HH0038 Liquid-solid Mixture

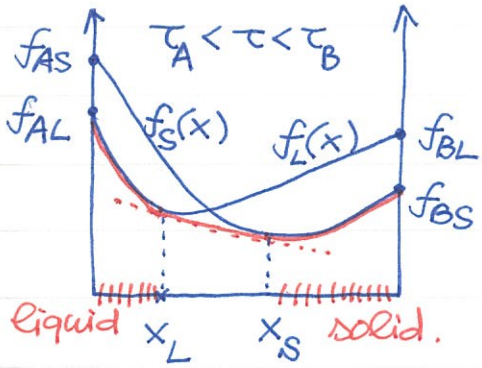
Suppose we mix two liquids A and B together. As described in HH0037,

$$u_{AB} - \frac{1}{2}u_{AA} - \frac{1}{2}u_{BB} < 0 \longrightarrow \text{no solubility gap}$$

Something like this...

If we start to cool the homogeneous liquid, what will happen? It turns out that the solution is rather simple yet interesting ☺

⊘ Liquidus / Solidus curves:



Suppose the melting temperatures for A & B are τ_A, τ_B. We assume $\tau_A < \tau_B$. For $\tau > \tau_B$, the phase is homo liquid. For $\tau < \tau_A$, the phase is homo solid.

What about $\tau_A < \tau < \tau_B$? It's tricky ☹.

The free energy curves for homo liquid $f_L(x)$ and homo solid $f_S(x)$ are shown in above. Three regimes can be found for $\tau_A < \tau < \tau_B$

(1) $x < x_L$: homo liquid
(2) $x_L < x < x_S$: hetero liquid-solid mixture ← heterogeneous phase.
(3) $x > x_S$: homo solid

In the hetero phase, neither $f_L(x)$ nor $f_S(x)$ are the minima.

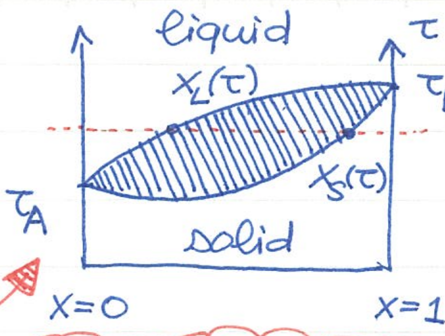
$$f_{hetero} = \frac{x_S - x}{x_S - x_L} f_L(x_L) + \frac{x - x_L}{x_S - x_L} f_S(x_S)$$

← a straight line

f_{hetero} is the minimum and the homogeneous phase is unstable. By changing τ between τ_A and τ_B, one can find $x_L = x_L(\tau)$ and $x_S = x_S(\tau)$.

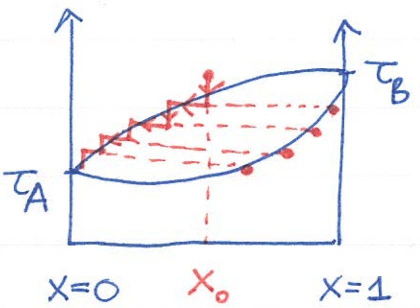
Collecting all $x_L(\tau)$ and $x_S(\tau)$ together, we obtain the typical phase diagram for liquid-solid mixture without solubility gap.

