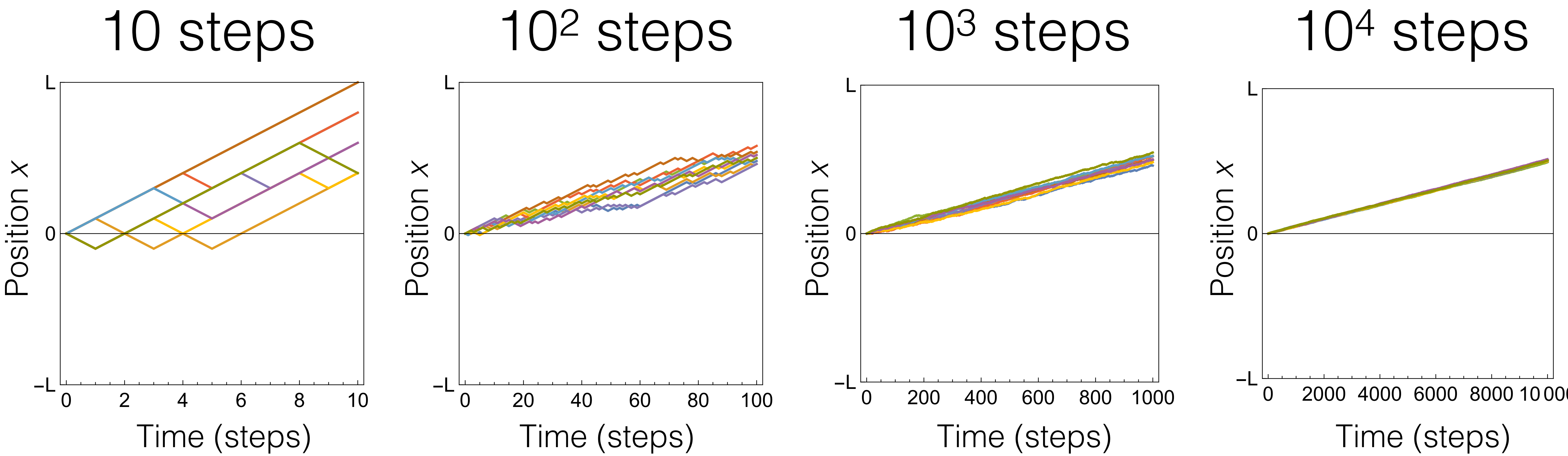
Physics 170:
Statistical Mechanics and Thermodynamics

Lecture 1B

Monika Schleier-Smith
schleier@stanford.edu
Varian 238

Last Time: Random Walk



- Final position follows *binomial distribution*
- Today: large-*N (thermodynamic)* limit

Names:

EXERCISE 1B: FROM BINOMIAL TO GAUSSIAN STATISTICS

New concepts and mathematical tools:

- The model system of the **paramagnet**
- **Microstates, macrostates**, and the **thermodynamic limit**
- **Stirling's approximation**

Useful results from last time:

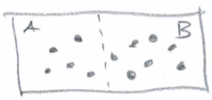
- $P_N(X) = \frac{N!}{(\frac{N-X}{2})!(\frac{N+X}{2})!} p^{\frac{N+X}{2}}(1-p)^{\frac{N-X}{2}}$
- $\langle X \rangle = (2p-1)N$
- $\Delta X = 2\sqrt{Np(1-p)}$

1. Last time, you derived the *binomial distribution*, the probability distribution for the outcome of a random walk in one dimension. List a few other scenarios or physical phenomena that are ...

   a. ...described by the binomial distribution:

* Coin toss

* Partitioning a group of people



* Binary alloy

A	B	B	A	A
B	A	A	B	A
A	A	A	B	B

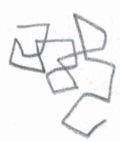
e.g. brass: A = Cu
B = Zn

* Paramagnet ↑↓↑↑↓ unpaired e^- spins in a solid, non-interacting
(e.g., Lithium)

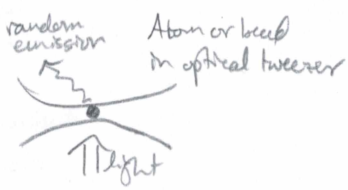
   b. ...analogous to random walks in higher dimensions:

* Diffusion, e.g. spreading of dye in solution (radius $\propto \sqrt{T}$)
= Brownian motion

* Polymer conformation



* Recoil heating in laser cooling or fluorescence imaging
= random walk in momentum space
... prevents us from knowing both x and p
... sets temperature limit in optical cooling



Names:

2. **Microstates and macrostates.** Consider a simple model of a paramagnet, consisting of N non-interacting spins, each of magnetic moment μ, in a magnetic field $B\hat{\mathbf{z}}$. A **microstate** of the system can be specified by the orientations ~~$\sigma_i^z = \pm 1$~~ ↑, ↓ of the N spins with respect to the field.

 a. How many different **microstates** are available to the system?

