Landau theory of phase Transitions:

Landau theory is a symmetry based analysis of the equilibrium behavior of a system near a phase transition.

* A system changes from one phase to another (by tuning an external parameter, say, temperature) through a transition, at which physical observables show non-smooth (singular, non-analytic) behavior.

* Landau noted that a system cannot change smoothly between two phases of different symmetries.

Phase transitions are usually associated with spontaneous breakdown of one (or more) symmetry.

In fact, the symmetry of one phase must be higher than the other.

What is Symmetry breaking: If the Hamiltonian of a system posseses a symmetry, but the ground state wave functn does not respect it.

Examples: ⊙ Hamiltonian of a solid and liquid for a particular system (say, water and ice) are same, having continuous translation symmetry, ~~however~~, The wave-fn. of water respects it, but that of solid breaks the continuous translation symmetry to only discrete translation by lattice vectors.

⊙ Ferromagnet / ferroelectric breaks the spin-rotation / polarization-rot^n symmetry, but the paramagnet / paraelectric respects that.

⊛ Landau theory characterizes phase transitions in terms of an order parameter, a physical entity that is zero in the high-symmetry (or disordered) phase, and finite, increasing continuously when the symmetry is lowered (ordered phase).

⊙ For paraelectric to ferroelectric transition, the order parameter is polarization (P), for ~~ferro~~ para magnet to ferromagnet, the order parameter is magnetization (m).

⊛ In Landau theory, the free energy density, f, (such that the total free energy $F = \int f\, dV$) in the vicinity of a transition is expanded in a power series of the order parameter, where only the symmetry compatible terms are retained.

$$f(P) = \alpha P^2 + \beta P^4 + \gamma P^6 + \dots \text{ etc.}$$

$$f(m) = \alpha m^2 + \beta m^4 + \gamma m^6 + \dots \text{ etc.}$$

Only the even powers occur, as the free energy is invariant under polarization/magnetization inversion.

$$\text{i.e. } f(P) = f(-P) \quad \text{or} \quad f(m) = f(-m)$$

⊙ The state of the system is found by minimizing $f(P)$ w.r.t. P or m. (to obtain P_0 or m_0 that minimizes f).

⊙ Other thermodynamic quantities are subsequently calculated by taking appropriate derivatives of f.

⊙ For simplicity, we consider only spatially uniform, scalar order parameter (P or m), but a generalization to vector or even tensor order parameter is conceptually straight-forward (though calculationally tedious at times!).

⊛ Landau theory is a straight-forward phenomenology for linking measurable thermodynamic quantities in the vicinity of a phase transitions.

⊛⊛ However, the predictions of Landau theory are as good as its input parameters (e.g. α, β, γ) - the co-efficients of the series expansion of f. They are only determined from experiments or a first principle calculations based on a microscopic models.

⊙⊙ At a first look, the central ansatz of Landau theory - the free energy being represented as a power series - might ~~look~~ appear surprising. This is because the singular behavior associated with a phase transition are describable by such a simple analytic (regular) expansion!

⊛⊛ This is so, because the value of the order parameters, such as P_0 or m_0, that minimizes f is itself non-smooth (singular / discontinuous) function of the expansion co-efficients, which are T-dependent.

Aside; Landau theory is generally not valid very very close to the transitions. Ginzburg developed a criterion that decides the regime of ~~the~~ T, in which Landau theory is good, and the regime varies from transition to transitions in different systems.

General Phenomenology:

We start with:

$$f(P) = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \cdots - EP$$

or, $$f(m) = \frac{1}{2}am^2 + \frac{1}{4}bm^4 + \frac{1}{6}cm^6 + \cdots - mB$$

Note that we add the coupling to the electric field or magnetic field respectively. (This should not be taken as an indication to allow odd power term in free energy in general. The even power expansion is the ansatz for a field free situation, and we just added a known term in free energy that couples the field to the system.)

- Also, we assumed that the field free, unpolarized medium to have a free energy $f_0 = 0$, otherwise it would be a constant and irrelevant for thermodynamic behavior.
- We truncate the series at the sixth power term. The co-efficient of the highest power term must be positive. This ensures thermodynamic stability (we leave the explanation here). Basically, we must expand upto the highest even power for which the co-efficient is positive.

The equilibrium is determined by ~~of~~ the free energy minimum: $\frac{\partial f}{\partial P}\Big|_{P_0}=0$ or $\frac{\partial f}{\partial m}\Big|_{m_0}=0$

$$\Rightarrow \quad E = aP_0 + bP_0^3 + cP_0^4 \qquad B = am_0 + bm_0^3 + cm_0^4$$

get susceptibility: $\chi_p = \frac{P_0}{E}\Big|_{P_0=0} = \frac{1}{a}$; $\chi_m = \frac{m_0}{B}\Big|_{m_0=0} = \frac{1}{a}$.

