

Thermal Physics

PHYS/BMME 441

Chapter 2

Lectures 3 - 6

When & Where: Mon. / Wed. 08:45- 10:00 AM, Phillips 247

Textbook: *An Introduction to Thermal Physics*, Daniel V. Schroeder

Website: sakai.unc.edu

Outlook for Chapter 2

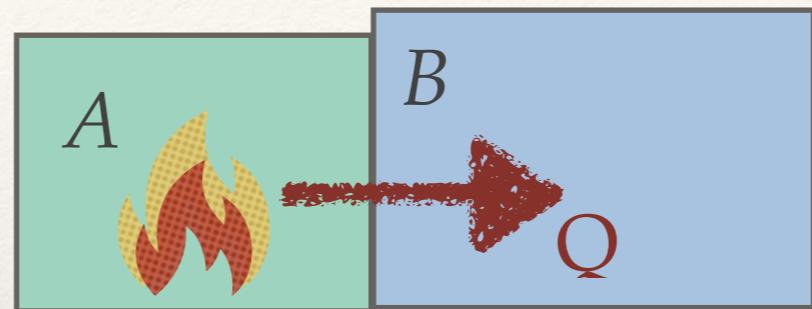
Chapter 2: The Second Law (chapters 2.1 to 2.6)

read chapters:

- 2.1 Two-state systems
- 2.2 Einstein Model for Solids
- 2.3 Interacting Systems
- 2.4 Large Systems
- 2.5 Ideal Gas (again...)
- 2.6 Entropy

Outlook for Chapter 2

So far we have seen how large ($N \sim 10^{23}$) systems behave



Why does energy flow from hot to cold? Why not the other way?

Microscopic laws of motion are time reversible

(Newton's Laws, Maxwell's Equations, Schrödinger Equation etc..)

Why do thermodynamic processes happen one way and not the other?

Why is there an arrow of time?

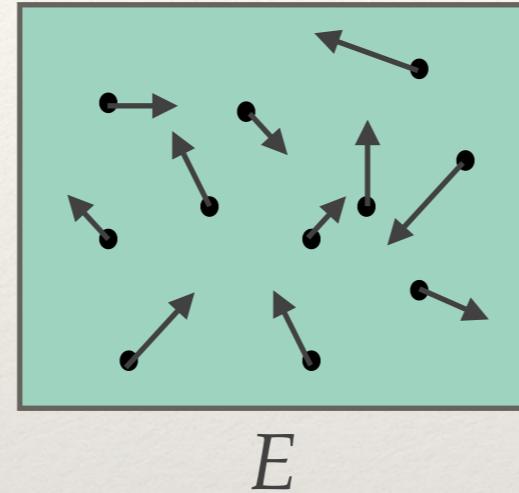
First Law: $\Delta E = Q + W$ interplay between work and heat

Can we convert heat entirely into work?

The answers lie within the Second Law

Outlook: entropy

How does energy of individual particles can be arranged such that $E_{\text{system}} = E$?



$$N \sim 10^{23}$$

$$E$$

There is A LOT of different ways to distribute energy to each particle such that $E_{\text{system}} = E$

The notion of *entropy* is the way to quantify this.

Let's begin with a simple example in combinatorics...

Two-state system

e.g. toss 3 coins: what are the possible outcomes ("states") ?

Ω	Penny	Nickel	Dime	
1	H	H	H	
3	H	H	T	 <i>macrostate</i> (e.g. two H one T)
	H	T	H	
	T	H	H	
3	H	T	T	 <i>microstate</i> (e.g. THH)
	T	H	T	
	T	T	H	
1	T	T	T	

- There are 4 macrostates, 8 microstates
- *Multiplicity (Ω)*: Number of microstates in a macrostate
- probability of macrostate n : $P(n) = \frac{\Omega(n)}{\sum_n \Omega(n)}$

Two-state system

e.g. toss 100 coins: what are the possible outcomes ("states") ?

- How many microstates:
- How many macrostates:

Two-state system

e.g. toss 100 coins: what are the possible outcomes ("states") ?

- How many microstates: 2^{100}
- How many macrostates: 100

If you were to bet on a macrostate which one would you pick?

Two-state system

e.g. toss 100 coins: what are the possible outcomes ("states") ?

- How many microstates: 2^{100}
- How many macrostates: 100

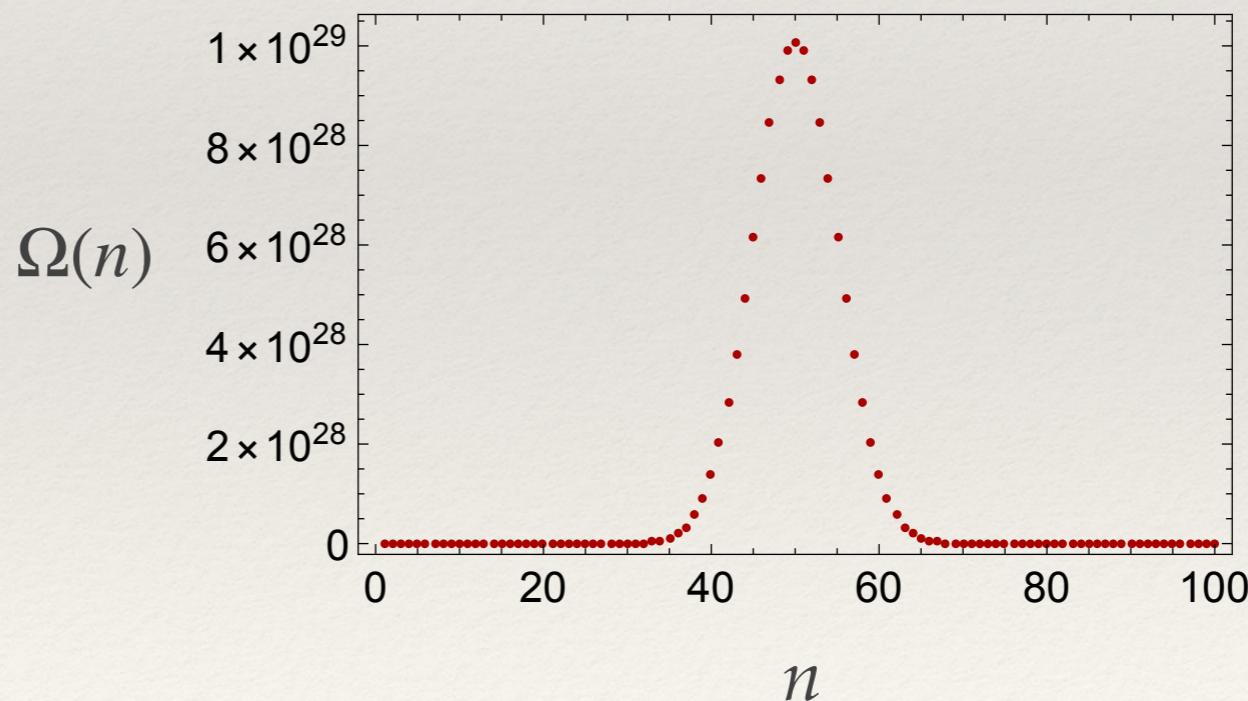
If you were to bet on a macrostate which one would you pick?

$$\Omega(\text{all H}) = 1$$

$$\Omega(\text{one T}) = 100$$

⋮

$$\Omega(n) = \frac{100!}{n!(100-n)!}$$



Two-state paramagnet

Lattice of spins:

- Each atom has a magnetic moment μ
- each lattice site is either *spin up* or *down* ('`H or T")
- *energy:* per site: $E_i = - \vec{B} \cdot \vec{s}_i$, total: $E_{system} = B(N_\downarrow - N_\uparrow)$



- number of up spins : N_\uparrow
 - number of down spins : N_\downarrow
- $N_\uparrow + N_\downarrow = N$: fixed

Multiplicity of macrostates: $\Omega(N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!}$

Einstein Solid

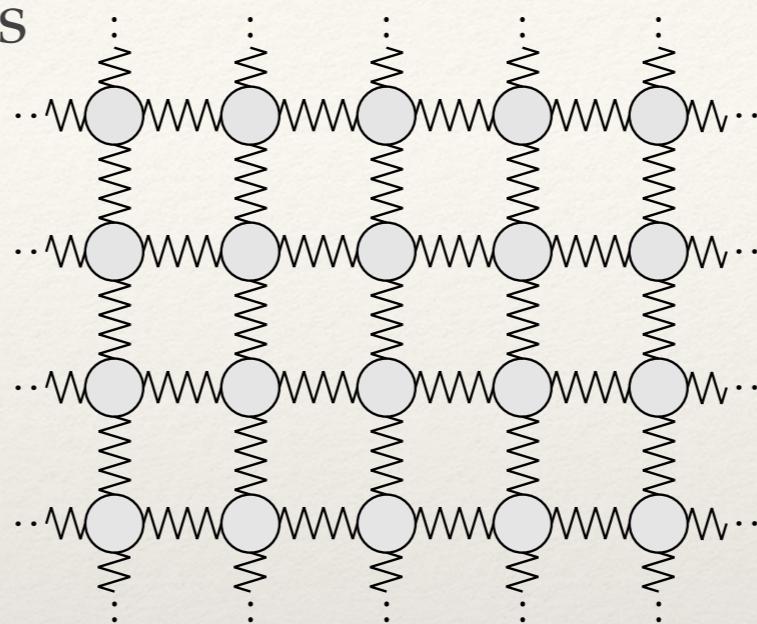
1 atom per site, each atom vibrates

Modeled by a quantum simple harmonic oscillator

$$E_{\text{site}} = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right)$$

constant

integers



Einstein solid:

N oscillators with integer energy levels

each atom = 3 oscillators

$$E_i \propto n$$

$$i \in \{1, \dots, N\}$$

3 x (# of atoms)

Einstein Solid

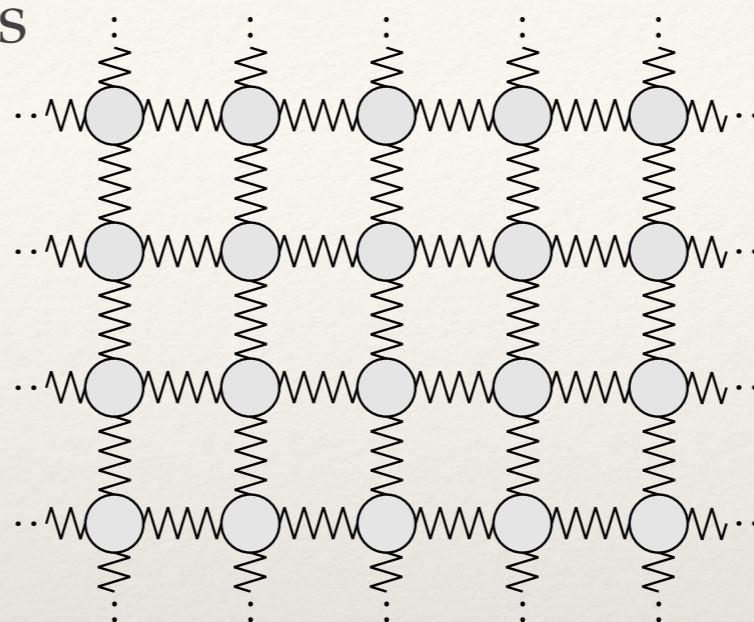
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constant

integers



Einstein solid:
 N oscillators with integer energy levels

$$E_i \propto n$$

$$i \in \{1, \dots, N\}$$

of atoms / 3

Microstates: Each microstate corresponds to a set of N integers

oscillator (i):	1	2	3	4	5	6	7	8	N
e.g. energy level (n):	5	12	7	124	39	4	42	234	E_N

Macrostates: Each macrostate corresponds to a single integer $q = \sum_{i=1}^N E_i$

Einstein Solid

e.g. three oscillators ($N=3$)

$$\Omega(0) = 1$$

Oscillator:	#1	#2	#3
$q=0$	0	0	0

$q=1$	1	0	0
	0	1	0
	0	0	1

Oscillator:	#1	#2	#3
Energy:	3	0	0

$$\Omega(1) = 3$$

$q=2$	2	0	0
	0	2	0
	0	0	2
	1	1	0
	1	0	1
	0	1	1

$$\Omega(2) = 6$$

Energy:	3	0	0
	0	3	0
	0	0	3
	2	1	0
	2	0	1
	1	2	0
	0	2	1
	1	0	2
	0	1	2
	1	1	1

$$\Omega(3) = 10$$

$q=3$

Any guesses for $\Omega(q)$?

Einstein Solid

N oscillators, multiplicity of macrostate q :

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}$$

Einstein Solid

N oscillators, multiplicity of macrostate q :

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In how many different ways one can write q as a sum of N integers?

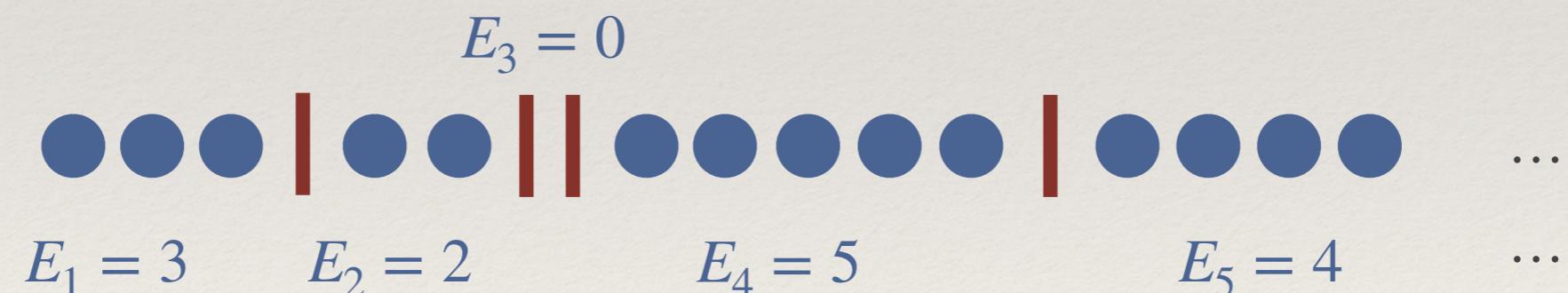
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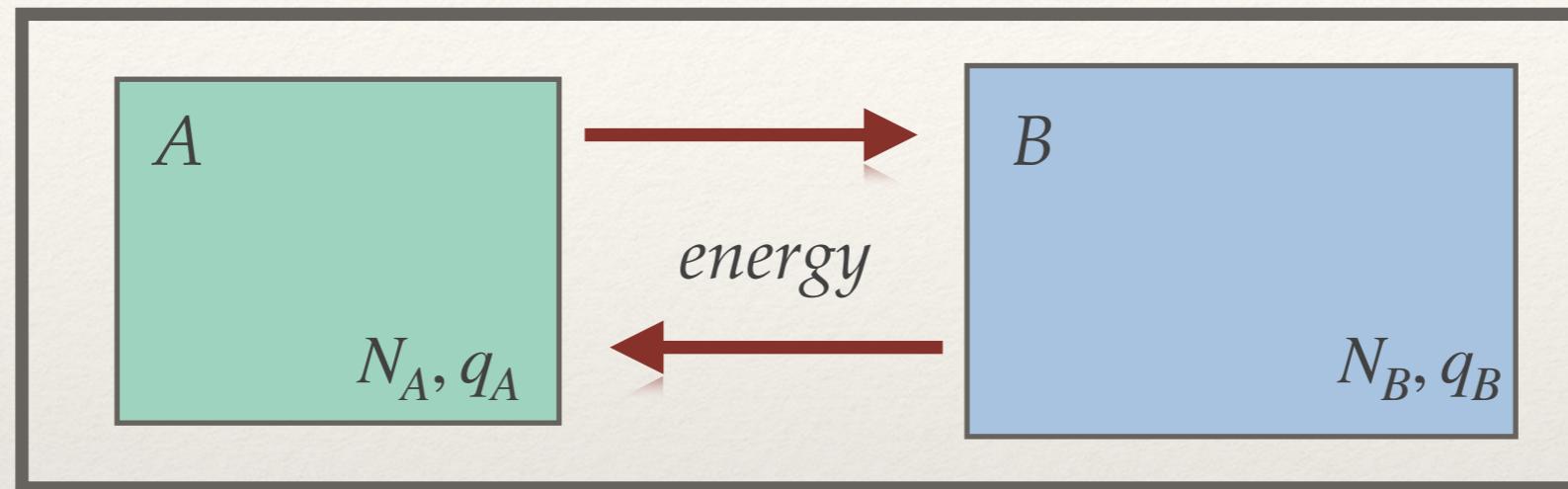
In how many different ways one can write q as a sum of N integers?

