4.5 Landau theory of phase transitions

4.5.1 Landau free energy

- In order to develop a general theory of phase transitions it is necessary to extend the concept of the free energy. . . .

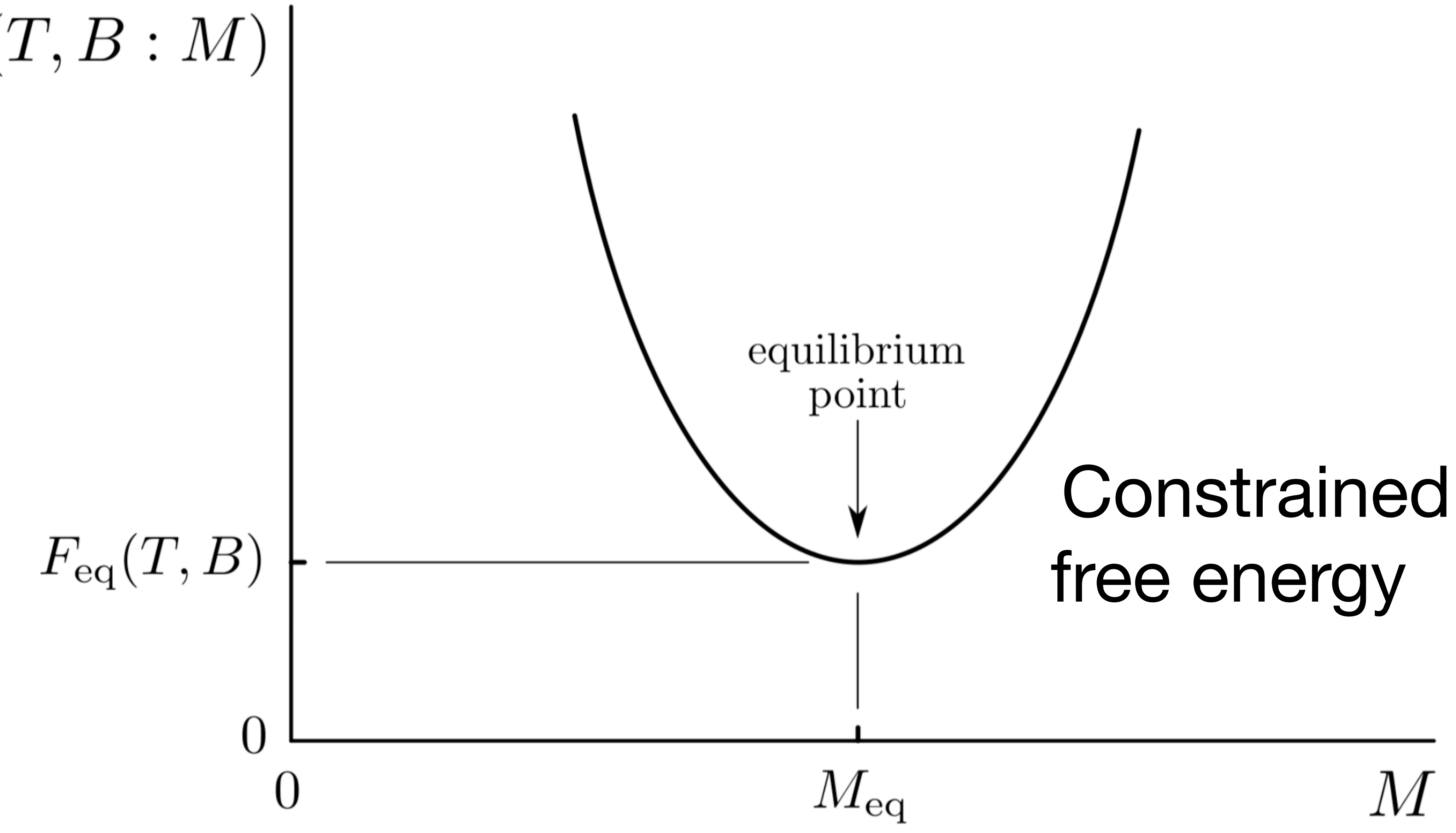
- The (magnetic) Helmholtz free energy has "proper variables" T and B. $F = F(T, B)$. And in differential form

$$\mathrm{d}F = -S\mathrm{d}T - M\mathrm{d}B.$$

- Thus S and M are given by

$$S = -\left.\frac{\partial F}{\partial T}\right|_B, \qquad M = -\left.\frac{\partial F}{\partial B}\right|_T.$$

- This free energy describes a system in *equilibrium* $F_{\rm eq}(T,B)$.
- Now let us hold the system away from equilibrium, by constraining the value of M. Write the corresponding free energy as $F(T,B:M)$.
- Upon releasing the constraint on M, the system will relax to its equilibrium state; M will move towards its equilibrium $-\partial F/\partial B\,|_T$.
- This will be the minimum of $F(T,B:M)$ (Generalisation of the law of maximal entropy)



- These ideas were used by Landau. The *constraint* on the free free energy is the order parameter.

- Thus Landau's free energy is a function of the order parameter.

- And the equilibrium value of the order parameter is found by minimising the Landau (constrained) free energy.

- For definiteness we will, in this section, consider the case of a ferromagnet, but it should be appreciated that the ideas introduced apply more generally.

4.5.2 Landau free energy for ferromagnet

Motivation for Landau theory

- Calculate the constrained free energy for the Weiss model

$$F = E - TS\,.$$

- The order parameter is the magnetisation M (actually M/M_0)
- Evaluate the internal energy and the entropy separately.
- Since we require the *constrained* free energy we must be sure to keep M as an explicit variable.
- The internal energy is

$$E = -\int B\,.\,\mathrm{d}M.$$

- **Internal energy** is

$$E = -\int B \,.\, \mathrm{d}M.$$

- In the Weiss model, B is the sum of the applied field B_0 and the local (mean) field b.

$$B = B_0 + b.$$

- Write b in terms of T_c:

$$b = \frac{Nk}{M_0^2} T_\mathrm{c} M.$$

- Integrate up internal energy:

$$E = -B_0 M - \frac{NkT_\mathrm{c}}{2}\left(\frac{M}{M_0}\right)^2.$$

- Consider the case where there is no external applied field: $B_0 = 0$.
- In terms of $m = M/M_0$ (the order parameter), E is

$$E = -\frac{NkT_\mathrm{c}}{2}m^2.$$

- **Entropy** — (Gibbs entropy in Boltzmann ensemble)

$$S = -Nk \sum_j p_j \ln p_j \,.$$

- Consider spin 1/2, so only two spin states

$$S = -Nk \left[p_\uparrow \ln p_\uparrow + p_\downarrow \ln p_\downarrow \right].$$

- In terms of m, the fractional magnetisation

$$p_\uparrow = \frac{1}{2}(1+m), \qquad p_\downarrow = \frac{1}{2}(1-m)$$

- So entropy (expressed as a function of m) is

$$S = \frac{1}{2}Nk \left[2\ln 2 - (1+m)\ln(1+m) - (1-m)\ln(1-m) \right].$$

- Assemble the free energy $F = E - TS$:

$$F = -\frac{1}{2}Nk\left\{T_c m^2 + T\left[2\ln 2 - (1+m)\ln(1+m) - (1-m)\ln(1-m)\right]\right\}$$

