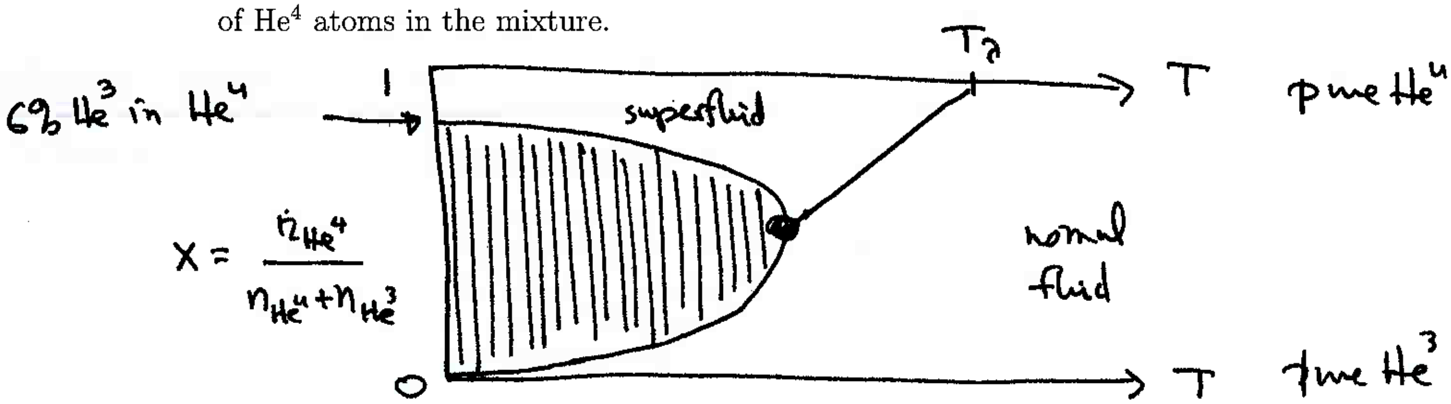
May 20

Multi-Critical Points

In the previous lecture, we discussed the phase diagram of a material with gas, liquid, and solid phases. We saw that this diagram includes two special points, a *critical point* that is an endpoint of a line of discontinuous phase transitions, and a *triple point* that is a point where three distinctly different phases coexist. More complex phase diagrams are possible. I will present some more complex critical points in this lecture.

A system that exhibits a more complex sort of critical point is a He^3–He^4 mixture at low temperatures. Pure He^4 has a critical point that separates the normal liquid from the superfluid phase. This critical point is described by the Landau theory of the XY ferromagnet. In pure He^3, the liquid turns continuously from a normal liquid into a degenerate Fermi liquid as the temperature is lowered. At very low temperature, the presence of He^3 dissolved in He^4 reduces the tendency to form a superfluid. Conversely, He^4 atoms are expelled from the He^3 liquid. The He^3–He^4 system thus has an interesting phase diagram in the plane of T versus x, the fraction of He^4 atoms in the mixture.



The shaded region in the figure is an excluded region denoting phase separation into He^3-rich and He^4-rich phases.

Blume, Emery, and Griffiths introduced a lattice spin model that reproduces the important aspects of this phase diagram (Phys. Rev. A4, 1071 (1971)). I will now present this model and work out its phase structure.

The Blume-Emery-Griffiths model has a square lattice in d dimensions with spins S_i on the lattice sites. The spins take the values

$$S_i \in \{+1, 0, -1\}$$

The values $S_i = \pm 1$ represent the He^4 atoms. The superfluid order parameter has XY symmetry, but it is represented here by an Ising model. Long-range order with

$$\langle S_i \rangle \neq 0$$

will represent superfluidity. The value $S_i = 0$ represents a He^3 atom. The lattice with $S_i = 0$ on every site has zero entropy, a characteristic of the degerate Fermi system of pure He^3.

I will take the Hamiltonian of this system to be

$$H = -J \sum_{\langle ij \rangle} S_i S_j + \Delta \sum_i S_i^2$$

The parameter J induces magnetic (or superfluid) order. The parameter Δ is a relative chemical potential for He^4 with respect to He^3. The limits

$$\Delta \to -\infty \qquad \text{gives pure } He^4$$

$$\Delta \to +\infty \qquad \text{gives pure } He^3$$

The system has two order parameters

$$m = \langle S_i \rangle \qquad\qquad x = \langle S_i^2 \rangle$$

A value $m \neq 0$ indicates superfluidity. The value of x gives the fraction of He^4 atoms.

