

Landau Theory of Phase Transitions

In this section we'll have a quick look at Landau's theory of phase transitions. We will be looking at a general approach rather than any specific system.

We will consider systems at constant temperature and volume, so the Helmholtz free energy is a minimum when in thermal equilibrium. We suppose that the phase of a system is determined by some parameter. For example, in the ferromagnetic system we discussed last time, the magnetization, M , was the parameter of interest. It had a value different from zero for temperatures below the Curie temperature, went to zero at the Curie temperature, and stayed 0 for higher temperatures. We will denote the parameter by ξ ; in the generic case, it's called the *order parameter*. Sometimes I call it "wiggly."

At thermal equilibrium, the order parameter will have some value, $\xi_0(\tau)$, but we suppose that we can calculate the free energy for other values of ξ . That is, we write

$$F_L(\xi, \tau) = U(\xi, \tau) - \tau\sigma(\xi, \tau),$$

where the subscript L indicates the "Landau free energy." Of course the free energy, energy, and entropy depend on the volume and number of particles as well, but we're assuming they're constant and we're not bothering to show them.

When the system is in thermal equilibrium, the order parameter will take on the value which minimizes the free energy and we have

$$F(\tau) = F_L(\xi_0, \tau) \leq F_L(\xi, \tau),$$

for all $\xi \neq \xi_0$. Given $F_L(\xi, \tau)$, we can determine its minimum. It's the appearance of a new minimum as τ is varied that is a sign of phase transition.

Suppose F_L is an even function of the order parameter. Also suppose F_L can be expanded in a power series in the order parameter. (Both assumptions are reasonable, but are certainly not guaranteed to always be true!) We have

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 + \frac{1}{6}g_6(\tau)\xi^6 + \dots,$$

where the indices on the g 's indicate the corresponding power of ξ , and the fractions are put in for later convenience.

Now we need to look at this power series to see under what conditions there is a minimum which moves around as we change the temperature. First of all, suppose all the g functions are positive. Then all of them increase the Landau free energy for all values of ξ^2 . So the minimum occurs when the order parameter is zero. Not very exciting!

To get a minimum somewhere other than $\xi = 0$, we need at least one of the g functions to be negative and for this function to be large enough compared to the other functions that it can shift the minimum away from zero. Also, to have a transition, we would like the minimum to depend on the temperature. We suppose that

$$g_2(\tau) = \alpha(\tau - \tau_0) ,$$

where α is a positive constant. The temperature τ_0 is the temperature at which the phase transition will occur and this expression for g_2 should only be taken as valid in a neighborhood of τ_0 . It clearly can't work all the way down to $\tau = 0$! We suppose that $g_4(\tau) > 0$ and that α and $g_4(\tau)$ are sufficiently large that all the interesting behavior occurs for small ξ so we don't have to worry about g_6 and higher order functions. With all these caveats, the Landau free energy is

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 .$$

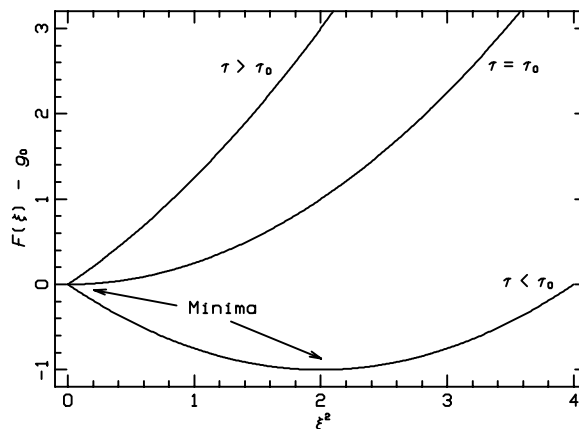
To find the minimum, we set the derivative with respect to the order parameter to zero,

$$0 = \left(\frac{\partial F_L}{\partial \xi} \right)_{\tau} = \alpha(\tau - \tau_0)\xi + g_4(\tau)\xi^3 ,$$

