

Statistical Mechanics

- **Goal**
 - calculation/prediction of TD (macroscopic) properties from molecular (microscopic) properties
- **Overall approach**
 - use QM to describe molecular properties and invoke statistical connection between microscopic and macroscopic properties
- **Options**
 - 1) most general - canonical and grand canonical ensembles (ensemble or **Gibbs method**)
 - 2) isolated system of independent particles → find connection to entropy, then use TD state equations (**Maxwell-Boltzmann method**)

Enumeration of Microstates-1
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M-B Method Outline

- Given **isolated** macroscopic system with specified energy (E or U) and volume (V) made up of N microscopic particles (with N large)
- **Microscopic model**
 - each particle has well-defined, quantized/discrete energy levels ($\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_m$)
 - total energy is sum of energies of particles
 - *implicitly assuming energy levels of one particle are independent of presence of other particles*
⇒ energy levels not perturbed by molecular interactions
 - *equivalent to perfect gas, ideal solution assumptions*
- **Probability and Statistics**
 - number ways to distribute N particles over individual energy levels (ϵ_i) while maintaining same overall energy E ?
 - which is most “likely”?
- **Macroscopic TD properties**
 - answer will lead to entropy then other TD properties

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Enumeration of Microstates

- Macroscopic TD state
 - E, V, N sufficient to define TD state
- Microscopic state
 - need more to define **microstate**
 - how are particles distributed over the molecular energy levels?
 - large number of microstates (unique quantum states) consistent with macrostate, e.g., total E and N
 - example: four $\epsilon, N=4, E=8$

$\epsilon_1=0$	$\epsilon_2=2$	$\epsilon_3=2$	$\epsilon_4=4$	
•	•	•	•	1
••			••	2
•	••		•	3
•		••	•	4
	••	••		5
	•••	•		6
	•	•••		7
	••••			8
		••••		9
•••			•	10
•	•		•	11

$E \neq 8$
Same as microstate 1 if indistinguishable particles

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Enumeration of Microstates

- Could also divide into 3 energy levels with one having degeneracy of 2
- So each microstate is a unique quantum state of the system, but has same TD E, N constraints
 - define Ω** = total number of microstates with same E, N
- Want to find Ω
 - will later relate to S
 - use indistinguishable particles

$\epsilon_1=0$	$\epsilon_2=2$	$\epsilon_3=2$	$\epsilon_4=4$
•	•	•	•

$\epsilon_1=0$	$\epsilon_2=2$	$\epsilon_3=4$
•	• •	•

$$\Omega = \sum_{\substack{\text{microstates with} \\ \sum N_i = N \\ \sum N_i \epsilon_i = E}} 1$$

Enumeration of Microstates-4

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Particle Statistics

- Approach to finding Ω
 - consider indistinguishable particles (**balls**)
 - each must exist in some energy level (**big box**)
 - each energy level can have degeneracy (**little boxes**)
 - can be “true” degeneracy $\varepsilon_a = \varepsilon_b$
 - or can be near degeneracy $\varepsilon_a \approx \varepsilon_b$

$\varepsilon_1=0$	$\varepsilon_2=2$	$\varepsilon_3=4$
		

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Matter Models

- Examine 5 situations
 - 1) Distinguishable balls in set of boxes with number of balls in each box (N_i) prespecified
→ Boltzmann statistics without degeneracy (model for crystals)
 - 2) Same as (1) with degeneracy
→ Boltzmann statistics with degeneracy
 - 3) Same as (2) but indistinguishable particles and dilute ($g_i \gg N_i$) = low probability of >1 particle in small box
→ Corrected Boltzmann statistics
 - if dilute, reduce to (3) { 4) Same as (3) but no restrictions on # particles per small box
→ Bose-Einstein statistics
 - 5) Same as (3) but only one particle per small box
→ Fermi-Dirac statistics (follow Pauli Exclusion Principle)

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Macrostate

- Definitions
 - macrostate $\equiv$ given distribution of N particles across energy levels (big boxes), i.e., given N_i distribution
 - $W(N_i) \equiv$ # of microstates in specific macrostate
- So multiple macrostates per TD state
- Total number of microstates in TD state related to W

$$\Omega = \sum_{\substack{\text{macrostates with} \\ \sum N_i = N \\ \sum N_i \varepsilon_i = E}} W(N_i)$$

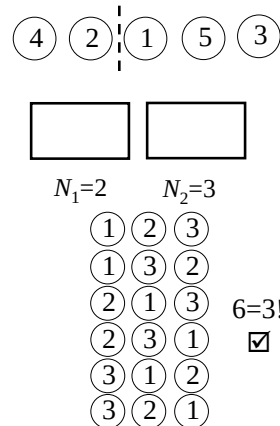
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Counting Microstates

- State with N “balls” (particles) and M “large boxes” (energy levels)
- Imagine 1) lining up the N balls then 2) sorting in order into large boxes
- 1st step – how many ways to line up N balls?
 - 1st ball: N choices
 - 2nd ball: $N-1$ choices
 - etc. $\Rightarrow N!$
- 2nd step – sorting into boxes



Enumeration of Microstates-8

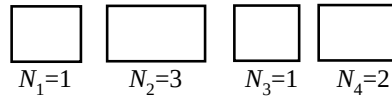
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Sorting into Energy Levels

- Case 1) **Boltzmann Statistics w/o degeneracy**

- example $N=7, M=4$



- one of $N!$ lineups



- no different (can't "order" molec. in same state)



