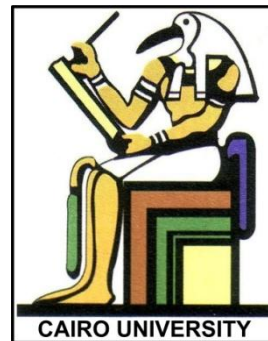


Medical Equipment I - 2009

Chapter 3

Professor Yasser M. Kadah

Web: <http://ymk.k-space.org/courses.htm>



Introduction

- Is it possible to use classical mechanics to describe systems of many particles ?
- Example: particles in 1 mm³ of blood

- Compute translational motion in 3D

$$v_i(t + \Delta t) = v_i(t) + F_i \Delta t / m \quad , \quad (i = x, y, z)$$

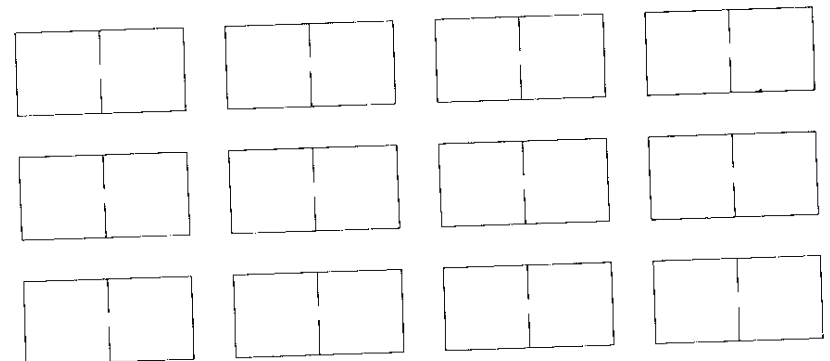
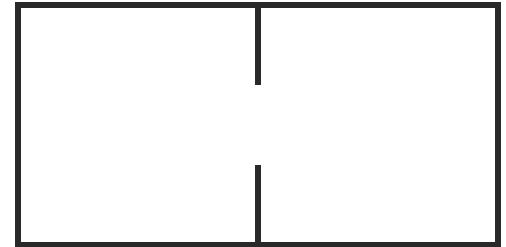
- 6 multiplications + 6 additions / particle
- For 10¹⁹ particle, 10²⁰ operations required/interval
- 10⁸ s (3 years) on a 1G operations/s computer !!

Statistical Mechanics

- Do not care about individual molecules
 - Impossible to trace practically
- Average macroscopic properties over many particles are what we need
- Such properties are studied under statistical physics / statistical mechanics
 - e.g., Pressure, Temperature, etc.
 - Average and probability distribution

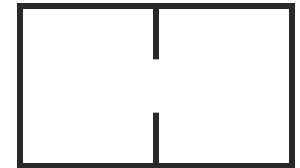
Gas Molecules in a Box

- Total number of molecules = N
- Box with imaginary partition
- Particles in left half = n
- $P(n)$ can be computed from an ensemble of boxes



Gas Molecules in a Box

- Example: $N=1$
 - $P(0)=0.5$, $P(1)=0.5$
- Example: $N=2$



Molecule 1	Molecule 2	n	$P(n; 2)$
R	R	0	$\frac{1}{4}$
R	L	1	$\frac{1}{2}$
L	R	1	$\frac{1}{2}$
L	L	2	$\frac{1}{4}$

Gas Molecules in a Box

- Example: $N=3$

Molecule 1	Molecule 2	Molecule 3	n	$P(n; 3)$
R	R	R	0	$\frac{1}{8}$
R	R	L	1	
R	L	R	1	$\frac{3}{8}$
L	R	R	1	
L	L	R	2	
L	R	L	2	$\frac{3}{8}$
R	L	L	2	
L	L	L	3	$\frac{1}{8}$

