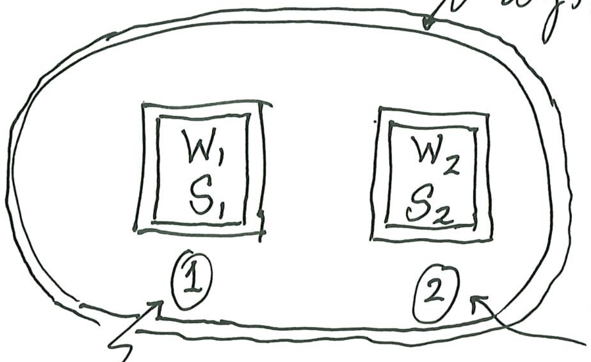
G. $S = k \ln W$ Makes sense and Making sense of $S = k \ln W$

> Regarding 2 systems as 1 composite system, # microstates Multiply and Entropy adds, Boltzmann's Formula works this way (14)

System taking ① and ② subsystems



W_2 = # microstates of subsytem ②
$(S_2 = k \ln W)$

W_1 = # Microstates of subsystem ①
$(S_1 = k \ln W_1)$

$S_{①+②}$ = Entropy of whole system $= S_1 + S_2$ (entropy is extensive)

Aside: An important Point on Counting: "Triple Trio" in Horse Racing.

Race #1 : 13 Horses [assume equally fit]

Race #2 : 13 Horses [assume equally fit]

Race # 3 : 14 Horses [assume equally fit]

A "Trio" for a race is the first three horses, and the order is irrelevant

[e.g. Horses #6, #12, #7 are 1st, 2nd, 3rd in race, as long as your ticket has "6, 7, 12" printed on it, it is a winning ticket]

"Triple Trio": Get the Trio right in $\underbrace{\text{three different races}}$

(also called "3T")

Note: one race is independent of the other races

Race # 1: How many possible tickets are there?

Counting Problem is: Out of 13 horses, pick 3 horses (order doesn't matter), how many lists of 3 horses can you make?

Answer: $_{13}C_3 = \frac{13!}{3!\,10!}$

Why? 13 choices for 1^{st} entry, 12 choices for 2^{nd} entry, 11 choices for 3^{rd} entry

[Note: so far order matters, i.e. "6, 7, 12", "7, 6, 12", ... occur]

$13 \times 12 \times 11$ ways $= \frac{13 \times 12 \times 11 \times 10 \times \cdots 1}{10 \times 9 \times \cdots 1} = \frac{13!}{10!}$

To correct for repeated listing of the same three horses, divide by 3!

[because 3 horses have 6 ordered listings]

possible outcomes $= \frac{13!}{3!\,10!} = {}_{13}C_3 \quad (= 286)$

Similarly, Race #2 has ${}_{13}C_3$ possible outcomes (286)

Race #3 has ${}_{14}C_3$ possible outcomes (364)

For "Triple Trio", how many possible outcomes are there?

Answer: $\underbrace{{}_{13}C_3}_{\#\text{ in Race 1}} \times \underbrace{{}_{13}C_3}_{\text{Race 2}} \times \underbrace{{}_{14}C_3}_{\text{Race 3}}$ (29,773,744)

Why? One Race has nothing to do (independent of) with other races

One outcome in Race #1 can go with any outcome in Race #2 and go with any outcome in Race #3

In Stat. Mech., when (sub)system ① has W_1 microstates and (sub)system ② has W_2 microstates, the whole system [taking ① & ② together] has

$W_{①+②} = W_1 \times W_2$ microstates

For our composite system, $W_{1+2} = W_1 \cdot W_2$

[product!] # microstates multiply

Boltzmann Formula $S_{1+2} = k \ln W_{1+2} = k \ln [\underbrace{W_1 \cdot W_2}]$

$= k \ln W_1 + k \ln W_2$

$= S_1 + S_2$

entropies add!

