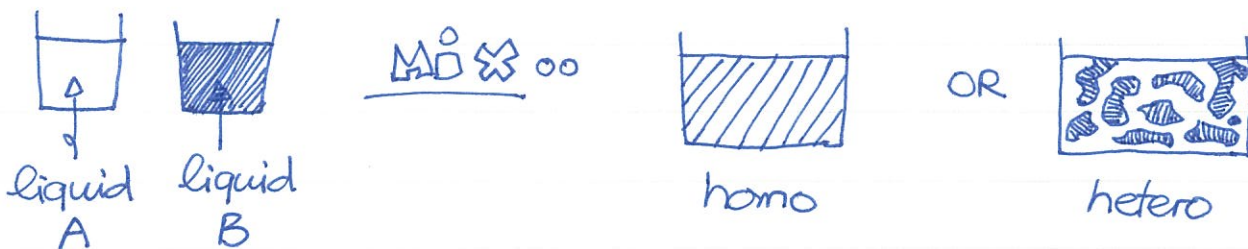


# HH0037 Solubility Gap in Binary Mixture

When we mix two different liquids together, they may form a homogeneous mixture, or a heterogeneous mixture.

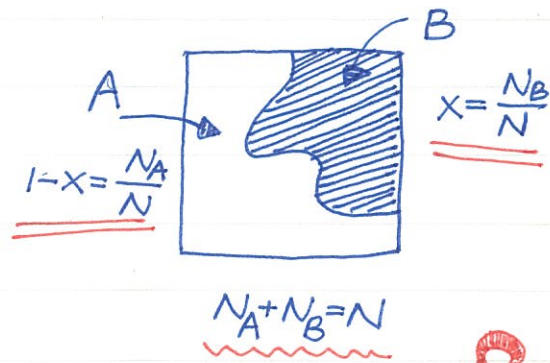


When a heterogeneous mixture shows up, it exhibits a solubility gap. In the following, we assume the volume change due to mixing is small. Thus, the external pressure can be ignored.

→ Use  $F = F(\tau, V, N)$  instead of  $G = G(\tau, P, N)$ . important ☺

① Free energy after mixing :

Ignoring the interfacial interactions and the mixing entropy, It is expected that the free energy should be



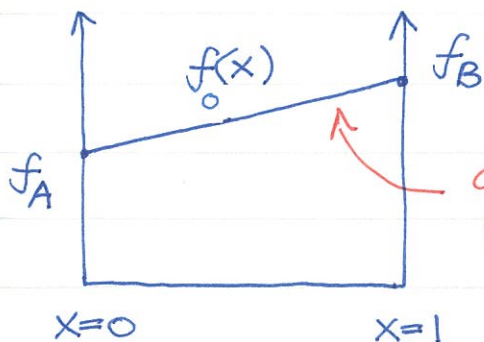
$$f_0(x) \equiv \frac{F}{N} = \frac{1}{N} (N_A f_A + N_B f_B)$$

→  $f_0(x) = (1-x)f_A + x f_B$

Is this true? ☹️

This is probably too naive...

One need to include the corrections  $u_{mix}$  and  $\sigma_{mix}$  due to interfacial interactions and mixing entropy.

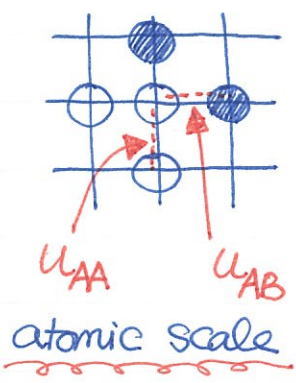


According to Shannon entropy,

$$\sigma_{mix} \equiv \frac{\sigma_m}{N} = -x \log x - (1-x) \log(1-x) \geq 0$$

simple!





Zooming into atomic scale, the average energy of a neighboring bond surrounding an A atom is

$$u_A = (1-x)u_{AA} + x u_{AB}$$

Similarly, the average bond energy surrounding a B atom is

$$u_B = (1-x)u_{AB} + x u_{BB}$$

Suppose there are  $p$  bonds surrounding each atom, the energy per atom is

$$u = \frac{1}{2} p [(1-x)u_A + x u_B]$$

$$= \frac{1}{2} p [(1-x)^2 u_{AA} + x^2 u_{BB} + 2x(1-x)u_{AB}]$$

Separate the average energy into two parts:  $u = u_0 + u_{mix}$

$$u_0 = (1-x) \left( \frac{1}{2} p u_{AA} \right) + x \left( \frac{1}{2} p u_{BB} \right)$$

