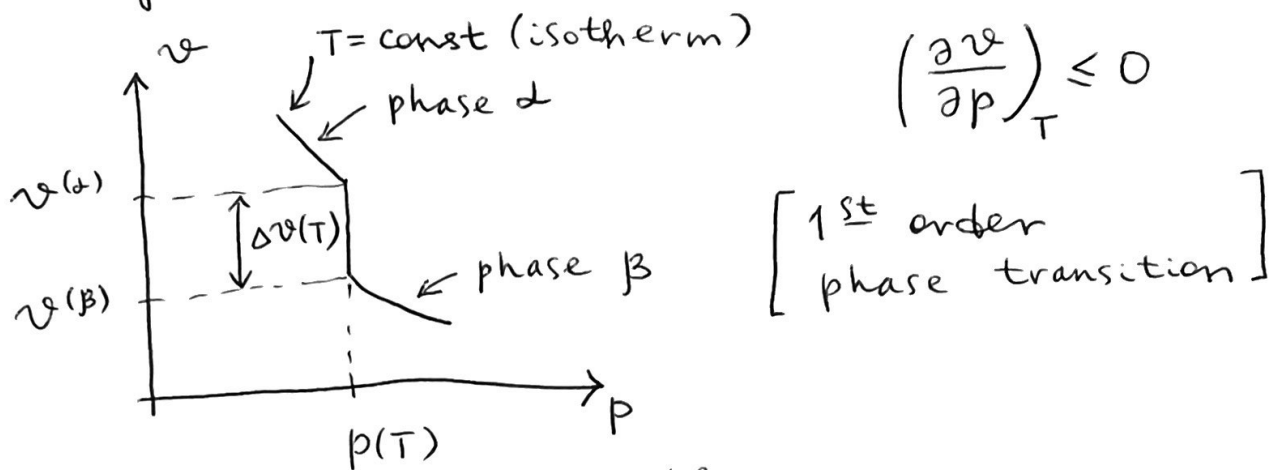


Lecture 5

Now consider the p - v plane in a one-component ($r=1$) system.



Solution of the (CC) Clausius-Clapeyron eq'n

$v^{(\alpha)}$ = volume per mole of phase α @ equil. with phase β at a temp. T

$v^{(\beta)}$ = same for phase β

$$\left\{ \begin{array}{l} p(T) = p^{(\alpha)}(T, v^{(\alpha)}) = p^{(\beta)}(T, v^{(\beta)}) \\ \mu(T) = \mu^{(\alpha)}(T, v^{(\alpha)}) = \mu^{(\beta)}(T, v^{(\beta)}) \end{array} \right.$$

\downarrow can be used to get $v^{(\alpha)}(T), v^{(\beta)}(T)$
 from CC eq's

Note that the CC eq'n in the μ - T plane requires

$$p^{(\alpha)}(\mu, T) = p^{(\beta)}(\mu, T) \leftarrow \text{inversion of } \mu^{(\alpha)}(p, T) = \mu^{(\beta)}(p, T)$$

But then the GD eq'n gives

$$dp = \underbrace{\frac{S}{V}}_S dT + \underbrace{\frac{h}{V}}_p d\mu$$

per unit volume

Next, $dp^{(\alpha)}(\mu, T) = dp^{(\beta)}(\mu, T)$ along the co-existence line, yielding

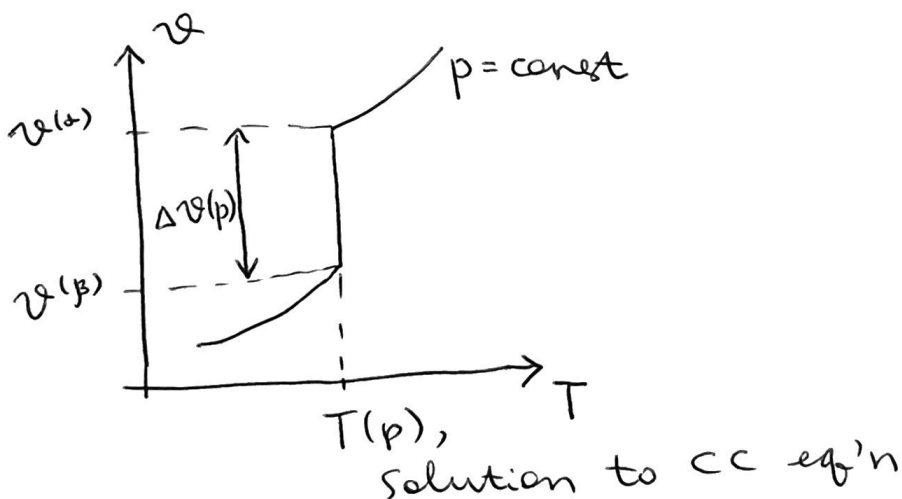
$$S^{(\alpha)} dT + p^{(\alpha)} d\mu = S^{(\beta)} dT + p^{(\beta)} d\mu,$$