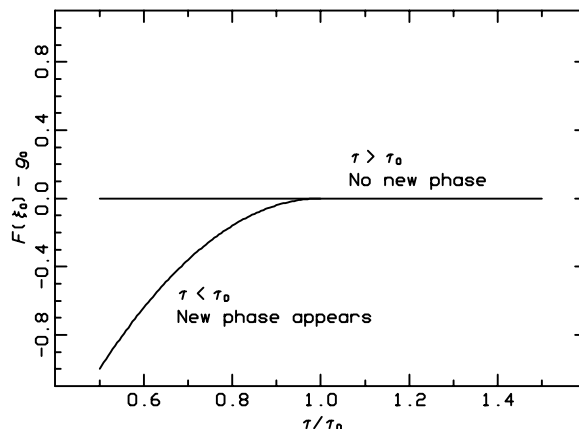
which has the roots

$$\xi = 0 , \quad \text{and} \quad \xi = \pm \sqrt{(\tau_0 - \tau) \frac{\alpha}{g_4(\tau)}} .$$

The root at 0 is always at least an extremum of the free energy. The other roots are imaginary and unphysical if $\tau > \tau_0$. For temperatures lower than the transition temperature, τ_0 , the roots are real, physical and are actually the global minima of the free energy. The figure shows plots of the free energy versus the square of the order parameter for several values of the temperature. For $\tau > \tau_0$ the minimum is at $\xi = 0$. For $\tau < \tau_0$, the minimum moves away from 0 with decreasing τ .



The figure shows the minimum value of the free energy as a function of the temperature. Both ξ_0 and the minimum free energy are continuous functions of temperature. The minimum free energy below τ_0 joins smoothly to the minimum curve $g_0(\tau)$ at $\tau = \tau_0$. Presumably the entropy is also a continuous function of temperature through τ_0 . This means there is no latent heat and we are dealing with a second order transition. The ferromagnetic system we discussed last time is a phase transition of this sort. To show this, we need to express the energy and the entropy as functions of the magnetization which will be our order parameter. Recall that M is the magnetic dipole moment per unit volume, so we will express these quantities per unit volume. The energy of an aligned magnet in a magnetic field is $-\mu B$. In terms of magnetization, this becomes $U(M) = -MB$. With our mean field approximation where $B = \lambda M$, this becomes $U(M) = -\lambda M^2$. **But...** It is the magnetic dipoles which are the source of the field so we have a double counting problem. Each magnet contributes once in the B factor of $-\mu B$ and once in the μ factor. We need a factor of $1/2$. Then the energy density is $U(M) = -\lambda M^2/2$. What about the entropy? In homework 1, problem 3, you worked out the entropy of our spin system. When the magnetization is small (that is, near the transition temperature), the entropy is



$$V\sigma(s) = V\sigma_0 - \frac{2s^2}{N},$$

where N is the number of dipoles and $2s$ is the spin excess as usual. We've written the volume explicitly, so σ refers to entropy density. We have

$$M = n\mu \frac{2s}{N},$$

so

$$\sigma = \sigma_0 - \frac{M^2}{2n\mu^2},$$

where n is the concentration of magnetic moments, μ . Then the free energy as a function of M is

$$F_L(M, \tau) = -\frac{\lambda M^2}{2} - \tau\sigma_0 + \tau \frac{M^2}{2n\mu^2} + \text{higher order terms}.$$

The higher order terms arise because our approximation for the entropy is only accurate when the magnetization is close to zero. When the magnetization is large, then the entropy is small. Ignoring the higher order terms, we can rearrange this expression as

$$F_L(M, \tau) = \underbrace{-\tau\sigma_0}_{g_0} + \frac{1}{2} \underbrace{\frac{1}{n\mu^2} (\tau - n\mu^2\lambda)}_{g_2 = \alpha(\tau - \tau_0)} M^2,$$

and the higher order terms will produce M^4 and higher powers. So the Landau free energy for our mean field approximation for a ferromagnet has exactly the form we've been considering for a second order phase transition. This method of analysis correctly yields the existence of a Curie temperature and the functional dependence of the order parameter (magnetization) on temperature near the Curie point, but does not tell us what happens as $\tau \rightarrow 0$ (we neglected the higher order terms—what did you expect?).

How would we go about making a first order transition? To have a first order transition, we need a discontinuous entropy so that we have a latent heat. This means that the free energy must be discontinuous. In the second order transition which we've just examined, the “new” minimum of the free energy first appears ($\tau = \tau_0$) at the same location ($\xi = 0$) as the old minimum and then moves to non-zero values of the order parameter as the temperature is lowered below the transition point. What we want is for the new minimum to first appear at a non-zero order parameter. Then the order parameter (and the free energy) will jump discontinuously to the new minimum. In terms of our expansion of the free energy around $\xi = 0$, we need a function that starts at 0 (we imagine subtracting off g_0), rises, dips below zero, and then rises again as ξ increases. Since we are dealing with a power series in ξ^2 , the ξ^2 term must be responsible for the initial rise. Then the ξ^4 term takes over and produces the dip. For larger ξ , the ξ^6 term wins and the function rises again. All this means that g_4 must be negative and g_6 must be positive. Our expansion for the free energy looks like

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)\xi^2 - \frac{1}{4}|g_4(\tau)|\xi^4 + \frac{1}{6}g_6(\tau)\xi^6 + \dots$$

We're allowing the ξ^2 coefficient to be either positive or negative depending on whether τ is larger or smaller than τ_0 . Note that τ_0 is not the transition temperature in this case.

