Physics 212 – Statistical Mechanics

Multicritical Points

Before going on to more advanced topics in the theory of order-disorder transitions, I would like to spend a lecture on other possibilities for singularities in the phase diagram that can appear when we consider systems depending on additional thermodynamic variables.

It is obvious that, if we add a new variable to a statistical mechanics problem, the phase diagram must extend into another dimension. In this case, it is possible that a single critical point can extend to a line of critical points. More interesting phenomena are also possible in this setting. Let's now explore some of these.

A real physical system that has interesting behavior in a multiparameter phase diagram is that of He^3–He^4 mixtures. Pure He^4 has a superfluid transition at $T_\lambda = 2.2^\circ$K. Earlier in the course, we saw that such a transition is expected for a gas of bosonic atoms such as He^4 and corresponds to the transition to a superfluid state.

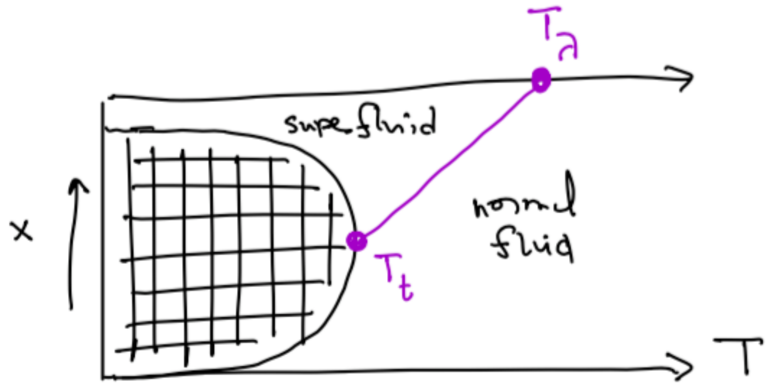
He^3, on the other hand, is a fermionic atom. As the temperature is lowered, it evolves continuously, without a phase transition, to a system in which the atoms repel one another both by their interactions and by the Pauli exclusion principle. This system is "Fermi liquid", similar to that of electrons in a metal, but more strongly interacting. The low-energy excitations are similar to those in a free fermion gas – excitation of individual atoms from just below to just above the Fermi surface.

In an earlier lecture, we saw that the electron gas undergoes pair condensation to a superconductor at a few °K. In a similar way, He^3 atoms undergo pair condensation to a superfluid at temperatures of about 2 mK. But, that is not my subject here.

If we mix He^3 and He^4, we find an interesting phase diagram in the plane of T and the density fraction

$$x = \frac{n_{He4}}{n_{He4} + n_{He3}} \ . \tag{1}$$

Pure He^3 expels He^4 atoms, since the He^3 atoms, constrained by the Pauli principle, want as much space as possible for themselves. On the other hand, He^3 has a small but nonzero solubility in superfluid He^4. Then one finds the phase diagram



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A line of critical points extends from T_λ to T_t. At T_t, this line turns into a line of discontinuous (first-order) transitions with 2-phase coexistence.

Martin Blume, Victor Emery, and Robert Griffiths introduced a lattice spin model that reproduces the main features of this phase diagram in Phys. Rev. A4, 1071 (1971). I will now analyze this BEG model using mean field theory.

The BEG model is a spin system on a square lattice in d dimensions. The spin takes the values

$$S_i = \{1, 0, -1\} \tag{3}$$

Here, the states $S_i = \pm 1$ represent He^4 atoms in the superfluid state. The two spin orientations and the Z_2 symmetry connecting them replace the manifold of ground states and the $U(1)$ symmetry of a superfluid. The state $S_i = 0$ represents a He^3 atom. Thus, this model is a lattice gas representation of He^3–He^4 mixtures.

The Hamiltonian of the BEG model is

$$\mathcal{H} = -J \sum_{i,\nu} S_i S_{i+\nu} + \Delta \sum_i S_i^2 \ . \tag{4}$$

The coupling $J > 0$ induces magnetic or superfluid order. The parameter Δ is analogous to the relative chemical potential of He^3 vs. He^4 atoms. That is

$$\begin{array}{lll} \Delta \to -\infty & \text{gives} & \text{pure He}^4 \\ \Delta \to +\infty & \text{gives} & \text{pure He}^3 \end{array} \tag{5}$$

Let

$$m = \langle S_i \rangle \qquad x = \left\langle S_i^2 \right\rangle \ . \tag{6}$$

Then $x \to 1$ is the pure He^4 system and $m \neq 0$ signals superfluid order.

