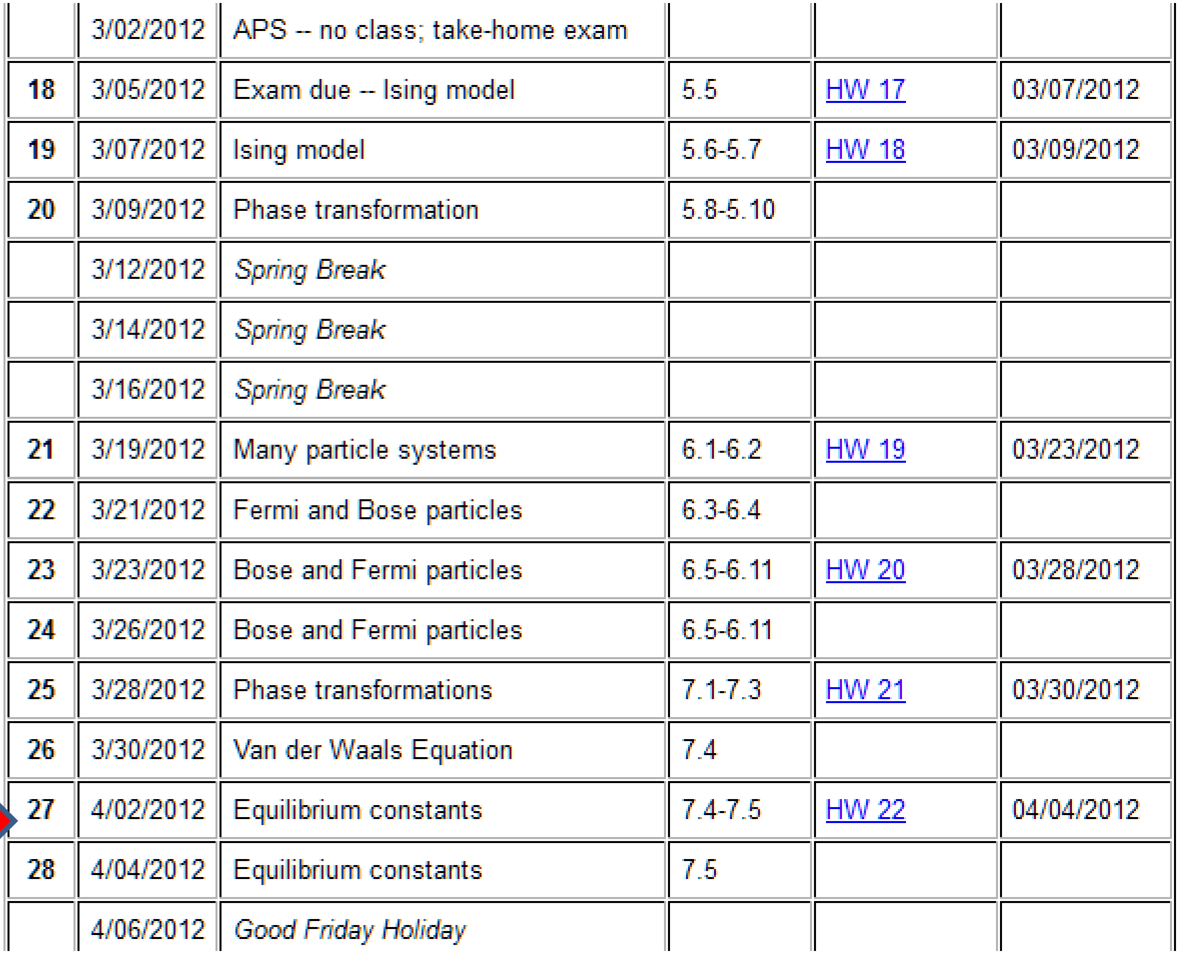
PHY 341/641
Thermodynamics and Statistical Physics

Lecture 27

Chemical potentials and phase equilibria (Chapter 7 in STP)

