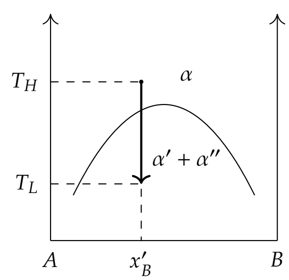
Spinodal Decomposition

Consider a binary alloy system with a miscibility gap, i.e.,

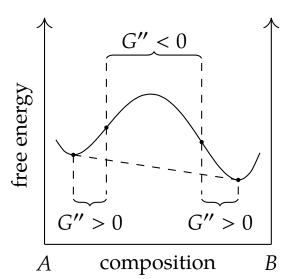


now, consider a transformation which must occur when an alloy with composition x'_B is quenched from temperature T_H to a lower temperature $T_L{}'$, i.e.,

$$\alpha \longrightarrow \alpha' + \alpha''.$$

In order to properly deal with the transformation, we need to analyze, not surprisingly, the G_{sol} vs composition relation at the transformation temperature T_L!

I.e.,



In particular,

1. If x'_B inside the $G'' < 0$ region, then small fluctuations in composition $\Rightarrow$ $G \downarrow$ about x'_B. $\therefore$ system is unstable and decomposition continues via "uphill" diffusion!

On the other hand,

2. If x'_B outside the $G'' < 0$ region, small variations in composition $\Rightarrow$ increase in the total free energy of the system (i.e., $G \uparrow$). $\therefore$ system is metastable and requires large fluctuations to develop $\alpha' + \alpha''$ (i.e., N and G required here).

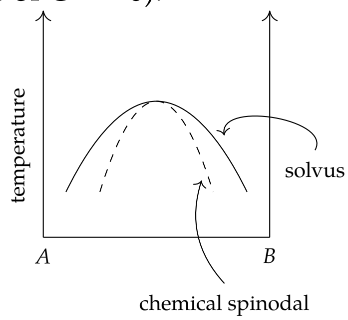
Expand $G(c)$ about c_0, then

$$G(c_0 + \Delta c) = G(c_0) + G'(c_0) \cdot \Delta c + G''(c_0) \cdot \frac{(\Delta c)^2}{2!} + \cdots,$$
$$G(c_0 - \Delta c) = G(c_0) - G'(c_0) \cdot \Delta c + G''(c_0) \cdot \frac{(\Delta c)^2}{2!} + \cdots.$$

$$\therefore \Delta G = \frac{G(c_0 + \Delta c) + G(c_0 - \Delta c)}{2} - G(c_0) = \frac{G''(c_0)(\Delta c)^2}{2},$$

which is to say that $\Delta G < 0$ if $G''(c_0) < 0$ and $\Delta G > 0$ if $G''(c_0) > 0$.

If we plot $G'' = 0$ points at various temperature, we obtain the chemical spinodal (i.e., line of $G'' = 0$).



Inside the spinodal → spontaneous decomposition can occur via "uphill" diffusion process, i.e.,