Lecture 6
Observability

O'Connell & Haile
Chapter 8

Topics:

- **Stability**
  - Differential & Global Criteria
  - Pure Components
    - Spinodals & Phase Boundaries
    - Clapeyron Equation & Enthalpies
  - Mixtures
  - Applications
    - VLE
    - LLE

STABILITY I.

Basic Question:
Will a proposed thermodynamic state be observed?

Answer:
In general, if equilibrium criteria not met or entropy can be generated by changing to alternative state, it will, when it can overcome existing free energy barriers

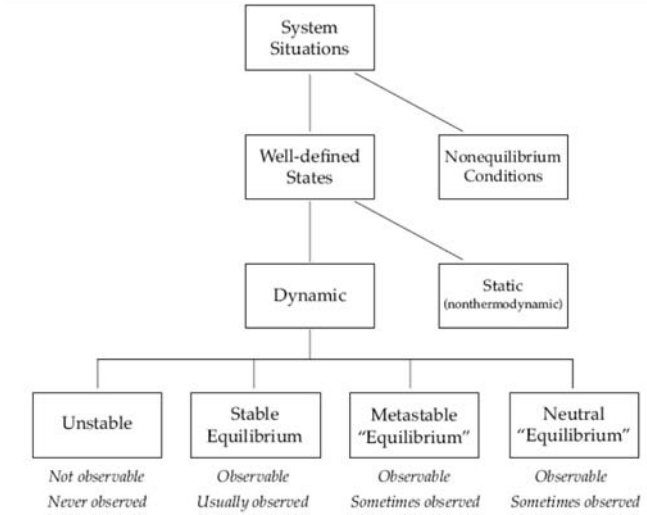
Next Question:
How to test stability in terms of measurables?

Answer: Do some derivation & some modeling

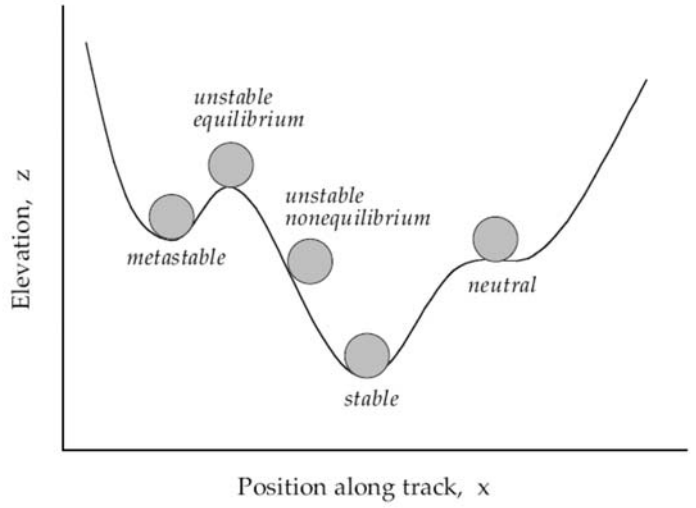
Prominent example:
Will system be 1 phase if *T* & *P* are specified?

Answer: Yes or no; find lowest possible *G* value

Hierarchy of possible well-defined states:
Cases: Unstable, Stable, Metastable, Neutral



Analogs in mechanical situation



Unstable *never* observed: since molecules always provide disturbance

In mechanical case, no balancing force if $\frac{dz}{dx} \neq 0$

Neutral equilibrium is point of inflection.

Stable equilibrium = *global* minimum; metastable = *local* minimum

<u>Differential</u> criterion $\frac{dz}{dx} = 0$, $\frac{d^2z}{dx^2} > 0$ **gives same result for both stable & metastable**

System can get from local (metastable) to global (stable) only if finite disturbance occurs (Δx) to overcome local increase in *z*