We can analyze this system using mean field theory. The effective single spin Hamiltonian is

$$-J \cdot 2d\, m \cdot S_i + \Delta S_i^2 \qquad\qquad m = \langle S_i \rangle$$

Then the mean field equations for $\langle S_i \rangle$ and $\langle S_i^2 \rangle$ are

$$\langle S_i \rangle = \frac{\left[e^{2d\beta Jm} \cdot (+1) + e^{-2d\beta Jm}(-1)\right] e^{-\beta\Delta} + 0}{\left(e^{2d\beta Jm} + e^{-2d\beta Jm}\right) e^{-\beta\Delta} + 1}$$

$$\langle S_i^2 \rangle = \frac{\left(e^{2d\beta Jm} + e^{-2d\beta Jm}\right) e^{-\beta\Delta}}{\left(e^{2d\beta Jm} + e^{-2d\beta Jm}\right) e^{-\beta\Delta} + 1}$$

Now impose self-consistency:

$$\langle S_i \rangle = m \qquad \qquad \langle S_i^2 \rangle = x$$

This gives the equations

$$m = \frac{2 \sinh(2d\beta Jm)}{2\cosh(2d\beta Jm) + e^{\beta\Delta}}$$

$$x = \frac{2\cosh(2d\beta Jm)}{2\cosh(2d\beta Jm) + e^{-\beta\Delta}}$$

If we solve the first equation for m, x is rather simply determined by the second equation,

$$\frac{m}{x} = (\tanh 2d\beta Jm) < 1$$

For $\Delta \to -\infty$, which gives $x = 1$ or pure He^4, the self consistency equation becomes

$$m = \tanh(2d\beta J m)$$

This is just the mean-field equation for the magnetization of the Ising model. Just as we found there, this model has a critical point at a temperature T_C given by

$$2d\beta_c J = 1 \quad \text{or} \quad T_c = 2dJ$$

Next, consider finite values of Δ. The equation for m always has the solution

$$m = 0$$

The value of x associated with this solution is

$$x_0 = \frac{2}{2 + e^{\beta\Delta}}$$

We can now study the equations in the vicinity of this point. Expand the right-hand side of the m equation in powers of m,

$$m = \frac{2\left[(2d\beta J m) + \frac{1}{6}(2d\beta J m)^3 + \cdots\right]}{2\left[1 + \frac{1}{2}(2d\beta J m)^2 + \cdots\right] + e^{\beta\Delta}}$$

$$= \frac{2}{2+e^{\beta\Delta}}(2d\beta J m)\left[1 + \frac{1}{6}(2d\beta J m)^2 - \frac{1}{2+e^{\beta\Delta}}(2d\beta J m)^2 + \cdots\right]$$

This gives, finally,

$$m = x_0 \; 2d\beta J \; m \cdot \left[1 - \tfrac{1}{2}(x_0 - \tfrac{1}{3})(2d\beta J m)^2 + \ldots\right]$$

The slopes on the left- and right-hand sides match for

$$2d\beta_c J x_0 = 1 \qquad \text{or} \qquad T_c(\Delta) = x_0(\Delta) \cdot 2dJ$$

This implies that the superfluid transition temperature depends on x_0 as

$$T_c = x_0(\Delta) \cdot 2dJ$$

As long as $x_0 > \frac{1}{3}$, we can solve for m at temperatures just below the transition.