Now I will analyze this system using mean field theory. To do this, I will assume that, for each spin S_i, the neighboring spins take the value $m = \langle S_i \rangle$. With this substitution, the spin S_i has the one-site Hamiltonian

$$\mathcal{H}_{MF} = -J \cdot 2dm \cdot S_i + \Delta\, S_i^2 \ . \tag{7}$$

We can work out the statistical mechanics of this simple model and determine the value of m by self-consistency.

$$m = \langle S_i \rangle = \frac{\left((+1)e^{2d\beta Jm} + (-1)e^{-2d\beta Jm}\right)\, e^{-\beta\Delta}}{\left(e^{2d\beta Jm} + e^{-2d\beta Jm}\right)\, e^{-\beta\Delta} + 1} \ . \tag{8}$$

From the 1-site Hamiltonian, the expectation value of the spin is Similarly, the prediction for x is

$$x = \left\langle S_i^2 \right\rangle = \frac{\left(e^{2d\beta Jm} + e^{-2d\beta Jm}\right)\, e^{-\beta\Delta}}{\left(e^{2d\beta Jm} + e^{-2d\beta Jm}\right)\, e^{-\beta\Delta} + 1} \ . \tag{9}$$

These equations can be written more simply as

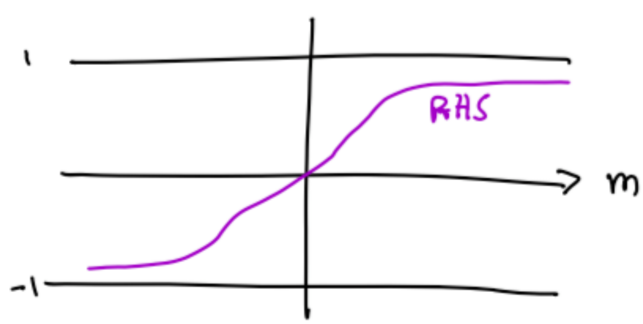
$$\begin{aligned} m &= \frac{2\sinh(2d\beta Jm)}{2\cosh(2d\beta Jm) + e^{\beta\Delta}} \\ x &= \frac{2\cosh(2d\beta Jm)}{2\cosh(2d\beta Jm) + e^{\beta\Delta}} \end{aligned} \tag{10}$$

If we find a solution for m, then x is given by

$$x = \frac{m}{\tanh(2d\beta Jm)} \tag{11}$$

The formulae (10) make clear that both m and x will be have values between 0 and 1.

As in our study of mean field theory for the Ising model, the right-hand side (RHS) of the equation for m is a monotonically increasing function of m that transitions from -1 to 1 as m is increased from $-\infty$ to ∞



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We can find solutions to the m equation graphically by intersecting this curve with the line $m = m$.

At high temperatures, β is small and so the RHS has very slow dependence on m. Then there is only one solution to the equation, the obvious solution $m = 0$. However, as the temperature is lowered or β is increased, new solutions appear. In our earlier discussion, the RHS was the derivative of the Gibbs free energy with respect to m. Thus, the solutions to the equation were alternately minima and maxima of the Gibbs free energy. That is also correct in this case and will be a useful source of insight.

If we send $\Delta \to -\infty$, we have the pure He^4 system, and the mean field theory problem becomes precisely the one that we solved earlier. Mean field theory predicts an order-disorder transition at the temperature T_c given by

$$2d\beta_c J = 1 \qquad \text{or} \qquad T_c = 2dJ \tag{13}$$

at which the $m = 0$ solution becomes unstable with respect to solutions at $m = \pm m_0$. For finite Δ, the value $m = 0$ remains a solution. For this value of m, the parameter x takes the value

$$x_0 = \frac{2}{2 + e^{\beta\Delta}} \tag{14}$$

which decreases from 1 to 0 as Δ is increased. Let's now follow this solution and examine its stability in this more complex problem.

