

Lecture 11

- Calculating property changes from PVT EOS and *ideal gas heat capacity*
- Fugacity and fugacity coefficient
- Phase equilibrium
 - general consideration
 - Clapeyron equation; Clausius-Clapeyron equation

Read Chs. 9, 10 Sandler, Chs. 9 and 11 Callen

Objectives

- Calculate property changes from *ideal gas heat capacity* and EOS
- Understand fugacity and be able to calculate fugacity coefficient from EOS
- Understand and remember Clapeyron and Clausius-Clapeyron equations

Changes in U and H in Terms of T, V or T, P

Start from fundamental equation

$$dU = TdS - PdV$$

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

similarly

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

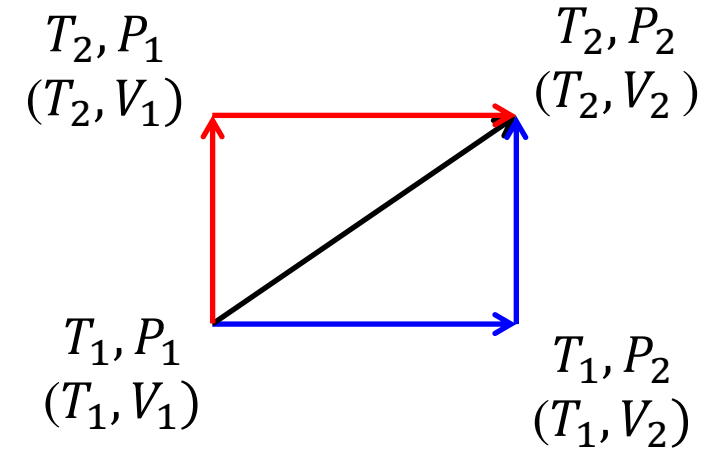
Calculating Property Changes

Example

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

or

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

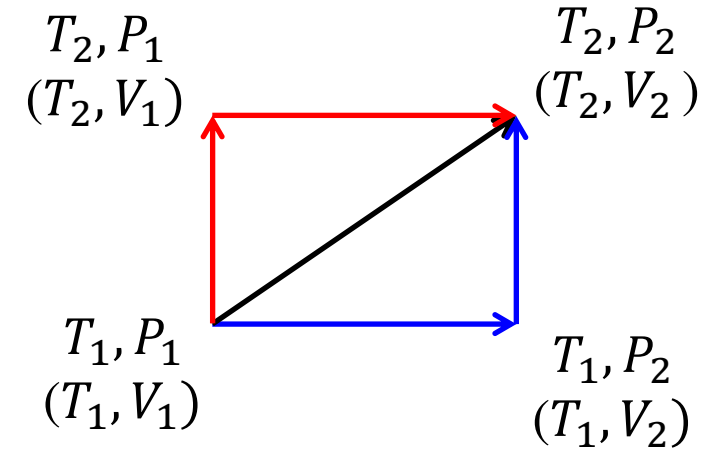
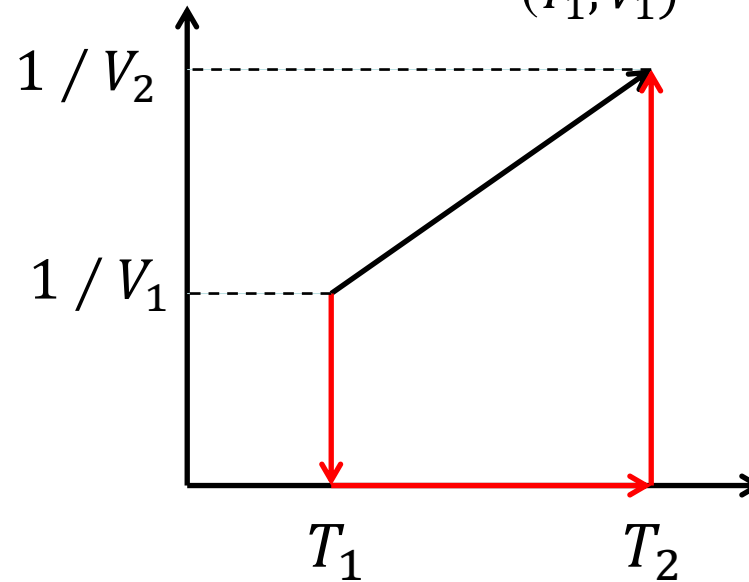
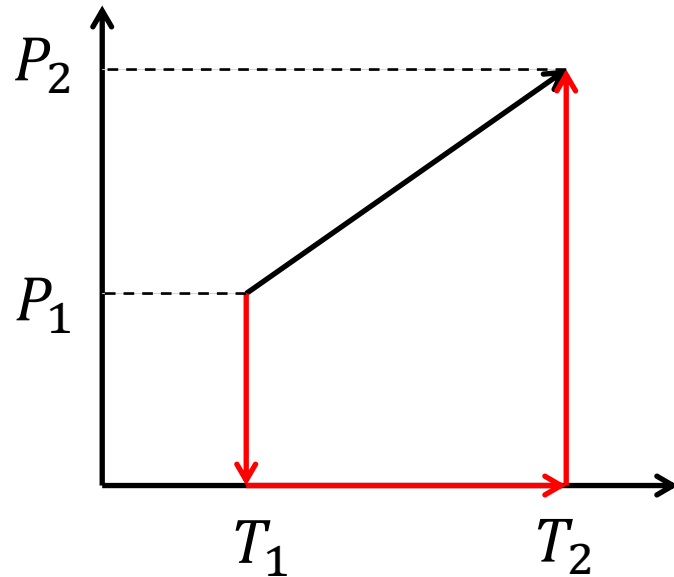


- Separate into isothermal and isobaric (isocoric) steps
- Using EOS and **pressure/density dependence of C_p and C_v**

$$H(T_2, P_2) = H(T_1, P_1) + \underbrace{\int_{T_1}^{T_2} C_P \Big|_{P_1} dT}_{\text{isobaric}} + \underbrace{\int_{P_1}^{P_2} \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] \Big|_{T_2} dP}_{\text{isothermal}}$$

Calculating Property Changes

- Pressure/density dependence of C_p and C_v are not easily available
- Using EOS and *ideal-gas* C_p (or C_v), which only has temperature dependence



Isothermal segment done at zero pressure or infinite volume

All gases become ideal in the limit of zero pressure or density
(infinite molar volume)

$$P = \rho RT[1 + B\rho + C\rho^2 + \dots] = \rho RTZ$$

$$Z = 1 + B\rho + C\rho^2 + \dots = 1 + B'P + C'P^2 + \dots$$

$$\lim_{\rho \rightarrow 0} Z = 1$$

Pressure Explicit vs. Volume Explicit EOS

Pressure explicit (more common)

$$P = P(v, T)$$

more natural to use v as variable

Volume explicit

$$v = v(P, T)$$

more natural to use P as variable

Example

$$S(T_2, V_2) - S(T_1, V_1) = S(T_2, V_2) - S(T_2, \infty) + S(T_2, \infty) - S(T_1, \infty) + S(T_1, \infty) - S(T_1, V_1)$$

isothermal
compression

heating/cooling of
ideal gas

isothermal
expansion

$$R \ln \frac{V_2}{V_1} + \int_{T_1}^{T_2} \frac{C_V^{I.G.}}{T} dT + \int_{V_1}^{\infty} \left[\left(\frac{\partial P}{\partial T} \right)_{T=T_1} - \frac{R}{V} \right] dV - \int_{V_2}^{\infty} \left[\left(\frac{\partial P}{\partial T} \right)_{T=T_2} - \frac{R}{V} \right] dV$$

