

Lecture 9

- Stability criteria
- Common stability criteria – thermal, mechanical, diffusional
- Physical meaning of stability criteria
- Le Chatelier's principle
- Spinodal and Critical state
- The 3rd law

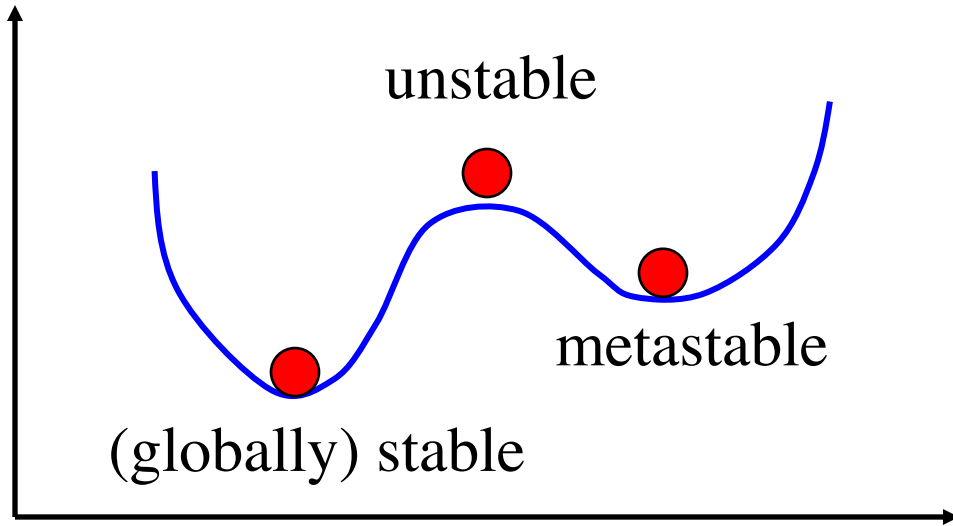
Read Ch. 7 Sandler, Chs. 8 and 11 Callen

Objectives

- Aware of stability conditions
- Know the common stability conditions
- Know how to determine critical point for fluids from EOS
- Know the consequences of the 3rd law

Stable, Metastable and Unstable Equilibrium

- Equilibrium originally a mechanical concept – vanishing of force
- Stability has to do with how system responds to perturbation



- Unstable: infinitesimal perturbation leads system away from its initial equilibrium state
- Metastable: system stable with respect to small local perturbations, but large perturbation will lead to transition to a more stable state
- (Globally) stable state: lowest energy state

Local stability determined by curvature

Entropy Maximization Principle

Like the equilibrium condition, stability condition comes from 2nd law

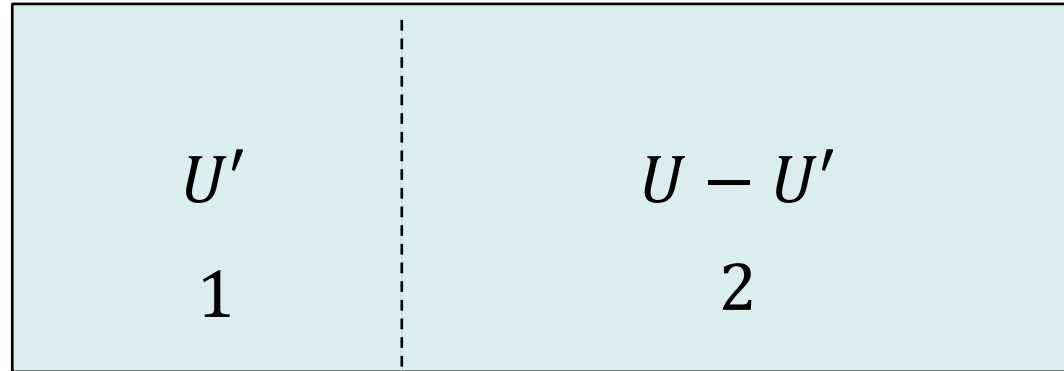
$$\left(\frac{\delta S}{\delta X}\right)_{V,U} = 0 \qquad \left(\frac{\delta^2 S}{\delta X^2}\right)_{V,U} < 0$$

For multiple variables

$$\left(\frac{\delta S}{\delta X_i}\right)_{V,U,X_{j \neq i}} = 0 \qquad \left(\frac{\delta^2 S}{\delta X_i \delta X_j}\right)_{V,U,X_{k \neq i,j}} \text{ is a matrix}$$

In general need to look at eigenvalue of the matrix, and ensure that the largest eigenvalue remains negative.