To find the locations of the minima, we differentiate with respect to the order parameter,

$$0 = \left(\frac{\partial F_L}{\partial \xi} \right)_{\tau} = \alpha(\tau - \tau_0)\xi - |g_4(\tau)|\xi^3 + g_6(\tau)\xi^5,$$

which has solutions $\xi = 0$ and

$$\xi^2 = \frac{|g_4| \pm \sqrt{g_4^2 - 4g_6\alpha(\tau - \tau_0)}}{2g_6}.$$

If τ is sufficiently large, the argument of the square root is negative and there are no extrema other than the one at $\xi = 0$. In particular,

$$\tau - \tau_0 < \frac{g_4^2}{4\alpha g_6},$$

in order to have two more real solutions for ξ^2 . The smaller one (the negative sign above) is a local maximum and the larger one (the positive sign) is a local minimum. In order

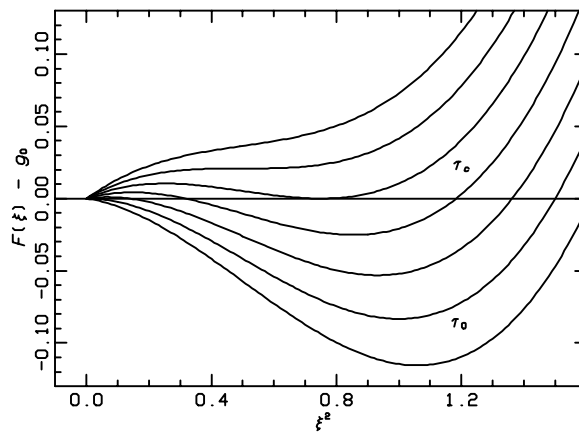
to have a new minimum of the free energy (and a phase transition), this minimum must be less than the one at $\xi = 0$. The critical temperature occurs when the free energy at this second minimum is 0. This takes a bit of messy algebra—we plug the expression for ξ^2 with the positive sign back into the expression for $F_L(\xi, \tau) - g_0(\tau)$, set the result to 0 (which means we can divide out a ξ^2), and solve for the temperature. Assuming I did this correctly, the critical temperature (with this simple model) is given by

$$\alpha(\tau_c - \tau_0) = \frac{3g_4^2}{16g_6},$$

which satisfies the condition above. The value of the order parameter at the critical temperature is

$$\xi_c^2 = \frac{3|g_4|}{4g_6}.$$

The figure shows the free energy versus the square of the order parameter for several values of the temperature. From bottom to top, the temperature increases by the same amount from curve to curve. The curves are plotted with $g_4 = -1$ and $g_6 = 1$. The curve labeled τ_c is the critical curve; it is tangent to $F_L - g_0 = 0$ at $\xi^2 = \xi_c^2 = 3/4$. For temperatures below this temperature the equilibrium phase is the phase at the second minimum. The next curve above the τ_c curve is plotted for temperature τ_1 where $\alpha(\tau_1 - \tau_0) = g_4^2/4g_6$. This is the highest temperature for which the



second minimum exists. For temperatures between the critical temperature and τ_1 , the equilibrium phase is the phase with $\xi = 0$, not the phase at the second minimum. The curve at the highest temperature is an example of a free energy curve with only the $\xi = 0$ minimum. The curve labeled τ_0 is the lowest curve for which $\xi = 0$ is a local minimum. There are a couple of sample curves shown with $\tau_0 < \tau < \tau_c$ and one curve with $\tau < \tau_0$. To summarize: with this model, the disordered phase ($\xi = 0$) can exist for temperatures higher than τ_0 . The ordered phase (which occurs at the other minimum) can exist for temperatures lower than τ_1 . The equilibrium phase below the critical temperature is the ordered phase and above the critical temperature it's the disordered phase. In the range between τ_0 and τ_1 , the system must make a discontinuous jump to get from one phase to another. If we imagine cooling the system from a temperature above τ_1 , we know the system is in the disordered phase when we start. If we're careful about how we cool it, the system can remain in the disordered phase past τ_c . There is a free energy "barrier" between the disordered and ordered phases. However, the barrier shrinks with decreasing temperature until at τ_0 , the barrier disappears and the system must switch to the ordered phase. In other words, the system may be supercooled down to τ_0 . Similarly, if we start