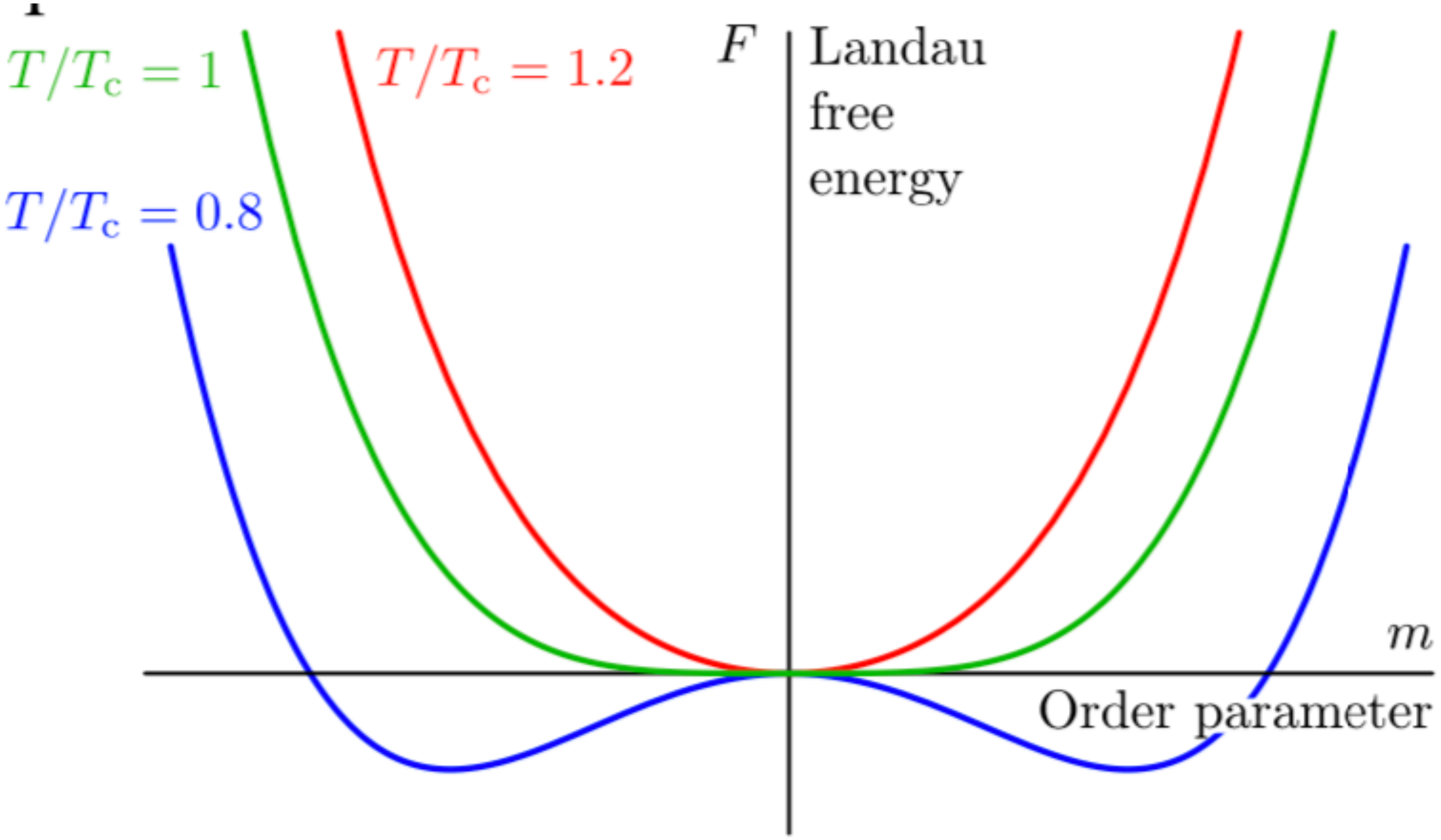


Fig. 4.25 *Landau free energy for Weiss model ferromagnet*

- Above T_c the minimum is at $m = 0$.
- Below T_c there are minima at finite m.
- This is a 2nd order transition because $m \to 0$ continuously as $T \to T_c$ (from below).
- Strictly this picture applies for a *scalar* order parameter .

- The XY model - m is a 2d vector

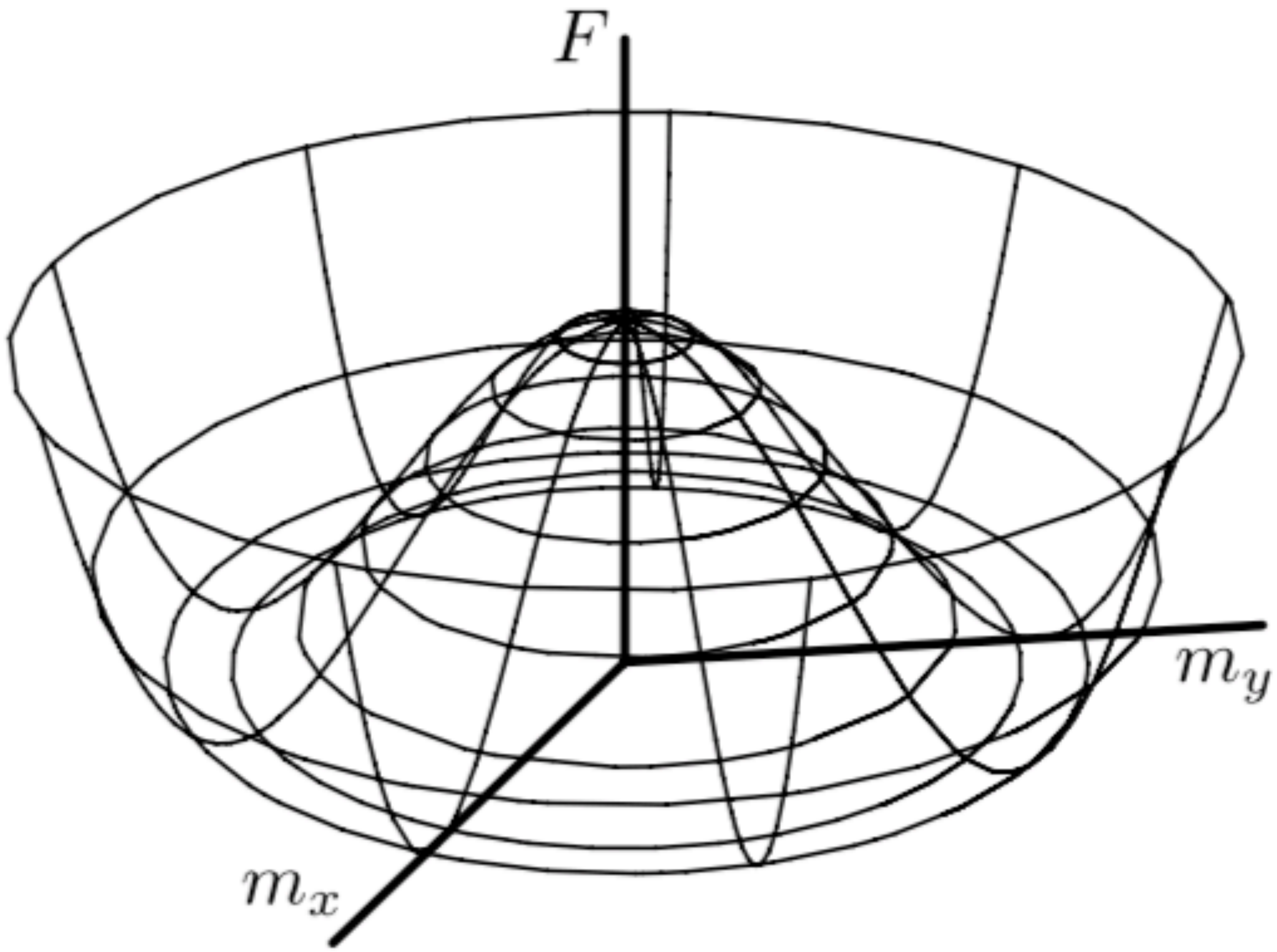


Figure 4.27: Landau free energy for XY model

Discrete *vs* continuous symmetry breaking

In the vicinity of the critical point

- Close to the critical point m is small so we can expand F in powers of m:

$$F = \frac{1}{2}Nk\left\{\left(T - T_{\mathrm{c}}\right)m^2 + \frac{1}{6}m^4\right\}$$

Prob 4.2

plus higher order terms.

- BUT . . . This is all you need for a 2nd order transition!!!!!!!!!!!!!!!!!!!!!!!!
You need just the shape of the quartic.

- So although we started with a “complicated” F, its precise details are not important (in the vicinity of the critical point). — Emergence.

- This is why Landau theory is so wonderful: you put in so little and you get out so much.

4.5.3 Landau theory - 2nd order transition

Actual Landau theory

- Applies in the *vicinity* of the critical point.
- I.e. order parameter (let's call it φ) is small and T is close to T_{c}.
- Assumption: F is an analytic function of φ;
  i.e. can expand F in powers of φ. (!?!?)
- Landau theory is equivalent to mean field (in the vicinity of the transition).

Landau procedure

- Expand F as a power series in φ

$$F = F_0 + F_1\varphi + F_2\varphi^2 + F_3\varphi^3 + F_4\varphi^4 + \ldots$$

- Can ignore F_0 here (to find equilibrium we differentiate wrt φ)
- Symmetry (here) allows discarding of odd terms — only $M \, . \, M$ gives a scalar.
- So we have

$$F = F_2\varphi^2 + F_4\varphi^4$$

ignoring higher order terms.

This is all we need for F !!

Equilibrium state

- Minimise F – set $\mathrm{d}F/\mathrm{d}\varphi = 0$

$$\frac{\mathrm{d}F}{\mathrm{d}\varphi} = 2F_2\varphi + 4F_4\varphi^3 = 0.$$

- This has solutions

$$\varphi = 0 \qquad \text{and} \qquad \varphi = \pm\sqrt{\frac{-F_2}{2F_4}}.$$

- F_4 must be positive to ensure stability.
- If $F_2 < 0$ there are three stationary points
- If $F_2 > 0$ there is only one stationary point (φ must be real).