Gas Molecules in a Box

- Histogram representation

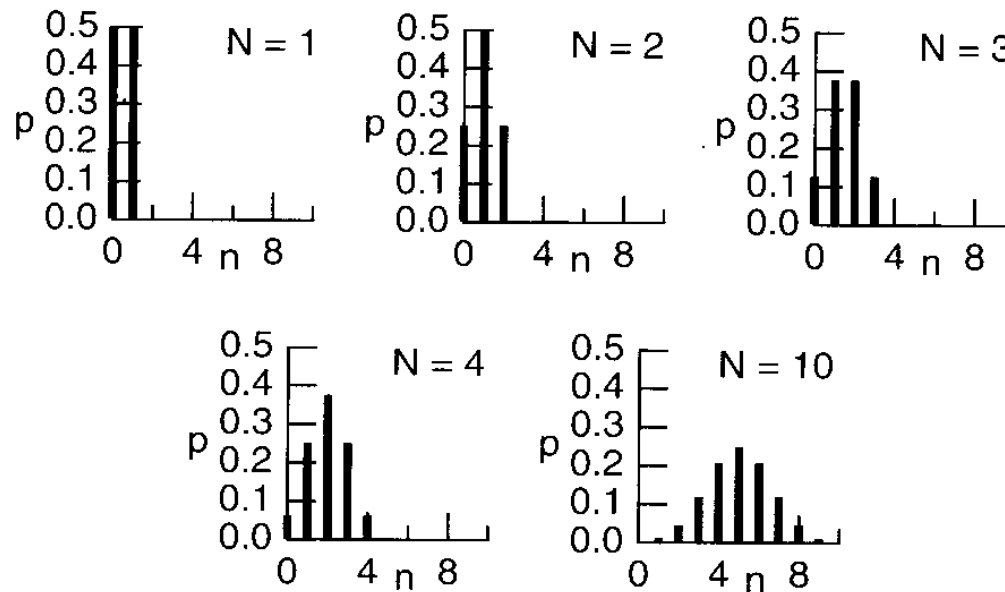
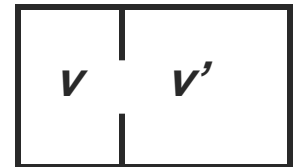


FIGURE 3.2. Histograms of $P(n; N)$ for different values of N .

Gas Molecules in a Box

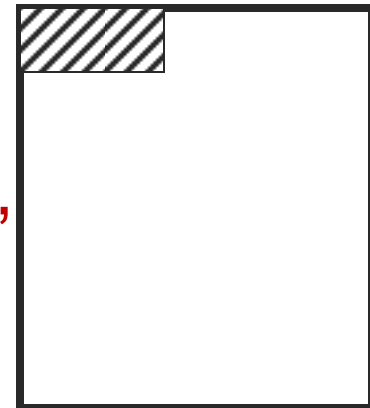
- General case: binomial distribution
- Assume a general box partitioning into two volumes v (left) and v' (right) such that $p=v/V$, $q=v'/V$, then $p+q=1$
- Probability of n particles in volume v given by

$$P(n; N, p) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}$$



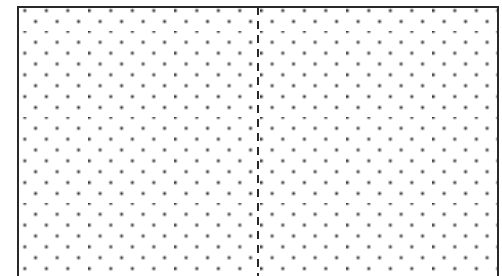
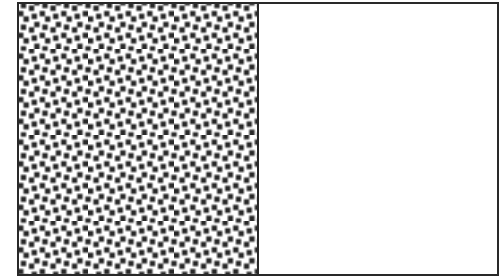
Microstates and Macrostates

- Microstates: all information about a system
 - Position and velocity of all molecules
- Macrostates: average properties
 - Number of molecules in each half
- Example: Toys in a room
 - Microstate: position of every toy
 - Macrostate: “picked-up” or “mess”



[Gas Box Example]

- Partition in between
- Partition suddenly removed
 - Many more microstates available
 - Improbable to remain all on left
 - Equilibrium: half on each side
 - Macroscopic states not changing with time
 - Most random, most probable