- Van der Waals equation of state
- Chemical reactions

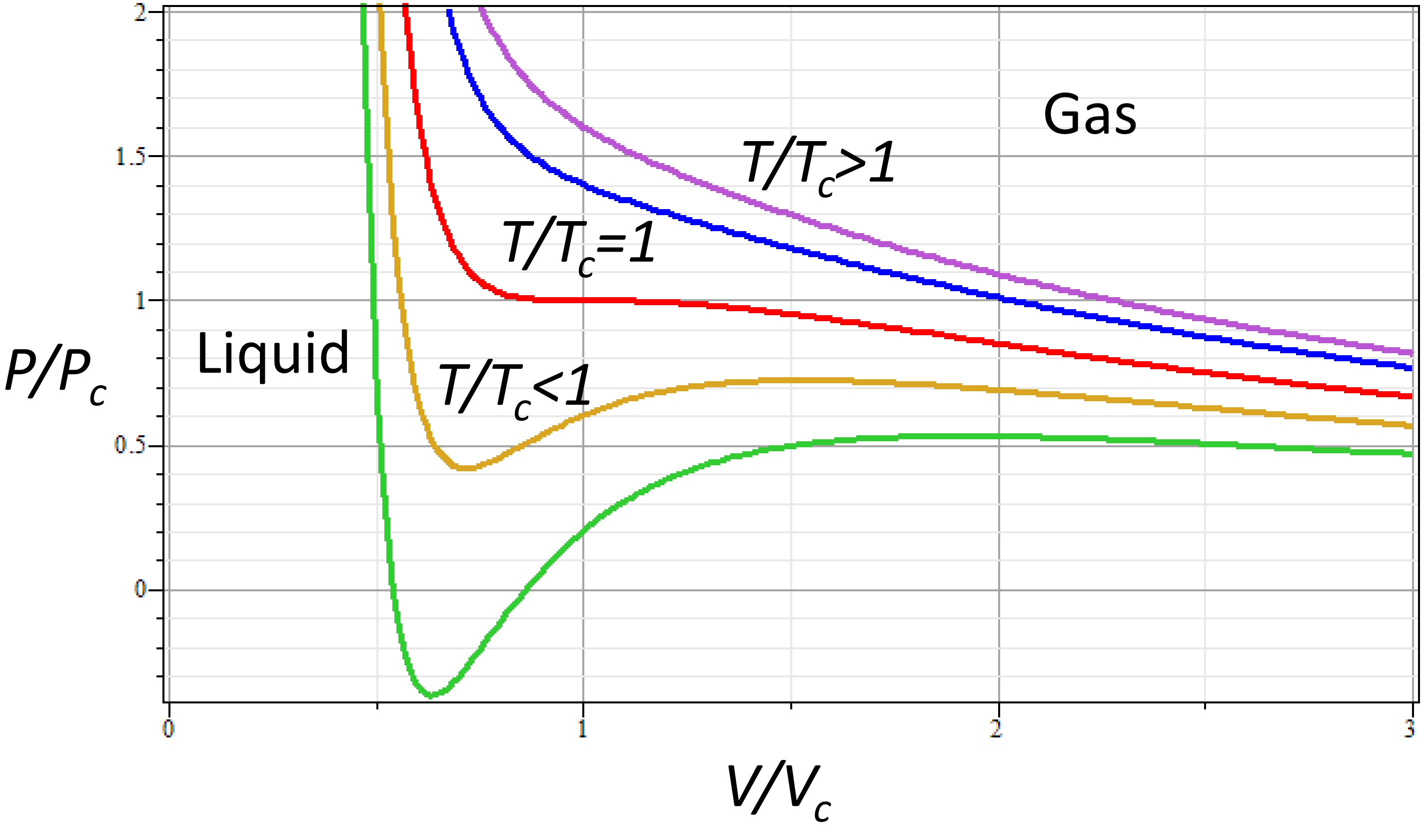


	3/02/2012	APS -- no class; take-home exam			
18	3/05/2012	Exam due -- Ising model	5.5	HW 17	03/07/2012
19	3/07/2012	Ising model	5.6-5.7	HW 18	03/09/2012
20	3/09/2012	Phase transformation	5.8-5.10		
	3/12/2012	*Spring Break*			
	3/14/2012	*Spring Break*			
	3/16/2012	*Spring Break*			
21	3/19/2012	Many particle systems	6.1-6.2	HW 19	03/23/2012
22	3/21/2012	Fermi and Bose particles	6.3-6.4		
23	3/23/2012	Bose and Fermi particles	6.5-6.11	HW 20	03/28/2012
24	3/26/2012	Bose and Fermi particles	6.5-6.11		
25	3/28/2012	Phase transformations	7.1-7.3	HW 21	03/30/2012
26	3/30/2012	Van der Waals Equation	7.4		
27	4/02/2012	Equilibrium constants	7.4-7.5	HW 22	04/04/2012
28	4/04/2012	Equilibrium constants	7.5		
	4/06/2012	*Good Friday Holiday*			

