(Equilibrium) Statistical Mechanics

- **What statistical mechanics provides**
  1. calculation/prediction of equilibrium thermodynamic (macroscopic) properties from molecular/microscopic properties
  - examples
    - specific heats: c_p, c_v
    - compressibility coefficients: α, β, κ
  2. insights into entropy, meaning of temperature
- **Overall strategy**
  - use QM to describe microscopic properties of system of interest
  - invoke statistical connection between microscopic and macroscopic properties (through entropy)
- An extension, *nonequilibrium statistical mechanics*, provides information on how systems evolve between equilibrium states
  - not a subject of this presentation

Statistical Mechanics Approaches

- Two approaches to use statistical mechanics for calculating macroscopic thermodynamic properties from microscopic properties
- **Ensemble (Gibbs) method**

  more powerful method, but more abstract
  - most general approach
  - works for non-ideal (real) and ideal systems
    - ideal = independent "particles" (atoms/molecules, electrons, photons, …); no interactions between particles
- **Maxwell-Boltzmann method**

  easier to interpret (learning ✓) and useful for ideal gases
  - original formulation
  - assumes isolated system of independent particles
    - works for ideal gases, electron gases, crystal solids, radiation
- Both assume large number of microscopic components, so that statistical/probabilistic methods apply

Ensemble (Gibbs) Method

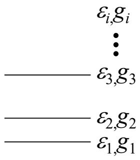
- For completeness, begin by briefly introducing Gibbs method
- **What is an ensemble?**
  - theoretical collection of large number of systems, each replicates macroscopic TD system of interest; entire ensemble is isolated
- For example, consider a system of N particles, with a total energy E and volume V (named the **microcanonical ensemble**)
  - very large number (nearly infinite) of combinations of the 3N positions and 3N momenta satisfy the (N,E,V) requirement
  - each combination is one element of the ensemble
  - time-averaged TD equilibrium properties based on ensemble-averaged properties
- Two other general ensembles
  - **canonical ensemble**: closed isothermal system (known N,V,T)
  - **grand canonical ensemble**: open isothermal sys. (known μ,V,T)

chemical potential

Maxwell-Boltzmann Method Outline

- Developed for isolated macroscopic system with specified (N,E,V) of ***independent*** particles
  - essentially *microcanonical ensemble* of independent particles

1. **Need to describe microscopic systems**
   - *each particle* has well-defined, possible **quantum states**
     - independent because allowed quantum states not impacted by molecular interactions
   - quantum states with same energy can be grouped into **energy levels** (ε_i) with **degeneracies** (g_i)
   - total energy is sum of energies of particles



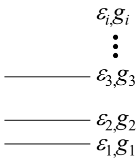
Maxwell-Boltzmann Method Outline

2. Use probability and statistics

- determine number of different ways to distribute *N* particles over energy levels (ε_i) while maintaining same overall energy *E* (for given *V*)
- each distribution with unique combination of quantum numbers for each particle is known as a **microstate**
- all microstates that have same number of particles in each energy level are said to be part of the same **macrostate**

3. Macroscopic TD properties

- determine which macrostate is most likely
- relate this macrostate to macroscopic TD properties through entropy



M-B: Enumeration of Microstates

- Let's look at simplified example to understand microstates
  - macroscopic system with *N*=4 *indistinguishable* particles and with total energy *E*=8
  - microscopic system with 4 quantum states having energies
    - $\varepsilon_1=0$, $\varepsilon_2=2$, $\varepsilon_3=2$, $\varepsilon_4=4$
  - some different *unique* ways we can distribute our 4 particles among these energy quantum states

$\varepsilon_1=0$	$\varepsilon_2=2$	$\varepsilon_3=2$	$\varepsilon_4=4$	
•	•	•	•	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 the 4 quantum states into 3 energy levels, with one having degeneracy of 2
- So each microstate is a unique quantum configuration (state) of the system, but has same TD/ macroscopic constraints (*E*,*V*,*N* here)
  - **define Ω** = total number of microstates with required macroscopic properties
- Want to find Ω
  - will later relate to *S*
  - use indistinguishable particles

ε_1=0	ε_2=2	ε_3=2	ε_4=4
●	●	●	●

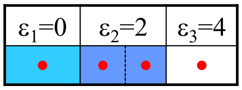
ε_1=0	ε_2=2	ε_3=4
●	● ●	●

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

constraints for MB approach

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, quantum states have exactly same energy, $\varepsilon_a=\varepsilon_b$
    - or can be near (extended) degeneracy $\varepsilon_a \approx \varepsilon_b$