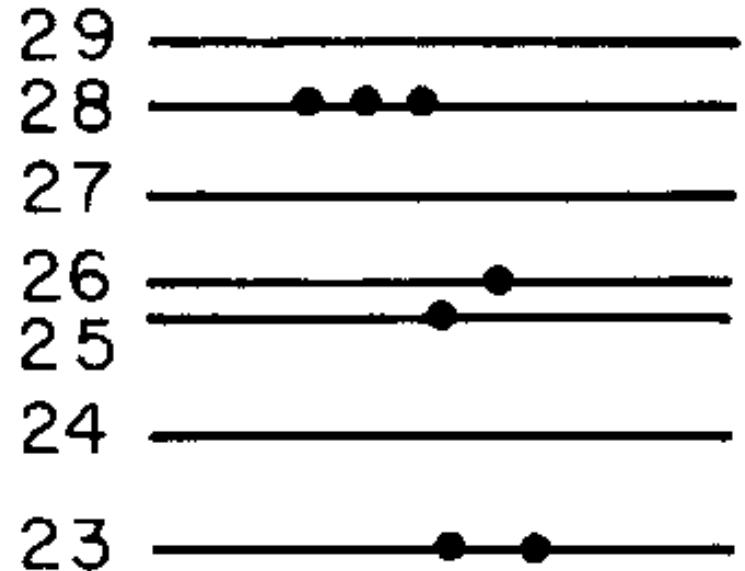
[Microstates]

- Energy levels defined by a set of quantum numbers = $3N$ (in 3D)
 - Discrete levels
- Total number of quantum numbers required to specify state of all particles is called *degrees of freedom (f)*
- *Microstate*: specified if all quantum numbers for all particles are specified

First Law of Thermodynamics

- Total energy $U = \text{sum of particle energies}$

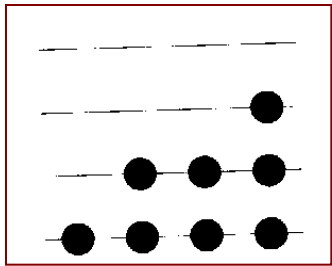
$$U = 2u_{23} + u_{25} + u_{26} + u_{28}$$



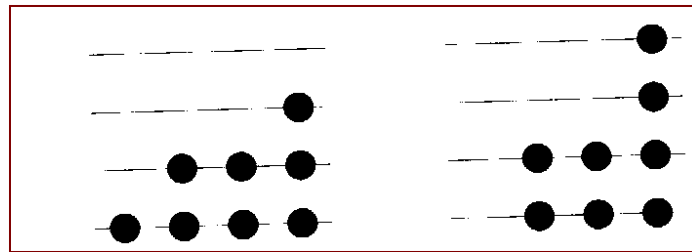
[Exchange of Energy]

- Exchange forms: Work and Heat

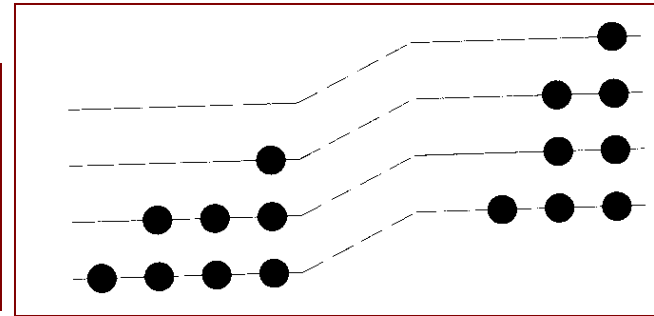
$$\Delta U = Q - W$$



No work – No heat flow



No work – Heat added



Work done – No heat flow
(Adiabatic change)



[Exchange of Energy]

- Pure heat flow involves a change in the average number of particles in each level
 - No change in positions of levels
- Work involves a change in the macroscopic parameters
 - Change in positions of some levels
 - Change in average populations in levels
- General case: both heat flow and work
 - Sum of changes due to both

Specifying Microstates and Macrostates

- Microstates
 - quantum numbers of each particle in the system
- Macrostates
 - All of external parameters
 - Total energy of the system

