Sharif University of Technology
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Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 16

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Statistical Definitions

- Microstate: Exact specification of the system at microscopic level, it tells us all needed information.

- Microstate can be expanded by degeneracy or quantum states or molecular way.

- Macrostate: Listing the particles in energy levels for, N_j, with

$$\text{constraints } N = \sum_j N_j \text{ and } U = \sum_j N_j e_j$$

N = No. of particles, U = Energy of the system, and e_j = Energy level

- Degeneracy, g_j, is a way of describing the number of ways a particle can acquire the same energy level or state.

- Thus, a degenerate state is one in which there is more than one way of obtaining an energy level.

- In a non-degenerate state, there is only one way.

Example

- Information & constraints: $N = \sum_j N_j$ and $U = \sum_j N_j e_j$
- Consider a system with two independent particles and three energy levels , e_0, e_1, and e_2 with $N = 2$ and $U = 2$
- For $g_j = 0$:
  - Macro I: $N_0 = 1$, $N_1 = 0$, and $N_2 = 1$
  - Macro II: $N_0 = 0$, $N_1 = 2$, and $N_2 = 0$
- For $g_j = 1$:

$g_j = 2$ degeneracy

$e_0 = 0$	$2\boxed{1}$	$2\boxed{2}$
$e_1 = 1$	$1\boxed{1}$	$1\boxed{2}$
$e_2 = 2$	$0\boxed{1}$	$0\boxed{2}$

- Degeneracy of a system with only translational kinetic energy:
- C is the number of the translational kinetic energy.

$$g = \frac{(c+2)(c+1)}{2}$$

- Statistical models
  - Classical mechanics: particles are distinguishable, no limit for No. of particles per quantum state, Boltzmann-Model
  - Quantum mechanics: particles are indistinguishable
    - Maximum 1 per quantum state, Paoli (Fermi-Dirac)
    - No limit, Bose-Einstain

$$w = \text{ Thermodynamic Probability}$$

$$w_{Bol.} = N!\prod_j \left[\frac{g_j^{N_j}}{N_j!}\right]$$

$$w_{B.E.} = \prod_j \left[\frac{(g_j + N_j - 1)!}{(g_j - 1)!N_j!}\right]$$

$$w_{F.D.} = \prod_j \left[\frac{g_j!}{(g_j - N_j)!N_j!}\right]$$

$$w_{\text{Corrected Boltzmann}} = \frac{w_{\text{Boltzmann}}}{N!} = \prod_j \left[\frac{g_j^{N_j}}{N_j!}\right]$$

- Note! In reals ystems $N_j << g_j$