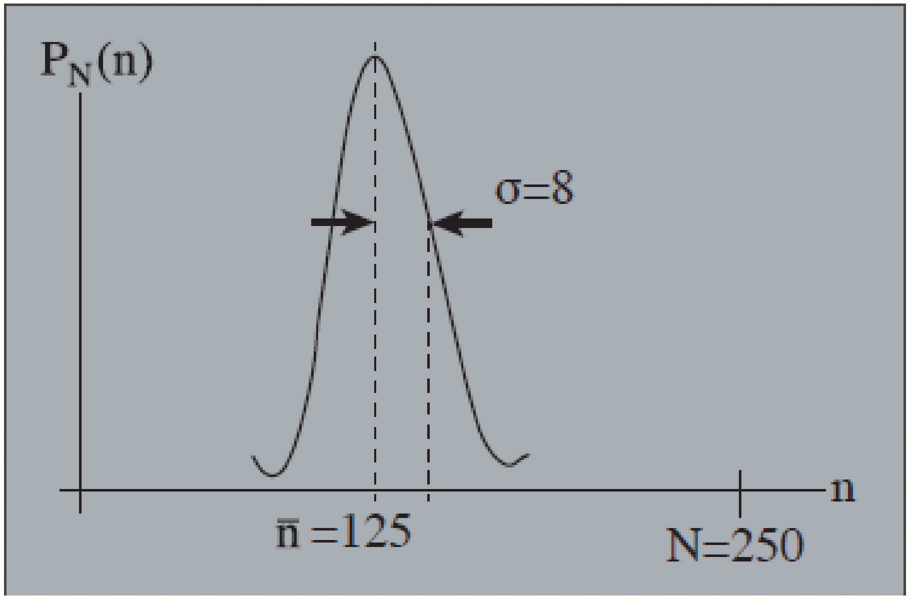




Example 9: system of 100 COINS

-system of 100 flipped coins: what are;

average number of H (head),

the standard deviation,

the relative fluctuation?

Ans:

$\bar{n} = pN = (1/2)(100) = 50$

$\sigma = (Npq)^{1/2} = ((100)(.5)(.5))^{1/2} = 5$

$\sigma/\bar{n} = 5/50 = 10\ \%$

- now N = 10,000 flipped coins

$\bar{n} = pN = (1/2)(10\ 000) = 5\ 000$

$\sigma = (Npq)^{1/2} = ((10\ 000)(.5)(.5))^{1/2} = 50$

$\sigma/\bar{n} = 50/5\ 000 = 1\ \%$

note:

A binomial probability distribution must meet each of the following:

1. There are a fixed number of trials

2. The trials must be independent

3. Each trial must have outcomes classified into two categories

4. The probabilities remain constant for each trial

Gaussian Distribution

Gaussian Distribution

The Gaussian distribution is useful where binomial formula is not

The probability $P_N(n) \cong P(n)$

P(n) – a continuous function of n

Criteria for increase accuracy;

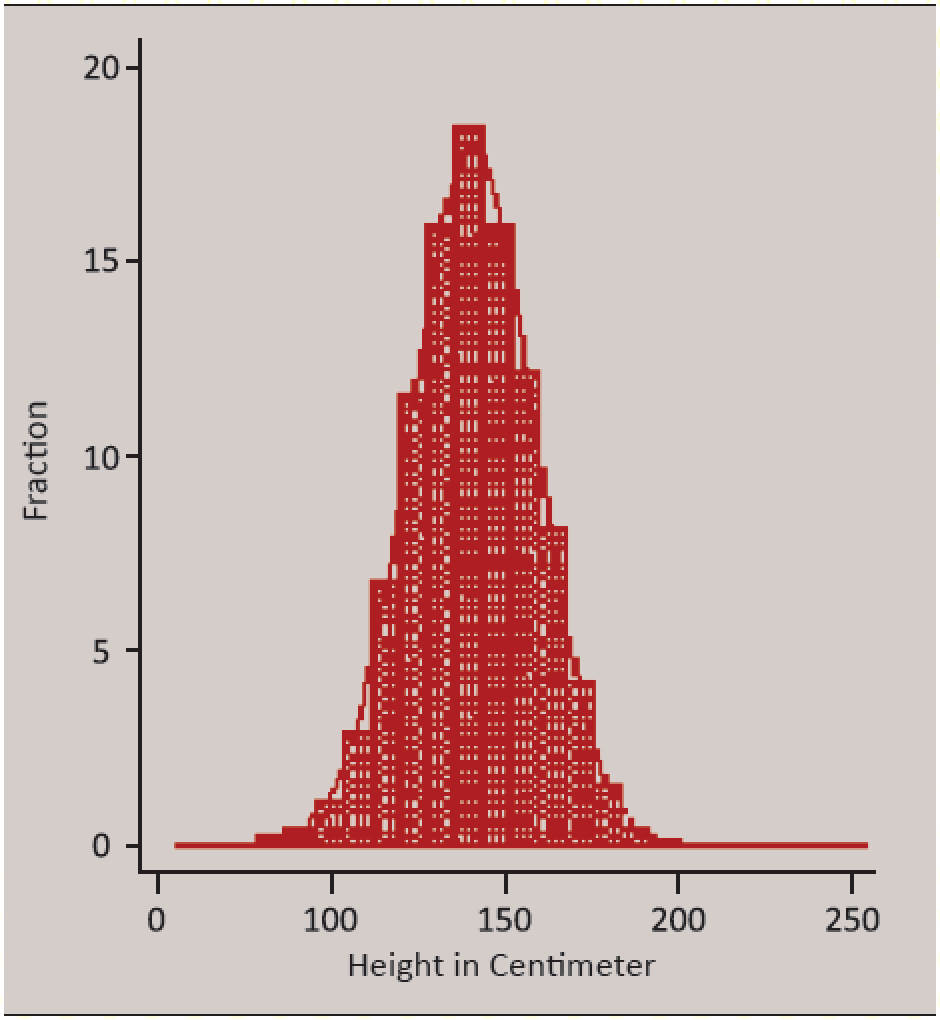
i) choose as smooth a function as possible