Second exam: April 9-13

-- student presentations 4/30, 5/2 (need to pick topics) van der Waals equation of state: $P = \frac{NkT}{(V - bN)} - a\frac{N^2}{V^2}$

$$P_c = \frac{a}{27b^2} \qquad kT_c = \frac{8a}{27b} \qquad V_c = 3bN$$



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

$$F \quad = -NkT\ln\left(V-bN\right) - a\frac{N^2}{V} + NkTw(T)$$

Gibb's free energy:

$$G = F + PV = -NkT\ln\left(V-bN\right) - a\frac{N^2}{V} + PV + NkTw(T)$$

$$g = \frac{G}{N} = -kT\ln\left(V-bN\right) - a\frac{N}{V} + \frac{PV}{N} + kTw(T)$$

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: $P = \frac{NkT}{\left(V-bN\right)} - a\frac{N^2}{V^2}$

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

Using scaled variables with

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

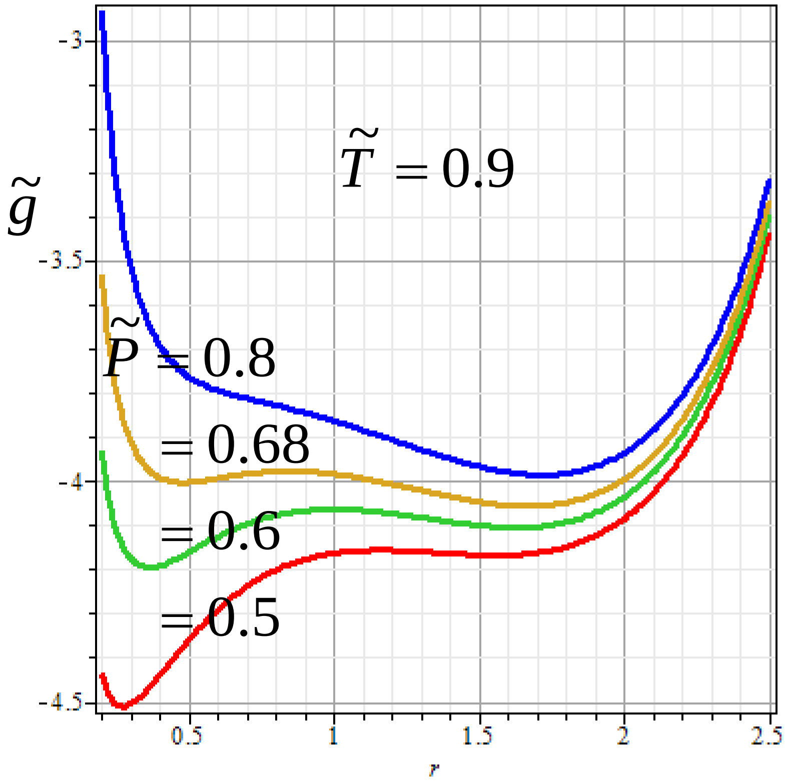
$$G = F + PV = -NkT\ln\left(V - bN\right) - a\frac{N^2}{V} + PV + NkTw(T)$$