trivial part

$$u_{mix} = x(1-x) p \left[ u_{AB} - \frac{1}{2} (u_{AA} + u_{BB}) \right]$$

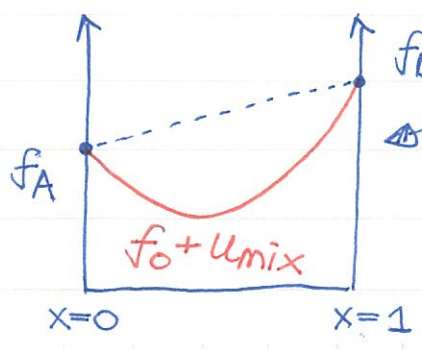
due to mixing !!

$x(1-x)$  is the probability to find a hetero bond  $\text{A-B}$  and  $u_{AB} - (u_{AA} + u_{BB})/2$  is the energy difference between a hetero bond and a homo bond. Collecting all results together, the free energy after mixing is

$$f = f_0 + u_{mix} - \tau \sigma_{mix}$$

$f_0 = (1-x)f_A + x f_B$  linear.  
 $u_{mix} - \tau \sigma_{mix}$  non-linear.

At  $\tau = 0$ , the mixing entropy term can be dropped,

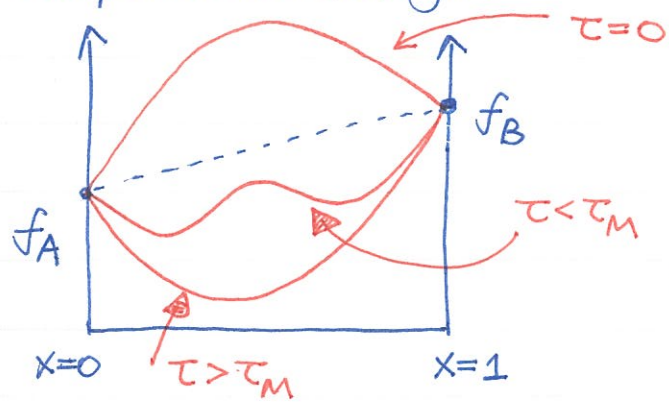
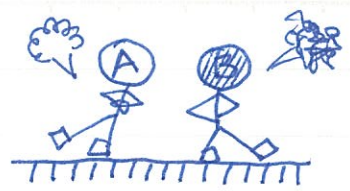


For  $u_{AB} - \frac{1}{2} (u_{AA} + u_{BB}) < 0$ , atoms love to mix up. Nothing interesting happens even for  $\tau > 0$ .





For  $u_{AB} - \frac{1}{2}(u_{AA} + u_{BB}) > 0$ , the profile of  $f(x)$  shows interesting evolution upon temperature change.



There exists a temperature  $\tau_M$  —  
 (1)  $\tau > \tau_M$ ,  $\frac{d^2f}{dx^2} > 0$ .  
 (2)  $\tau < \tau_M$ ,  $\frac{d^2f}{dx^2}$  can be negative in some regimes.

Finding  $\tau_M$  is the same as looking for  $\frac{d^2f}{dx^2} < 0$ .

$$\frac{d^2f}{dx^2} = \frac{d^2f_0}{dx^2} + \frac{d^2u_{mix}}{dx^2} - \tau \frac{d^2\sigma_{mix}}{dx^2} < 0$$

lower limit of  $\tau$  to exhibit a solubility gap

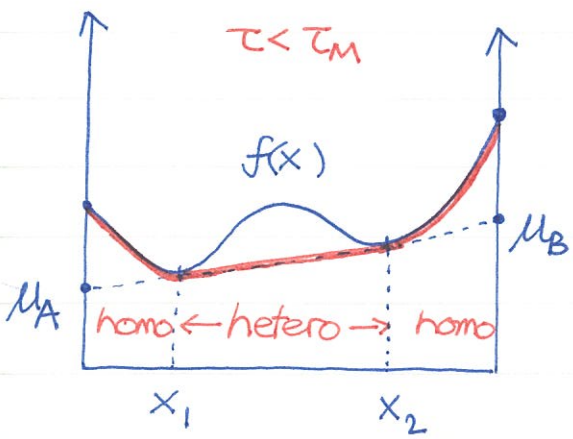
$$\rightarrow \frac{d^2u_{mix}}{dx^2} = -2p [u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})]$$

$$\Rightarrow \tau_M = \frac{p}{2} [u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})]$$

