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

\[
\begin{align*}
T &= \text{const (isotherm)} \quad \left( \frac{\partial v}{\partial p} \right)_T \leq 0 \\
\Delta v(T) &\quad \text{phase \(\alpha\)} \\
&\quad \text{phase \(\beta\)} \\
&\quad [1^{\text{st}} \text{order phase transition}] \\
\end{align*}
\]

\[p(T)\]

Solution of the Clausius-Clapeyron eq'n

\[v^{(\alpha)} = \text{volume per mole of phase } \alpha \text{ at equil. with phase } \beta \text{ at a temp. } T\]

\[v^{(\beta)} = \text{same for phase } \beta\]

\[
\begin{cases}
 p(T) = p^{(\alpha)}(T, v^{(\alpha)}) = p^{(\beta)}(T, v^{(\beta)}) \\
 M(T) = M^{(\alpha)}(T, v^{(\alpha)}) = M^{(\beta)}(T, v^{(\beta)})
\end{cases}
\]

\[\text{from CC eq's}\]

\[v^{(\alpha)}(T), v^{(\beta)}(T)\]

Note that the CC eq'n in the \(M-T\) plane requires
\[ p^{(\omega)}(\mu, T) = p^{(\beta)}(\mu, T) \quad \text{inversion of} \quad \mu^{(\omega)}(p, T) = \mu^{(\beta)}(p, T) \]

But then the GD eq'n gives
\[ dp = \frac{\delta}{V} dT + \frac{n}{V} d\mu \]
\[ \delta p \quad \text{per unit volume} \]

Next, \[ dp^{(\omega)}(\mu, T) = dp^{(\beta)}(\mu, T) \]
along the co-existence line, yielding
\[ s^{(\omega)} dT + p^{(\omega)} d\mu = s^{(\beta)} dT + p^{(\beta)} d\mu, \]

or
\[ \frac{dT}{d\mu} = \frac{p^{(\beta)} - p^{(\omega)}}{s^{(\omega)} - s^{(\beta)}} = -\frac{\Delta p}{\Delta s}, \]

\[ \left\{ \begin{array}{l}
\Delta p = p^{(\beta)} - p^{(\omega)} \\
\Delta s = s^{(\beta)} - s^{(\omega)}
\end{array} \right. \]

Can also look at the \( u-T \) plane:

\[ \text{solution to CC eq'n} \]
Maxwell Construction

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

Consider \( T = \text{const} \) \( \Rightarrow a = a(v) \)

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

At equilibrium, \( p(a\uparrow)(T, V(a\uparrow)) = p(b\downarrow)(T, V(b\downarrow)) = p(T) \).

Slope of \( a \) at \( V = V(a\uparrow) \) is the same as that at \( V = V(b\downarrow) \).

\[
\frac{a(T, V(a\uparrow)) - a(T, V(b\downarrow))}{V(a\uparrow)(T) - V(b\downarrow)(T)} = -p(T) \text{, or}
\]

\[
(a + p V)(a\uparrow) = (a + p V)(b\downarrow)
\]

\[
M(a\uparrow) = M(b\downarrow)
\]

\[-3-\]
Finally, we realize that $p = p(T) \Rightarrow$

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

$$a_{two-phase} = a^{(\alpha)} + \frac{\nu - \nu^{(\alpha)}}{\nu^{(\beta)} - \nu^{(\alpha)}} \left[ a^{(\beta)} - a^{(\alpha)} \right] =$$

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

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

Ex. In a model system, one may observe

The curvature of $a(\nu)$ changes sign between $\nu_1$ & $\nu_2$.
But then \( \left( \frac{\partial^2 \mathcal{A}}{\partial \mathbf{v} \partial \mathbf{v}} \right)_T = -\left( \frac{\partial p}{\partial \mathbf{v}} \right)_T \leq 0 \)

\[
\text{instability}
\]

Need to replace the solid line between \( \mathcal{V}^{(1)} \) and \( \mathcal{V}^{(2)} \) by the Maxwell construction (dashed tangent line).

[Phase diagram of a simple]

[material like Ar]

\[
\begin{align*}
\text{critical point} & \\
\text{liquid - gas equil.} & \\
\text{liquid - solid equil.} & \\
\text{triple point} & \\
\text{solid lines} = \text{locus of all } \mathcal{V}^{(1)}(T), \mathcal{V}^{(2)}(T), \mathcal{V}^{(3)}(T) \text{ values as } T \\
\end{align*}
\]
Plane interfaces

Two phases at equil. \( \Rightarrow \) \( \Gamma \) interface between them

\[
\begin{array}{c}
\text{interface} \\
\beta \\
\end{array}
\]

dividing surface, area \( \delta \)

\( \delta = \text{interface width} \)

\[
E = E^{(\alpha)} + E^{(\beta)} + E^{(s)}
\]

\( E \) surface energy

Introduce

\[
\Gamma = \left( \frac{\partial E}{\partial \delta} \right)_{s, v, n}
\]

surface tension

Then

\[
dE = TdS - pdV + \mu d\delta + \gamma d\delta
\]

\( \gamma < 0 \) would lead to an unstable interface: \( E \) as \( \delta \) \( \uparrow \), the surface will spread over the entire system.

