Thermal & Statistical Physics

PHYS 343

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LECTURE 4

Entropy and Exchange between systems

- Counting microstates of *combined* systems
- Volume exchange between systems
- Definition of Entropy and its role in equilibrium

Review: Some definitions

- State: The details of a particular particle, e.g., what volume bin it is in, the orientation of its spin, what velocity it has, etc.

- Microstate: The configuration of states for a set of particles, e.g., which bin each particle is in, the specific orientation of the spins --
- ↑↑↓↑↓, etc.

- Macrostate: The collection of all microstates that satisfy some constraint, e.g.,
  - all the particles on the left side
  - all the particles in *any* bin
  - 1/3 of the particles with their spins "up"
  - no particles as a gas (all as liquid)

ACT 1: Microstates

Consider 10 coins (labeled by their position).
Which microstate is least likely?

a. HHHHH HHHHH
b. HHHHH TTTTT
c. HTHTH THTHT
d. HHTHT TTHHH
e. TTHTH HHTTH

ACT 1: Microstates

Consider 10 coins (labeled by their position).
Which microstate is least likely?

a. HHHHH HHHHH
b. HHHHH TTTTT
c. HTHTH THTHT
d. HHTHT TTHHH
e. TTHTH HHTTH

Every microstate is equally likely! (This assumes the system is in equilibrium – it has had a chance to reach every microstate).

If instead we ask which *macrostate* is least likely, it is the one with all the coins ‘heads’ (or ‘tails’). Why is that that least likely macrostate? Because there’s only one microstate that gives it.

Basic reminders and new definition

- When an isolated system can explore some number Ω of microstates, they each become equally likely.
- So the probability that you find some *macro*state A is just the fraction of all the microstates that look like A.

$$P(A) = \Omega(A) / \Omega,$$

$$S(A) \equiv \ln \Omega(A)$$

To keep track of the large numbers of states, we define Entropy

$$P(A) \propto e^{S(A)}$$

The most likely macrostate in equilibrium has the biggest net entropy S. We call that the "equilibrium state" even though there are really small fluctuations around it. If the system is BIG (many particles), the relative size of these fluctuations is negligible.

Counting Microstates (revisited)

Last lecture we considered binomial (two-state) systems:

Coins land with either heads or tails, electronic spins have magnetic moments m pointing either along or counter to an applied field, and 1-dimensional drunks can step a distance either left or right. We defined the terms "microstate" and "macrostate" to describe the spins, and by analogy the other systems:

System	One particular Microstate	Macrostate (usually what we measure)
Spins	↑↓↓↑↓↑↑↑↓↑	Total magnetic moment = $\mu\,(N_{up} - N_{down})$
Coins	HTTHTHHHTH	Net winnings = $(N_{heads} - N_{tails})$
Steps	RLLRLRRRLR	Total distance traveled = $\ell_x(M_{right} - M_{left})$ (N = # drunks, or # particles diffusing)

Now we will study systems that occupy more than two states. This "bin problem" is directly related to particles in gases and solids.

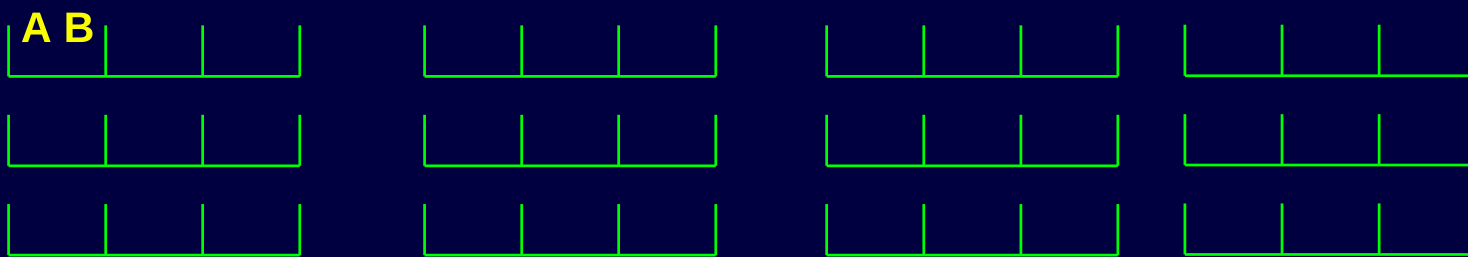
→

Counting arrangements of objects

<u>Problem #1</u>: <u>Distinct objects</u> in bins with <u>unlimited</u> <u>occupancy</u>.