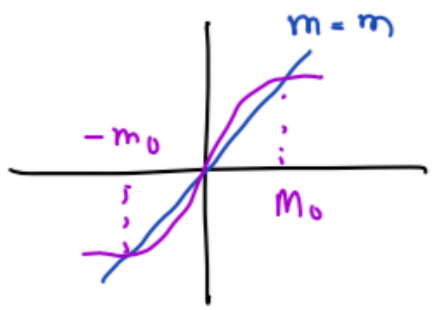
Expand the self-consistency equation about $m = 0$. We find

$$\begin{aligned} m &= \frac{2((2d\beta Jm) + \frac{1}{6}(2d\beta Jm)^3 + \cdots)}{2(1 + \frac{1}{2}(2d\beta Jm)^2 + \cdots) + e^{\beta\Delta}} \ . \\ &= \frac{2 \cdot (2d\beta Jm)}{2 + e^{\beta\Delta}} \left\{ 1 + (\frac{1}{6} - \frac{1}{2 + e^{\beta\Delta}}) \, (2d\beta Jm)^2 + \cdots \right\} \end{aligned} \tag{15}$$

Then

$$m = m \cdot x_0 \cdot 2d\beta J \left(1 - \frac{1}{2}(x_0 - \frac{1}{3}) \, (2d\beta Jm)^2 \right) \ . \tag{16}$$

The slope of the RHS at $m = 0$ is $x_0 \cdot 2d\beta J$. When this slope becomes equal to 1, the RHS and the line $m = m$ are tangent. For larger values of the slope, the RHS lies above the line. But, since the RHS is always less than 1, the curve must cross back and give another solution. As long as the coefficient of the m^3 term is negative, the curve bends back very close to $m = 0$.



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These considerations give the location of the critical point at

$$1 + x_0 \cdot 2d\beta_c J \qquad \text{or} \qquad T_c = x_0 \cdot 2dJ \ . \tag{18}$$

For $T < T_c$ but close to T_c, we can solve for the nontrivial solutions

$$m(x_0 2d\beta J - 1) = \frac{1}{2} x_0 (x_0 - \frac{1}{3})(2d\beta J)^3 \ m^3 \tag{19}$$

On the right-hand side, we can set $\beta = \beta_c$. Then

$$m(\frac{T_c}{T} - 1) = \frac{1}{2}(x_0 - \frac{1}{3})\frac{1}{x_0^2} \ m^3 \ . \tag{20}$$

Finally, we find

$$m_0 = \pm \Big(\frac{2x_0^2}{x_0 - 1/3} \frac{T_c - T}{T_c} \Big)^{1/2} \ . \tag{21}$$

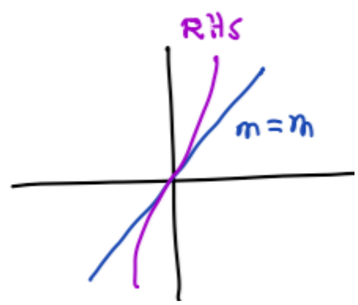
This analysis is correct for values of Δ such that $x_0 > 1/3$. It gives a line of critical points parametrixed by Δ or x_0. However, when x_0 crosses 1/3, the picture changes. Along the line of critical points, this happens at a temperature T_t given by

$$T_t = 2dJ/3 \ . \tag{22}$$

at the value of Δ such that

$$x(T_t, \Delta) = \frac{1}{3} \ . \tag{23}$$

As we pass this point, the term in parentheses on the RHS of (16) becomes curved upward, so there is no longer a solution for m close to $m = 0$.



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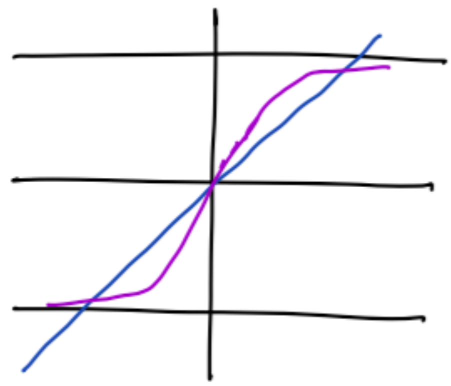
Still, the RHS is bounded above by 1, so the curve must bend back eventually. We conclude that, when the slope of the RHS equals 1, there is already a nontrivial solution at large values of m.