- The nature of the solution depends crucially on the sign of F_2

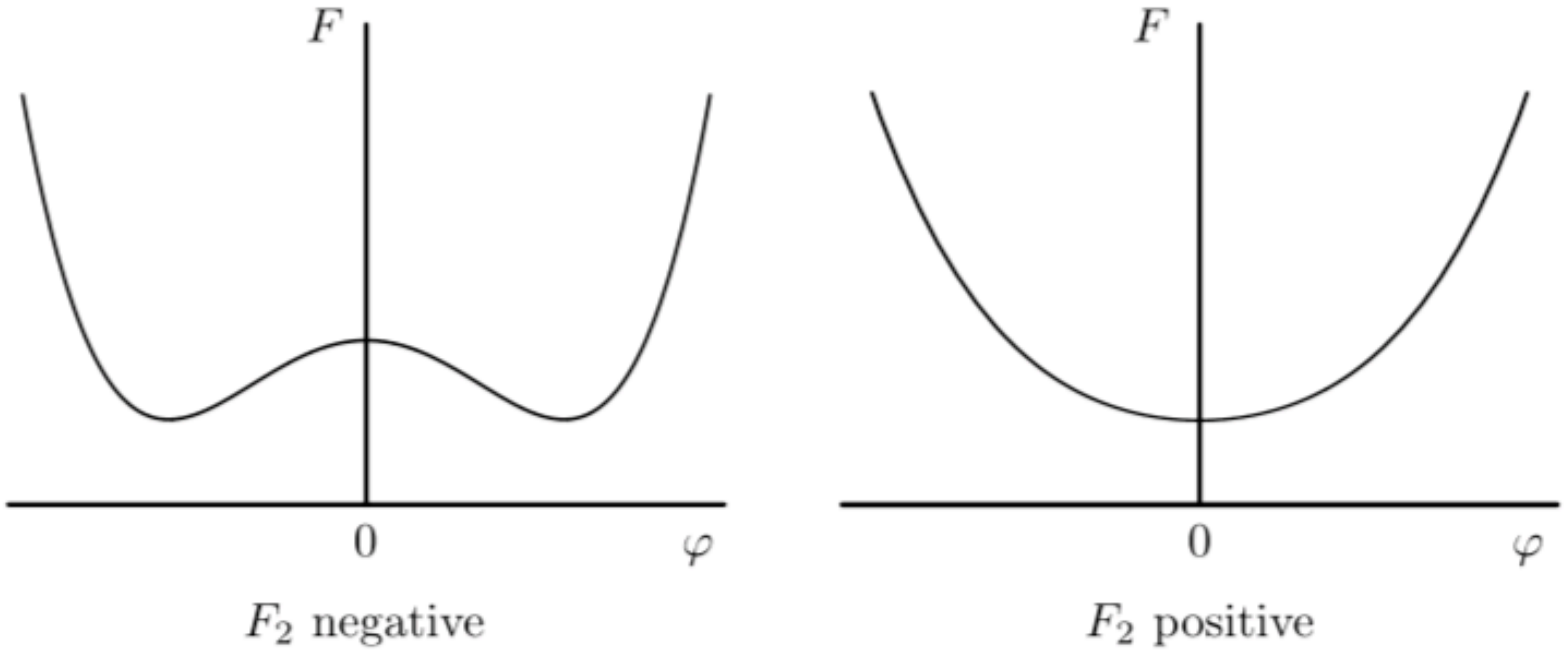


Figure 4.28: Minima in free energy for positive and negative F_2.

- The *critical point* is the point where F_2 changes sign

- The *critical point* is the point where F_2 changes sign.

- Thus expand F_2 and F_4 in powers of $T - T_c$ to leading order:

$$F_2 = a(T - T_c) \quad \text{and} \quad F_4 = b.$$

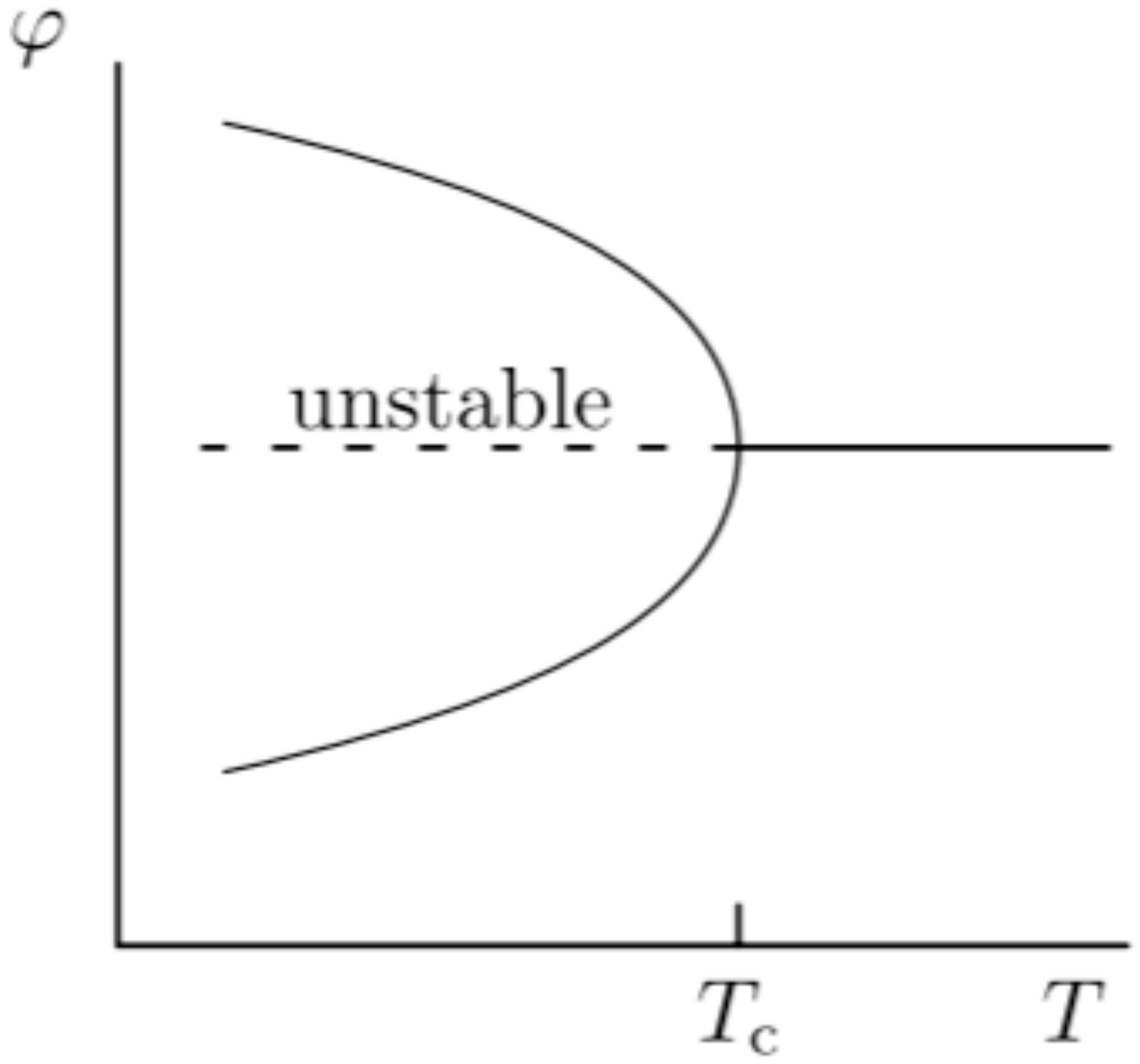
(Recall expansion of the Weiss F).

- So then

$$\varphi = 0 \qquad T > T_c$$

$$\varphi = \pm\sqrt{\frac{a(T_c - T)}{2b}} \qquad T < T_c$$

Gives $\beta = \frac{1}{2}$.



- Only terms up to *fourth order* required to give second order transition:
  — smooth transition from double well to single well.

- Landau's key insight here was to appreciate that it is not that the higher order terms *may* be discarded, it is that they *must* be discarded in order to exhibit the *generic* properties of the transition.

- When terms above φ^4 are discarded this is known as the φ^4 model.

4.5.4 Heat capacity in the Landau model

- Weiss model $\Longrightarrow$ discontinuity in heat capacity ($\alpha = 0$).
- Look at this in Landau theory.
- Landau free energy:

$$F = F_0(T) + a(T - T_\mathrm{c})\varphi^2 + b\varphi^4.$$

  - Have included F_0 term (indep. of φ) and allowed it to have a (weak) T dependence.
  - Have put in the established $T-$dependence of F_2 and F_4

- $$F = F_0(T) + a(T - T_c)\varphi^2 + b\varphi^4$$
- Find S by differentiating F:

$$S = -\frac{\partial F}{\partial T} = S_0 - a\varphi^2.$$

- This shows: — how S drops as the ordered phase is entered
  — S is continuous at the transition.
- $T > T_c,\quad \varphi = 0 \quad S = S_0(T)$

  $T < T_c,\quad \varphi = \pm\sqrt{\frac{a(T_c - T)}{2b}} \quad S = S_0(T) + \frac{a^2}{2b}(T - T_c)$

