Chapter 4 Statistics for Systems of Many Elements

As the number of elements in a system increases, the Binomial distribution becomes impossibly unwieldy. We need something else.

Fluctuations

For large systems (large meaning 'many elements'), we can characterize a distribution by a mean and a fluctuation about that mean.

Eg:

$$P_{1000}(0) = 9.3 \times 10^{-302} \quad \leftarrow \text{all tails}$$

$$P_{1000}(1) = 9.3 \times 10^{-299} \quad \leftarrow \text{1 head, 999 tails}$$

$$\vdots$$

$$P_{1000}(495) = 0.0240$$

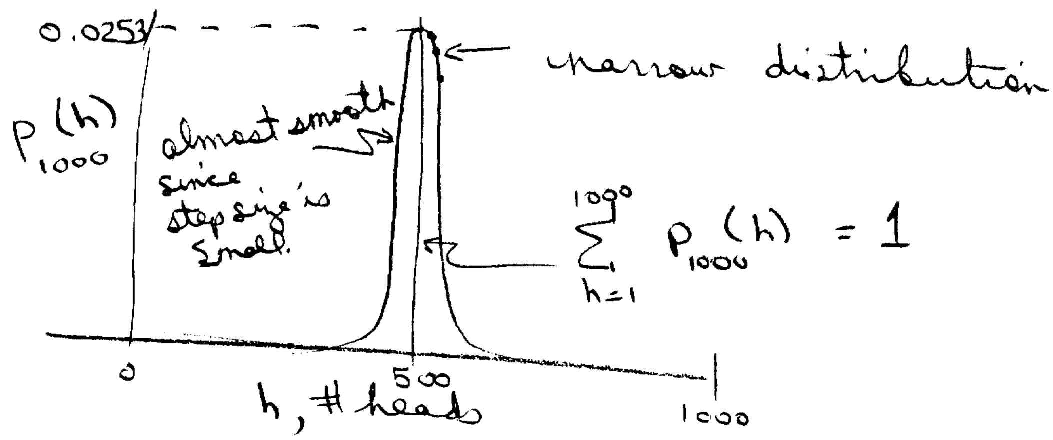
$$\vdots$$

$$P_{1000}(500) = 0.0253 \quad \leftarrow \text{mean}$$

$$\vdots$$

$$P_{1000}(1000) = 9.3 \times 10^{-302} \quad \leftarrow \text{all heads}$$

Possible outcomes to flipping 1000 coins



All we really need is:

1. mean
2. fluctuation

$\bar{n} = pN \leftarrow$ Number of elements in system

$\uparrow$ mean $\nwarrow$ prob. of single element 'true'

(this is really the definition of $p \equiv \frac{\bar{n}}{N}$

Average fluctuation : $\overline{(n-\bar{n})} \equiv \overline{\Delta n}$

$= \bar{n} - \bar{n} = 0$

(recall : $\overline{f+g} = \bar{f} + \bar{g}$)

$\uparrow$ + & - cancel out.

So this is not a good measure of fluctuations.

Use: $\overline{(n-\bar{n})^2}$ so that all terms add.

$\equiv$ (standard deviation)^2

$= \sigma^2$

$$\sigma^2 = \overline{(n-\bar{n})^2} = \sum_n P_n (n-\bar{n})^2 = \sum_{n=0}^{N} \left[\frac{N!}{n!(N-n)!} p^n q^{N-n} \right] (n-\bar{n})^2$$

$= Npq$ (after some math - see App. 4A if interested)