$$\text{or } \frac{dT}{d\mu} = \frac{p^{(\beta)} - p^{(\alpha)}}{S^{(\alpha)} - S^{(\beta)}} = - \frac{\Delta p}{\Delta S},$$

$$\left(\text{where } \begin{cases} \Delta p = p^{(\beta)} - p^{(\alpha)} \\ \Delta S = S^{(\beta)} - S^{(\alpha)} \end{cases} \right.$$

get $T(\mu)$
or $\mu(T)$

Can also look at the v - T plane:



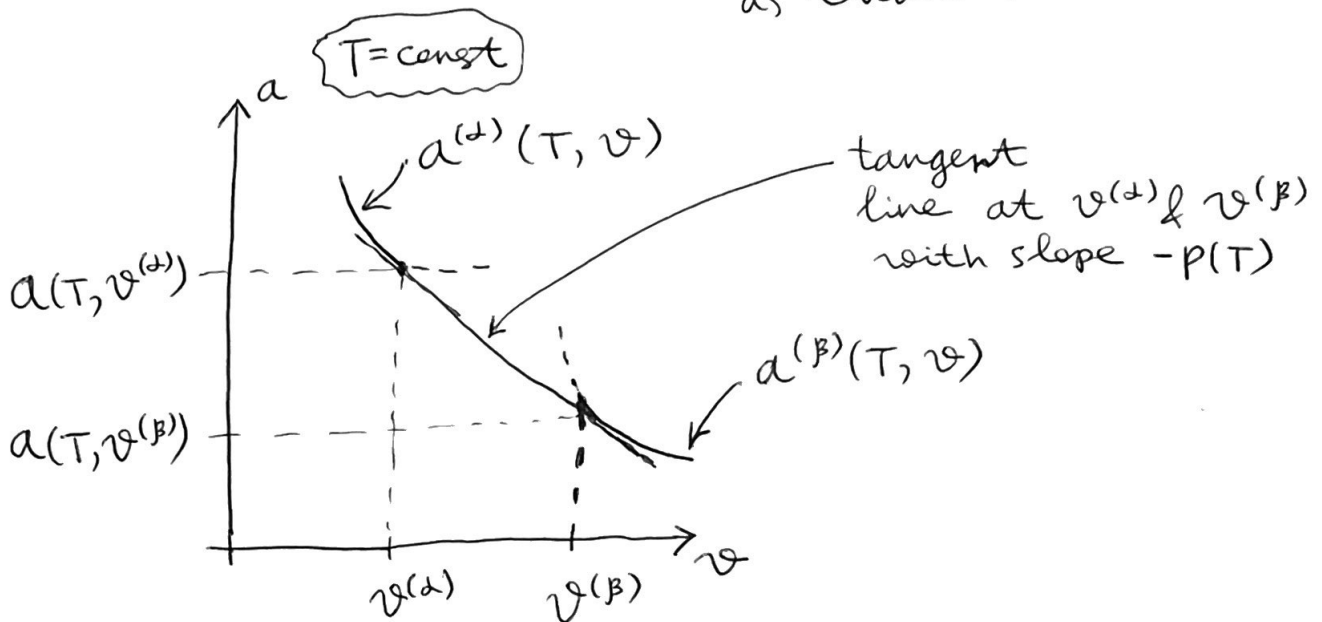
Maxwell construction

Let $a = \frac{A}{n}$ if $n = \text{const}$, $A = A(T, V)$

Consider $T = \text{const} \Rightarrow a = a(v)$ as well Imagine $\alpha \rightarrow \beta$ phase transition occurs

Recall that $\left(\frac{\partial A}{\partial V}\right)_T = -P \Rightarrow \left(\frac{\partial a}{\partial v}\right)_T = -P.$