Specifying Microstates and Macrostates

- Statistical physics: ensemble of identical systems
- At some instant of time, “freeze” ensemble

$$P(\text{microstate } i) = \frac{\text{Number of systems in microstate } i}{\text{Total number of systems in the ensemble}}$$

- “Unfreeze” then wait and repeat “freeze”
- Ergodicity:
 - Equivalence of time and ensemble averages

[Basic Postulates]

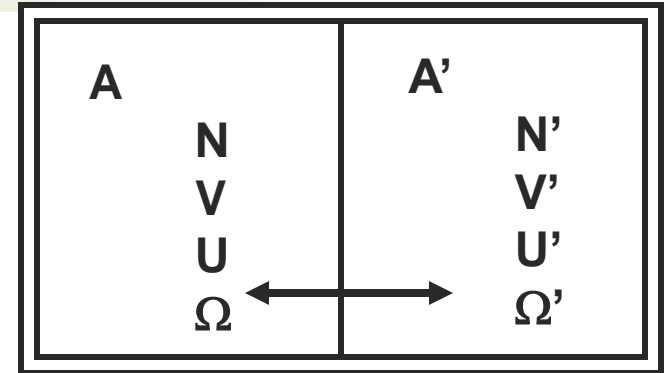
1. If an isolated system is found with equal probability in each one of its accessible microstates, it is in equilibrium
 - Converse is also true
2. If it is not in equilibrium, it tends to change with time until it is in equilibrium
 - Equilibrium is the most random, most probably state.

[Thermal Equilibrium]

- Idealization: system that does not interact with surroundings
 - Adiabatic walls can never be realized
- Much can be learned by considering two systems that can exchange heat, work or particles but isolated from the rest of the universe
 - One of them is our system and the other can be taken to be the rest of the universe

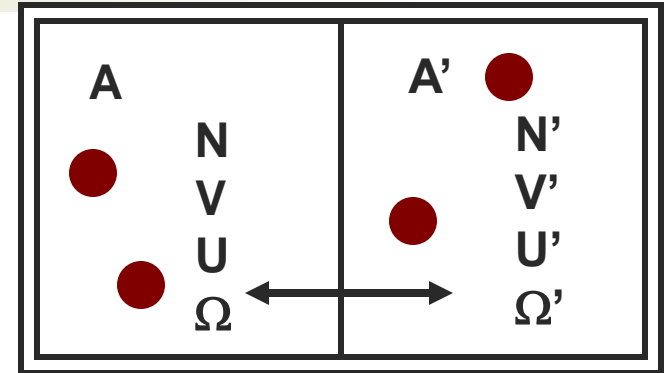
[Thermal Equilibrium]

- Consider only heat flow
- Total system A^*
 - Number of particles $N^* = N + N'$
 - Total energy $U^* = U + U'$
- Two systems can exchange heat
 - U and U' may change as long as $U^* = \text{const}$
 - Barrier prevents exchange of particles or work



Thermal Equilibrium

- Number of microstates
 - $\Omega^*(U) = \Omega(U) \times \Omega'(U)$
- Probability of microstate
 - $P(U) = \Omega^*(U) / \Omega_{\text{tot}}^*$
 - $\Omega_{\text{tot}}^* = \sum_U \Omega^*(U)$
- Example: system of 2 particles in A and A'
 - Total energy $U^* = 10u$
 - Possible energy levels for particles = $1u, 2u, \dots$



[Thermal Equilibrium]

- Ex: $U = 2u \rightarrow U' = U^* - U = 10u - 2u = 8u$
 - Possible A microstates: $(1u, 1u)$
 - $\Omega(U) = 1$
 - Possible A' microstates: $(1u, 7u), (2u, 6u), (3u, 5u), (4u, 4u), (5u, 3u), (6u, 2u), (7u, 1u)$
 - $\Omega'(U) = 7$
 - $\Omega^*(U) = \Omega(U) \times \Omega'(U) = 7$

Thermal Equilibrium

System A		System A'		System A*
U	Ω	U'	Ω'	Ω^*
$2u$	1	$8u$	7	7
$3u$	2	$7u$	6	12
$4u$	3	$6u$	5	15
$5u$	4	$5u$	4	16
$6u$	5	$4u$	3	15
$7u$	6	$3u$	2	12
$8u$	7	$2u$	1	7
				$\Omega_{\text{tot}}^* = 84$