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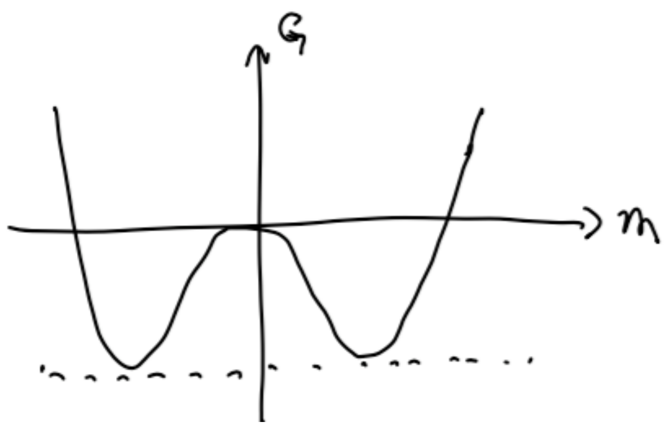
By the Z_2 symmetry of the problem, there must also be corresponding solution at large negative values of m. Since the solutions of the self-consistency equation are extrema of the variational Gibbs free energy, this function must have the form



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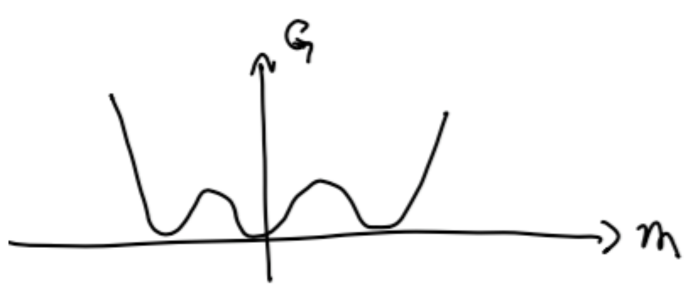
The Gibbs free energy has minima at $\pm m_0$ as, near $m = 0$, the order m^2 coefficient goes through zero. Note that, at the point where the m^2 coefficient vanishes, the curve bends downward at the origin , so the coefficient of the m^4 term is negative.

For any even slightly higher temperature, G will have a minimum at $m = 0$. But then, as we increase the temperature, we will find a temperature $T_T(\Delta)$ at which G has three degenerate minima,



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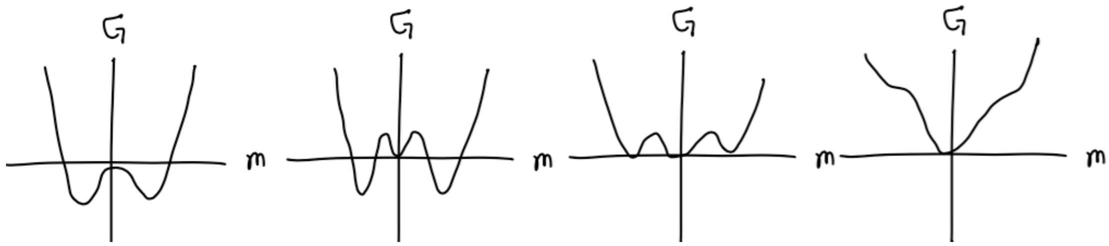
This is a *triple point*, a point where 3 different thermodynamic phases can simultaneously be in equilibrium. A familiar example of a triple point is the equilibrium state of water, ice, and vapor in a glass of ice water. The evolution of the system from low to high temperatures at values of Δ such that $x_0 < 1/3$ then has the form