Thermal Stability



$$\left(\frac{\delta S}{\delta U'}\right)_V = 0$$

$$\delta^2 S = \delta^2 S_1 + \delta^2 S_2 = \left(\frac{\partial^2 S_1}{\partial U_1^2}\right) (\delta U_1)^2 + \left(\frac{\partial^2 S_2}{\partial U_2^2}\right) (\delta U_2)^2 < 0$$

$$\delta^2 S = \delta^2 S_1 + \delta^2 S_2 = \left(\frac{\partial(1/T_1)}{\partial U_1}\right) (\delta U_1)^2 + \left(\frac{\partial(1/T_2)}{\partial U_2}\right) (\delta U_2)^2 < 0$$

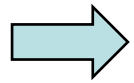
$$\delta^2 S = \delta^2 S_1 + \delta^2 S_2 = -\frac{1}{T^2} \left(\frac{1}{C_{V1}} + \frac{1}{C_{V2}} \right) (\delta U')^2 < 0$$

$$\left(\frac{\partial 1/T}{\partial U}\right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_V = -\frac{1}{T^2 C_V}$$

Thermal Stability

$$\left(\frac{1}{C_{V1}} + \frac{1}{C_{V2}} \right) < 0$$

True for any partitioning of the system



$$C_V > 0$$

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

$$\left(\frac{\partial S}{\partial T} \right)_{N,V} > 0$$

$T \Leftrightarrow S$, conjugates

Mechanical Stability

V'	$V - V'$
1	2

$$\left(\frac{\delta F}{\delta V'}\right)_T = 0$$

$$\delta^2 F = \delta^2 F_1 + \delta^2 F_2 = \left(\frac{\partial^2 F_1}{\partial V_1^2}\right) (\delta V_1)^2 + \left(\frac{\partial^2 F_2}{\partial V_2^2}\right) (\delta V_2)^2 > 0$$

$$\delta^2 F = \delta^2 F_1 + \delta^2 F_2 = -\left(\frac{\partial P_1}{\partial V_1}\right) (\delta V_1)^2 - \left(\frac{\partial P_2}{\partial V_2}\right) (\delta V_2)^2 > 0$$

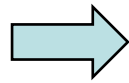
$$\delta^2 F = \delta^2 F_1 + \delta^2 F_2 = \left(\frac{1}{V_1 \kappa_{T1}} + \frac{1}{V_2 \kappa_{T2}}\right) (\delta V')^2 > 0$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

Mechanical Stability

$$\left(\frac{1}{V_1 \kappa_{T1}} + \frac{1}{V_2 \kappa_{T2}} \right) > 0$$

True for any partitioning of the system



$$\kappa_T > 0$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$-\left(\frac{\partial P}{\partial V} \right)_{N,T} > 0$$

$-P \Leftrightarrow V$, conjugates

Summary of Common Stability Conditions

Thermal

$$C_p > C_V > 0$$

Mechanical

$$\kappa_T > \kappa_S > 0$$

Diffusional

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{V,T,n_{j \neq i}} > \left(\frac{\partial \mu_i}{\partial n_i}\right)_{P,T,n_{j \neq i}} > 0$$