⊙ Landau realized, ~~that~~ looking at the behavior of f vs. P/m that a phase transition (i.e. a singularity in χ) can be obtained by assuming the parameter a to change sign across the transition temperature, say, T_0.

He then postulates the simplest T-dependence of a, as

$$a(T) = a_0(T-T_0) + (\text{higher order terms.})$$

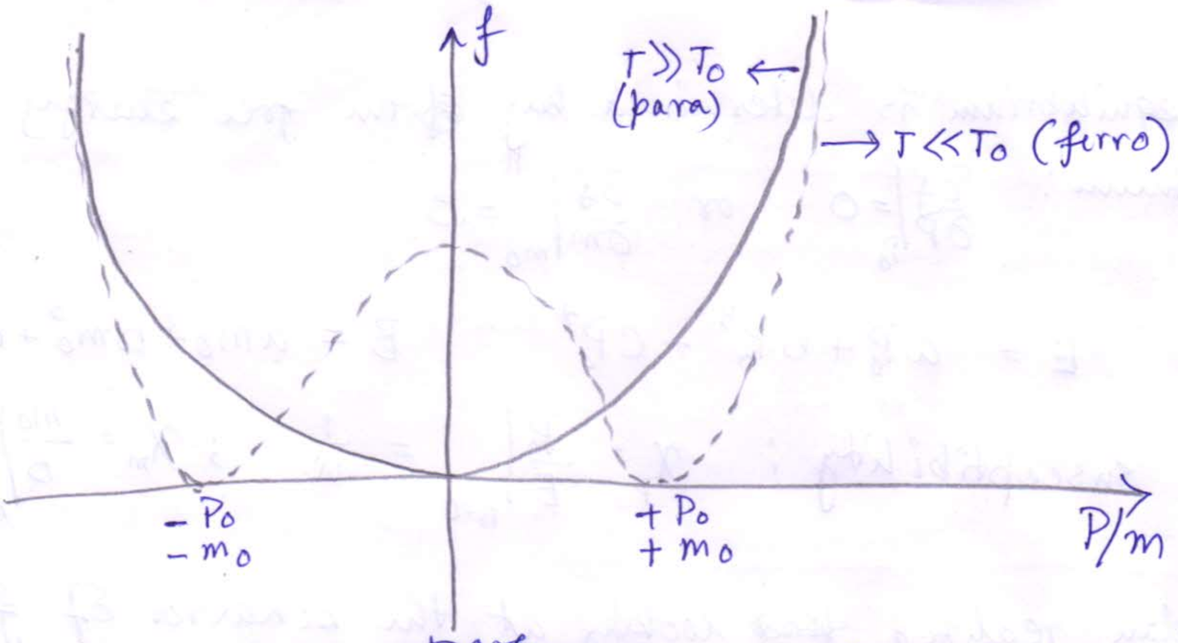
(a_0 is +ve and this is valid for $T>T_0$)

As we will see, this is sufficient, the T-dependence of higher order terms are ignored: $b(T)=b$; $C(T)=c$ etc.

The chosen form automatically ensures $\chi(T_0)$ diverges, at the phase transition temperature T_0.

How does f vs. P/m evolve with T, showing a transition?

To plot free energy vs. order parameter, we need a_0, b, c etc., which actually comes from experiments ~~/~~ or model calculations. But the qualitative behavior does not depend on these values! (as long as we are taking their correct signs). Because we truncated at c-term, $c>0$, ~~too~~ $a_0>0$ by construction. The qualitative behavior for f vs. P/m for $T\gg T_0$ & $T\ll T_0$ (irrespective of b being +ve or -ve) is shown below;



We see that the ~~ferro~~ para phase is characterized by P/m = 0 at the free energy minimum, whereas, the ferro phase develops a finite value of the order parameter ($\pm P_0/m_0$) when the free energy is minimum.

sgn(b) and the order of transition:

(A) b > 0 leading to 2nd order or continuous transitions:

In this case sixth power term is not really required and simplification in calculation occurs in ignoring it.

$$\frac{\partial f}{\partial P} = 0 \Rightarrow aP_0 + bP_0^3 = 0 \Rightarrow P_0 = \left[\frac{a_0}{b}(T_0 - T)\right]^{1/2} \text{ for } T < T_0$$

(ignoring applied electric field)

Clearly P_0 vanishes @ $T = T_0$ $\qquad = 0$ for $T > T_0$

$$\chi = \frac{1}{a_0(T_0 - T)} \quad \text{for } T < T_0$$

$$= \frac{1}{a_0(T - T_0)} \quad \text{for } T > T_0$$

shows Curie-Weiss behavior, and a divergence @ T_0.

