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**)

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 (ε_1, ε_2, ε_3, $\ldots\varepsilon_m$)
  - 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

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 ε, ***N*=4, *E*=8**

$\varepsilon_1=0$	$\varepsilon_2=2$	$\varepsilon_3=2$	$\varepsilon_4=4$	
●	●	●	●	1
●●			●●	2
●	●●		●	3
●		●●	●	4
	●●	●●		5
	●●●	●		6
	●	●●●		7
	●●●●			8
		●●●●		9
~~●●●~~			~~●~~	10
~~●~~	~~●~~	~~●~~	~~●~~	11

***E*≠8**

Same as microstate 1 if indistinguishable particles

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

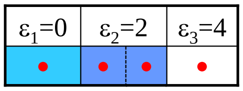
$\varepsilon_1=0$	$\varepsilon_2=2$	$\varepsilon_3=2$	$\varepsilon_4=4$
●	●	●	●

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

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

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 $\varepsilon_a\approx\varepsilon_b$



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 ($g_i>>N_i$)=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)

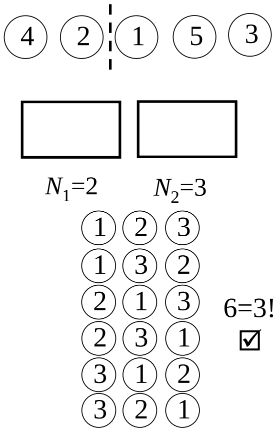
Macrostate

- Definitions
  - macrostate ≡ 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

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

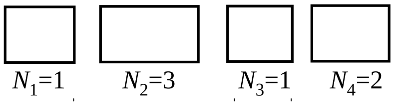
Counting Microstates

- 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

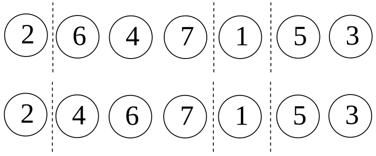


Sorting into Energy Levels

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

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

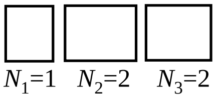
←total # lineups

←total # equiv. lineups

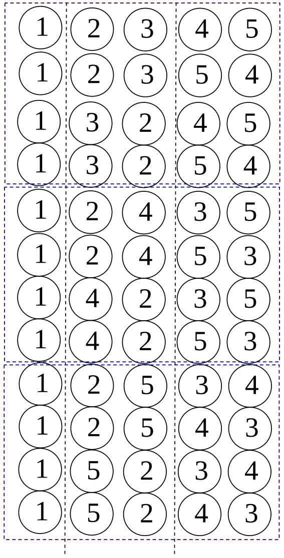
lots of microstates even for only a few particles and boxes

Another Example

- N=5, M=3



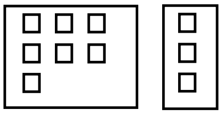
- Every four configurations are the "same"
  - $N_1! \cdot N_2! \cdot N_3!$ = 1·2·2=4 ☑



1	2	3	4	5
1	2	3	5	4
1	3	2	4	5
1	3	2	5	4
1	2	4	3	5
1	2	4	5	3
1	4	2	3	5
1	4	2	5	3
1	2	5	3	4
1	2	5	4	3
1	5	2	3	4
1	5	2	4	3

Sorting into Energy Levels

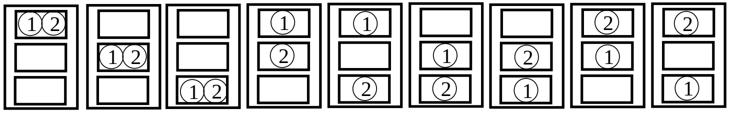
- Case 2) **Boltzmann Statistics w/ degeneracy**
  - N particles, M large boxes, g_i small boxes in large box
  - ignoring g_i, already know $W(N_i)=\dfrac{N!}{\prod_{i=1}^{M} N_i!}$
  - but now within each large box (energy level) g_i places to put a particle $W(N_i)=\dfrac{N!}{\prod_{i=1}^{M} N_i!}\times\left(\begin{array}{c}\text{\# ways to arrange}\\ \text{balls into small boxes}\end{array}\right)$
  - how many particles allowed in each small box?
    - with no exclusion rule, as many as N_i



$N_1\,;g_1$=7 $N_2\,;g_2$=3

Sorting into Energy Levels

- Case 2) **Boltzmann Statistics w/ degeneracy**
  - how many was to arrange N_i balls into g_i small boxes?
  - e.g., N_i=2, g_i=3 gives 9 (=3^2)



$\Rightarrow g_i^{Ni}$

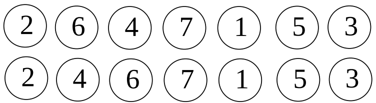
  - since each big box (energy level) independent

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

Sorting into Energy Levels

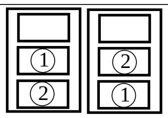
- Case 3) **(Corrected) Boltzmann Statistics**
  - now make balls/particles **indistinguishable**

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



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

- 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 $g_i \gg N_i$**



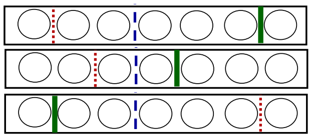
N_i=2,g_i=3

now the same microstate

or number of quantum states available >> number of particles

Sorting into Energy Levels

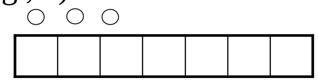
- Case 4) **Bose-Einstein Statistics**
  - indistinguishable particles
  - no limit on number of particles per quantum state (small box) **Bosons**
  - to avoid dilute requirement consider one large box (energy level) with N_i=7, g_i=4; but use g_i–1=3 partitions to mark them
  - gives us N_i+g_i–1 (10) 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



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

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)



$$g_i\left(g_i-1\right)\ldots\left(N_i+g_i-1\right)=\frac{g_i!}{\left(g_i-N_i\right)!}$$

  - but particles indistinguishable, overcounted by N!
  - since each big box independent

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

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

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Boltzmann Limit

- Look at B-E and F-D cases for
  g_i>>N_i Boltzmann Limit

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

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

$$=W_{CB}$$

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