 2^N

 b. Many of these microstates are, for all practical purposes, equivalent. Suggest a macroscopic property that could be used to provide a simpler description of the state of the paramagnet. (*Note:* there is more than one correct answer!)

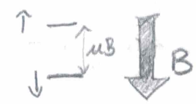
 Magnetization $M \equiv \mu(N_\uparrow - N_\downarrow)$

 Energy $E = -\mu B(N_\uparrow - N_\downarrow)$

 "Spin excess" $X \equiv N_\uparrow - N_\downarrow$

 m_s quantum # ($s=\frac{1}{2}$): $m = \frac{N_\uparrow - N_\downarrow}{2}$

 # of up spins $N_\uparrow$



 c. Sketch all microstates of the paramagnet for $N = 3$. Based on your answer in b., circle groups of microstates that correspond to the same **macrostate**.

↑↑↑
↑↑↓
↑↓↑
↑↓↓
↓↑↑
↓↑↓
↓↓↑
↓↓↓

Awkwardly organized...

microstates	X	m
↑↑↑	3	3/2
↓↑↑, ↑↓↑, ↑↑↓	1	1/2
↓↓↑, ↓↑↓, ↑↓↓	−1	−1/2
↓↓↓	−3	−3/2

Better organized...

d. For general N, how many **macrostates** are available to the paramagnet?

$0 \leq N_\uparrow \leq N \Rightarrow N+1$ macrostates

e. Suppose that we know the total magnetization $M = \mu(N_\uparrow - N_\downarrow)$ and hence the spin excess $X \equiv N_\uparrow - N_\downarrow$. Write down the **multiplicity** $g_N(X)$ of microstates corresponding to this macrostate.

$$g_N(X) = \binom{N}{N_\uparrow} \qquad X = N_\uparrow - (N - N_\uparrow) = 2N_\uparrow - N$$

$$= \binom{N}{\frac{N+X}{2}} = \frac{N!}{\left(\frac{N-X}{2}\right)!\left(\frac{N+X}{2}\right)!}$$

f. If each individual spin has probability p of pointing along $+\hat{\mathbf{z}}$, how is the probability $P_N(X)$ of finding the paramagnet in a state of spin excess X related to the multiplicity $g_N(X)$?

Probability = (multiplicity of microstates) × (probability of individual microstate)

$$P_N(X) = g_N(X)\, p^{\frac{N+X}{2}} (1-p)^{\frac{N-X}{2}}$$

g. How does the relationship between probability $P_N(X)$ and multiplicity $g_N(X)$ simplify if $p = 1/2$? Explain.

If $p = 1/2$, $P_N(X) = g_N(X)/2^N$.

This makes sense: for $p = 1/2$, all microstates are equally likely. In this case, probability is just directly proportional to multiplicity.

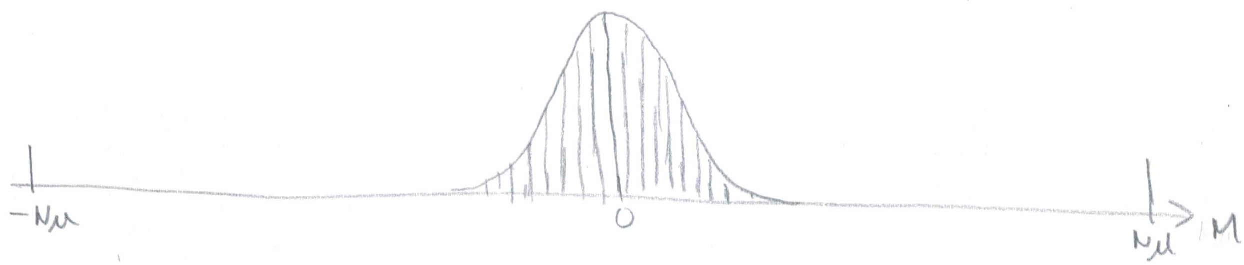
Ex: if $\vec{B} = 0$, $\uparrow$ and $\downarrow$ should be equally probable.