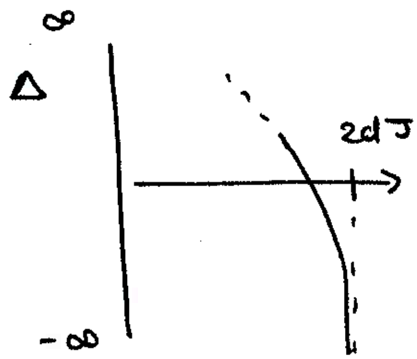
$$m\,[x_0 2d\beta J - 1] = x_0 \; 2d\beta J \; \tfrac{1}{2}(x_0 - \tfrac{1}{3})(2d\beta J)^2 m^3$$

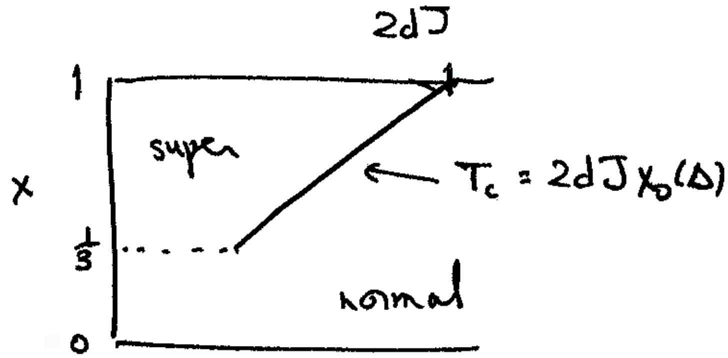
$$\left(\frac{T_c}{T} - 1\right) = \frac{T_c}{T} \cdot \frac{1}{2}(x_0 - \tfrac{1}{3})\left(\frac{T_c}{T x_0}\right)^2 m^2$$

so that

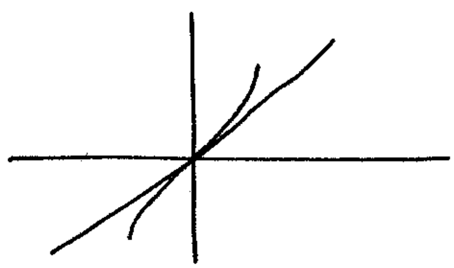
$$m \cong \left(\frac{2x_0^2}{x_0 - \frac{1}{3}}\right)^{\frac{1}{2}} \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}}$$