with the system below τ_0 , it is necessarily in the ordered state. If we raise the temperature carefully it can remain in the ordered state past τ_c , all the way to τ_1 . Again, there is a free energy barrier and τ_1 is the temperature of maximum superheating. Note that if we raise and lower the temperature in this range, the possibility of supercooling and superheating means that the state of the system on the way up in temperature does not have to be the same as the state of the system on the way down in temperature. When this occurs, the system is said to exhibit *hysteresis*.

If we write

$$\frac{4g_6\alpha(\tau - \tau_0)}{g_4^2} = x,$$

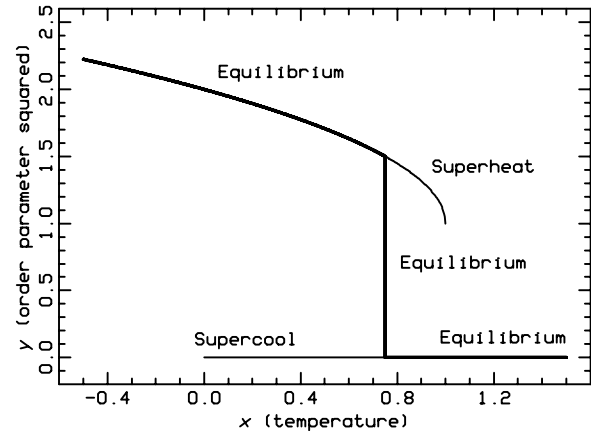
and

$$\frac{2g_6\xi^2}{|g_4|} = y,$$

so that x and y are the temperature and the square of the order parameter in convenient, dimensionless units, then we have

$$y = 1 + \sqrt{1 - x},$$

for the order parameter when the system is in the ordered phase. This relation is plotted as the upper curve in the figure. It ends at $x = 1$ corresponding to $\tau = \tau_1$. Also shown is the order parameter for the disordered phase. It's just the straight line at $y = 0$. It goes no lower than $x = 0$ which corresponds to $\tau = \tau_0$. The thick curve is the equilibrium order parameter versus temperature. The thin curves show the extensions corresponding to supercooling and superheating.



Mixtures

So far we've considered fairly simple phase transitions. Things can get quite a bit more complicated if we consider mixtures of various elements or compounds. For example, a mixture of water and salt has a lower melting temperature than water by itself.