At equil., $p^{(\alpha)}(T, v^{(\alpha)}) = p^{(\beta)}(T, v^{(\beta)}) = P(T).$ \leftarrow slope of a at $v = v^{(\alpha)}$ is the same as that at $v = v^{(\beta)}$



$$\frac{a(T, v^{(\alpha)}) - a(T, v^{(\beta)})}{v^{(\alpha)}(T) - v^{(\beta)}(T)} = -P(T), \text{ or}$$

$$(a + Pv)^{(\alpha)} = (a + Pv)^{(\beta)},$$

$$\mu^{(\alpha)} = \mu^{(\beta)}$$

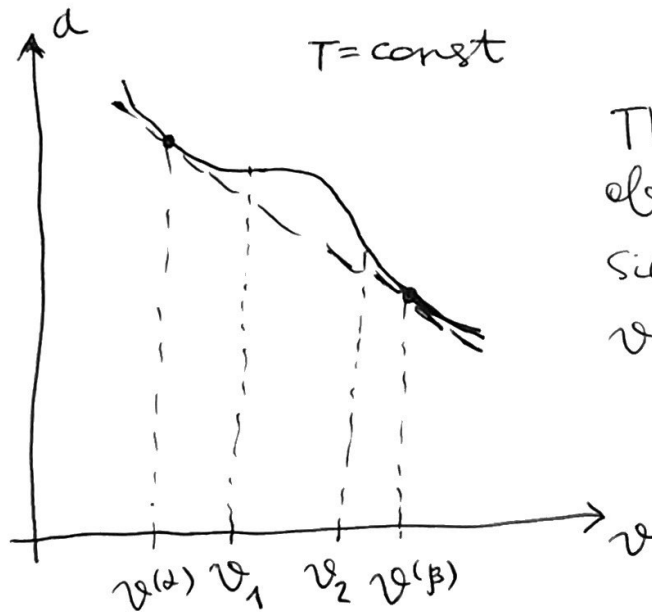
Finally, we realize that $p = p(T) \Rightarrow$
 \Rightarrow the slope is fixed $[= -p(T)]$ for
 any mixture of α & β phases with
 $v^{(\alpha)} < v < v^{(\beta)}$. So, the tangent line
is the free energy in the two-phase
 region. Hence

$$a_{\text{two-phase}} = a^{(\alpha)} + \frac{v - v^{(\alpha)}}{v^{(\beta)} - v^{(\alpha)}} [a^{(\beta)} - a^{(\alpha)}] =$$

$$= a^{(\alpha)} \frac{v^{(\beta)} - v}{v^{(\beta)} - v^{(\alpha)}} + a^{(\beta)} \frac{v - v^{(\alpha)}}{v^{(\beta)} - v^{(\alpha)}}, \text{ where}$$

$$\begin{cases} a^{(\alpha)} = a(T, v^{(\alpha)}(T)), \\ a^{(\beta)} = a(T, v^{(\beta)}(T)) \end{cases}$$

Ex. In a model system, one may
 observe

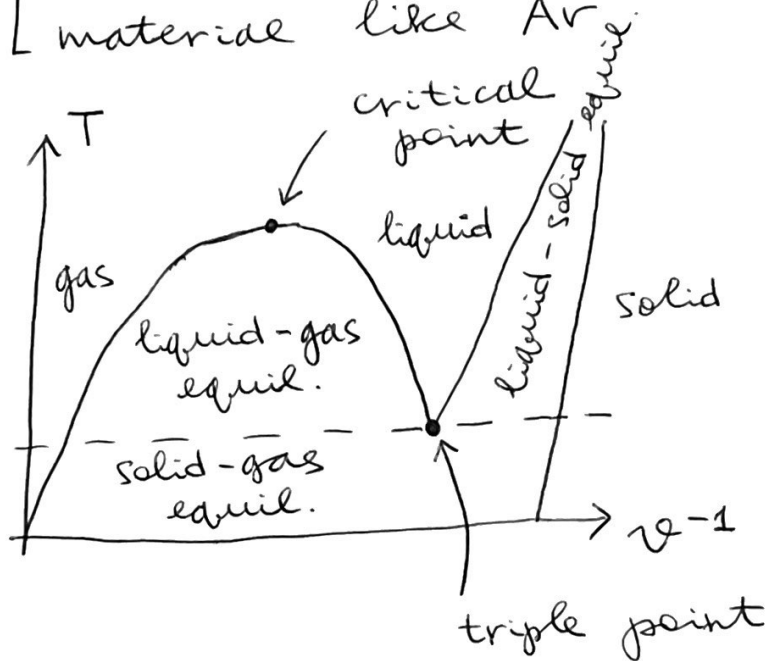


The curvature
 of $a(v)$ changes
 sign between
 v_1 & v_2

But then
$$\left(\frac{\partial^2 a}{\partial v^2}\right)_T = - \underbrace{\left(\frac{\partial p}{\partial v}\right)_T}_{\text{instability}} < 0$$

Need to replace the solid line between $v^{(\alpha)}$ & $v^{(\beta)}$ by the Maxwell construction (dashed tangent line).