The model then has a *line* of critical points

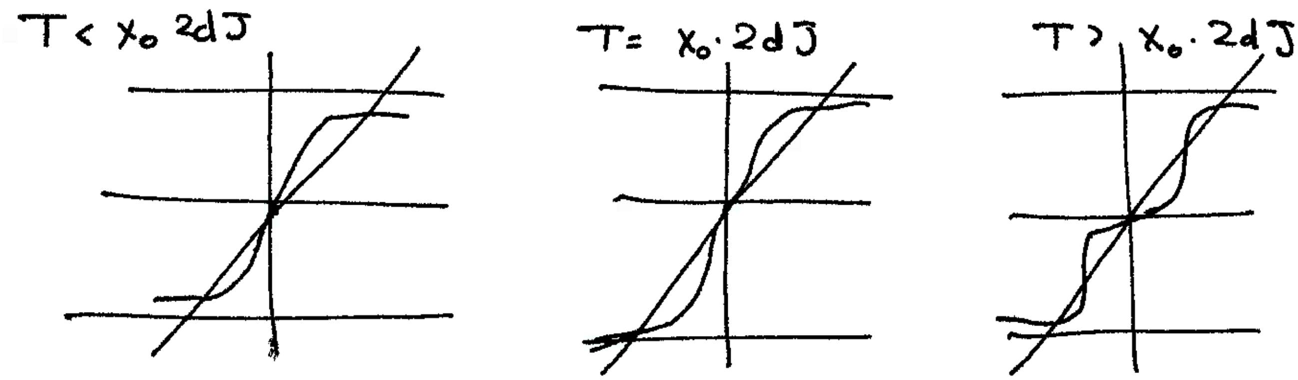




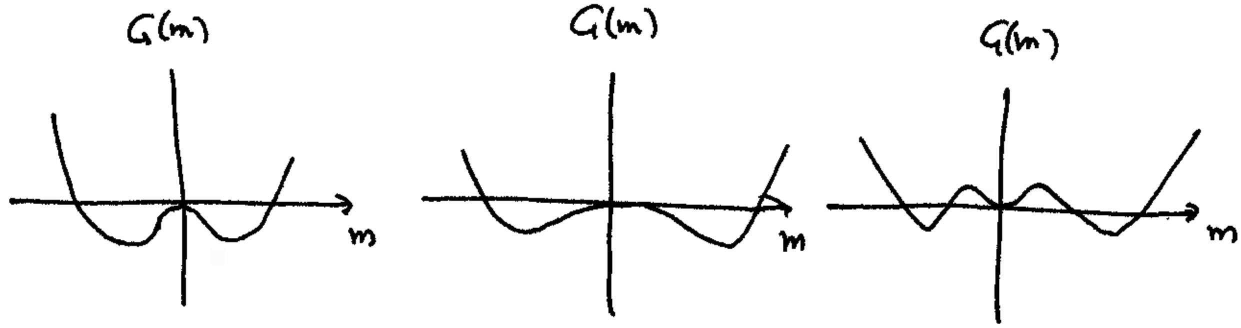
The behavior of the solution for m changes when $x_0 < \frac{1}{3}$. In this case, the right-hand side of the m equation near $m = 0$ bends the wrong way. At $T = x_0 2dJ$, the right-hand side has the form



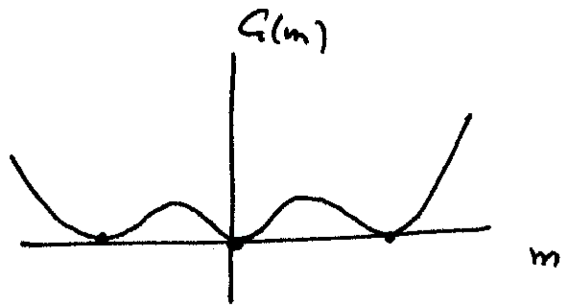
Since this expression goes to ± 1 has $m \to \pm\infty$, the full shape of the curve must be



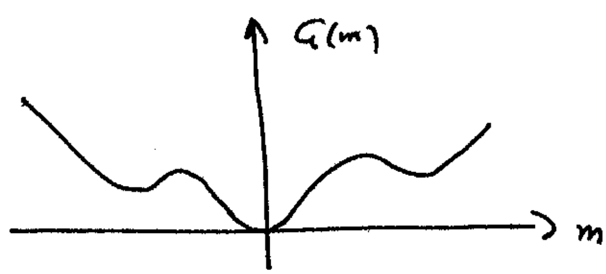
Recall from our discussion of the Ising model that, when the right-hand side of the self-consistency equation is greater than m, the Gibbs free energy decreases as m increases. We can infer that, in the three situations just pictured, the Gibbs free energy has the form



This implies that there is a temperature T somewhat higher than $x_0 2dJ$ at which G has the form

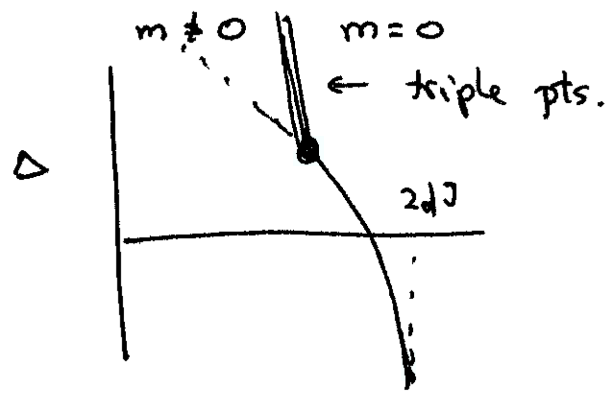


This is the Gibbs free energy of a triple point—coexistence of three distinct phases. At a slightly higher value of T, G has the form

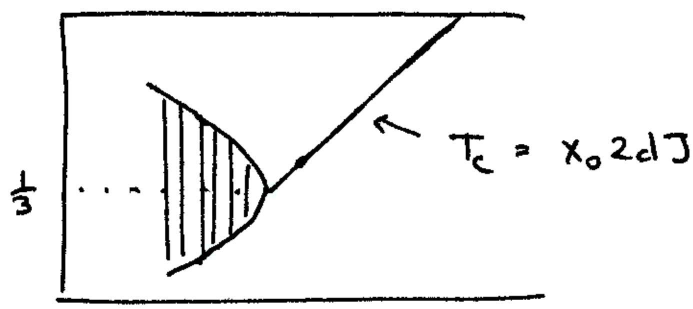


with a single minimum representing the normal fluid.

From all of this information, we can reconstruct the phase diagram in the (T, Δ) plane. This diagram contains a line of critical points but, superceding this behavior for $x_0(\Delta) < \frac{1}{3}$, a line of triple points.



