

Phys 112 : Lecture 27

Notes for the Fall 2017 Physics 112 Course taught by Professor Holzapfel
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Recall from last time that we had Van der Waals equation given by:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = N\tau$$

Now, we can introduce characteristic constants:

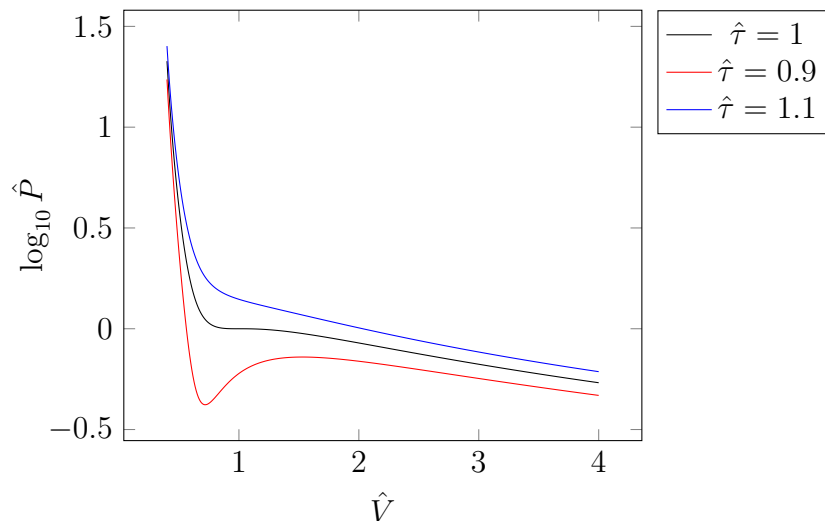
$$P_c = \frac{a}{27b^2}; \quad V_c = 3Nb; \quad \tau_c = \frac{8a}{27b}$$

And we can also, if we want, introduce some dimensionless 'indicator' variables:

$$\hat{P} = \frac{P}{P_c}; \quad \hat{V} = \frac{V}{V_c}; \quad \hat{\tau} = \frac{\tau}{\tau_c}$$

And we end up with a relation:

$$\hat{P} = \frac{(8/3)\hat{\tau}}{\hat{V} - (1/3)} - \frac{3}{\hat{V}^2}$$



Notice that we have a special point at $\hat{\tau} = \hat{P} = \hat{V} = 1$, where both the first and the second derivative of \hat{P} against \hat{V} vanishes. Now, also notice that we have:

$$G = F + PV = F + \frac{N\tau V}{V - Nb} - \frac{N^2 a}{V} = \frac{N\tau V}{V - Nb} - \frac{2N^2 a}{V} - N\tau \left[\ln \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right]$$

Now, we can also plot G as a function against \hat{P} . Note that when we have phase transitions, we always minimise the Gibbs free energy.

Now, suppose we have two components, a and b . Now we have that:

$$G = U + PV - \tau\sigma$$

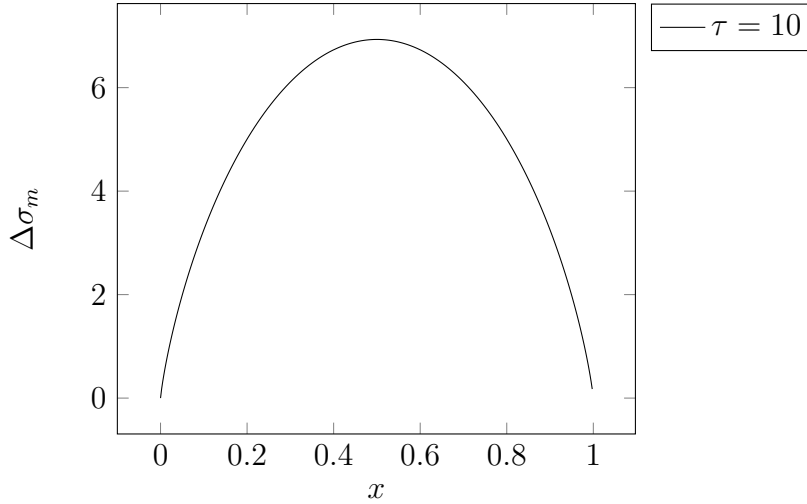
We can define a dimensionless quantity telling us the percentage of b , $x = N_b/(N_a + N_b)$. We have that:

$$G = (1 - x)G_A + xG_B$$

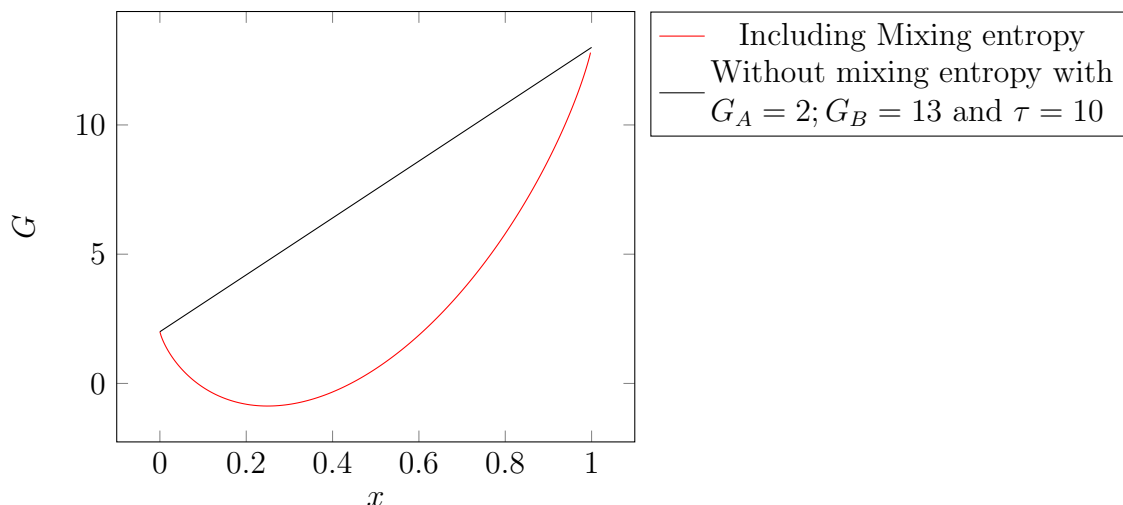
if we are ignoring the entropy of mixing. Now, when we mix the two quantities, we can assume under mild conditions that $\Delta U \sim \Delta V \sim 0$, so the only term that contributes is the change in entropy, the entropy of mixing, which we derived earlier:

$$\Delta\sigma_m = -N \left[(1 - x) \ln(1 - x) + x \ln x \right]$$

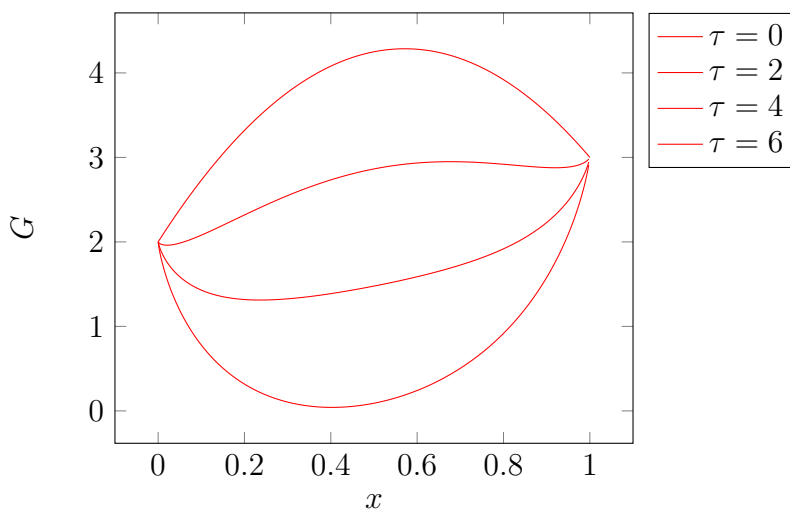
And we can make a plot of the change in entropy against x :



Now, we can find the real Gibbs free energy is 'bent downwards' by the $-\tau\sigma$ term in the Gibbs free energy:



Of course, if we want to be even more precise, there is an additional term due to the internal energy increasing or decreasing when you mix the two (for instance oil and water; the energy increases due to intermolecular interactions, oil and water don't like being mixed!). So you get a curve ΔU vs x that looks exactly like our $\Delta\sigma_m$ against x plot. Now, if we plot the G against x :



Notice that when $\tau = 0$, we have completely unmixed, since there is no mixing entropy contribution, so the oil and water don't want to mix. When τ is big, notice that the system is completely mixed, since it is concave, and has a global minimum near the middle. For inbetween temperatures, it is a bit hard to see, but you can imagine the two local minima of G in the middle, so we effectively have two different mixture phases, one more mixed and one less mixed.