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# Statistical Mechanics and Classical Thermodynamics.

## Section 5.5

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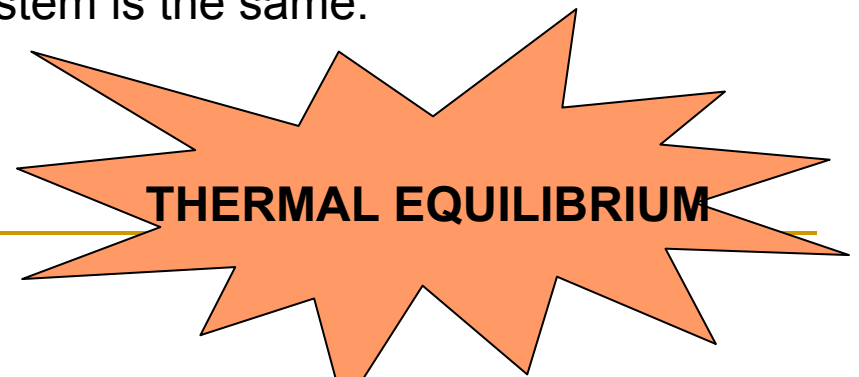
- *Dates back to 1902 when Gibbs published for the first time his discourse of statistical mechanics principle . He approached thermodynamics from the idea of particle statistics.*
  - Statistical Mechanics explains the following fundamental ideas about particles and their ensembles:
    - Fundamental configuration of particles:
      - Particle location and energy states.
    - Each configuration generates many microstates that are occupied by electrons having different spins.
    - Equilibrium between the configurations: multiplicity of the largest configuration.
    - Thermal equilibrium  $\longrightarrow$  Thermodynamics Principle
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# Continued..

- Equilibrium is defined as the tendency of a system to return back to its original state.
- Configurations with the greatest multiplicity indicates the highest probability of a system to exist in that particular state and is defined as \*System Equilibrium\*
- From lecture 10, multiplicity  $g(N,S)$  is defined as:

$$g(N,S) = \frac{N!}{\left(\frac{N}{2} + S\right)! \left(\frac{N}{2} - S\right)!}$$

- The multiplicity function  $g(N,S)$  is thus maximized at equilibrium keeping the total internal energy of a closed system constant.
- Temperature being the measure of internal energy of any system; at equilibrium temperature of each subsystem is the same.



- According to classical mechanics, the most complete description of a particle's energy and quantum state is given by the Schrödinger Equation.
- There have been two constraints laid down for particles enclosed in a closed system.
  - Conservation of energy
  - Conservation of mass

$$\sum E_i N_i = U$$

$$\sum N_i = N$$

Where  $E_i$  is the energy of the  $i^{\text{th}}$  state having  $N_i$  particles such that the total energy of the system is  $U$

- Having said that, the probability of finding a particle in a certain configuration having some energy  $E_i$  is simply the ratio of the multiplicity of the given configuration to the total multiplicity of the closed system.
- Based on Maxwell-Boltzmann Distribution this probability is defined as:

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_i e^{-\frac{E_i}{k_B T}}}$$

Where  $k_B$  defined as the Universal Boltzmann constant

- Thus the total energy of the system can be defined as the summation of the probability  $P_i$  of a particle to have energy  $E_i$  in the  $i^{\text{th}}$  state:

$$U(E) = \sum P_i E_i$$

- Using the Maxwell-Boltzmann Probability distribution function as defined in the previous slide, the total Energy can thus be expressed as

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Where  $\beta$  is  $1/k_B T$

- The classical partition function  $Z$  is henceforth defined as the sum over the Boltzmann factor

$$Z = \sum_i e^{-\frac{E_i}{k_B T}}$$

Therefore having said this, one can easily explain the thermodynamics of a particle enclosed in a closed system and its thermal equilibrium. This leads us to the Laws of Thermodynamics which are derived from the Postulates of Statistical Mechanics

# Laws of Thermodynamics

## ■ Zeroth Law:

- If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.

## ■ First Law:

- Conservation of energy for a closed system

- Energy can neither be created nor be destroyed. The change in the energy of a system is equivalent to the change in its internal energy and the work done by the system

$$dQ = dU + dW$$

## ■ Second Law:

- Entropy of a system remains conserved. The change in entropy of system leads to the change in its Energy ( for a reversible system) and is often represented as :

$$dS = \frac{dQ}{T}$$

## ■ Third Law:

- At absolute zero temperature, the entropy of the system becomes zero.