I.G. part

Correction due to nonideality

Fugacity and Fugacity Coefficient

Recall chemical potential of ideal gas

$$\mu^{I.G.}(P, T) = \mu^{\ominus}(T) + RT \ln \frac{P}{P^{\ominus}}$$

Nonideal gas – keep similar form

$$\mu(P, T) = \mu^{\ominus}(T) + RT \ln \frac{f}{P^{\ominus}}$$

Fugacity

$$f = \phi P$$

Fugacity coefficient

$$\phi = f/P$$

Fugacity and Fugacity Coefficient

Fundamental equation $d\mu = -sdT + vdP$

At constant T $d\mu = vdP$ (1)

For I.G. $d\mu^{I.G.} = v^{I.G.}dP = \frac{RT}{P}dP$ (2)

(1)-(2), and integrate between 0 and P

$$\mu(T, P) - \mu^{I.G.}(T, P) = \underbrace{\mu(T, 0) - \mu^{I.G.}(T, 0)}_0 + \int_0^P \left(v - \frac{RT}{P} \right) dP$$

$$\mu(T, P) = \mu^{I.G.}(T, P) + \int_0^P \left(v - \frac{RT}{P} \right) dP = \mu^{\ominus}(T) + RT \ln \frac{P}{P^{\ominus}} + \int_0^P \left(v - \frac{RT}{P} \right) dP$$

Fugacity and Fugacity Coefficient

$$\mu(T, P) = \mu^{\ominus}(T) + RT \ln \frac{\phi P}{P^{\ominus}}$$

with

$$\phi = \exp \left[\frac{1}{RT} \int_0^P \left(v - \frac{RT}{P} \right) dP \right] = \exp \left[\int_0^P \frac{(Z - 1)}{P} dP \right]$$

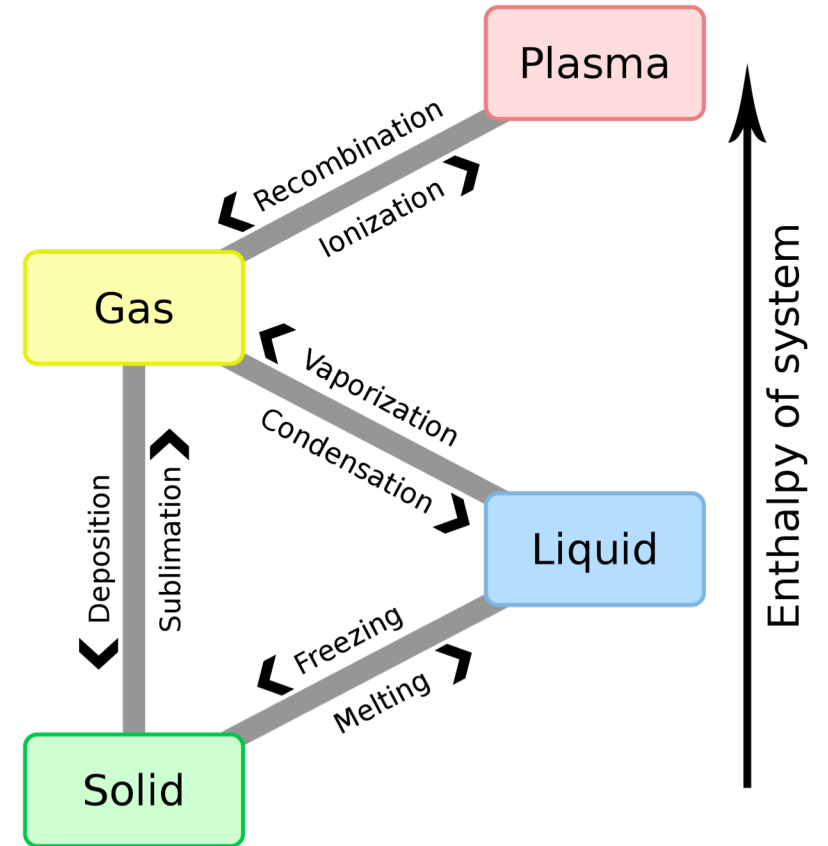
Note! $\mu^{\ominus}(T)$ chemical potential of the **ideal gas** at standard state pressure, even **though gas is nonideal** (used even for liquid)

All nonideality effects are contained in fugacity correction!

Phases and Phase Transitions

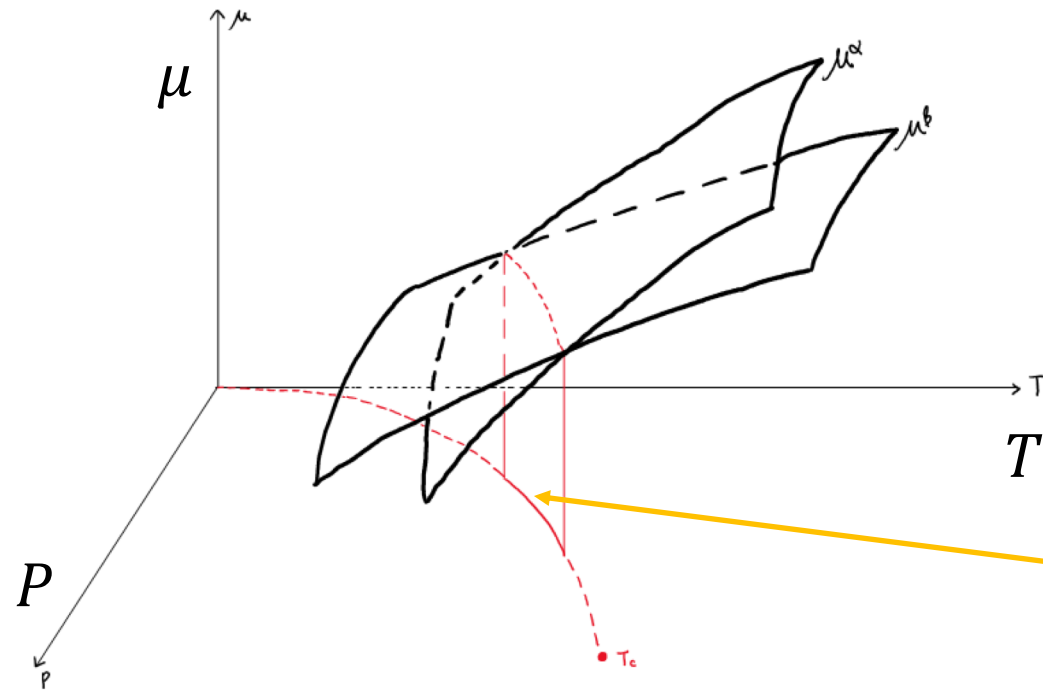
- Phase: a thermodynamic state of matter having uniform properties
- Often identified by their differences
- Phase transition: transformation from one phase to another

There are new states of matter (phases) not included in the traditional 4 states, e.g., liquid crystals



https://en.wikipedia.org/wiki/Phase_transition#/media/File:Phase_change_-_en.svg

Thermodynamics of Phase Transition



intersection of two free
energy surfaces

Clapeyron line

Slopes in the P-T plane:

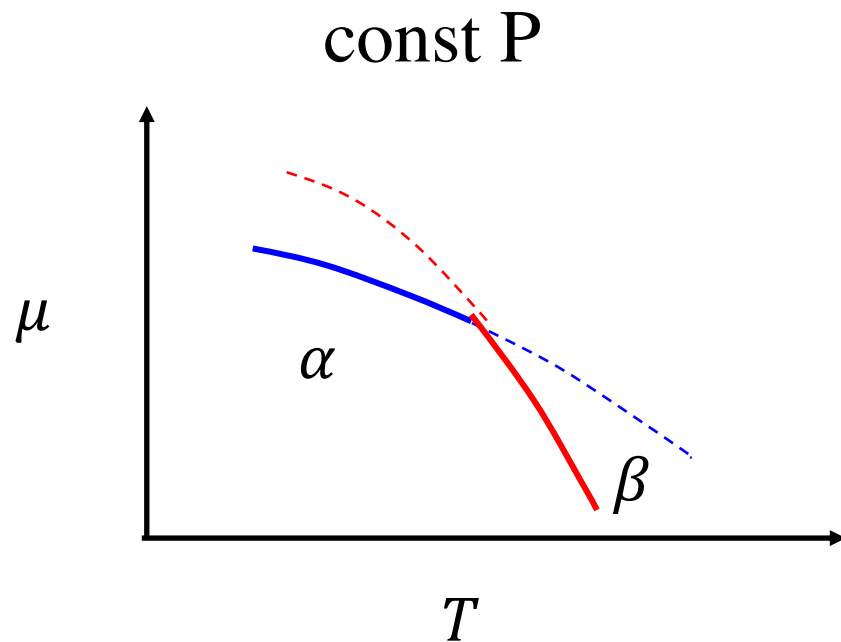
$$\left(\frac{\partial \mu^a}{\partial P}\right) = v^a$$

$$\left(\frac{\partial \mu^a}{\partial T}\right) = -S^a$$

$$\left(\frac{\partial \mu^\beta}{\partial P}\right) = v^\beta$$

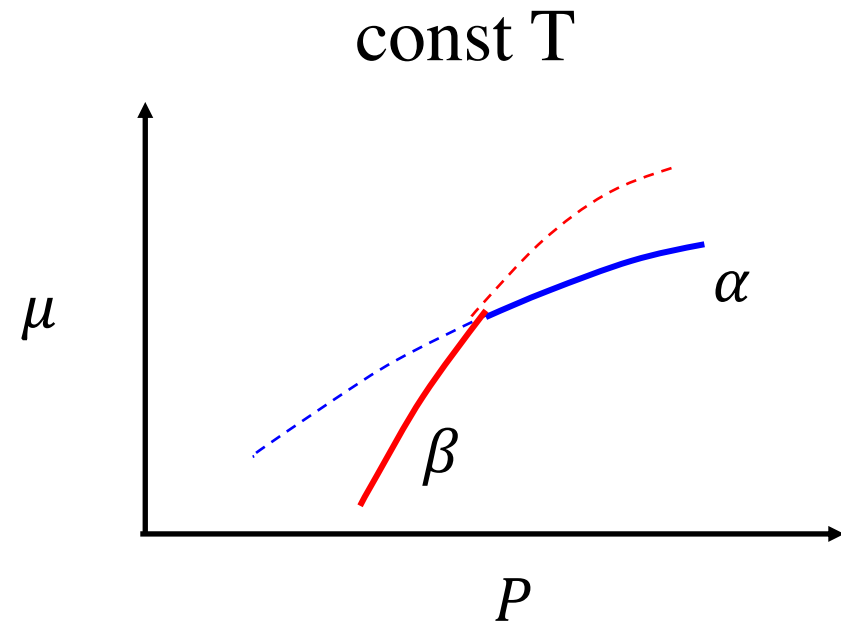
$$\left(\frac{\partial \mu^\beta}{\partial T}\right) = -S^\beta$$

Cross-sectional View



$$\left(\frac{\partial \mu^a}{\partial T}\right) = -S^a$$

$$\left(\frac{\partial \mu^\beta}{\partial T}\right) = -S^\beta$$



$$\left(\frac{\partial \mu^a}{\partial P}\right) = v^a$$

$$\left(\frac{\partial \mu^\beta}{\partial P}\right) = v^\beta$$

Ehrenfest Classification of Phase Transitions

First order transition:

Discontinuity in first derivatives
of free energy

$$v^a \neq v^\beta$$

$$s^a \neq s^\beta$$

Second order transition:

Continuous first derivatives but
discontinuous second derivatives

Examples: critical point in
L-V transition;
spontaneous magnetization

Clapeyron Equation

T-P relationship along the coexistence line, i.e., how transition temperature changes with pressure or vice versa

On the coexistence line $\mu_\alpha(T, P) = \mu_\beta(T, P)$
 $\mu_\alpha(T + dT, P + dP) = \mu_\beta(T + dT, P + dP)$

$$\frac{dP}{dT} = \frac{s^a - s^\beta}{v^a - v^\beta} = \frac{\Delta h}{T \Delta v}$$

Δh : latent heat of transition, usually defined as enthalpy of the Hi-T phase – enthalpy of the Lo-T phase

Clausius-Clapeyron Equation

If one phase is vapor, and approximating vapor as I.G.,

$$\Delta v = v^{vap} = \frac{RT}{P}$$

$$\frac{d \ln P}{dT} = \frac{\Delta h}{RT^2}$$

LHS: determined by EOS
RHS: a thermal property

Further approximating Δh as constant,

$$P_2 = P_1 \exp \left[\frac{\Delta h}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

Questions to Think about

- What's motivation for introducing fugacity?
- Why the reference chemical potential for a real gas is taken to be that of the same gas at a hypothetical ideal gas state?
- Why do the chemical potential curves in the cross-sectional view have these qualitative shapes (in terms of slopes and curvature)?
- What happens to the melting temperature of ice when the pressure increases?

Lecture 12

- Phase equilibrium
 - determination of L-V phase equilibrium from EOS
 - Helmholtz free energy perspective
 - Maxwell construction, double-tangent construction
- Phase diagram – stable, unstable and metastable states

