Landau Theory

- Introduction

  - Many phase transitions exhibit similar behaviors: critical temperature, order parameter…

  - Can one find a rather simple "unifying theory" that gives a general "phenomenological" overview of phase transitions ?

  - Several approaches :

    Molecular field (Weiss ~1925): solve the Schrödinger equation for a one particle system but with an effective interaction potential :

$$\hat{H} = \frac{p^2}{2m} + V_{eff}$$

    Microscopic model (Ising 1924): solve the Schrödinger equation for "pseudo spins" on a lattice with effective interaction Hamiltonian restricted to first neighbors

$$\hat{H} = \hat{H}_o - \frac{1}{2}\sum_{i,j} J\,\sigma_i\sigma_j$$

Landau Theory

- Introduction

  - **Landau Theory** :

    – **Express a thermo dynamical potential as a function of the order parameter (η), its conjugated external field (h) and temperature.**

    – **Keep close to a stable state → minimum of energy → power series expansion, eg. like:**

$$\Phi(\eta) = \Phi_o + \frac{A}{2}\eta^2 + \frac{B}{4}\eta^4 + \frac{C}{6}\eta^6 + \cdots - h\eta$$

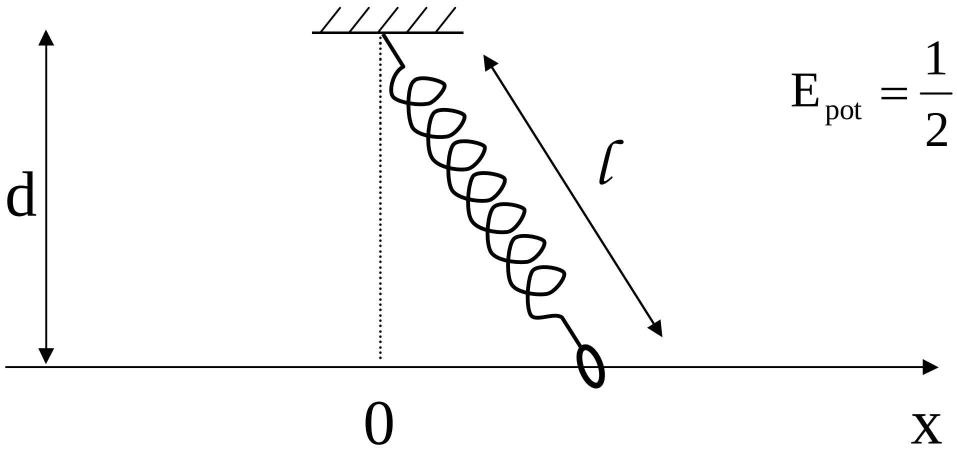
    – **Find and discuss minima of Φ versus temperature and external field.**

    – **Look at thermodynamics' properties (latent heat, specific heat, susceptibility, etc.) in order to classify phase transitions**

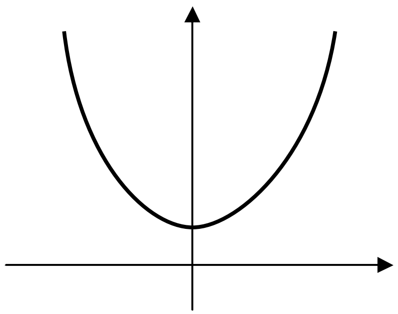
Landau Theory

- Broken symmetry

  - **a simple 1D mechanical illustration** :



$$E_{pot} = \frac{1}{2} k \cdot (l - l_o)^2 = \frac{1}{2} k \cdot (\sqrt{d^2 + x^2} - l_o)^2$$