Names:

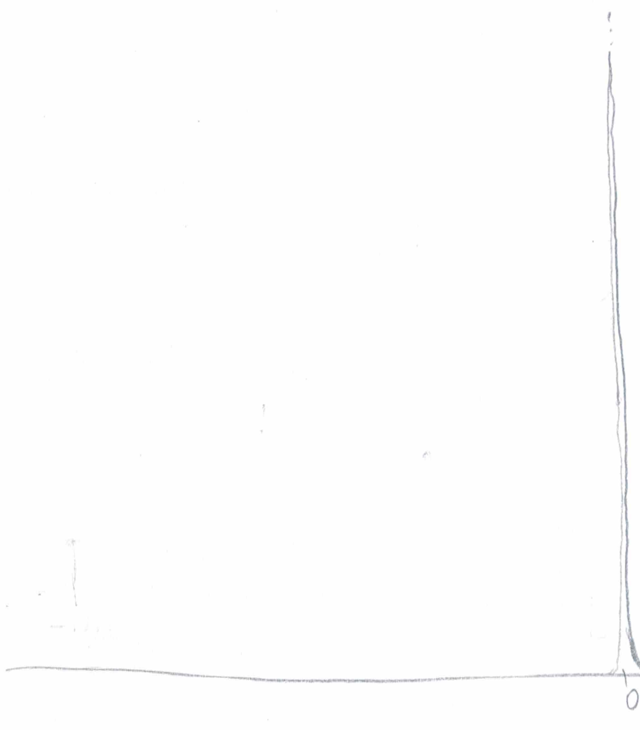
h. Sketch the multiplicity $g_N(M)$ as a function of magnetization M for a paramagnet of N spins over the full domain $-N\mu \leq M \leq N\mu$. Show three different cases: $N = 3$, $N = 100$, and $N = 10^{23}$.

$\boxed{N=3}$

$\boxed{N=100}$



$\boxed{N=10^{23}}$



Multiplicity is sharply peaked in the thermodynamic limit.

— This will be very useful for predicting behavior of many-particle system!

3. The probability distribution $P_N(X)$ is unwieldy. Let's find a simplified expression for the large-N (thermodynamic) limit.

   a. *Stirling's approximation*:
   Which of the following is the best approximation, for $N \gg 1$?

   A) $\ln N! \approx N \ln N$

   ~~**B)**~~ $\ln N! \approx N \ln N + N$

   → **C)** $\ln N! \approx N \ln N - N$

   ~~**D)**~~ $\ln N! \approx N \ln N + N - \ln N$

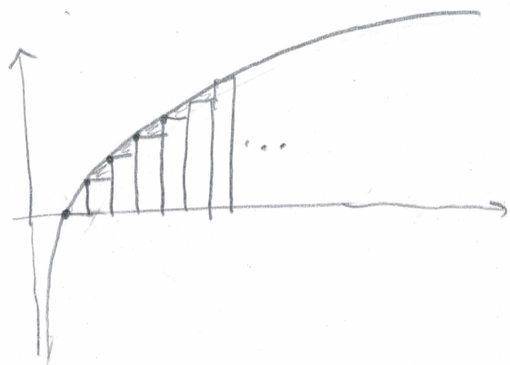
$N! = N(N-1)(N-2)\cdots 1 = \prod_{k=1}^{N} k \quad < N^N$

$\ln N! < N \ln N \Rightarrow$ maybe C?

$\ln N! = \sum_{k=1}^{N} \ln k \approx \int_1^N dk \ln k$

$= [k \ln k - k]_1^N$

$\approx \underbrace{N \ln N - N}\ \underbrace{+1}_{\ll N}$



This is a pretty good approximation. A more careful analysts shows

$\ln N! \approx N \ln N - N + \frac{1}{2} \ln(2\pi N) + \mathcal{O}(1/N)$

Let's just use the first two terms for now...

b. Using Stirling's approximation, find an approximation to the binomial distribution $P_N(X)$ in the large-N limit.

i. Write down an approximation for $\ln P_N(X)$. Simplify your expression into the form

$$\frac{N+X}{2}\ln(A)+\frac{N-X}{2}\ln(B), \tag{1}$$

where A and B depend on $N, p, \underbrace{q}_{=1-p}$, and X.

$$\ln P_N(X) \approx \underbrace{N\ln N}_{\frac{N+X}{2}\ln N+\frac{N-X}{2}\ln N} - \frac{N-X}{2}\ln\left(\frac{N-X}{2}\right) - \frac{N+X}{2}\ln\left(\frac{N+X}{2}\right) + \frac{N+X}{2}\ln p + \frac{N-X}{2}\ln(1-p)$$

$$\Rightarrow \ln P_N(X) \approx -\frac{N+X}{2}\ln\left(\frac{N+X}{2Np}\right) - \frac{N-X}{2}\ln\left(\frac{N-X}{2Nq}\right),$$ where $q=1-p$

$$\xrightarrow[p=1/2]{} -\frac{N+X}{2}\ln(1+\xi) - \frac{N-X}{2}\ln(1-\xi)$$

ii. You have shown that the typical fluctuation from the mean scales as $\Delta X \propto \sqrt{N}$. Thus, $\xi \equiv (X-\langle X\rangle)/N$ is a small parameter wherever the probability distribution is not negligibly small. Evaluate the probability distribution $P_N(X)$ by expanding for small ξ. You may set $p=1/2$ to minimize algebra.