$x_L = x_L(\tau)$: liquidus curve
$x_S = x_S(\tau)$: solidus curve



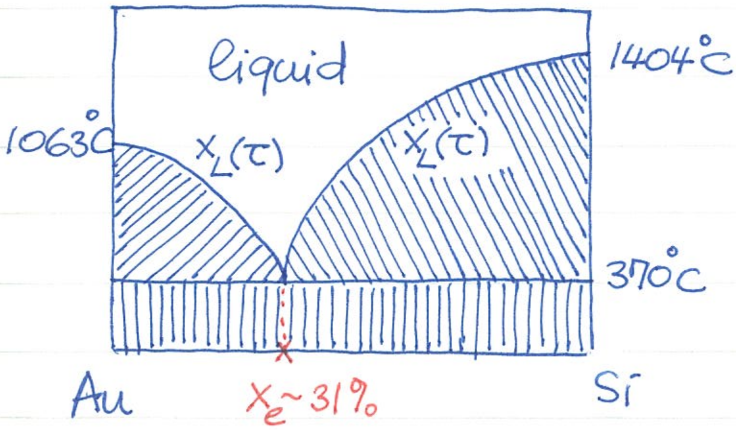
The unstable regime shrinks near τ_A or τ_B

Now we understand what happens when a homo liquid is gradually cooled down



Starting from $x=x_0$ homo liquid, solidification goes on and on until $\tau=\tau_A$. A series of alloys with varying x precipitates during the cooling process.

⑩ Eutectics : Many binary systems in the solid phase have a wide solubility gap. Thus, we would like to study how the phase diagram changes. An interesting example is $Au_{1-x}Si_x$ with the following phase diagram.



(1) Two liquidus curves join at $(x_e, \tau_e) = (31\%, 370°C)$

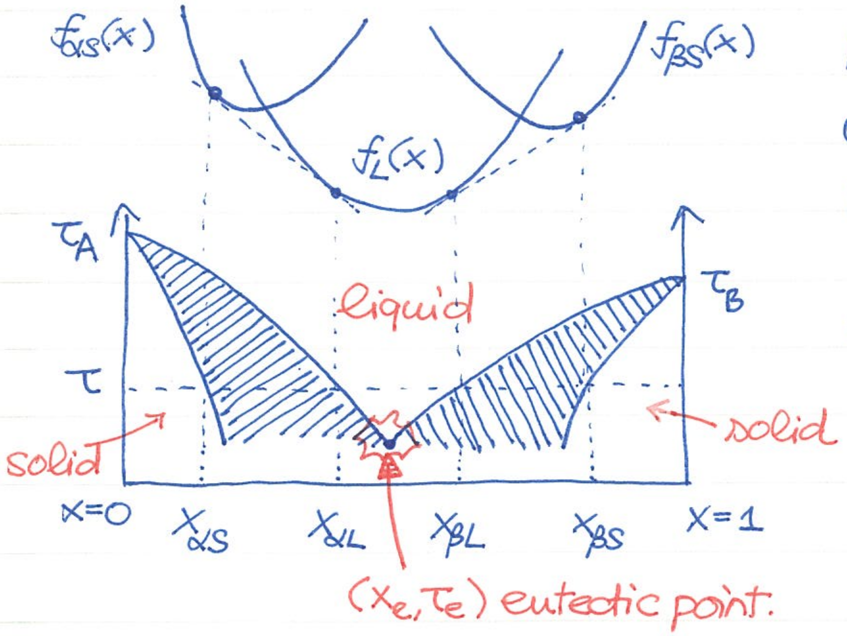
x_e : eutectic composition.

τ_e : eutectic temperature.

(2) Very large solubility gap... In fact, there's no homo solid mixture at all ಠ_ಠ

(3) By just adding some Si impurity in Au (and vice versa), the melting temperature drops significantly!

⊘ Explaining eutectics: Assuming the two solids are described by $f_{\alpha S}(x)$ and $f_{\beta S}(x)$ respectively (usually due to different crystal structures)