Thermal Equilibrium

- Most probable value of U has $\max P(U)$

$$\frac{d}{dU} P(U) = \frac{d}{dU} \left[\frac{\Omega^*(U)}{\Omega_{tot}^*} \right] = \frac{1}{\Omega_{tot}^*} \frac{d}{dU} [\Omega^*(U)] = 0$$

$$\Omega^*(U) = \Omega(U) \cdot \Omega'(U^* - U)$$

$$\frac{d\Omega^*(U)}{dU} = 0 = \underbrace{\Omega \Omega'}_{\neq 0} \left(\underbrace{\frac{1}{\Omega} \frac{d\Omega}{dU} - \frac{1}{\Omega'} \frac{d\Omega'}{dU'}}_{= 0 \text{ for equilibrium}} \right)$$

$\neq 0$

$= 0$ for equilibrium

Thermal Equilibrium

- Define a quantities τ and τ' with units of energy such that

$$\frac{1}{\tau} \equiv \frac{1}{\Omega} \frac{d\Omega}{dU} \quad \text{and} \quad \frac{1}{\tau'} \equiv \frac{1}{\Omega'} \frac{d\Omega'}{dU'}$$

- Equilibrium at $\tau = \tau'$,

- related to absolute temperature

$$\tau = k_B T$$

- $k_B =$ Boltzmann const = $1.38 \times 10^{-23} \text{ J K}^{-1}$
- $T =$ absolute temperature K

[Entropy]

- Develop a condition for thermal equilibrium
 - $\ln \Omega^* = \ln \Omega + \ln \Omega'$

$$\frac{1}{\tau} \equiv \frac{d}{dU} (\ln \Omega)$$

- Define entropy S as

$$S = k_B \ln \Omega$$



$$\Omega = e^{S/k_B}$$

[Entropy]

- Feature #1: temperature definition

$$\frac{dS}{dU} = \frac{k_B}{\tau} = \frac{1}{T}$$

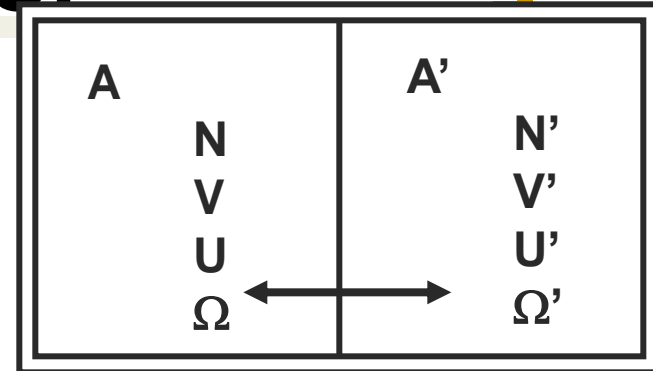
- Feature #2: entropy = sum of entropies

$$S^* = S + S'$$

- Feature #3: max entropy at equilibrium
 - Follows from max Ω^* at equilibrium
- Feature #4: entropy change related to heat flow

[The Boltzmann Factor]

- Two isolated systems
 - In thermal contact
- Let system A be a single particle
- Let system A' be a large system
 - “reservoir”
- Transfer of energy → Number of microstates in A and A' change
 - Ratio of number of states $\equiv G$



The Boltzmann Factor

- Consider system A has two different energies U_r and U_s
- Reservoir A' is very large
 - Its temperature T' remains the same
 - Has many energy levels
- Recall that $P(U) = \Omega^*(U) / \Omega_{\text{tot}}^*$
- Recall that $\Omega^*(U) = \Omega(U) \cdot \Omega'(U^* - U)$

The Boltzmann Factor

- Then,

$$\frac{P(U_s)}{P(U_r)} = \frac{\Omega^*(U_s)}{\Omega^*(U_r)} = \frac{\Omega(U_s) \cdot \Omega'(U^* - U_s)}{\Omega(U_r) \cdot \Omega'(U^* - U_r)}$$