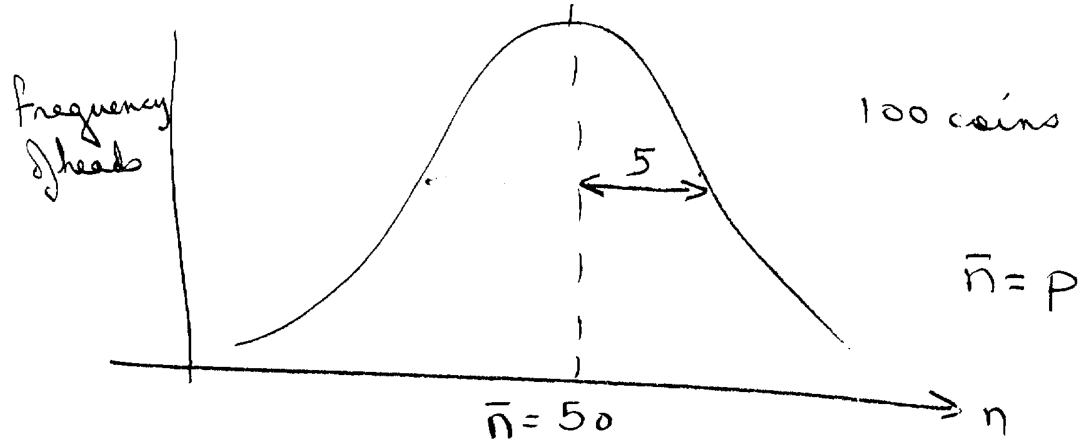
This is easy to calculate.

Note that $\frac{\sigma}{\bar{n}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{Np}} \propto \frac{1}{\sqrt{N}}$.

Thus the <u>relative</u> spread $\downarrow$ as $N \uparrow$

but the <u>absolute</u> " $\uparrow$ as $N \uparrow$

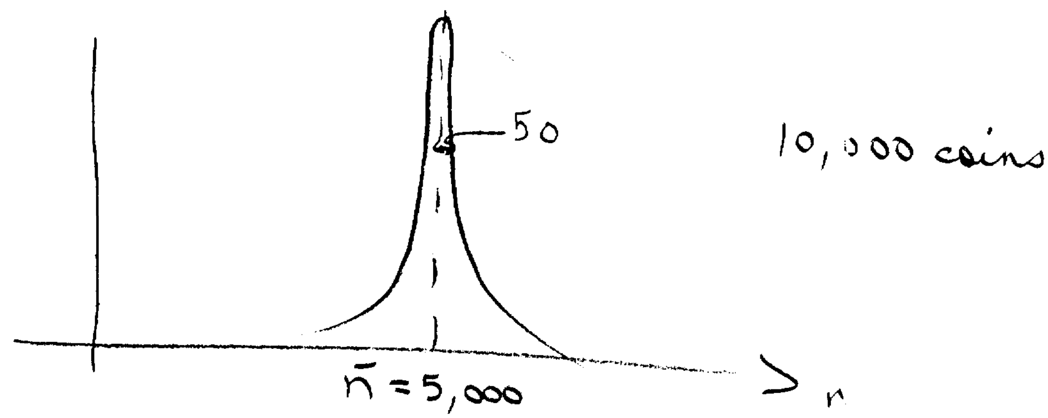
Example : coin flip



$\bar{n} = pN = \frac{1}{2} \cdot 100 = 50$

$\sigma_{100} = \sqrt{Npq} = \sqrt{100 \cdot \frac{1}{2} \cdot \frac{1}{2}} = \sqrt{25} = 5$ ⟵ absolute

$\frac{\sigma_{100}}{\bar{n}} = \frac{5}{50} = 0.2$ ⟵ relative



$\sigma_{10000} = \sqrt{10,000 \cdot \frac{1}{2} \cdot \frac{1}{2}} = 50$ ⟵ absolute fluctuation

$\frac{\sigma_{10,000}}{\bar{n}} = \frac{50}{5,000} = 0.01$ ⟸ relative fluctuation

<u>Example</u>: # of molecules in front $\frac{1}{3}$ of a room:

Case 1: 100 molecules

$$\bar{n} = pN = 33.\dot{3}$$

$$\sigma = \sqrt{Npq} = \sqrt{100 \cdot \tfrac{1}{3} \cdot \tfrac{2}{3}} \cong 4.7$$

$$\frac{\sigma}{\bar{n}} = 0.14$$

Case 2: 10^{28} molecules

$$\bar{n} = pN = 3.\dot{3} \times 10^{27}$$

$$\sigma = 4.7 \times 10^{13}$$

$$\frac{\sigma}{\bar{n}} = 1.4 \times 10^{-14}$$

Real scale systems have a very small <u>relative</u> fluctuation.

