Liquid-Liquid Phase Separation

A binary mixture has a free energy of mixing ($\mathrm{Jmol^{-1}}$) of

$$\Delta G_{\mathrm{mix}} = N_{\mathrm{A}} k_{\mathrm{B}} T \left[\Phi \log(\Phi) + 2[1-\Phi]\log(1-\Phi) + 4\Phi[1-\Phi] \right]$$

when T = 300 K. Plot the free energy of phase separation to the coexisting compositions (Φ_1 and Φ_2) as a function of the initial mole fraction Φ_0 (in the interval from Φ_1 to Φ_2). You should do a numerical or graphical solution to the problem and use some computer program to generate the plot.

Hint: Exercise 2.3 might be helpful!

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The first step is to find the coexisting compositions. Since this is not the regular solution model we must use the tangent method. The tangent function can be written as $y = k\Phi + m$ and we need to find the values of k and m. There are two ways: Either use a graphical solution by plotting the $\Delta G_{\text{mix}}(\Phi)$ function and try to fit a tangent manually or use a numerical method. We here do a more exact numerical solution (only a graphical one is also OK).

The tangent must have the same derivative and function value as ΔG_{mix} for both Φ_1 and Φ_2. The derivative is:

$$\frac{\partial \Delta G_{\text{mix}}}{\partial \Phi} = N_{\text{A}} k_{\text{B}} T \left[3 + \log(\Phi) - 2\log(1-\Phi) - 8\Phi \right]$$

The equations we must solve to find Φ_1 and Φ_2 are:

$$\left.\frac{\partial \Delta G_{\text{mix}}}{\partial \Phi}\right|_{\Phi=\Phi_1} = \left.\frac{\partial \Delta G_{\text{mix}}}{\partial \Phi}\right|_{\Phi=\Phi_2}$$

$$\Delta G_{\text{mix}}(\Phi_2) = \Delta G_{\text{mix}}(\Phi_1) + \left.\frac{\partial \Delta G_{\text{mix}}}{\partial \Phi}\right|_{\Phi=\Phi_1} \times \left[\Phi_2 - \Phi_1 \right]$$

This is a system of non-linear equations. It can be solved e.g. by "fsolve" in MATLAB. The function file can then be written as:

```
function y=HA1(phis)

y(1)=log(phis(1))-2*log(1-phis(1))-8*phis(1)-log(phis(2))+2*log(1-
phis(2))+8*phis(2);

y(2)=phis(2)*log(phis(2))+2*(1-phis(2))*log(1-phis(2))+4*phis(2)*(1-
phis(2))-phis(1)*log(phis(1))-2*(1-phis(1))*log(1-phis(1))-4*phis(1)*(1-
phis(1))-(phis(2)-phis(1))*(3+log(phis(1))-2*log(1-phis(1))-8*phis(1));

end
```

