Intermediate Physics for Medicine and Biology - Chapter 3

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

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Introduction

- Is it possible to use classical mechanics to describe systems of many particles ?
- Example: particles in 1 mm^3 of blood
  - Compute translational motion in 3D

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

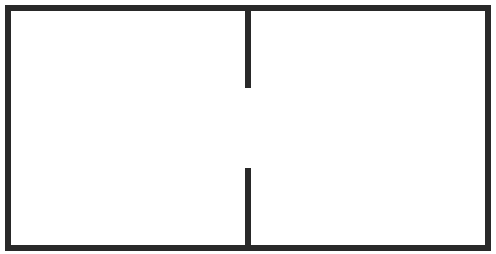
  - 6 multiplications + 6 additions / particle
  - For 10^{19} particle, 10^{20} operations required/interval
  - 10^8 s (3 years) on a 1G operations/s computer !!

Statistical Mechanics

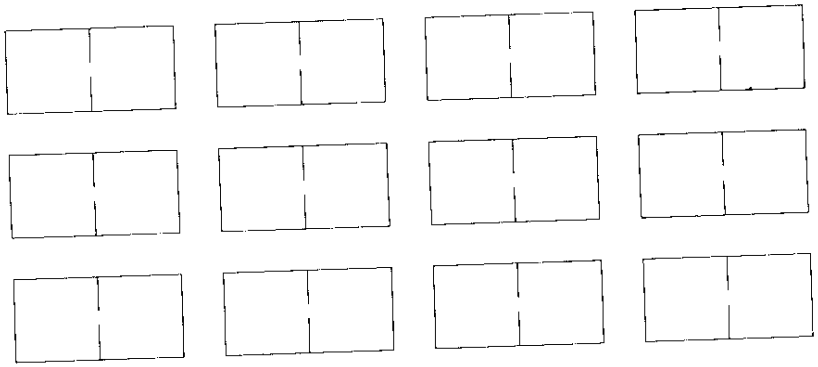
- Do not care about individual molecules
  - Impossible to trace practically
- Average macroscopic properties over many particles are what we need
- Such properties are studied under statistical physics / statistical mechanics
  - e.g., Pressure, Temperature, etc.
  - Average and probability distribution

Gas Molecules in a Box

- Total number of molecules = N
- Box with imaginary partition

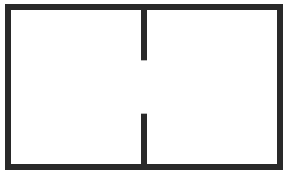


- Particles in left half = n
- P(n) can be computed from an ensemble of boxes



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	
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

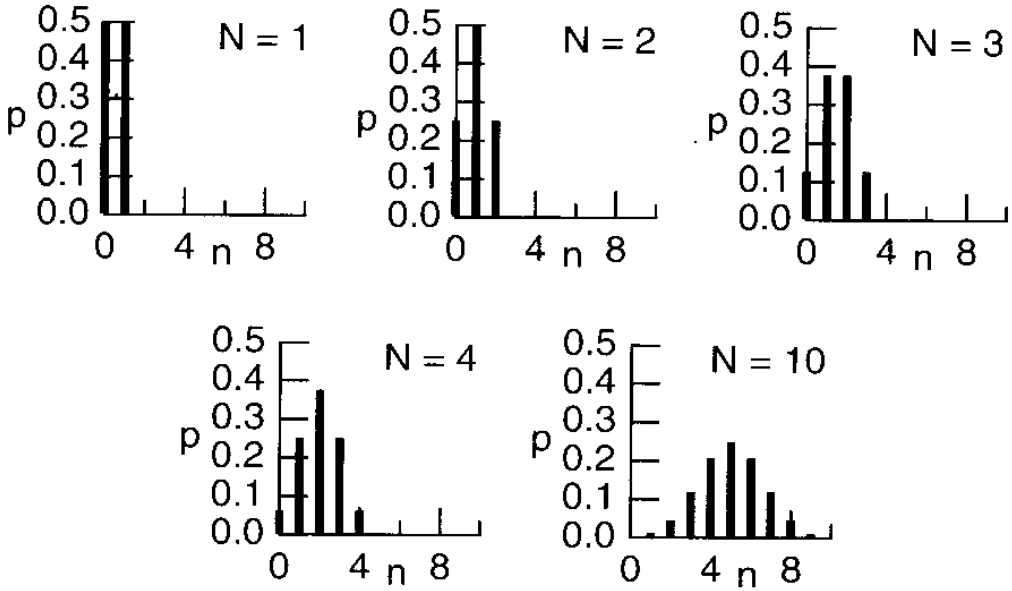
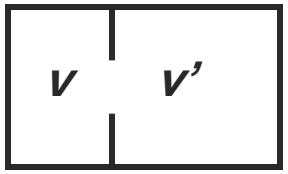