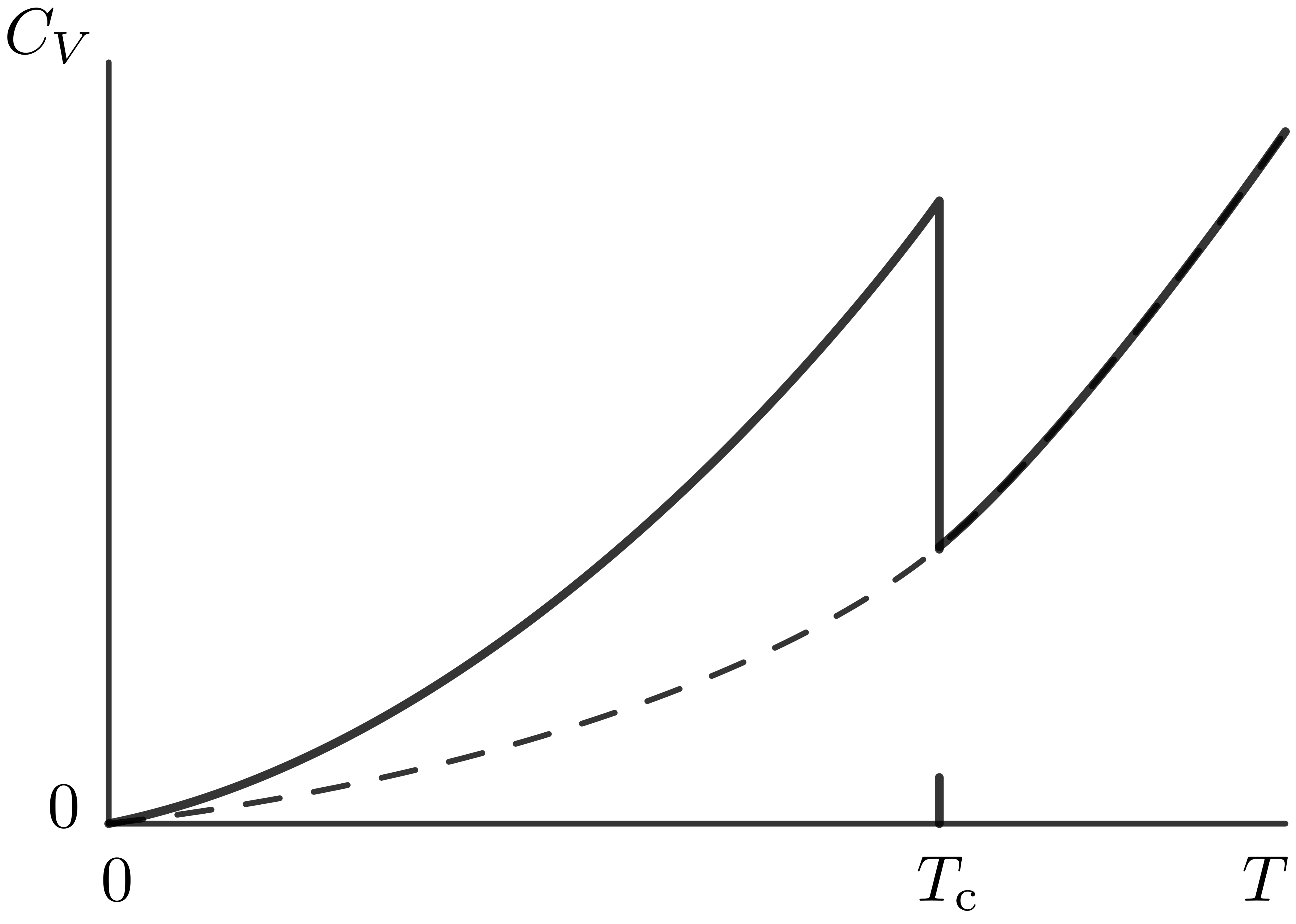
- $$T > T_c, \qquad S = S_0(T)$$
  $$T < T_c, \qquad S = S_0(T) + \frac{a^2}{2b}(T - T_c)$$
- Heat capacity is $$C = \frac{\partial Q}{\partial T} = T\frac{\partial S}{\partial T}$$
- $\Longrightarrow$ $$T > T_c, \qquad C = C_0(T)$$
  $$T < T_c, \qquad C = C_0(T) + \frac{a^2}{2b}T$$
- At the transition there is a discontinuity in the thermal capacity ΔC

$$\Delta C = \frac{a^2 T_c}{2b}$$

- At the transition there is a discontinuity in the thermal capacity, as we saw for the Weiss model.

- Discontinuity ΔC given in terms of the Landau parameters a, b and T_c

$$\Delta C = \frac{a^2 T_c}{2b}\,.$$



4.5.5 Ferromagnet in a magnetic field

- Magnetic field adds a term $-MB$ to the free energy.

- This now gives a term linear in φ .

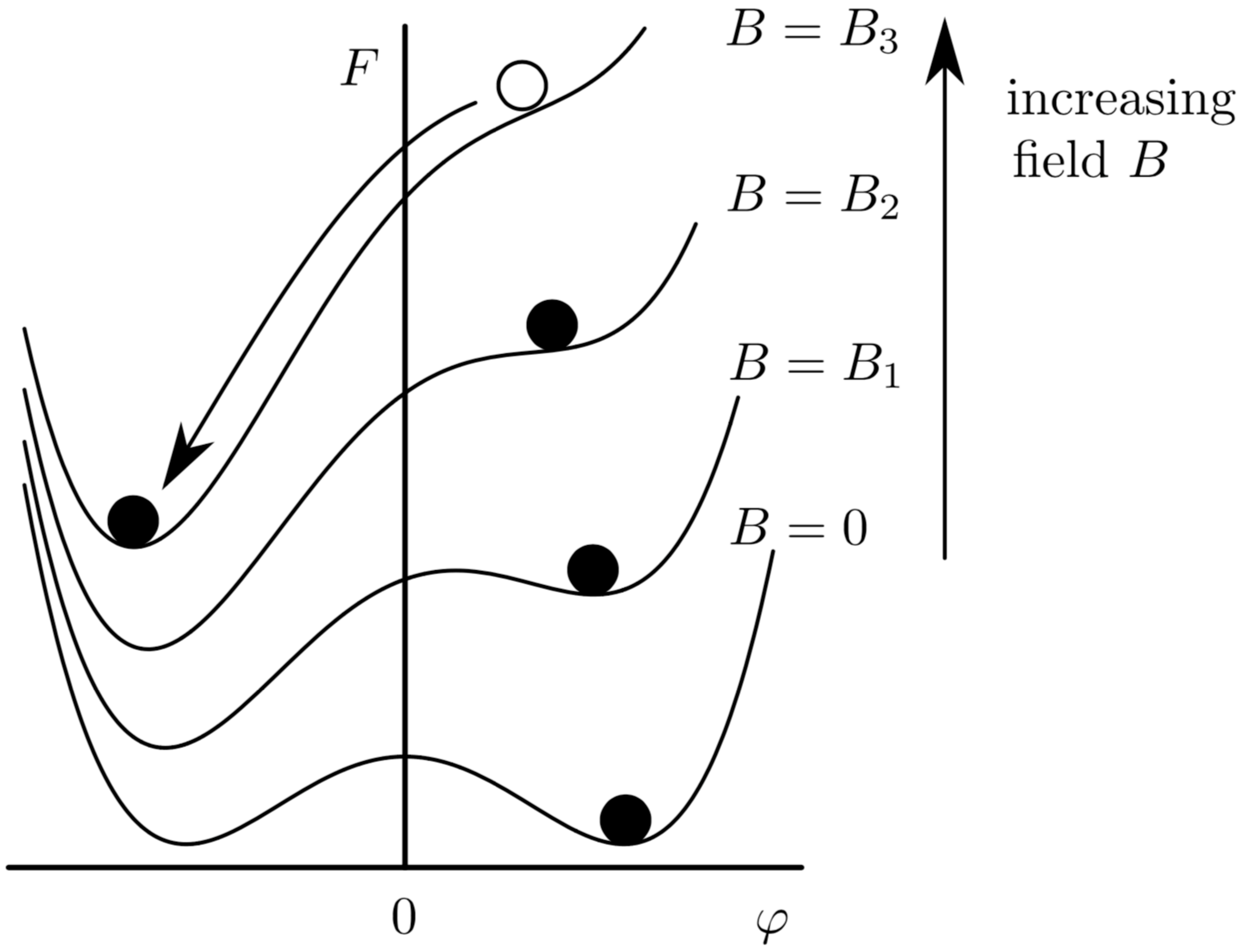
$$F = F_1\varphi + a(T - T_c)\varphi^2 + b\varphi^4.$$

- The F_1 is a constant proportional to the applied field.