Stable interfaces require two-phase equilibrium,

\[
\sum f = 2 + r - \# \text{DoF}
\]

by choice

\[
\gamma = \gamma (T, x_1, \ldots, x_{n-1}) \rightarrow \gamma = \gamma (T)
\]

\( \gamma \) mole fractions
E is \( n=1 \) homog. in \( S, V, n, \beta \):

\[
E = TS - pV + \mu n + \gamma \beta, \quad \sim N^{2/3}, \text{ negligible if } N \to \infty
\]

Imagine that both \( \alpha \) and \( \beta \) phases maintain their bulk properties right until the interface.

Consider:

\[
\begin{align*}
\frac{dE^{(\alpha)}}{dS} &= TdS^{(\alpha)} - pdV^{(\alpha)} + \mu dn^{(\alpha)}, \\
E^{(\alpha)} &= TS^{(\alpha)} - pV^{(\alpha)} + \mu n^{(\alpha)}, \\
\frac{dE^{(\beta)}}{dS} &= TdS^{(\beta)} - pdV^{(\beta)} + \mu dn^{(\beta)}, \\
E^{(\beta)} &= TS^{(\beta)} - pV^{(\beta)} + \mu n^{(\beta)}. \\
\end{align*}
\]

\[
V = V^{(\alpha)} + V^{(\beta)} \quad \Rightarrow \quad V^{(S)} = 0
\]

\( V \) total volume

Other extensive properties:

\[
X^{(S)} = X - X^{(\alpha)} - X^{(\beta)} \neq 0 \text{ in general}
\]

Consider:

\[
\begin{align*}
\mu^{(\beta)} &= \int_{-\infty}^{\infty} d\bar{z} \rho_{d}(\bar{z}), \\
\mu^{(\alpha)} &= \int_{-\infty}^{\infty} d\bar{z} \rho_{d}(\bar{z}), \\
\rho_{d}(\bar{z}) &\quad \text{density per unit length}
\end{align*}
\]

\( -7 - \)
\[ \omega = \text{interface width} \]

\[ h^{(s)} = h - h^{(\omega)} - h^{(\beta)} = \int_{-\infty}^{\infty} \mathrm{d}z \, p(z) - \int_{-\infty}^{\infty} \mathrm{d}z \, p_d(z) = \int_{-\infty}^{\infty} \mathrm{d}z \, [p(z) - p_d(z)] . \tag{*} \]

\[ \text{choice of } z_d \text{ s.t. } h^{(s)}(z_d) = 0 \Rightarrow \]

\[ \Rightarrow \text{gibbs dividing surface} \]

\[ z_d \text{ can be obtained by solving } h^{(s)}(z_d) = 0 \text{ in Eq. (*)} \]

Now, consider

\[ E^{(s)} \Rightarrow \]  

\[ dE^{(s)} = dE - dE^{(\omega)} - dE^{(\beta)} = \]

\[ = Tds^{(s)} + \gamma d\sigma + \mu dn^{(s)} \]

\[ \uparrow \]  

\[ dV = dv^{(\omega)} + dv^{(\beta)} \]

"0 for the gibbs dividing surface"

Then \[ E^{(s)} = TS^{(s)} + \gamma \sigma , \quad dE^{(s)} = Tds^{(s)} + \gamma d\sigma. \]
\[ \gamma = \frac{E(s) - TS(s)}{6} \leq \text{surface tension} \]

is free energy A per unit area

\[ \gamma dS \text{ is a restoring force that inhibits interface growth.} \]

What if \( r > 1 \)?

\[ dE(s) = TdS(s) + \gamma dS + \sum_{i=1}^{r} \mu_i dn_i(s) \]

Choose \( n_1(s) = 0 \) (i.e. set \( \xi_d \) to make \( n_1(s)(\xi_d) = 0 \))

Then \( dE(s) = TdS(s) + \gamma dS + \sum_{i=2}^{r} \mu_i dn_i(s) \)

If \( r = 2 \), \( dE(s) = TdS(s) + \gamma dS + \mu_2 dn_2(s) \),

which yields

\[ E(s) = TS(s) + \gamma S + \mu_2 n_2(s) \]

GD equation:

\[ 6d\gamma = -S^{(s)}dT - n_2^{(s)}d\mu_2. \]

If \( T = \text{const} \),

\[ 6d\gamma = -n_2^{(s)}d\mu_2 \]

Gibbs adsorption isotherm

-9-
Finally, \[
\frac{n_2(s)}{\bar{c}} = -\left( \frac{\partial f}{\partial \mu_2} \right)_T = -\left( \frac{\partial f}{\partial p_2} \right)_T \left( \frac{\partial p_2}{\partial \mu_2} \right)_T
\]

\(n_2\) as solute accumulates on the surface.

\[
\left( \frac{\partial f}{\partial p_2} \right)_T < 0 \Rightarrow \text{surface tension decreases as } p_2 \uparrow
\]

\(n_1\) = solvent, \(n_2\) = solute

\(> 0\) - leg stability