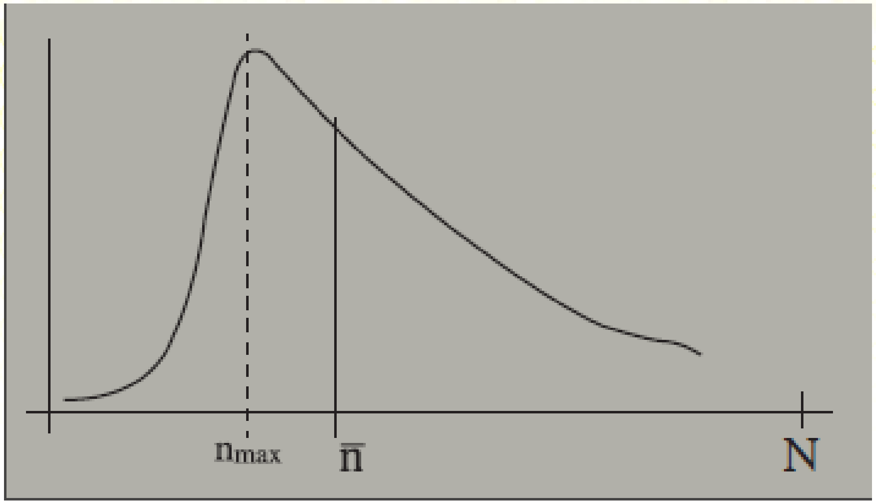
ii) choose reference point, as close to the value of n

to satisfy (i)—expand the logarithm of P(n)

to satisfy(ii) – choose reference as n_{max}

interested in values of P(n) for n near n_{max}


Fraction
20
15
10
5
0
0
100
150
200
250
Height in Centimeter



using Taylor series expansion

$$\ln P(n) = \ln P(\bar{n}) + \frac{\partial}{\partial n}\ln P(n)\Big|_{n=\bar{n}}(n-\bar{n}) + \frac{1}{2}\frac{\partial^2}{\partial n^2}\ln P(n)\Big|_{n=\bar{n}}(n-\bar{n})^2 + ..$$

but $\frac{\partial}{\partial n}\ln P(n)\Big|_{n=\bar{n}} = 0$ max. point

2^{nd} derivative using $\frac{\partial P(n)}{\partial n} = \frac{\Delta P(n)}{\Delta n} = \frac{P(n+1)-P(n)}{(n+1)-n} = \ldots$

$$\frac{\partial^2}{\partial n^2}\ln P(n)\Big|_{n=\bar{n}} = -\frac{1}{Npq} = -\frac{1}{\sigma^2}$$

therefore $\ln P(n) = \ln P(\bar{n}) - \frac{1}{2\sigma^2}(n-\bar{n})^2$

or

$$P(n) = P(\bar{n})e^{-(\frac{(n-\bar{n})^2}{2\sigma^2}}$$

to calculate P(n)

