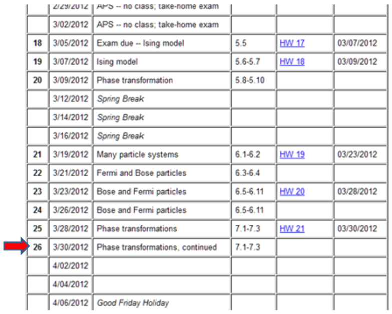
PHY 341/641
Thermodynamics and Statistical Physics

Lecture 26

Chemical potentials and phase equilibria (Chapter 7 in STP)

- Phase diagrams
- Van der Waals equation of state



	2/29/2012	APS -- no class; take-home exam			
	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	Phase transformations, continued	7.1-7.3		
	4/02/2012				
	4/04/2012				
	4/06/2012	*Good Friday Holiday*			

Reminder – second exam in April
-- student presentations 4/30, 5/2 (need to pick topics)

Review:

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

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

Example: A ≡ vapor B ≡⟹ water

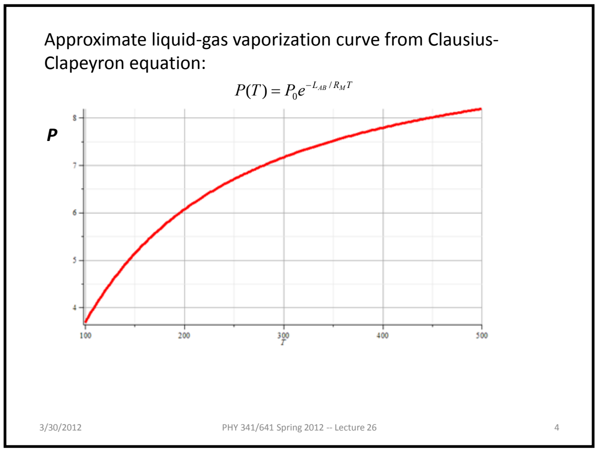
$$L_{AB} = 2.257\times 10^{6}\, J/kg = 40.7\times 10^{3}\, J/mole \qquad T \geq 373.15K$$

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

$$V_B \approx 0$$

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

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



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

$$P(T) = P_0 e^{-L_{AB}/R_M T}$$

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: $PV = NkT$

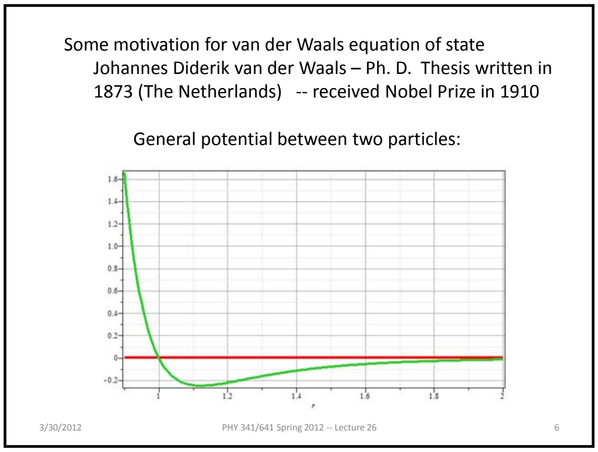
van der Waals equation of state: $\left(P + a\frac{N^2}{V^2}\right)(V - bN) = NkT$

here a, b are material-dependent parameters

Dimensionless variables:

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

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



Some motivation for van der Waals equation of state

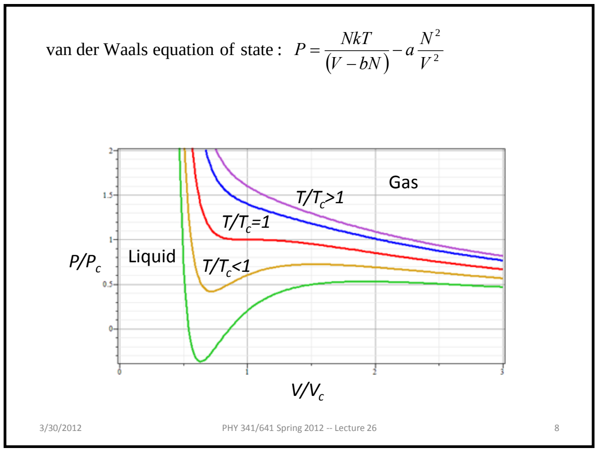
Johannes Diderik van der Waals – Ph. D. Thesis written in 1873 (The Netherlands) -- received Nobel Prize in 1910

General potential between two particles:

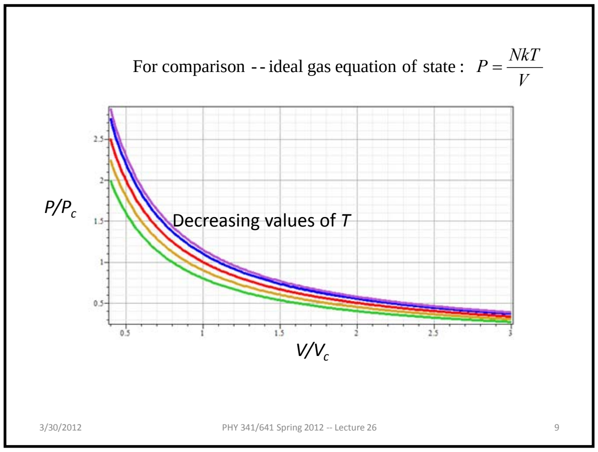
van der Waals equation of state : $P = \frac{NkT}{(V - bN)} - a\frac{N^2}{V^2}$