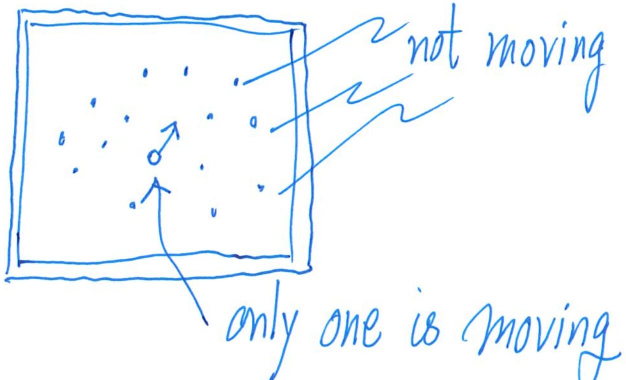
(as expected of entropy)

Only the "ln" function works this way!

$$\boxed{\text{Irreversible phenomena in macroscopic systems are related to going from "a restricted set of microstates" (non-equilibrium) to all accessible microstates (a huge number)}} \quad (15)$$

- Let's say we start with one particle (out of $\underbrace{N \sim 10^{24}}_{\text{a gas of } \sim m^3}$) taking ALL the available energy E

(this is more restrictive (technically there is one more constraint of assigning E to one particle) than simply (E, V, N) for the system)



- Even if E can be given to any of N particles, $S_{initial}$ is small ($W_{initial} \sim N$)

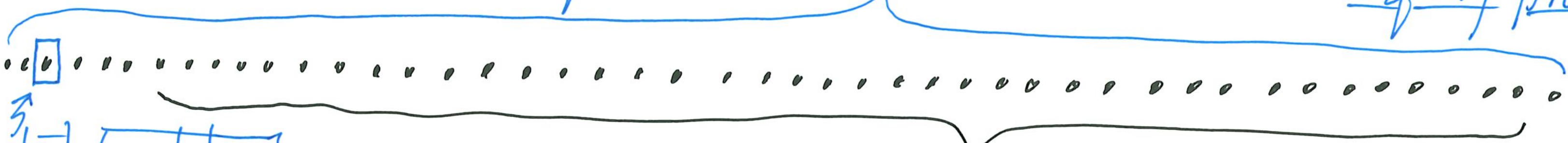
When constraint is relaxed, we have a system specified by (E, V, N)

[particles collide (share energy), energy shared by many particles, as time goes, approach equilibrium]

For a gas, $W(E,V,N) \sim E^N$ (a huge number)

[initial restricted # microstates are a tiny tiny subset of accessible microstates]

At equilibrium, all accessible microstates are equally probable



← E^N microstates

initial (a state or a small group of states) → let time evolve

a dominating number of microstates correspond to what we observe (i.e. "equipartition of energy", "uniform temperature", spreading uniformly in V)

Although the "all energy in one particle" microstates in 1 out of W (huge number) accessible microstates and all microstates are equally probable, the probability of seeing a system going to the "all energy in one particle" is simply too small. [$W \cdot \tau$ ~ time needed to wait, it is too long for us to wait!]

time between collision

This is the microscopic understanding of irreversible processes (phenomena that occur spontaneously) and the Arrow of Time!

Go to Examples of Applications

- To illustrate the method and the Math skills
- More important, bring out the physics in physical systems with a lot of stuff and how kT affects the behavior

Go To: Heat Capacity of Solids (insulators) at low temperatures

Go to Examples of Applications

- To illustrate the method and the Math skills
- More important, bring out the physics in physical systems with a lot of stuff and how kT affects the behavior

Go To : Number of Defects thermally generated in a solid

Go to Examples of Applications

- To illustrate the method and the Math skills
- More important, bring out the physics in physical systems with a lot of stuff and how kT affects the behavior

Go To : Classical Ideal Gas

After seeing how the microcanonical ensemble approach works, we look at how the ideas in $S = k \ln W$ have led to important developments in the subject and other subjects

- $S = -\sum_i P_i \ln P_i$ (information theory)
- Non-interacting (weakly interacting) particles
  - microstates, Distributions, macrostates
  - Most probable distribution
- Equilibrium condition for two systems in thermal contact
  - leads to another approach (Canonical Ensemble)