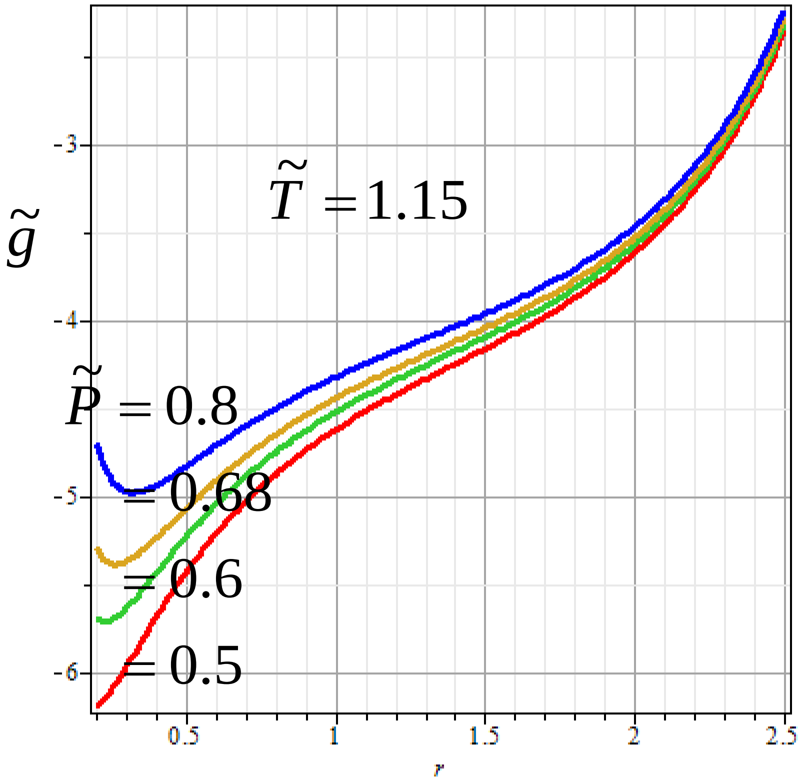
$$\tilde{g} = -\frac{8}{3}\tilde{T}\ln\left(\left(\frac{3}{\tilde{\rho}} - 1\right)bN\right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w'(\tilde{T})$$

Behavior of Gibbs chemical potential :

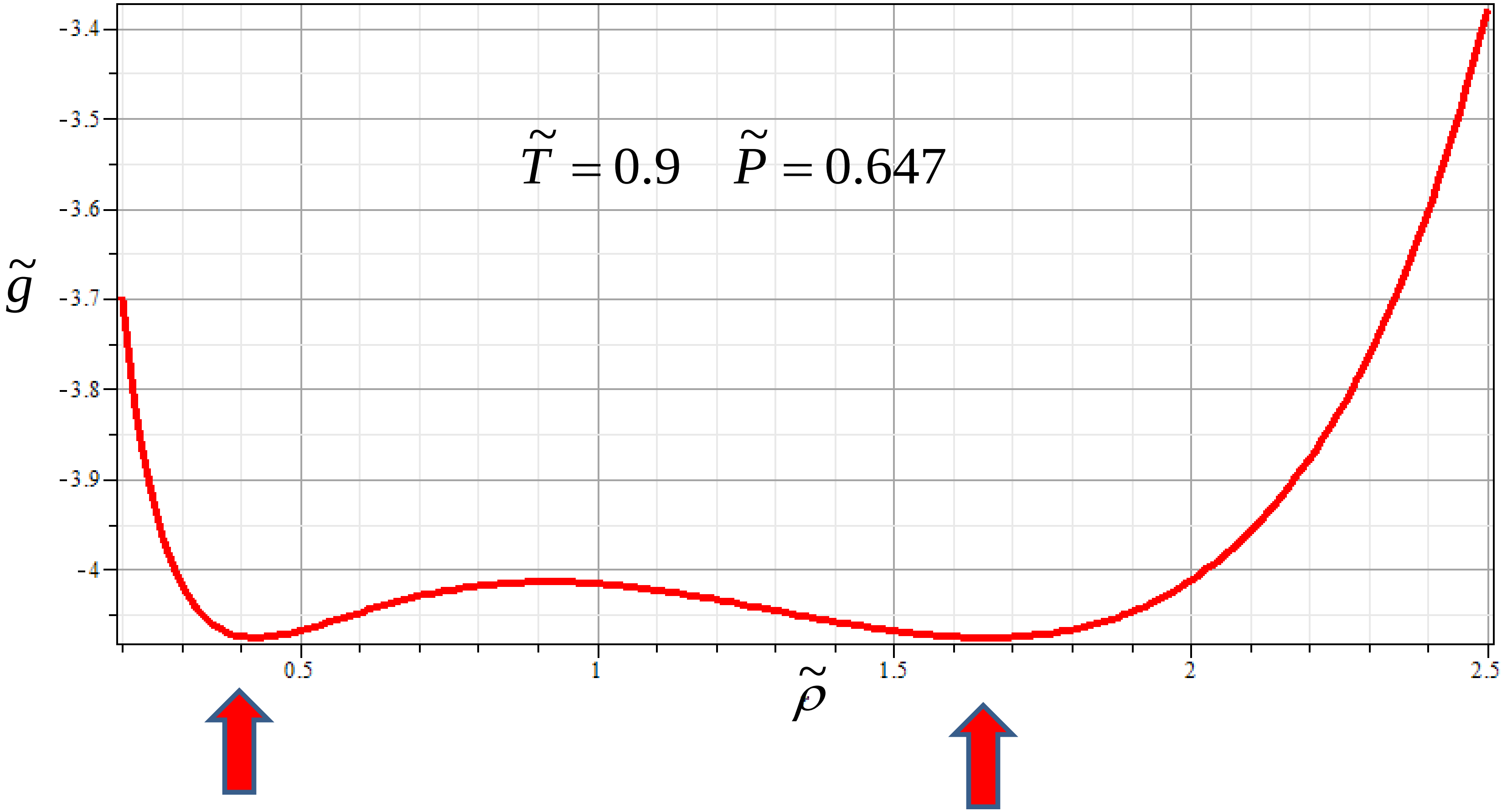
$$\tilde{g}(\tilde{T},\tilde{P},\tilde{\rho}) = -\frac{8}{3}\tilde{T}\ln\left(\left(\frac{3}{\tilde{\rho}}-1\right)bN\right) - 3\tilde{\rho} + \frac{\tilde{P}}{\tilde{\rho}} + w'(\tilde{T})$$