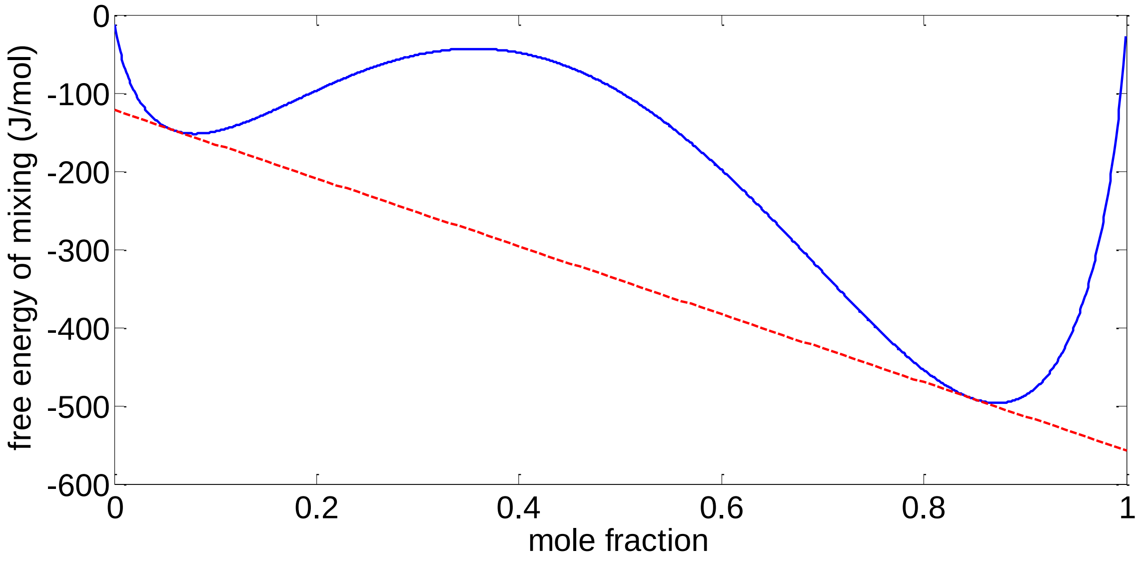
The starting guess can be taken from the plot of $\Delta G_{\text{mix}}(\Phi)$, for instance $\Phi_1 = 0.05$ and $\Phi_2 = 0.85$. Running "fsolve('HA1',[0.05,0.85])" gives $\Phi_1 = 0.0596$ and $\Phi_2 = 0.8491$. The tangent can then be evaluated by:

$$k = \left.\frac{\partial \Delta G_{\text{mix}}}{\partial \Phi}\right|_{\Phi=\Phi_1}$$

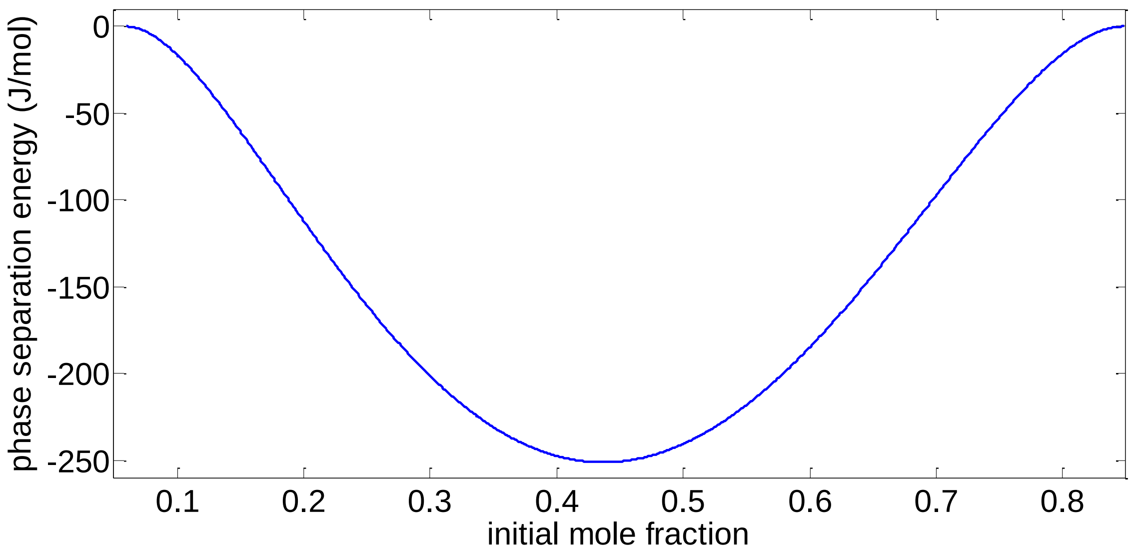
$$m = -k\Phi_1 + \Delta G_{\text{mix}}(\Phi_1)$$

This should give k = -434.6925 Jmol^{-1} and m = -122.3303 Jmol^{-1}.

The plot shows $\Delta G_{mix}(\Phi)$ and the tangent.



The free energy of phase separation is simply $y(\Phi_0) - \Delta G_{mix}(\Phi_0)$. The final plot is:



Note that the curve is not fully symmetric even though it appears so.