In the (T, x) plane, this behavior appears as



There are more surprises in the phase diagram. Turn on a magnetic field. In the He^3-He^4 system, there is no field that couples to the phase of the condensate wavefunction. But in a magnetic system, we could readily provide an external field that couples to S_i. Then the Hamiltonian would become

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j + \Delta \sum_i S_i^2 - h \sum_i S_i$$

In mean-field theory, the effective single-spin Hamiltonian is

$$-J\, 2d\, m\, S_i + \Delta S_i^2 - h S_i$$

The self-consistency equation for m is then

$$m = \frac{\left(e^{2d\beta J m} e^{\beta h} - e^{-2d\beta J m} e^{-\beta h}\right) e^{-\beta \Delta}}{\left(e^{2d\beta J m} e^{\beta h} + e^{-2d\beta J m} e^{-\beta h}\right) e^{-\beta \Delta} + 1}$$

or

$$m = \frac{2 \sinh (2d\beta J m + \beta h)}{2 \cosh (2d\beta J m + \beta h) + e^{\beta \Delta}}$$

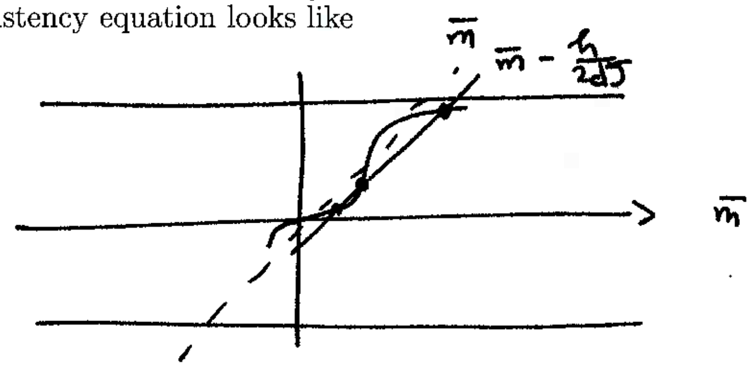
Let

$$\bar{m} = m + \frac{h}{2dJ}$$

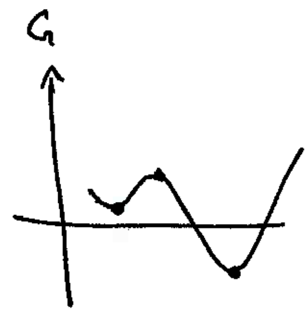
This this equation can be written as

$$\bar{m} - \frac{h}{2dJ} = \frac{2 \sinh (2d\beta J m + \beta h)}{2 \cosh (2d\beta J m + \beta h) + e^{\beta \Delta}}$$

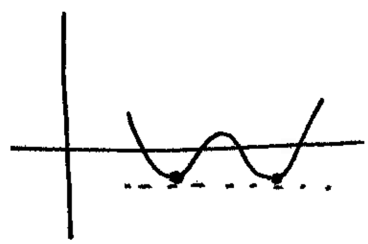
For $x_0(\Delta) > \frac{1}{3}$, the consequences of turning on h are similar to those in the Ising model. Howevere, let $x_0(\Delta) < \frac{1}{3}$ and $T < x_0 2dJ$. Then the graphical solution of the self-consistency equation looks like