- Based on these laws of thermodynamic system, the fundamental thermodynamic potentials can be derived. We know that the internal energy,  $U$ , is dependent on intensive properties and the *randomness* or the Entropy,  $S$ , of the system.

Thus  $U$  can be clearly represented as:

$$U = U(S, V, N_1, \dots, N_i)$$

where  $V$  is the system volume.

Linking the thermodynamic parameter,  $T$ , with the statistical mechanical parameter,  $\beta$  and partition function  $Z$ , we can easily define the internal energy  $U$ :

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

as:

$$U = -\frac{\partial(\ln Z)}{\partial \beta}$$



- But  $\beta$  is defined as

$$\beta = \frac{1}{k_B T}$$

Thus,

$$\partial\beta = -\frac{1}{k_B T^2} \partial T$$

$$\partial(\ln T) = \frac{\partial T}{T}$$

$$\partial\beta = -\frac{1}{k_B T} \partial(\ln T)$$

Internal Energy in terms of classical parameters is thus represented as:

$$U = -k_B T \frac{\partial(\ln Z)}{\partial(\ln T)}$$

# Derivation of Maxwell relations using Legendre Transformations:

- Legendre Transformations are carried out for any mathematical system to express dependent variables in terms of intensive properties or a combination of intensive and extensive properties.
- If we start from our first equation expressing  $U$  as a function of entropy, volume and number of particles,  $U=U(S, V, N_i)$ ; we can use the method of partial differentiation to attain the following result.

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V, N, P} dS + \left( \frac{\partial U}{\partial V} \right)_{P, N, S} dV + \sum_i \left( \frac{\partial U}{\partial N_i} \right)_{V, N, P, S} dN_i$$

- For closed systems as in our case, we have assumed that the mass of the system is conserved, i.e. the total number of particles in the system remains unchanged which basically implies that  $\partial N_i$  is zero.

Thus the system reduces down to

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V,N,P} dS + \left( \frac{\partial U}{\partial V} \right)_{P,N,S} dV + \left( \frac{\partial U}{\partial P} \right)_{V,N,P} dP$$

With the following definition of the thermodynamic parameters:

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N,P} ; P = \left( \frac{\partial U}{\partial V} \right)_{P,N,S}$$

The first law of Thermodynamics in terms of intensive and extensive properties can be reduced to

$$dU = TdS - PdV$$

# Legendre Transformations...

- In order to derive the remaining Maxwell relations for thermodynamic potentials, the following mathematical manipulation is carried out:

We know:  $dU = TdS - PdV$  (i)

$$d(TS) = TdS + SdT \quad \text{(ii)}$$

$$d(PV) = PdV + VdP \quad \text{(iii)}$$

Thus using these 3 equations we can derive the following relations:

$$d(U + PV) = TdS + VdP$$

$$d(U + PV - TS) = VdP - SdT$$

$$d(U - TS) = -SdT - PdV$$

The new functions thus generated are defined as follows:

Enthalpy :  $H = U + PV$

Gibbs Energy :  $G = U + PV - TS = H - TS$

Helmholtz Potential :  $F = U - TS$

# Maxwell Relations:

- Once the Legendre transformations are made as shown in previous slide, we can relate the thermodynamic potentials as follows:

$$dU = TdS - PdV \quad (i)$$

$$dH = TdS + VdP \quad (ii)$$

$$dF = -SdT - PdV \quad (iii)$$

$$dG = -SdT + VdP \quad (iv)$$

- In order to derive Maxwell relations, let us first consider equation (i) from above.

Dividing the equation with  $dS$  and evaluating it at constant volume we get an expression for  $T$  as:

$$dU = TdS - PdV$$

$$T = \left( \frac{dU}{dS} \right)_v$$

Using similar approach by taking derivatives and keeping one of the variables constant, we can arrive at expressions for  $T, V, S$  and  $P$  in terms of the thermodynamic potentials. These relations are called the Maxwell relations.