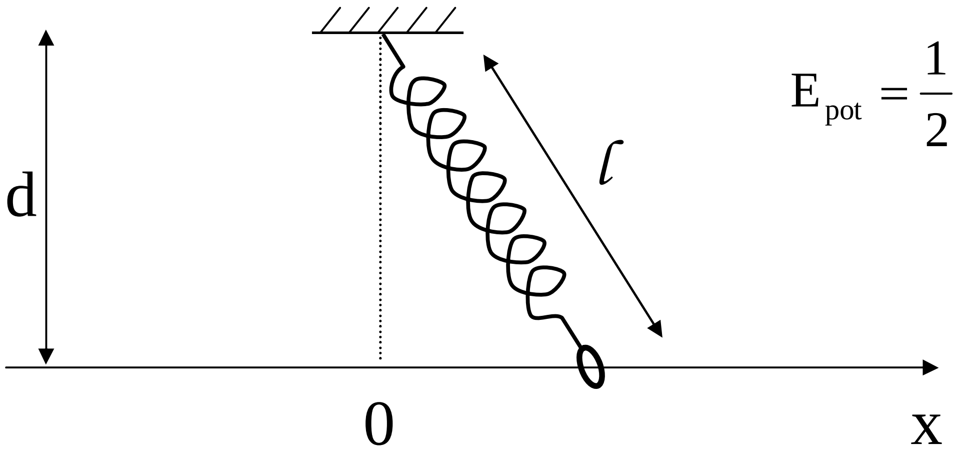


✓ let go with **d > ℓ_o** : equilibrium position (minimum energy) → $x = 0$

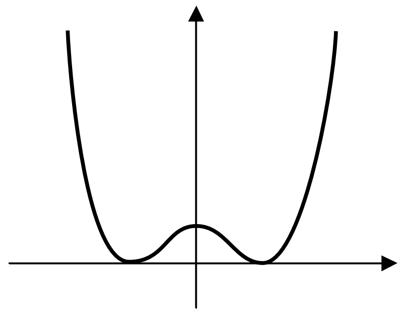
Landau Theory

- Broken symmetry

  - **a simple 1D mechanical illustration** :



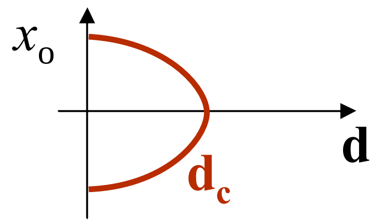
$$E_{pot} = \frac{1}{2}k\cdot(l-l_o)^2 = \frac{1}{2}k\cdot(\sqrt{\mathrm{d}^2+x^2}-l_o)^2$$



✓ let go with **d < ℓ_o** : equilibrium position (minimum energy) → $x = x_o \neq 0$

Order parameter

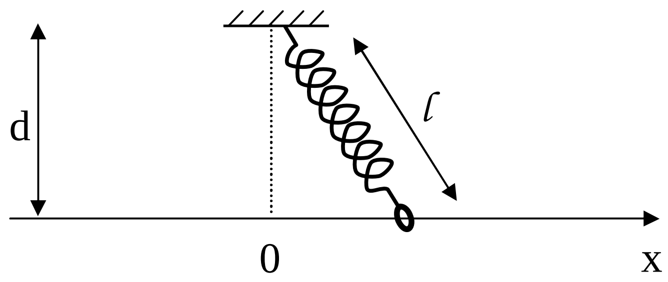
@ critical value $d_c = \ell_o$ → spontaneous symmetry breaking



Only irreversible microscopic events will make the system settle at +xo or –xo when the system slowly exchanges energy with external world

Landau Theory

- Broken symmetry
  - **a simple 1D mechanical illustration** :



$$E_{pot} = \frac{1}{2} k \cdot (l - l_o)^2 = \frac{1}{2} k \cdot (\sqrt{d^2 + x^2} - l_o)^2$$

✓ Taylor expansion of potential (elastic) energy

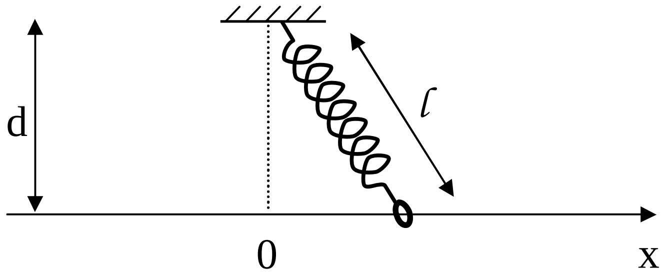
$$l = d \cdot \left(1 + \frac{x^2}{d^2}\right)^2 \approx d \cdot \left(1 + \frac{1}{2}\frac{x^2}{d^2} + \cdots\right)$$

$$(l - l_o)^2 \approx \left((d - l_o) + \frac{x^2}{2d^2}\right)^2$$

$$E_{pot} = \frac{1}{2} k \cdot (l - l_o)^2 \approx \frac{1}{2} k \cdot (d - l_o)^2 + \frac{1}{2} k \cdot 2(d - l_o) \cdot \left(\frac{x^2}{2d}\right) + \frac{1}{2} k \frac{x^4}{4d} + \cdots$$