FIGURE 3.2. Histograms of $P(n; N)$ for different values of N.

Gas Molecules in a Box

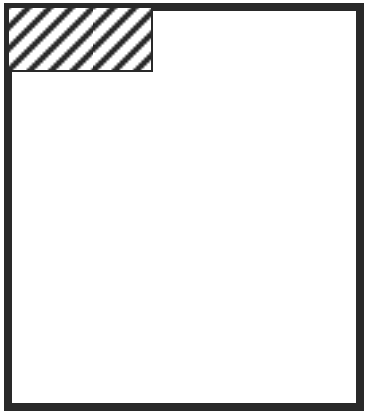
- General case: binomial distribution
- Assume a general box partitioning into two volumes v (left) and v' (right) such that *p=v/V*, *q= v'/V*, then *p+q=1*
- Probability of n particles in volume v given by



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

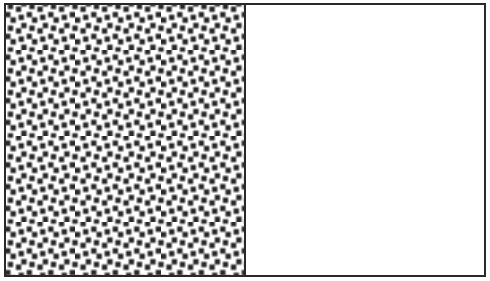
Microstates and Macrostates

- 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”

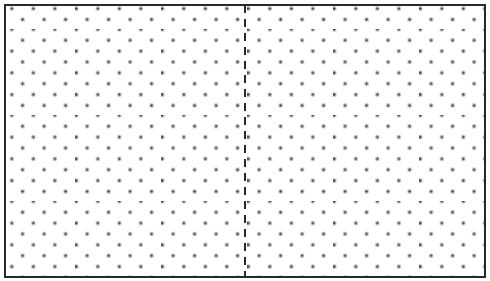


Gas Box Example

- Partition in between



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



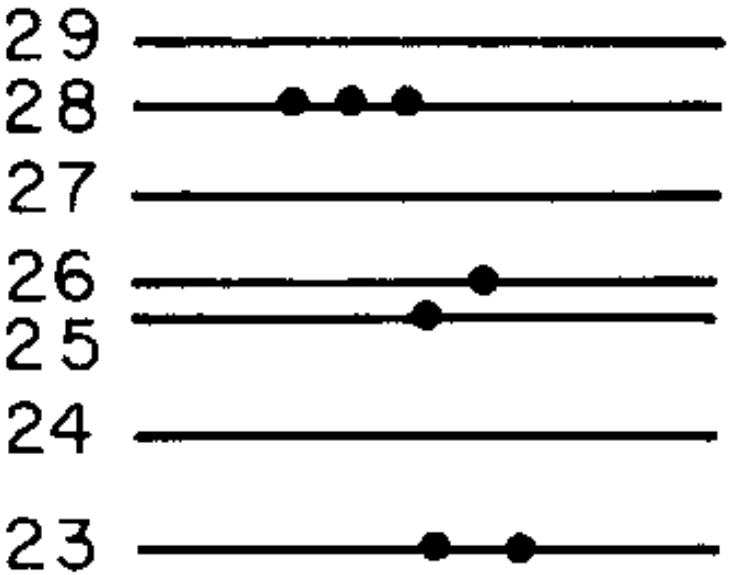
Microstates

- 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 = sum of particle energies