This corresponds to a Gibbs free energy of the form

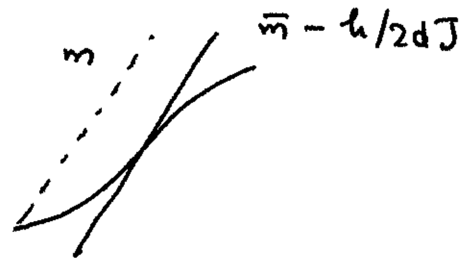


By adjustment of h, we can arrange that the two minima here become degenerate



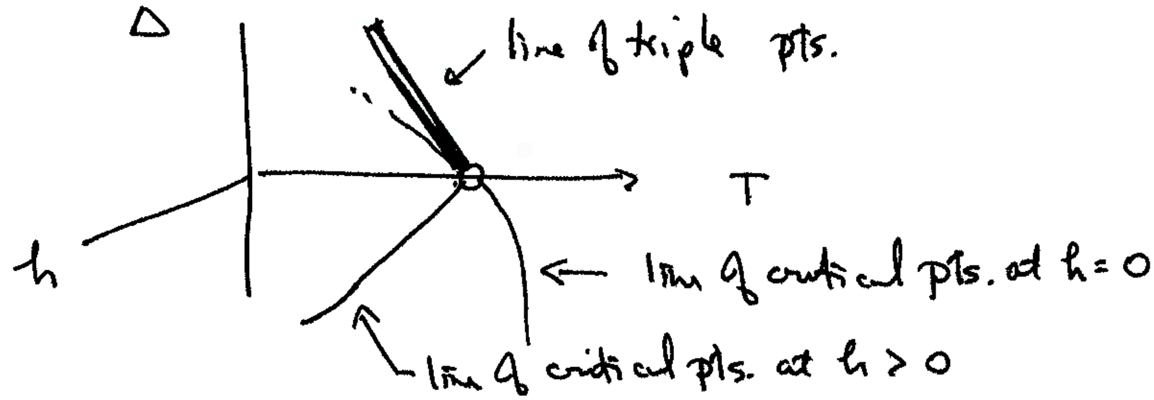
Then, in this region, we find phase coexistence between phases with two different values of m. This situation is present for a range of values of Δ, so we find here a line of discontinuous phase transitions.

By adjusting Δ, we can arrange, further, the the right-hand side of the self-consistency equation is *tangent* to the line $(\overline{m} - h/2dJ)$

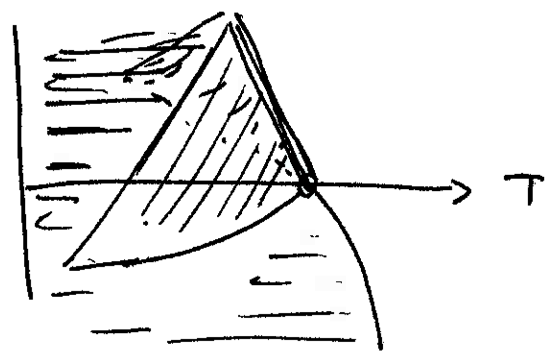


This situation would be the endpoint of the line of discontinuous phase transitions that I have just described. The whole structure is present for any T sufficiently small. Thus, the full structure is a *surface* of discontinuous phase transitions ending in a *line* of critical endpoints.

The whole structure is the (Δ, T, h) 3-dimensional space looks like



The lines are critical endpoints, boundaries of surfaces of discontinuous phase transitions. The double line is a line of *triple points.* Here is another view with the surfaces filled in:

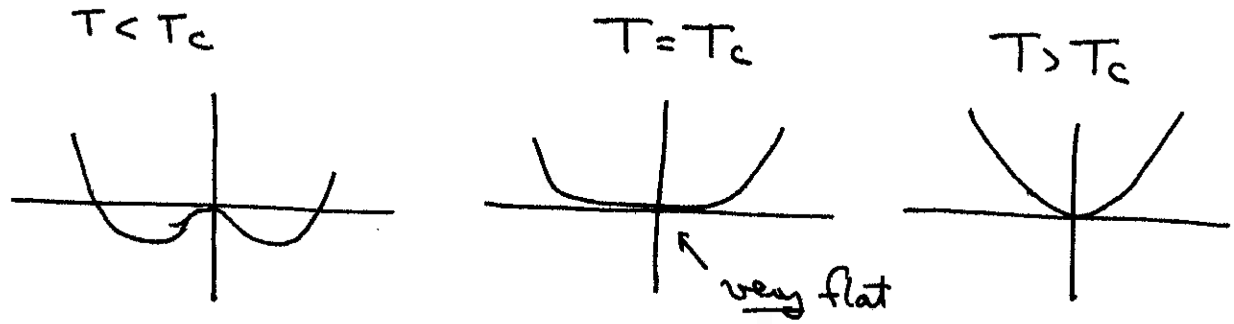


The point at the center, which is threefold three ways, is a special type of critical point called by Griffiths a *tricritical point.*

