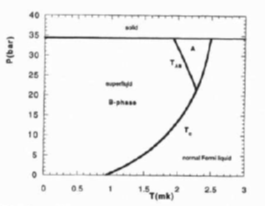
**Phases**

We’re generally interested in two things regarding phase transitions. First we want to map out the coexistence curves delineating different phases. Second we’d like to characterize how the potentials, and order parameter(s), change across these transitions. And third we’d like to work out how the intensive variables like specific heat capacity and thermal compressibility change.

**Phases and Why**

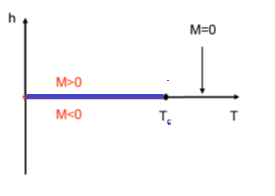
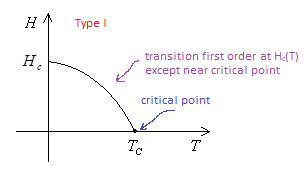
Substances exist in different phases, which can be delineated in terms of their independent variables, E, X, N, ψ (or one of their conjugates). I suppose, we can choose any two non-canonically conjugate variables, basically any independent variables of one of those thermodynamic potentials? Seems T, p, the Gibbs potential variables, are a favorite for liquids.

Liquid water: Liquid He:

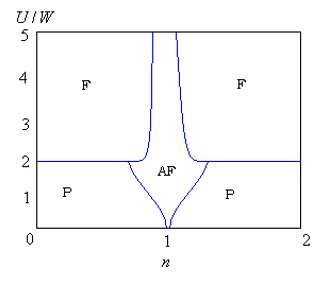
 

whereas T and h, the Helmholtz potential variables are favorites for when we have magnetic fields going on.

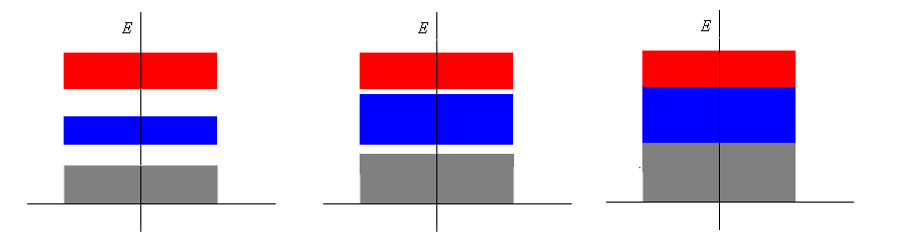
Ferromagnet: Superconductor:

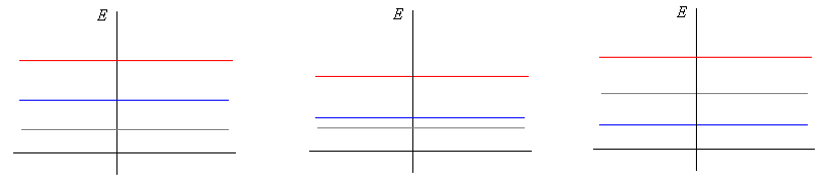
We can also change the composition of the substance, basically by changing its internal parameters, which is the subject of ‘quantum’ phase transitions. For instance, the doped Hubbard model of interacting electrons (n = # electrons per site, U = coulomb repulsion, W = band width)



Classical phase transitions are temperature induced. Basically the different phases occur at different energy levels. Consider the first picture below. In solid phase (grey) we might have lattice oscillations. In liquid phase (blue) the molecules are held by weaker VDW forces, and we might have longitudinal oscillations. In gas phase (red), we’d have no more interactions, and excitations would just be kinetic d.o.f. As we raise the temperature, the substance’s energy increases, and it obviously requires a finite amount of energy to jump phase (first order phase transition). But by changing the external parameters (second picture), like V, h, we change the energy levels, and perhaps bring them closer together. When they meet (third picture) is where we get a 2nd order phase transition as the crossover between phases is smooth (not necessarily all three, as i drew in the picture, though).



Quantum phase transitions are all at T = 0, so the system is always in its GS. They are caused by changing some external parameter which alters the character of the GS. In diagram we see the GS (grey in first and second pictures) changing, and when it crosses the second energy level (third picture), an abrupt (phase) transition occurs.



One last comment: phase transitions often won’t happen in systems of reduced dimensionality. There is a ‘lower critical dimension’ below which a phase transition can’t occur. For many cases, like the ferromagnetic transition, or liquid-gas transition, dlower\_critical = 2.