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





Gibbs chemical potential at coexistence point



gas

liquid

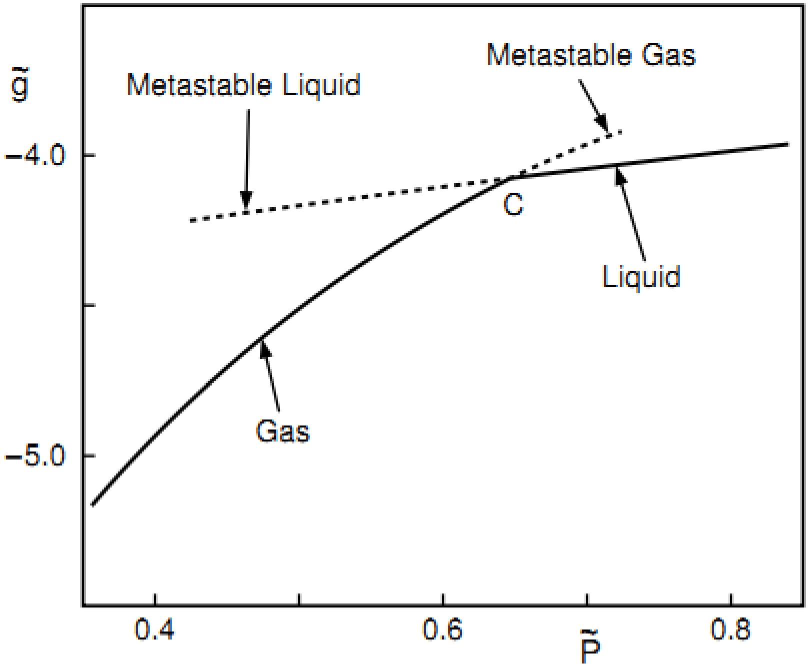


Figure 7.7: Plot of the dimensionless Gibbs free energy per particle $\tilde{g}$ as a function of $\tilde{P}$ at $T = 0.9T_c$ and fixed density. The system is metastable along the dashed curves.

