

PHY 770 -- Statistical Mechanics
12:30-1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
 Course Webpage: <http://www.wfu.edu/~natalie/s14phy770>

Lecture 6 -- Chapter 4
Review of Thermodynamics -- continued

1. Thermodynamics of phase transitions
2. Phase equilibria; Clausius-Clapeyron equation

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PHY 770 Statistical Mechanics

TR 12:30-1:45 PM OPL 107 <http://www.wfu.edu/~natalie/s14phy770/>

Instructor: Natalie Holzwarth Phone: 758-5510 Office: 300 OPL e-mail: natalie@wfu.edu

Course schedule for Spring 2014

(Preliminary schedule -- subject to frequent adjustment.) Please note that makeup lectures (indicated in red) are scheduled for Tuesdays or Thursdays at 11 AM - 12:15 PM in Olin 107.

Lecture date	Text Reading	Topic	Assign.	Due date
1 Tue: 01/14/2014	Chap. 3	Review of macroscopic thermodynamics	a1	02/04/2014
2 Thu: 01/16/2014	Chap. 3	Review of macroscopic thermodynamics	a2	02/04/2014
3 Tue: 01/21/2014	Chap. 3	Thermodynamic potentials	a3	02/04/2014
4 Tue: 01/21/2014	Chap. 3	Thermodynamic stability	a4	02/04/2014
5 Thu: 01/23/2014	Chap. 3	Thermodynamic stability	a5	02/04/2014
Tue: 01/28/2014		IAPW out of town - no class		
Thu: 01/30/2014		IAPW out of town - no class		
6 Tue: 02/04/2014	Chap. 4	Phase transitions	a6	02/11/2014
7 Thu: 02/06/2014	Chap. 2	Microscopic analysis of entropy	a7	02/11/2014
8 Thu: 02/06/2014	Chap. 2	Microscopic analysis of entropy	a8	02/11/2014

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News

Peter Diemer and Prof. Jurchescu receive Wake Forest Innovation Award

Article by Cory Hewitt and Prof. Carroll featured on the cover of Synthetic Metals

The Department Welcomes our new Administrative Assistant, Karen Logan

Events

Wed. Feb. 5, 2014
 Organic Materials
 Prof. Stangelin, London
 4:00 PM in Olin 101
 Reception:
 3:30 PM in Olin Lobby

Profiles in Physics

Wake Forest Physics... Nationally recognized for teaching excellence; internationally respected for

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WFU Physics Colloquium

TITLE: Unravelling electronic processes and phenomena in organic materials through polymer scientists' tools

SPEAKER: [Dr. Natalie Stingelin](#),
*Department of Materials and Centre for Plastic Electronics,
 Imperial College London, UK*

TIME: Wednesday February 5, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory


Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

In the past decade, significant progress has been made in the fabrication of organic semiconductor thin-film devices predominantly due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist. Key to commercial success is to make it technological practice to exploit the touted potential for low-cost manufacturing of these functional materials. This requires intimate knowledge of relevant structure/processing/performance interrelations. Here, examples are

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Thermodynamics of phase equilibria and transitions

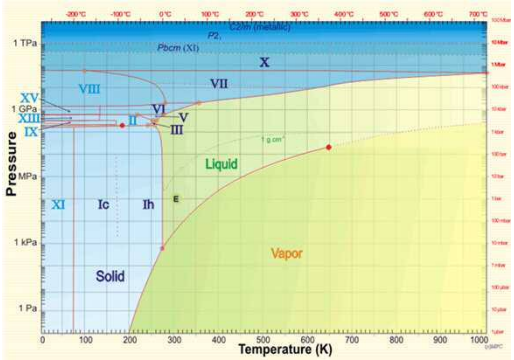


Initially, focus on one component systems with multiple phases

Example: water
 Phase I: Solid
 Phase II: Liquid
 Phase III: Gas

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Phase diagram of water (<http://www1.lsbu.ac.uk/water/phase.html>)



The diagram plots Pressure (Pa) on a logarithmic scale from 1 Pa to 1 TPa against Temperature (K) from 0 to 1000 K. It shows the boundaries between various phases of water, including solid (Ic, Ih, Ii, II, III, V, VI, VII, VIII, IX, X, XI, XII, XV), liquid, and vapor. Key points like the triple point (0.01°C, 611 Pa) and the critical point (374°C, 218 MPa) are indicated.