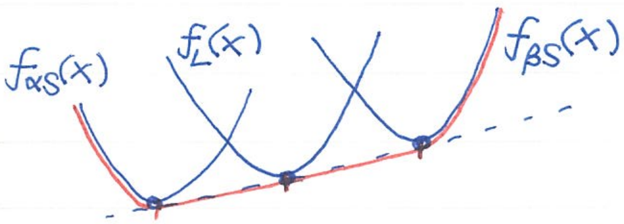


Here is a simple model to explain eutectics. For $\tau > \tau_e$, the liquid free energy $f_L(x)$ is lower than both $f_{\alpha S}(x)$ and $f_{\beta S}(x)$. Thus, there are two unstable regimes

$$x_{\alpha S} < x < x_{\alpha L}$$
$$x_{\beta L} < x < x_{\beta S}$$

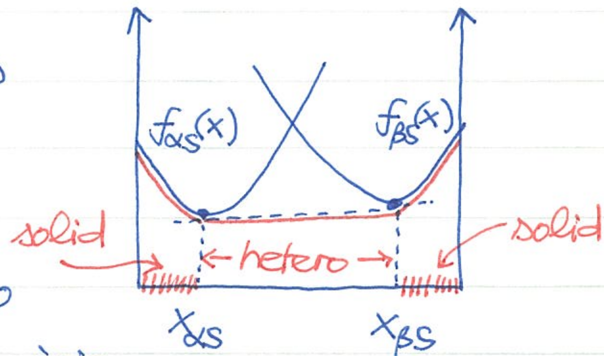
two hetero phases ☺

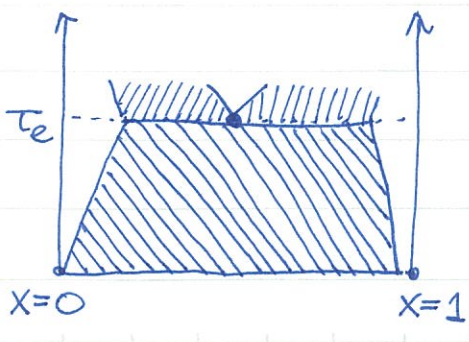
Right at $\tau = \tau_e$, all free energies share a common tangent.



Two unstable regimes meet and merge into one large unstable regime.

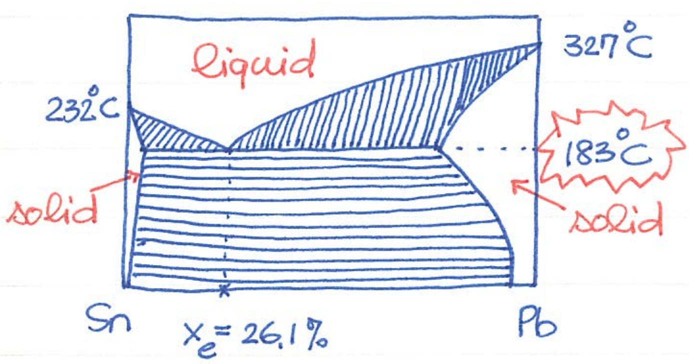
For $\tau < \tau_e$, $f_L(x)$ is out of the game. The story is then about the competition between $f_{\alpha S}(x)$ and $f_{\beta S}(x)$. The unstable regime $x_{\alpha S} < x < x_{\beta S}$ is a hetero phase of two homo solids $x_{\alpha S}$ and $x_{\beta S}$. One can plot the phase diagram below τ_e.



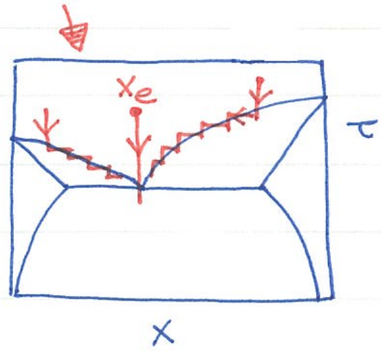


Basically, two hetero regimes join into one when cooling below the eutectic temperature τ_e.

Combine all results together, we get the complete eutectic phase diagram. Here is a real one for $Sn_{1-x}Pb_x$:



The cute thing about eutectic point is that $Sn_{1-x_e}Pb_{x_e}$ solidifies at a single temperature ☺



Again, the simple model here capture the essential physics about eutectics. But, of course, more complicated phase diagrams can be found ☺

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