How many ways to partition q balls into N bins (separated by $N-1$ bars)



Interacting Systems

Two Einstein solids in thermal contact & isolated from the rest of the universe:



total energy is fixed: $q = q_A + q_B$: fixed

Energy exchange between A and B is much slower
compared to relaxation times of A and B

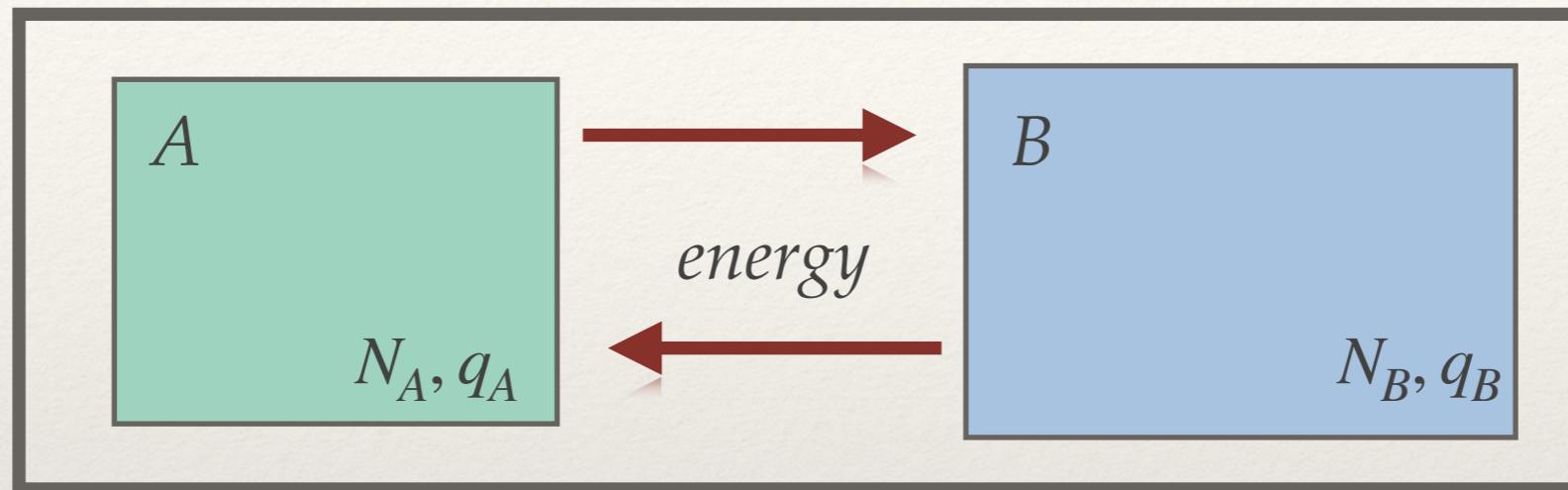
$$\tau_A, \tau_B \ll \tau_{A \leftrightarrow B}$$

Macrostates of A and B change slowly while A and B
remain in *local thermal equilibrium*

$$\Omega(q) = \Omega(q_A)\Omega(q_B)$$

Interacting Systems

Two Einstein solids in thermal contact & isolated from the rest of the universe:

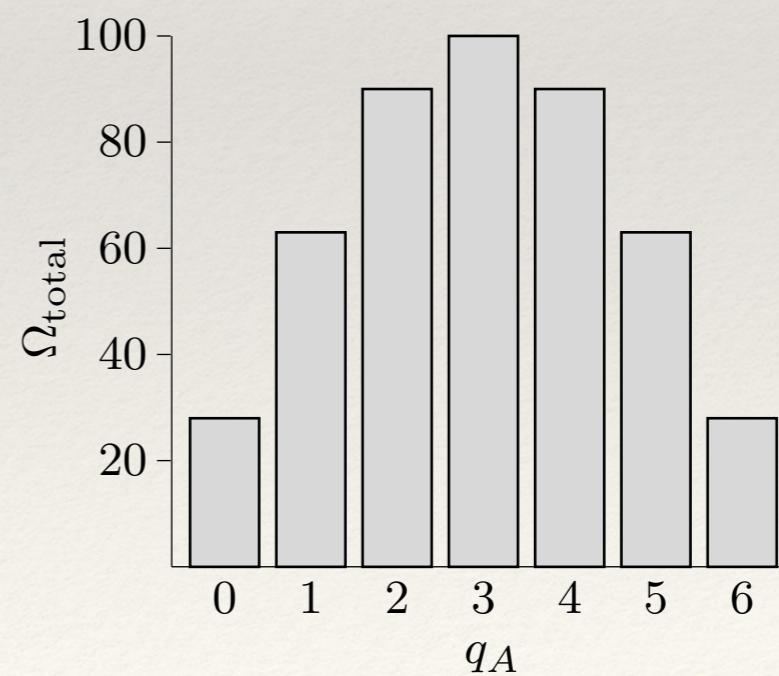


total energy is fixed: $q = q_A + q_B$: fixed

e.g.
 $N=3$
 $q=6$

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

$\frac{462}{462} = \binom{6+6-1}{6}$



Microcanonical ensemble

Fundamental assumption of statistical mechanics

For an isolated system in thermal equilibrium
all accessible microstates are equally probable

Remarks:

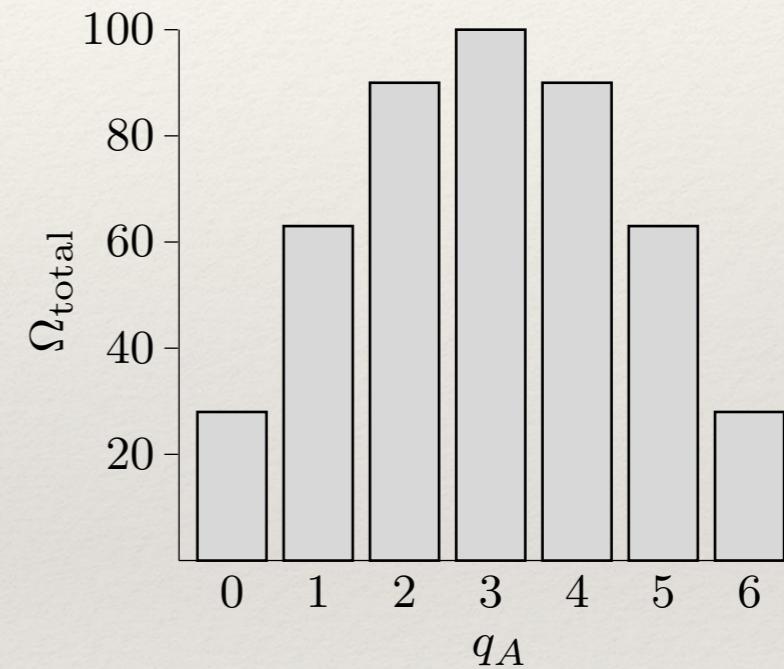
- Microscopic processes are time reversal* symmetric: state $X \leftrightarrow$ state Y
- Complete democracy among the microstates
- The system will eventually visit all the microstates uniformly (*ergodicity*)
- Practically only a tiny number of microstates will be visited
- They constitute a representative sample of the system
- Many ergodic systems also have a stronger property of *mixing*: two very similar initial microstates will eventually evolve into very different states

* actually CPT

Interacting Systems

All microstates are equally likely
Not the case for macrostates

	q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
e.g. $N=3$ $q=6$	0	1	6	28	28
	1	3	5	21	63
	2	6	4	15	90
	3	10	3	10	100
	4	15	2	6	90
	5	21	1	3	63
	6	28	0	1	28
					$\frac{462}{462} = \binom{6+6-1}{6}$



$$P(q_A = 3) = \frac{100}{462}$$

$$P(q_A = 6) = \frac{28}{462}$$

Interacting Systems

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Not the case for macrostates

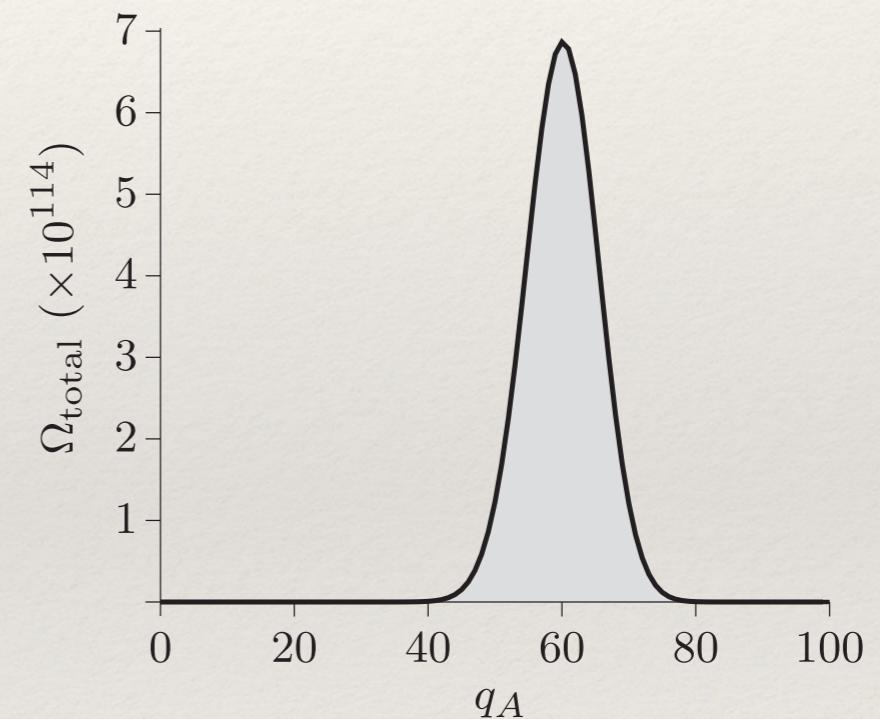
e.g.

$N_A = 300$

$N_B = 200$

$q=100$

q_A	Ω_A	q_B	Ω_B	Ω_{total}
0	1	100	2.8×10^{81}	2.8×10^{81}
1	300	99	9.3×10^{80}	2.8×10^{83}
2	45150	98	3.1×10^{80}	1.4×10^{85}
3	4545100	97	1.0×10^{80}	4.6×10^{86}
4	3.4×10^8	96	3.3×10^{79}	1.1×10^{88}
\vdots	\vdots	\vdots	\vdots	\vdots
59	2.2×10^{68}	41	3.1×10^{46}	6.7×10^{114}
60	1.3×10^{69}	40	5.3×10^{45}	6.9×10^{114}
61	7.7×10^{69}	39	8.8×10^{44}	6.8×10^{114}
\vdots	\vdots	\vdots	\vdots	\vdots
100	1.7×10^{96}	0	1	$\frac{1.7 \times 10^{96}}{9.3 \times 10^{115}}$



$$P(q_A < 10) \sim 10^{-20}$$

Interacting Systems

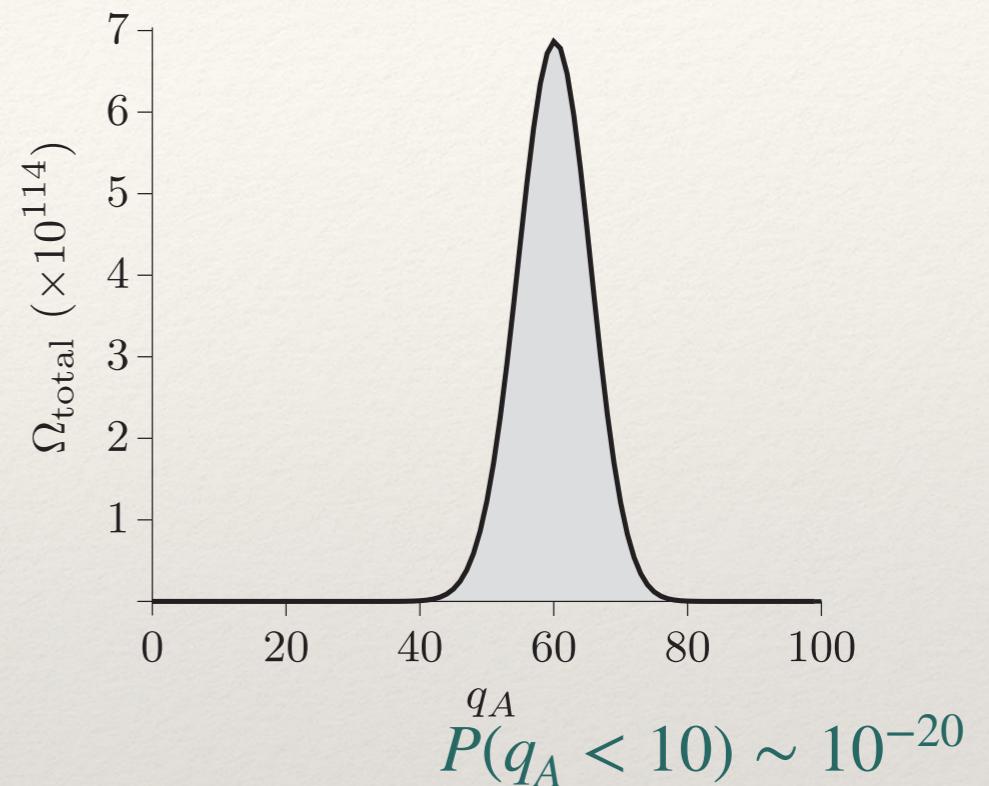
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Microstates with $q_A = 60$ have the highest probability of occurring.