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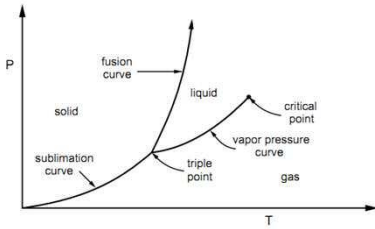
Comments about phase transitions at constant T and P (or more generally T and Y).

- $G^i(T,Y)=G^i(T,Y)$ and $\mu^i(T,Y)=\mu^i(T,Y)$
- Coexistence line defined by $Y^{i-II}_{coexist}(T)$.
- In this case, the coexistence of three phases is only possible at a point in the Y,T plane.
- Phase transition can be first order when G has discontinuous first derivatives
- Phase transition can be second order when G has continuous first derivatives

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Thermodynamic description of the equilibrium between two forms “phases” of a material under conditions of constant T and P

Review of Gibb's Free energy :

$$G = G(T, P, N) \equiv U - TS + PV = A + PV$$

$$dG = -SdT + VdP + \mu dN$$

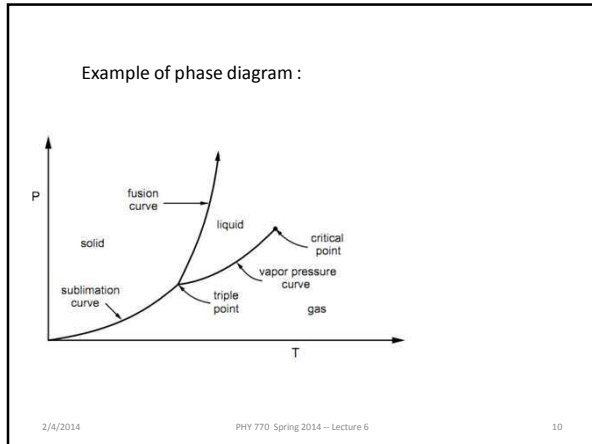
$$\mu = \mu(T, P) = \frac{G}{N} \equiv g(T, P)$$

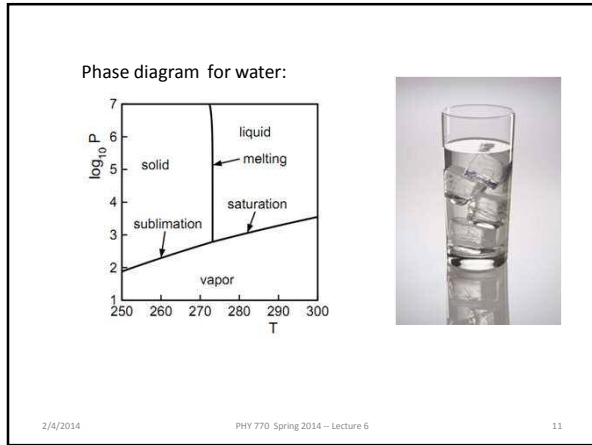
$$\left(\frac{\partial g}{\partial T}\right)_P = -\frac{S}{N} \quad \left(\frac{\partial g}{\partial P}\right)_T = \frac{V}{N}$$

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Consider a two phase system at constant T and P