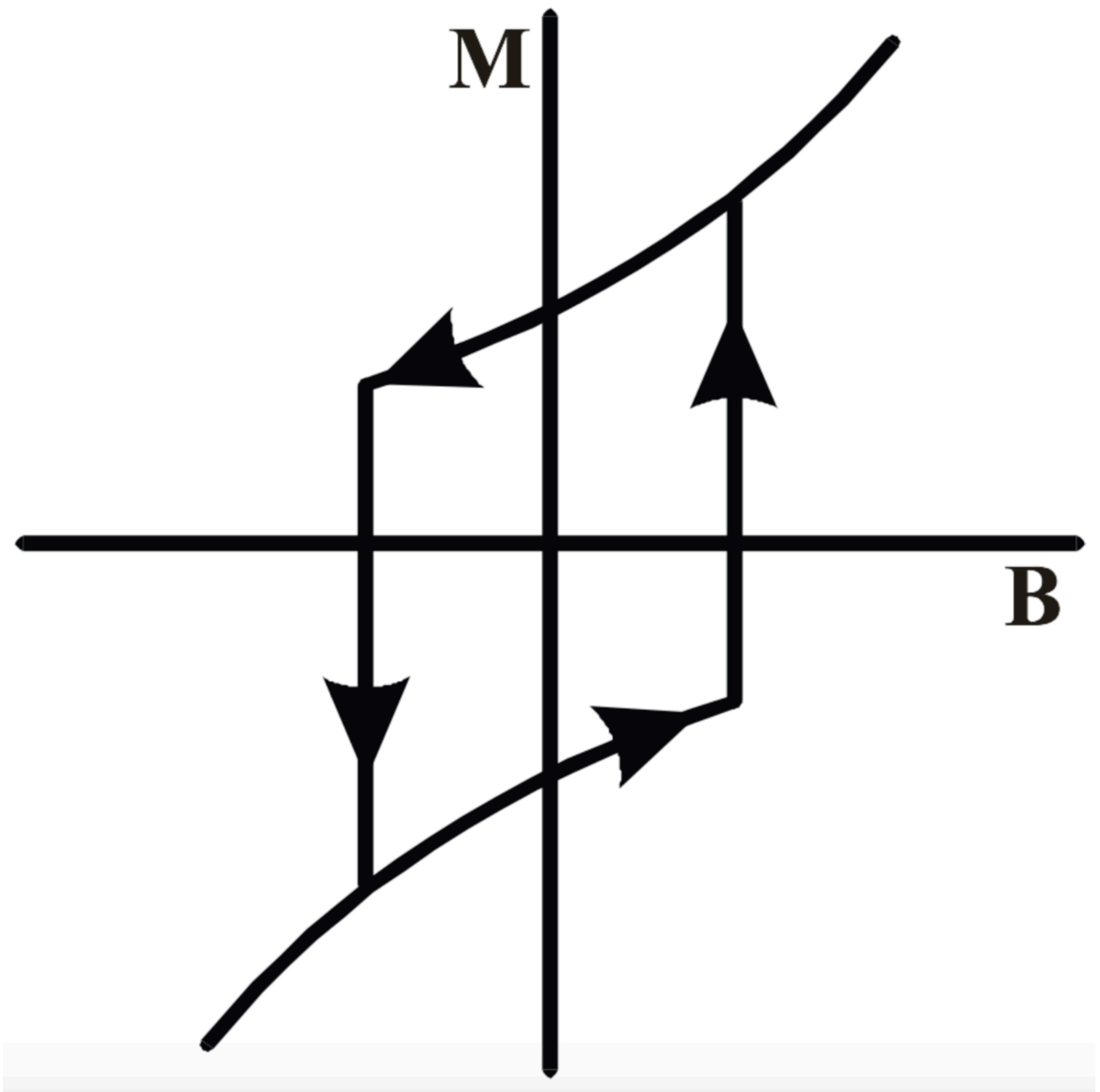
- This gives a *vertical shear* to the free energy curves.

Ising case

- Discrete symmetry



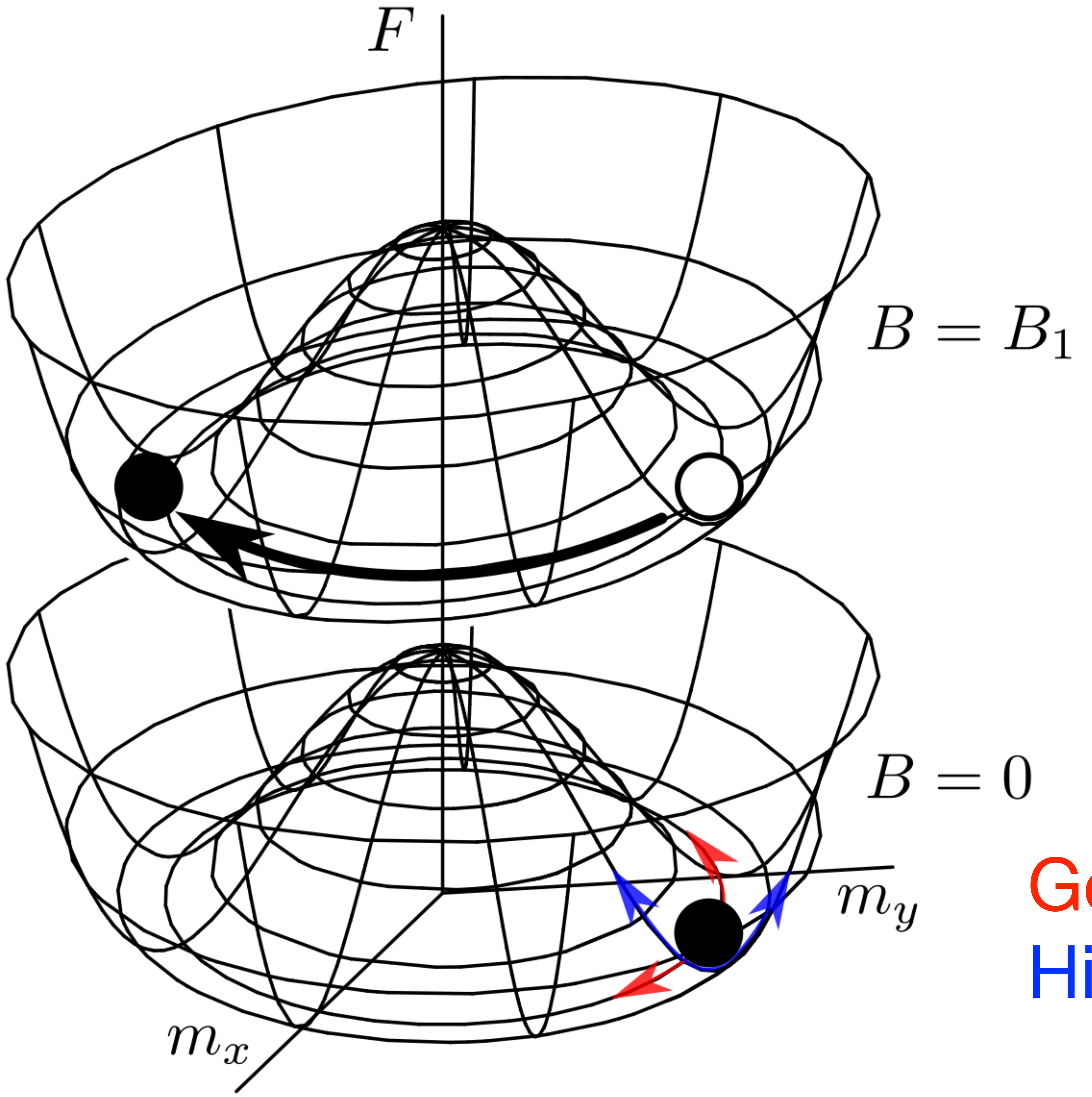
Hysteresis



XY, Heisenberg and higher cases

- Continuous symmetry

no hysteresis
(for this mechanism)



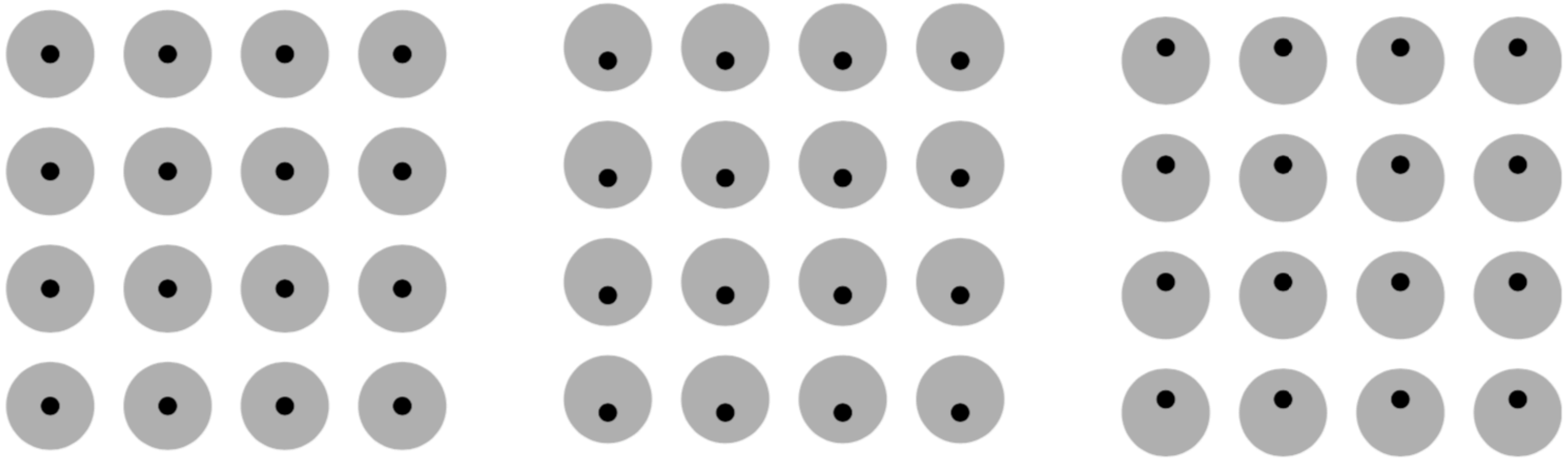
Goldstone mode
Higgs mode

4.6 Ferroelectricity

4.6.1 Description of the phenomenon

- In certain ionic solids a spontaneous electric polarisation can appear.
- Example: $BaTiO_3$, transition temperature 140°C.
- Nice discussion in Kittel *Introduction to Solid State Physics*.
- *Ferroelectric* means electrical analogue of ferromagnet — nothing to do with iron (ferrum).
- Transition can be 1st order or 2nd order.

- The “centre of charge” of the positive ion core becomes displaced from that of the negative electron cloud.