- **How many ways can you arrange 2 <u>distinct</u> objects (A and B) in 3 bins?**

Work space:



 # arrangements ≡ # "microstates" = Ω =

Now throw the 2 objects up and let them land randomly.

- **What is the probability of getting a specified microstate?**

- **How many microstates for <u>N different objects in M bins</u>?** **Ω =**
- **Find Ω for two <u>identical</u> objects (A and A) in 3 bins.** **Ω =**

Counting arrangements of objects

Problem #1: Distinct objects in bins with unlimited occupancy.

- How many ways can you arrange 2 distinct objects (A and B) in 3 bins?

Work space:

Bin 1	Bin 2	Bin 3
A B		
A	B	
A		B
B	A	
	A B	
	A	B
B		A
	B	A
		A B

 # arrangements ≡ # "microstates" = Ω = 9

Now throw the 2 objects up and let them land randomly.

- **What is the probability of getting a specified microstate?** 1/9
- **How many microstates for N different objects in M bins?** $\Omega = M^N$
- **Find Ω for two identical objects (A and A) in 3 bins.** $\Omega =$

ACT 2: Effect of indistinguishability

Consider 2 particles in a box with two bins (multiple occupancy allowed). Compare the total number of microstates Ω_d if the particles are distinguishable, with the total number of microstates Ω_i if the particles are indistinguishable.

a. $\Omega_i < \Omega_d$ b. $\Omega_i = \Omega_d$ c. $\Omega_i > \Omega_d$

ACT 2: Effect of indistinguishability -- Solution

Consider 2 particles in a box with two bins (multiple occupancy allowed). Compare the total number of microstates Ω_d if the particles are distinguishable, with the total number of microstates Ω_i if the particles are indistinguishable.

a. $\Omega_i < \Omega_d$ (circled) **b. $\Omega_i = \Omega_d$** **c. $\Omega_i > \Omega_d$**

For the distinguishable particles ("a" and "b"), the states are:

|ab|0| |0|ab| |a|b| |b|a|

For the indistinguishable particles ("a" and "a"), the states are:

|aa|0| |0|aa| |a|a|

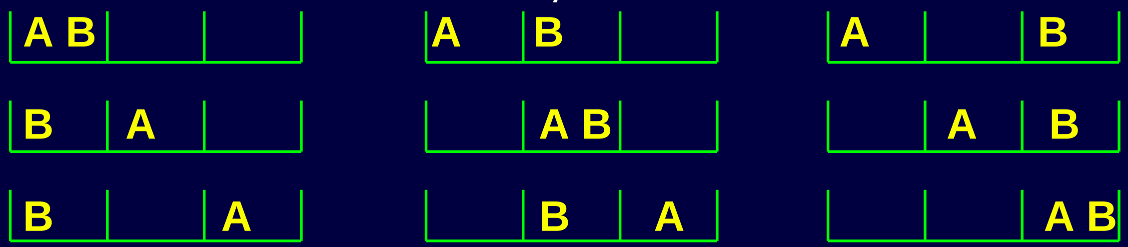
This is a general result – indistinguishable particles typically have fewer microstates.

Counting arrangements of objects

Problem #1: Distinct objects in bins with unlimited occupancy.

- How many ways can you arrange 2 distinct objects (A and B) in 3 bins?

Work space:



arrangements ≡ # "microstates" = Ω = 9

Now throw the 2 objects up and let them land randomly.

- What is the probability of getting a specified microstate? 1/9

- How many microstates for N different objects in M bins? $\Omega = M^N$

- Find Ω for two identical objects (A and A) in 3 bins. Ω = 6

Why do we consider IDENTICAL PARTICLES?

(Indistinguishable)

NATURE IS COMPOSED OF CLASSES OF IDENTICAL PARTICLES

All atoms of a given type are indistinguishable.

All molecules of a given type are indistinguishable.

But specifying ‘type’ you have to be complete, including all the isotopes, remembering spin states, etc.

Single occupancy

Problem # 2: Distinct objects in single-occupancy bins.

- How many ways can you arrange 2 distinct objects (A, B) in 4 bins?