Landau Theory

- Broken symmetry
  - **a simple 1D mechanical illustration** :



$$E_{pot} = \frac{1}{2}k\cdot(l - l_o)^2 = \frac{1}{2}k\cdot(\sqrt{d^2 + x^2} - l_o)^2$$

✓ Taylor expansion of potential (elastic) energy

$$E_{pot} \approx E_o + \frac{1}{2}A\cdot x^2 + \frac{1}{4}B\cdot x^4 + \cdots + O(x^6)$$

$$A = A(d) = \frac{k}{d}(d - d_c)$$ **Change sign at $d=d_c$!!!**

$$B > 0$$ **Does not change sign**

Landau Theory

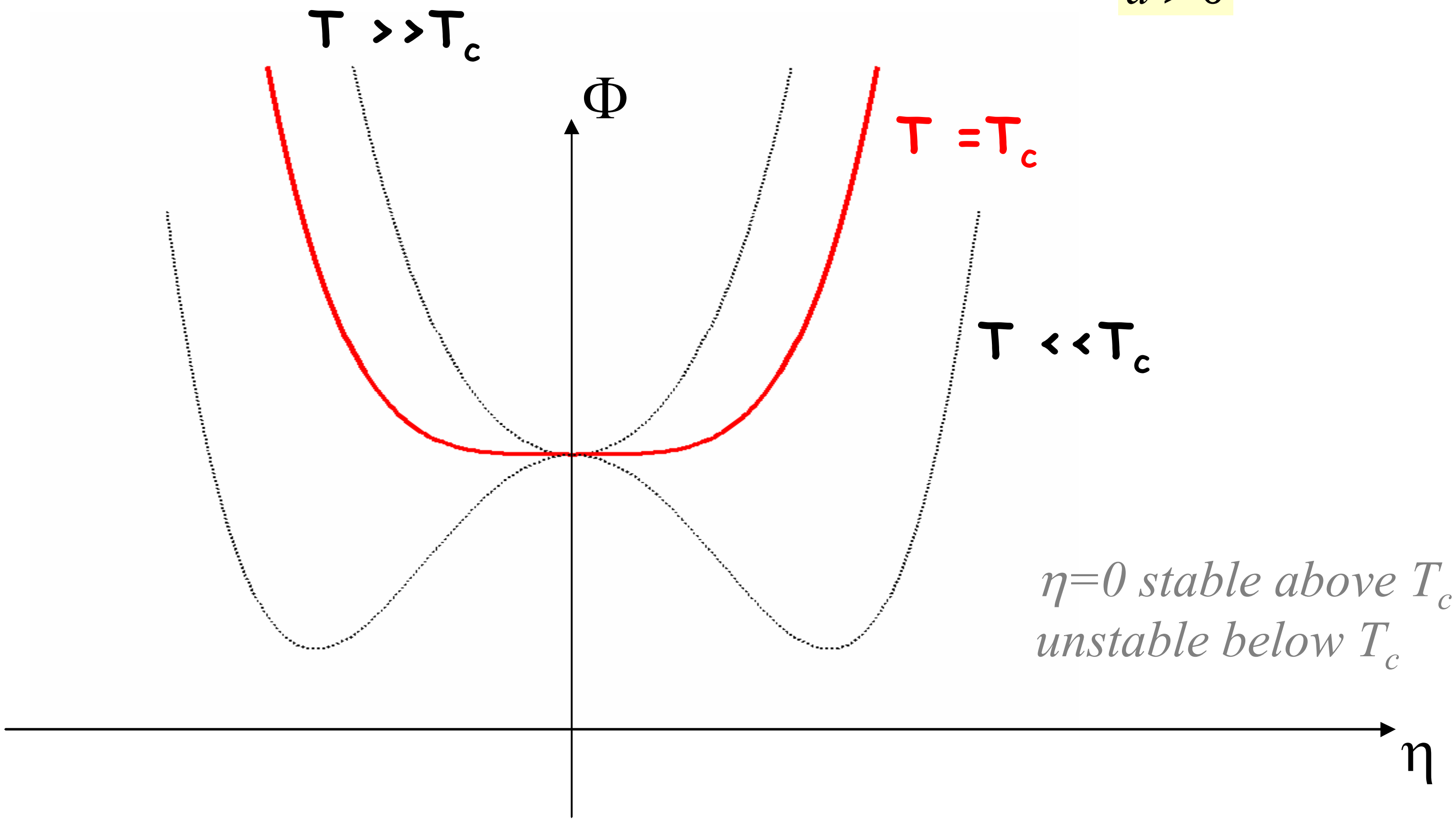
- Second Order Phase Transitions

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 - h\eta$$

$$A = a\cdot(T - T_c)$$

$$a > 0$$

h=0



η=0 stable above T_c, unstable below T_c

Landau Theory

•Second Order Phase Transitions

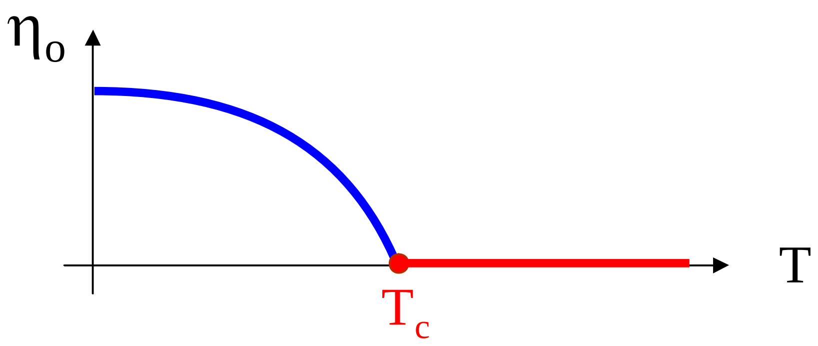
$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 - h\eta$$