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***



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

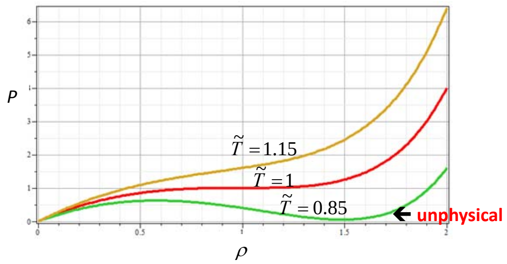


For comparison -- ideal gas equation of state : $P = \frac{NkT}{V}$

Dimensionless variables:

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

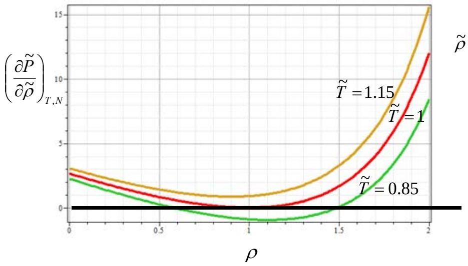
van der Waals equation of state: $\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3-\tilde{\rho}} - 3\tilde{\rho}^2$



Examination of compressibility in van der Waals material:

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_{T,N} \geq 0$$

for: $\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3-\tilde{\rho}} - 3\tilde{\rho}^2$



$$\tilde{P} \equiv 27\left(\frac{b^2}{a}\right)P$$

$$\tilde{T} \equiv \frac{27}{8}\left(\frac{b}{a}\right)kT$$

$$\tilde{\rho} \equiv 3b\frac{N}{V}$$

$$P_c = \frac{a}{27b^2}$$

$$kT_c = \frac{8a}{27b}$$

$$V_c = 3bN$$

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

$$F = -\int^V P dV + NkTw(T)$$

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

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

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

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

Gibb's free energy :

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

In scaled variables with

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

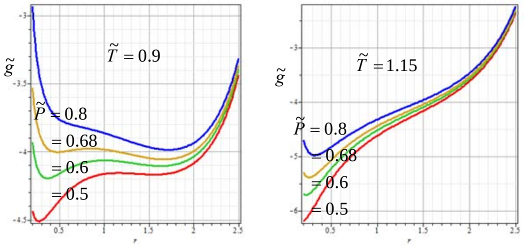
$$G = F + PV = -NkT\,\ln\left(V-bN\right) - a\frac{N^2}{V} + PV + NkTw(T)$$

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

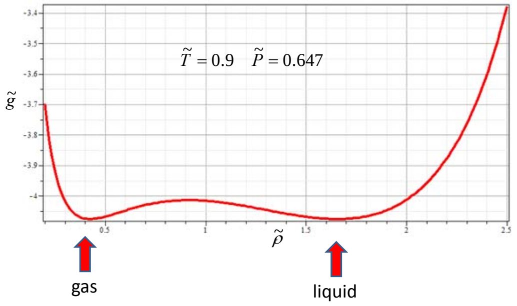
Behavior of Gibbs chemical potential :

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

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



Gibbs chemical potential at coexistence point



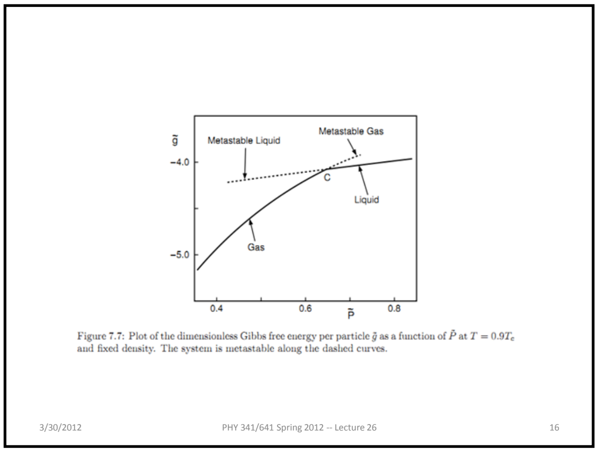


Figure 7.7: Plot of the dimensionless Gibbs free energy per particle $\tilde{g}$ as a function of $\tilde{P}$ at $T = 0.9T_c$ and fixed density. The system is metastable along the dashed curves.

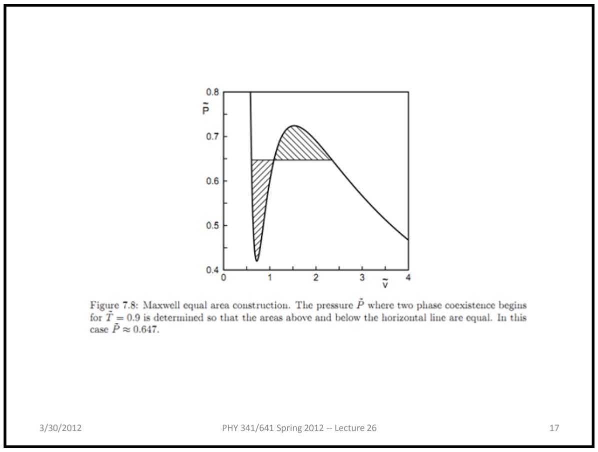


Figure 7.8: Maxwell equal area construction. The pressure $\tilde{P}$ where two phase coexistence begins for $\tilde{T} = 0.9$ is determined so that the areas above and below the horizontal line are equal. In this case $\tilde{P} \approx 0.647$.