- What is Ω for 3 objects (A, B, C) in 4 bins? $\Omega =$

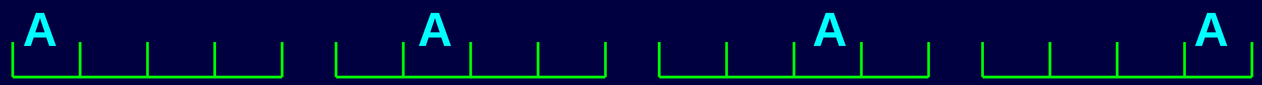
- How many ways can you arrange N different objects in M bins ?

Single occupancy

Problem # 2: Distinct objects in single-occupancy bins.

- **How many ways can you arrange 2 distinct objects (A, B) in 4 bins?**

Solution: There are 4 possible places for A:



Each of these **has 3 possible places for B.**

Therefore, the total number of microstates = Ω =

- **What is Ω for 3 objects (A, B, C) in 4 bins?** **Ω =**

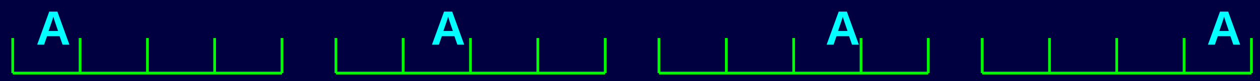
- **How many ways can you arrange N different objects in M bins?**

Single occupancy

Problem # 2: Distinct objects in single-occupancy bins.

- How many ways can you arrange 2 distinct objects (A, B) in 4 bins?

Solution: There are 4 possible places for A:



Each of these **has 3 possible places for B.**

Therefore, the total number of microstates = Ω = 4 x 3 = 12

- What is Ω for 3 objects (A, B, C) in 4 bins? **Ω = 4 x 3 x 2 = 24**

(each of the 3 possible places for B had 2 spots for C)

- How many ways can you arrange N different objects in M bins?

Answer:

$$\Omega = \frac{M!}{(M-N)!}$$

[Convince yourself.]

Consequence of Identical particles: single occupancy

- Imagine 4 distinct particles arranged in 10 single-occupancy bins. One possible arrangement (microstate):

A			B			C	D		

Switching C and D gives a different state.

$$\Omega = M!/(M-N)! = 10!/6! = \boxed{5040}$$

N objects ; M bins

- If we change to 4 identical particles, we have over-counted the number of microstates. By what factor is Ω reduced?

A			A			A	A		

Switching two A's gives the same state, so: **divide by N! = 4!**

Explanation: How many ways can ABCD be permuted?

A can be in 4 positions: Axxx xAxx xxAx xxxA

Each of these has 3 possibilities for B: Bxx xBx xxB

Each of these has 2 possibilities for C: Cx xC

Each of these has only one spot left for D. D

Total number of permutations = 4 x 3 x 2 x 1 = 4! = 24

So # microstates for Identical Particles: $\boxed{\Omega = 5040/24 = 210}$

Occupancy Rules and Particle Types

- The possible occupancy rules for bins are
  - unlimited occupancy
  - single occupancy
- The possible particle types are
  - distinct = distinguishable
  - identical = indistinguishable

4 cases total

- Note that for N<<M, the occupancy rule doesn't matter because there are relatively few multiple occupancies.

N objects ; M bins

Try M=10, N=2:

Predict: $\frac{M!}{(M-N)!} \approx M^N$ (O.K.)

$M^N = 10^2 = 100$

$$\frac{10!}{8!} = \frac{10 \cdot 9 \cdot 8 \cdots 1}{8 \cdot 7 \cdots 1} = 10 \cdot 9 = \boxed{90} \approx 100$$

(only 10 multiple occupancies)

Summary of Bin Statistics

M = # bins

N = # objects

$\Omega =$

	Unlimited Occupancy	Single Occupancy	Dilute gas (N << M)
Distinguishable	M^N	$\frac{M!}{(M-N)!}$	M^N
Identical	$\frac{(N+M-1)!}{(M-1)!N!}$	$\frac{M!}{(M-N)!N!}$	$\frac{M^N}{N!}$

For gases we will be concerned primarily with the low-density limit (N << M). In this limit, we need only:

$\Omega \approx M^N$ for distinguishable particles

$\Omega \approx \frac{M^N}{N!}$ for indistinguishable particles

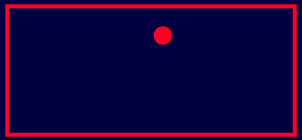
Our 1/N! for indistinguishable single-occupancy ~works for multiple–occupancy gases too because N<<M means multiple occupancy is rare.