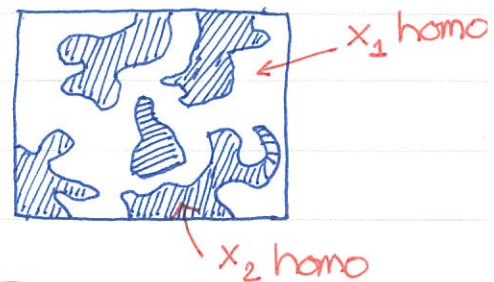
hetero-homo

$$\rightarrow \tau \frac{d^2\sigma_{mix}}{dx^2} = -\frac{\tau}{x(1-x)} \leq -4\tau$$

What happens below  $\tau_M$ ? For  $x < x_1$  OR  $x > x_2$ , homogeneous mixture is stable. On the other hand, for  $x_1 < x < x_2$ , a hetero mixture is more stable!



Within the solubility gap,  $x_1 < x < x_2$ , let's compare the homo and hetero free energy:



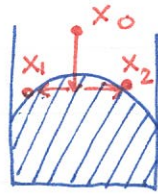
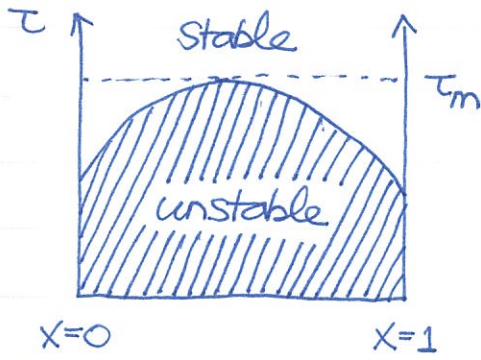
homo and hetero free energy:

$$\left\{ \begin{array}{l} \text{homo: } f(x) \leftarrow \text{upper curve} \\ \text{hetero: } \frac{x_2 - x}{x_2 - x_1} f(x_1) + \frac{x - x_1}{x_2 - x_1} f(x_2) \end{array} \right.$$

From the figure, it is clear that  $f(\text{hetero})$  is lower in the lower straight line!



① Phase diagram: One can plot the solubility gap for  $\tau < \tau_m$  and obtain the phase diagram. Note that the shaded area is unstable for homo liquid.



Suppose one cools  $x = x_0$  homo liquid below  $\tau_m$   
 → decompose into hetero mixture

$$f_1 = \frac{x_2 - x_0}{x_2 - x_1} \quad \text{and} \quad f_2 = \frac{x_0 - x_1}{x_2 - x_1}$$

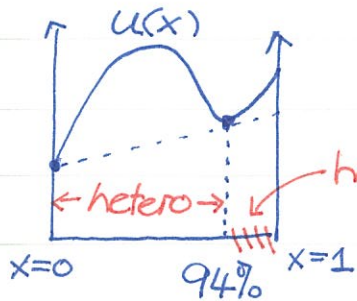
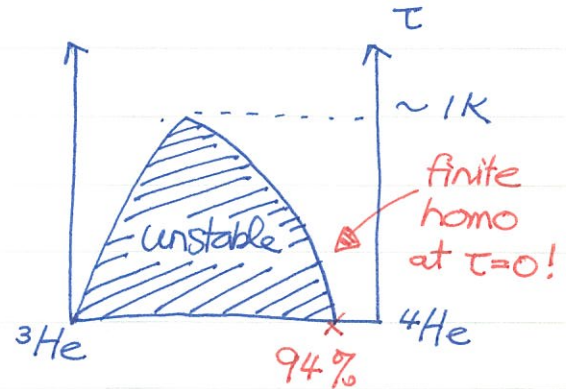
← fractions ☺

Clearly,  $f_1 + f_2 = 1$

It is also easy to show that  $f_1 x_1 + f_2 x_2 = x_0$ . Why? Well, we assume  $N_A, N_B$  remain constant during mixing process.

The simple model gets the essential physics right. The phase diagram for  $^3\text{He} - ^4\text{He}$  mixture exhibits similar structure.

The finite homo regime down to  $\tau = 0$  implies the interfacial energy  $u_{\text{mix}}$  is not as simple as a parabola.



At  $\tau = 0$ ,  $f(x) = u(x)$  as plotted on the left.

The solubility gap does not eat up the entire  $x$  regime ☺



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