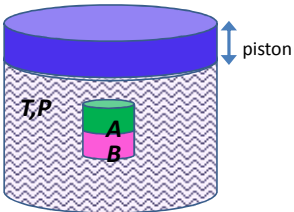
Note: A and B denote different phases (previously I and II)

$$dG_A + dG_B = 0$$

$$-S_A dT + V_A dP + g_A dN_A - S_B dT + V_B dP + g_B dN_B = 0$$

$$\Rightarrow g_A dN_A + g_B dN_B = 0$$

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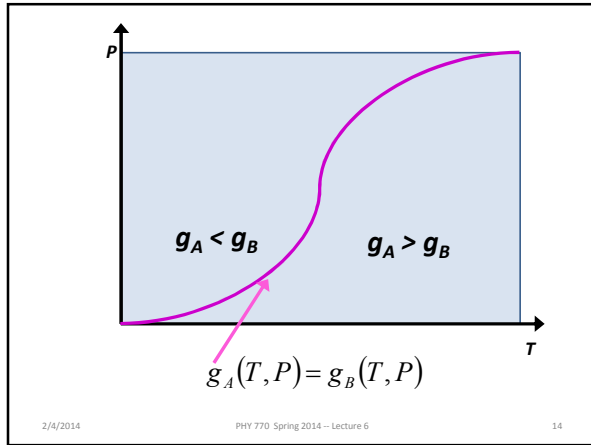
$g_A dN_A + g_B dN_B = 0$

Assuming: $N_A + N_B = N$

$\Rightarrow dN_B = -dN_A$

$\Rightarrow (g_A - g_B) dN_A = 0 \Rightarrow g_A = g_B$

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Clausius-Clapeyron Equation

$g_A(T, P) = g_B(T, P)$

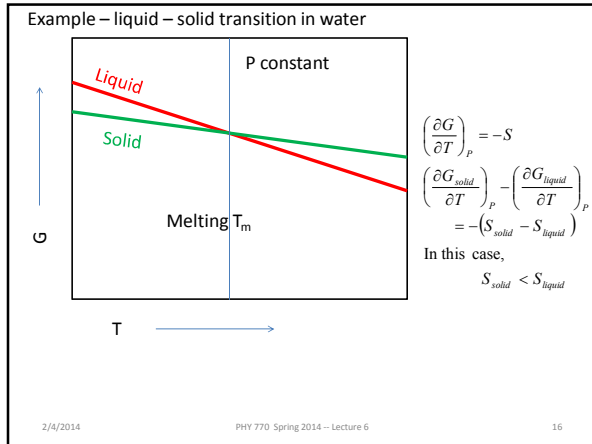
$dg_A(T, P) = dg_B(T, P)$

$$\left\{ \left(\frac{\partial g_A}{\partial T} \right)_P - \left(\frac{\partial g_B}{\partial T} \right)_P \right\} dT + \left\{ \left(\frac{\partial g_A}{\partial P} \right)_T - \left(\frac{\partial g_B}{\partial P} \right)_T \right\} dP = 0$$

$$- \left\{ \frac{S_A}{N_A} - \frac{S_B}{N_B} \right\} dT + \left\{ \frac{V_A}{N_A} - \frac{V_B}{N_B} \right\} dP = 0$$

$\Rightarrow \left(\frac{dP}{dT} \right)_{\text{coexist}} = \frac{\Delta(S/N)}{\Delta(V/N)}$

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Clausius - Clapeyron Equation

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{\Delta(S/N)}{\Delta(V/N)}$$

For a phase change involving the "Latent Heat":

$$\Delta S = \frac{L_{AB}}{T}$$

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{L_{AB}}{T(V_A - V_B)}$$

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More details

In terms of enthalpy : $G = H - TS$

At the coexistence condition :

$$G_A = H_A - TS_A = G_B = H_B - TS_B$$

$$\Delta H \equiv H_{AB} \equiv H_B - H_A = T\Delta S$$

$$\Delta S = \frac{H_{AB}}{T}$$

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{H_{AB}}{T(V_{AB})}$$

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Clausius - Clapeyron Equation

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{H_{AB}}{T(V_A - V_B)}$$

Example : A ≡ ice B ≡ water

$H_{AB} = 3.35 \times 10^5 \text{ J / kg}$ $T = 273.15 \text{ K}$

$V_A = 1.09070 \times 10^{-3} \text{ m}^3 / \text{kg}$

$V_B = 1.00013 \times 10^{-3} \text{ m}^3 / \text{kg}$

$$\left(\frac{dP}{dT}\right)_{coexist} = -1.35 \times 10^7 \text{ Pa / K}$$

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Clausius - Clapeyron Equation