H. Another Form of $S = k\ln W$ and a Generalized Form of Entropy

The $W(E,V,N)$ accessible microstates are equally probable

$$P_i^{(MCE)} = \frac{1}{W} = \text{probability of microstate } i \text{ occuring}$$

$$\ln P_i^{(MCE)} = -\ln W$$

W terms (sum over i)

$$\sum_{\substack{\text{all accessible}\\ \text{microstates } i \\ \text{(all members in ensemble)}}} P_i^{(MCE)} \ln P_i^{(MCE)} = -\sum_{i=1}^{W} P_i^{(MCE)} \ln W = \sum_{i=1}^{W} -\frac{1}{W}\ln W = (W)\cdot\left(-\frac{1}{W}\ln W\right)$$

$$= -\ln W$$

$$\therefore \boxed{S = \underbrace{-k\sum_i P_i^{(MCE)} \ln P_i^{(MCE)}}_{\text{Gibbs}} = \underbrace{k\ln W}_{\text{Boltzmann}}} \qquad (16)$$

Gibbs (general formula, applicable to other ensembles)

$$\boxed{\text{Shannon Entropy } H = -\sum_i p_i \ln p_i \text{ is the beginning of Information Theory}}$$

I. Non-interacting Systems: A powerful idea emerges

- Oscillators problem: Independent oscillators ("non-interacting" oscillators)
- Defects problem: Each atom excited or not is treated independently
- $E = 3\varepsilon$ to $N = 3$ particles: Single-particle energy states $\left\{ \begin{array}{l} \vdots \\ 4\varepsilon \\ 3\varepsilon \\ 2\varepsilon \\ \varepsilon \\ 0 \end{array} \right.$

These are Non-interacting Systems

Step 1 (Find spectrum of single-particle states)

E.g.

$$\begin{array}{l} \vdots \\ 4\varepsilon \\ 3\varepsilon \\ 2\varepsilon \\ \varepsilon \\ 0 \end{array} \quad \text{OR} \quad \begin{array}{l} \varepsilon \\ 0 \end{array} \quad \text{OR} \quad \begin{array}{l} \varepsilon/2 \\ -\varepsilon/2 \end{array}$$

(defect) ($\vec{\mu}$ in $\vec{B}$-field)

Step 2

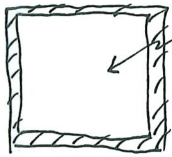
Fill each particle into single-particle states, under some given conditions

This was how we introduced the idea of accessible microstates

VIII - 7

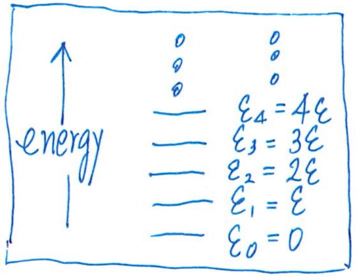
B. Basic Ideas on What microstates are through a simple example

- Pay attention: Key ideas here



3 particles (let's say they are distinguishable (A, B, C) for simplicity) OR (red, green, blue)

For each particle, the allowed single-particle states are found to be (again for simplicity here)



Meaning: a particle can be in a single-particle state of energy of "0", "1ε", "2ε", "3ε", "4ε", "5ε", and so on (unbounded spectrum)

The system of 3 particles has, say, a total energy of $E = 3\varepsilon$.

Macrostate: $E = 3\varepsilon$, $N = 3$

Question: What are the microstates compatible with the given macrostate?