-the sum of the probabilities of all possible values of n must be equal to 1

$$\sum_n P(n) = 1$$

$$\sum_n P(n) = 1$$

$$= \sum_n P(n)\Delta n \approx \int_{n=-\infty}^{\infty} P(n)dn$$

$$= P(\bar{n}) \int_{n=-\infty}^{\infty} e^{-\left[(n-\bar{n})^2/2\sigma^2\right]} dn = P(\bar{n})(\sqrt{2\pi\sigma}$$

$$= \frac{1}{\sqrt{2\pi\sigma}} e^{-\left[(n-\bar{n})^2/2\sigma^2\right]}$$

because

$$P(\bar{n}) = \frac{1}{\sqrt{2\pi\sigma}}$$

Gaussian Distribution

$$P(n) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(n-\bar{n})^2}{2\sigma^2}}$$

$$x = (n - \bar{n})$$

Properties of Gaussian distribution

$$\bar{x} = \int_{-\infty}^{\infty} xP(x)\,dx = 0$$

$$\int_{-\sigma}^{\sigma} P(x)\,dx = 0.683$$

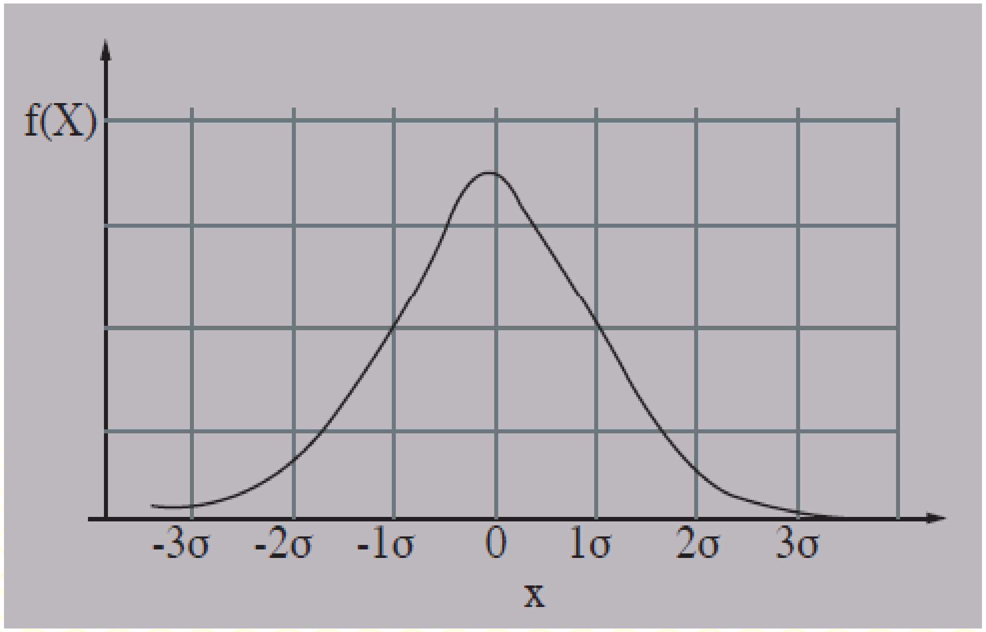
$$\int_{-2\sigma}^{2\sigma} P(x)\,dx = 0.954$$

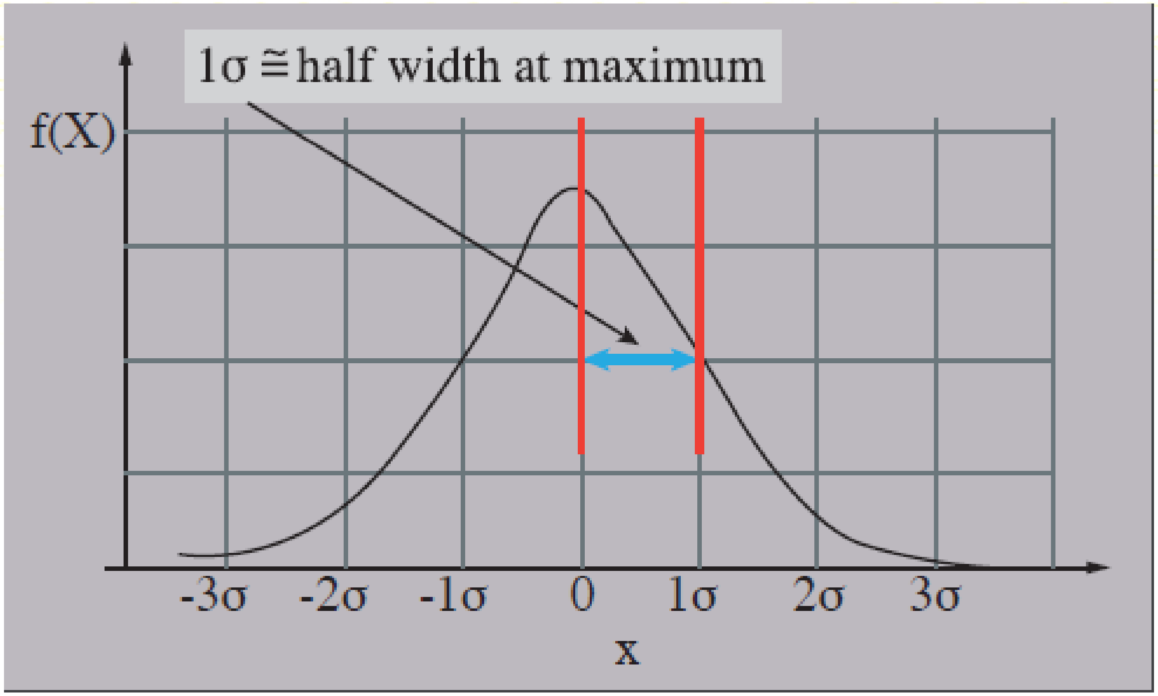
$$\int_{-3\sigma}^{3\sigma} P(x)\,dx = 0.997$$