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{H_{AB}}{T(V_A - V_B)}$$

Example : A ≡ vapor B ≡ water

$H_{AB} = 2.257 \times 10^6 \text{ J / kg}$ $T = 373.15 \text{ K}$

$V_A = 1.673 \text{ m}^3 / \text{kg}$

$V_B = 1.043 \times 10^{-3} \text{ m}^3 / \text{kg}$

$$\left(\frac{dP}{dT}\right)_{coexist} = 3.62 \times 10^3 \text{ Pa / K}$$

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Clausius - Clapeyron Equation -- approximate $P(T)$ for liquid - gas coexistence

$$\frac{dP}{dT} = \frac{L_{AB}}{T(V_A - V_B)}$$

Example : A ≡ vapor B ≡ water

$L_{AB} = 2.257 \times 10^6 \text{ J / kg} = 40.7 \times 10^3 \text{ J/mole}$ $T \geq 373.15 \text{ K}$

$V_A \approx \frac{R_M T}{P}$ (per mole) $R_M = kN_{Av}$

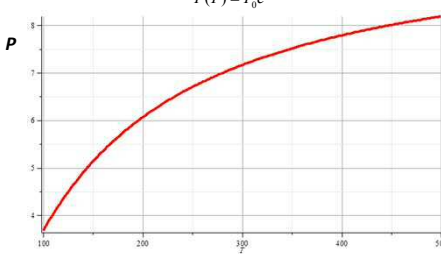
$V_B \approx 0$

$$\frac{dP}{dT} = \frac{L_{AB}}{R_M} \frac{P}{T^2} \Rightarrow \frac{dP}{P} = \frac{L_{AB}}{R_M} \frac{dT}{T^2}$$

$$\ln(P) = \text{constant} - \frac{L_{AB}}{R_M T} \Rightarrow P(T) = P_0 e^{-L_{AB}/R_M T}$$

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Approximate liquid-gas vaporization curve from Clausius-Clapeyron equation:

$$P(T) = P_0 e^{-L_{lg}/R_u T}$$


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The van der Waals equation of state
 -- More realistic than the ideal gas law; contains some of the correct attributes for liquid-gas phase transitions.

Ideal gas equation of state: $PV = NkT$

van der Waals equation of state: $\left(P + a \frac{N^2}{V^2}\right)(V - bN) = NkT$

here a, b are material - dependent parameters

Dimensionless variables:

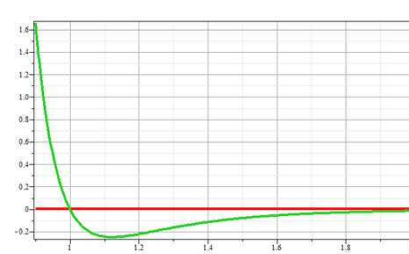
$$\tilde{P} \equiv 27 \left(\frac{b^2}{a}\right) \frac{P}{P_c} \quad \tilde{T} \equiv \frac{27}{8} \left(\frac{b}{a}\right) kT \frac{T}{T_c} \quad \tilde{\rho} \equiv 3b \frac{N}{V} \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

van der Waals equation of state: $\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3 - \tilde{\rho}} - 3\tilde{\rho}^2$

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Some motivation for van der Waals equation of state
 Johannes Diderik van der Waals – Ph. D. Thesis written in 1873 (The Netherlands) -- received Nobel Prize in 1910

General potential between two particles:



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van der Waals equation of state: $P = \frac{NkT}{(V - bN)} - a \frac{N^2}{V^2}$

Substance	a (10^{-30}eV m^3)	b (10^{-30}m^3)
water	9.55	50.7
SO ₂	11.9	94.7
CO ₂	6.3	71.3
O ₂	2.38	52.9
Ar	2.36	53.8
N ₂	2.36	64.3
H ₂	0.428	44.3
⁴ He	0.0597	39.4