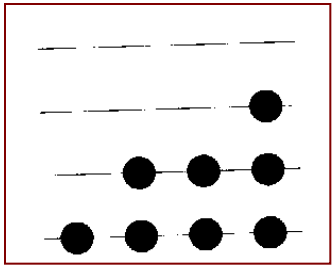
$$U = 2u_{23} + u_{25} + u_{26} + u_{28}$$



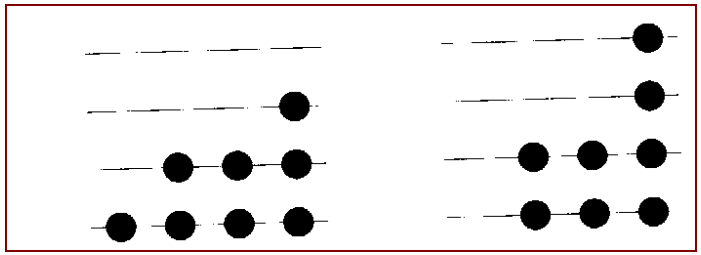
Exchange of Energy

- Exachange forms: Work and Heat

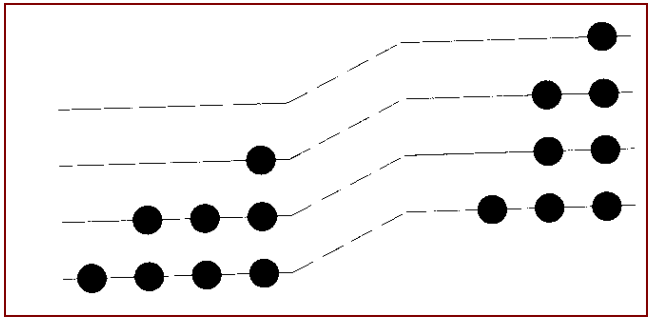
$$\Delta U = Q - W$$



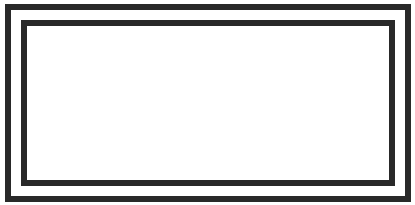
No work – No heat flow

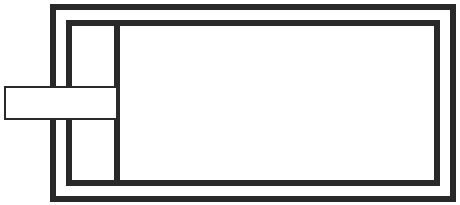


No work – Heat added



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”
- Edgodicity:
  - Equivalence of time and ensemble averages

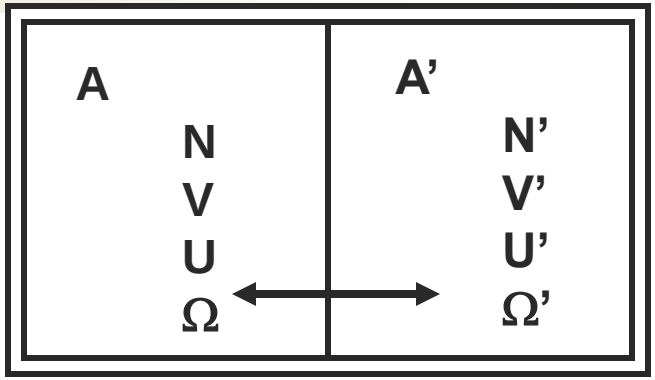
Basic Postulates

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

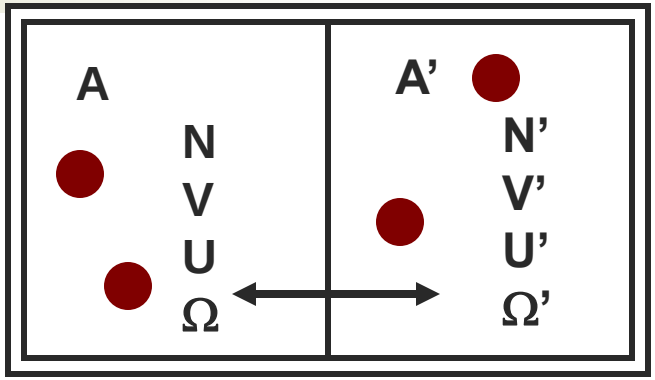
- Idealization: system that does not interact with surroundings
  - Adiabatic walls can never be realized
- Much can be learned by considering two systems that can exchange heat, work or particles but isolated from the rest of the universe
  - One of them is our system and the other can be taken to be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