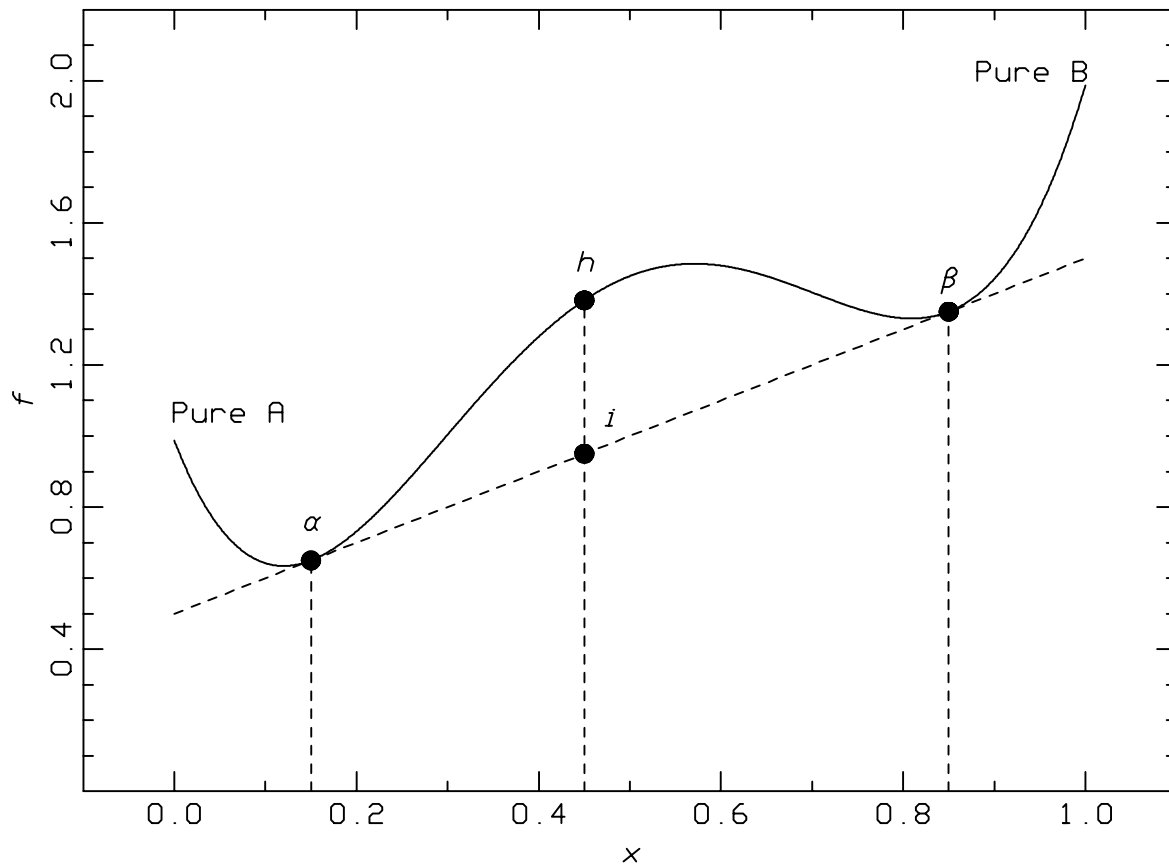
An example discussed in K&K is a gold-silicon alloy. Melting temperatures of pure gold and pure silicon are 1063°C and 1404°C , respectively. A 69% gold, 31% silicon mixture melts at 370°C . You're probably thinking, what's the big deal, we just formed a chemical compound something like Au_2Si which just happens to have a low melting point. Wrong! If one looks at the material under a microscope, one finds crystals of nearly pure gold next to crystals of nearly pure silicon. Such a mixture is called a heterogeneous mixture. A homogeneous mixture, on the other hand, is mixed down to the atomic scale. A homogeneous mixture is a single phase system while a heterogeneous mixture is a two (or more) phase system. The situation with crystals of gold and silicon existing side by side is similar to the situation with liquid water and ice existing side by side at the melting point of water.

When we have a homogeneous mixture, we say the two elements or compounds are dissolved in each other. We can understand the formation of heterogeneous phases by considering the free energy. If the free energy of a two phase, heterogeneous system is lower than that of the single phase, homogeneous solution, then we will wind up with the heterogeneous mixture. When this happens, there is a *solubility gap*. If we are dealing with solids or liquids, we can generally ignore any work done due to volume changes. So we can take the volume to be constant and consider the Helmholtz free energy. Also, we will assume that no chemical reactions occur in the mixtures. Whatever elements and compounds we start out with are what we'll end up with.

We will start with binary mixtures. We suppose we have N_A atoms of type A and N_B of type B . The total is $N_A + N_B = N$. We can specify the composition of the mixture by the fraction of B atoms,

$$x = \frac{N_B}{N}, \quad 1 - x = \frac{N_A}{N}.$$

We want to consider what happens when we keep N fixed, but vary the composition, x . So, we consider the free energy per atom $f = F/N$, which must be a function of x . A typical



free energy curve is shown in the figure. Note that this free energy is for the homogeneous mixture. The key feature of this curve is the bump in the middle. Given that there's a bump in the middle, we can draw a straight line which is tangent to the free energy curve at points α and β . Consider the free energy at a point somewhere between α and β like the point labeled h in the figure. We will show that by constructing a heterogeneous mixture with the compositions x_α and x_β , we can reproduce the overall composition of point h , but with a free energy that's on the straight line tangent curve just below h . This point is labeled i for inhomogeneous. Let the free energy of the homogeneous mixture with composition x_α be f_α . Similarly, the free energy at β is f_β . Consider the expression

$$f_i = f_\beta \frac{x - x_\alpha}{x_\beta - x_\alpha} + f_\alpha \frac{x - x_\beta}{x_\alpha - x_\beta} .$$

This is a linear function of x which, by construction, goes through the two tangent points, so f_i must be the value of the tangent line at composition x . What this function is telling us to do is to make a mixture with the fraction

$$\frac{x - x_\alpha}{x_\beta - x_\alpha} ,$$

having composition x_β and the fraction

$$\frac{x - x_\beta}{x_\alpha - x_\beta} ,$$

having composition x_α . The overall composition is

$$x_\beta \frac{x - x_\alpha}{x_\beta - x_\alpha} + x_\alpha \frac{x - x_\beta}{x_\alpha - x_\beta} = x .$$

This is the actual composition and this means that the free energy is minimized if the mixture breaks up into two phases, one with some B dissolved in A (composition x_α) and one with some A dissolved in B (composition x_β). The range from x_α to x_β is the solubility gap in this case.