Any initial condition away from that (say all the energy is in solid B i.e. $q_A = 0$) evolve into $q_A = 60$ with almost 100% probability.

Heat flow from B to A: macrostate with the highest multiplicity occurring with the highest probability

Second Law

The spontaneous flow of energy continues until the macrostate with highest multiplicity is reached.

Multiplicity of macrostates ("almost certainly") always increases.

Entropy $\sim \log(\text{multiplicity})$

Entropy ("almost certainly") always increases.

"The law that entropy always increases, holds, I think, the supreme position among the laws of Nature.

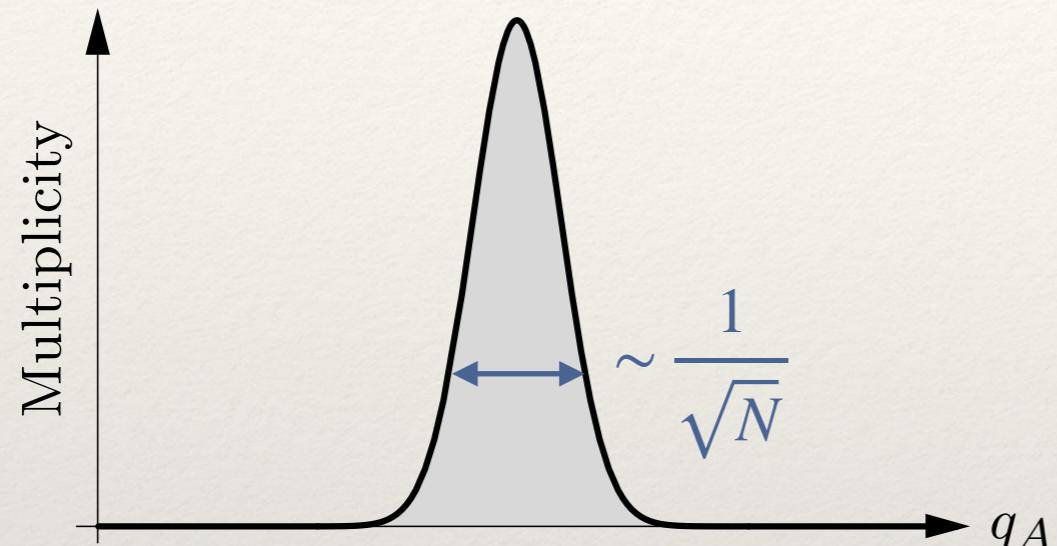
If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes.

But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation."

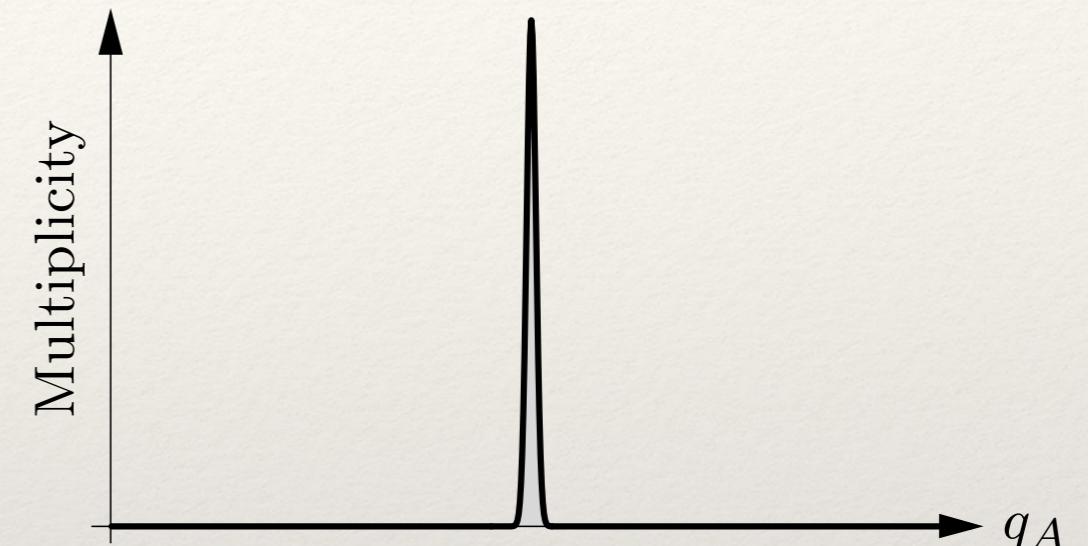
—Arthur Eddington

VERY LARGE NUMBERS

$N, q \approx \text{few hundred}$



$N, q \approx \text{few thousand}$



At large N fluctuations around the mean are suppressed

For $N \sim 10^{23}$ typical multiplicities are like $10^{10^{23}}$



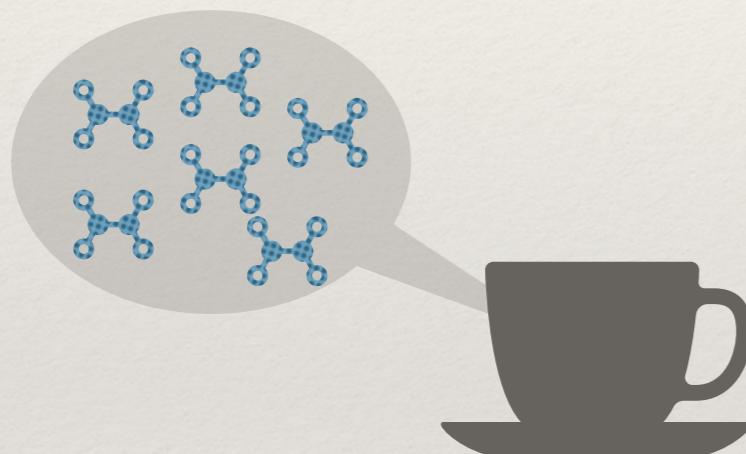
e.g. two-state paramagnet $\sim 2^{10^{23}}$

VERY LARGE NUMBERS



``Small numbers'' 2, 23, 42,...

Everyday units



``Large numbers'' $N \sim 10^{23}$ $10^{23} + 42 = 10^{23}$

Exponentiation of small numbers

Typically macroscopic quantities in microscopic units

``Very large numbers'' $10^{10^{23}}$ $10^{10^{23}} \times 10^{23} = 10^{10^{23}}$

$\Omega(1), \Omega(2), \Omega(3), \dots$

Exponentiation of large numbers

*Ridiculously large, don't count actual physical objects,
Combinatoric problems, count number of possible outcomes*



Manipulating Very Large Numbers

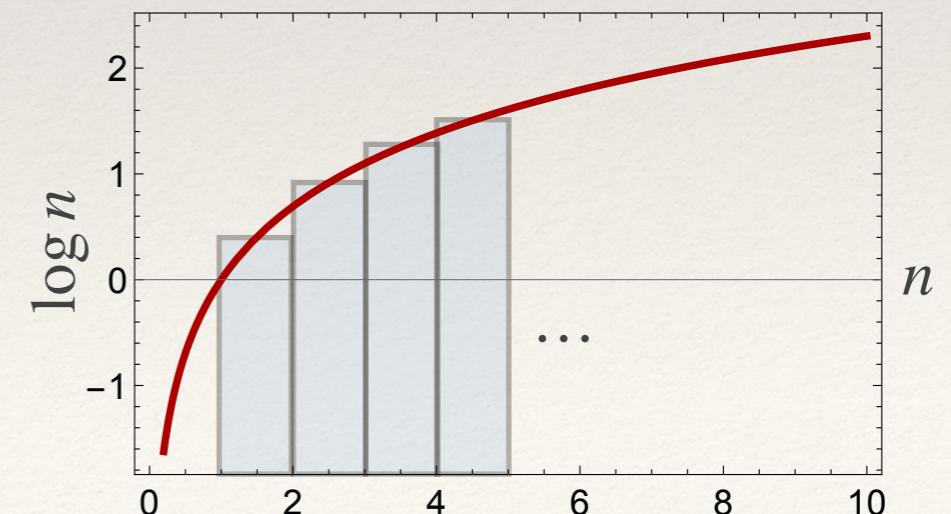


Stirling approximation $N! \sim N^N e^{-N} \sqrt{2\pi N}$ for $N \gg 1$

N factors of $\left(\frac{N}{e}\right)$ *correction*

For most cases $\log N! \sim N \log N - N$ *is good enough*

$$\log N! = \sum_{n=1}^N \log n \approx \int_{n=1}^N \log n \, dn = N \log N - N + 1$$

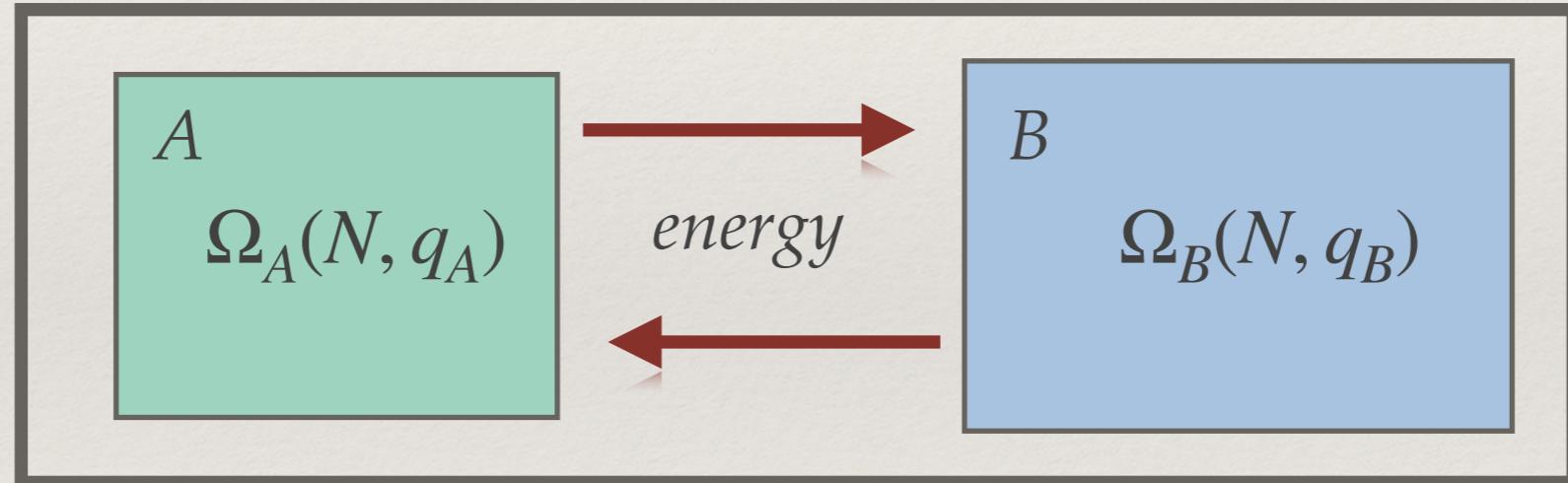


Einstein Solid Revisited

multiplicity of each solid $\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!} \approx \frac{(q + N)!}{q!N!}$

High temperature limit: $\log \Omega \approx N \log \left(\frac{q}{N} \right) + N$ or $\Omega \approx \left(\frac{eq}{N} \right)^N$

e.g.
 $N_A = N_B = N$



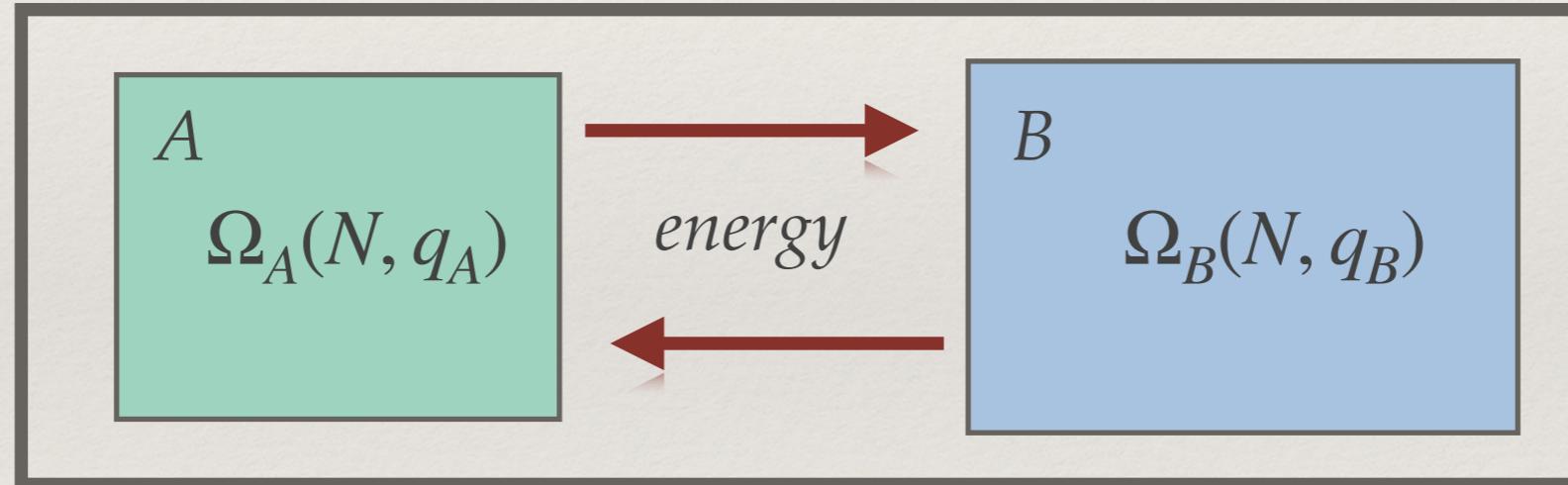
$$\Omega = \Omega_A \Omega_B \approx \left(\frac{e}{N} \right)^N (q_A q_B)^N$$