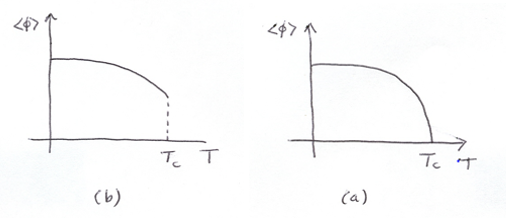
**First and Second Order Phase Transitions**

Transitions are often characterized by an order parameter which are related to the entropy, and more or less characterize some macroscopic feature of the substance. These are often zero in the ‘disordered’ phase, and finite in the ‘ordered’ phase. An example is net magnetization for ferromagnets. Or minimum # of particles in the GS of a bosonic gas. Or the difference in molar volume of the liquid vs. gas phase of a fluid at same T and p. In first order phase transitions, the order parameter makes a discreet jump when it crosses the phase boundary line. For second order phase transitions, the jump is 0. Quantum phase transitions are also characterized by such a parameter, but these occur at T = 0, and so the changes of the order parameter are w/r to some other independent variable, like concentration, or interaction strength, etc..

**First order phase transition:** characterized by discontinuity in order parameter, generally.

**Second order phase transition:** characterized by continuity in order parameter

Here plotting order parameter vs. T, but that isn’t necessary, can be p, etc.



Graphs below show how the order parameter as a function of some independent variable at different T’s (blue, red, black, in order of T), and can see how it goes from 1st order to 2nd order as we change T. Generally, as we approach the critical point, the first order discontinuities shrink, until they vanish at the critical point. As illustrated below.

Graphical user interface

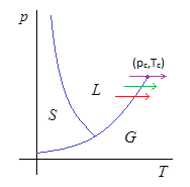
Description automatically generated with medium confidence

We can also characterize phase transitions by their potentials. I believe the potentials themselves are continuous across the phase boundaries. But their derivatives may not be/probably aren’t, and likewise their second derivatives.

**First order phase transition:** characterized by discontinuity in first derivative of potentials, generally.

**Second order phase transition:** characterized by discontinuity in second derivatives of potentials.

Consider the phase diagram below,



Since we’re dealing with T and p, the relevant potential is G(T,p), which, in differential form is dG = -SdT – Vdp. So the first derivatives are S and V basically. Therefore we ‘expect’ these to be discontinuous across the phase boundary, at least up till the critical point. This coheres with our order parameter discusion: first order phase transitions are characterized by a discrete change in entropy across the boundary, and second order phase transitions by a continuous change. This generally indicates that the PE/structure of the system is changing. Some second derivative quantities are, among other choices, C = T∂S/∂T, and κT = V-1(∂V/∂T)p. So note how the first derivatives, second derivatives, change as we closer to the critical point:

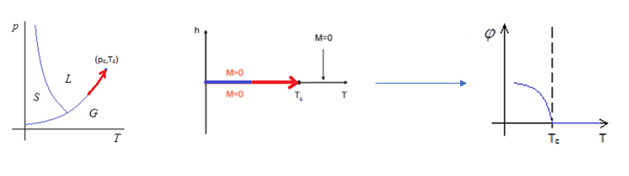
Chart, radar chart, line chart

Description automatically generated

Generally, as we approach the critical point, the first order discontinuities shrink, until they vanish at the critical point. But often the singularities in the derivatives remain. What about other potentials and their natural variables? Say S(E,V), and dS = (1/T)dE – (p/T)dV. So we’d allege that 1/T, and p/T are discontinuous functions of E and V across the boundary? Well holding V constant across the solid-liquid boundary, certainly E will increase while 1/T will remain flat. So maybe not discontinuous, but certainly the second derivative ∂(1/T)/∂E|V will be (which is related to Cv). Anyway, I suspect there are at least non-analytic features across these phase boundaries.

**Introducing critical point parameters/exponents**

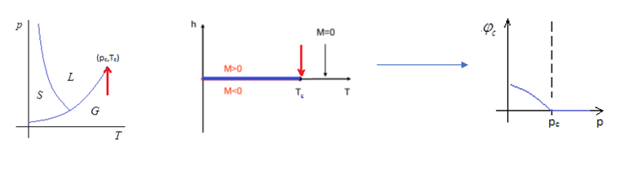
To characterize the functional form of the order parameters/derivatives as a function of T, p, across the transition and near the critical point, we’ll introduce the following functions. Probably doesn’t matter how we approach the critical point in the last three. So first we’d like to examine how the order parameter behaves along the coexistence curve as we approach the critical point:



As you go up the line, approaching TC, the order parameter will go to zero. In fluids, the order parameter is usually taken to be φ = Vg - VL (difference in volume per particle or molar volume between the gas and liquid phases). In magnetic systems, the order parameter, φ could be written as φ = <mh+> - <mh-> where h+ and h- mean just a shade above 0 and just a shade below 0. These two will be equal and opposite though, so we could say φ = 2<mh+>, but instead we just say φ = <mh+>. Turns out they both go to zero according to the same power law, which defines the first critical exponent, β:



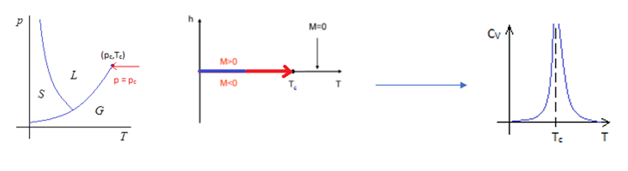
Now consider approaching from a different direction, at constant temperature.