Read Chs. 9 and 10 Sandler

Objectives

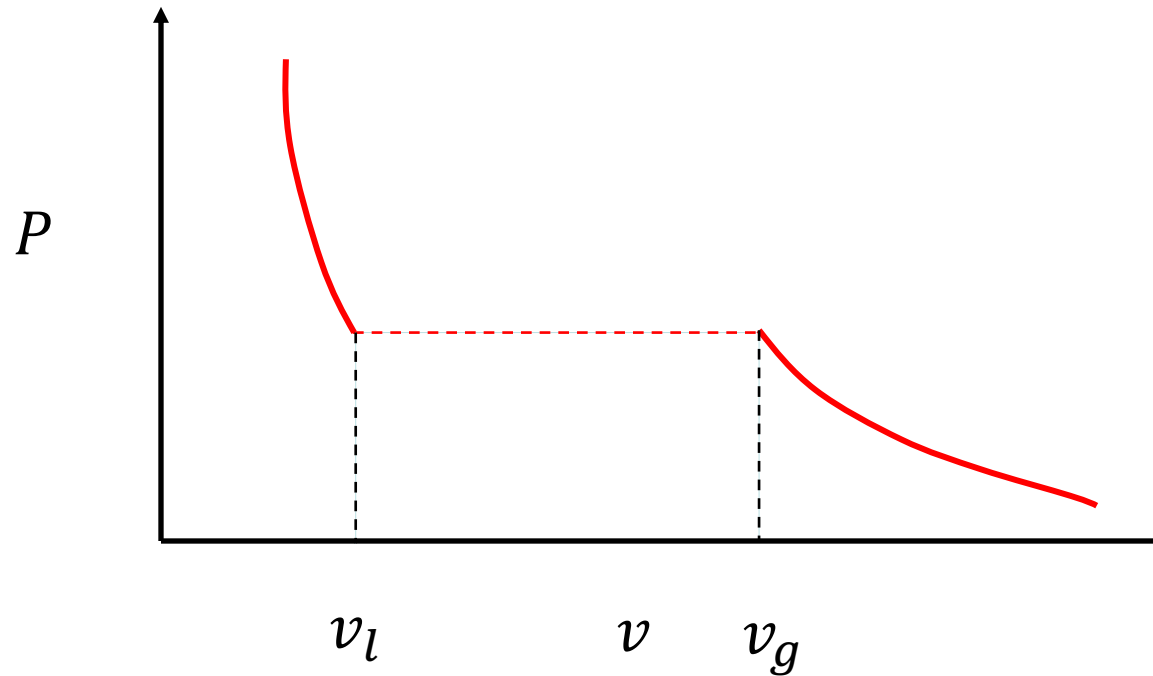
- Able to calculate vapor-liquid equilibrium from EOS
- Understand relationship between double tangent, equality of chemical potential and Maxwell construction
- Able to read and understand phase diagram

L-V Equilibrium from EOS

Given an equation of state for a fluid

$$P(T, v^a) = P(T, v^b)$$

$$\mu(T, v^a) = \mu(T, v^b)$$



Real Gases

- **Van der Waals**

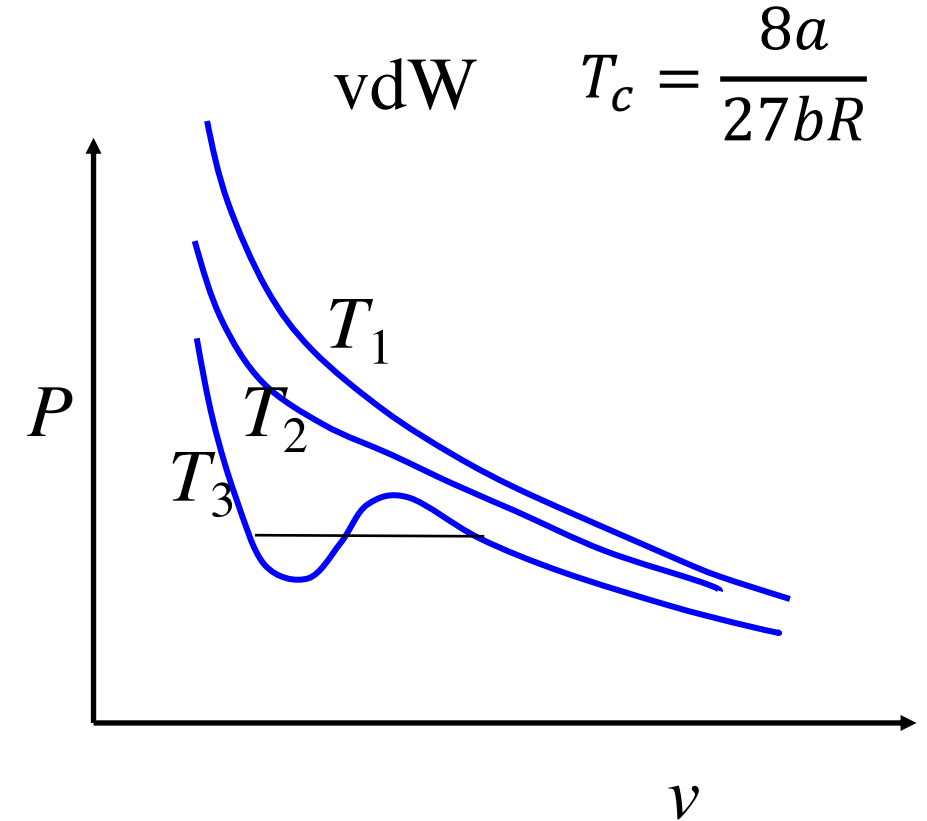
$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

- Redlich-Kwong

$$P = \frac{RT}{v - b} - \frac{a}{T^{1/2}v(v + b)}$$

- Peng-Robinson

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}$$



- Part of the EOS becomes unphysical due to mean-field approximations
- How do we determine the physical coexistence curve?

L-V Equilibrium Condition

Equality of pressure

$$P(T, v_l) = P(T, v_g)$$

$$\frac{RT}{v_l - b} - \frac{a}{v_l^2} = \frac{RT}{v_g - b} - \frac{a}{v_g^2}$$

L-V Equilibrium Condition

Equality of chemical potential

$$\mu(T, v_l) = \mu(T, v_g)$$

Fundamental equation

$$df = -Pdv$$

$$f(T, v) = f_0(T, v_0) - RT \ln \frac{v - b}{v_0} - \frac{a}{v} + \frac{a}{v_0}$$

$$f(T, v) = f^*(T, v_0) - RT \ln \frac{v - b}{b} - \frac{a}{v}$$

$$\mu = f + pv = f^*(T, v_0) + \frac{RTv}{v - b} - RT \ln \frac{v - b}{b} - \frac{2a}{v}$$

$$\mu = f + pv = \mu^*(T, v_0) + \frac{RTb}{v - b} - RT \ln \frac{v - b}{b} - \frac{2a}{v}$$

$$\frac{RTb}{v_l - b} - RT \ln \frac{v_l - b}{b} - \frac{2a}{v_l} = \frac{RTb}{v_g - b} - RT \ln \frac{v_g - b}{b} - \frac{2a}{v_g}$$

L-V Equilibrium Condition

Equality of pressure:

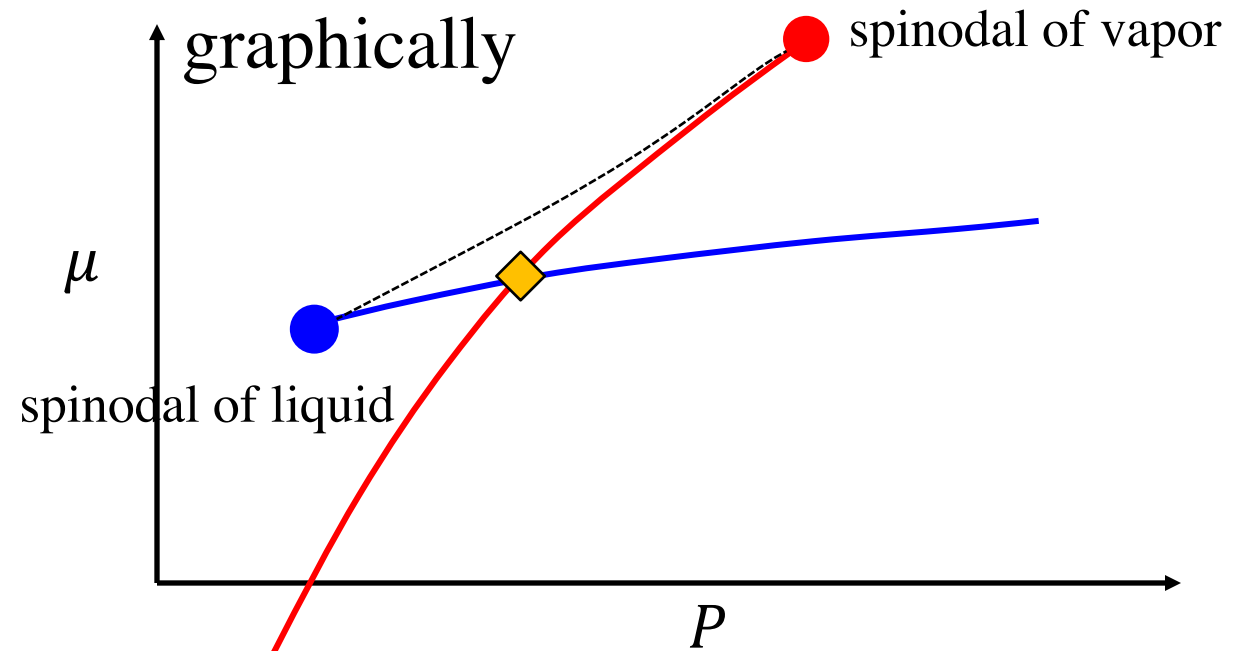
$$\frac{RT}{v_l - b} - \frac{a}{v_l^2} = \frac{RT}{v_g - b} - \frac{a}{v_g^2}$$

Equality of chem. potential:

$$\frac{RTb}{v_l - b} - RT \ln \frac{v_l - b}{b} - \frac{2a}{v_l} = \frac{RTb}{v_g - b} - RT \ln \frac{v_g - b}{b} - \frac{2a}{v_g}$$

2 equations for 2 unknowns v_l and v_g

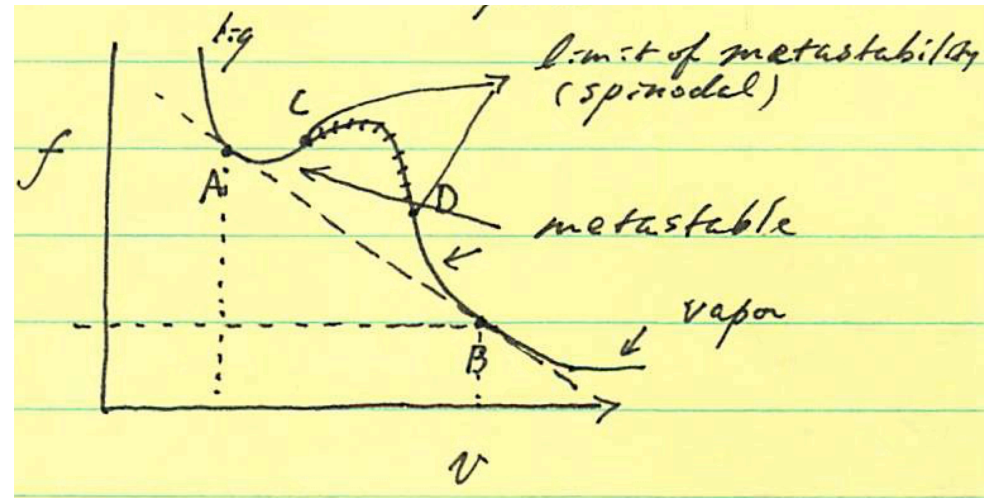
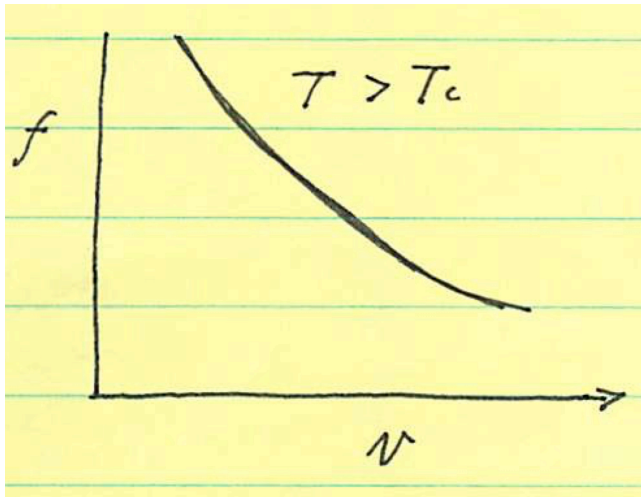
- Crossing gives coexistence pressure and chemical potential
- Slopes give v_l and v_g



Helmholtz Free Energy Perspective

Van der Waals
$$f(T, v) = f^*(T, v_0) - RT \ln \frac{v - b}{b} - \frac{a}{v}$$

$$T_c = \frac{8}{27} \frac{a}{Rb}$$



Coexistence given by common tangent

Equivalent to equality of pressure and chemical potential and to

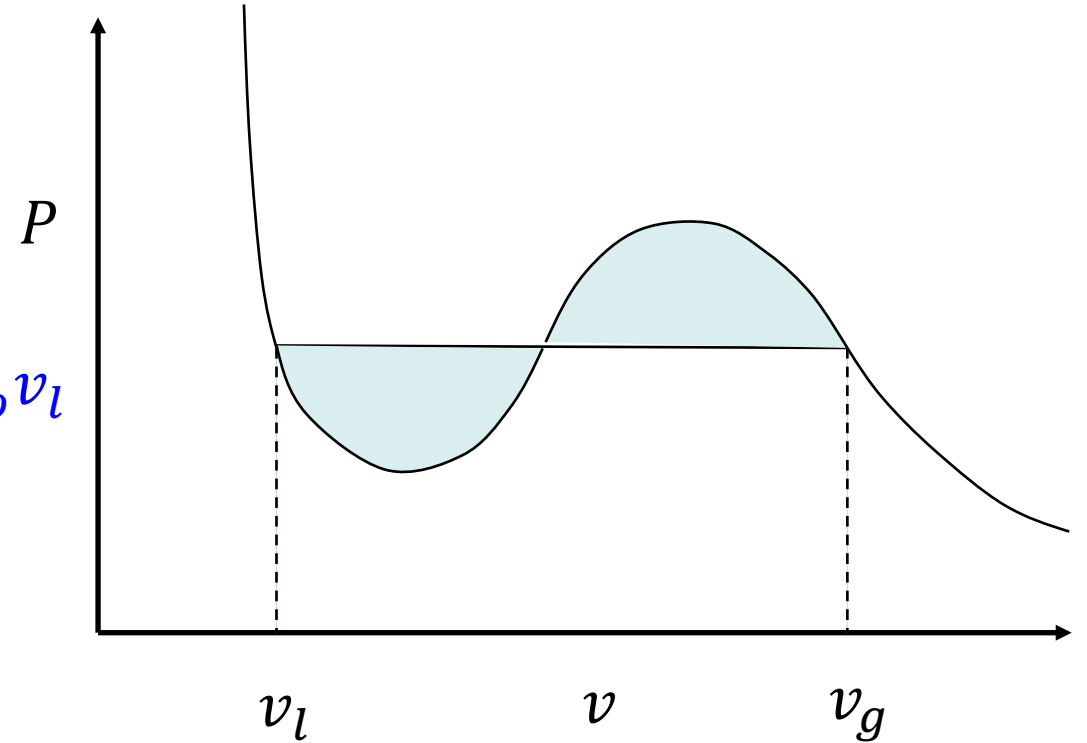
Maxwell equal area construction in P-v diagram