Microstates Compatible with Given Macrostate

Let's list all the accessible microstates

Particles										
A	ε	3ε	0	0	2ε	2ε	ε	ε	0	0
B	ε	0	3ε	0	ε	0	2ε	0	2ε	ε
C	ε	0	0	3ε	0	ε	0	2ε	ε	2ε
	I (1)	II (3)			III (6 microstates)					

There are 10 microstates compatible with $(E=3\varepsilon, N=3)$ macrostate

$$\therefore \; W(E=3\varepsilon, N=3) = 10$$

Ex: Try $(E=8\varepsilon, N=8)$, same E/N, and find W. (Will see W increases rapidly as system is bigger)

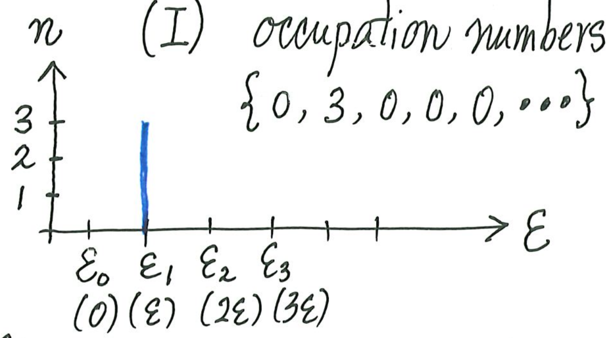
How about $N \sim 10^{23}$? W is a huge number! ($\ln W$ is better behaved)

What are the labels I, II, III? Let's pick up the discussion here.

- The 10 microstates divide naturally in 3 groups (3 distributions)
- Each group is characterized by a distribution†

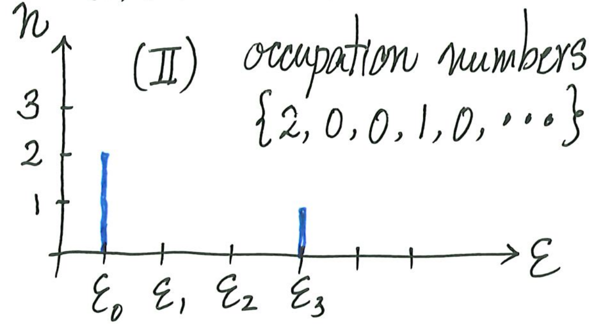
Group I: "3 particles all in $\varepsilon_1 = \varepsilon$ s.p. energy level"

(1 corresponding microstate)



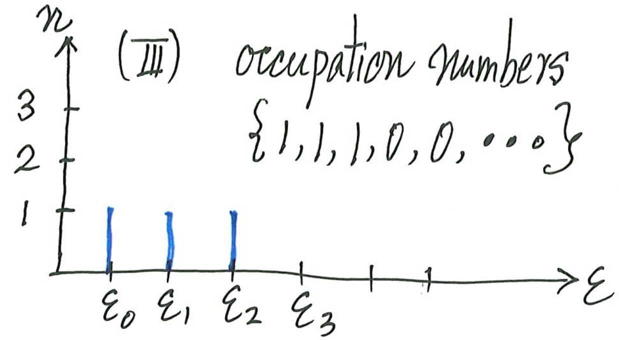
Group II: "one particle in $\varepsilon_3 = 3\varepsilon$ and two particles in ε_0"

(3 corresponding microstates)



Group III: "one particle in $\varepsilon_2 = 2\varepsilon$, one in $\varepsilon_1 = \varepsilon$, and one in $\varepsilon_0 = 0$"

(6 corresponding microstates)



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† At this point, the notion of a distribution enters.

A distribution can be described by a string of "occupation numbers"

$$\{ n_0, n_1, n_2, n_3, \cdots, n_i, \cdots \}$$

n_0: # particles in level 0 of energy ε_0

n_1: # particles in level 1 of energy ε_1

n_i: # particles in level i of energy ε_i

a long string because usually there are infinitely many s.p. states

[see occupation numbers in figure]

In our context of given E and given E, each string (distribution) satisfies

$$\boxed{\begin{aligned} \sum_i n_i &= N \\ \sum_i n_i \varepsilon_i &= E \end{aligned}} \qquad (18)$$

specified by macrostate[+]

Two constraints on allowed distributions (occupation numbers)

[+] Remember we started the discussion on $S = k \ln W$ emphasizing that it is for isolated systems at equilibrium

$$10 = \underbrace{1} + \underbrace{3} + \underbrace{6}$$

$$W = W\begin{pmatrix}\text{Type I}\\ \text{distribution}\end{pmatrix} + W\begin{pmatrix}\text{Type II}\\ \text{distribution}\end{pmatrix} + W\begin{pmatrix}\text{Type III}\\ \text{distribution}\end{pmatrix}$$

Given a string $\{n_0, n_1, n_2, \ldots\}$, how to count W(distribution)?

