Sharif University of Technology
School of Mechanical Engineering
Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 17

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Thermodynamic Probability

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

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

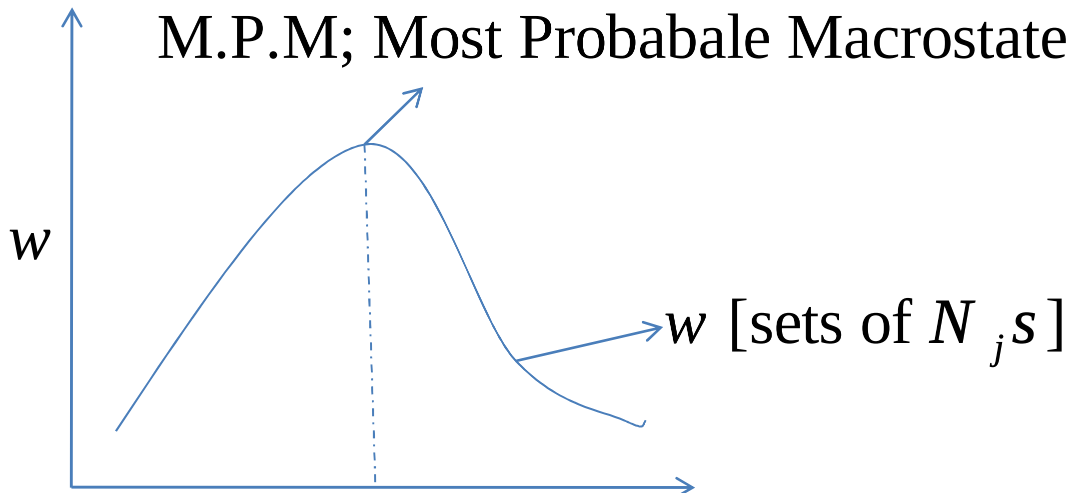
$$w_{B.E.} = \prod_j\left[\frac{(g_j + N_j - 1)!}{(g_j - 1)!N_j\,!}\right]$$

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

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

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

Thermodynamic Probability …



$$\left.\begin{array}{l}\ln\left(w_{Bol.}\right)=\ln\left(N!\right)+\sum_j\left[N_j\ln\left(g_j\right)-\ln\left(N_j!\right)\right]\\ \text{Stirling Law}\rightarrow\ln N!=N\ln N-N\end{array}\right\}$$

$$\rightarrow\ln w=N\ln N+\sum_j\left[N_j\ln g_j-N_j\ln N_j\right]$$

$$d\ln w=\sum_j\left[\ln g_j dN_j-\ln N_j dN_j-dN_j\right]=0$$

$$N_{j\text{ M.P.}}=g_j\,e^{-a}e^{-b\,e_j}$$

$$\begin{cases} \dfrac{w_{M.P.M-1}}{w_{M.P.M}} < 1 \\ \dfrac{w_{M.P.M+1}}{w_{M.P.M}} < 1 \end{cases}$$

$$d \ln w = \sum_j \left[\ln g_j dN_j - \ln N_j dN_j - dN_j \right] = 0$$

$$N_j / g_j \ll 1 \rightarrow e^{-a} \ll 1 \rightarrow e^{a} \gg 1$$

- Lagrangian undetermined multipliers may be used to solve such problems.

$$N = e^{-a} \sum g_j e^{-b e_j}$$

$$U = e^{-a} \sum e_j g_j e^{-b e_j}$$

$$\sum g_j e^{-b e_j} = \text{Partition Function} \equiv Z$$

$$N = e^{-a} \sum g_j e^{-b\,e_j} \rightarrow e^{-a} = \frac{N}{\sum g_j e^{-b\,e_j}} = \frac{N}{Z}$$

- Partition function (Z), statistical core, is sum of all quantum states.
- The thermodynamics properties such as *G*, *S*, and *H* may be stated in terms of *Z*.

$$e^{-a} = \frac{N}{Z} \quad \text{Eq. (1)}$$

$$N_{j\ \text{M.P.}} = \frac{N}{Z} g_j e^{-b\,e_j} \quad \text{Eq. (2)}$$

$$\left.\begin{aligned} U &= \sum_j N_j e_j = \frac{N}{Z} \sum g_j e_j e^{-b\,e_j} \quad \text{Eq. (3)} \\ Z &= \sum g_j e^{-b\,e_j} \rightarrow \frac{\partial Z}{\partial b} = -\sum e_j g_j e^{-b\,e_j} \quad \text{Eq. (4)} \end{aligned}\right\} \rightarrow U = -\frac{N}{Z}\left(\frac{\partial Z}{\partial b}\right)$$

$$U=\sum_j N_j e_j \rightarrow dU=\sum_j e_j dN_j+\sum_j N_j de_j$$

$$\rightarrow dU=\underbrace{\sum_j e_j dN_j}_{\text{I: Heat interaction}}+\underbrace{\sum_j N_j\left(\frac{de_j}{dV}\right)dV}_{\text{II: Work interaction}} \quad \text{Eq. (1)}$$

- I: dU variation due to particles distribution among the energy levels
- I: dU variation due to shift in energy No. at each energy level or quantum states group.

1st Law: $dU=dQ-dW$

For Quasi-Static Process: $dQ=Tds$ and $dW=PdV$

$$\text{Eq. (1)}\Rightarrow\begin{cases} dW=PdV=-\sum_j N_j\left(\frac{de_j}{dV}\right)dV \\ dQ=Tds=\sum_j e_j dN_j \end{cases}$$