<u>STABILITY II. (Closed Systems)</u>

Disturb isolated homogeneous system to A & B

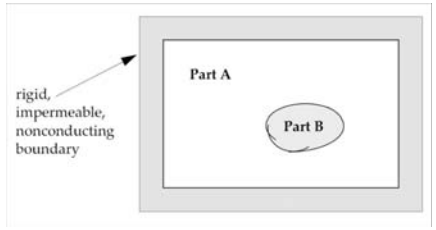
Variational treatment says

$$\Delta S = \delta S + \delta^2 S + \ldots$$

System *S* maximum,

$\Delta S < 0$, $\delta S = 0$ **&**

$\delta^2 S + \delta^3 S \leq 0$



with

$$0 = \delta S = \sum_{\alpha=A}^{B} \left[\left(\frac{\partial S^\alpha}{\partial U^\alpha} \right)_{V^\alpha} \delta U^\alpha + \left(\frac{\partial S^\alpha}{\partial V^\alpha} \right)_{U^\alpha} \delta V^\alpha \right]$$

$$= \frac{1}{T^A}\delta U^A + \frac{1}{T^B}\delta U^B - \frac{P^A}{T^A}\delta V^A - \frac{P^B}{T^B}\delta V^B$$

$$\Rightarrow \; T^A = T^B; P^A = P^B$$

<u>STABILITY III.</u>

$$0 > \delta^2 S = \sum_{\alpha=A}^{B} [S^\alpha_{uu}(\delta U^\alpha)^2 + 2S^\alpha_{uv}\delta U^\alpha \delta V^\alpha + S^\alpha_{vv}(\delta V^\alpha)^2]$$

where $S^\alpha_{uu} \equiv \left[\left(\frac{\partial^2 S}{\partial U^2} \right)_V \right]^\alpha \quad S^\alpha_{uv} \equiv \left[\left(\frac{\partial^2 S}{\partial U \partial V} \right) \right]^\alpha$**, etc.**

or $0 > \delta^2 S = (\delta U \delta V)$**S, symmetric matrix**

$S = \begin{vmatrix} S_{uu} S_{uv} \\ S_{uv} S_{vv} \end{vmatrix}$ **S must be *negative definite* for differential stability**

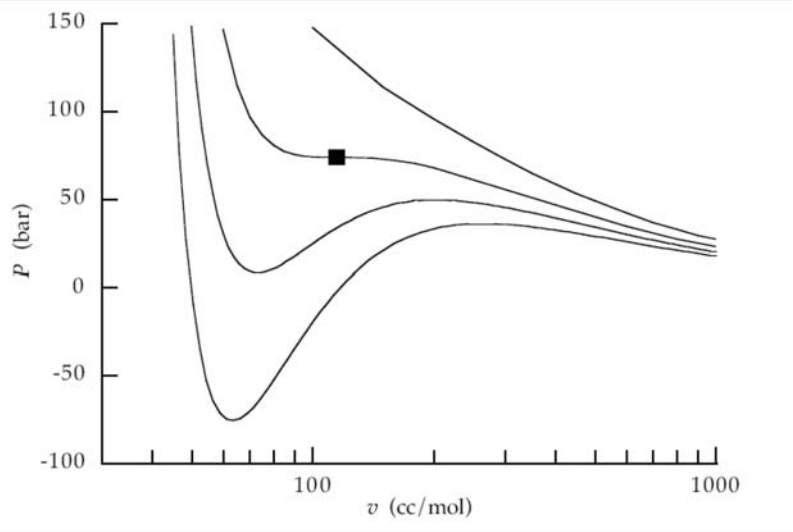
Two consequences:

$$S_{uu} = -\frac{1}{T^2 c_v} < 0 \qquad \textbf{or} \quad c_v > 0$$

$$S_{uu}S_{vv} - S^2_{uv} = \frac{1}{T^3 c_v v \kappa_T} > 0 \;\; \textbf{or}$$

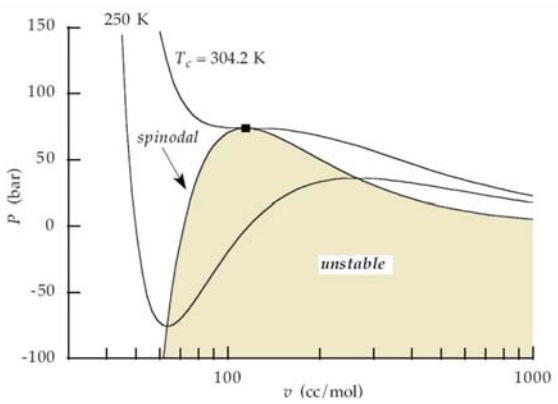
$$\kappa_T \equiv -\left(\frac{\partial \ln v}{\partial P} \right)_T > 0 \Rightarrow \left(\frac{\partial P}{\partial v} \right)_T < 0$$