W(distribution) = # microstates of a distribution

Generally,

$$\boxed{W = \sum_{\text{distributions}} W(\text{distribution})} \qquad (19)$$

Suggests another way in obtaining W

So far, everything is exact.

- List all microstates (most detailed)
- Distributions (intermediate)
- Macrostate (roughest)

But Eq. (19) and Eq. (18) suggest an alternative and efficient way of getting W: The idea of the <u>Most Probable Distribution</u>.

Observation: $W(\text{Type II distribution}) = 6$

$$\frac{\ln 6}{\ln 10} \cong 0.778$$

So, there is one "dominating" distribution: The Most Probable Distribution

"Perhaps, we could simply look for the most probable distribution, expecting its W(most probable distribution) almost represents W"

especially when system is Macroscopic.

One more example: $E = 6\varepsilon$, $N = 6$

Distributions ↓	The 6 particles are distributed in energy levels:		Number of microstates ↓	$W(\{n_i\})$ $\{n_0, n_1, n_2, n_3, n_4, n_5, n_6, n_7, \cdots\}$
I	$6\varepsilon, 0, 0, 0, 0, 0$		6	$\{5,0,0,0,0,0,1,0,0,\cdots\}$
II	$5\varepsilon, \varepsilon, 0, 0, 0, 0$		30	$\{4,1,0,0,0,1,0,0,0,\cdots\}$
III	$4\varepsilon, 2\varepsilon, 0, 0, 0, 0$		30	$\{4,0,1,0,1,0,0,0,0,\cdots\}$
IV	$4\varepsilon, \varepsilon, \varepsilon, 0, 0, 0$		60	$\{3,2,0,0,1,0,0,0,0,\cdots\}$
V	$3\varepsilon, 3\varepsilon, 0, 0, 0, 0$		15	$\{4,0,0,2,0,0,0,0,0,\cdots\}$
VI	$3\varepsilon, 2\varepsilon, \varepsilon, 0, 0, 0$	(most probable) →	$\boxed{120}$	$\{3,1,1,1,0,0,0,0,0,\cdots\}$
VII	$3\varepsilon, \varepsilon, \varepsilon, \varepsilon, 0, 0$		60	$\{2,3,0,1,0,0,0,0,0,\cdots\}$
VIII	$2\varepsilon, 2\varepsilon, 2\varepsilon, 0, 0, 0$		20	$\{3,0,3,0,0,0,0,0,0,\cdots\}$
IX	$2\varepsilon, 2\varepsilon, \varepsilon, \varepsilon, 0, 0$		90	$\{2,2,2,0,0,0,0,0,0,\cdots\}$
X	$2\varepsilon, \varepsilon, \varepsilon, \varepsilon, \varepsilon, 0$		30	$\{1,4,1,0,0,0,0,0,0,\cdots\}$
XI	$\varepsilon, \varepsilon, \varepsilon, \varepsilon, \varepsilon, \varepsilon$		1	$\{0,6,0,0,0,0,0,0,0,\cdots\}$

Total number of microstates $= W = 462$

The dominating distribution contributes 120 microstates out of 462

$$\frac{\ln 120}{\ln 462} \approx 0.780$$

Reasonable to expect W is dominated by one distribution as system becomes macroscopic

Also why after system achieves equilibrium, its macroscopic properties do not change with time, as properties are dominated by one dominating (most probable) distribution.