Can do Problems 4.1 at this point
4.2
4.3
4.4 ← Assign # 1

The Poisson Distribution (not in Stowe)

We had $P_N(n) = \dfrac{N!}{n!\,(N-n)!}\, p^n\, q^{N-n}$ ← Binomial Dist^n

$q = (1-p)$

= prob. of n successful events out of N given p prob. of success per event.

Hard to evaluate when N large.

We can simplify this when:

$p \ll 1$ (success is rare)

$\bar{n} = pN \ll N$

We have:

$$P_N(n) = \frac{1}{n!}\frac{N!}{(N-n)!}\, p^n (1-p)^{-n} (1-p)^N$$

$$\frac{N!}{(N-n)!} = N(N-1)(N-2)\cdots(N-n+1) \simeq (N)^n \quad \text{since } n \ll N$$

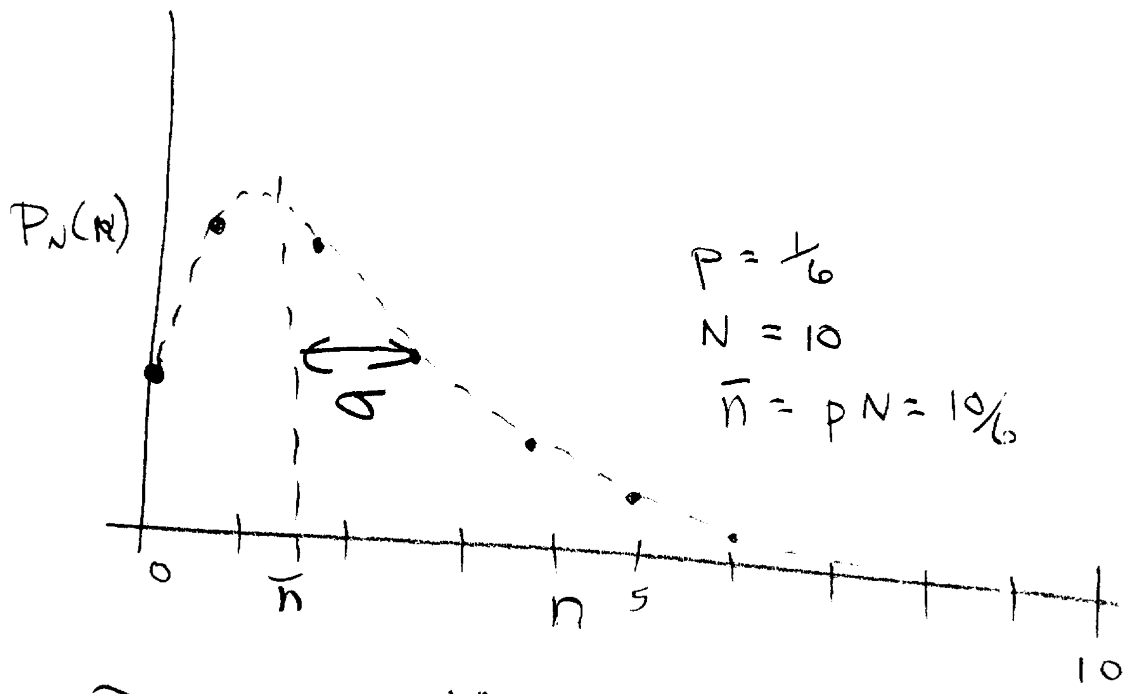
$$= \frac{1}{n!}(Np)^n (1-p)^{-n} (1-p)^N$$

$(Np)^n = (\bar{n})^n$

$(1-p)^{-n} \sim \left(1 + np + \frac{n(n+1)}{2}p^2 + \dots\right)$ (binomial series) ~ 1 as $p \to 0$

$(1-p)^N = (1-p)^{\bar{n}/p} \simeq e^{-\bar{n}}$ when $p \to 0$

$$\therefore \boxed{P_N(n) \simeq \frac{(\bar{n})^n}{n!} e^{-\bar{n}} \quad \text{Poisson Dist}^n}$$



Poisson ~~Dist~~ Dist^n is still a discrete dist^n & still has $n!$ to evaluate.