Consider R-K EOS isotherms on *P-v* graph



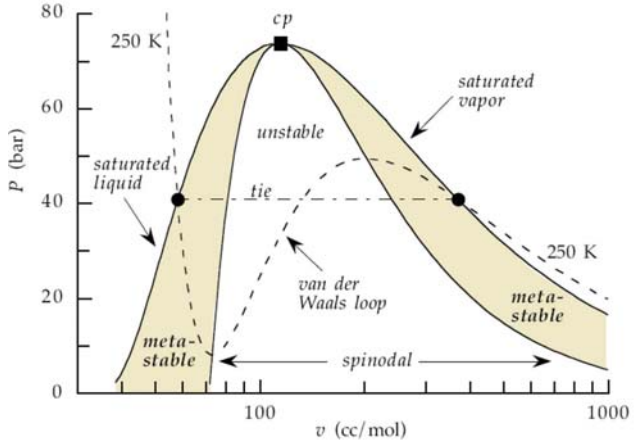
Region of instability bounded by spinodal

$$1/\kappa_T \equiv -1/\left.\frac{\partial \ln v}{\partial P}\right)_T = \infty \Rightarrow \left.\frac{\partial P}{\partial v}\right)_T = 0$$



Metastable bounded by spinodal & phase boundary

Critical point is on <u>both</u> spinodal & phase boundary



Spinodal is locus of $\left.\frac{\partial P}{\partial v}\right)_T = 0$ **(Note:** $\therefore \kappa_T = \infty$**)**

For R-K EoS

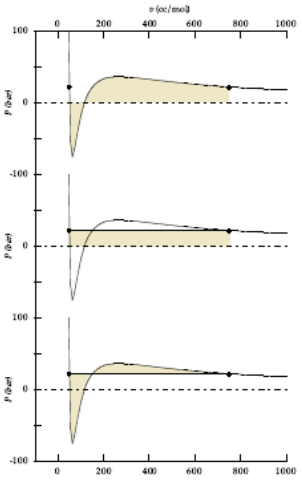
$$T_{sp}(v) = \left[\frac{a(2v+b)(v-b)^2}{Rv^2(v+b)^2}\right]^{2/3}$$

Phase Boundary where

$$P^v = P^l \equiv P^s,\ T^v = T^l \equiv T,$$
$$f^v = f^l,\ \phi^v = \phi^l$$

Gives 3 relations of *PV*

Also gives 3 equations to solve for P^s, v^v, v^l for $T<T_c$



$$P^s \equiv P(T, v^v) = P(T, v^l) = \frac{1}{v^v - v^l}\int_{v^l}^{v^v} P(T, \psi)d\psi$$

STABILITY IV.

EOS gives enthalpies for phase change

$$\Delta h^{vap} = T\int_{v^l}^{v^v} \gamma_v(T, \psi)d\psi$$ **for $T < T_c$, but also**

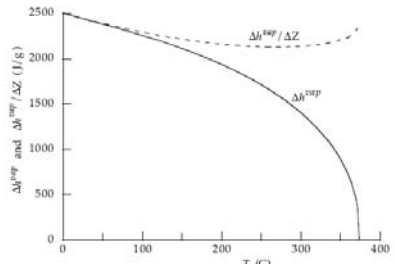
$$\frac{dP^s}{dT} = \frac{1}{v^v - v^l}\int_{v^l}^{v^v} \gamma_v(T, \psi)d\psi$$ **where** $\gamma_v \equiv \left.\frac{\partial P}{\partial T}\right)_v \Rightarrow$

Clapeyron Eq. $\frac{dP^s}{dT} = \frac{\Delta h^{vap}}{T(v^v - v^l)} = \frac{\Delta h^{vap}}{T\Delta v^{vap}} = \frac{\Delta h^{vap} P}{T^2 \Delta Z^{vap}}$

(With Δv, useful for *all* phase changes, with ΔZ, only for vaporizing, subliming)