Hint: You will need the Taylor series expansion $\ln(1+u) \approx u - u^2/2 + O(u^3)$.

$$\ln P_N(X) \approx -N\left(\frac{1+\xi}{2}\right)(\xi-\xi^2/2) - N\left(\frac{1-\xi}{2}\right)(-\xi-\xi^2/2)$$

$$= -\frac{N}{2}\left[(\cancel{\xi}-\xi^2/2)+(\cancel{-\xi}-\xi^2/2)\right] - \frac{N\xi}{2}\left[(\xi-\cancel{\xi^2/2})+(\xi+\cancel{\xi^2/2})\right]$$

$$= +\frac{N}{2}\xi^2 - N\xi^2 = -N\xi^2/2$$

$$\Rightarrow \boxed{P_N(X) \approx e^{-N\xi^2/2} = e^{-NX^2/(2N^2)} = e^{-X^2/(2N)}}$$

iii. Is your result for $P_N(\xi)$ properly normalized? Why or why not? If not, find the normalization factor.
Hint: You will need to evaluate a Gaussian integral of the form: $\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx$.

Getting the normalization right requires the next-order term in Stirling's Approximation. Alternatively, let's just find the general form of a properly normalized Gaussian integral... see attached notes.

$$P_N(X) = \frac{1}{\sqrt{2\pi N}}\, e^{-X^2/(2N)}$$

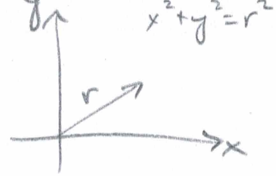
iv. Based on your work above, write down the properly normalized distribution $P_N(X)$. Is its standard deviation consistent with the result you obtained last class from the binomial distribution?

$$P_N(X) = \frac{1}{\sqrt{2\pi N}}\, e^{-X^2/(2N)}$$

$$(\Delta X)^2 = N \Rightarrow \Delta X = \sqrt{N} = 2\sqrt{Np(1-p)} \text{ @ } p = \tfrac{1}{2} \checkmark$$

You have just seen an example of a powerful statistical result known as the **Central Limit Theorem**, which explains why the Gaussian distribution is so ubiquitous in nature. You will prove the central limit theorem in the homework and examine how it applies to the paramagnet in class on Monday.

We want: $P(x) = Ae^{-\alpha x^2}$ s.t. $\int_{-\infty}^{\infty} dx\, P(x) = 1$



We have $I \equiv \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$

$$I^2 = \left[\int_{-\infty}^{\infty} e^{-\alpha x^2} dx\right]\left[\int_{-\infty}^{\infty} e^{-\alpha y^2} dy\right] = \int_0^{\infty} dr \cdot 2\pi r\, e^{-\alpha r^2}$$

$u = +\alpha r^2 \Rightarrow du = +2\alpha r$

$$= +\int_0^{\infty} \frac{\pi}{\alpha} du \cdot e^{-u} = -\frac{\pi}{\alpha} e^{-u}\Big|_0^{\infty} = \frac{\pi}{\alpha} \Rightarrow I = \sqrt{\frac{\pi}{\alpha}}$$

$$\Rightarrow \int_{-\infty}^{\infty} dx\, Ae^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} A \overset{!}{=} 1 \Rightarrow A = \sqrt{\frac{\alpha}{\pi}}$$

$$\Rightarrow P(x) = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha x^2}$$

The <u>standard deviation</u> can be found from

$$\langle x^2 \rangle = A\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = -A \frac{\partial}{\partial \alpha} \overbrace{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx}^{I}$$

$$= -A \frac{\partial}{\partial \alpha} \sqrt{\frac{\pi}{\alpha}} = \frac{A}{2}\sqrt{\pi/\alpha^3} = \frac{1}{2}\sqrt{\frac{\alpha}{\pi}}\sqrt{\frac{\pi}{\alpha^3}} = \frac{1}{2\alpha}$$

For the Gaussian under consideration, $\langle x \rangle = 0$ (mean zero), so

$$\sigma \equiv \Delta x = \sqrt{\langle x^2 \rangle} = 1/\sqrt{2\alpha} \Longleftrightarrow \alpha = \frac{1}{2\sigma^2}$$

General form of Gaussian with std. dev. σ and mean $\langle x \rangle$:

$$\boxed{P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\langle x \rangle)^2/[2\sigma^2]}}$$

<u>Useful to remember!</u>