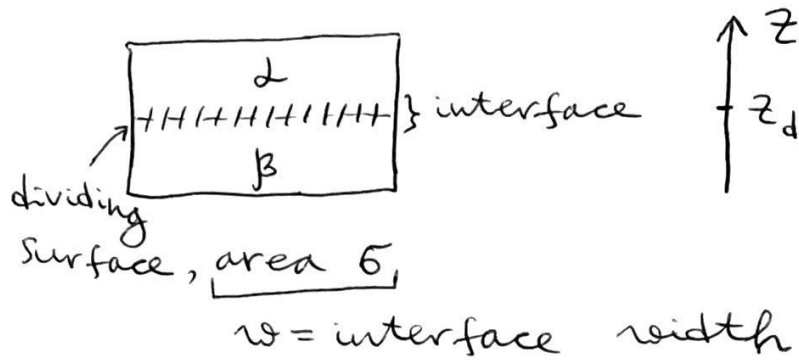
[Phase diagram of a simple material like Ar]



solid lines = locus of all $v^{(\alpha)}(T)$, $v^{(\beta)}(T)$, $v^{(\gamma)}(T)$ values as T changes

plane interfaces

Two phases at equil. \Rightarrow } interface between them



$$E = E^{(\alpha)} + E^{(\beta)} + \underbrace{E^{(s)}}_{\text{surface energy}}$$

Introduce $\gamma = \left(\frac{\partial E}{\partial \sigma} \right)_{S, V, n} \geq 0$ intensive
 surface tension

Then $dE = TdS - pdV + \mu dn + \gamma d\sigma$

$\gamma < 0$ would lead to an unstable interface: $E \downarrow$ as $\sigma \uparrow$, the surface will spread over the entire system.

Stable interfaces require two-phase equilibrium, $f = 2 + r - J = r$.

by choice #DoF \uparrow \downarrow $r=1$

$$\gamma = \gamma(T, x_1, \dots, x_{r-1}) \Rightarrow \gamma = \gamma(T)$$

mole fractions

E is $n=1$ homog. in S, V, n, σ :

$$E = TS - pV + \mu n + \gamma \sigma.$$

$\underbrace{\hspace{1.5cm}}_{\sim N}$
 $\underbrace{\hspace{1.5cm}}_{\sim N^{2/3}}$
, negligible
if $N \rightarrow \infty$

Imagine that both α and β phases maintain their bulk properties right until the interface.

$$\text{Consider } \begin{cases} dE^{(\alpha)} = TdS^{(\alpha)} - pdV^{(\alpha)} + \mu dn^{(\alpha)}, \\ E^{(\alpha)} = TS^{(\alpha)} - pV^{(\alpha)} + \mu n^{(\alpha)}. \end{cases}$$

$$\begin{cases} dE^{(\beta)} = TdS^{(\beta)} - pdV^{(\beta)} + \mu dn^{(\beta)}, \\ E^{(\beta)} = TS^{(\beta)} - pV^{(\beta)} + \mu n^{(\beta)}. \end{cases}$$