$\mathbf{P} = 0$ $\mathbf{P} \downarrow$ $\mathbf{P} \uparrow$

- In this way an electric polarisation appears.

- Transition associated with a *structural displacement*.
- So $\mathbf{P}$ will point parallel or antiparallel to a specific direction.
- Symmetry broken is *inversion symmetry*, a discrete symmetry.
- While polarisation is the order parameter, strictly it is the (scalar) length P.

  I.e. the order parameter for the ferroelectric is a *scalar*.

- Transition has a non-conserved order parameter and can be 1st or 2nd order.
- Different approach — we will *start* from the Landau free energy we don't invoke a microscopic model (hamiltonian).

4.6.2 Landau free energy

- Write the Landau free energy expansion (φ is the order parameter)

$$F = F_0 + F_1\varphi + F_2\varphi^2 + F_3\varphi^3 + F_4\varphi^4 + F_5\varphi^5 + F_6\varphi^6 + \dots$$

- Inversion symmetry $\Longrightarrow$ axis of symmetry ($+\varphi \equiv -\varphi$), so odd terms vanish.
- Usual argument: can ignore F_0 for determining equilibrium polarisation, so

$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6 + \dots$$

- $$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6 + \ldots$$

- For the ferromagnet we could terminate at φ^4 since F_4 was positive. (Justified from the Weiss model).

- For the ferroelectric F_4 *may* be negative.

- Then we *cannot* terminate there.

- We will *assume* F_6 is positive. The we can terminate at φ^6.

- So then

$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

- Two cases:
  - F_4 positive, terminate at φ^4, same as the ferromagnet, 2nd order transition
  - F_4 negative, terminate at φ^6. Will see this leads to a 1st order transition.

- φ^6 case — everything follows from the simple Landau free energy

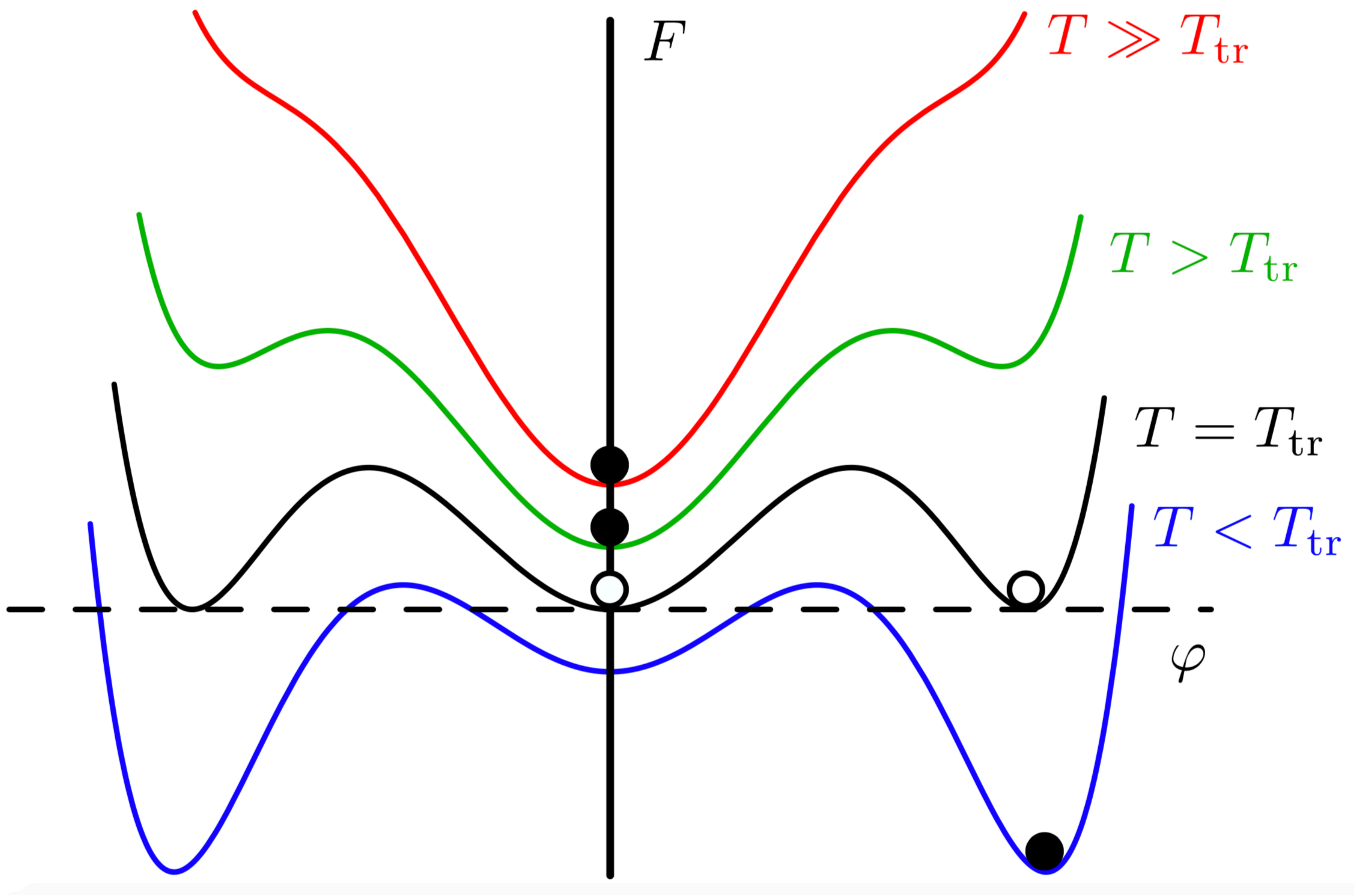
$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

regardless of the microscopic description.

Moreover we can see what is happening *without solving any equations*; all follows from the fact we have a (n even) sextic equation.

No-math discussion — φ^6 case

- Blue curve shows general form for a 6th order even equation.



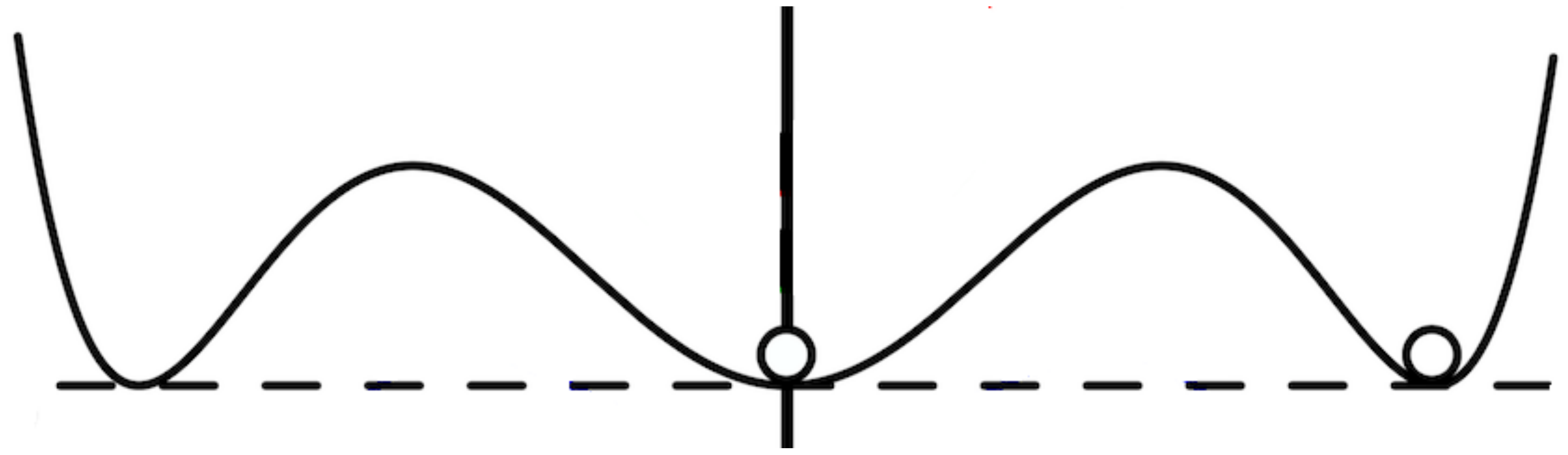
- Large $\pm\varphi$, F increases since $F_6 > 0$.
- In general, have 6 roots, 5 stationary pts.
- 3 minima. One at $\varphi = 0$, other two at $\varphi = \pm$ same.
- Red curve shows equilibrium $\varphi = 0$
- Blue curve shows equilibrium φ finite
- Black curve shows transition: equilibrium φ jumps — first order transition. Possibility of hysteresis — barrier must be climbed.

Now comes the math part . . .

- We have $$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

  and note that $F_4 < 0$ and $F_6 > 0$.

- At the transition the 3 minima have the same $F = 0$.



- So transition point specified by $F(\varphi) = 0$ and $\partial F(\varphi)/\partial\varphi = 0$.