- Let

$$G = \frac{\Omega(U_s)}{\Omega(U_r)}$$

and

$$R = \frac{\Omega'(U^* - U_s)}{\Omega'(U^* - U_r)}$$

The Boltzmann Factor

- Recall that

$$\frac{1}{\tau} \equiv \frac{1}{\Omega} \frac{d\Omega}{dU} \quad \text{and} \quad \frac{1}{\tau'} \equiv \frac{1}{\Omega'} \frac{d\Omega'}{dU'}$$

- Equilibrium at $\tau = \tau'$,

- related to absolute temperature

$$\tau' = k_B T'$$

- $k_B =$ Boltzmann const = $1.38 \times 10^{-23} \text{ J K}^{-1}$
- $T =$ absolute temperature K

- Consider solving the above equation for Ω'
 - T' is constant

The Boltzmann Factor

$$\frac{1}{\Omega'} \left(\frac{d\Omega'}{dU'} \right) = \frac{1}{k_B T'} \Rightarrow \frac{d\Omega'}{dU'} = \left(\frac{1}{k_B T'} \right) \Omega'$$

- Then,

$$\Omega'(U') = \text{constant} \times e^{U'/k_B T'}$$

- Hence, at equilibrium $T = T'$

$$R = \frac{\text{constant} \times e^{(U^* - U_s)/k_B T'}}{\text{constant} \times e^{(U^* - U_r)/k_B T'}} = e^{-(U_s - U_r)/k_B T}$$

The Boltzmann Factor

- R is called the “Boltzmann factor”
 - Factor by which the number of microstates in the reservoir decreases when the reservoir gives up energy $U_s - U_r$
- Relative probability of finding system A with energy U_r or U_s is given by

$$\frac{P(U_s)}{P(U_r)} = G \cdot R = \left[\frac{\Omega(U_s)}{\Omega(U_r)} \right] \cdot e^{-(U_s - U_r)/k_B T}$$

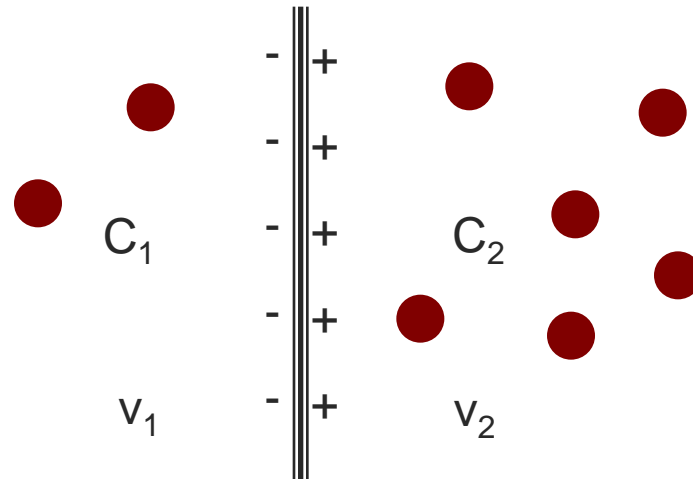
[The Boltzmann Factor]

- G factor: “density of states factor”
 - Property of the system
 - Ex: single atom with discrete energy levels, $G=1$
 - Degeneracy: G may be different

Example 1: Nernst Equation

- Concentration of ions on the two sides of a semi-permeable membrane and its relation to the voltage across the membrane

$$\frac{P(2)}{P(1)} = \frac{C_2}{C_1}$$



Nernst Equation

- $U = E_k + E_p$ (E_k is the same)
 - *Potential energy is $E_p = zev$*

- Then,

$$\frac{C_2}{C_1} = e^{-ze(v_2 - v_1)/k_B T}$$

- Since $R = N_A K_B$ and $F = N_A e$

*Nernst
Equation*

$$v_2 - v_1 = \frac{RT}{zF} \ln \left(\frac{C_1}{C_2} \right)$$

Example 2: Pressure variation in the atmosphere

- Atmospheric pressure decreases with altitude
- Potential energy: gravitational = $m \times g \times y$

$$\frac{C(y)}{C(0)} = e^{-mgy/k_B T}$$

[Problem Assignment]

- Posted on class web site

Web: <http://ymk.k-space.org/courses.htm>