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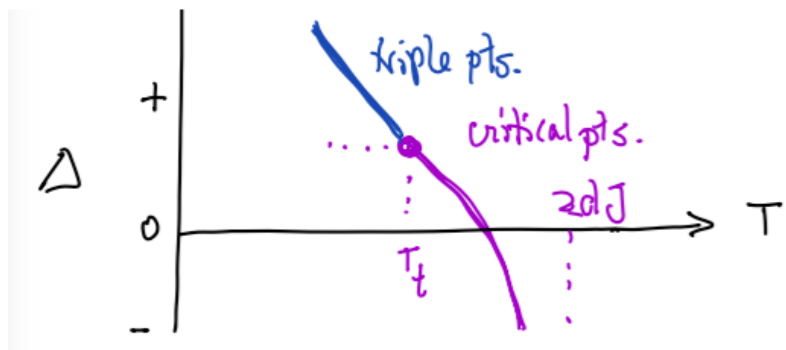
The phase diagram in the (T, Δ) plane then looks like



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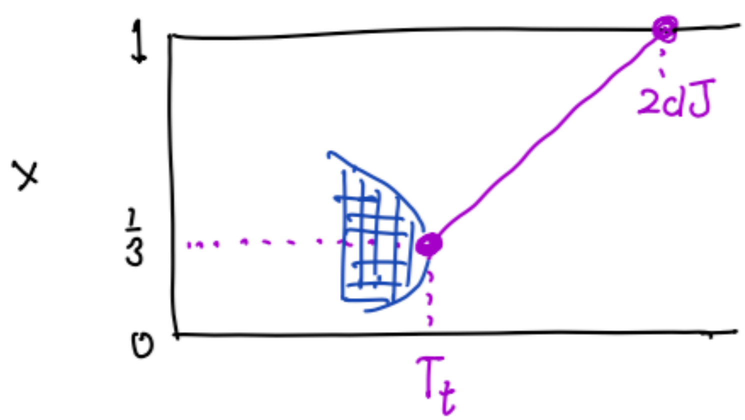
In the (T, x) plane this looks like



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The hatched region is not thermodynamically stable; it is the region of coexistence of two phases, one with a high density and the other with a low density of He^4. The line from $T = 2dJ$ to $T_t = 2dJ/3$ is a line of second-order phase transitions. The region to the left of this line is has superfluid order. At the temperature T_t, this line ends and continues as a line of triple points.

This is still not the full picture. In the whole plane shown in (30), the Hamiltonian is symmetric under the Z_2 symmetry. Let's now break this symmetry by adding an external magnetic field H coupling to the spins. This adds a third dimension to the phase diagram, with $H > 0$ filling the space behind this plane and $H < 0$ filling the space in front. The Hamiltonian is now

$$\mathcal{H} = -J \sum_{i,\nu} S_i S_{i+\nu} + \Delta \sum_i S_i^2 - H \sum_i S_i \ . \tag{31}$$

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

$$\mathcal{H}_{MF} = -J \cdot 2dm \cdot S_i + \Delta\, S_i^2 - H S_i \ . \tag{32}$$

This generates the self-consistency equation

$$m = \langle S_i \rangle = \frac{\left(e^{2d\beta Jm} e^{\beta H} - e^{-2d\beta Jm} e^{-\beta H}\right)\, e^{-\beta\Delta}}{\left(e^{2d\beta Jm} e^{\beta H} + e^{-2d\beta Jm} e^{-\beta H}\right)\, e^{-\beta\Delta} + 1} \ . \tag{33}$$

or

$$m = \frac{2\sinh(2d\beta Jm + \beta H)}{2\cosh(2d\beta Jm + \beta H) + e^{\beta\Delta}} \tag{34}$$

If we define

$$\overline{m} = m + \frac{H}{2dJ} \ , \tag{35}$$

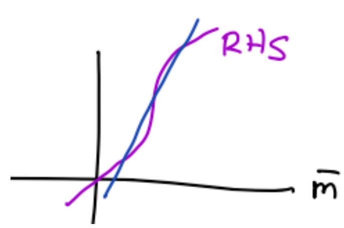
then we find the equation

$$\overline{m} - \frac{H}{2dJ} = \frac{2\sinh(2d\beta J\overline{m})}{2\cosh(2d\beta J\overline{m}) + e^{\beta\Delta}} \tag{36}$$

The RHS of this equation is the same function that we studied earlier. But now we must intersect this curve with the line

$$\overline{m} - \frac{H}{2dJ} \quad \text{vs.} \quad \overline{m} \tag{37}$$

which lies (for $H > 0$) somewhat to the right of the origin. In the interesting region where 3 phases come close to coexistence, the construction looks like