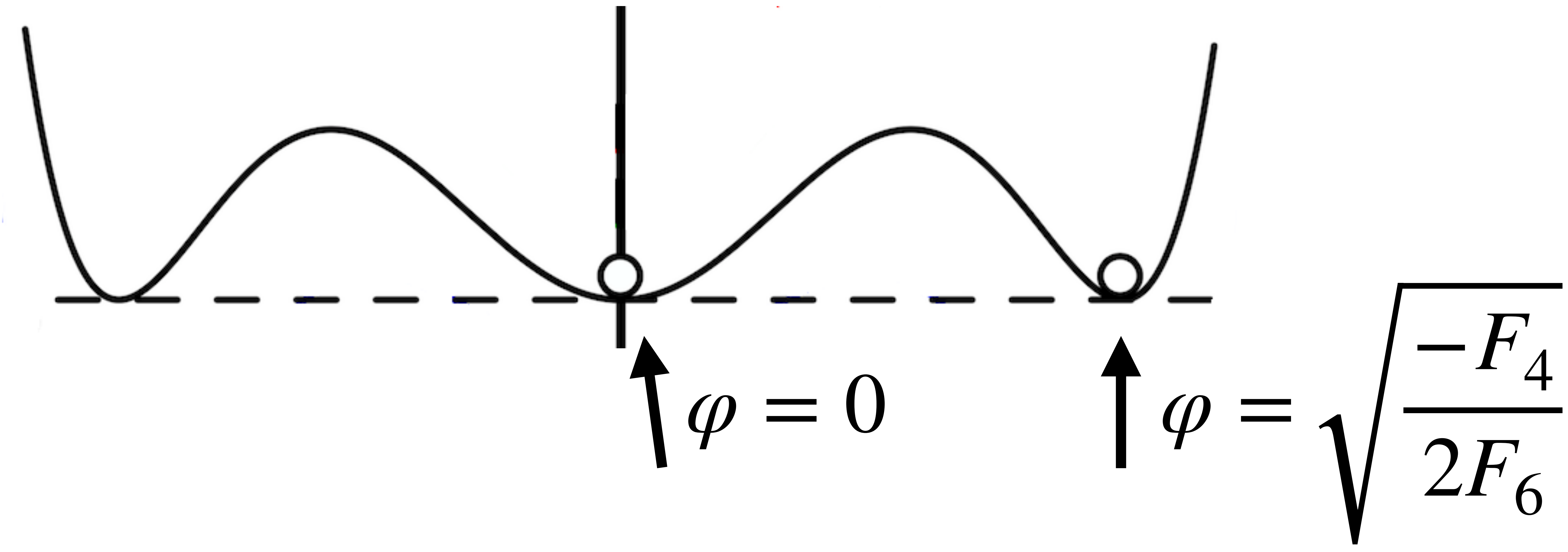
- That is
$$\left.\begin{aligned} F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6 &= 0 \\ 2F_2\varphi + 4F_4\varphi^3 + 6F_6\varphi^5 &= 0 \end{aligned}\right\}$$

- We have the $\varphi = 0$ solution; this can be factored out, giving

$$\left.\begin{aligned} F_2 + F_4\varphi^2 + F_6\varphi^4 = 0 \\ 2F_2 + 4F_4\varphi^2 + 6F_6\varphi^4 = 0 \end{aligned}\right\}$$

- Simultaneous equations — solve for φ in terms of F_4 and F_6:

$\varphi^2 = -\dfrac{F_4}{2F_6}$ or $\varphi = \pm\sqrt{\dfrac{-F_4}{2F_6}}$ (put – upstairs: F_4 negative, F_6 positive)

- 

- Jump in φ at the transition

$$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}}$$

- $\Delta\varphi \to 0$ when $F_4 \to 0$; transition becomes 2nd order
Transition is 2^{nd} order when F_4 is positive — as seen previously (ferromagnet).

- Order parameter jump at transition

$$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}}$$

- $\Delta\varphi \to 0$ when $F_4 \to 0$; transition becomes 2nd order
- Transition is 2nd order when F_4 is positive — as seen previously (ferromagnet).
- As F_4 varies the transition changes order.
- Point of changeover ($F_4 = 0$) is called the *tricritical* point.

Transition temperature

- At the transition we solved for φ as a function of F_4 and F_6.

- What about F_2? This can be regarded as the other solution to the simultaneous equations pair

$$F_2 = \frac{F_4^2}{4F_6}.$$ There is a reason for doing it this way.

- Assume F_2 varies with T as in the 2nd order case

$$F_2 = a(T - T_c)$$

and that F_4 and F_6 are independent of T.

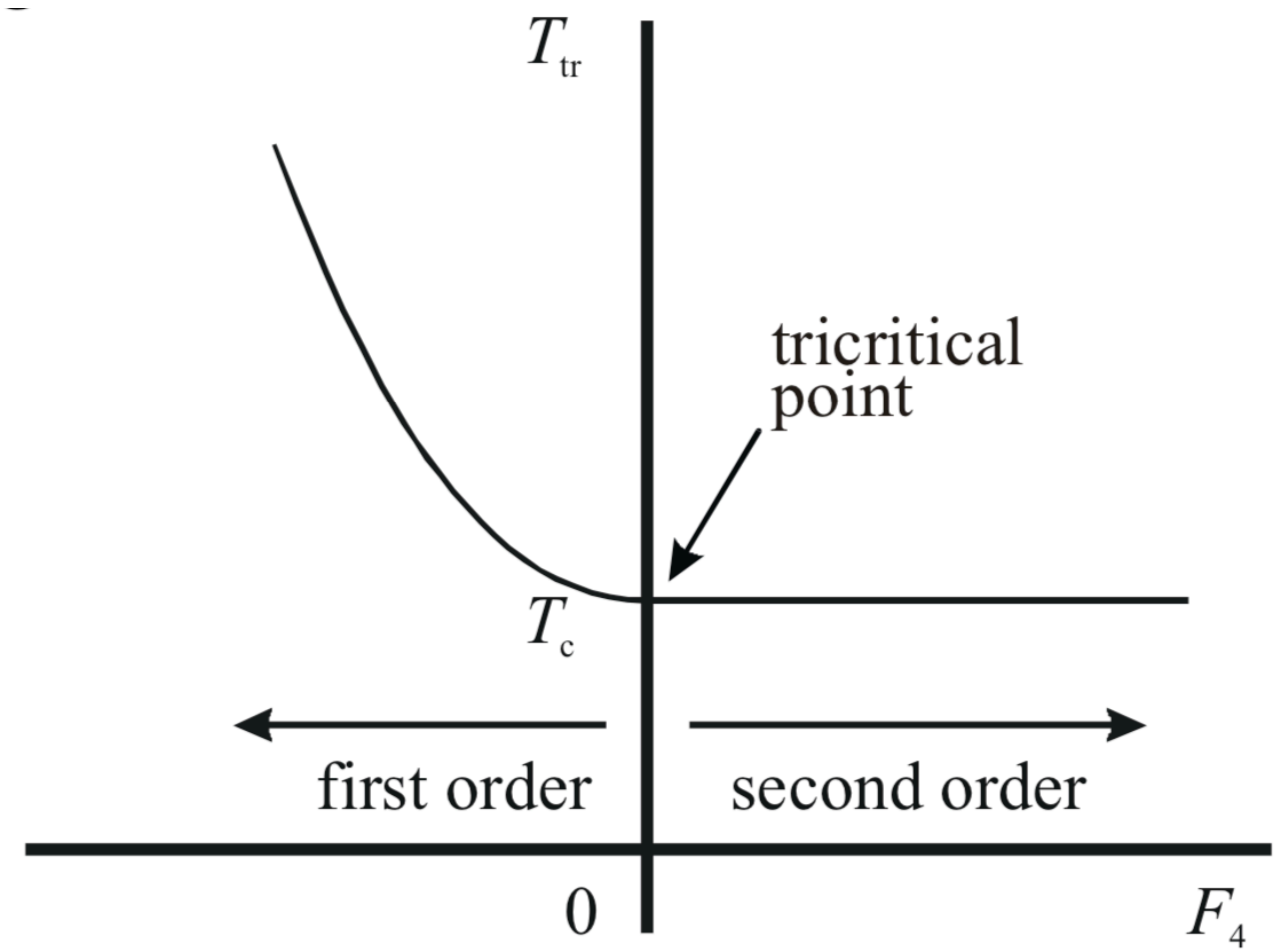
- At the transition $$a(T_{tr} - T_c) = \frac{F_4^2}{4F_6}$$ a constant.

- At the transition $$a(T_{\rm tr} - T_{\rm c}) = \frac{F_4^2}{4F_6}$$ a constant.

- In the first order case the transition does *not* correspond to the vanishing of F_2, which, nevertheless, we continue to call the critical point.