Distributions of Gas molecules

We apply counting to real particles

Consider gas particles in a container:

Volume V:



Let's say that in each volume V, the number of different states M available to a particle is proportional to V, as you would correctly expect.
So we write:

$$M = n_T V.$$

n_T here just means the number of states per unit volume for a particle. (Because particles with different velocities in the same volume count as different states, this number depends on T.)

Why not an uncountable infinity of states? Quantum mechanics! ($\Delta x\, \Delta p > \hbar$)

Simplest math:

Begin with <u>distinguishable</u> particles and with # bins >> # particles ($M = n_T V >> N$), i.e., dilute system

<u>N particles; M states</u>

If there are M states (e.g, M = 100), probability that the particle will be in a particular state is just 1/M: = 1%

Total number of states for 2 distinguishable particles:

$$\Omega = M \cdot M = M^2 \qquad = 10{,}000$$

Total number of states for N distinguishable particles:

$$\Omega = M^N$$

($= 100^N = 10^{2N} = 10^{20}$ *just for 10 particles*)

<u>N particles; M states</u>

ACT 3: Counting states

Consider N particles in a box of volume V. This has a total number of states (e.g., cells) M, and a total number of microstates $\Omega = M^N$. If we double the volume (2V), what is the new number of microstates Ω'?

a. $\Omega' = \Omega$

b. $\Omega' = 2\,\Omega$

c. $\Omega' = 2^N\Omega$

d. $\Omega' = \Omega^2$

ACT 3: Counting states -- Solution

Consider **N particles** in a box of volume V. This has a **total number of states** (e.g., cells) **M**, and a total number of microstates $\Omega = M^N$. If we double the volume (2V), what is the new number of microstates Ω'?

a. $\Omega' = \Omega$

b. $\Omega' = 2\,\Omega$

c. $\Omega' = 2^N\Omega$

d. $\Omega' = \Omega^2$

If you double the volume, M doubles.

$$\Omega' = (2M)^N = 2^N M^N = 2^N\Omega$$

Let's say the volume only increases by 1%:

$$\Omega' = (1.01\,M)^N = 1.01^N\,\Omega$$

If $N = 10^{23}$ (e.g., gas in a room), this increase in the number of states is enormous: $(1 + 0.01)^N$ will overflow your calculator.

Counting states for two combined systems – the concept of equilibrium

- Divide a box into two parts, volumes V_1 and V_2 . $V_1 + V_2 = V$
- Put N_1 particles in V_1 and N_2 particles in V_2 . $N = N_1 + N_2$
- The position of the partition (or value of V_1) defines a "macrostate".

V_1 $V_2 = V - V_1$

N_1 $N_2 = N - N_1$

Ω_1 = # microstates in left side = $(n_T V_1)^{N_1}$

Ω_2 = # microstates in right side = $(n_T V_2)^{N_2}$

Total number of microstates in the macrostate with volume V_1 :

$$\underline{\Omega = \Omega_1 \cdot \Omega_2} = n_T^{N_1} n_T^{N_2} V_1^{N_1} \cdot V_2^{N_2} = (n_T^{N}) \cdot V_1^{N_1} \cdot V_2^{N_2}$$

Equilibrium Volume Exchange

We now allow the partition to move (the macrostate to change) and ask, "What is the most probable macrostate? (most likely V_1?)" .

(For big systems the average V_1 and the most likely V_1 are nearly the same.)