$$V = V^{(\alpha)} + V^{(\beta)} \Rightarrow V^{(s)} = 0$$

$\underbrace{\hspace{1.5cm}}_{\text{total volume}}$

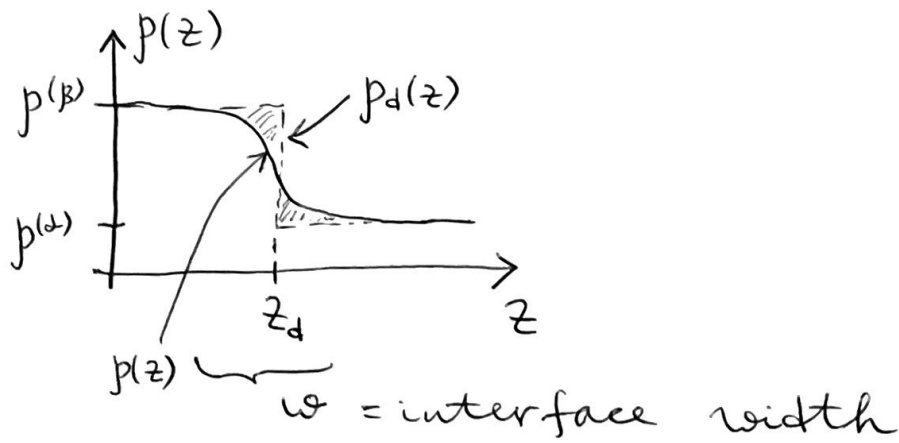
Other extensive properties:

$$X^{(s)} = X - X^{(\alpha)} - X^{(\beta)} \neq 0 \text{ in general}$$

$$\text{Consider } n^{(\beta)} = \int_{-\infty}^{z_d} dz \rho_d(z)$$

$$n^{(\alpha)} = \int_{z_d}^{\infty} dz \rho_d(z)$$

$\underbrace{\hspace{1.5cm}}_{\text{density per unit length}}$



$$\rightarrow n^{(s)} = n - n^{(\alpha)} - n^{(\beta)} = \int_{-\infty}^{\infty} dz p(z) - \int_{-\infty}^{\infty} dz p_d(z) = \int_{-\infty}^{\infty} dz [p(z) - p_d(z)] \quad (*)$$

\exists choice of z_d s.t. $n^{(s)} = 0 \Rightarrow$
 \Rightarrow Gibbs dividing surface

z_d can be obtained by solving
 $n^{(s)}(z_d) = 0$ in Eq. (*)



Now, consider

$$\rightarrow E^{(s)} \Rightarrow dE^{(s)} = dE - dE^{(\alpha)} - dE^{(\beta)} =$$

$$= TdS^{(s)} + \gamma d\sigma + \underbrace{\mu dn^{(s)}}_{=0 \text{ for the Gibbs dividing surface}}$$

$$\uparrow$$

$$dV = dV^{(\alpha)} + dV^{(\beta)}$$

"0 for the
Gibbs dividing surface

Then $E^{(s)} = TS^{(s)} + \gamma\sigma$, $dE^{(s)} = TdS^{(s)} + \gamma d\sigma$.

$$\gamma = \frac{E^{(s)} - TS^{(s)}}{\sigma} \Leftarrow \begin{array}{l} \text{surface tension} \\ \text{is free energy } A \\ \text{per unit area} \end{array}$$

$\gamma d\sigma$ is a restoring force that inhibits interface growth.

—○—

what if $r > 1$?

$$dE^{(s)} = TdS^{(s)} + \gamma d\sigma + \underbrace{\sum_{i=1}^r \mu_i dn_i^{(s)}}_{\text{no gibbs surface}}$$

Choose $n_1^{(s)} = 0$ (i.e. set z_d to make $n_1^{(s)}(z_d) = 0$)

$$\text{Then } dE^{(s)} = TdS^{(s)} + \gamma d\sigma + \sum_{i=2}^r \mu_i dn_i^{(s)}$$

$$\text{If } r=2, \quad dE^{(s)} = TdS^{(s)} + \gamma d\sigma + \mu_2 dn_2^{(s)},$$

which yields

$$E^{(s)} = TS^{(s)} + \gamma\sigma + \mu_2 n_2^{(s)}$$

GD equation:

$$\sigma d\gamma = -S^{(s)}dT - n_2^{(s)}d\mu_2$$

$$\text{If } T = \text{const}, \quad \underbrace{\sigma d\gamma = -n_2^{(s)}d\mu_2}_{\text{gibbs adsorption isotherm}}$$

Finally,

$$\frac{n_2^{(s)}}{\Gamma} = - \left(\frac{\partial \sigma}{\partial \mu_2} \right)_T = - \left(\frac{\partial \sigma}{\partial p_2} \right)_T \underbrace{\left(\frac{\partial p_2}{\partial \mu_2} \right)_T}_{>0}$$

$\underbrace{\quad}_{>0}$; $\begin{cases} n_1 = \text{solvent,} \\ n_2 = \text{solute} \end{cases}$
 \uparrow as solute
accumulates on
the surface

by stability

$\left(\frac{\partial \sigma}{\partial p_2} \right)_T < 0 \Rightarrow$ surface
tension
decreases
as $p_2 \uparrow$