$$\frac{\partial P(x)}{\partial x} = 0 \quad \text{at} \quad x = 0 \qquad (\text{or} \quad n = \overline{n})$$

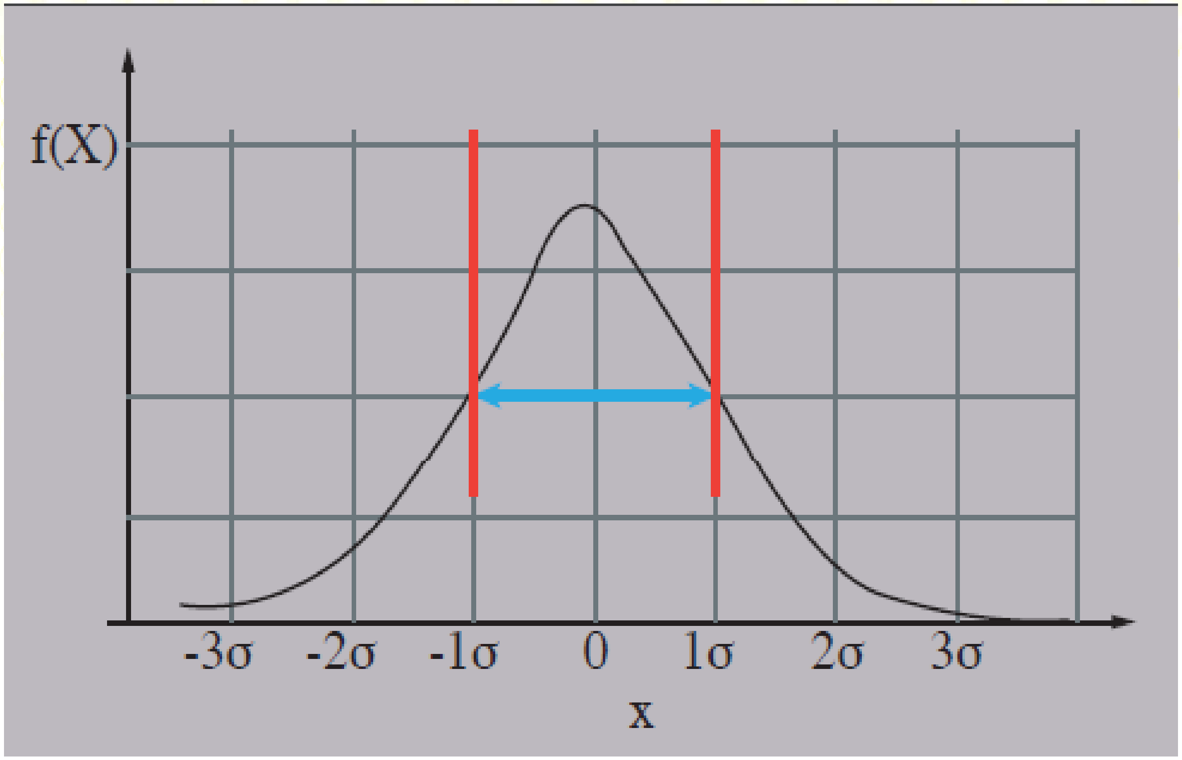
$$\frac{\partial^2 P(x)}{\partial x^2} = 0 \quad \text{at} \quad x = \sigma$$

