

PHY 341/641
Thermodynamics and Statistical Physics

Lecture 6

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

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Variables and functions:

Internal energy U

Entropy S

Pressure P

Volume V

Temperature T

[Number of particles N] (fixed for now)

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Internal energy: $U = U(S, V)$

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

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

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

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

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Entropy: $S = S(U, V)$

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

From First Law: $dU = TdS - PdV$

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

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

Note: This is consistent with internal energy derivatives:

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

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

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Enthalpy: $H = H(S, P) = U + PV$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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Maxwell's relations for a fixed number of particles

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

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

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

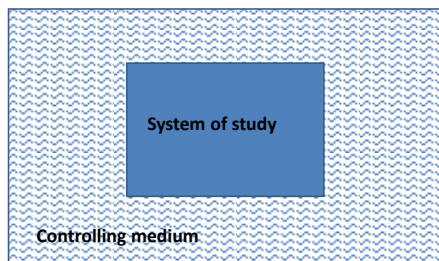
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

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Realization of variable control by use of "controlling medium"



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Variables and functions:

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

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

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

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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: $dU = TdS - PdV + \mu dN$

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

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

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

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

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

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

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

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Additional Maxwell's relations:

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

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

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

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

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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???

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

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

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