ORDER/DISORDER

Long-Range Order (l.r.o.) **2 sublattices**

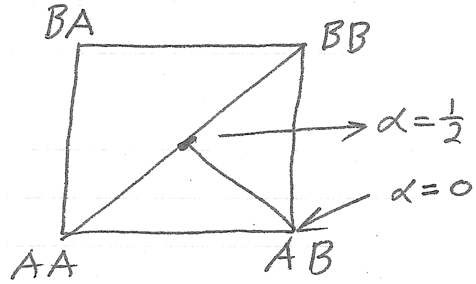
$$\underset{(1-\alpha)}{A_A} + \underset{(1-\alpha)}{B_B} = \underset{\alpha}{A_B} + \underset{\alpha}{B_A}$$

$\alpha = 0 \Rightarrow 100\%$ l.r.o.
$\alpha = \frac{1}{2} \Rightarrow 0\%$ l.r.o.
$\alpha =$ l.r.o. parameter

Let: $2\omega = (2g^{\circ}_{AB} - g^{\circ}_{AA} - g^{\circ}_{BB})$

where $(g^{\circ}_{AB} = g^{\circ}_{BA})$

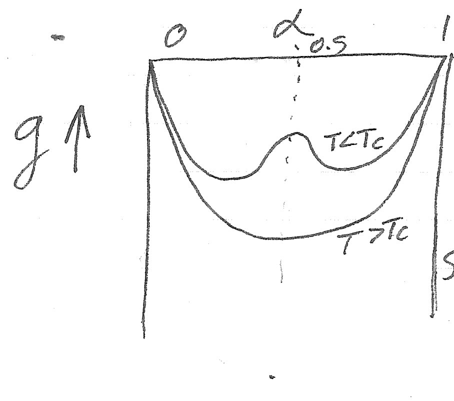
$\omega = 0 \Rightarrow \alpha = \frac{1}{2}$
$\omega = -\infty \Rightarrow \alpha = 0$



$$\Delta S = 2RT(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha))$$

Then: $G = \alpha^2 g^{\circ}_{BA} + (1-\alpha)^2 g^{\circ}_{AB} + \alpha(1-\alpha) g^{\circ}_{AA} + \alpha(1-\alpha) g^{\circ}_{BB}$
$- T\Delta S$

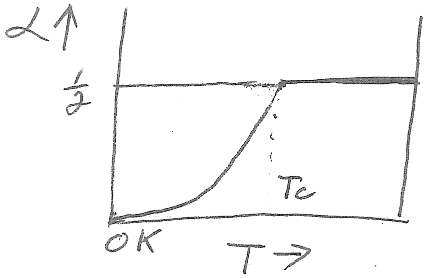
$$\left(\frac{dG}{d\alpha}\right) = 0 \Rightarrow 2\alpha g^{\circ}_{AB} - (2-2\alpha) g^{\circ}_{BA} + (1-2\alpha) g^{\circ}_{AA} + (1-2\alpha) g^{\circ}_{BB}$$
$$+ 2RT(\ln\alpha - \ln(1-\alpha))$$
$$= 2\omega(2\alpha - 1) + 2RT \ln\frac{\alpha}{1-\alpha} = 0$$
$$\ln\left(\frac{\alpha}{1-\alpha}\right) = e^{-\omega(2\alpha-1)/RT}$$



Always a solution at $\alpha = \frac{1}{2}$
For $T < T_c$ there are solutions for $\alpha \leq 1/2$

set $\left(\frac{d^2G}{d\alpha^2}\right)_{\alpha=\frac{1}{2}} = 0$

$$2\omega(2) + 2RT\left(\frac{1}{\alpha} + \frac{1}{1-\alpha}\right) = 0$$
$$4\omega + 2RT(2+2) = 0$$
$$T_c = \frac{-\omega}{2R}$$



<u>Also consider short-range order</u> (s.r.o.)