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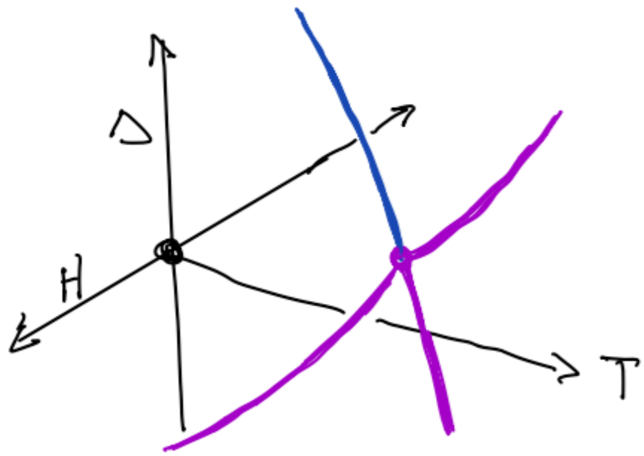
Starting from the region of high temperature, where there is only one solution to the self-consistency equation, we reach the situation of three-phase coexistence when the line (37) is tangent to the RHS. This corresponds to a new critical point or, in the (T, Δ, H) space, a line of critical points emerging from the special point at $T = T_t$. This structure is repeated on the other side when $H < 0$.

We are now in a better position to see the full picture. There are three lines of critical points that connect at the point $x = 1/3, T = T_t$. The line of triple points also connects to this point. Then we have the framework in 3 dimensions



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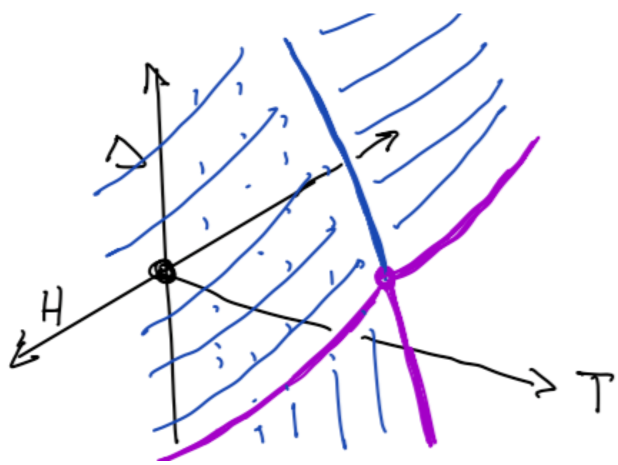
Each line of critical points is the edge of a surface of discontinuous transitions from one minimum of G to another. The three surfaces intersect on the line of triple points. Then, finally



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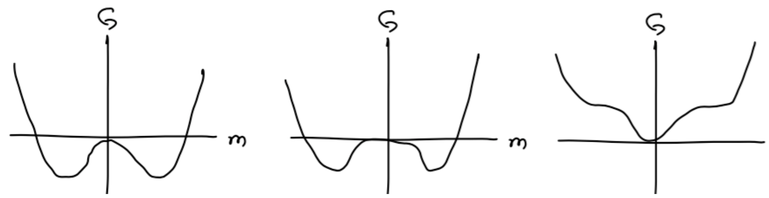
Griffiths called the point at $T = T_t$, $x = 1/3$ the *tricritical point.* This point is triple in two different ways, since it controls the three lines of critical points and the three surfaces of discontinuity.

We might now ask how the tricritical point appears in Landau theory. Actually, there is a description ready at hand. Within Landau theory, we can add a parameter to dial the coefficient of the M^4 term in the local free energy down to zero. In this case, we need an M^6 term for stability. Then we have the Landau freee energy

$$G = \int d^3x \left\{ \frac{1}{2}(\vec{\nabla} m)^2 + \frac{a}{2}(T - T_c)m^2 + \frac{b}{4}(y - y_t)m^4 + \frac{c}{6}m^6 \right\} . \tag{41}$$

For $T < T_c$ and $y = y_t$, the evolution of the free energy as a function of temperature is



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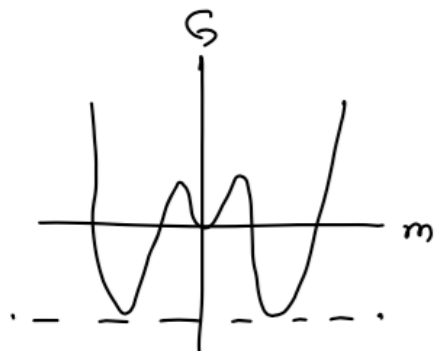
These forms can be perturbed in either direction by turning on a positive or negative M^4 term.