$$\int_{-\infty}^{\infty} x^2 P(x)\, dx = \sigma^2$$

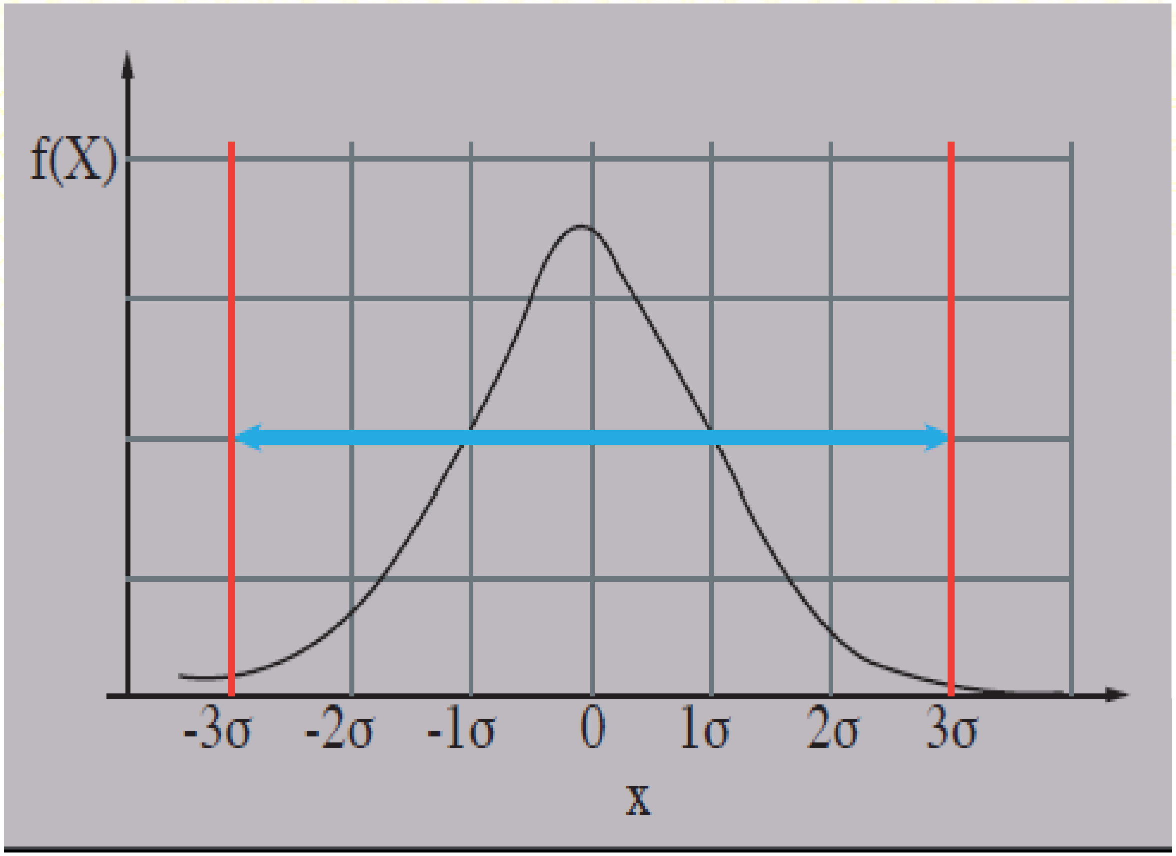




Probability of a measurement falling within -σ to +σ of the mean is 0.683



Probability of a measurement falling within -2σ to +2σ of the mean is 0.954



Probability of a measurement falling within -3σ to +3σ of the mean is 0.997

Random Walk

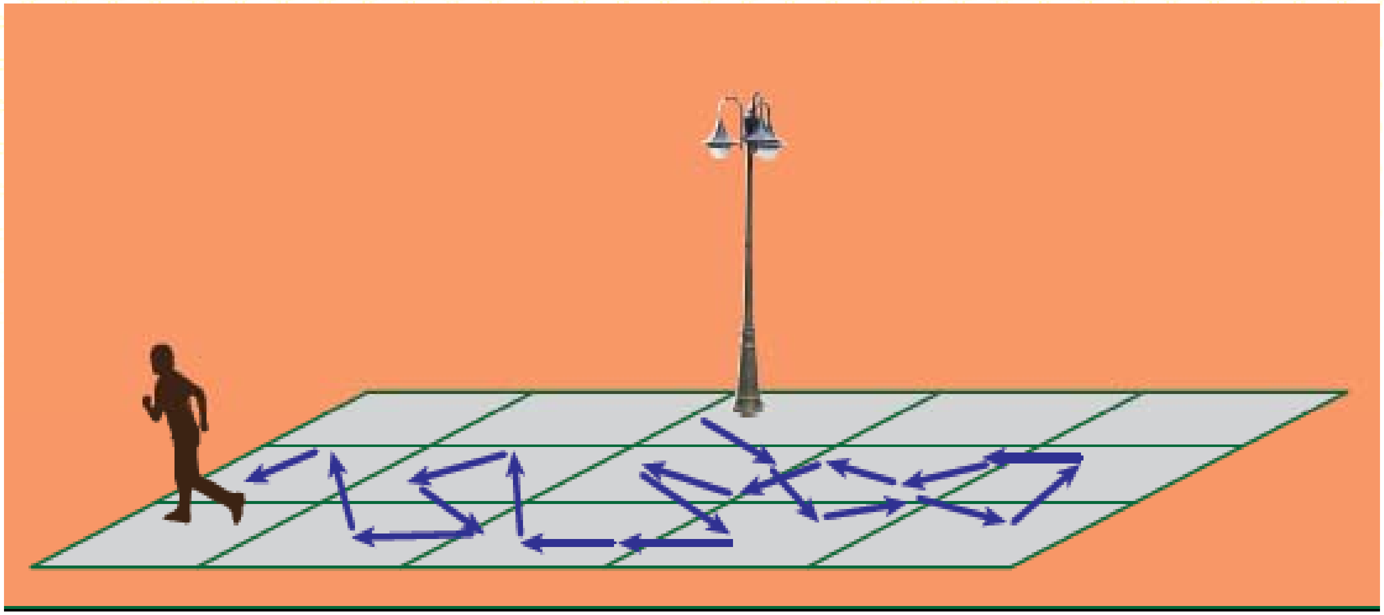
Random Walk

A random process consisting of a sequence of discrete steps of fixed length

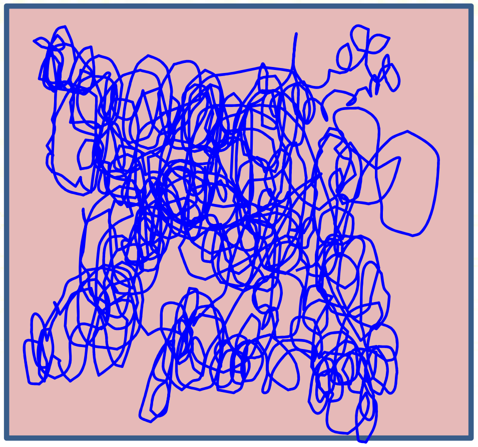
The random walk is central to statistical physics.

-predicting how fast one gas will diffuse into another,
-how fast heat will spread in a solid,

-how big fluctuations in pressure will be in a small container,
-and etc……….



Problem: to find the probability of landing at a given spot after a given number of steps, or to find how far away the girl is on average from where she started.