X_{AB} = fraction of A_A–B_B pairs $= (1-\alpha)^2 + y$

X_{BA} = $= \alpha^2 + y$

X_{AA} = $= \alpha(1-\alpha) - y$

X_{BB} = $= \alpha(1-\alpha) - y$

<u>y = s.r.o. parameter</u>

<u>Let</u>: $2\omega' = \frac{Z}{2}(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$ $\quad(\epsilon_{AB} = \epsilon_{BA})$

where: ϵ_{ij} = energy of $(i-j)$ <u>pair</u>

Use quasichemical model.

$$G = \left(\alpha^2 g^\circ_{AB} + (1-\alpha)^2 g^\circ_{BA} + \alpha(1-\alpha) g^\circ_{AA} + \alpha(1-\alpha) g^\circ_{BB}\right)$$
$$+ y\frac{Z}{2}(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$$
$$+ 2RT(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha))$$
$$+ ZRT\left[(\alpha^2+y)\ln\frac{\alpha^2+y}{\alpha^2} + ((1-\alpha)^2+y)\ln\frac{(1-\alpha)^2+y}{(1-\alpha)^2} + 2(\alpha(1-\alpha)-y)\ln\frac{\alpha(1-\alpha)-y}{\alpha(1-\alpha)}\right]$$

(<u>More completely</u>: $G = \left(\alpha^2(g^\circ_{BA} - \epsilon_{BA}) + (1-\alpha)^2(g^\circ_{AB} - \epsilon_{AB}) + \cdots\right)$

$$+Z\left[(\alpha^2+y)\epsilon_{BA} + ((1-\alpha)^2+y)\epsilon_{AB} + (\alpha(1-\alpha)-y)\epsilon_{AA} + \cdots\right]$$

etc.)

Assume $g^E = 0$

$$\left(\frac{\partial G}{\partial y}\right)_{\alpha=cst} \Rightarrow RT\ln\frac{(\alpha^2+y)((1-\alpha)^2+y)}{(\alpha(1-\alpha)-y)^2} = -2w' \quad (1)$$

$$\left(\frac{dG}{d\alpha}\right)_{y=cst} \Rightarrow 2w(2\alpha-1) + 2RT\ln\frac{\alpha}{1-\alpha} \quad (2)$$
$$+ZRT\left(2\alpha\ln\frac{\alpha^2+y}{\alpha^2} - 2(1-\alpha)\ln\frac{(1-\alpha)^2+y}{(1-\alpha)^2}\right.$$
$$\left. + 2(1-2\alpha)\ln\frac{\alpha(1-\alpha)-y}{\alpha(1-\alpha)}\right) = 0$$

Substitute (1) into (2)

$$2w(2\alpha-1) + 2RT\ln\frac{\alpha}{1-\alpha} - 4w'\alpha + 2ZRT\ln\frac{(\alpha(1-\alpha)-y)(1-\alpha)}{\alpha((1-\alpha)^2+y)} = 0$$

Set $\left(\frac{d^2G}{d\alpha^2}\right)_{\substack{y=cst\\ \alpha=\frac{1}{2}}} = 0$

$$4(w-w') + 2RT\left(\frac{1}{\alpha} + \frac{1}{1-\alpha}\right) + 2ZRT\left(\frac{1-2\alpha}{\alpha(1-\alpha)-y} - \frac{1}{1-\alpha} - \frac{1}{\alpha} + \frac{2(1-\alpha)}{(1-\alpha)^2+y}\right) = $$

$$T_c = \frac{-(w-w')\ (4y+1)}{2R}$$

If $w'=0,\ y=0,\ T_c = -w/2R$ (no s.r.o.)

- If $w=w'$, then $T_c=0$ and there is no l.r.o., only s.r.o.

  $y=0$ for $T=\infty$ $\quad$ $y=1$ for $T=0$

- General case: $\quad T_c < -w/2R$ for $T>T_c$ $\quad y\neq 0$

  That is s.r.o. persists above T_c