Einstein Solid Revisited

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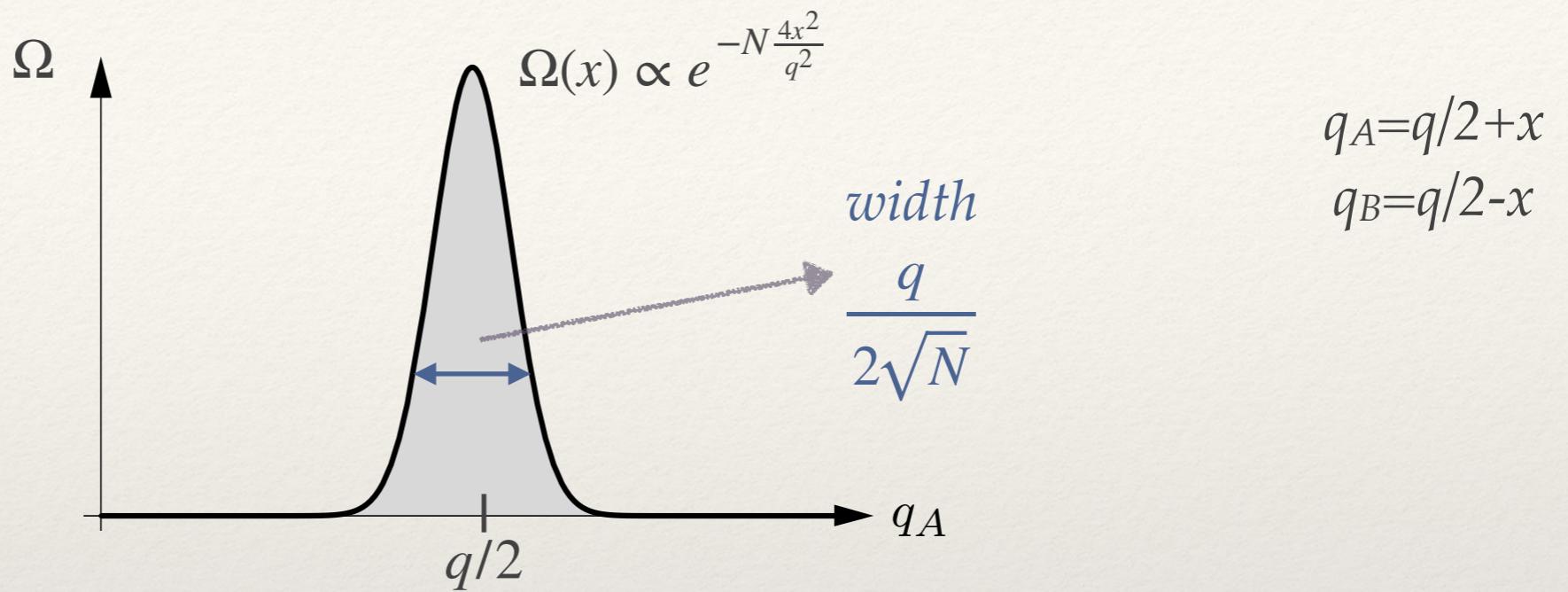


$$q_A = q/2 + x$$

$$q_B = q/2 - x$$

$$\Omega = \Omega_A \Omega_B \approx \left(\frac{e}{N} \right)^N (q_A q_B)^N = \left(\frac{e}{N} \right)^N e^{N \log(q^2/4 - x^2)} = \left(\frac{e}{N} \right)^N e^{N \log(q^2/4) + N \log(1 - 4x^2/q^2)} \approx \left(\frac{eq^2}{4N} \right)^N e^{-N \frac{4x^2}{q^2}}$$

Thermodynamic Limit



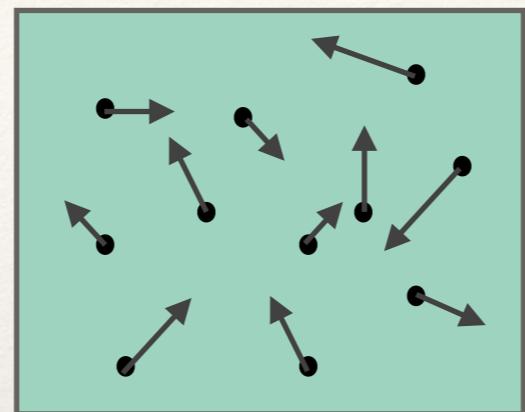
Extremely narrow: $\Omega(x \sim 10 \times q/2\sqrt{N}) \sim 10^{-44}$

Once the system settles in the most likely macrostate,
finding the system in any other state is practically impossible*

Formally the fluctuations vanish for an infinitely large system:
thermodynamic limit

*unless one has the patience to wait for much much much longer than the age of the universe

Back to the Ideal Gas

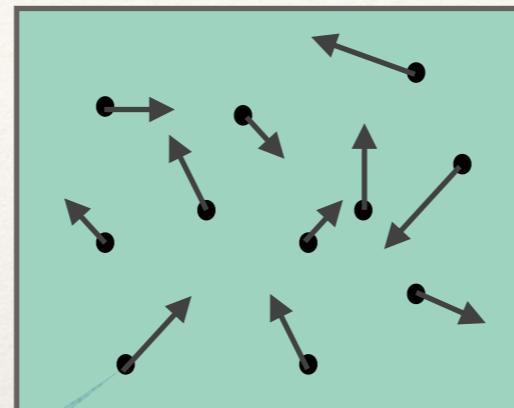


energy=U

$$N \sim 10^{23}$$

What are the microstates?

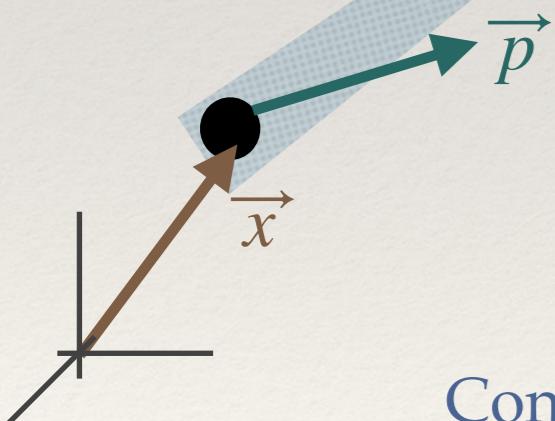
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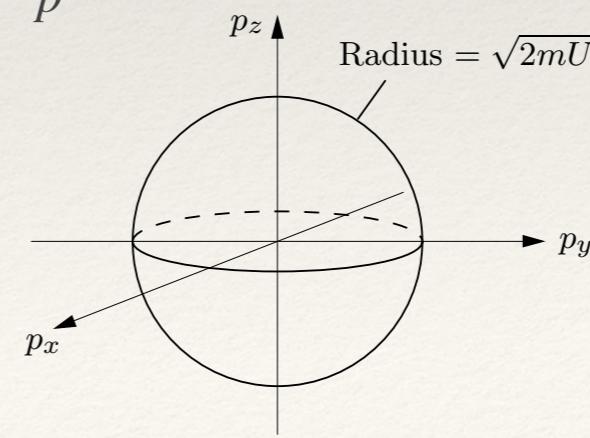
Each atom has a position and momentum *phase space*

dimension: $3+3=6$

$$\Omega_1 \propto V \times V_p$$

Conservation of energy:

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = U$$

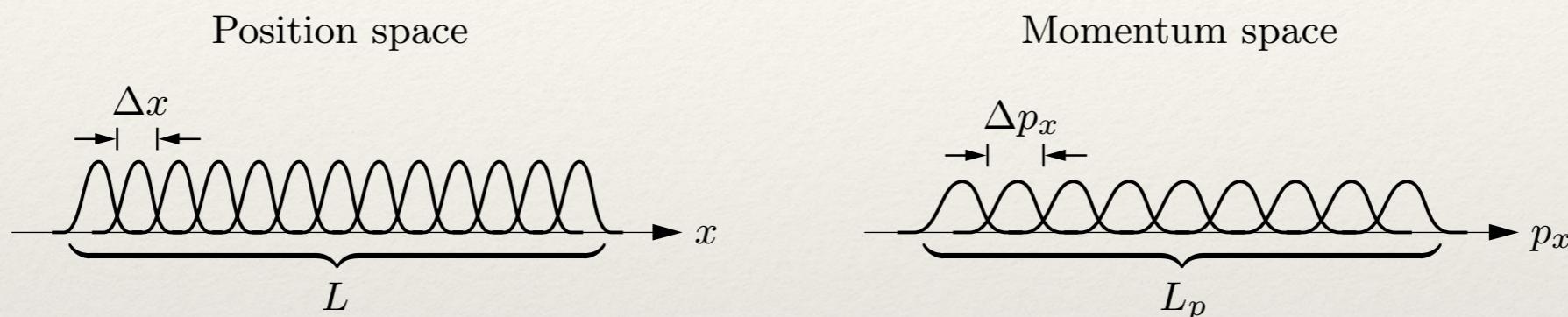


phase space
dimension: $3+2=5$

A Little bit of Quantum Mechanics

$$\Omega_1 \propto V \times V_p \quad \text{How do we actually count microstates?}$$

Microscopic states are described by QM wavefunctions

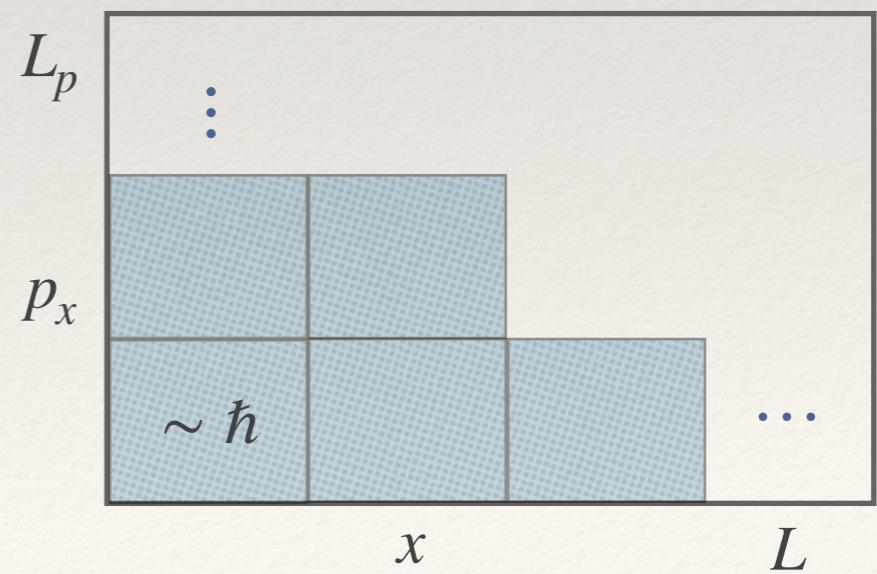


In a finite box there are *finitely many* wavefunctions

Uncertainty principle: $\Delta x \Delta p \sim \hbar$

wavefunctions: $\frac{L}{\Delta x} \times \frac{L_p}{\Delta p_x}$

$$\Omega_1 \propto \left(\frac{L}{\Delta x}\right)^3 \left(\frac{L_p}{\Delta p}\right)^3 \sim \frac{V V_p}{\hbar^3}$$



Ideal Gas

but we have not 1 but $\sim 10^{23}$ particles...

Let's take $N=2$

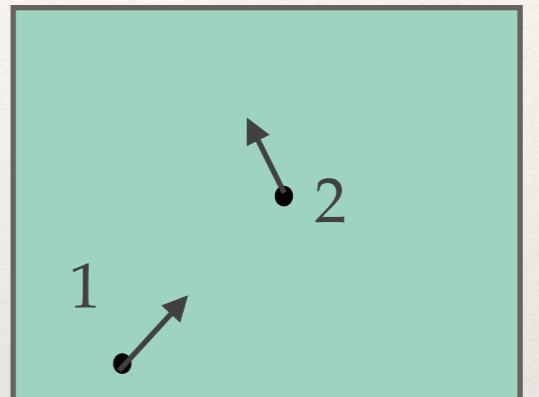
$$\frac{1}{2m}(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2) = U$$

area: $S_5 = \frac{8\pi^2}{3}R^5$

5d sphere

$$\text{radius: } R = \sqrt{2mU}$$

$$\Omega_2 \sim \frac{1}{2!} \frac{V^2}{(2\pi\hbar)^6} \times S_5$$



Ideal Gas

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Let's take $N=2$

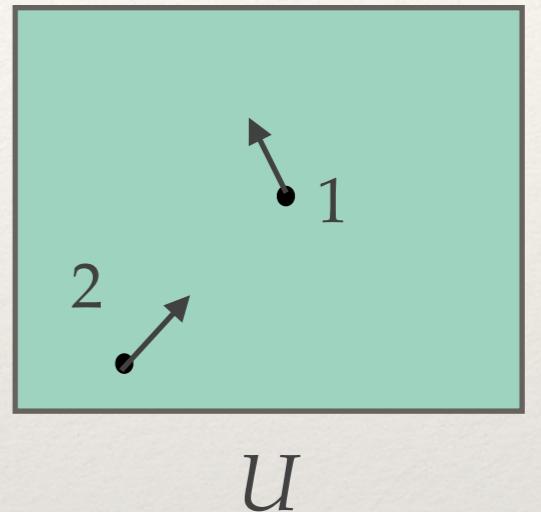
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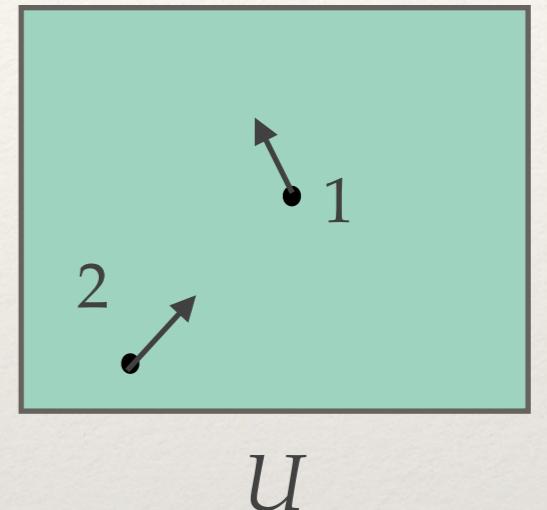
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5d sphere

$$\text{area: } S_5 = \frac{8\pi^2}{3} R^5$$

$$\text{radius: } R = \sqrt{2mU}$$

$$\Omega_2 \sim \frac{1}{2!} \frac{V^2}{(2\pi\hbar)^6} \times S_5$$



N identical particles

$$\Omega_N = \frac{1}{N!} \frac{V^N}{(2\pi\hbar)^{3N}} \times S_{3N-1} = \frac{1}{N!} \frac{V^N}{(2\pi\hbar)^{3N}} \times \frac{2\pi^{\frac{3N}{2}}}{(3N/2 - 1)!} (\sqrt{2mU})^{3N-1}$$

area of d-sphere: $S_{d-1} = \frac{2\pi^{\frac{d}{2}} R^{d-1}}{(d/2 - 1)!}$

Ideal Gas

but we have not 1 but $\sim 10^{23}$ particles...