It is relatively easy to locate the tricritical point in Landau theory. For this, I will allow the coefficient of the M^4 term to become negative, in a way controlled by a new parameter y. I must add an M^6 term with a positive coefficient for stabilization. Then

$$G = \int d^3x \left\{ \frac{a}{2}(T - T_c) M^2 + \frac{b}{4}(y - y_t) M^4 + \frac{c}{6} M^6 \right\}$$

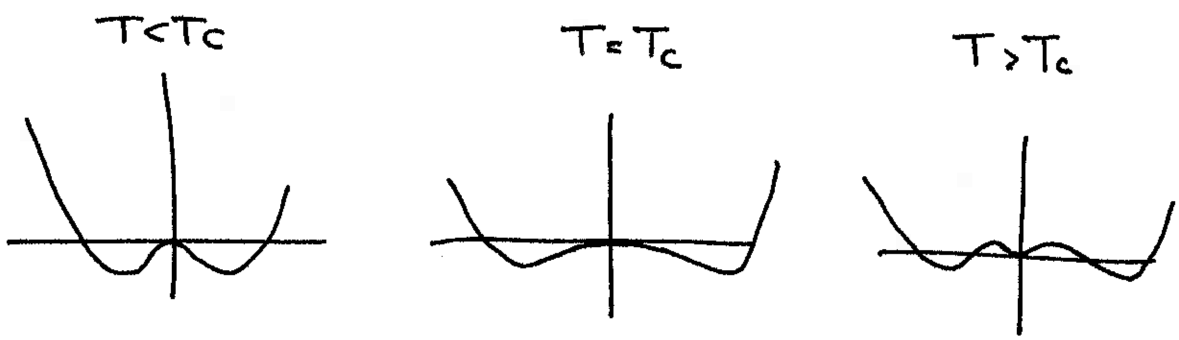
For $y > y_t$, we have the standard behavior discussed earlier in the course. There is spontaneous symmetry breaking for $T < T_C$ and a critical point at $T = T_C$. Just at $y = y_t$, the Gibbs free energy has the form



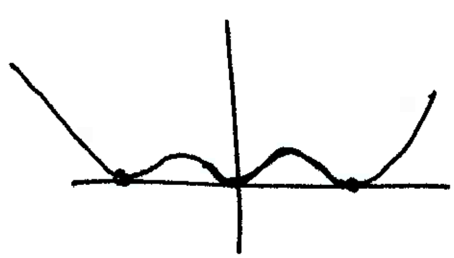
Since the stabilizing M^4 term is now replaced by an M^6 term, some of the predictions for non-analytic behavior change when $y = y_t$,

$$T < T_c \quad h = 0 \qquad M \sim (T_c - T)^{1/4} \qquad\qquad T = T_c \qquad M \sim h^{1/5}$$

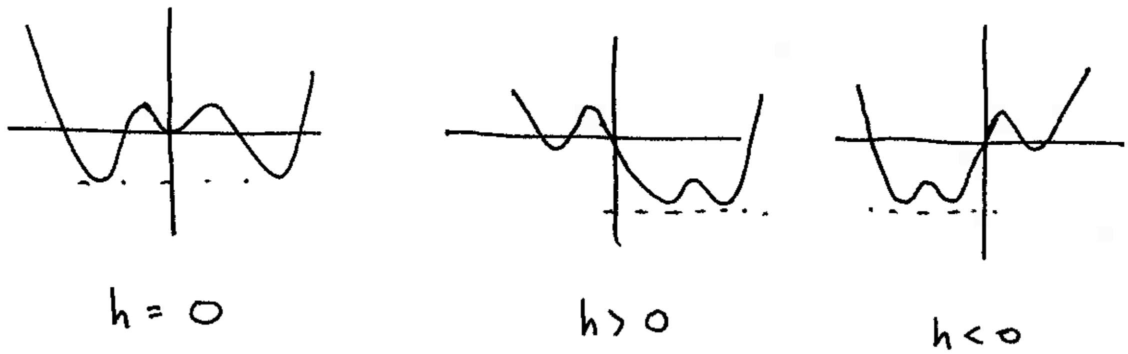
When $y < y_t$, the free energy has the form



In the first two pictures, the phase transition has already occured when we reach $T = T_C$. At a temperature somewhat higher than T_C, we will have a free energy of the form