Thermal Equilibrium



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

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)

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

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

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

Thermal Equilibrium

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

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

- Equilibrium at $\tau = \tau'$,
  - related to absolute temperature $\boxed{\tau = k_B T}$
    - k_B= Boltzmann const= 1.38×10^{-23} J K^{-1}
    - T= absolute temperature K

Entropy

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

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

- Define entropy S as

$$\boxed{S = k_B \ln \Omega} \longrightarrow \boxed{\Omega = e^{S/k_B}}$$

Entropy

- Feature #1: temperature definition

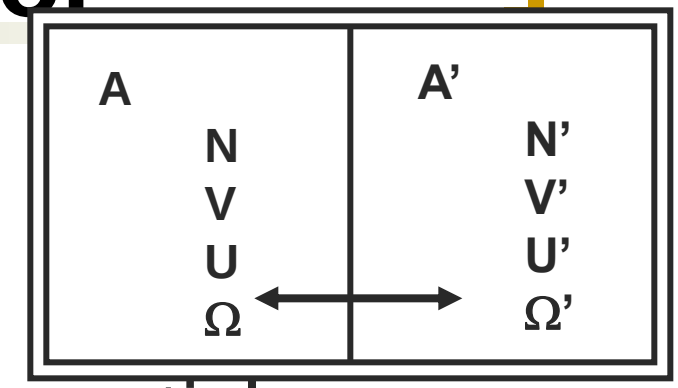
$$\boxed{\frac{dS}{dU} = \frac{k_B}{\tau} = \frac{1}{T}}$$

- Feature #2: entropy = sum of entropies

$$\boxed{S^* = S + S'}$$

- 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 ≡ 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 $P(U) = \Omega^*(U) / \Omega^*_{tot}$
- Recall that $\Omega^*(U) = \Omega(U) \cdot \Omega'(U^* - U)$

The Boltzmann Factor

- Then,

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

- Let

$$\boxed{G = \frac{\Omega(U_s)}{\Omega(U_r)}} \quad \text{and} \quad \boxed{R = \frac{\Omega'(U^* - U_s)}{\Omega'(U^* - U_r)}}$$

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 $\tau = \tau'$,

$$\tau' = k_B T'$$

  - related to absolute temperature
    - k_B= Boltzmann const= 1.38×10^{-23} 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

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

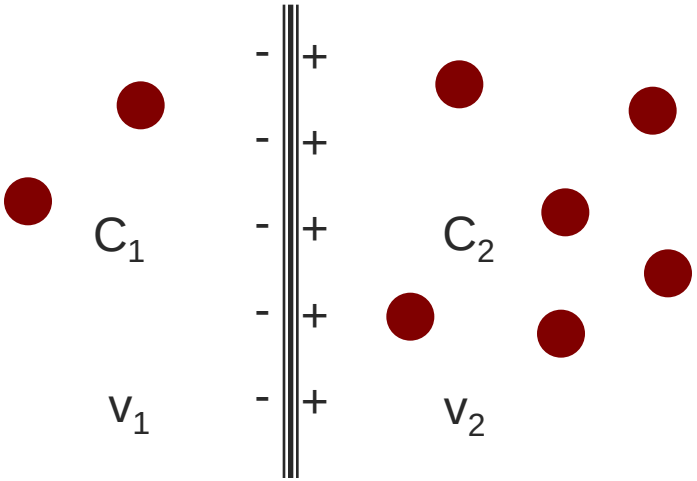
The Boltzmann Factor

- *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 $= m \times g \times y$

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

Problem Assignment

- Posted on class web site

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