PHY 341/641
Thermodynamics and Statistical Physics

Lecture 7

1. Chemical potential
2. Gibbs-Duhem equation
3. Thermodynamic derivatives

Summary of thermodynamic potential functions

Name	Potential	Differential Form
Internal energy	$E(S,V,N)$	$dE = TdS - PdV + \mu dN$
Entropy	$S(E,V,N)$	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H(S,P,N) = E + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F(T,V,N) = E - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G(T,P,N) = F + PV$	$dG = -SdT + VdP + \mu dN$
Landau potential	$\Omega(T,V,\mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

Variables and functions:

Internal energy	U
Entropy	S
Pressure	P
Volume	V
Temperature	T
Number of particles	N
Chemical potential	μ

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Categories of functions and variables
Extensive → depends on system size
Intensive → independent of system size

Extensive		Intensive	
Number of particles	N	Temperature	T
Volume	V	Pressure	P
Entropy	S(U,V,N)	Density	ρ
Internal energy	U(S,V,N)	Chemical potential	μ
Enthalpy	H(S,P,N)		
Helmholz Free energy	F(T,V,N)		
Gibbs Free energy	G(T,P,N)		

Chemical potential

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

From first law of thermo evaluated at constant U and V :

$$\left(\frac{\partial S}{\partial N}\right)_{V,U} = \frac{-\left(\partial U / \partial N\right)_{S,V}}{\left(\partial U / \partial S\right)_{N,V}} = \frac{-\mu}{T}$$

Special relationship of μ to $G(T,P,N)$:

Argue that: $G(T,P,N) = Ng(T,P)$

$$\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu = g(T,P) \qquad \Rightarrow \mu = \frac{G(T,P,N)}{N}$$

In terms of Gibbs free energy density $g(T,P)$ (intensive function) --

Gibbs-Duhem equation:

$$dg = d\mu = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$$

$$dg = d\mu = -\frac{S}{N}dT + \frac{V}{N}dP \equiv -sdT + vdP$$

Some materials parameters based on thermodynamic variables and functions

Heat capacity at constant V :

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

In fact, this should be easy, but as we have seen the "natural" variables of U are *U=U(S,V,N)* and *S=S(U,V,N)*.

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial S}\right)_V = \left(\frac{\partial^2 U}{\partial S^2}\right)_V$$

$$\Rightarrow C_V = \frac{T}{\left(\partial^2 U / \partial S^2\right)_V} = \frac{\left(\partial U / \partial S\right)_V}{\left(\partial^2 U / \partial S^2\right)_V}$$

Some materials parameters based on thermodynamic variables and functions -- continued

Heat capacity at constant P:

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

This again should be easy, but as we have seen the "natural" variables of H are *H=H(S,P,N)* and *S=S(U,V,N)*.

$$T = \left(\frac{\partial H}{\partial S}\right)_P \qquad \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial^2 H}{\partial S^2}\right)_P$$

$$\Rightarrow C_P = \frac{T}{\left(\partial^2 H / \partial S^2\right)_P} = \frac{\left(\partial H / \partial S\right)_P}{\left(\partial^2 H / \partial S^2\right)_P}$$

Internal energy with its "natural variables": $U = U(S, V, N)$

$$dU = TdS - PdV + \mu dN = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$$

Example for ideal Gas :

$$U = \frac{NkT}{\gamma - 1} \qquad PV = NkT$$

$$S = \frac{Nk}{\gamma - 1} \ln\left(\frac{T}{T_1}\left(\frac{V}{V_1}\right)^{\gamma - 1}\right) \qquad \Rightarrow T = \frac{T_1 e^{\left(\frac{\gamma - 1}{Nk} S\right)}}{(V/V_1)^{\gamma - 1}}$$

$$U(S, V) = \frac{NkT_1}{\gamma - 1} \frac{e^{\left(\frac{\gamma - 1}{Nk} S\right)}}{(V/V_1)^{\gamma - 1}}$$

$$\text{Internal energy with its "un-natural variables":} \quad U = U(T, V, N)$$

$$dU = TdS - PdV + \mu dN = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV + \left(\frac{\partial U}{\partial N}\right)_{T,V} dN$$

$$\text{It is therefore convenient to assume:} \qquad S = S(T, V, N)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V,N} dT + \left(\frac{\partial S}{\partial V}\right)_{T,N} dV + \left(\frac{\partial S}{\partial N}\right)_{T,V} dN$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \qquad \left(\frac{\partial U}{\partial V}\right)_{T,N} = -P + T\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

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

Other useful thermodynamic derivatives

Isothermal compressibility:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

Isobaric expansion:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

Example from your text on functional dependences in black body radiation following analysis by Boltzmann in 1884.

Assume that we have a system characterized by:

Internal energy: $U(T,V) \equiv u(T)V$ Entropy: $S(T,V)$

Pressure: $P(T) \equiv \frac{1}{3}u(T)$

$$dS = \frac{V}{T}\frac{du}{dT}dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{V}{T}\frac{du}{dT}\right) = \left(\frac{\partial}{\partial T}\right)_V \left(\left(\frac{\partial S}{\partial V}\right)_T \right) \Rightarrow u(T) = KT^4, \; S(T,V) = \frac{4}{3}KT^3V$$