V = total volume

Answer: **Find V_1 that maximizes Ω . That will be the most probable V_1 .**

$$\Omega = (\text{constant}) \cdot V_1^{N_1} \cdot V_2^{N_2} = (\text{constant}) \cdot V_1^{N_1} \cdot (V - V_1)^{N_2}$$

Shortcut: **Maximize** $\ln(\Omega) = \ln(\Omega_1) + \ln(\Omega_2)$

------ a sum rather than a product:

$$\ln(\Omega) = N_1 \ln(V_1) + N_2 \ln(V - V_1) + \text{constant}$$

$$\frac{d\ln(\Omega)}{dV_1} = 0$$

← **Condition for maximum $\ln(\Omega)$**

Result

$$\frac{d\ln(\Omega)}{dV_1} = \left(\frac{\partial \ln(\Omega)}{\partial V_1}\right)_{V_2} + \frac{dV_2}{dV_1}\left(\frac{\partial \ln(\Omega)}{\partial V_2}\right)_{V_1} = \left(\frac{\partial \ln(\Omega)}{\partial V_1}\right)_{V_2} - \left(\frac{\partial \ln(\Omega)}{\partial V_2}\right)_{V_1} = 0$$

$$\therefore \left(\frac{\partial \ln(\Omega)}{\partial V_1}\right)_{V_2} = \left(\frac{\partial \ln(\Omega)}{\partial V_2}\right)_{V_1} \quad \Rightarrow \frac{N_1}{V_1} = \frac{N_2}{V_2}$$

Reasonable result: It is most likely that the gases have equal densities, N/V

(Recall ideal gas law: p = (N/V) kT

If the two chambers are at the same T, then the partition will move to equalize p.)

Given the freedom to move, the partition will move so that

$$\left(\frac{\partial \ln(\Omega_i)}{\partial V_i}\right)$$ **is the same on each side.**

Then trading V can't increase net ln(Ω).

And that's what gives equal particle densities on each side.

Entropy

Define a quantity called the Entropy = natural log of the number of accessible microstates

$$S \equiv \ln(\Omega)$$

Why?

Combine two systems. Ω_{tot} is a product. σ_{tot} is a sum.

$$\Omega_{Tot} = \Omega_1 \cdot \Omega_2 \qquad so$$

$$S_{Tot} = \ln(\Omega_1 \cdot \Omega_2) = \ln(\Omega_1) + \ln(\Omega_2) = S_1 + S_2$$

Property of system 1 **Property of system 2**

Entropy is *additive* →
much more convenient to maximize.

Entropy is a <u>state function</u> … determined by the macrostate of the system

Summary

Total entropy of an isolated system is maximum in equilibrium.

So if two parts (1 and 2) can trade V, equilibrium requires:

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}$$

← **General!**

So long as systems are big enough for the derivative to be meaningful

---

For N distinguishable independent gas particles in a volume V:

$$\Omega \propto V^N \quad so \quad S = N \ln V + const.$$

Remember number for σ because we didn't know how to calculate n_T, but this tells us how σ depends on V. In particular, for an ideal gas that isothermally changes volume from V_i to V_f the entropy change is

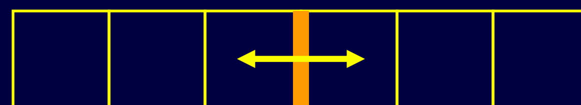
$$S_f - S_i = N \ln(V_f / V_i)$$

(We can compute some entropy *changes* exactly – no arbitrary constants.)

Exercise: Microstates and Entropy

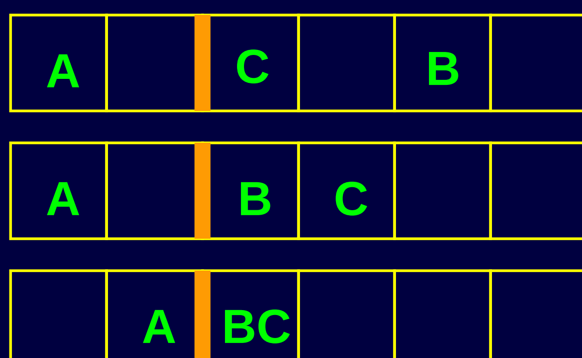
a case where the numbers are small, and the whole distribution matters, the average and the most likely may not be very close

Consider 3 particles (A, B, C) in a two-chamber system with 6 single-state cells partitioned by a movable barrier Take N_1=1 (particle A) and N_2=2 (particles B and C).



Count the number of microstates for each side and for the whole system as a function of the partition position.