Maxwell (Equal-area) Construction

Draw a const. pressure line such that area above and area below are equal

$$\int_{v_l}^{v_g} (P - P_{co}) dv = 0$$

$$\begin{aligned} \int_{v_l}^{v_g} (P - P_{co}) dv &= f(v_l) - f(v_g) - P_{co}v_g + P_{co}v_l \\ &= \mu(v_l) - \mu(v_g) \end{aligned}$$



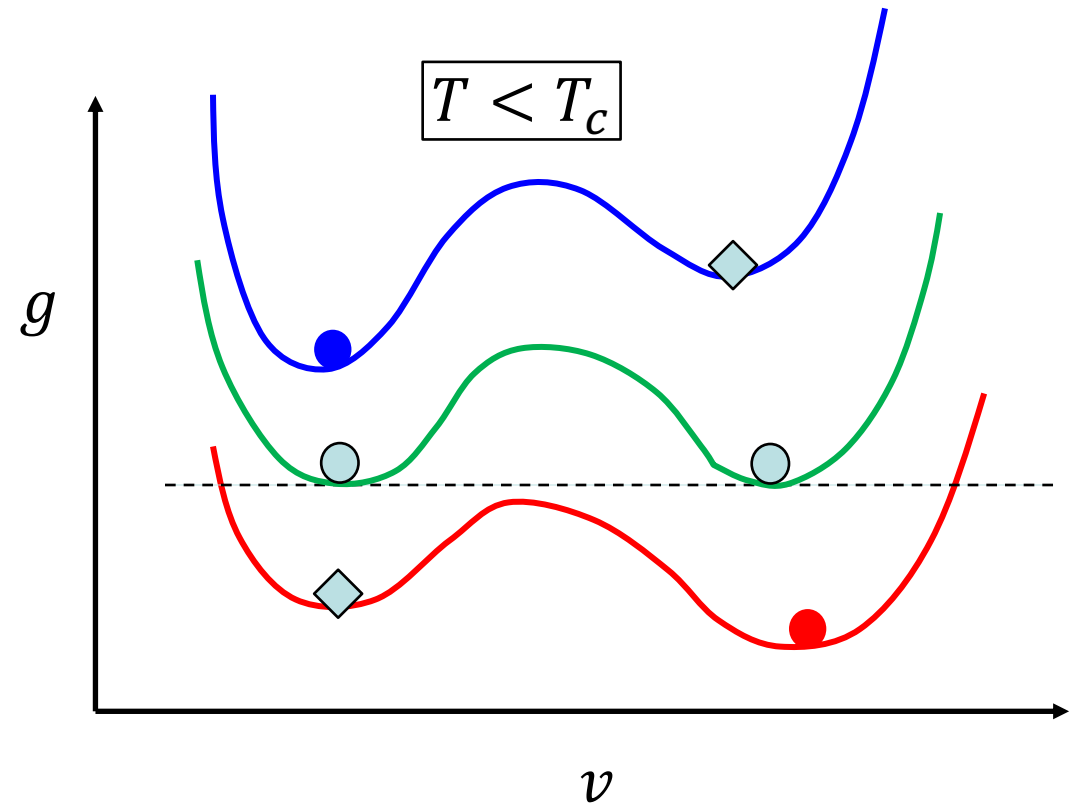
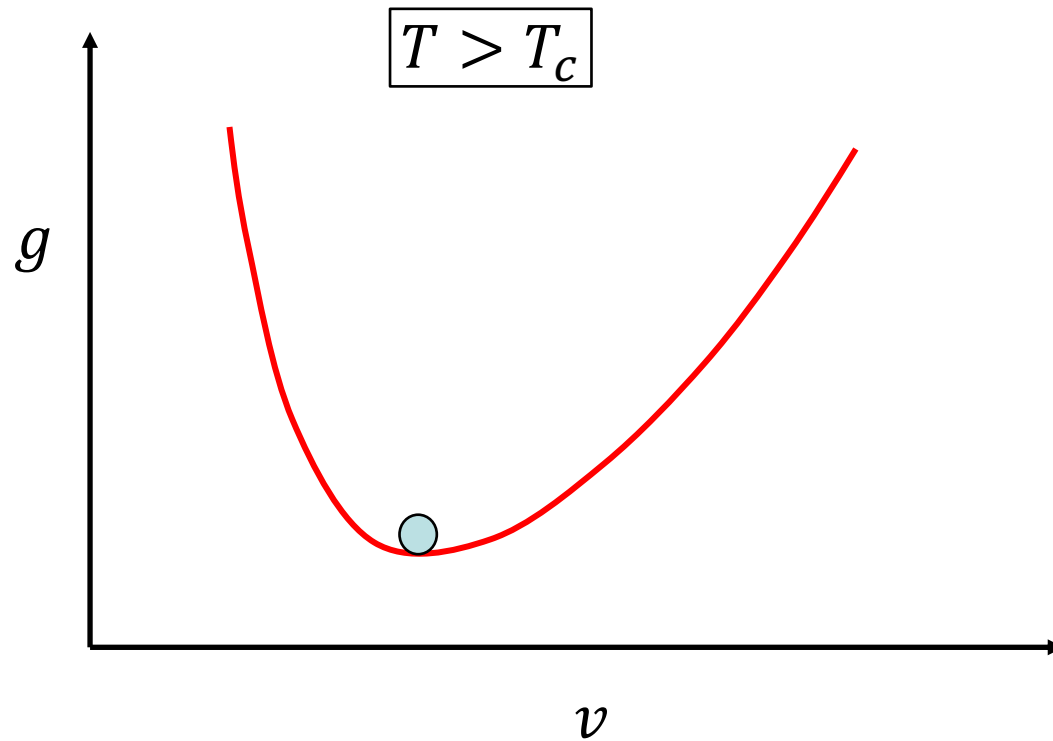
Maxwell construction is equivalent to equality of pressure and equality of chemical potential

