Chapter 3: Systems of Many Particles – Part II

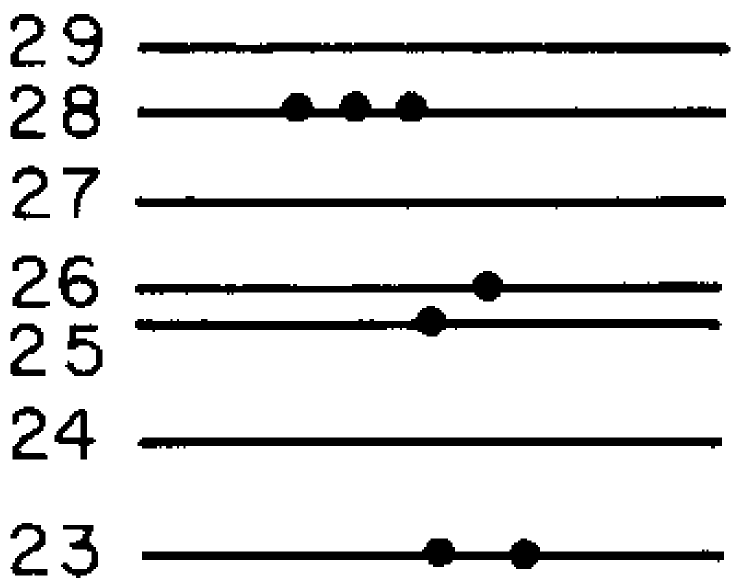
Medical Equipment I

2008-2009

First Law of Thermodynamics

- Total energy U = sum of particle energies

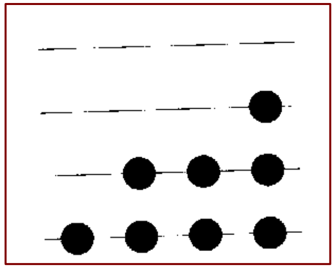
$$U = 2u_{23} + u_{25} + u_{26} + u_{28}$$

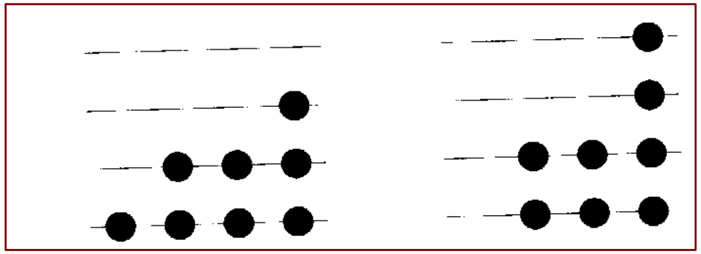


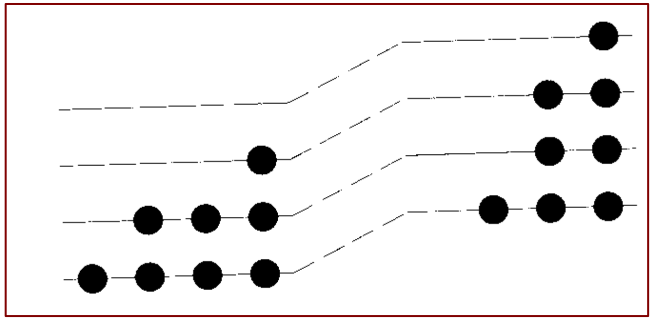
Exchange of Energy

- 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

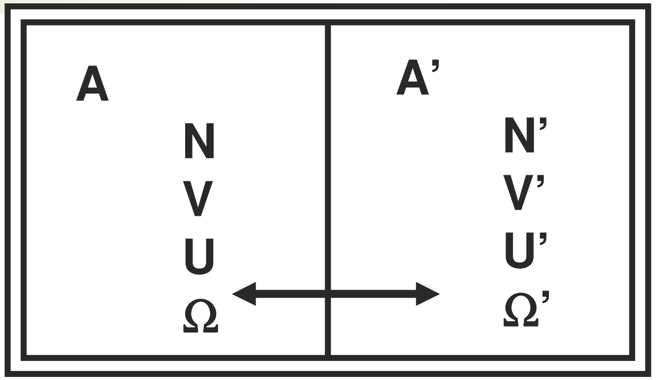
Basic Postulates

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

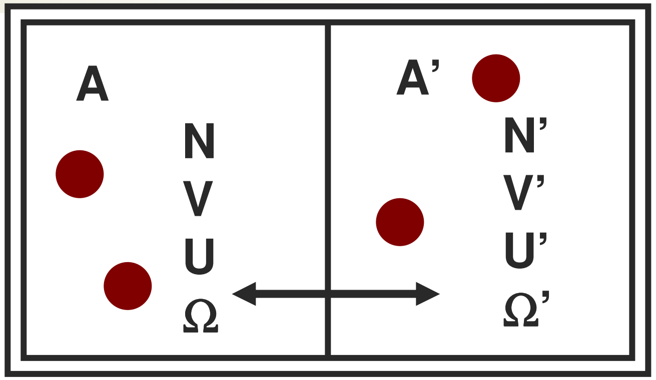
- Idealization: system that does not interact with surroundings
  - Adiabatic walls can never be realized
- Much can be learned by considering two systems that can exchange heat, work or particles but isolated from the rest of the universe
  - One of them is our system and the other can be taken to be 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
  - $P(U) = \Omega^*(U) / \Omega^*_{tot}$
  - $\Omega^*_{tot} = \Sigma_U \Omega^*(U)$
- Example: system of 2 particles in A and A'
  - Total energy U*=10u
  - Possible energy levels for particles = 1u, 2u, ..

Thermal Equilibrium

- Ex: $U = 2u \longrightarrow U' = U^* - U = 10u - 2u = 8u$
  - 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)

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

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

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

≠ 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= 1.38×10^{-23} 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

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

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

Assignment

- Problem assignment on web site