More generally

$$\left(\frac{\partial \xi_i}{\partial X_i}\right)_{Y,Z} > 0$$

$$\xi_i \Leftrightarrow X_i$$

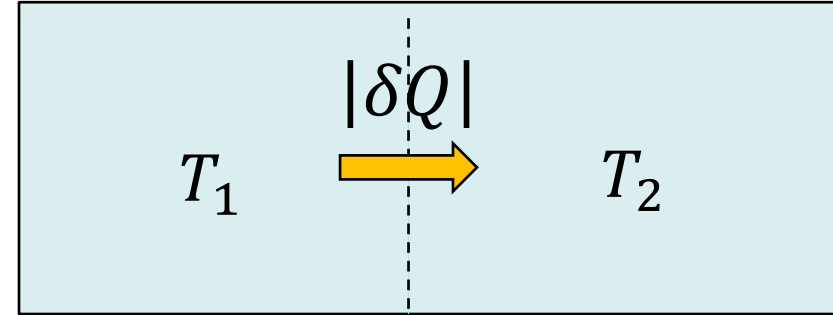
conjugates

Physical Interpretation of Stability Condition

Take thermal stability as example

$$T_1 > T_2$$

Then, according to direction of change



$$Q_1 = -|\delta Q| \quad Q_2 = |\delta Q|$$

$$\text{Now, } C_V = \frac{\delta Q}{\delta T} \quad \Rightarrow \quad \delta T_1 = \frac{\delta Q_1}{C_{V1}} = -\frac{|\delta Q|}{C_{V1}} \quad \delta T_2 = \frac{\delta Q_2}{C_{V2}} = \frac{|\delta Q|}{C_{V2}}$$

If $C_V < 0$ then $\delta T_1 > 0$ $\delta T_2 < 0$ \Rightarrow Hotter side gets hotter
Cooler side gets cooler

\Rightarrow More heat flow \Rightarrow Larger temperature difference \Rightarrow Runaway!

Le Chatelier's Principle

When a system at equilibrium is perturbed by the application of an action, the reaction of the system is such as to decrease the effect of the action.

Any change in status quo prompts an opposing reaction in the responding system

Spinodal

Susceptibility (response function) diverges

Spinodal: limit of local stability $\left(\frac{\partial^2 F}{\partial X^2}\right) = 0$

For fluid $\left(\frac{\partial P}{\partial V}\right)_T = 0$

For parameters $\kappa_T < 0$ system spontaneously phase separate into a stable liquid and vapor with $\kappa_T > 0$ in each

Critical States

When $\left(\frac{\partial^2 F}{\partial X^2}\right) = 0$ need to go to higher order

$$\delta F = \overset{0}{\cancel{\delta F^{(1)}}} + \overset{0}{\cancel{\delta F^{(2)}}} + \delta F^{(3)} + \delta F^{(4)} \dots$$

Now $\delta F^{(3)} = \frac{1}{3!} \left(\frac{\partial^3 F}{\partial X^3}\right) (\delta X)^3$ Sign depends on δX

$$\Rightarrow \left(\frac{\partial^3 F}{\partial X^3}\right) = 0 \quad \text{and} \quad \left(\frac{\partial^4 F}{\partial X^4}\right) > 0$$

More generally

$$\left(\frac{\partial \xi_i}{\partial X_i}\right) = 0 \quad \text{and} \quad \left(\frac{\partial^2 \xi_i}{\partial X_i^2}\right) = 0 \quad \xi_i \text{ intensive conjugate to extensive } X_i$$

Critical States

For fluid

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

determined from EOS

Third Law

The entropy of a system at absolute zero Kelvin is a finite constant.

$$\lim_{T \rightarrow 0} S = S_0$$

Planck: The entropy of a perfect crystal at T=0 K is zero

With Boltzmann's statistical definition, 3rd is automatically satisfied.

$$S = k \ln \Omega$$

Consequences of Third Law

Calculating absolute entropy

$$S(T) = \int_0^T \frac{C_P}{T} dT$$

If there are phase transitions, including latent heat.

Example gas

$$S(T) = \int_0^{T_m} \frac{C_{P,s}}{T} dT + \frac{\Delta_{fus}H}{T_m} + \int_{T_m}^{T_b} \frac{C_{P,l}}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^T \frac{C_{P,g}}{T} dT$$

Consequences of Third Law

$$\lim_{T \rightarrow 0} C_X = 0$$

X can be anything, P , V , E , etc.

Proof:

$$S(0) = S(T) + \left(\frac{\partial S}{\partial T} \right) (0 - T) + O(T^2)$$

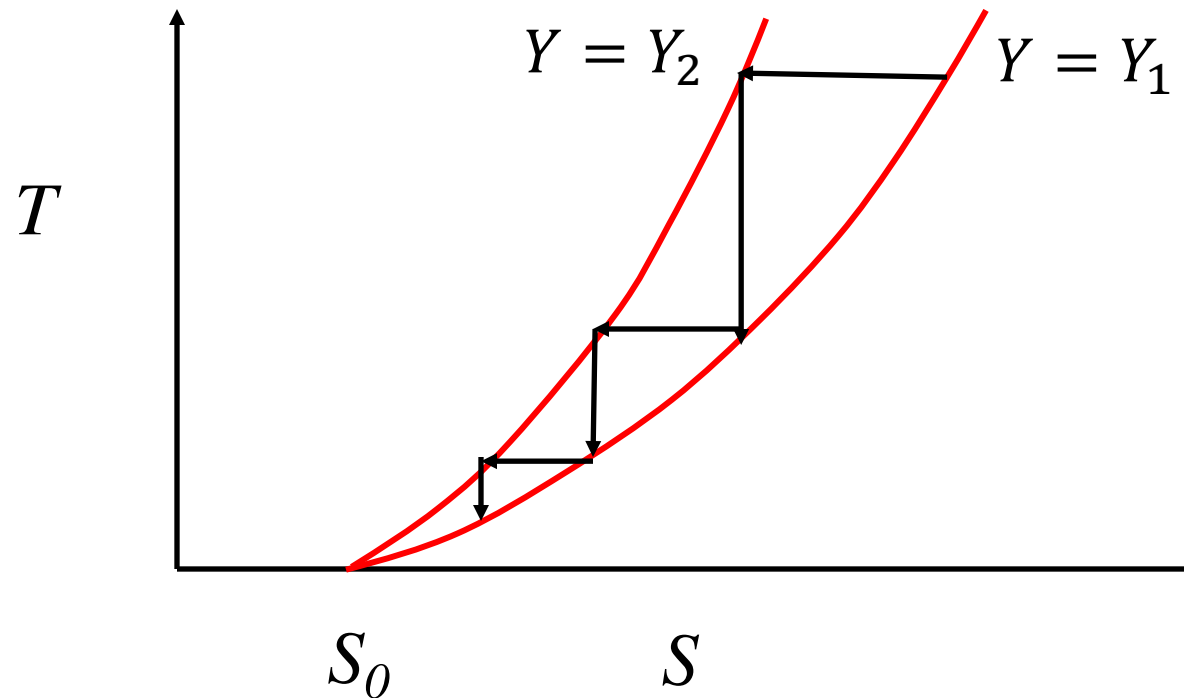
$$S(0) = S(T) - T \left(\frac{\partial S}{\partial T} \right) + O(T^2)$$

Since $\lim_{T \rightarrow 0} S(T) = S(0) \quad \Rightarrow \quad \lim_{T \rightarrow 0} T \left(\frac{\partial S}{\partial T} \right) = 0$

i.e. $C_X(0) = 0$

Consequences of Third Law

It is impossible to reach absolute zero K by a finite number of isothermal-adiabatic steps



Y can be magnetic field

T-S diagram: useful for analyzing reversible heat
(analogue of P-V diagram for work)

$$Q_{rev} = \int T dS$$

Questions to Think about

- Think physically why $C_p > C_V$ $\kappa_T > \kappa_S$
- Repeat the physical interpretation for mechanical and diffusional stability
- Is it necessary to know the absolute value of entropy?

Lecture 11

- Ideal gas
 - fundamental equation perspective
 - entropic origin of EOS
 - chemical potential
 - properties
- Real gas
 - virial EOS
 - van der Waals
 - hard sphere (Carnahan-Starling)
 - Redlich-Kwong, Peng-Robinson
 - properties

Read Ch. 7 Sandler, Chs. 9 and 11 Callen

Objectives

- Know *everything* about ideal gas
- Memorize vdW EOS
- Be able to calculate property and property changes for vdW EOS and virial EOS

Ideal Gas

Defined by IG EOS

$$PV = nRT$$

$$Pv = RT$$

Fundamental equation

$$s = s_0 + f(u) + R \ln(v/v_0)$$

$$S = ns_0 + nf(U/n) + nR \ln(V/Nv_0)$$

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

$$\longrightarrow \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{n,V} = f'_u$$

$$\left(\frac{\partial^2 S}{\partial U^2} \right)_{n,V} = \left(\frac{\partial (\frac{1}{T})}{\partial U} \right)_{n,V} = -\frac{1}{T^2 C_V} = -\frac{1}{n} f''_{uu} \quad \text{so} \quad C_V = -\frac{n}{T^2 f''_{uu}}$$