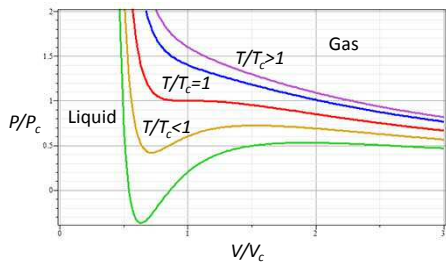
From: Baierlein, *Thermal Physics*

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van der Waals equation of state: $P = \frac{NkT}{(V - bN)} - a \frac{N^2}{V^2}$
 $P/P_c = \frac{8(V/V_c)T/T_c - 3(V/V_c)^2}{3 - (V/V_c)}$

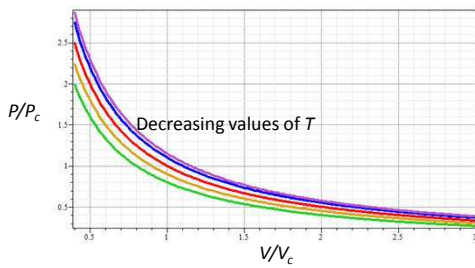


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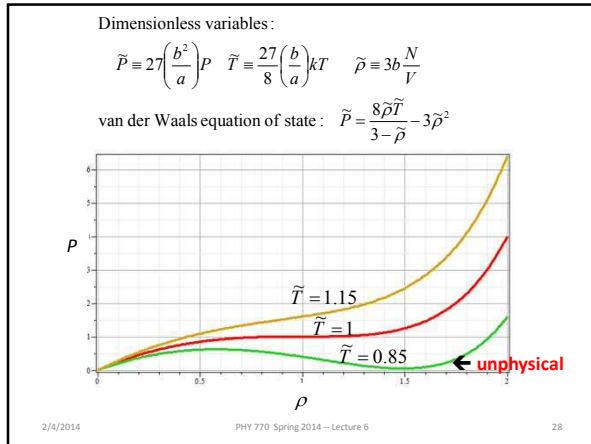
For comparison -- ideal gas equation of state: $P = \frac{NkT}{V}$

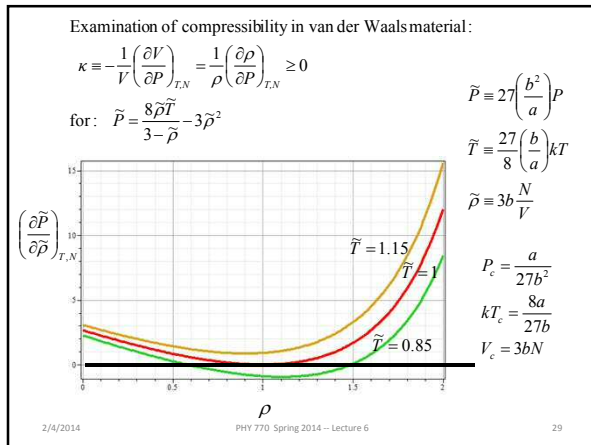


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Behavior of the thermodynamic potentials for the van der Waals equation of state

In terms of unscaled variables: $\left(P + a \frac{N^2}{V^2} \right) (V - bN) = NkT$

Helmholz free energy A : $P = - \left(\frac{\partial A}{\partial V} \right)_{T,N}$

$$A = - \int^V P dV + NkT w(T)$$

$$= - \int^V \left(\frac{NkT}{V - bN} - a \frac{N^2}{V^2} \right) dV + NkT w(T)$$

$$= -NkT \ln(V - bN) - a \frac{N^2}{V} + NkT w(T)$$

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Behavior of the thermodynamic potentials for the van der Waals equation of state

$$A = -NkT \ln(V - bN) - a \frac{N^2}{V} + NkT w(T)$$

Gibb's free energy :

$$G = A + PV = -NkT \ln(V - bN) - a \frac{N^2}{V} + PV + NkT w(T)$$

In terms of scaled variables with

$$\tilde{g} \equiv \frac{G}{N} \frac{8}{3kT_c} = \frac{G}{N} \frac{9b}{a} \quad \tilde{P} \equiv 27 \left(\frac{b^2}{a} \right) P \quad \tilde{T} \equiv \frac{27}{8} \left(\frac{b}{a} \right) kT \quad \tilde{\rho} \equiv 3b \frac{N}{V}$$

$$\tilde{g} = -\frac{8}{3} \tilde{T} \ln \left(\left(\frac{3}{\tilde{\rho}} - 1 \right) bN \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w'(\tilde{T})$$

$$= -\frac{8}{3} \tilde{T} \ln \left(\frac{3}{\tilde{\rho}} - 1 \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w''(\tilde{T}, N)$$