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 :

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

Integating 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:

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

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

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

$$\tilde{P}\left(\tilde{V}_{liq}-\tilde{V}_{gas}\right)-\int_{\tilde{V}_{gas}}^{\tilde{V}_{liq}}\tilde{P}\,d\tilde{V}=0$$

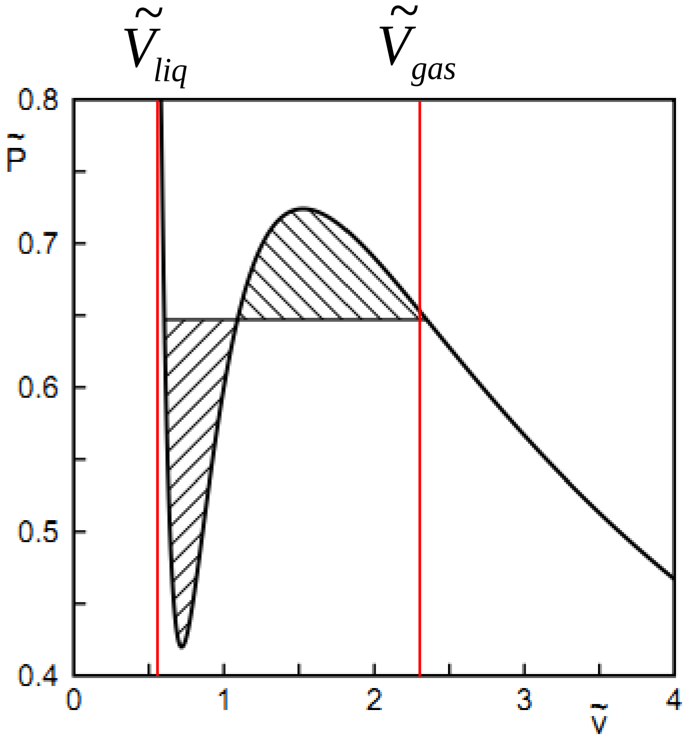
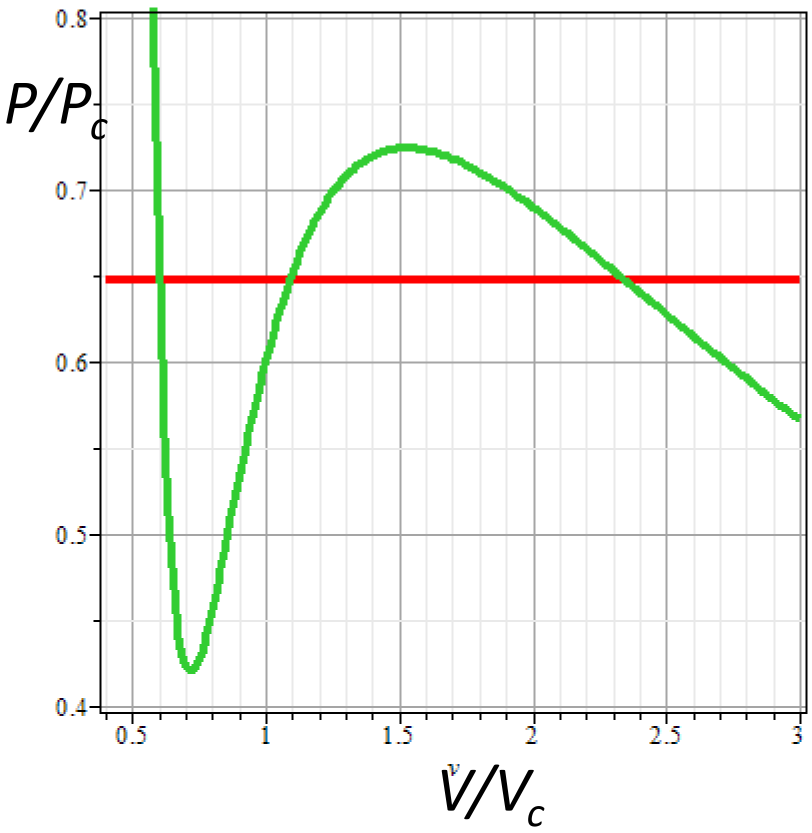


Figure 7.8: Maxwell equal area construction. The pressure $\tilde{P}$ where two phase coexistence begins for $\tilde{T}=0.9$ is determined so that the areas above and below the horizontal line are equal. In this case $\tilde{P}\approx 0.647$.