Let's take $N=2$

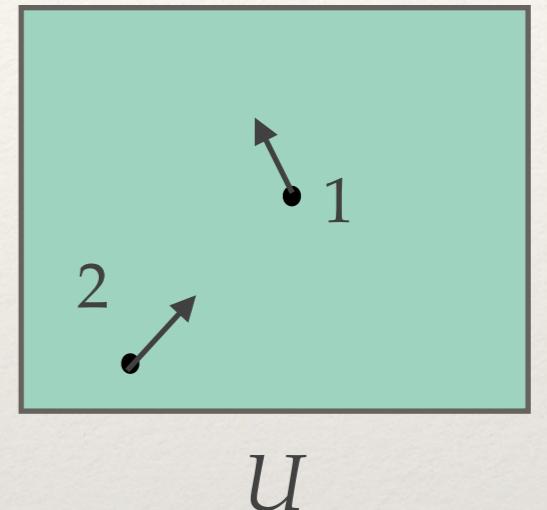
$$\frac{1}{2m}(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2) = U$$

5d sphere

$$\text{area: } S_5 = \frac{8\pi^2}{3} R^5$$

$$\text{radius: } R = \sqrt{2mU}$$

$$\Omega_2 \sim \frac{1}{2!} \frac{V^2}{(2\pi\hbar)^6} \times S_5$$



N identical particles

$$\Omega_N = \frac{1}{N!} \frac{V^N}{(2\pi\hbar)^{3N}} \times S_{3N-1} \approx \frac{1}{N!} \frac{V^N}{(2\pi\hbar)^{3N}} \times \frac{\pi^{\frac{3N}{2}}}{(3N/2)!} (\sqrt{2mU})^{3N}$$

area of d-sphere: $S_{d-1} = \frac{2\pi^{\frac{d}{2}} R^{d-1}}{(d/2 - 1)!}$

Ideal Gas

but we have not 1 but $\sim 10^{23}$ particles...

Let's take $N=2$

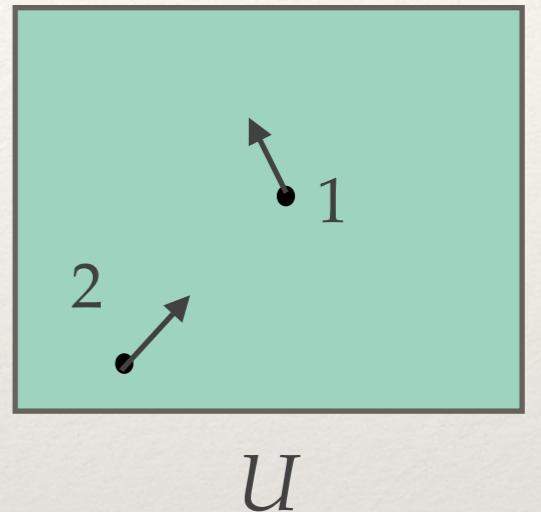
$$\frac{1}{2m}(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2) = U$$

area: $S_5 = \frac{8\pi^2}{3}R^5$

5d sphere

$$\text{radius: } R = \sqrt{2mU}$$

$$\Omega_2 \sim \frac{1}{2!} \frac{V^2}{(2\pi\hbar)^6} \times S_5$$



N identical particles

$$\Omega_N(V, U) = f(N) V^N U^{\frac{3N}{2}}$$

Ideal Gas

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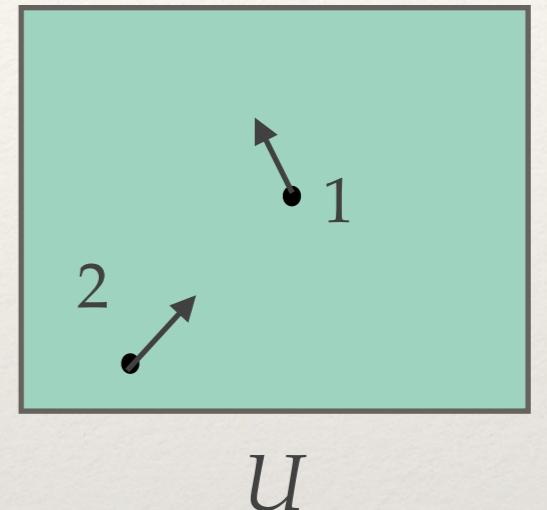
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N identical particles

$$\Omega_N(V, U) = f(N)V^N U^{\frac{3N}{2}}$$



$$\frac{3N}{2} = \frac{N_{dof}}{2}$$

true for any system with quadratic degrees of freedom

Ideal Gas

but we have not 1 but $\sim 10^{23}$ particles...

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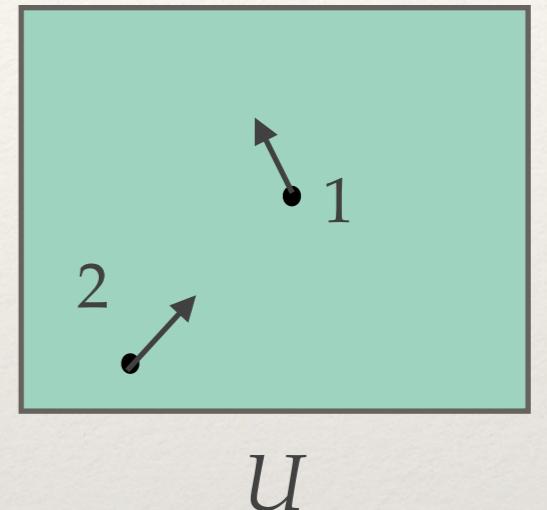
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N identical particles

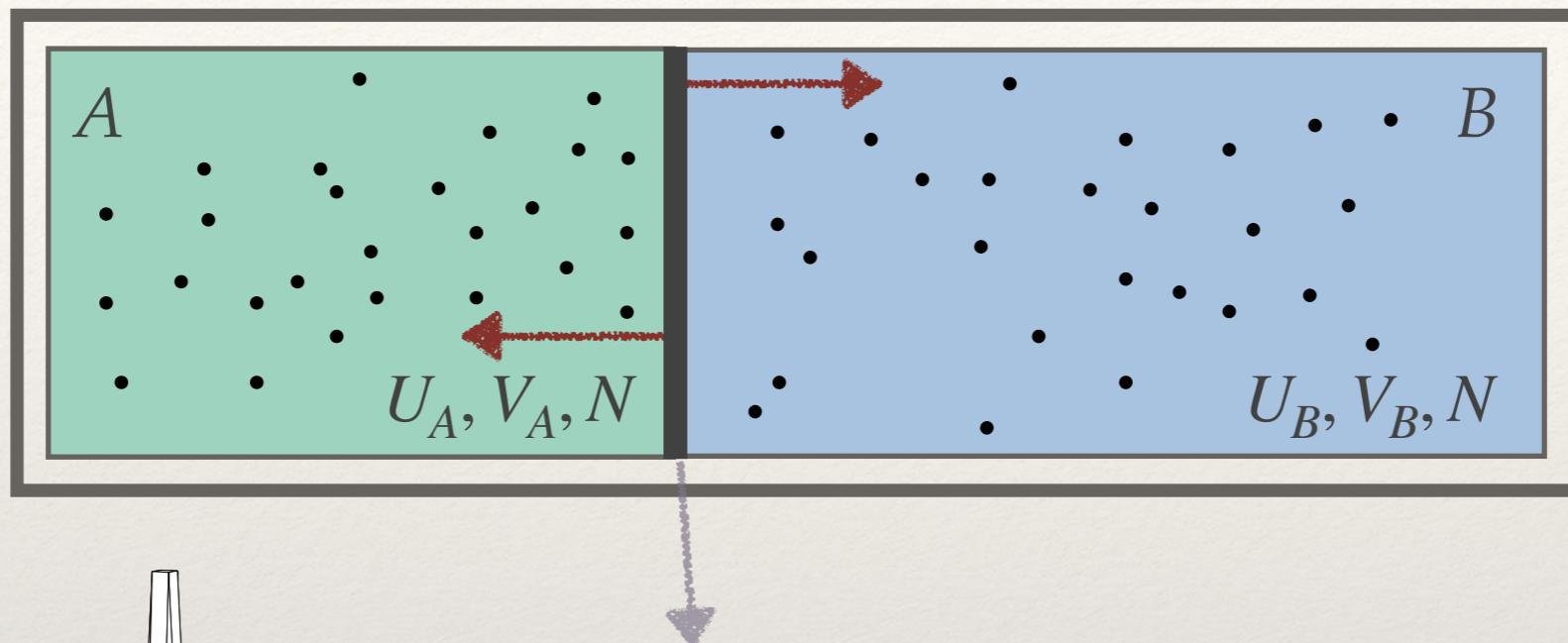
$$\Omega_N(V, U) = f(N)V^N U^{\frac{3N}{2}}$$



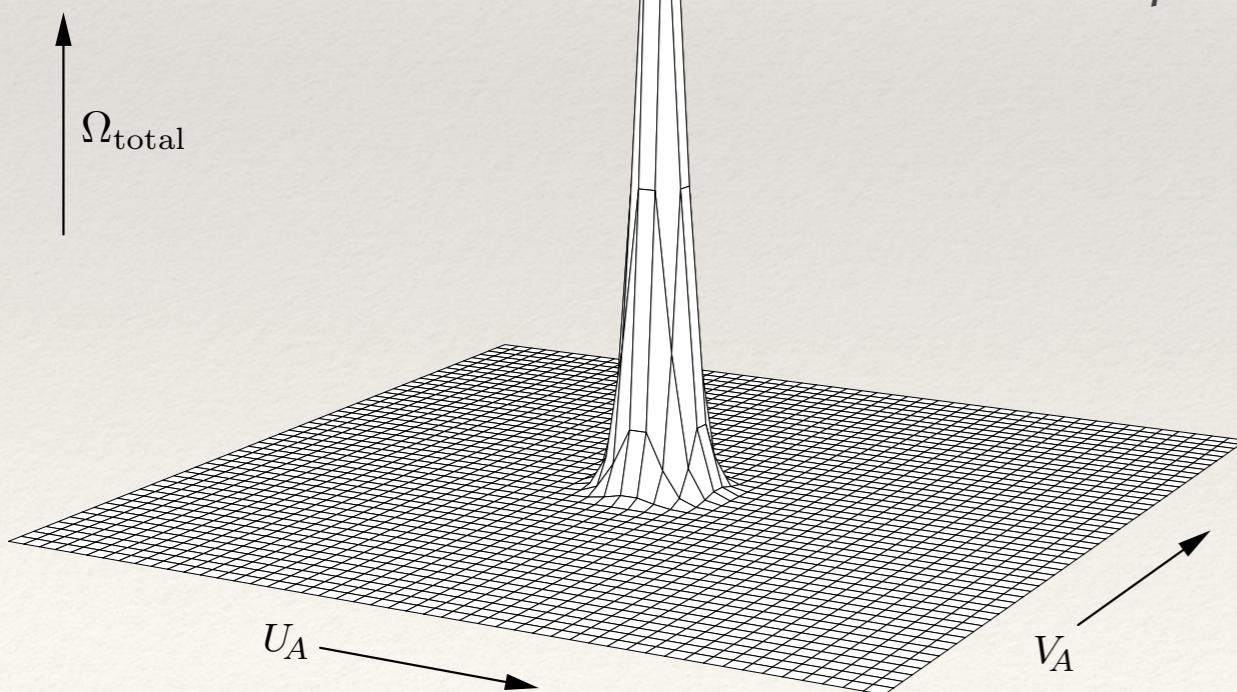
$$\frac{3N}{2} = \frac{N_{dof}}{2}$$

true for any system with quadratic degrees of freedom

Interacting Ideal Gases



movable partition: gases exchange, volume and energy

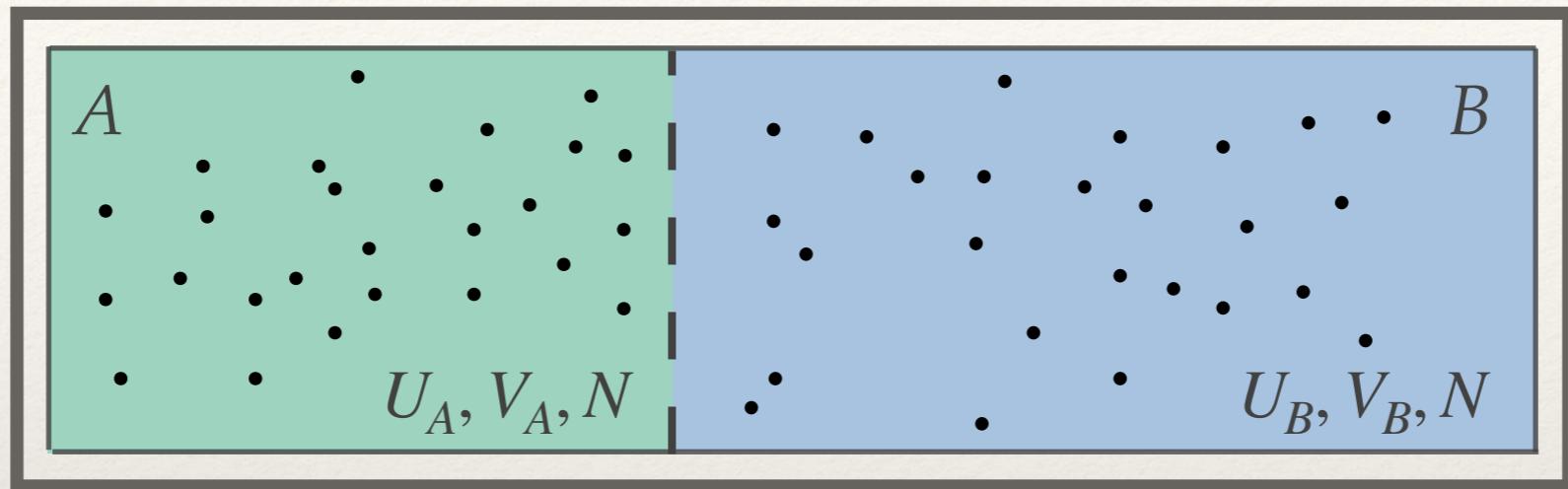


$$\Omega = \Omega_A \Omega_B = f^2(N) (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$$