In the fluid case, we would be interested in φc = Vg - Vc, and c references the critical point. In the magnetic systems case, rather φc = <mh+> - <mc> = <mh+> (‘cause <mc> = 0) is what we’d calculate. In any event, this too should go to zero, and does so according to the exponent δ (of course hc = 0).



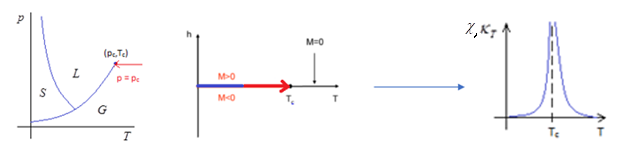
Now take a look at the heat capacity along this curve…



If go along this line, the heat capacity will diverge as approach Tc.



and finally, consider the compressibility, magnetic susceptibility:



It too will diverge, something like:



If we were to subject our substance to an inhomogeneous field, or perhaps pressure, then we can generalize the susceptibility to something like (illustrated for case of spins in a magnetic field) the Green’s function thingy there.



The δ/δ derivative stands for functional derivative, and this would be appropriate here because by the theory of Green’s functions, m(r) would be a functional of h(r). It’s useful to see that we can also get the usual homogeneous susceptibility, χ, from the GF. The definition of the susceptibility implies:



Now we’ll look at the total ‘magnetization’, and also presume the susceptibility is a function of only the difference of the two arguments so that we can introduce a Fourier transform. And we’ll also presume h(**r**) is uniform.



So we have:



which says that the uniform susceptibility is just the k = 0 component of the Fourier transform of the inhomogeneous susceptibility χ(r-r´). Apropos the thermal relaxation time, we don’t really have the apparatus for calculating such things until get to statistical mechanics one might think, but apparently it is also governed by a critical exponent. Interesting that it diverges near phase transition.

**Scaling Relations**

The critical exponents are not all independent. There appears to be just two independent critical exponents. This fact can be shown to follow from Widom’s scaling hypothesis (which itself can be shown to follow from an RG group analysis – see Stat Mech folder/RG file). Namely that close to the critical point, the free energy f = F/V (well, actually, f = βF/V) conforms to the following general form,



where is some well-behaved function. And t = β(T – Tc), j = β(h-hc) or β(p-pc), etc. Note in the T → Tc limit, we can say β → βc = 1/kBTc, and so we will presume to set β = βc already. Recalling (using units where kB = 1 now),



the specific heat at critical field, or pressure, is,



So,



as we expect. Now let’s look at the magnetization (or could do pressure in case of gas). It’s given by:



And so the magnetization at the critical field,



So,



And the whatever that other one is called,



For this limit to give rise to a power of j (which it’s supposed to), and not just blow up or go to zero, it must be that ψ´(x) ~ xp such that t2-α-Δ(j/tΔ)p is finite in t = 0 limit → 2-α-Δ = Δp → p = (2-α-Δ)/Δ. So then,



and magnetic susceptibility



So,



These give rise then, to a bunch of scaling relations between the critical exponents. For one,



And we can get one involving the η, and ν. Consider the generic expression for the uniform susceptibility discussed above.



where Ωd is the area of a d-dimensional unit sphere. Filling in ξ,



The stuff in the [ ] is just a prefactor that doesn’t blow up in the vicinity of Tc, so we don’t care. And recognizing the form of χ, we see that we must have:



I think we can also say, well we did already say, that the correlation length assumes a universal form near the critical point,



**Hyperscaling**

There is one more scaling equation that relates the critical exponents explicitly to dimensionality. This relationship only holds for d < dupper\_critical, where dupper\_critical = 4 for things like the liquid-gas transition, and ferromagnetic transition, etc. The argument is that near the critical point, the system is grouped into clumps of size on the order of the correlation length, ξ. Presuming the system to be composed of independent blocks of size ξd, then the total partition function is just Z0N (this would also depend on t and j, but ought to not depend in a singular way), where N = (L/ξ)d. And so filling stuff in we get (note we can take T → Tc = constant near the critical point):



and so f(t, j = 0) = βF/Ld = |t|dνβcF0(t, j=0). And I think we’d assume that F0(t,j=0) doesn’t go to 0 as t does, but rather to some constant. Therefore, comparing with the form Widom established for f(t,j) above, we’d conclude that:



But again, this doesn’t seem to hold past the upper critical dimension, as indeed this would often make α negative.

**MI transition**

In metal-insulator transitions, one may hypothesize other scaling relations, like:



where nc is a critical impurity concentration, at which the conductivity vanishes, when T = 0.

**Appendix**

Here are some critical exponents of the Ising model from Chaiken-Lubensky. I think the liquid-gas transition exponents are similar?

Table

Description automatically generated