P-V diagram for van der Waals material at T/T_c=0.9



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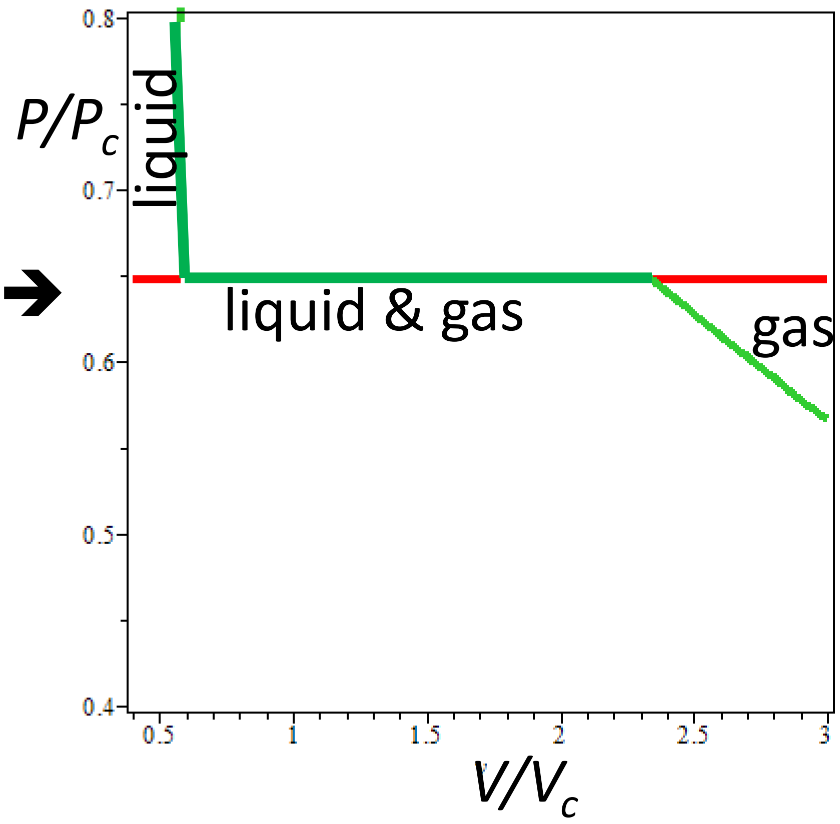