ε_1=0	ε_2=2	ε_3=4
●	● ●	●

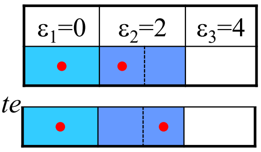
Different Statistical Situations

- 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
  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)

if dilute, reduce to (3) $\}$ (4), (5)

Ω and Macrostates

- Recall definition of macrostate
  - macrostate ≡ given unique distribution of N particles across energy levels (big boxes)
  - so a macrostate has specific N_i distribution
  - let $W(N_i)$ ≡ number of microstates in specific macrostate



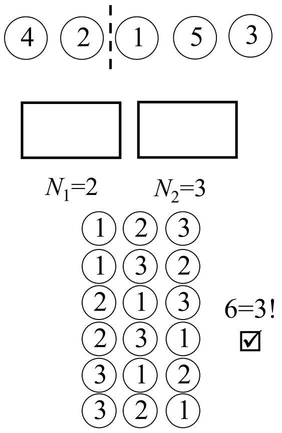
both part of same macrostate

- Also there are multiple macrostates per TD state
- Total number of microstates in TD state related to W

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

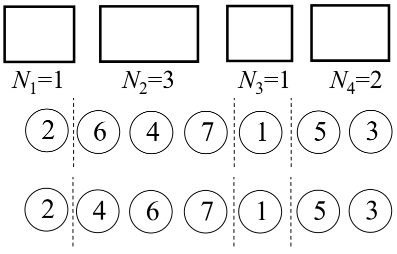
Counting Microstates

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



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

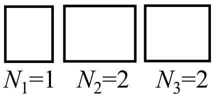
← total # lineups

← total # redundant lineups

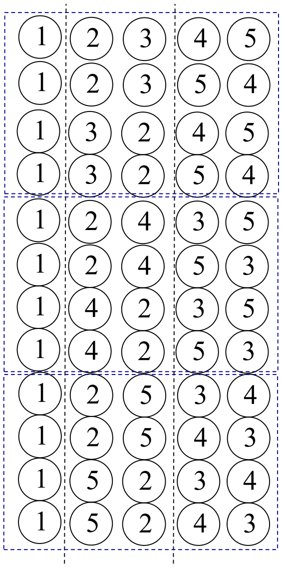
lots of microstates even for only a few particles and boxes

Another Example

- N=5, M=3



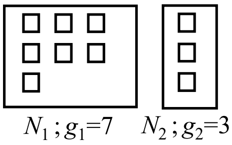
- Every four configurations are the "same"
  - $N_1! \cdot N_2! \cdot N_3! = 1{\cdot}2{\cdot}2{=}4$ ☑



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

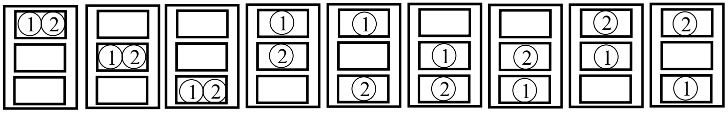
- Case 2) **Boltzmann Statistics w/ degeneracy**
  - N particles, M large boxes, g_i small boxes in large box



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

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)



$\Rightarrow g_i^{N_i}$

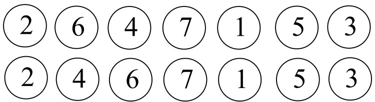
  - since each big box (energy level) independent

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

Sorting into Energy Levels

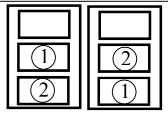
- Case 3) **(Corrected) Boltzmann Statistics**
  - now make balls/particles **indistinguishable**

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



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

- 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



now the same microstate

N_i=2,g_i=3

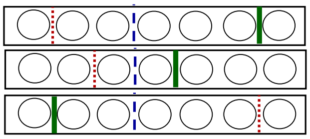
$\Rightarrow$ **corrected Boltzmann statistics**

so dilute **only valid for g_i>>N_i**

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

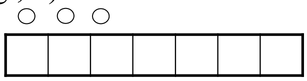


  - gives us N_i+g_i–1 (10) things to arrange
    - if distinguishable (N_i+g_i–1)! ways to line them up
  - but both balls and partitions are indistinguishable
    - N_i! (g_i–1!) overcounts (balls distinguishable from partitions)
  - since each big box independent

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

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)



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

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

note: requires $g_i \geq N_i$ or would have more than one particle per quantum state
so constrains (max) N_i

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

Boltzmann Limit

- Look at B-E and F-D cases for $g_i >> N_i$, dilute, also known as the **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 Bose-Einstein and Fermi-Dirac statistics