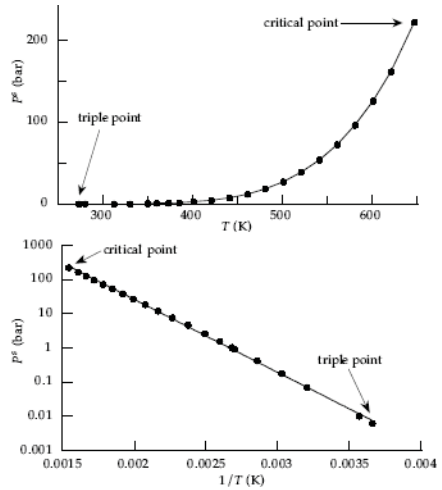
Gives <u>slope</u> of 2-phase curve on *P-T* diagram

Note variation of Δh^{vap} but not of $\frac{\Delta h^{vap}}{\Delta Z^{vap}}$

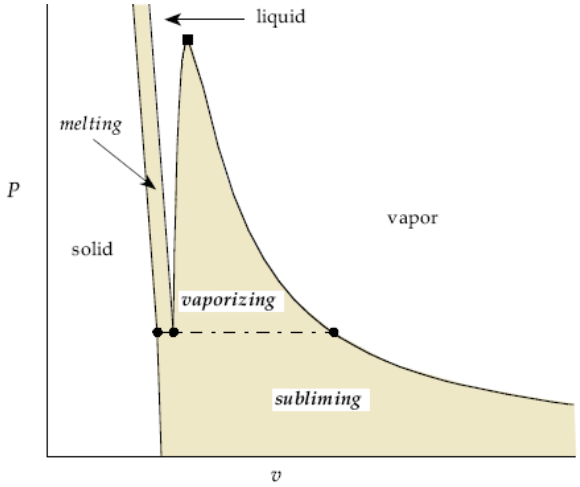


Rearrange to linear plot via $\frac{d \ln P^s}{d(1/T)} = -\frac{\Delta h^{vap}}{R(Z^v - Z^l)}$

Slope on lnP^s-1 / T plot (~constant $= -\frac{\Delta h^{vap}}{R}$) at low T



Solids complicated; no EOS for solids



STABILITY V.

Isolated binary system with open parts

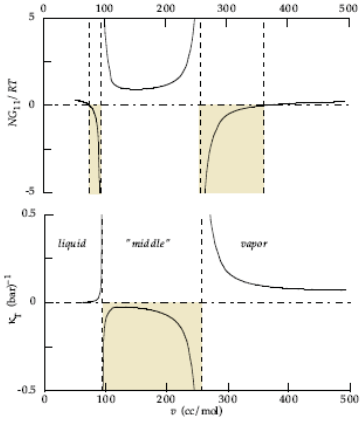
Same Derivation: negative definite matrix

$$S = \begin{vmatrix} S_{uu} & S_{uv} & S_{un_1} & S_{un_2} \\ S_{uv} & S_{vv} & S_{vn_1} & S_{vn_2} \\ S_{un_1} & S_{vn_1} & S_{n_1n_1} & S_{n_1n_2} \\ S_{un_2} & S_{vn_2} & S_{n_1n_2} & S_{n_2n_2} \end{vmatrix}$$

Ultimately, stability requires principal minors > 0

$$\frac{1}{T^4 c_v \nu \kappa_T} \frac{\partial \overline{G}_1}{\partial N_1}\Big)_{T,P,N_2} \equiv \frac{\overline{G}_{11}}{T^4 c_v \nu \kappa_T} > 0$$

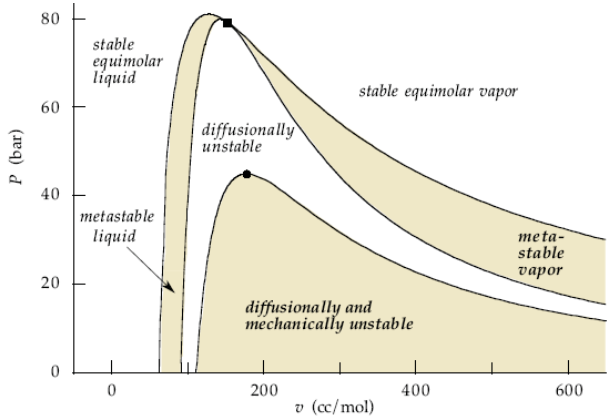
Use full expression - c_v & k_T may both be < 0