Becomes more symmetric as $p \uparrow$

Poisson Dist^n is good for working with <u>rare</u> statistical events where n is not too large (since we must calc. $n!$)

Pretty good approx. to Binomial Dist^n even for small n.

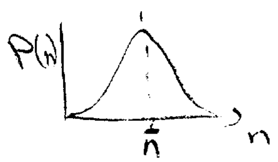
Gaussian Distribution

Let's take a large system.

$\mathcal{P}_N(n) \rightarrow P(n)$ (N so big we don't worry about its specific value)
(Binomial)

Expand $\ln P(n)$ about $\bar{n}$ (the mean)

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



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

Assume $n_{max} = \bar{n}$ (ie distn peaks at the mean).

$$\therefore \frac{\partial}{\partial n} \ln P(n)\Big|_{n=\bar{n}} = 0$$

$$\& \frac{\partial^2}{\partial n^2} \ln P(n)\Big|_{n=\bar{n}} < 0 = -\frac{1}{\sigma^2} \quad \text{(see App. 4c)}$$

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

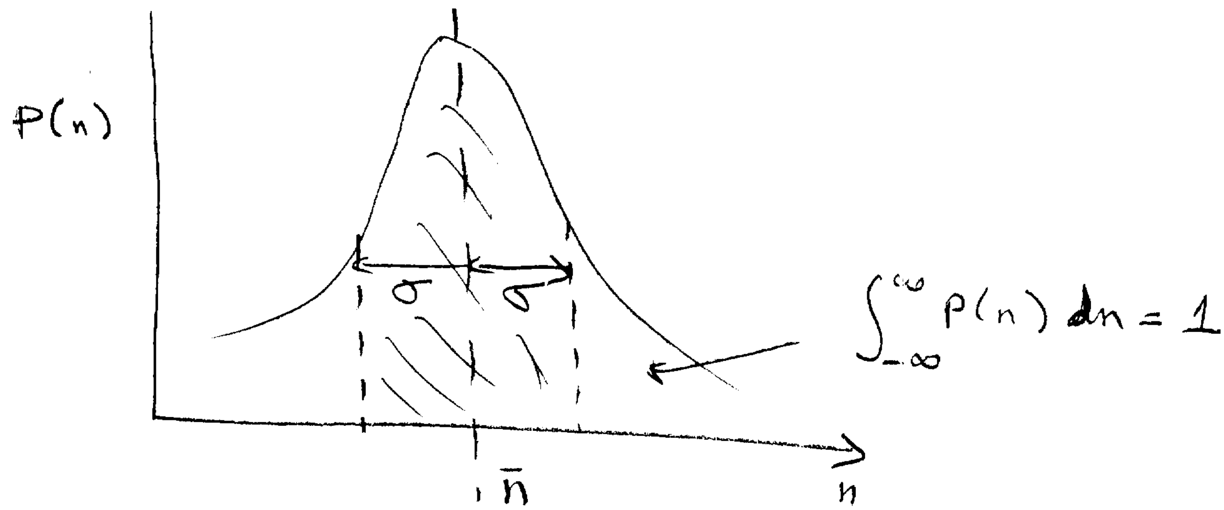
$$\text{ie } P(n) = P(\bar{n})\, e^{-\frac{(n-\bar{n})^2}{2\sigma^2}}$$

Now since $\sum_n' P(n) = 1 \simeq \int_{n=-\infty}^{\infty} P(n)\,dn = P(\bar{n})\sqrt{2\pi}\,\sigma$

$$\therefore \boxed{P(n) = \frac{1}{\sqrt{2\pi}\,\sigma}\, e^{-(n-\bar{n})^2/2\sigma^2}}$$ Gaussian Distribution

Valid only for large systems where $(n-\bar{n}) \ll \sigma^2$

comes from limitations of the Taylor series expansion



What is prob. that $\bar{n}-\sigma < n < n+\sigma$?
That is just the shaded area.

$$\int_{\bar{n}-\sigma}^{\bar{n}+\sigma} P(n)\,dn \quad \text{where } P(n) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(n-\bar{n})^2/2\sigma^2}$$

Do this integral numerically to find
prob $= 0.68$
ie 68% of the time we are within $\pm 1\sigma$.