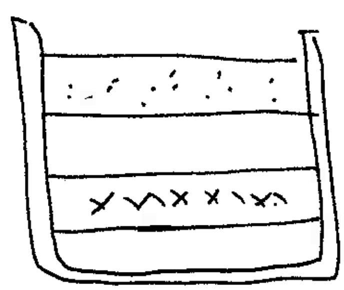


This form of G gives 3-phase coexistence. The point $T = T_C$, $y = y_t$, $h = 0$ is then the intersection of a line of critical points and a line of triple points. Moving away from this point (and possibility turning on h) there are three surfaces of two-phase coexistence. On these surfaces, G has the form

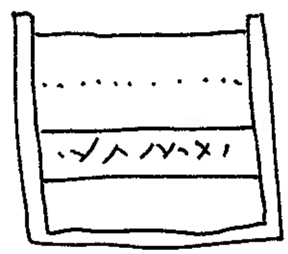


We could have discovered all of this structure in Landau theory without going through the explicit analysis of the Blume-Emery-Griffiths model. But probably you would have thought it silly of me to add higher-order polynomials to the Landau free energy. It is interesting that these quite abstruse behaviors actually appear in physical systems.

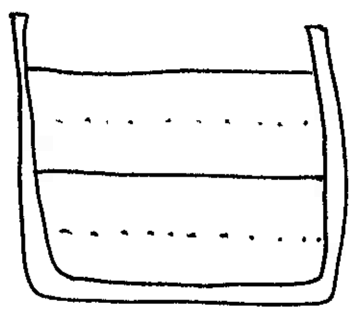
It is possible to create even more exotic higher-order critical points in the laboratory. Here is one more example, Consider a multicomponent fluid system with 4 distinct immiscible solvents:



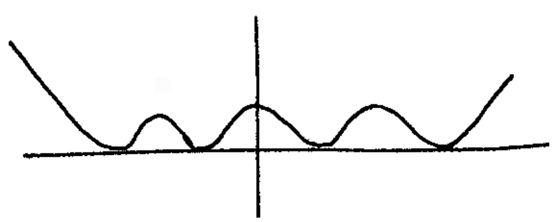
This is a case of 4-phase coexistence. When we dissolve solutes in this system, the solutes will have a different concentration in each layer, regulated by the requirement that the chemical potentials in the four layers should be equal. By adjusting the concentrations or chemical potentials of solutes, it is possible to cause a pair of layers to merge, so that the interface disappears. The point of disappearance of the interface is a critical endpoint.



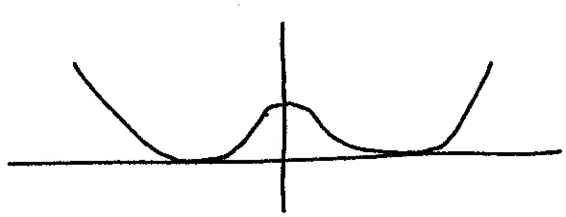
If there are several solutes, we can continue to adjust their chemical potentials so that a second interface disappears. The intersection of the two critical endpoints is called a *bicritical point.*



It is easy to make a description of the bicritical point in Landau theory. Four-phase coexistence is described by an 8th-order polynomial with 4 degenerate minima.



We can adjust two parameters so that pairs of minima just merge, so that the behavior near each minimum M_* is $G(M) \sim (M - M_*)^4$,



Clearly, we can add to this complexity arbitrarily.

A century ago, Gibbs studied the systematics of multi-component fluid mixtures. He proposed a rule to systematize the search for special points in the thermodynamic space. Consider a system with c component species. This system is parametrized by c chemical potentials, plus temperature T and pressure P. Only differences of chemical potentials are relevant, and there are $(c-1)$ such differences, so the system has

$$f = c + 1$$

degrees of freedom.

Two-phase coexistence is one restriction on the parameters. Every additional coexisting phase requires another constraint. For m phase coexistence, there are $(m-1)$ constraints. If, in addition, we constrain the system to be at a critical endpoint, there is an additional restriction on the parameters.

In all, a system with c components, m-phase coexistence, at critical endpoints in e directions, has

$$f = c + 2 - m - e$$

remaining degrees of freedom. This is the *Gibbs phase rule.* It expresses the way in which the various special thermodynamic points form nested subspaces of lower dimension in the full thermodynamic space.