Gibbs Free Energy Perspective

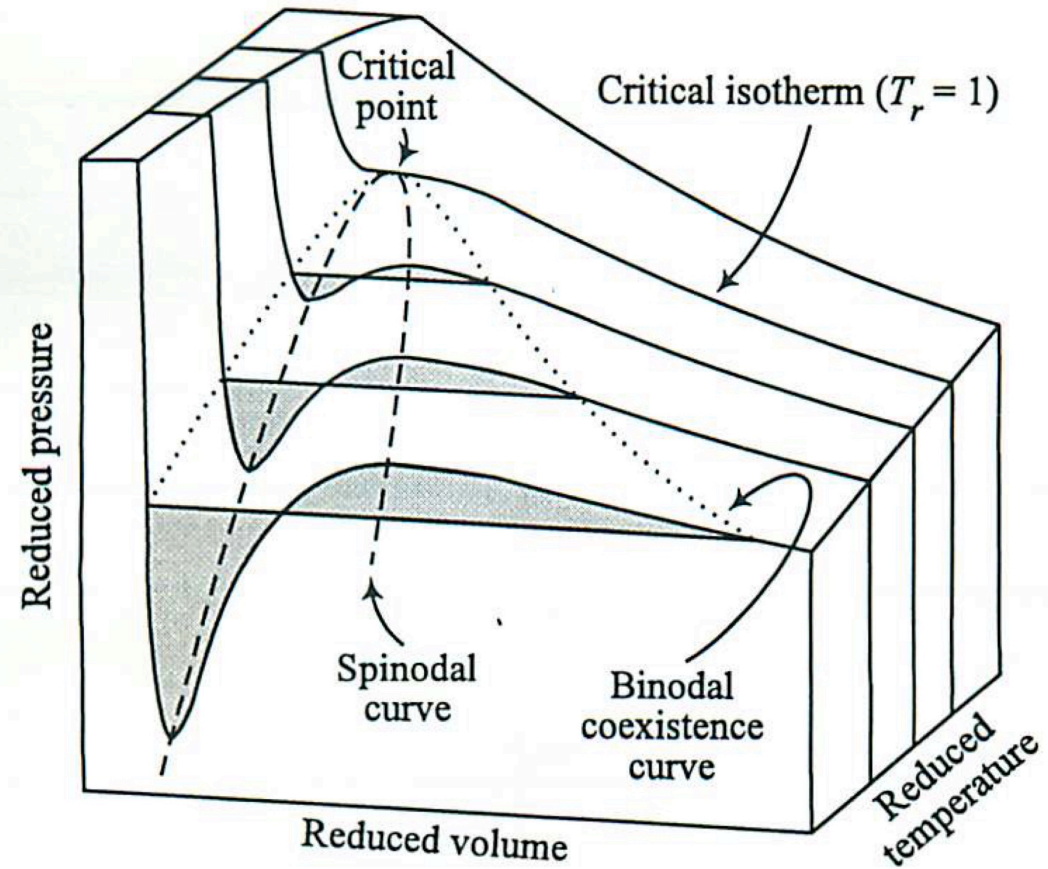
Variational Gibbs free energy

$$g(T, P; v) = f^*(T, v_0) - RT \ln \frac{v - b}{b} - \frac{a}{v} + Pv$$

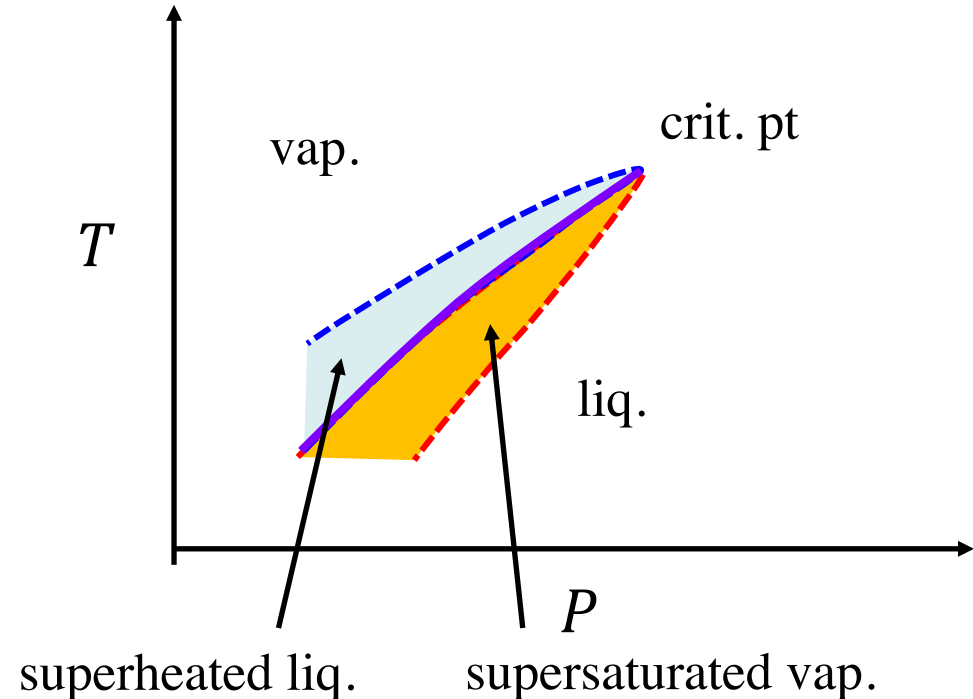
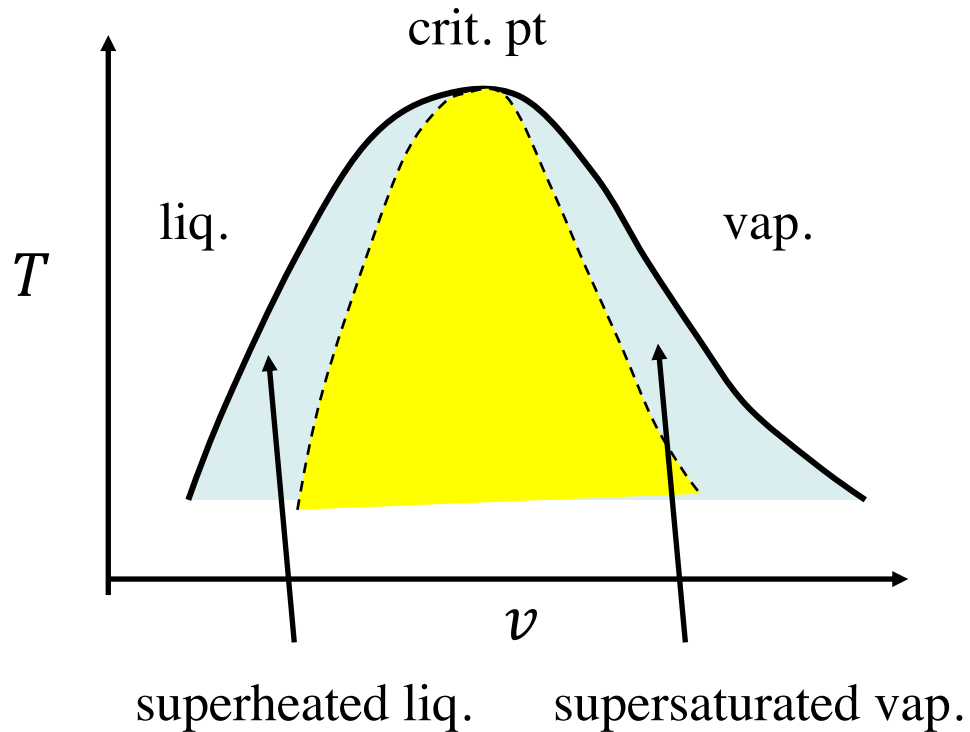
At given pressure, g is minimized over v , i.e., equilibrium state is one with a minimum g .