…after many many steps

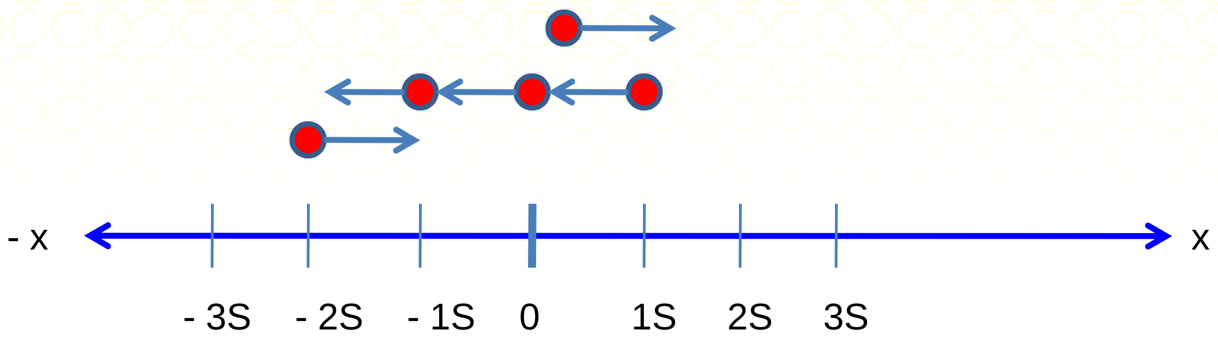
The simplest random walk is

a path constructed according

to the following rules:

- There is a starting point.
- The distance from one point in the path to the next is a constant.
- The direction from one point in the path to the next is chosen at random, and no direction is more probable than another.

Consider each step is of length s_0,
It can be either forward (right) or backward (left).

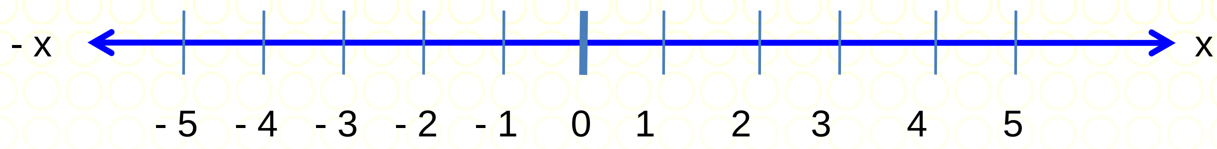


Probability of going forward (right) is p.
Probability of going backward (left) is q = 1 - p

After N steps, if n are forward (right), the distance traveled is,

$$S = [n - (N - n)]s_0 = (2n - N)\, s_0$$

The progression of the walk and it's different outcomes are nicely organized in Pascal's triangle.