Thus the Maxwell relations are obtained based on the equations (i) through (iv) and are presented below

$$\begin{aligned} T &= \left( \frac{\partial U}{\partial S} \right)_V & S &= - \left( \frac{\partial F}{\partial T} \right)_V \\ P &= - \left( \frac{\partial U}{\partial V} \right)_S & P &= - \left( \frac{\partial F}{\partial V} \right)_T \\ T &= \left( \frac{\partial H}{\partial S} \right)_P & S &= - \left( \frac{\partial G}{\partial T} \right)_P \\ V &= \left( \frac{\partial H}{\partial P} \right)_S & S &= - \left( \frac{\partial G}{\partial P} \right)_T \end{aligned}$$

Further mathematical manipulation is carried out on Maxwell relations as shown below to relate the slopes of each variable S,V,T and P with respect to each other.

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_S$$

$$\Rightarrow \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

$$\frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right)_P = \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right)_P$$

$$\Rightarrow \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

$$\frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)_T$$

$$\Rightarrow \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$$

$$\frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)_P = \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right)_T$$

$$\Rightarrow - \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P$$

# Statistical Mechanics and Thermodynamic Potentials:

- From previous slides we saw how thermodynamic potentials U, F, G and H were obtained using Maxwell Relations in terms of the T, V, S and P.
- Using Maxwell- Boltzmann Distribution theory one can express each of these four potentials in terms of the partition function Z, where Z is given by

$$Z = \sum_i e^{-\frac{E_i}{k_B T}}$$

- Let us derive these potentials in terms of Z.



# Deriving U:

- From previous slides, we know that U is the total energy of the system. Thus if the probability that a particle in the  $i^{\text{th}}$  state has energy  $E_i$  is given by  $P_i$ , then the total energy of the system is nothing but the summation over all the individual probabilities.
- Thus with further simplifications we can write U as a function of Z and T as shown in the right.  
We derived this previously (slides 8 and 9) to arrive at the following relationship, where  $k_B$  is the universal Boltzmann Constant.

$$U(E) = \sum_i P_i E_i$$

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_i e^{-\frac{E_i}{k_B T}}}$$

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$U = -k_B T \frac{\partial(\ln Z)}{\partial(\ln T)}$$

# Deriving Entropy, S:

- Consider a particle in the  $i^{\text{th}}$  energy state such that its energy is represented by  $E_i$ . Let  $x$  be any arbitrary variable ( it can be  $V, P, S$  or  $T$ ) that characterizes the  $i^{\text{th}}$  energy state. Let us assume that  $E_i$  changes in one dimension as a result of the quasi-static changes in  $x$  from  $x$  to  $x+dx$ . (*quasi-static process refers to a very slowly changing process such that it almost always appears to be in equilibrium*)

- The resulting change in energy can be defined as

$$\Delta E_i = \frac{\partial E_i}{\partial x} dx$$

- Work done by a system is defined as the change in the energy of a system due to displacement. When a system is displaced from its equilibrium due to an applied force, its internal energy is raised and is often described as  $dW$ , or the work done.

- According to Maxwell- Boltzmann Distribution, the mean value of any physical observable is given by:

$$y = \frac{\sum_i y_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

where  $\beta = 1/k_B T$

Thus, the macroscopic work  $dW$ , can be expressed in a similar fashion as:

$$dW = \frac{\sum_i -\Delta E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Substituting for  $\Delta E_i$  in the expression above, we get:

$$dW = \frac{\sum_i \left( -\frac{\partial E_i}{\partial x} dx \right) e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

- Using mathematical manipulations, we can express the derivative of  $E_i$  in terms of a summation series.

$$\sum_i e^{-\beta E_i} \left( -\frac{\partial E_i}{\partial x} dx \right) = -\frac{1}{\beta} \frac{\partial}{\partial x} \left( \sum_i e^{-\beta E_i} \right) dx$$
$$\Rightarrow -\frac{1}{\beta} \frac{\partial(Z)}{\partial x} dx$$

- Thus work  $dW$  can be expressed in terms of partition function as:

$$dW = \frac{\frac{1}{\beta} \frac{\partial(Z)}{\partial x}}{Z} dx$$
$$\Rightarrow dW = \frac{1}{\beta} \frac{\partial}{\partial x} (\ln Z) dx$$
$$\Rightarrow \frac{\partial(\ln Z)}{\partial x} dx = \beta dW$$

- Partition function,  $Z$ , being a function of  $x$  and  $\beta$ , can be expanded in the following form:

$$d(\ln Z) = \frac{\partial(\ln Z)}{\partial x} dx + \frac{\partial(\ln Z)}{\partial \beta} d\beta$$

From previous slides, we have shown that, average energy  $U$  can be expressed in terms of  $\beta$  and  $Z$ .