width in V : $\frac{V_{\text{tot}}}{\sqrt{N/2}}$

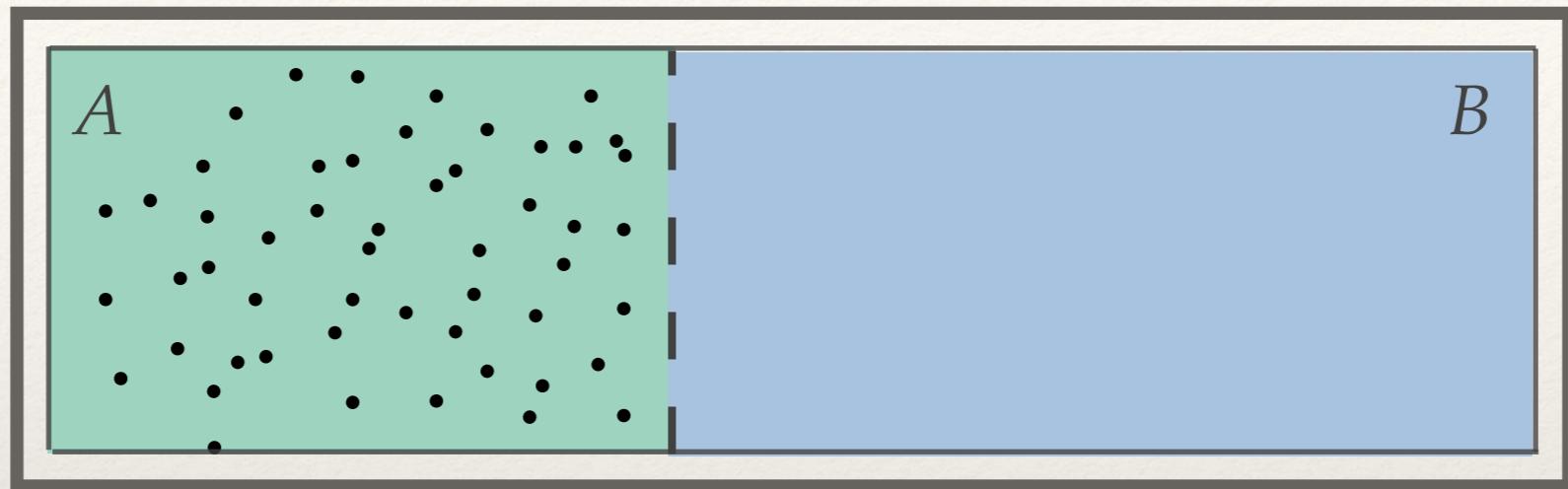
width in U : $\frac{U_{\text{tot}}}{\sqrt{3N/2}}$

Interacting Ideal Gases



Particles can move freely between containers

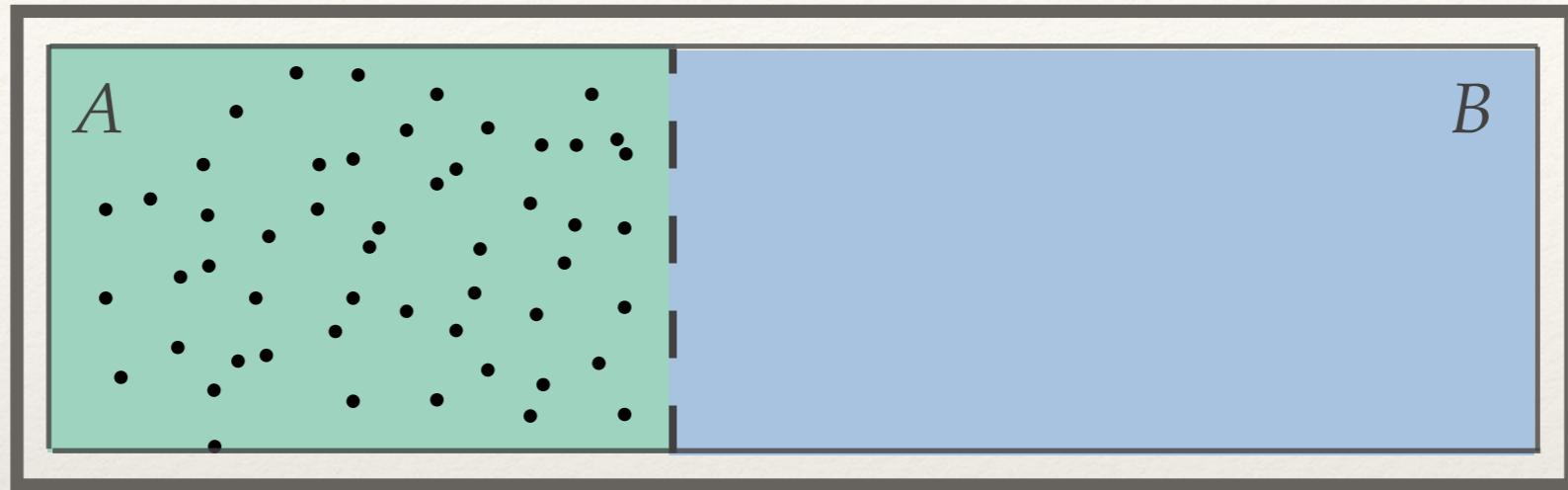
Interacting Ideal Gases



Particles can move freely between containers

What is the likelihood of this arrangement?

Interacting Ideal Gases



Particles can move freely between containers

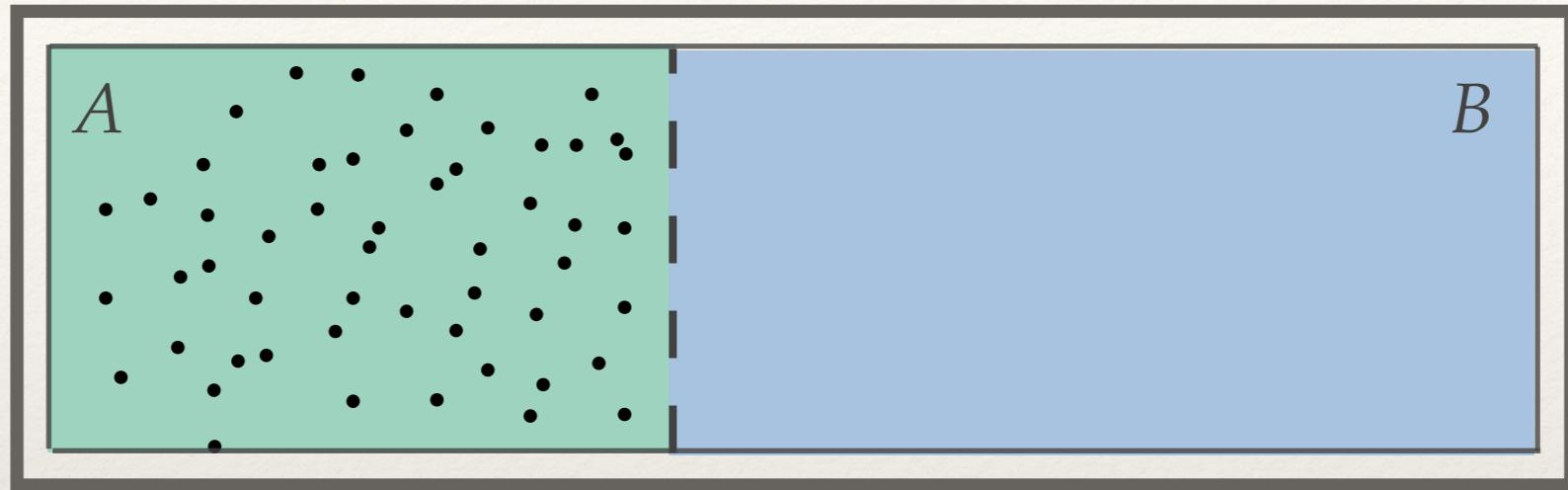
What is the likelihood of this arrangement?

$$\Omega(V) \propto V^N \rightarrow \Omega(V/2) \propto 2^{-N} \times V^N$$

For $N=100$, and a measurement rate of 10^{14} Hz it would take $\sim 10^8$ years
to observe 1 such configuration

Age of the universe: $H_0^{-1} \sim 10^{10}$ years

Interacting Ideal Gases



Particles can move freely between containers

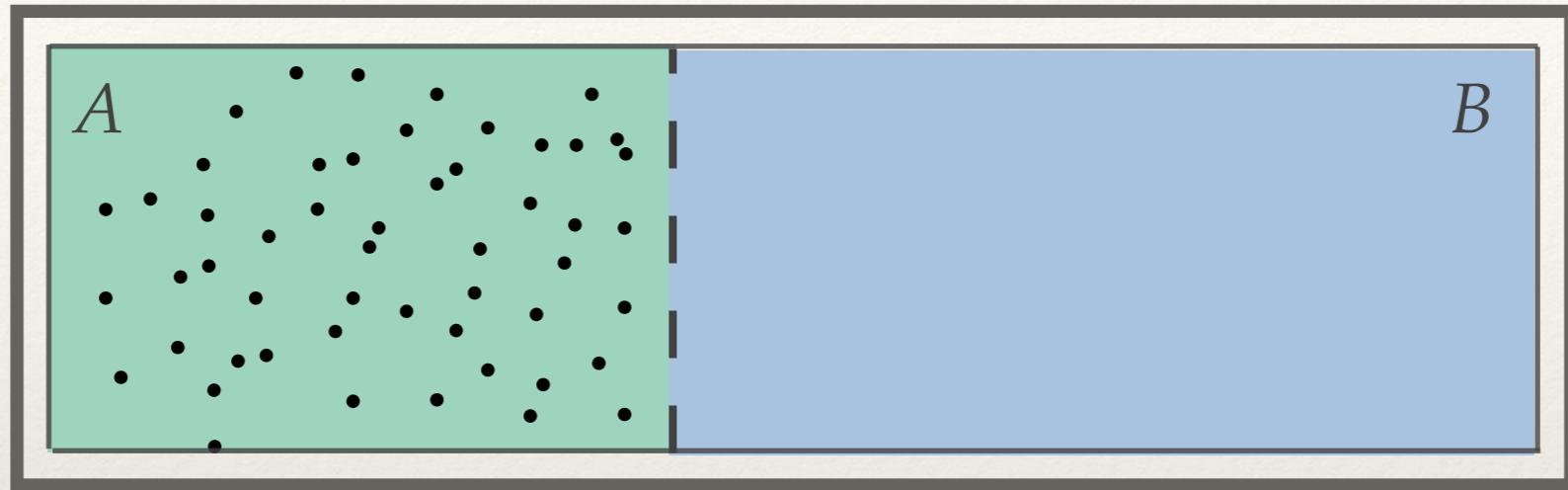
What is the likelihood of this arrangement?

$$\Omega(V) \propto V^N \rightarrow \Omega(V/2) \propto 2^{-N} \times V^N$$

For $N=110$, and a measurement rate of 10^{14} Hz it would take $\sim 10^{14}$ years
to observe 1 such configuration

Age of the universe: $H_0^{-1} \sim 10^{10}$ years

Interacting Ideal Gases



Particles can move freely between containers

What is the likelihood of this arrangement?

$$\Omega(V) \propto V^N \rightarrow \Omega(V/2) \propto 2^{-N} \times V^N$$

For $N=1000$, and a measurement rate of 10^{14} Hz it would take $\sim 10^{279}$ years
to observe 1 such configuration

Age of the universe: $H_0^{-1} \sim 10^{10}$ years

Entropy

A system in thermodynamic equilibrium is found in the macrostate that has the highest multiplicity.



Boltzmann's grave in Vienna

$$S = k \log \Omega$$

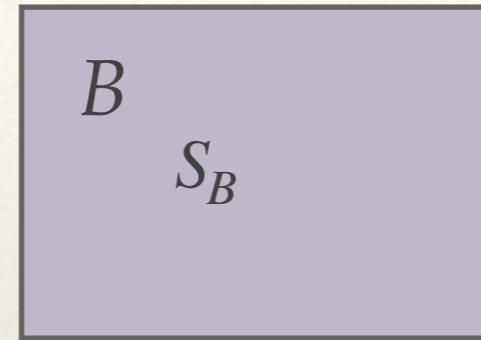
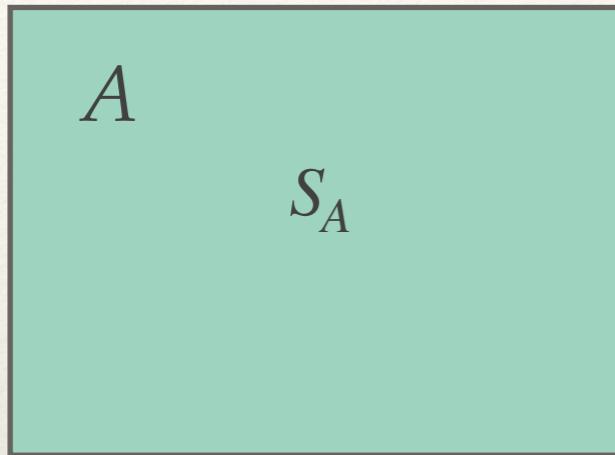
[Boltzmann, 1872]

Boltzmann constant, [S]=J/K

Second Law: ``Entropy tends to increase''

Thermodynamic equilibrium: state with highest entropy

Entropy



Un-interacting, composite system

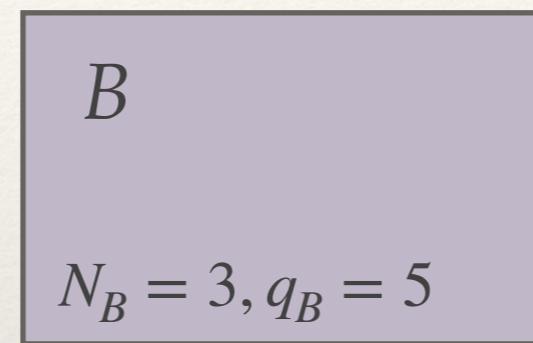
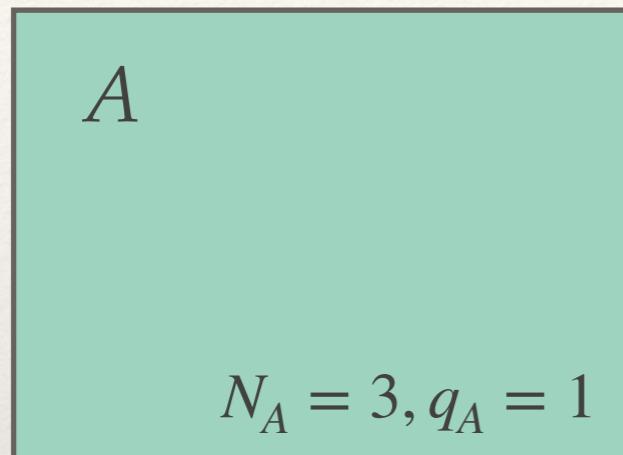
$$S_{tot} = \log(\Omega_A \Omega_B) = S_A + S_B$$