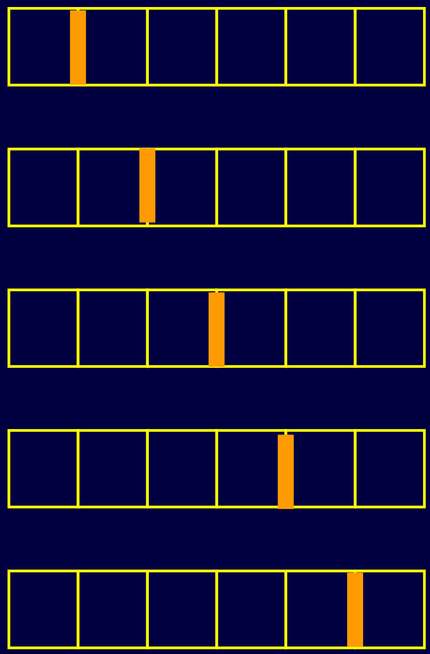
For example, for the partition as shown below, possible states are:



1 particle on left of partition and 2 particles on right. Allow <u>multiple occupancy</u>.

Worksheet for this problem

Fix the partition at:



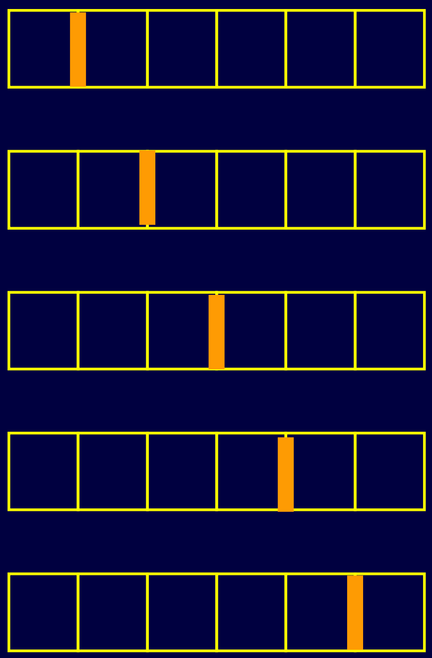
Ω_1	Ω_2	$\Omega = \Omega_1\Omega_2$	$\sigma = \ln(\Omega)$
1	$5^2 = 25$	25	3.22
2	$4^2 = 16$	32	
	$1^2 = 1$		

Constraint: 1 particle on left of partition and 2 particles on right. Allow multiple occupancy.

Average $V_1 = \langle V_1 \rangle = ?$

Worksheet for this problem

Fix the partition at:



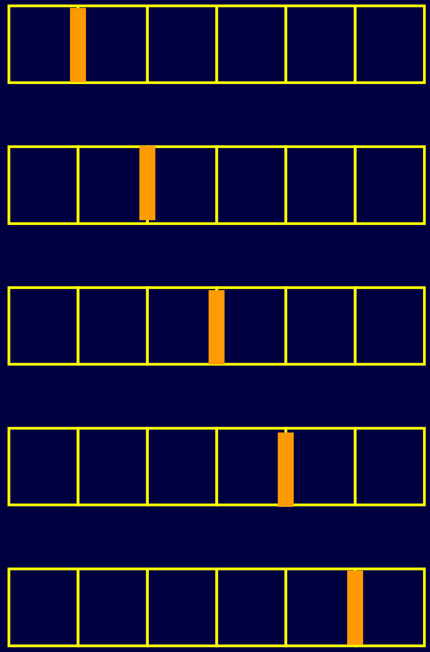
Ω_1	Ω_2	$\Omega = \Omega_1\Omega_2$	$\sigma = \ln(\Omega)$
1	$5^2 = 25$	25	3.22
2	$4^2 = 16$	32	3.47
3	$3^2 = 9$	27	3.30
4	$2^2 = 4$	16	2.77
5	$1^2 = 1$	5	1.61

Constraint: 1 particle on left of partition and 2 particles on right. Allow <u>multiple occupancy</u>.

Average $V_1 = \langle V_1 \rangle =$

Worksheet for this problem

Fix the partition at:



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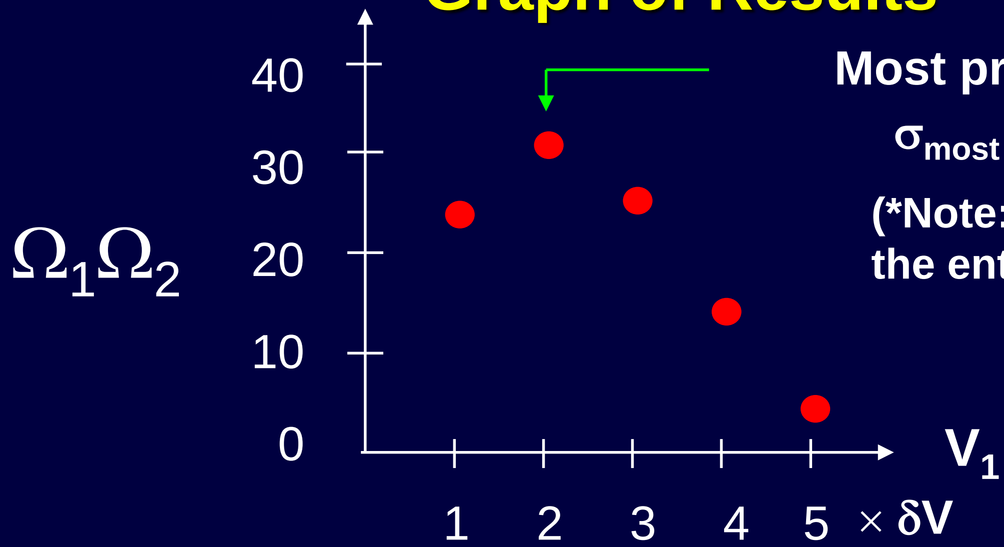
4	$2^2 = 4$	16	2.77
5	$1^2 = 1$	5	1.61

Constraint: 1 particle on left of partition and 2 particles on right. Allow multiple occupancy.

Average $V_1 = \langle V_1 \rangle =$ (1*25+2*32+3*27+4*16+5*5)/(25+32+27+16+5) = 259/105 = 2.47

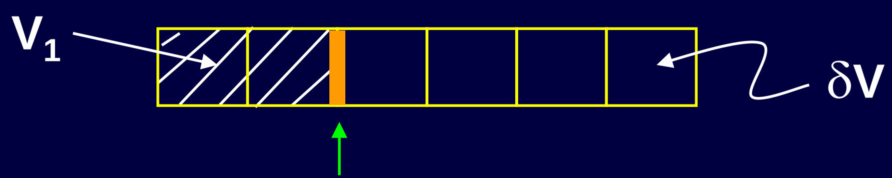
Graph of Results



Most probable V_1→

$\sigma_{\text{most likely}} = \ln(32) = 3.47$*

(*Note: without this constraint, the entropy of this system is $\sigma = \ln(105) = 4.65$)



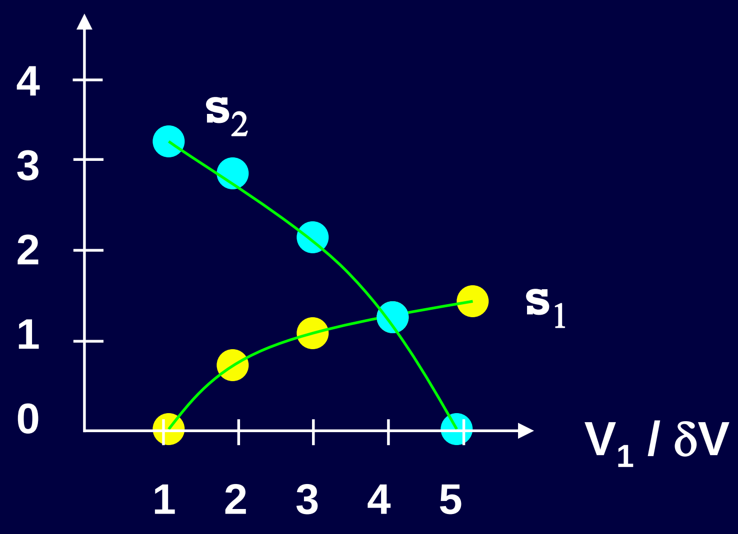
Letting the partition range over all 5 positions, most likely position occurs when