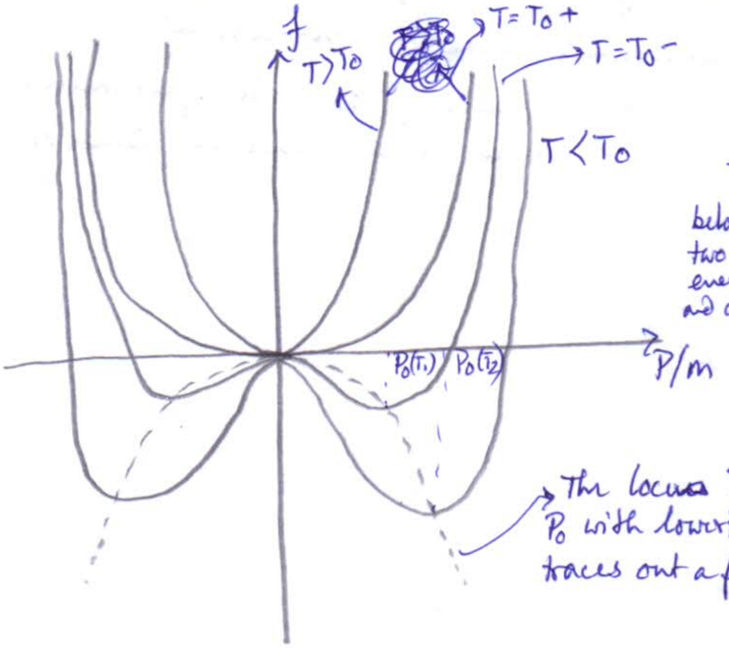
specific heat $C_v = -T\frac{\partial^2 f}{\partial T^2}$ shows jump across transition. $\Delta C_v = C_v(T = T_0^+) - C_v(T = T_0^-) = \frac{a_0^2 T_0}{2b}$

At $T = T_0$, and with electric field on: $\frac{\partial f}{\partial P} = 0 \Rightarrow -E + bP_0^3 = 0$

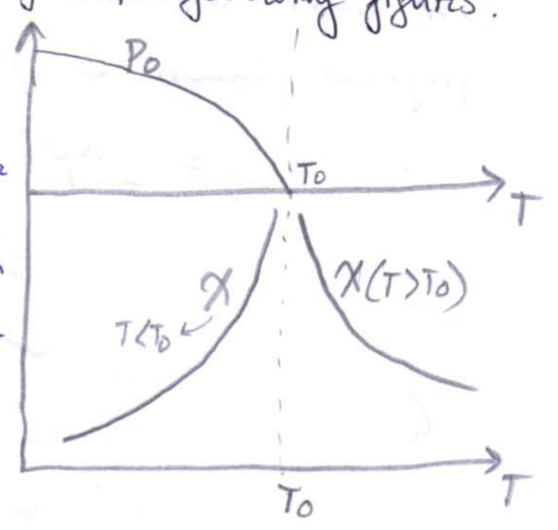
$$\Rightarrow P_0^{(T_0)} = \left(\frac{1}{b}\right)^{1/3} E^{1/3} \text{ etc.}$$

The magnetic analogues are obtained by replacing $P \rightarrow m$ & $E \rightarrow B$.

The qualitative behavior is well understood from the following figures:

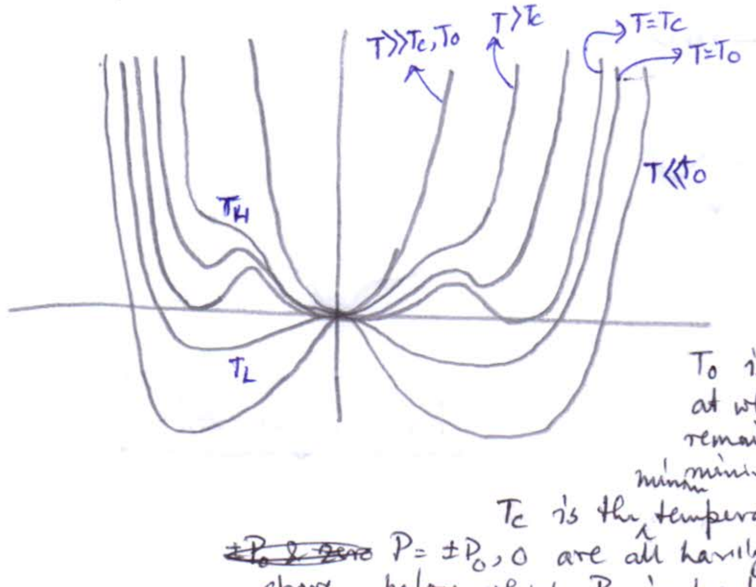


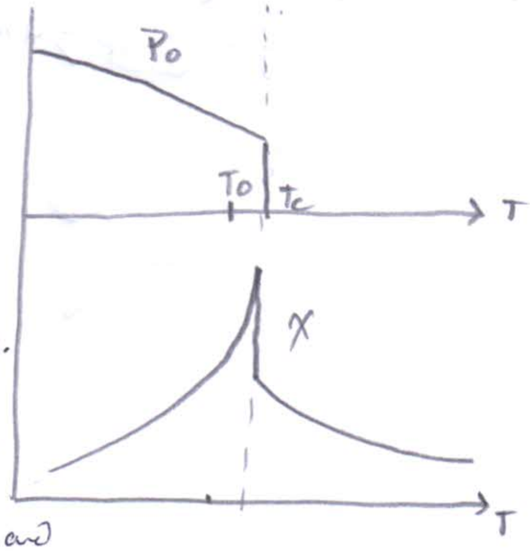
T_0 is the temperature below which there are two minima in free energy @ non-zero P/m and above which only a single minimum at P/m = 0



(B) <u>b<0 leading to 1st order or ~~continuous~~ discontinuous transition</u>:

Devonshire realized that b<0 leads to qualitative changes. In this case we must keep the 6^{th} power term in the expansion of f. The above diagram modifies as follows:





T_0 is the max. temp. at which finite $\pm P_0$ remains as global minimum of free energy.

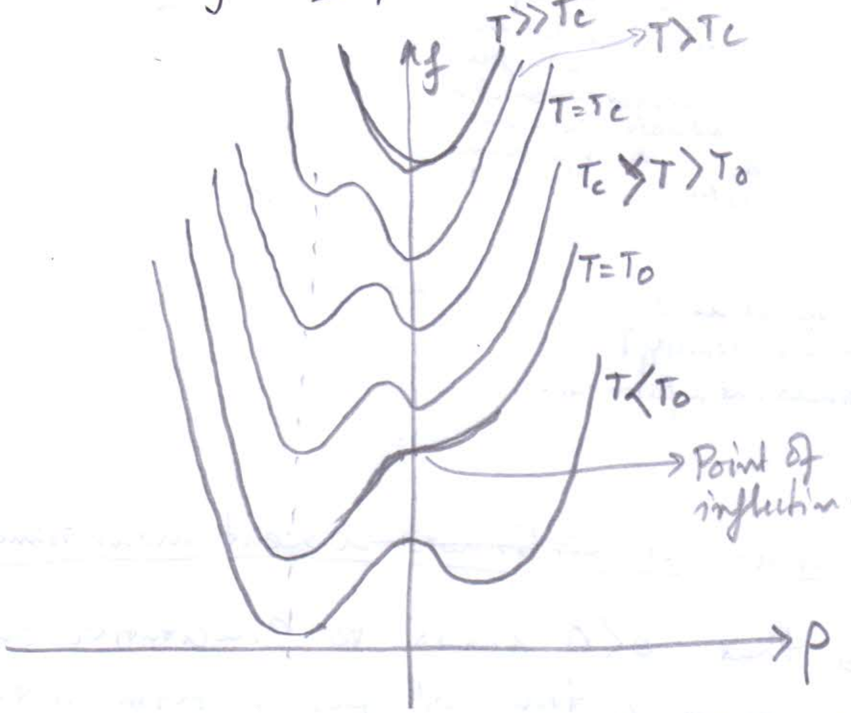
T_c is the temperature @ which ~~$\pm P_0$ & zero~~ $P = \pm P_0, 0$ are all having same energy and above ~~below~~ which P_0 jumps to zero.

Firstly, at $T=T_c$, the energy at $\pm P_0$ co-incides with that at $P=0$. Thus at T_c, the ordered and disordered phases co-exist.

Secondly, the system behaves differently as it is cooled or heated across the Transition. If the system is heated ~~up~~ from a low T, it exists in one of the two global minima, even across T_c (all the way until T_H), as the global minimum still persist as local minimum ~~as~~ in the "wrong" phase. On the other hand, if it is cooled from high T, it starts ~~at T=~~ with P=0, and cannot show ~~an~~ ordering until ~~heated~~ cooled below T_c. This is the origin of <u>thermal hysteresis</u>.

1st order transition occurs even for $b>0$, if for some other physical reason ~~as~~ free energy becomes cubic invariant.

i.e. $f = \frac{1}{2}a\rho^2 + d\rho^3 + \frac{1}{4}b\rho^3$ || here ρ is order parameter as in a solid liq. transition



Also ~~as~~ for a field driven transition in a ferromagnet (which shows a 2nd order transition ($b>0$) with T)

$$f = \cancel{\tfrac{1}{2}a\rho}\ \frac{1}{2}am^2 + \frac{1}{4}bm^4 - mB$$