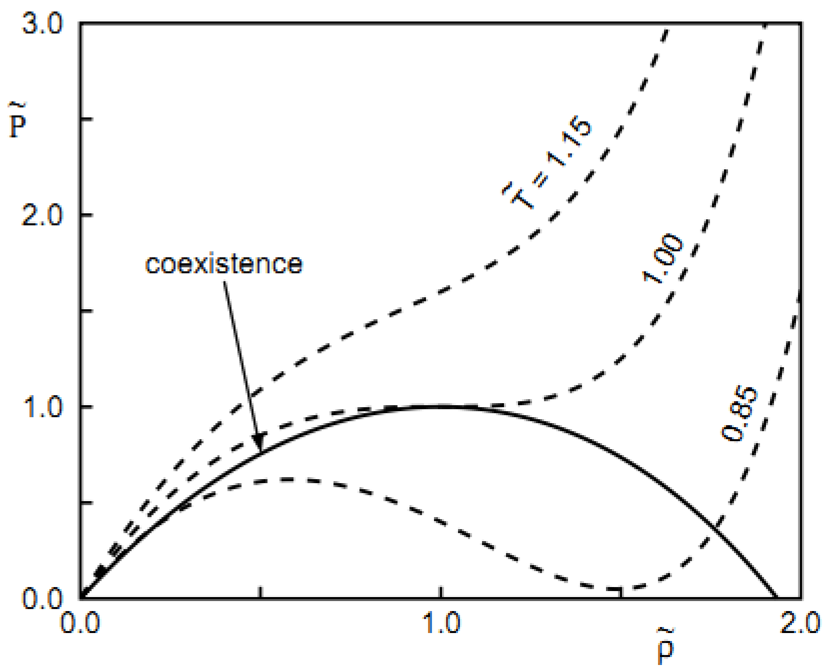
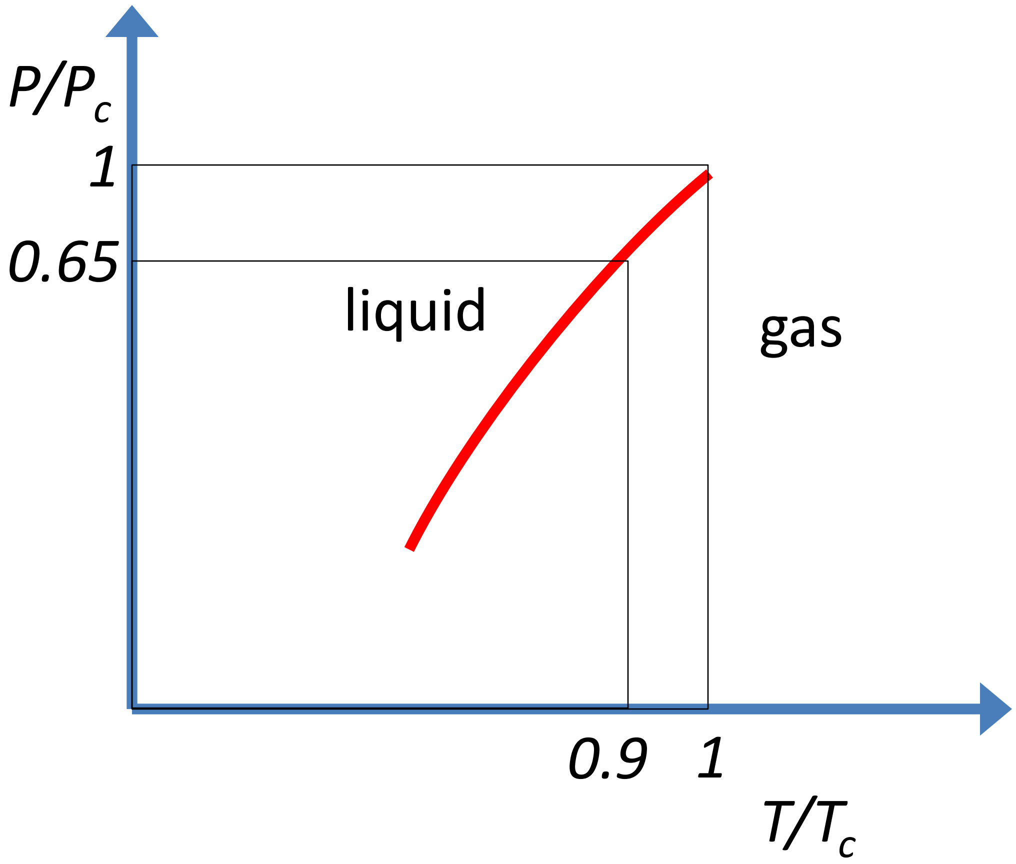


Figure 7.9: The coexistence curve for the van der Waals equation of state as a function of the dimensionless density $\tilde{\rho}$. Also plotted are three isotherms (dashed lines). For $\tilde{T} < 1$ the isotherms intersect the coexistence curve (solid line) at two points whose coordinates give the equilibrium values of $\tilde{P}$, $\tilde{\rho}_{\rm gas}$, and $\tilde{\rho}_{\rm liq}$. For $\tilde{T} = 1$ the isotherm intersects the coexistence curve at one point where $\tilde{P} = 1$ and $\tilde{\rho} = \tilde{\rho}_{\rm gas} = \tilde{\rho}_{\rm liq} = 1$.

Phase diagram for van der Waals material



Extension of analysis of Gibbs Free energy to analyze chemical equilibria:

Consider the following example:

$$\mathrm{H_2O} \Leftrightarrow \mathrm{H^+} + \mathrm{OH^-}$$

Constraint on number of molecules of each type:

$$+1N_{H^+} + 1N_{OH^-} - 1N_{H_2O} = 0 \equiv \sum_i \nu_i N_i$$

Change in Gibbs Free energy for this system:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

At equilibrium: $dG = 0$

At equilibrium with constant T and P: $\sum_i \mu_i dN_i = 0$