When they are in thermal contact, the macrostates of each sub-system will reorganize until the system reaches thermal equilibrium.

the new entropy: $S_{fin} \geq S_{A,in} + S_{B,in}$

Entropy

e.g. Einstein solid

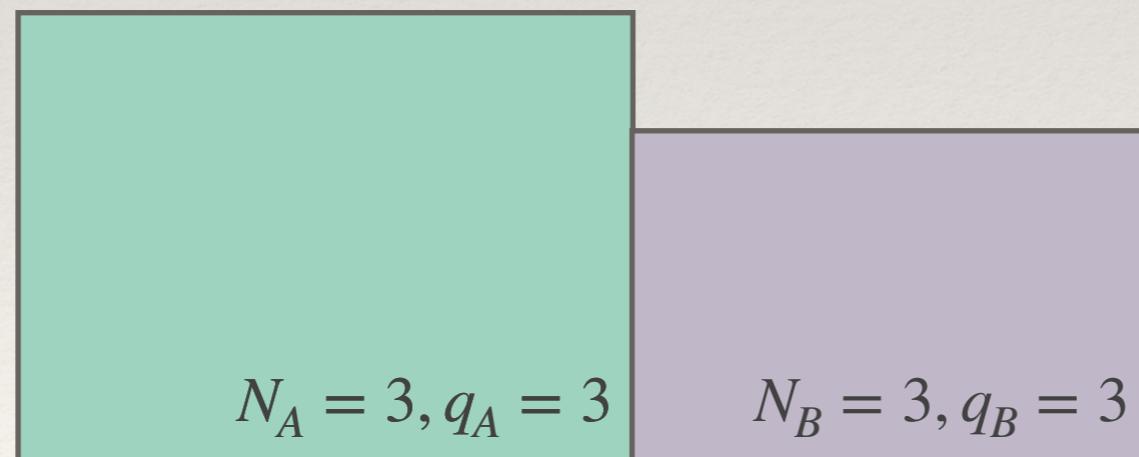


$$S_A = k \log 3$$

$$S_B = k \log 21$$

$$S_{in} = k \log 61$$

After reaching equilibrium:



$$S_A = k \log 10$$

$$S_B = k \log 10$$

$$S_{fin} = k \log 100 > S_{in}$$

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28
				$\frac{462}{462} = \binom{6+6-1}{6}$

Entropy of Ideal Gas

$$\Omega_N(U, V) = \frac{V^N \pi^{\frac{3N}{2}} (2mU)^{3N/2}}{N! (3N/2)! (2\pi\hbar)^{3N}}$$

$$S = Nk \left[\log \left(\frac{V}{N} \left(\frac{mU}{3N\pi\hbar^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

Sackur -Tetrode equation

Entropy of Ideal Gas

$$\Omega_N(U, V) = \frac{1}{N!} \frac{V^N \pi^{\frac{3N}{2}} (2mU)^{3N/2}}{(3N/2)! (2\pi\hbar)^{3N}}$$

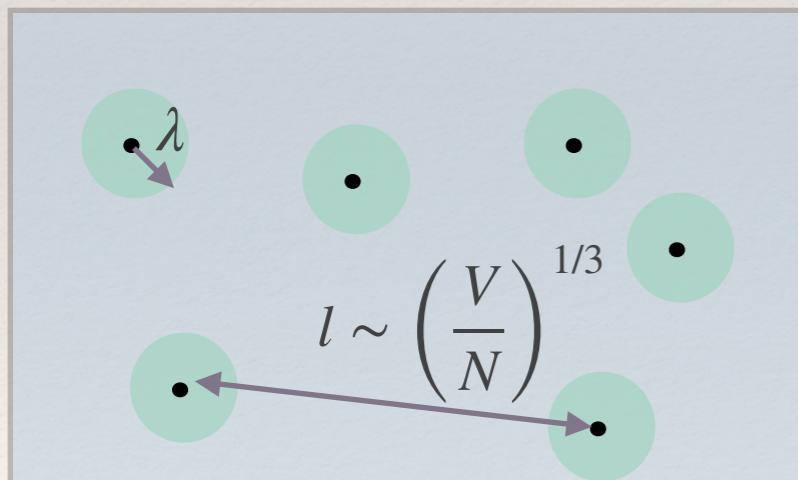
$$S = Nk \left[\log \left(\frac{V}{N\lambda^3} \right) + \frac{5}{2} \right]$$

Recall: $U = \frac{3}{2} N k T$

$$\left(\frac{mU}{3N\pi\hbar^2} \right)^{1/2} = \left(\frac{mkT}{2\pi\hbar^2} \right)^{1/2} = \frac{1}{\lambda}$$

Sackur -Tetrode equation

thermal de Broglie wavelength



V

*indistinguishable particles
``Gibbs Paradox''*

$$\lambda \ll l = (V/N)^{1/3} \rightarrow \text{interparticle distance (ideal gas)}$$

Number of configurations: $C = \frac{K!}{N!(K-N)!}$

number of available slots for each particle

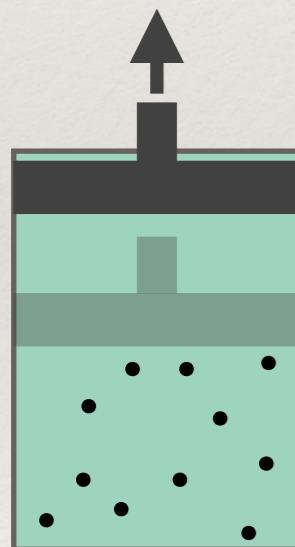
$$S = k \log C \sim kN \log(K/N) = kN \log(V/(N\lambda^3))$$

Entropy of Ideal Gas

e.g. 1 mole of helium at room temp and 1 atm:

$$U_{\text{thermal}} = \frac{3}{2}nRT = 3700\text{J}$$
$$S = 126\text{J/K}$$

Entropy *differences* are measurable classically
(via heat capacity, next chapter...)



e.g. isothermal expansion: N, U remains fixed

$$\Delta S = S_f - S_i = Nk \log \frac{V_f}{V_i}$$

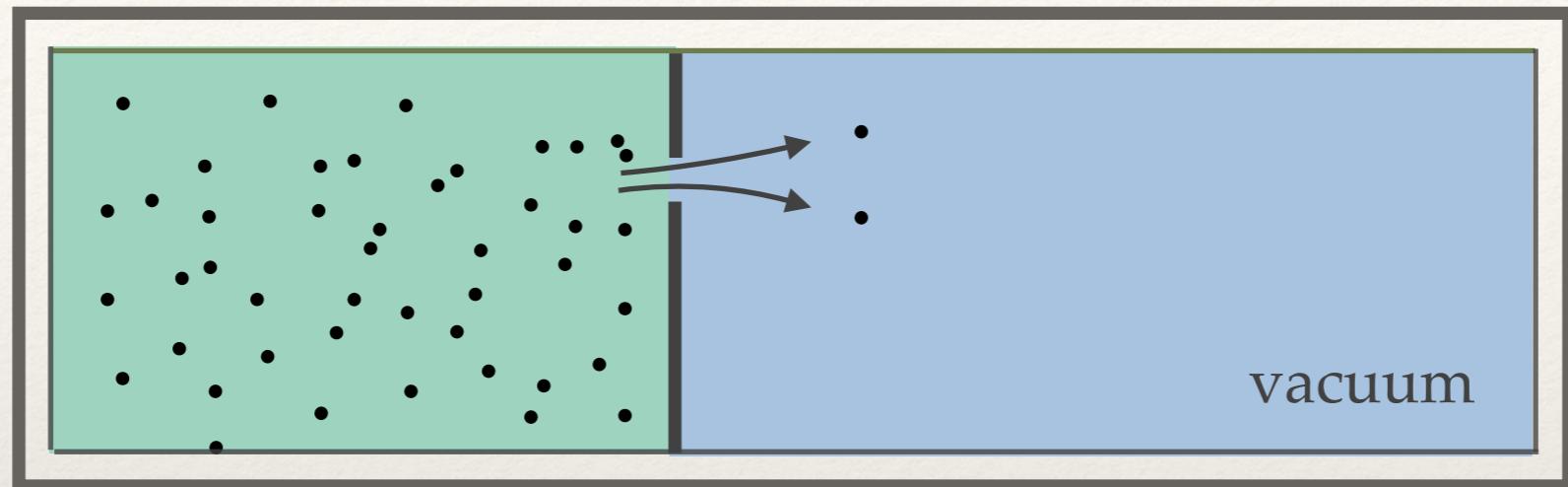
Recall: $\Delta U = Q + \Delta W = 0$

work to push the piston



Heat input from outside : increases entropy (next chapter)

Free Expansion



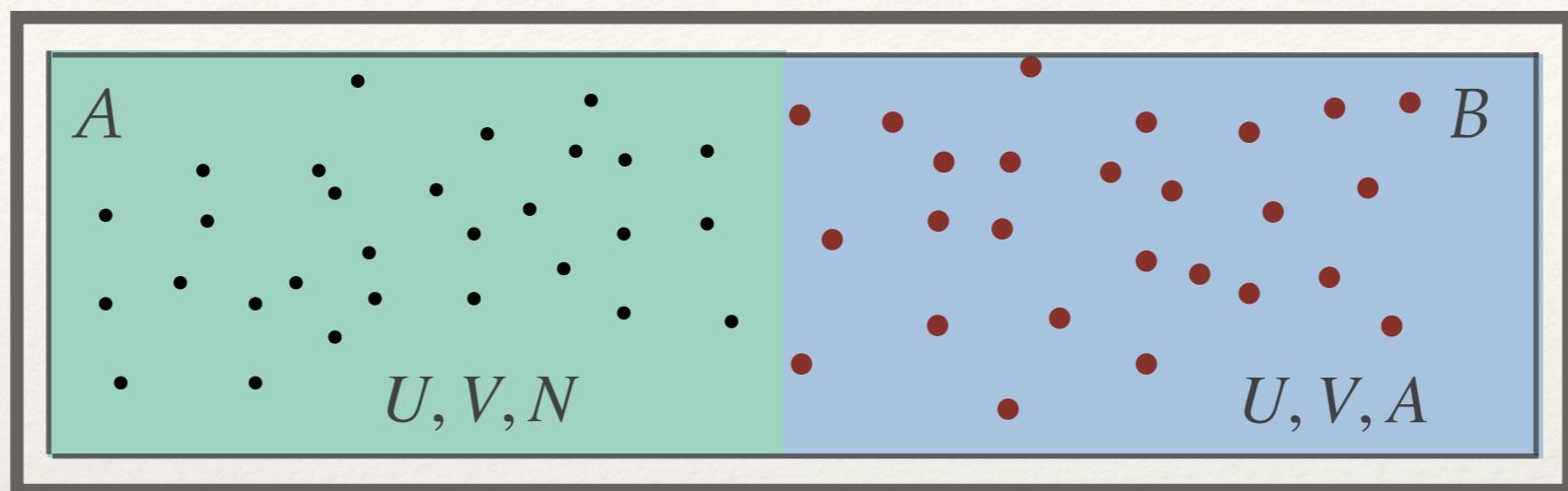
$$\Delta U = 0, \quad Q = 0, \quad \Delta W = 0$$

[Joule, 1845]

$$\Delta S = S_f - S_i = Nk \log \frac{V_f}{V_i}$$

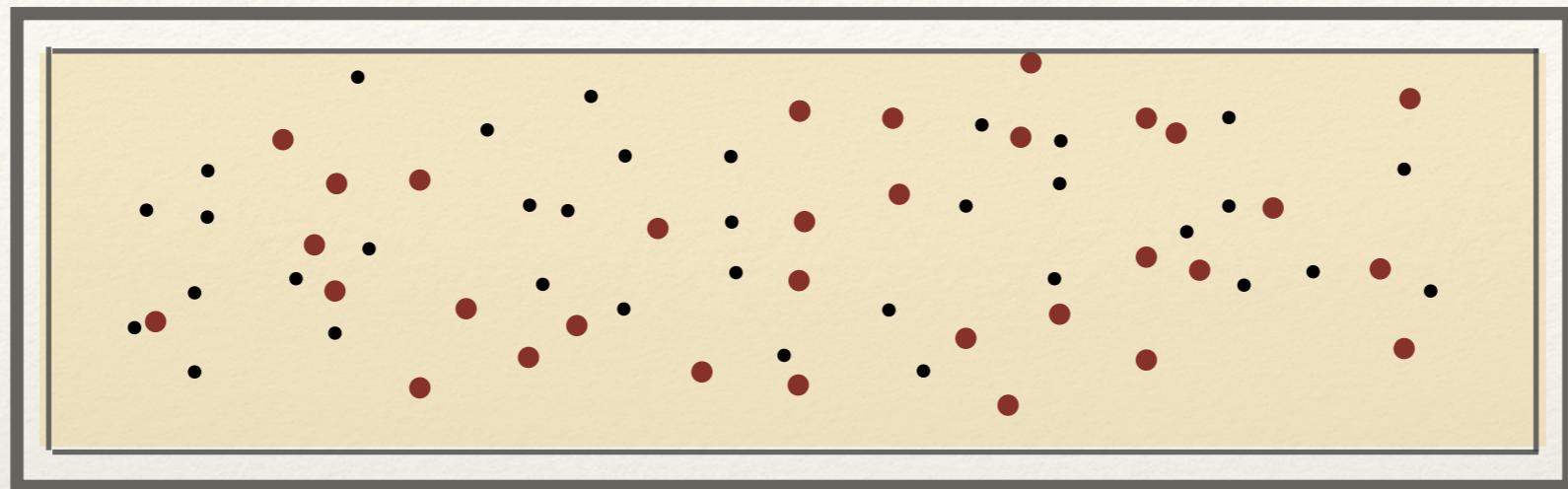
No heat input, but entropy still increased!