Initial:	1
After 1 step:	1q 1p
After 2 steps:	$1q^2$ 2pq $1p^2$
After 3 steps:	$1q^3$ $3pq^2$ $3p^2q$ $1p^3$
After 4 steps:	$1q^4$ $4pq^3$ $6p^2q^2$ $4p^3q$ $1p^4$

This is known as a binomial distribution.

Define the probability function $f_N(n)$

-- the probability that in a walk of N steps, point n.

For the nonzero probabilities.

For a walk of no steps, $f_0(0) = 1$.

For a walk of 1 step, $f_1(-1) = ½$, $f_1(1) = ½$.

For a walk of 2 steps, $f_2(-2) = ¼$, $f_2(0) = 2 \times ¼ = ½$, $f_2(2) = ¼$.

……. $f_3(-3) = 1/8$, $f_3(-1) = 3/8$, $f_3(1) = 3/8$, $f_3(3) = 1/8$.

…… $f_4(4) = 1/16$, $f_4(2) = ¼$; $f_4(0) = 3/8$, …….

n	-5	-4	-3	-2	-1	0	1	2	3	4	5
$f_0(n)$						1					
$f_1(n)$					½		½				
$f_2(n)$				¼		½		¼			
$f_3(n)$			⅛		⅜		⅜		⅛		
$f_4(n)$		1/16		¼		⅜		¼		1/16	
$f_5(n)$	1/32		5/32		5/16		5/16		5/32		1/32

Factor by $(1/2)^N$

n	-5	-4	-3	-2	-1	0	1	2	3	4	5
$f_0(n)$						1					
$2f_1(n)$					1		1				
$2^2f_1(n)$				1		2		1			
$2^3f_3(n)$			1		3		3		1		
$2^4f_4(n)$		1		4		6		4		1	
$2^5f_5(n)$	1		5		10		10		5		1

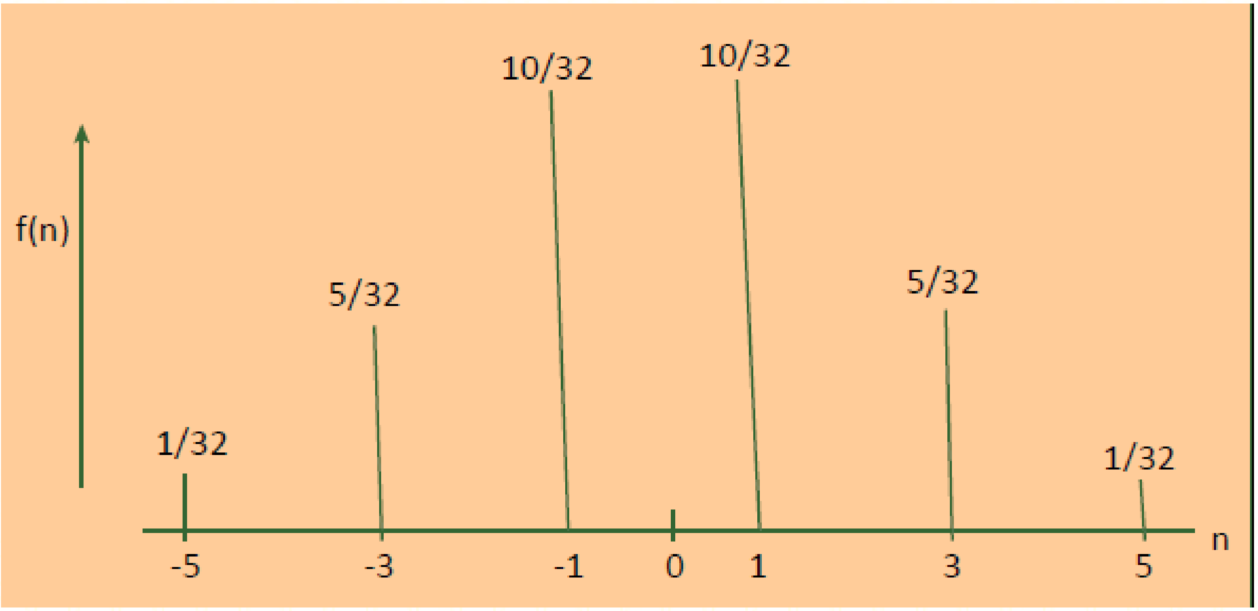
This is *Pascal's Triangle*—every entry is the sum of the two diagonally above

These numbers are in fact the coefficients that appear in the binomial expansion of $(\mathbf{p} + \mathbf{q})^N$