<u>Note of warning</u>!
The Gaussian tails extend beyond $n=0$ & $n=N$.
This is a small error that is not a practical problem.
Remember, Gaussian is valid when $(n-\bar{n})^2 \ll \sigma^2$
and the extremes do not satisify this criterion

Example:

What is prob. ~~that~~ exactly 1000 of 3000 molecules are in the front $\frac{1}{3}$ of a room?

$N = 3000$
$n = 1000$
$p = \frac{1}{3}, q = \frac{2}{3}$

$$\bar{n} = pN = \frac{1}{3} \times 3000 = 1000$$

$$\sigma = \sqrt{Npq} = \sqrt{3000 \times \frac{1}{3} \times \frac{2}{3}} = 25.8$$

$n = \bar{n}$ (for this case)

$$\therefore P_{3000}(1000) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(n-\bar{n})^2/2\sigma^2}$$

$$= \frac{1}{\sqrt{2\pi}\,\sigma} e^{0} = 1.6 \times 10^{-2}$$

What is prob. of exactly 1100 being in front $\frac{1}{3}$?

$$\frac{(n-\bar{n})^2}{2\sigma^2} = \frac{(100)^2}{2 \times (25.8)^2} = 7.5$$

$$\therefore P_{3000}(1100) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-7.5} = 8.8 \times 10^{-6}$$

So we are $\frac{1.6 \times 10^{-2}}{8.8 \times 10^{-6}} \simeq 2 \times 10^{3}$ times more likely to see exactly 1000 molecules in the front $\frac{1}{3}$ (ie a uniform distribution) than we are to see 1100 molecules (ie a non-uniform distn).

Example continued

How many ways to have 1100 molecules in front 1/3 ?

$$\frac{N!}{n!\,(N-n)!} = \frac{3000!}{1100!\;1900!}$$

We use Stirling's formula: ($\ln m! \simeq m \ln m - m$)

$$\ln 3000! \simeq 3000 \ln 3000 - 3000 = 21{,}019.10$$

$$\ln 1100! \simeq 6{,}603.37$$

$$\ln 1900! \simeq 12{,}444.26$$

Now $\ln \frac{3000!}{1100!\,1900!} \simeq \ln 3000! - \ln 1100! - \ln 1900!$

$$\simeq 1{,}971.47$$

$$\therefore \frac{3000!}{1100!\,1900!} \simeq e^{1971.47} \simeq 10^{1971.47/\ln 10} = 10^{1971.47/2.3026}$$

$$\simeq 10^{856} \quad 854.37$$

your calculator won't be able to handle this. ← spreadsheet

That is a lot of possible combinations

Can do problems 4-5, 4-6, 4-7 this pt, 4-8 ← Assign!

How does this compare to uniform?

$$\frac{3000!}{1000!\;2000!} \simeq e^{1905.37} \simeq 10^{827.5} \quad \text{ie } 10^{-26.9} \text{ lower}$$

Also $p^{1000} q^{2000}$ cf $p^{1100} q^{1900}$

$$\left(\tfrac{1}{3}\right)^{1000}\left(\tfrac{2}{3}\right)^{2000} \text{ cf } \left(\tfrac{1}{3}\right)^{1100}\left(\tfrac{2}{3}\right)^{1900}$$

$$\frac{\frac{1}{3}^{1000}\cdot\left(\frac{2}{3}\right)^{2000}}{\left(\frac{1}{3}\right)^{1100}\cdot\left(\frac{2}{3}\right)^{1900}} = \frac{\left(\frac{2}{3}\right)^{100}}{\left(\frac{1}{3}\right)^{100}} = 2^{100} = 10^{30}$$

$$\therefore \frac{P_{3000}(1000)}{P_{3000}(1100)} \simeq 10^{+3.1} \simeq 1.26\times10^{3}$$

compares to previous answer

Math aside:

Base conversion:

In general $(b1)^{x1} = (b2)^{x2}$

$$\Rightarrow \quad x2 = x1 \frac{\ln(b1)}{\ln(b2)}$$

Example:

$$e^{x} = 10^{y} \Rightarrow y = \frac{x \ln(e)}{\ln(10)} = \frac{x}{\ln 10}$$

$$= \frac{x}{2.3026}$$

$$\therefore e^{x} = 10^{x/\ln 10}$$

Example:

$$\left(\tfrac{1}{2}\right)^{x} = 10^{y} \Rightarrow y = \frac{x \ln(1/2)}{\ln 10}$$

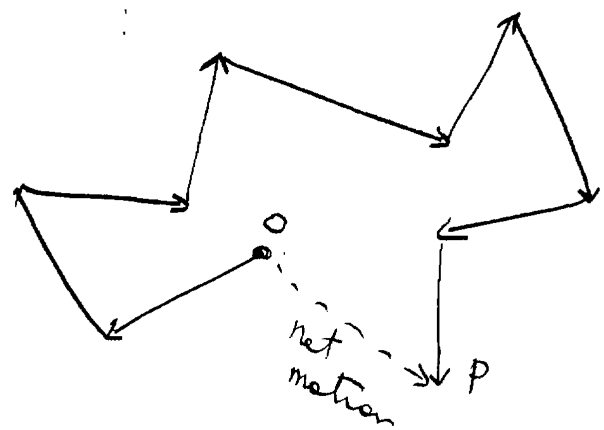
$$= -0.30103\, x$$

$$\therefore \left(\tfrac{1}{2}\right)^{x} = 10^{-0.30103 x}$$

The Random Walk

We can use probability theory to investigate random motion;

eg: diffusion of a gas
charge carriers in a metal or semiconductor
Brownian motion
arrangement of long polymer chains
⋮



Typically we want to know:

- average position w.r.t. start
- standard deviation (spread)

Single Step

Let s = step size

Let $P(s)ds$ = prob. of step having length between s & $s+ds$

$$\bar{s} = \int_{-\infty}^{\infty} s\, P(s)\,ds$$

$$(\text{standard deviation})^2 = \overline{(s-\bar{s})^2} \equiv \overline{(\Delta s)^2}$$

$$= \int_{-\infty}^{\infty} (s-\bar{s})^2\, P(s)\,ds$$

Now

$$\overline{(s-\bar{s})^2} = \overline{s^2 - 2s\bar{s} + \bar{s}^2}$$

$$= \overline{s^2} - 2\bar{s}\bar{s} + \bar{s}^2$$

$$= \overline{s^2} - \bar{s}^2$$

$$\overline{s^2} = \int_{-\infty}^{\infty} s^2\, P(s)\,ds \qquad \bar{s}^2 = \left[\int_{-\infty}^{\infty} s\,P(s)\,ds\right]^2$$

For N steps

$$\bar{S} = N\bar{s} \qquad \sigma^2 = N\,\overline{(\Delta s)^2}$$

(proof given in text if interested - p62)

Note: aver. dist travelled, $\bar{S}$, $\propto N$

$$\sigma \propto \sqrt{N}$$

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

Example :

Calculate $\bar{S}$ + σ for electron motion in electric field after 1 second.

Given : $N = 10^{12}$ collisions/sec. , $\bar{s} = 10^{-4}$Å

$\overline{\Delta s^2} = (1\text{Å})^2$ $\quad$ $1\text{Å} = 10^{-10}$m.

Sol'n

$$\bar{S} = N\bar{s} = 10^{12} \times 10^{-4} \times 10^{-10}\ \text{m} = 10^{-2}\ \text{m}.$$

$$\sigma^2 = N\left(\overline{\Delta s^2}\right) = 10^{12} \cdot (10^{-10}\ \text{m})^2 = 10^{-8}\ \text{m}^2$$

$$\therefore \sigma = 10^{-4}\ \text{m}$$

Note $\sigma \ll \bar{S}$ ie predictable behaviour for large N.

Can do problems 4.9 ← assign #1 at this pt.
4.10
4.11