Mixing



A, B : different gases, same number same energy

Mixing



A, B : different gases, same number same energy

After mixing $\Delta S_A = Nk \log 2$ $\Delta S_B = Nk \log 2$

Entropy of mixing: $\Delta S = \Delta S_A + \Delta S_B = 2Nk \log 2$

$$S = Nk \left[\log \left(\frac{V}{N} \left(\frac{mU}{3N\pi\hbar^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

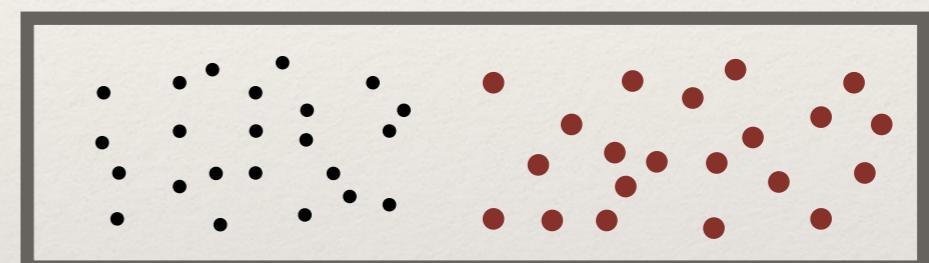
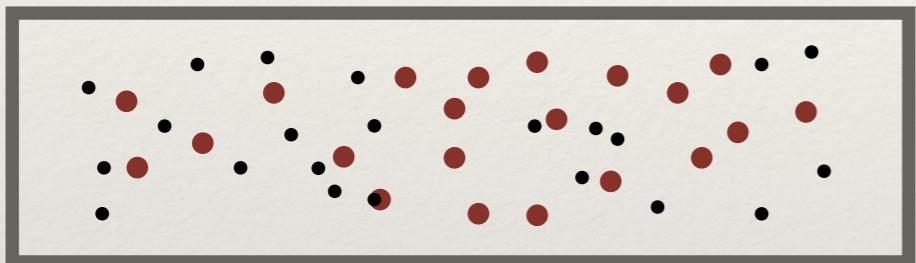
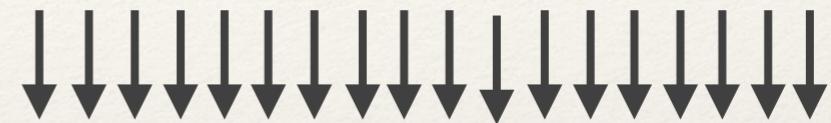
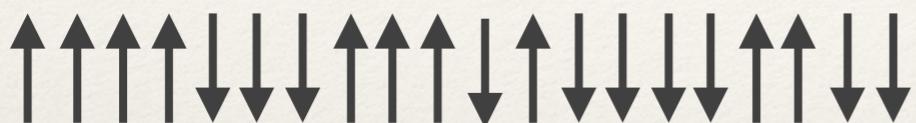
- add gas A first and then gas B $S_{A+B} = S_A + S_B = 2S$
- add gas A first and then gas A again
 $S_{A+A} = S(N \rightarrow 2N) \neq 2S$

$$S_{A+B} - S_{A+A} = 2Nk \log 2 \quad (\text{entropy of mixing})$$

Entropy and Disorder

Entropy is often understood as a measure of *disorder*

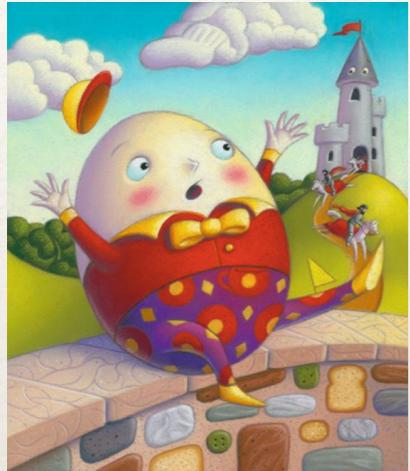
This depends on what is seen as ``disordered''



A disordered system has more possible arrangements

Is tidying up a messy room or ordering a shuffled deck of cards against the Second Law?

Reversible and Irreversible Processes



No process which increases the total entropy of the universe can be reversed.

This is true even if underlying microscopic processes can be reversed!

Emergent arrow of time!

e.g. heat transfer from hot to cold objects, sudden expansion of a gas, mixing, diffusion,...

e.g. reversible process: Quasi-static, slow expansion of a gas

QM energy levels shift very slowly but the particles do not jump from one state to the other.

Gibbs Entropy

Microcanonical ensemble: all microstates are equally probable

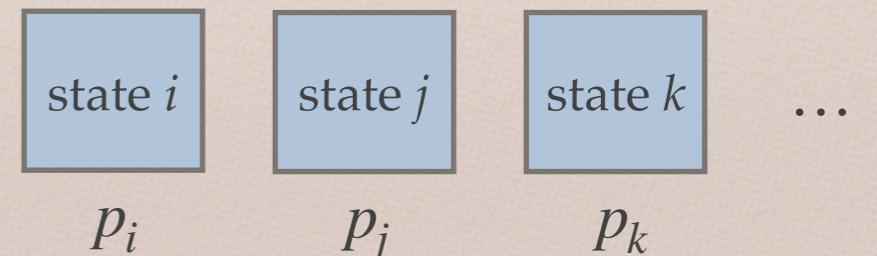
Relax this condition: Each microstate i occurs with a probability p_i

$$\text{Gibbs entropy} \quad S = -k \sum_i p_i \log p_i$$

microcanonical ensemble

``Replica trick'': Take W copies of the system

On average there are $p_i W$ copies of the system in state i



$$\text{Total number of configurations: } \Omega_{tot} = \frac{W!}{(p_1 W)!(p_2 W)!(p_3 W)! \dots}$$

$$\text{entropy for a single copy of the system: } S = \frac{1}{W} \times (k \log \Omega_{tot}) \sim -k \sum_i p_i \log p_i$$

Microcanonical Ensemble Revisited

microcanonical ensemble: all p_i s are constant

$$S = -k \sum_i p_i \log p_i$$

$$p_i = \frac{1}{N_{total}} = \frac{1}{\Omega} \Rightarrow S = -k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \log \frac{1}{\Omega} = k \log \Omega$$

Which probability distribution for the microstates maximizes the entropy?

For which set $\{p_1, p_2, \dots, p_n\}$ the Gibbs entropy, $S = -k \sum_i p_i \log p_i$, is maximum?

$$\frac{\delta}{\delta p_i} \left[-k \sum_i p_i \log p_i + \Lambda \left(\sum_i p_i - 1 \right) \right] = 0 \Rightarrow p_i = \text{constant}$$

Lagrange multiplier *Total prob.=1*

Microcanonical ensemble: the ensemble that maximizes the Gibbs entropy!
(with the constraint that all states have the same energy)

Information (Shannon) Entropy

- A thermodynamic system has an absurdly large number of microstates.
- Yet we disregard all that information and quantify it with a few number of macroscopic quantities (*energy, volume, etc..*).
- Entropy is a measure of the information we disregard.

entropy  *information*

Encode a message as a sequence of symbols and reproduce it elsewhere

What is the most economical way of doing that for a generic message?

e.g. an outcome of a game of coin toss with 100 fair coins

Heads: 0, Tails: 1

Outcome for each coin=one symbol

00001001001110101010....

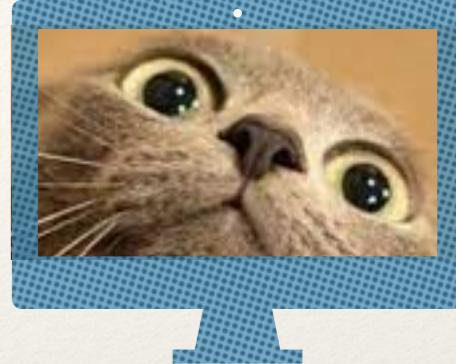
Most economical encoding: 1 bit/ symbol

Information Entropy



Message: a sequence of symbols sampled from the set $\{s_1, s_2, s_3, \dots, s_n\}$

each symbol s_i appears with a probability p_i



Information Entropy:

Minimum number of bits / symbol on average needed to encode a message

$$S = - \sum_i p_i \log_2 p_i$$

[Shannon, 1948]

e.g. coin toss: $S = - \sum_{i \in \{H,T\}} p_i \log_2 p_i = -2 \frac{1}{2} \log_2 \frac{1}{2} = 1$ (1 bit/symbol)

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points
p: 1/2 1/4 1/4

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

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♠ or ♣ = 0, ♥=10, ♦=11
1 bit 2 bits

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

p: 1/2 1/4 1/4

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♠ or ♣ = 0, ♥=10, ♦=01
1 bit 2 bits

e.g. English language: 27 characters (space= 1 character)
[Shannon, 1951]

- Assume each letter appears equally frequent $S_0 = \log_2(27) \approx 4.75$

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

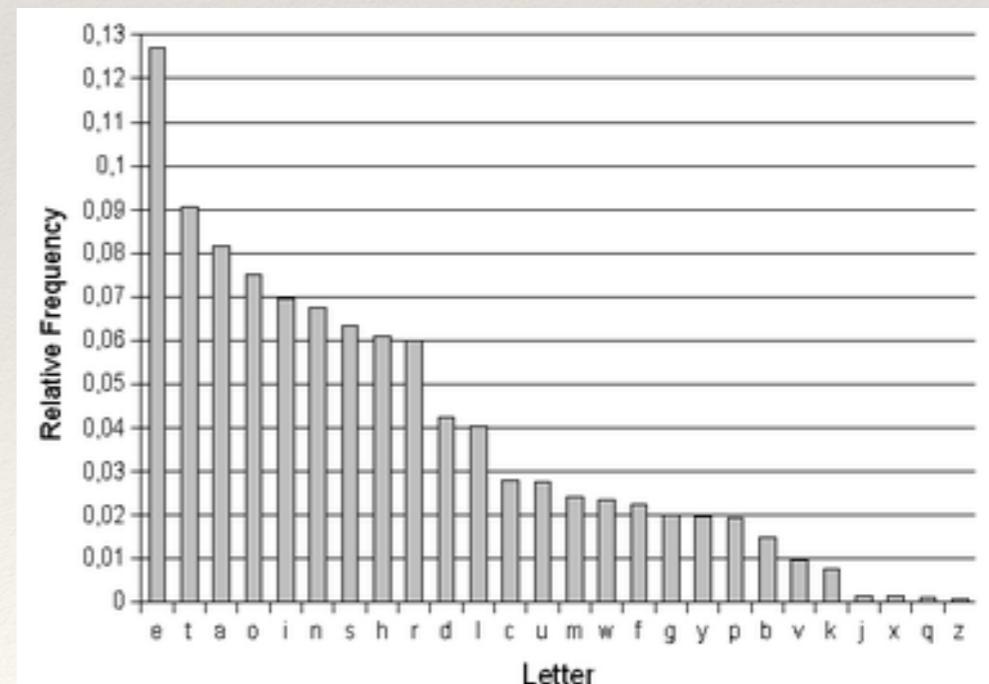
$$p: \quad \begin{matrix} 1/2 \\ 1/4 \\ 1/4 \end{matrix}$$

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

$$\begin{matrix} \spadesuit \text{ or } \clubsuit & =0, \\ 1 \text{ bit} & \end{matrix} \quad \begin{matrix} \heartsuit & =10, \\ 2 \text{ bits} & \end{matrix} \quad \begin{matrix} \diamondsuit & =01 \end{matrix}$$

e.g. English language: 27 characters (space= 1 character)
[Shannon, 1951]

- Assume each letter appears equally frequent $S_0 = \log_2(27) \approx 4.75$
- 1st order approximation: (letter frequency) $S_1 \approx 4.03$



Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

p: 1/2 1/4 1/4

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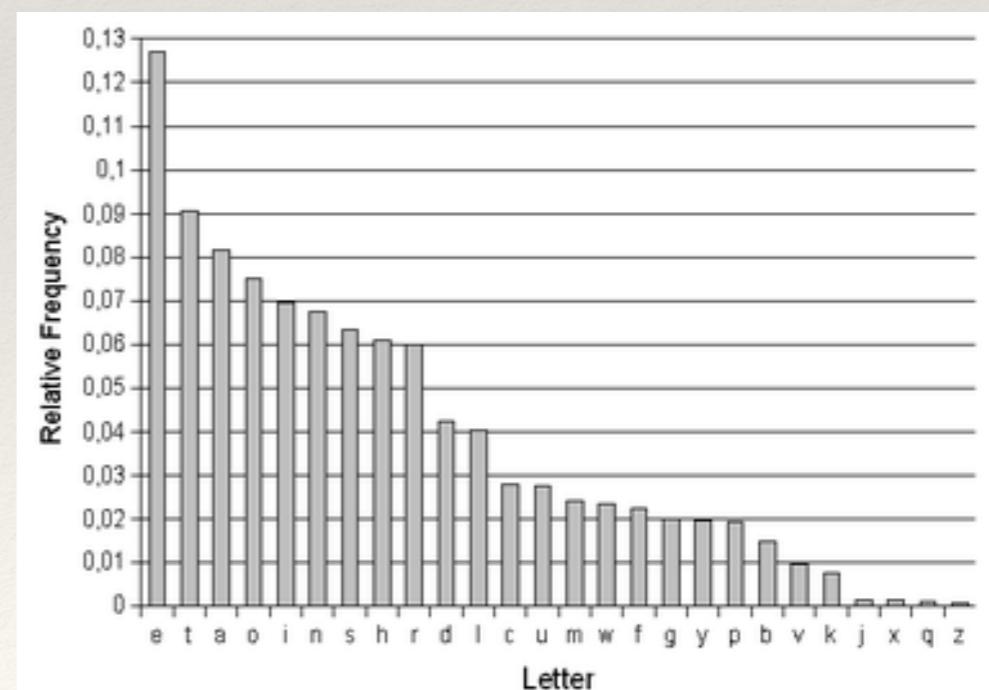
Correlations between letters:

- 2nd order approximation: (“bigrams”) $S_2 \approx 3.32$

e.g. TH is more common than TW

三

$$S_{English} \approx 2.14$$



Information Entropy



Claude Shannon

$$S = - \sum_i p_i \log_2 p_i$$

not sure what to call this....
maybe uncertainty?

“You should call it entropy, for two reasons:

In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name.

In the second place, and more important, nobody knows what entropy really is, so in a debate you will always have the advantage.”



John von Neumann

von Neumann Entropy

In Quantum Mechanics an ensemble of states is described by a *density matrix*

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i| \quad |\psi_i\rangle : \text{QM state}$$

$$\langle \hat{O} \rangle = \text{tr}(\hat{O}\hat{\rho}) \quad p_i : (\text{classical}) \text{ probability of finding the system in state } i$$

von Neumann entropy: $S = -\text{tr}(\hat{\rho} \log \hat{\rho})$

Pure state *i.e.* $\hat{\rho} = |\phi\rangle\langle\phi|$: $S = 0$

Mixed state: $S > 0$

e.g. entangled state $|AB\rangle = (|00\rangle - |11\rangle)/\sqrt{2}$ ``*EPR state*''

``*reduced density matrix*'' $\hat{\rho}_B = \text{tr}_A |AB\rangle\langle AB| = \frac{1}{2}I_{2\times 2}$

“*entanglement entropy*”
 $S = -\text{tr}_B(\hat{\rho}_B \log \hat{\rho}_B) = \log 2$

In general: entangled state \longleftrightarrow Entanglement entropy is nonzero

Thank you!