Phase Diagram for vdW



T-v and T-P Projections



Kinetic implications:

- unstable: system spontaneously phase separation via spinodal decomposition
- metastable: appearance of more stable phase via nucleation and growth

Lever Rule

fraction of molecules in liquid x_l

fraction of molecules in vapor x_g

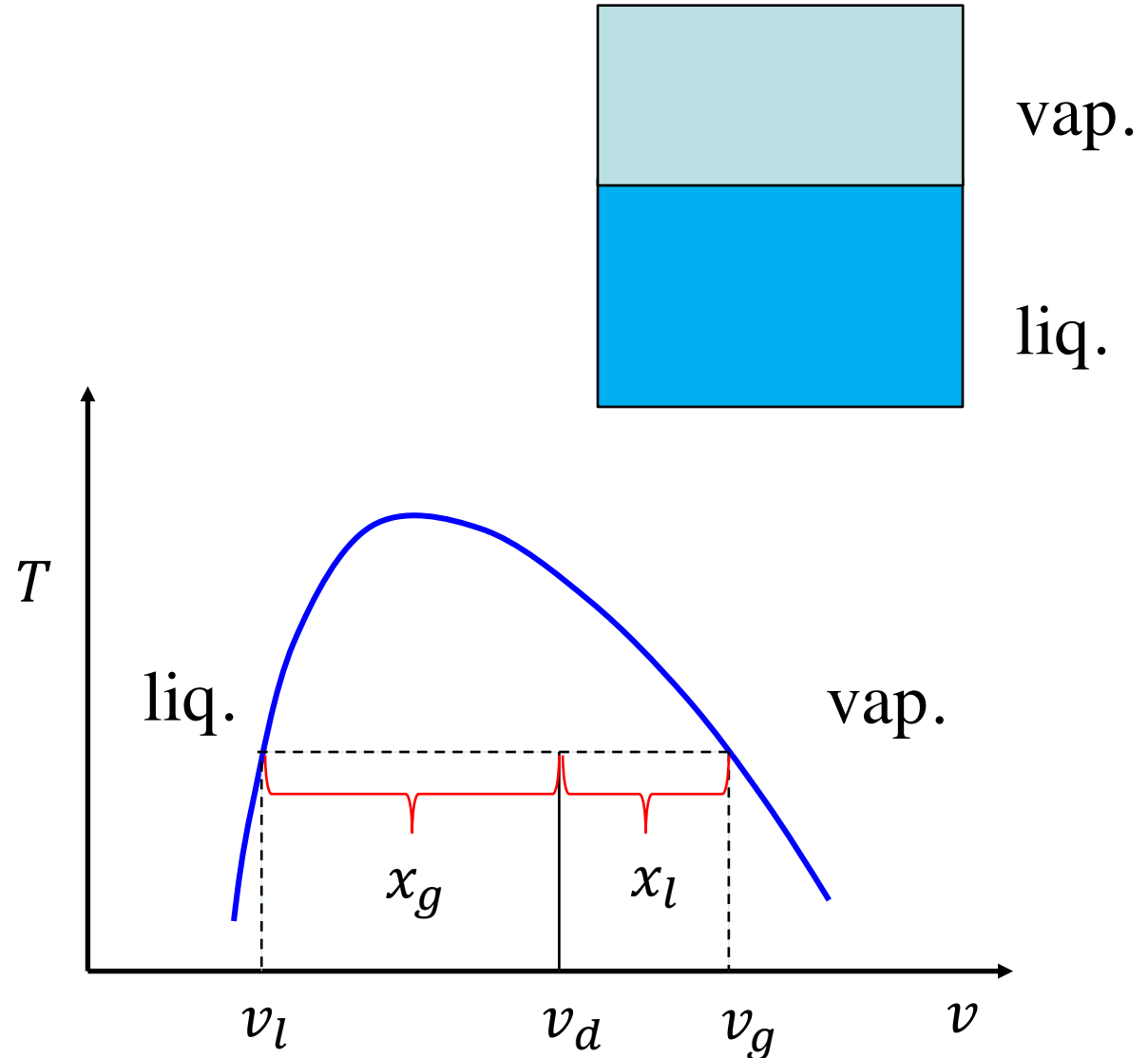
overall molar volume v_d

$$v_d n = v_g n_g + v_l n_l$$

$$v_d = v_g x_g + v_l x_l$$

$$v_d (x_g + x_l) = v_g x_g + v_l x_l$$

$$\frac{x_l}{x_g} = \frac{v_g - v_d}{v_d - v_l}$$



Supercritical Fluids (SCF)

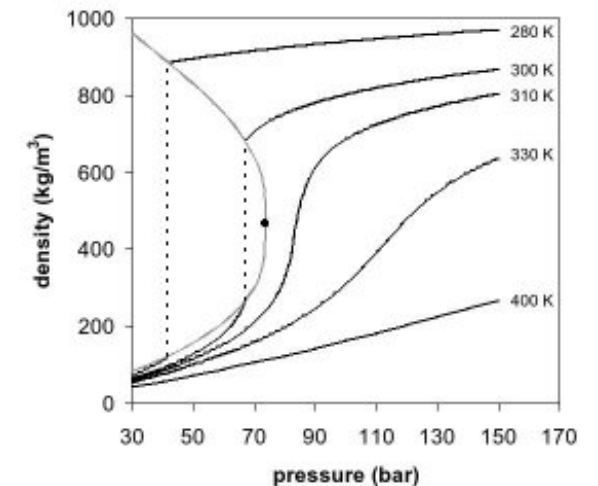
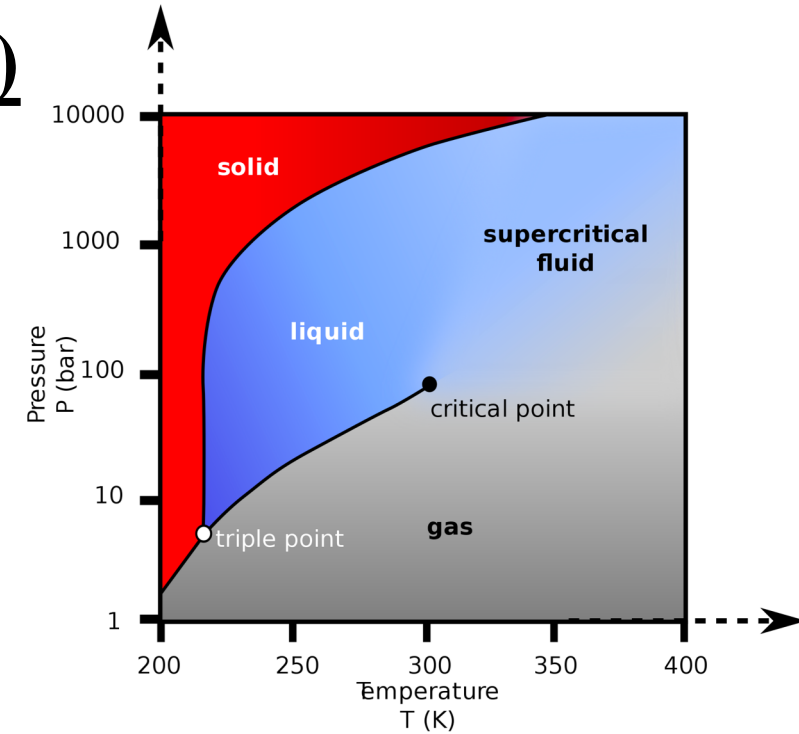
Fluids are supercritical when $T > T_c, P > P_c$

- No distinction between liquid and gas
- Allows continuous change in density with pressure
- Low viscosity/high diffusivity compared with liquid at normal conditions
- Good solvent properties

Applications:

- Extraction
- Dry cleaning
- Impregnation/dyeing
- Pharmaceuticals
- ...

CO₂



$$T_c = 304.1\text{K}$$

$$P_c = 7.38\text{ MPa}$$

Questions to Think about

- Why the minima in f vs. v do not yield the coexistence condition?
- How would the variational Gibbs free energy curves look like for different temperatures at a given pressure?
- What information is needed to determine the reference chemical potential or Helmholtz free energy for the vdW fluid?