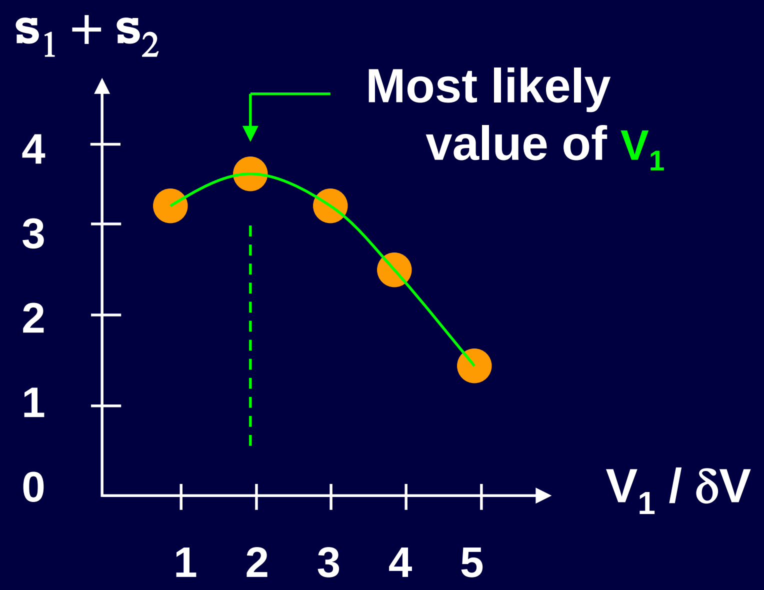
$$\frac{N_1}{V_1} = \frac{N_2}{V_2} \quad \left(= \frac{1}{2} \right)$$

What is the probability $P(2)$ of finding (V_1/ δV) = 2?

$$P(2) = \frac{32}{25+32+27+16+5} = \frac{32}{105} = 30.5\%$$

Maximizing the total entropy





If the partition is allowed to move freely among all positions (macrostates):

- **Most likely configuration occurs at maximum** $S = S_1 + S_2$

This corresponds roughly to $\frac{\partial s_1}{\partial V_1} \quad \frac{\partial s_2}{\partial V_2}$ **not** $s_1 = s_2$

Number of bins and particles large → distribution is very sharply peaked. (Recall probability distributions for binomial cases.)

Lessons from Volume exchange

- The number of states of the whole was the product of the number of states of the parts.

$$\Omega_{TOT} = \Omega_1 \Omega_2$$

- The log of the total number is the sum of the logs of the numbers of the parts.
  - We call the ln(number of microstates) the entropy σ

$$\ln(\Omega) \equiv \sigma$$

$$\sigma_{TOT} = \sigma_1 + \sigma_2$$

- For big systems, in equilibrium we almost certainly see the macrostate that maximizes total number
  - To find it we maximize entropy by maximizing the sum of the entropies of the parts.
- If parts can exchange volume, in equilibrium each must have the same derivative of its entropy with respect to its volume.
  - Otherwise volume could shift and increase net entropy
    - » argument doesn't rely on the parts being the same at all

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}$$

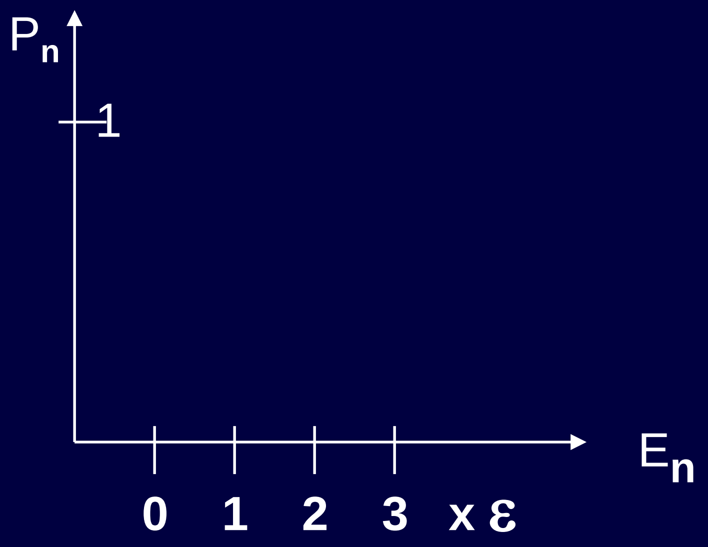
@fixed N, etc.

- We will next use the same principles for systems that trade ENERGY

Probability P_n decreases with increasing E_n
Home Exercise

- For a system of 3 oscillators with $U = 3 \cdot \varepsilon$ plot:

  P_n = probability that oscillator *#1* has energy $E_n = n \cdot \varepsilon$



Can you state in words why P_n decreases with increasing E_n?