Note : In principle $g = g(P, T)$ so that we should eliminate the N and V dependence using the

van der Waals equation of state : $P = \frac{NkT}{(V - bN)} - a \frac{N^2}{V^2}$

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Behavior of Gibbs chemical potential :

$$\tilde{g}(\tilde{T}, \tilde{P}, \tilde{\rho}) = -\frac{8}{3} \tilde{T} \ln \left(\left(\frac{3}{\tilde{\rho}} - 1 \right) bN \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w'(\tilde{T})$$

$$= -\frac{8}{3} \tilde{T} \ln \left(\frac{3}{\tilde{\rho}} - 1 \right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w''(\tilde{T}, N)$$

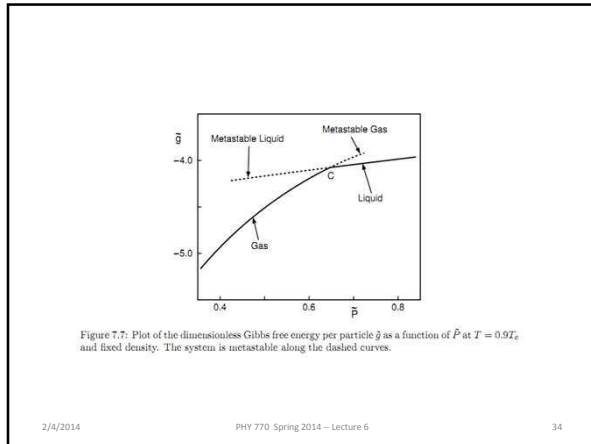
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Gibbs chemical potential at coexistence point

$\tilde{T} = 0.9 \quad \tilde{P} = 0.647$

gas liquid

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Analysis of gas-liquid coexistence conditions

General conditions on Gibbs free energy

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

$$\left(\frac{\partial g}{\partial P}\right)_T = \frac{V}{N} = \frac{1}{\rho}$$

When both liquid and gas phases are present at fixed T :

$$g(P_{liq}, T) - g(P_{gas}, T) = \int_{P_{gas}}^{P_{liq}} \left(\frac{\partial g}{\partial P}\right)_T dP = \int_{P_{gas}}^{P_{liq}} \frac{dP}{\rho}$$

Integrating by parts :

$$\int_{P_{gas}}^{P_{liq}} \frac{dP}{\rho} = \int_{P_{gas}}^{P_{liq}} \left\{ d\left(\frac{P}{\rho}\right) - Pd\left(\frac{1}{\rho}\right) \right\} = \frac{P(\rho_{liq}, T)}{\rho_{liq}} - \frac{P(\rho_{gas}, T)}{\rho_{gas}} - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} PdV$$

$$\Rightarrow g(P_{liq}, T) - g(P_{gas}, T) = \frac{P(\rho_{liq}, T)}{\rho_{liq}} - \frac{P(\rho_{gas}, T)}{\rho_{gas}} - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} PdV$$

Analysis of gas-liquid coexistence conditions -- continued

On coexistence curve :

$$g(P_{liq}, T) - g(P_{gas}, T) = 0 \quad \text{and} \quad P = P_{liq} = P_{gas}$$

$$g(P_{liq}, T) - g(P_{gas}, T) = \frac{P(\rho_{liq}, T)}{\rho_{liq}} - \frac{P(\rho_{gas}, T)}{\rho_{gas}} - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} PdV$$

$$\Rightarrow \frac{P}{N} (V_{liq} - V_{gas}) - \frac{1}{N} \int_{V_{gas}}^{V_{liq}} PdV = 0$$