The Problem of Finding the Most Probable Distribution

Idea 1

$$S = k \ln W = k \ln \Big[\underbrace{\sum_{\text{distributions}} W(\text{distribution})}_{\text{one term } W(\text{most probable}) \text{ dominates (out numbered sum of other terms)}} \Big] \quad \text{exact}$$

$$\approx k \ln W(\text{most probable}) \quad \text{(should be an excellent approximation)}$$

$$= k \ln W_{mp}$$

Question becomes: Set up formalism for obtaining the most probable distribution

Idea 2 [Key concepts here]

Most Probable distribution: A string of yet-to-be-determined occupation numbers

(a) $\{n_i\}_{mp} = \{n_1, n_2, n_3, n_4, \ldots\}_{mp}$

symbol for a string

unknowns

energy : $\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \ldots$

(b) Count # microstates corresponding to $\{n_i\}_{mp}$

$W(\{n_i\}_{mp})$ = a function of the unknowns $\{n_i\}_{mp}$

(c) there are constraints (Eq. (19))

$$\sum_i n_i = N \quad ; \quad \sum_i n_i \varepsilon_i = E \qquad (19)$$

(d) Mathematical Statement of finding $\{n_i\}_{mp}$

$$\boxed{\begin{array}{l}\text{Find } \{n_i\}_{mp} \text{ such that } W(\{n_i\}_{mp}) \text{ or} \\ \ln W(\{n_i\}_{mp}) \text{ is a maximum subject to the constraints} \\ \sum_i n_i = N \quad \text{and} \quad \sum_i n_i \varepsilon_i = E \end{array}} \qquad (20)$$

- A topic[+] in partial differentiation (using Lagrange multiplers)
- $W(\{n_i\})$ depends on further details of the non-interacting particles
  - a single-particle state can either be empty or occupied at most by one particle (fermions)

  (the result is the "Fermi-Dirac distribution")

+ Eq.(20) is finding the extremum of a function $\mathcal{F}(n_1, n_2, \ldots)$ under constraints. Naturally, we would vary each n_i, i.e. δn_i's, but the constraints say not all δn_i's are independent.

- a single-particle state can be empty or occupied by any number of particles (bosons)

  (the result is the Bose-Einstein distribution)

All particles are either fermions (spin $1/2, 3/2, \ldots$) or bosons (spin $0, 1, \ldots$)

- There are cases in which we don't need to care about fermionic or bosonic nature of particles ("classical particles")

  Why?

  when $\underbrace{\text{\# particles ("}n_i\text{") per single-particle states}}_{\text{many s.p. states available to one particle}} \ll 1$

  (never need to worry having more than 1 particle in a s.p. state)

Summary

- Eq. (20) is an $\underbrace{\text{easy method}}$ with profound consequences

  but with solid Stat. Mech. Foundation

- Can take (20) to work out all systems of non-interacting particles
- This Section connects to
  - Deriving the Fermi-Dirac distribution by Eq. (20)
  - Deriving the Bose-Einstein distribution by Eq. (20)

Aside: A bit of Quantum Thinking (Can skip and Move on)

$$\hat{H}_N \Psi(\vec{r}_1, \cdots, \vec{r}_N) = E\, \Psi(\vec{r}_1, \cdots, \vec{r}_N)$$ [N-particle state ↔ E pairs]

(Can't talk about single-particle states in general)

Non-interacting: $\hat{H}_N = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$ (no interaction terms)

$$\underbrace{\hat{H}_N = \sum_{i=1}^{N} \hat{h}_i}, \quad \hat{h}_i = \frac{\vec{p}_i^{\,2}}{2m}$$ (single-particle Hamiltonian)

⇒ Separation of Variables Works

$\Psi(\vec{r}_1, \cdots, \vec{r}_N)$ = Product of $\varphi_i(\vec{r}_i)$

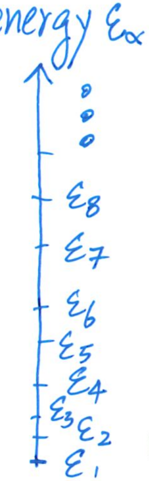
E = Sum of ε_i (one for each particle)

$$\underbrace{\hat{h}\,\varphi(\vec{r}) = \varepsilon\, \varphi(\vec{r})}$$

$\varphi_\alpha(\vec{r}) \leftrightarrow \varepsilon_\alpha$ pairs

single-particle states

single-particle allowed energies



This is the bases of the Counting Problems in Non-interacting Systems.