- $N_i!$ "lineups" are identical for each i

- here $W = \frac{7!}{1!3!1!2!} = 420$

$$W(N_i) = \frac{N!}{\prod_{i=1}^M N_i!}$$

← total # lineups

← total # equiv. lineups

lots of microstates even for only a few particles and boxes

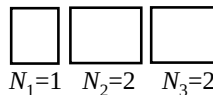
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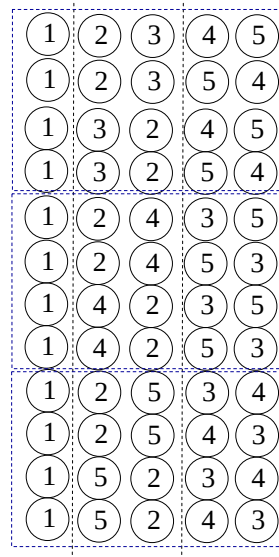
Another Example

- $N=5, M=3$



- Every four configurations are the "same"

- $N_1! \cdot N_2! \cdot N_3! = 1 \cdot 2 \cdot 2 = 4$ ✓



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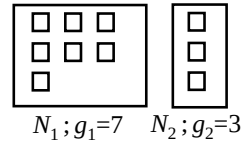
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Sorting into Energy Levels

- Case 2) **Boltzmann Statistics w/ degeneracy**

- N particles, M large boxes, g_i small boxes in large box

- ignoring g_i , already know
$$W(N_i) = \frac{N!}{\prod_{i=1}^M N_i!}$$



- but now within each large box (energy level) g_i places to put a particle
$$W(N_i) = \frac{N!}{\prod_{i=1}^M N_i!} \times \left(\begin{matrix} \text{\# ways to arrange} \\ \text{balls into small boxes} \end{matrix} \right)$$

- how many particles allowed in each small box?

- with no exclusion rule, as many as N_i

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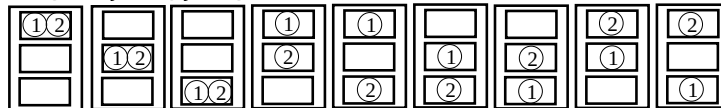
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Sorting into Energy Levels

- Case 2) **Boltzmann Statistics w/ degeneracy**

- how many ways to arrange N_i balls into g_i small boxes?

- e.g., $N_i=2$, $g_i=3$ gives 9 ($=3^2$)



$\Rightarrow g_i^{N_i}$

- since each big box (energy level) independent

$$W(N_i) = \frac{N!}{\prod_{i=1}^M N_i!} \prod_{i=1}^M g_i^{N_i}$$

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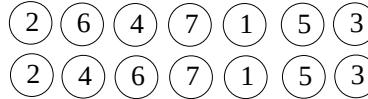
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Sorting into Energy Levels

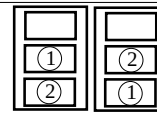
- Case 3) **(Corrected) Boltzmann Statistics**
 - now make balls/particles **indistinguishable**

$$W(N_i) = \frac{1}{\prod_{i=1}^M N_i!} \prod_{i=1}^M g_i^{N_i}$$



- Does not matter how we initially lineup balls
- BUT note from previous example we have now overcounted
- Not a problem if chance of overcounting negligible
 - ⇒ **corrected Boltzmann statistics** only valid for $g_i \gg N_i$

$$W_{CB}(N_i) = \frac{\prod_{i=1}^M g_i^{N_i}}{\prod_{i=1}^M N_i!}$$



$N_i=2, g_i=3$

now the same microstate

or number of quantum states available $\gg$ number of particles

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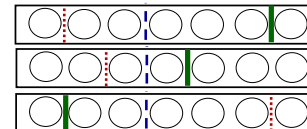
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Sorting into Energy Levels

- Case 4) **Bose-Einstein Statistics**
 - indistinguishable particles
 - no limit on number of particles per quantum state (small box)

Bosons

- to avoid dilute requirement consider one large box (energy level) with $N_i=7, g_i=4$; but use $g_i-1=3$ partitions to mark them



- gives us $N_i + g_i - 1$ (10) things to arrange
 - if distinguishable $(N_i + g_i - 1)!$ ways to line them up
- but both balls and partitions are indistinguishable
 - $N_i!$ ($g_i - 1!$) overcounts (balls distinguishable from partitions)
- since each big box independent

$$W_{BE}(N_i) = \prod_{i=1}^M \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!}$$

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Sorting into Energy Levels

- Case 5) **Fermi-Dirac Statistics**
 - now only one particles per quantum state (small box)
 - Fermions** (e.g., e^- spin)
 - place N_i (e.g, 3) particles in g_i (e.g., 7)
 - g_i (=7) places to put 1st ball
 - $g_i - 1$ (=6) places to put 2nd ball
 - continue until no balls left $g_i - N_i + 1$ (=5)
 - but particles indistinguishable, overcounted by $N_i!$
 - since each big box independent

Note: requires $g_i \geq N_i$ or would have more than one particle per quantum state

$$W_{FD}(N_i) = \prod_{i=1}^M \frac{g_i!}{N_i!(g_i - N_i)!}$$

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Boltzmann Limit

- Look at B-E and F-D cases for **$g_i \gg N_i$ Boltzmann Limit**

$$W_{FD} = \prod_{i=1}^M \frac{g_i!}{N_i!(g_i - N_i)!} = \prod_{i=1}^M \frac{g_i(g_i - 1) \cdots (g_i - N_i + 1)}{N_i!} \approx (\leq) \prod_{i=1}^M \frac{g_i^{N_i}}{N_i!}$$

$$W_{BE} = \prod_{i=1}^M \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!} = \prod_{i=1}^M \frac{(g_i + N_i - 1)(g_i + N_i - 2) \cdots (g_i)}{N_i!} \approx (\geq) \prod_{i=1}^M \frac{g_i^{N_i}}{N_i!}$$

$$= W_{CB}$$

- So in Boltzmann limit, no practical difference between Boson and Fermion statistics

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