Recall the significance of $\mu_i = \frac{\partial G}{\partial n_i}$

the change in energy associated with the change in the amount of mass $i$ in the system.

The Gibbs-Duhem expression arises from the fact that intensive properties are not affected by the size of the system, but extensive properties are. So, for each phase we can write

$$dG = \sum_{i=1}^{\infty} n_i d\mu_i + \sum_{i=1}^{\infty} n_i \mu_i d\mu_i$$

making the expression for $dG = -SdT + VdP + \sum_i \mu_i d\mu_i$

we get the Gibbs-Duhem expression for each phase

$$-SdT + VdP - \frac{1}{2} n_i d\mu_i = 0$$

Thus, for any group of coexisting phases we can write the following relation for each phase in the system.

$$\sum_i n_i \mu_i = VdP - \Sigma SdT$$
so first let's consider a 2 component system and a univariate equilibrium. recall that in a one component system at a univariate equilibrium we showed that

\[ \frac{dT}{dp} = \frac{\Delta \mu}{\Delta S} \]

for two components and 3 phases (A, B and C) the gibbs phase looks like the following...

\[ x_A \mu_A + x_B \mu_B = \bar{\mu}_A dp - \bar{\mu}_A dT \]

\[ x_B \mu_B + x_C \mu_C = \bar{\mu}_B dp - \bar{\mu}_B dT \]

\[ x_C \mu_C + x_C \mu_C = \bar{\mu}_C dp - \bar{\mu}_C dT \]

rearranging...

\[ \bar{\mu}_A = \bar{\mu}_A dp - x_A \mu_A \frac{dT}{3\phi} - x_A \mu_A \frac{dT}{3\phi} \]

\[ \bar{\mu}_B = \bar{\mu}_B dp - x_B \mu_B \frac{dT}{3\phi} - x_B \mu_B \frac{dT}{3\phi} \]

\[ \bar{\mu}_C = \bar{\mu}_C dp - x_C \mu_C \frac{dT}{3\phi} - x_C \mu_C \frac{dT}{3\phi} \]

we can solve this system of equations using cramer's rule because we are using the ratio of these...
Note that for a one-coroant system, the equivalent expression would be

\[
\frac{dP}{dT} = \frac{\Xi \bar{X}_{1B}}{\Xi_{AB} X_{1B}} \quad \text{since} \quad \Xi_{1A} = \Xi_{1B} = 1
\]

This reduces to

\[
\frac{dP}{dT} = \frac{\Delta S_{2\text{r}}}{\Delta V_{2\text{r}}}
\]

Now consider the case where we have a 2-phase coexistence in a binary system. For example,

\[
T \quad \begin{array}{c}
A \\
B
\end{array}
\]

we use the relation \( \bar{X}_{1A} = 1 - \bar{X}_{2A} \) and substitute

\[
(1 - \bar{X}_{2A}) d\mu_1 + \bar{X}_{2A} d\mu_2 = \bar{V}_A dP - \bar{S}_0 dT
\]

\[
d\mu_1 + \bar{X}_{2A} d(\mu_2 - \mu_1) = \bar{V}_A dP - \bar{S}_A dT
\]

Phase 1 - have 4 unknowns \( d\mu_0, d(\mu_2 - \mu_1), dP, dT \)

We also obtain the total differential \( d(\mu_2 - \mu_1) \) can also be written as

\[
dG_A = \frac{\partial G_A}{\partial P} dP + \frac{\partial G_A}{\partial T} dT
\]

\[
= \frac{\partial P}{\partial \Xi} dP - \frac{\partial S_0}{\partial T} dT + C_{G_0A} \Xi_{2\text{r}}
\]
$$\Delta G_A = (\bar{V}_{2A} - \bar{V}_{1A}) dP - (\bar{S}_{2A} - \bar{S}_{1A}) dT + \Delta x_x dX_2$$

$$dG_A = d(\mu_2 - \mu_1)A$$ slopes at tangent planes are the same, for two phases in equilibrium.

So rearrange and solve:

$$d(\mu_2 - \mu_1) = (\bar{V}_{2A} - \bar{V}_{1A}) dP - (\bar{S}_{2A} - \bar{S}_{1A}) dT + \Delta x_x dX_2$$

$$d\mu_1 + x_{2A} d(\mu_2 - \mu_1) = -\bar{S}_A dT + \bar{V}_A dP$$

$$d\mu_1 + x_{2B} d(\mu_2 - \mu_1) = -\bar{S}_B dT + \bar{V}_B dP$$

$$d\mu_1 = -x_{2A} d(\mu_2 - \mu_1) - \bar{S}_A dT + \bar{V}_A dP$$

$$d\mu_{11} = -x_{2B} d(\mu_2 - \mu_1) - \bar{S}_B dT + \bar{V}_B dP$$

$$0 = (x_{2B} - x_{2A}) d(\mu_2 - \mu_1) + (\bar{S}_B - \bar{S}_A) dT + (\bar{V}_B - \bar{V}_A) dP$$

Plug in the expression for $d(\mu_2 - \mu_1)$.
\[ (x_{2B} - x_{2A}) \frac{d(x_2 - M)}{dP} = (\bar{v}_B - \bar{v}_A) dP - (\bar{s}_B - \bar{s}_A) dT \]

\[
(x_{2B} - x_{2A}) \left[ (\bar{v}_{2A} - \bar{v}_{1A}) dP - (\bar{s}_{2A} - \bar{s}_{1A}) dT + A_{xx} dX_2 \right] =
\]

\[
(\bar{v}_B - \bar{v}_A) dP = (\bar{s}_B - \bar{s}_A) dT
\]

\[
(x_{2B} - x_{2A}) A_{xx} dX_2 = \left[ (\bar{v}_B - \bar{v}_A) - (\bar{v}_{2A} - \bar{v}_{1A})(x_{2B} - x_{2A}) \right] dP
\]

\[
+ \left[ (\bar{s}_{2A} - \bar{s}_{1A})(x_{2B} - x_{2A}) - (\bar{s}_B - \bar{s}_A) \right] dT
\]

2nd
2nd
wrt conf
wrt conf
does to 3400
since \( dX_2 = 0 \)
Walker et al. discuss concerns with cryptal melt buoyancy and effects of multicomponent equilibria. P. 318 bottom left last sent.

P. 319 changes in slope of liquids - why not important?