Picturing the Probability Distribution

Visualizing this probability distribution →

For **5** steps, it looks like:



-a walk of **100** steps → n steps forward and $100 - n$ steps backward

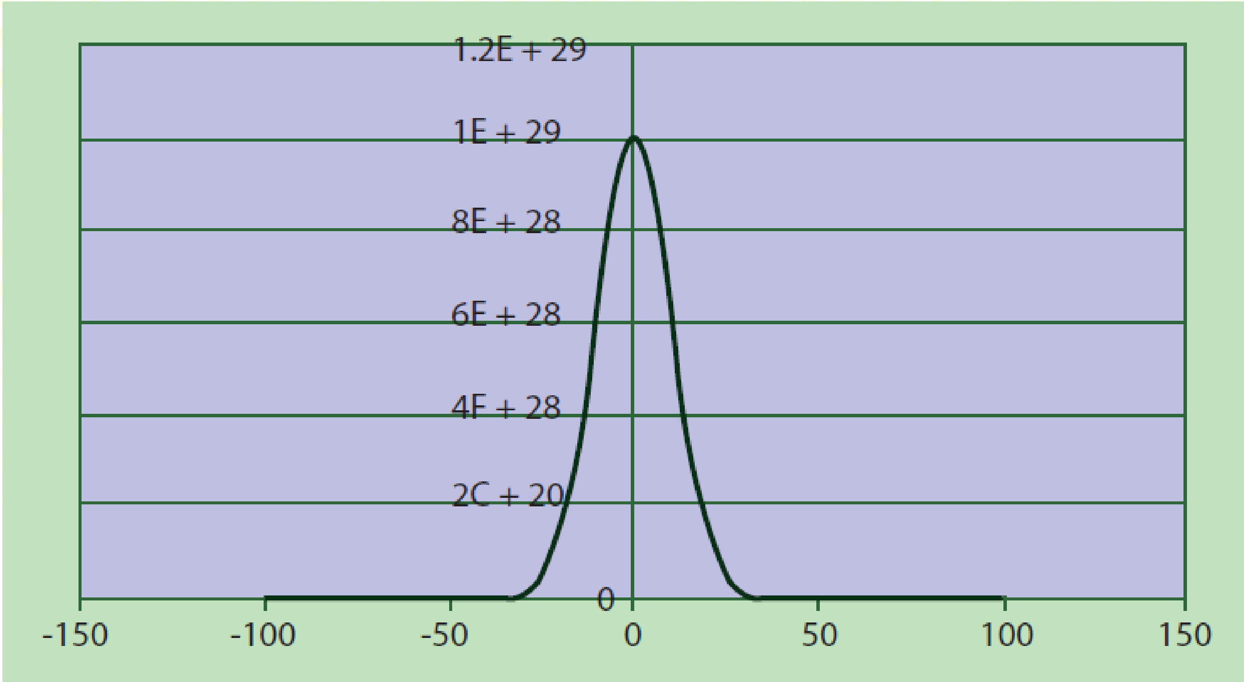
-the final landing place is $n - (100 - n) = 2n - 100$ paces in the forward direction.

Note that this is an even number, and goes from -100 to $+100$.

The total number of 100-step walks having just n forward steps is

$$(100)!/n!(100 - n)!$$

The probability of landing at $2n - 100$ after a random 100-step walk is proportional to the number of such walks that terminate there



The probability of this occurring is,

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

The average distance covered after N steps is,

$$\overline{S} = (2\overline{n} - N)s_0 = (2pN - N)s_0$$

$$\overline{S} = N(2p-1)s_0 \quad \text{and} \quad \text{For } p = \tfrac{1}{2}, \quad \overline{S} = 0$$

note: $\overline{n} = pN$

Standard deviation

$$\sigma^2 = \overline{(S - \overline{S})^2} = \overline{[(2n - N)s_0 - (2\overline{n} - N)s_0]^2}$$

$$\sigma^2 = 4s_0^2\overline{(n - \overline{n})^2} = 4s_0^2 Npq$$

$$\sigma^2 = N4pqs_0^2 \qquad \sigma = 2s_0\sqrt{Npq}$$

$$\frac{\sigma}{\overline{S}} = \frac{2s_0\sqrt{Npq}}{N(2p-1)s_0} = \frac{2\sqrt{pq}}{(2p-1)}\frac{1}{\sqrt{N}}$$

$$\frac{\sigma}{\overline{S}} \propto \frac{1}{\sqrt{N}}$$

AT

LAST!!

THE END….

REFERENCES:

1. REAF,F : “Fundamentals Of Statistical And Thermal Physics”, McGraw-Hill

2. KITTEL & KROMER: “Thermal Physics”, W.H. Freeman &   Company