PHY 341/641
Thermodynamics and Statistical Physics

Lecture 6

1. Variable dependences of thermodynamic relationships
2. Thermodynamic energy functions
3. Maxwell relations

Variables and functions:

Internal energy U

Entropy S

Pressure P

Volume V

Temperature T

[Number of particles N] (fixed for now)

$$\text{Internal energy:} \quad U = U(S,V)$$

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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

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

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

Maxwell relation

$$\text{Entropy:} \qquad S = S(U,V)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

$$\text{From First Law:} \qquad dU = TdS - PdV$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

Note: This is consistent with internal energy derivatives:

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

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	$\Omega(T,V,\mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

$$\text{Enthalpy}: \quad H = H(S,P) = U + PV$$

$$dH = dU + PdV + VdP = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

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

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

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

Maxwell relation

Helmholz free energy: $F = F(T,V) = U - TS$

$$dF = dU - TdS - SdT = -SdT - PdV = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

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

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

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

Maxwell relation

Gibbs free energy: $G = G(T,P) = F + PV$

$$dG = dF + PdV + VdP = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

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

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

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

Maxwell relation

Maxwell's relations for a fixed number of particles

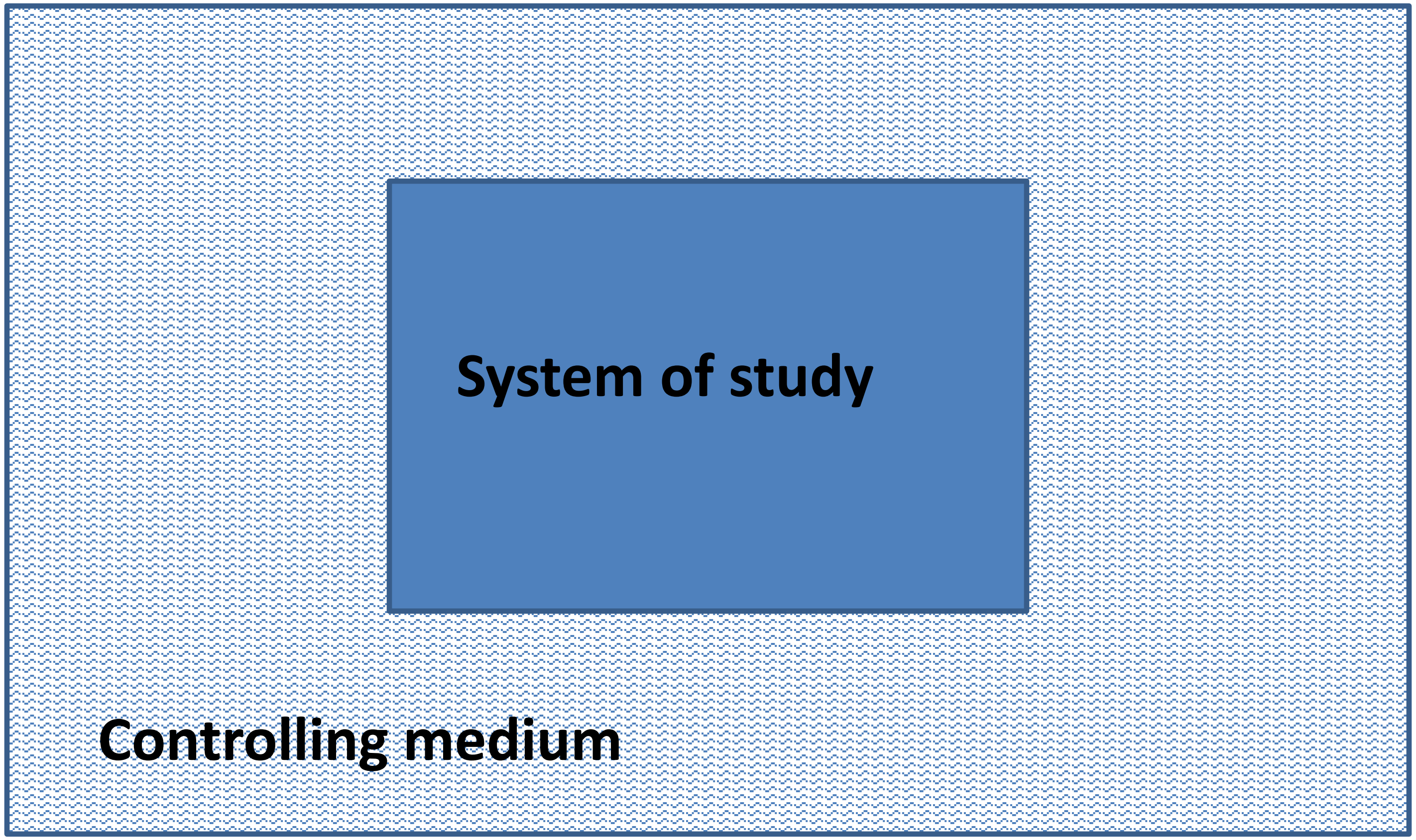
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

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

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

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

Realization of variable control by use of "controlling medium"



Variables and functions:

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

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

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	$\Omega(T,V,\mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

Entropy with variable particles: $S = S(U, V, N)$

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

From First Law: $dU = TdS - PdV + \mu dN$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

$$\text{Internal energy with variable particles:} \quad U = U(S, V, N)$$

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

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

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

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

Additional Maxwell's relations:

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

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

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

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

Check consistency :

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

From internal energy : $\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$

Is this consistent???

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

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