Making further mathematical manipulations, as shown, we can express  $Z$  in terms of  $\beta$  and  $U$ . Making substitution for  $U \delta \beta$ , we can express  $d(\ln Z)$  as shown in the equations on the right.

From the 1<sup>st</sup> law of Thermodynamics, change in internal energy,  $U$ , and the work done in the system is equivalent to the heat gained/lost.

With these substitutions,  $Z$  can be expressed in terms of  $U$  and  $Q$  as shown.

According to the 2<sup>nd</sup>. Law of thermo, the change in enthalpy of a system is equivalent to the change in  $Q$  per unit temperature at a constant  $T$ .

Integrating this system, we get an expression for the entropy,  $S$ , in terms of  $Z$  and  $U$  as shown  $\longrightarrow$

$$\frac{\partial(\ln Z)}{\partial \beta} d\beta = -U d\beta; \beta = \frac{1}{k_B T}$$

$$d(\ln Z) = \beta dW - U d\beta$$

$$d(U\beta) = U d\beta + \beta dU$$

$$\Rightarrow U d\beta = d(U\beta) - \beta dU$$

$$\Rightarrow d(\ln Z) = \beta dW - d(U\beta) + \beta dU$$

$$\Rightarrow d(\ln Z) = \beta(dW + dU) - d(U\beta)$$

$$dU + dW = dQ$$

$$\rightarrow d(\ln Z) = \beta dQ - d(U\beta)$$

$$\Rightarrow d(\ln Z + U\beta) = \beta dQ$$

$$dS = dQ/T = k_B \beta dQ$$

$$\Rightarrow dQ = dS / k_B \beta$$

$$\therefore dS = k_B d(\ln Z + U\beta)$$

$$\Rightarrow S = k_B \left( \ln Z + \frac{U}{k_B T} \right)$$

# Deriving Helmholtz potential, F:

From the expression derived for entropy in the previous slide, we can derive an expression for Helmholtz potential  $F$  in terms of  $Z$  and  $T$ .

$$dS = dQ/T = k_B \beta dQ$$

$$S = k_B \left( \ln Z + \frac{U}{k_B T} \right)$$

Start with the expression for  $S$ , and multiply throughout with  $T$ .

$$TS = k_B T (\ln Z) + U$$

$$\Rightarrow U - TS = -k_B T (\ln Z)$$

We know that  $F$  is defined as  $F = U - TS$ ,

Thus, substituting from above, an expression for  $F$  can be found.

$$F = U - TS$$

$$\Rightarrow F = -k_B T (\ln Z)$$

# Deriving Enthalpy and Gibb's Energy:

Knowing the expressions for U, S and F, we can derive equations for H and G using the Maxwell relations as defined in previous slides.

First, we need to find an expression for the product of pressure and volume in terms of Z.

Using maxwell equation of Entahlpy, H we get

Similarly for Gibb's free energy:

$$U = -k_B T \frac{\partial(\ln Z)}{\partial(\ln T)}$$

$$S = k_B \left( \ln Z + \frac{\partial(\ln Z)}{\partial(\ln T)} \right)$$

$$F = -k_B T (\ln Z)$$

$$PV = - \left( \frac{dF}{dV} \right)_T V$$

$$\Rightarrow PV = \frac{-d(-k_B T (\ln Z))}{dV/V}$$

$$\Rightarrow PV = \frac{k_B T d(\ln Z)}{d(\ln V)}$$

$$H = U + PV$$

$$\Rightarrow H = -k_B T \left[ \frac{\partial(\ln Z)}{\partial(\ln T)} + \frac{d(\ln Z)}{d(\ln V)} \right]$$

$$G = H - TS$$

$$\Rightarrow G = -k_B T \left[ \frac{\partial(\ln Z)}{\partial(\ln T)} + \frac{d(\ln Z)}{d(\ln V)} \right] - T k_B \left( \ln Z + \frac{\partial(\ln Z)}{\partial(\ln T)} \right)$$

$$\Rightarrow G = -k_B T \left( \ln Z - \frac{\partial(\ln Z)}{\partial(\ln V)} \right)$$

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