Special Case of Constant Cv

$$dU = C_V dT \quad U = C_V T \quad dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dn$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{n,V} = f'_u \quad \longrightarrow \quad f(u) = aR \ln(u/u_0)$$

$$\longrightarrow \quad u = aRT$$

$$C_V = naR$$

PVT Equation of State

from $S = ns_0 + nf(U/n) + nR\ln(V/Nv_0)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dn$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{n,U} = \left(\frac{\partial s}{\partial v}\right)_{n,u} = \frac{nR}{V}$$

$\longrightarrow PV = nRT$

Pressure of IG is **entropic in origin**

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\overset{0}{\cancel{\left(\frac{\partial U}{\partial V}\right)_T}} + T\left(\frac{\partial S}{\partial V}\right)_T$$

Chemical Potential of Ideal Gas

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial n}\right)_{U,V} = s_0 + f(u) - \frac{u}{T} + R \ln \frac{v}{v_0} - R \quad dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dn$$

For special case $f=aR\ln(u/u_0)$

$$\mu = -Ts_0 - aR \ln \frac{aRT}{u_0} + R \ln \frac{Pv_0}{RT} + (a+1)R$$

From Euler equation $U = TS - PV + \mu n \quad \longrightarrow \quad G = U - TS + PV = \mu n$

$\mu(T, P)$ is molar Gibbs free energy

Knowing $\mu(T, P)$ we obtain $G(n, T, P) = n\mu(T, P)$

Fundamental equation!

Chemical Potential of Ideal Gas

Alternatively, since m is molar Gibbs free energy, we have

$$d\mu = -s dT + v dP$$

Integrating at constant T

$$\mu(P, T) = \mu(P_0, T) + RT \ln \frac{P}{P_0}$$

Often choose P_0 as standard pressure P^\ominus (1 bar)

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

Reference chemical potential is given by fundamental equation (we derive it in stat. mech.)

Properties of Ideal Gas

- U and H are functions of temperature only and independent of density or pressure
- Joule coefficient

$$\left(\frac{\partial T}{\partial V}\right)_{N,U} = 0$$

- Joule-Thomson coefficient

$$\left(\frac{\partial T}{\partial P}\right)_{N,H} = 0$$

- Chemical potential

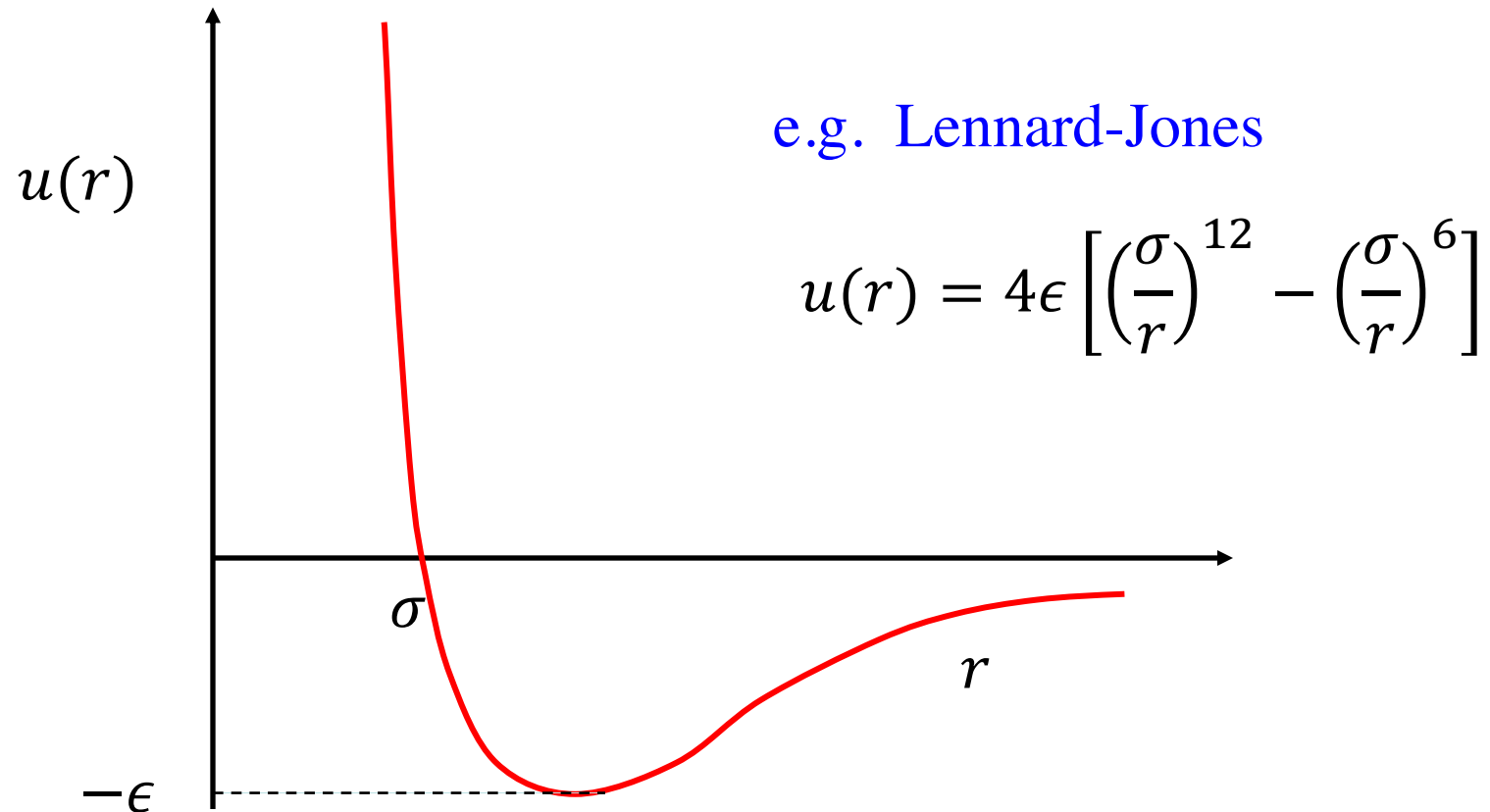
$$\mu = \mu^{(0)}(T) + RT \ln(p / p^{(0)})$$