A stable 6th order polynomial has a maximum of three possible minima. In a system with Z_2 symmetry, one of these minima must lie at $m = 0$ and the other two must be symmetric about this point. By adjusting parameters, we can find the situation in which the two nontrivial minima are in coexistence



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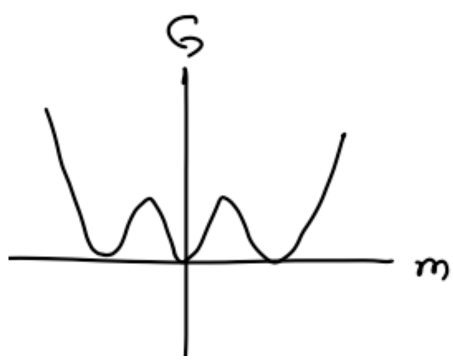
or the situation of the triple point



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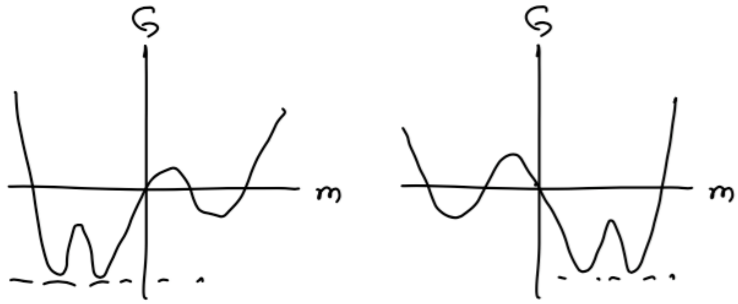
Adding an external field to break the Z_2 symmetry, other coexistence patterns are possible



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and, in these cases, there are new critical points where the two minima merge. This extended Landau theory then contains all of the features that we found in the BEG model.

For $y = y_t$ and temperatures just below T_t, the Landau theory predicts

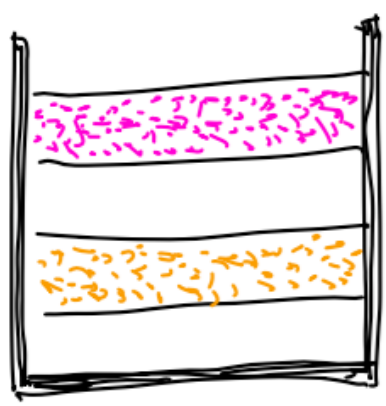
$$M \sim (T_c - T)^{1/4} . \tag{46}$$

At $y = y_t$ and $T = T_t$,

$$M \sim H^{1/5} . \tag{47}$$

This is a new set of critical exponents characteristic of a tricritical point. You can easily check that the operator M^6 is marginal around the Gaussian fixed point in 3 dimensions. Then $d = 3$ is the upper critical dimensionality for the tricritical point, and so these exponents are expected to be exact in 3-dimensional systems.

It is possible to create even more exotic higher-order critical points in the laboratory. Multi-component fluid systems can have a large number of degrees of freedom that we can adjust to find these. Consider, for example, a system of 4 immiscible fluids in equilibrium



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This is a 4-phase coexistence. By dissolving solutes in the fluids, one can adjust the relative chemical potentials of the fluids and create critical points at which pairs of fluids merge. In this way, it is possible to find a situation in which the discontinuities between two pairs of fluids are disappearing simultaneously

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Such a system has critical opalescence in both phases. This is a *bicritical point.*

In Landau theory, 4-phase coexistence requires an 8th-order polynomial. The bicritical point is the point of simultaneous merger of two pairs of minima. Following this path, higher-order critical points can be built up to any level of complexity.