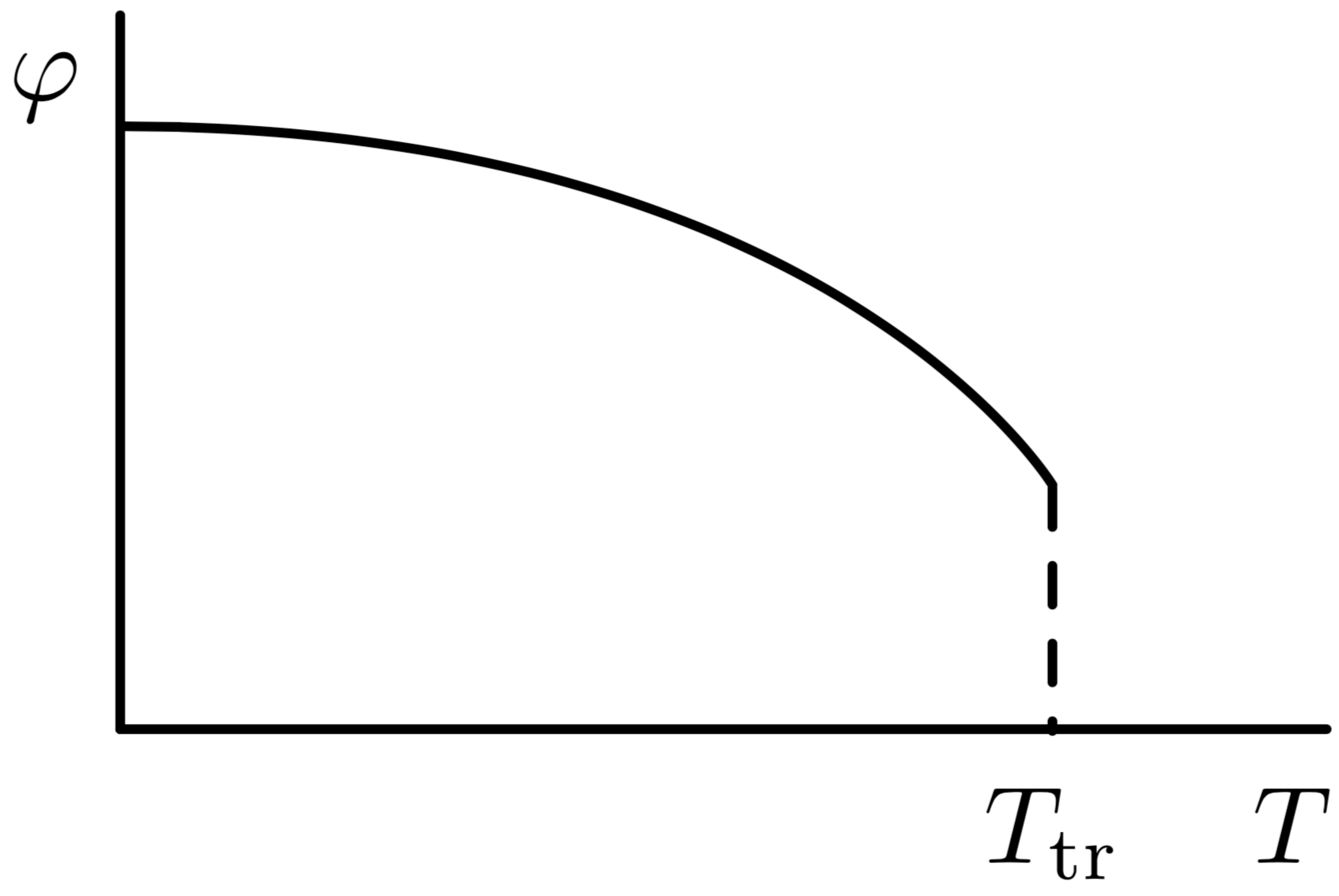
- $F_4 > 0, \quad T_{\rm tr} = T_{\rm c},$ 2nd order

  $F_4 < 0, \quad T_{\rm tr} = T_{\rm c} + \frac{1}{4a}\frac{F_4^2}{F_6},$ 1st order



- Solution for order parameter

$$\varphi^2 = \frac{|F_4|}{3F_6}\left\{1+\sqrt{\frac{4T_{\mathrm{tr}}-3T_{\mathrm{c}}-T}{4\left(T_{\mathrm{tr}}-T_{\mathrm{c}}\right)}}\right\}$$



Caveat

- Landau requires φ to be small

- Cannot really accommodate jump in φ

- OK for *weakly first order* transitions.
  Nice treatment of tricritical point as F_4 goes through zero.

4.6.5 Entropy and latent heat

- The Landau free energy is

$$F = F_0(T) + a(T - T_c)\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

- Entropy: $S = -\partial F/\partial T$ so that

$$S = S_0 - a\varphi^2$$

  just as in 2nd order case.

- But now there is a discontinuity in $\varphi \implies$ discontinuity in S: $\Delta S = a\varphi^2$.

- Latent heat $L = T_{\text{tr}}\Delta S$
  so that

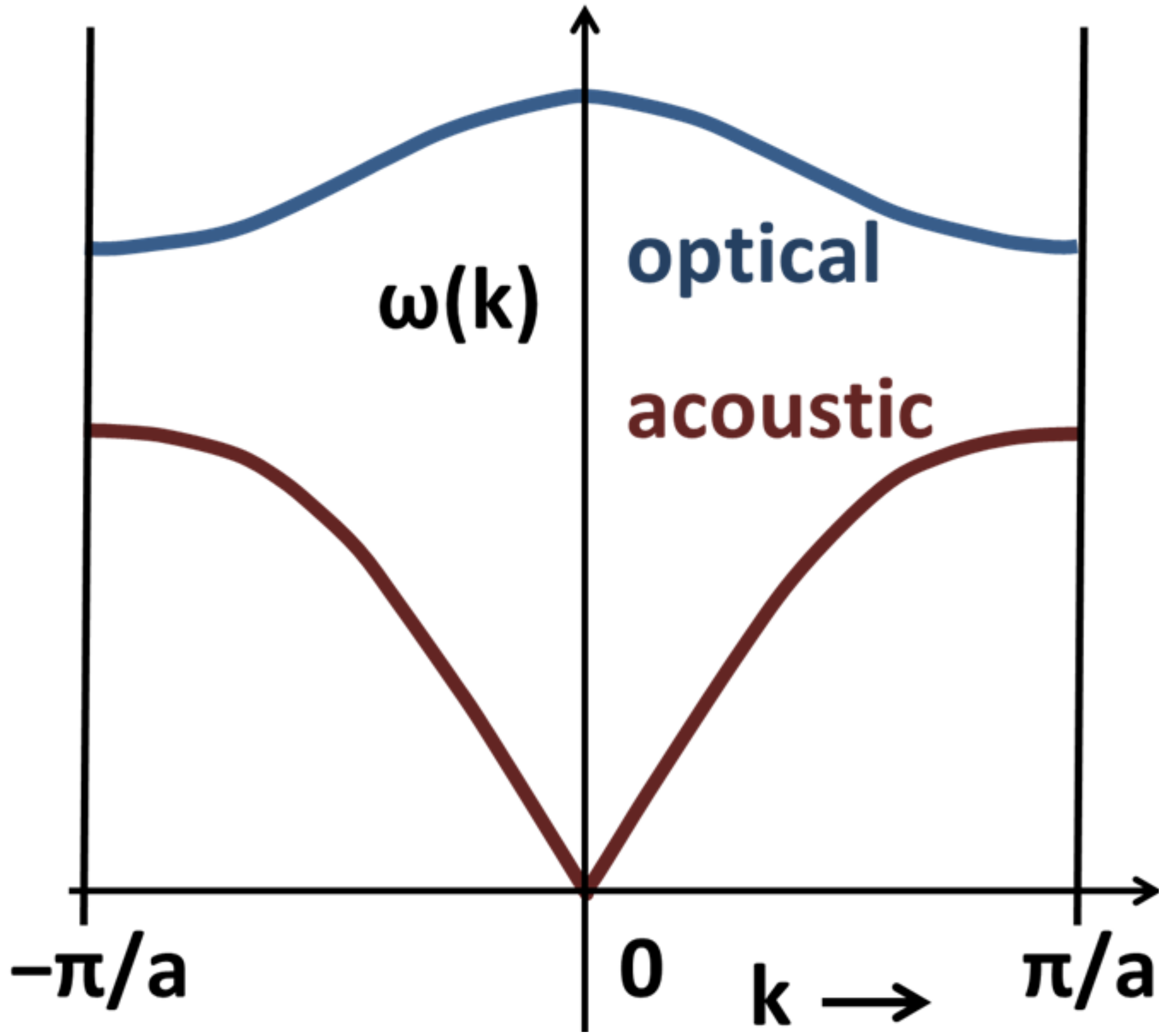
$$L = aT_{\text{tr}}\Delta\varphi^2$$

- $$L = aT_{\text{tr}}\Delta\varphi^2$$
- This shows how the latent heat is directly related to the discontinuity in the order parameter—both characteristics of a first order transition.
- Discontinuity in φ is $$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}}$$
- So L is $$L = aT_{\text{tr}}\frac{|F_4|}{2F_6}$$ ($F_4 < 0$ for 1st order trans.)
- This shows how L vanishes when the transition becomes 2nd order.

  (L vanishes at the tricritical point).

4.6.6 Soft modes

- In the ferroelectric the excitations of the order parameter are *optical* phonons.
- Not Goldstone bosons since it is not a continuous symmetry that is broken.
- Indeed the excitations have a finite energy (frequency) in the $p \to 0$ ($k \to 0$) limit. This is a characteristic of optical phonons.



- The frequency of the optical phonons depends on the restoring force of the interatomic interaction and the mass of the ions.

- At the critical point the Landau free energy exhibits anomalous broadening; the restoring force vanishes and the crystal becomes unstable.

  Talking about 2nd order case here

- At the transition the frequency of the optical phonon modes will go to zero: they become “soft”.

  (See books by Burns and by Kittel for more details)

- So as you cool down, the optical phonons go soft and the ferroelectric transition occurs.