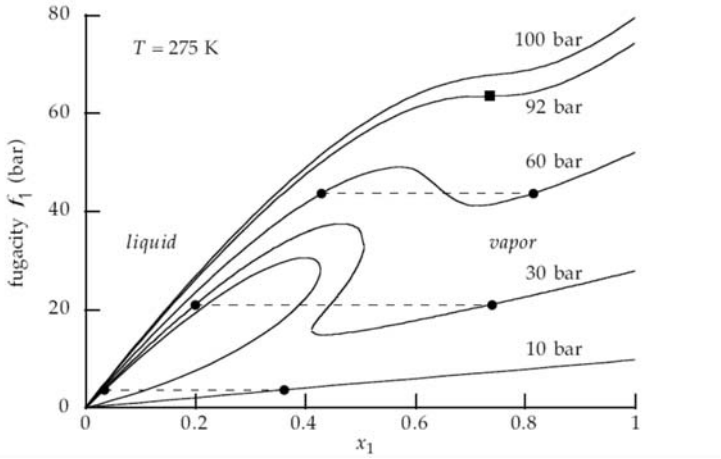
Also order of EOS criteria

Diffusional $\left.\frac{\partial \overline{G}_1}{\partial N_1}\right)_{T,P,N_2} > 0$ **violated 1st,**

Mechanical 2nd, $\left.\frac{\partial P}{\partial v}\right)_T > 0$**, Thermal 3rd** $c_v < 0$



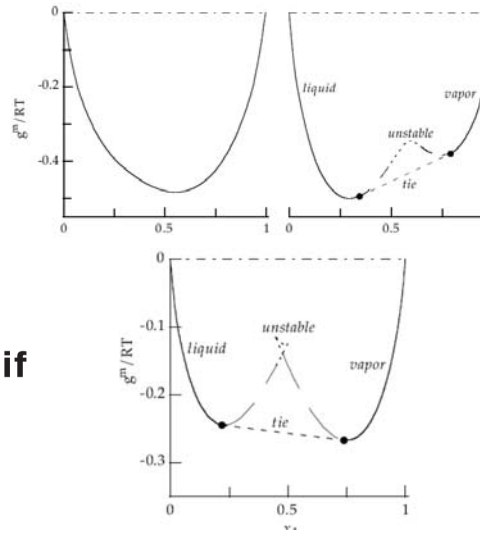
Fugacity also shows meta- & instabilities



STABILITY VI.

Ignore mechanical/thermal criteria - use mixing(*g*^{m}) + EOS

Diffusional stability derivative gives different cases



Using R-K EOS with

$$\frac{g^m}{RT} = \sum_{i=1}^{2} x_i \ln\left(\frac{x_i \phi_i}{\phi_{pure\ i}}\right)$$

(Branches on *g*^{m} line if have multiple *v*'s)

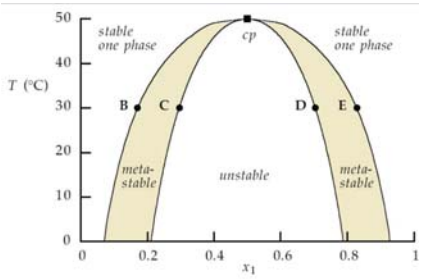
Also use ideal solution reference for *g*^{m}

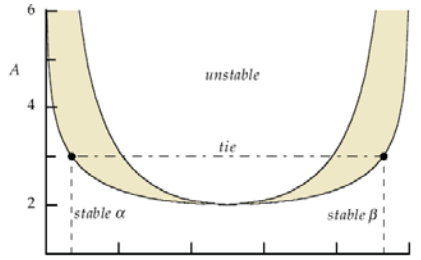
$\Rightarrow \left.\frac{\partial^2 (g^E/RT)}{\partial x_1^2}\right|_{T,P} + \frac{1}{x_1 x_2} > 0$ **at stability/metastability) -instability boundary; e.g., for Porter Model**

$g^E/RT = Ax_1x_2 \Rightarrow$ stability if $A < 2$

Case

$A = 2 + 0.02[323.15 - T(K)]$





Can use other independent variables (*e.g., T, v*)