a fundamental equation

Real Gases

Interactions

- Short-range hard repulsion (excluded volume)
- Long-range attraction (dispersion interaction)



Real Gases

- Virial EOS

$$P = \rho RT[1 + B\rho + C\rho^2 + \dots] = \rho RTZ \quad \text{Z: compressibility factor}$$

$$Z = 1 + B'P + C'P^2 + \dots \quad B' = \frac{B}{RT}, C' = \frac{C - B^2}{(RT)^2}$$

- Hard-spheres (Carnahan-Starling) $b_0 = N_a(\pi/6)\sigma^3$

$$P = \frac{RT}{v} \left[\frac{v^3 + b_0v^2 + b_0^2v - b_0^3}{(v - b_0)^3} \right]$$

- Hard-spheres + attraction

$$P = \frac{RT}{v} \left[\frac{v^3 + b_0v^2 + b_0^2v - b_0^3}{(v - b_0)^3} \right] - \frac{a}{v^2}$$

Real Gases

- **Van der Waals**

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

a : two-body attraction
 b : excluded volume

- **Redlich-Kwong**

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

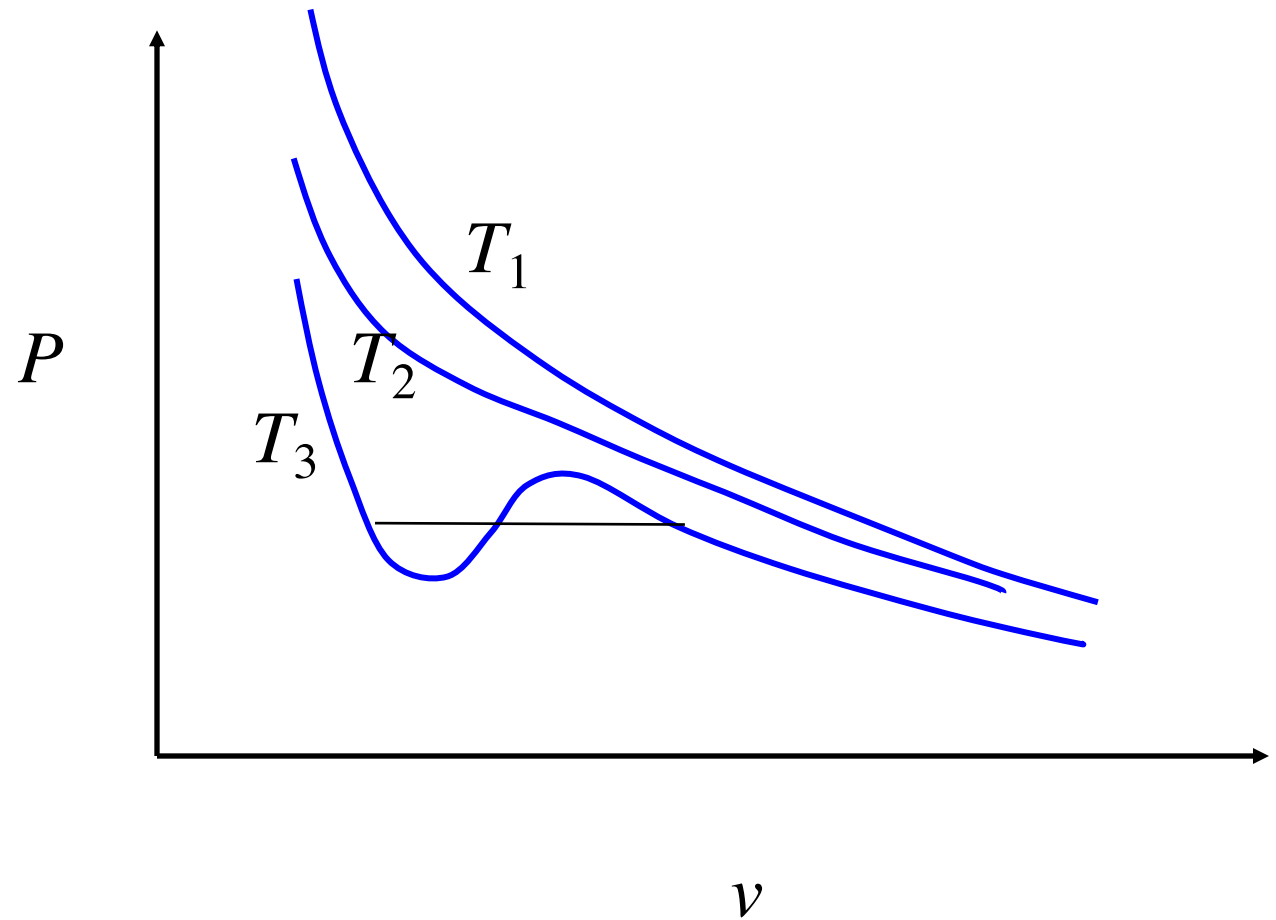
- **Peng-Robinson**

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

accurate up to high pressures
widely used in industrial modeling

P-V Isotherm

- Pressure increases with T and decreases with v
- At sufficiently low T , can have nonmonotonic behavior, signaling vapor-liquid transition
- Some portion violates stability condition
- Use Maxwell construct to get rid of unphysical region



Properties of Real Gases

- U, H, functions of T and P (or V)
- Nonzero Joule and Joule-Thompson coefficients