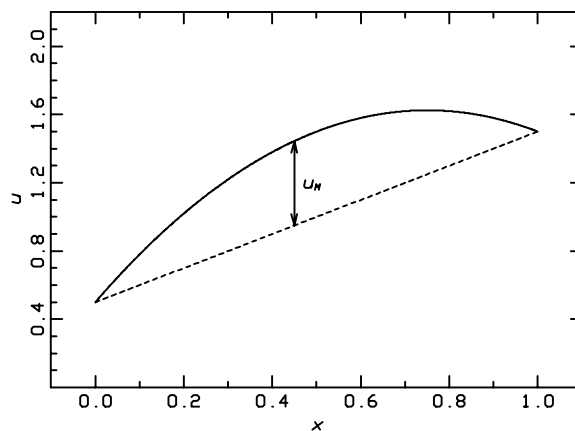
The next question of course, is how do you get a free energy curve like that shown in the figure? Recall that the Helmholtz free energy is $F = U - \tau\sigma$. We need to consider how both the energy and the entropy vary as the composition is changed. First of all, if we have a pure A , then the energy is Nu_A and if we have pure B , the energy is Nu_B , where u_A and u_B are the energy per atom of the pure elements. If we assume that the interactions between A and B are the same as the A - A and B - B interactions then the energy per atom of the mixture would be

$$u(x) = (N_A u_A + N_B u_B)/N = u_A + x(u_B - u_A) .$$

However, there probably is a difference in the interactions! One might imagine that (at least in some cases) A - B interactions are less strong than A - A or B - B interactions. So there will be an increase in energy when there is a mixture compared to separate phases. In any case, one usually has an *energy of mixing* and this can produce a bump in the energy curve. In other words the energy per atom might be

$$u = u_A + x(u_B - u_A) + u_M(x) ,$$

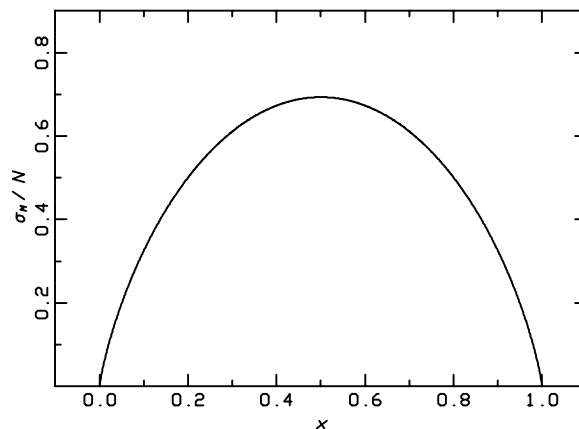
where M is the energy of mixing and may be positive in the neighborhood of $x = 1/2$ and must be 0 for $x = 0$ and $x = 1$.



Now, what about the entropy of mixing?
You should be able to show that

$$\sigma_M = -N[(1-x)\log(1-x) + x\log x].$$

In lecture 14 we considered the entropy of mixing in a situation where $x = 1/2$ and we found it to be $N \log 2$ in agreement with the expression just given. This is plotted in the figure. An important point is the entropy of mixing goes to zero at both ends with infinite slope! Now if we consider the change to the free energy as a result of the mixing, we have



$$\Delta f = u_M(x) - \tau \sigma_M(x)/N.$$

Now we can see what happens. At low temperatures, the bump in the energy of mixing curve wins and we have the situation that leads to a heterogeneous mixture. The infinite slopes in the entropy of mixing are responsible for the rise in free energy near the ends of the curve. This means that pure states are not the equilibrium configuration in the heterogeneous case. Instead, the equilibrium is the almost pure states at the “tangent points.” At high temperatures, the entropy of mixing wins, the free energy curve no longer has a bump and we have a homogeneous mixture. It’s competition between minimizing energy and maximizing entropy!