- Can condense into liquid phase at sufficiently low temperature and/or high pressure

usually $\left(\frac{\partial T}{\partial V}\right)_U < 0$

but $\left(\frac{\partial T}{\partial P}\right)_H$ can change sign

Joule Coefficient for vdW Gas

$$\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{c_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right]$$

For vdW gas

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

$$\left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] = \frac{a}{v^2}$$

$$\left(\frac{\partial T}{\partial v}\right)_u = -\frac{a}{v^2 c_V}$$

Joule coefficient usually negative

Joule-Thomson Coefficient for vdW Gas

$$\left(\frac{\partial T}{\partial P}\right)_H = \left[\frac{2a}{RT} \left(\frac{v-b}{v}\right)^2 - b \right] \left[\frac{5R}{2} - \frac{3a}{vT} \left(\frac{v-b}{v}\right)^2 \right]^{-1}$$

low density $v \rightarrow \infty$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{2}{5R} \left(\frac{2a}{RT} - b \right)$$

inversion temperature

$$T_{inv} = \frac{2a}{Rb}$$

$T < T_{inv}$ cooling upon throttling (liquefaction)

$T > T_{inv}$ heating upon throttling

Questions to Think about

- What's the physical reason that the Joule coefficient is negative?
- Why the Joule coefficient of the vdW gas doesn't depend on the parameter b ?
- How does the chemical potential behave as the pressure or density approaches zero?