$$A = a\cdot(T - T_c)$$

$$a > 0$$

✓ Stationary solution : $\dfrac{\partial\Phi}{\partial\eta} = 0$ & $\dfrac{\partial^2\Phi}{\partial\eta^2} \geq 0$

$$\left.\frac{\partial\Phi}{\partial\eta}\right|_{\eta_o} = \eta_o\cdot\left(A + B\eta_o^2\right) = 0 \Rightarrow \begin{cases} \eta_o = 0 & T \geq T_c \\ \eta_o^2 = -\dfrac{A}{B} = \dfrac{a(T_c - T)}{B} & T < T_c \end{cases}$$

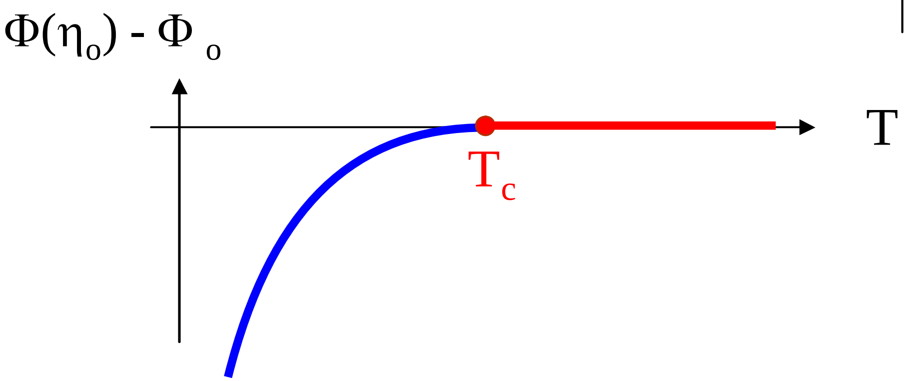


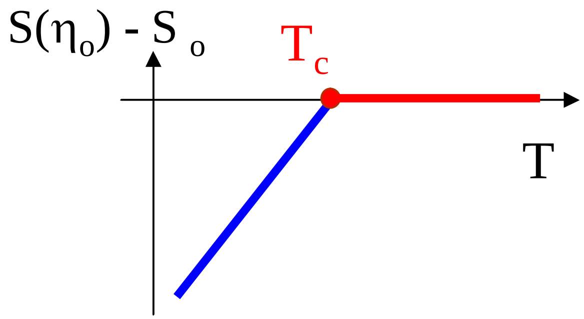
Landau Theory

•Second Order Phase Transitions

✓ Free energy :

$$\Phi_h(\eta_o) - \Phi_o = \begin{cases} 0 & T \geq T_c \\ -\dfrac{a^2}{2B}(T_c - T)^2 & T < T_c \end{cases}$$





✓ Entropy : $S = -\dfrac{\partial \Phi_h(\eta)}{\partial T} = -\dfrac{\partial \Phi_o}{\partial T} - \dfrac{a^2}{2B}(T - T_c)$

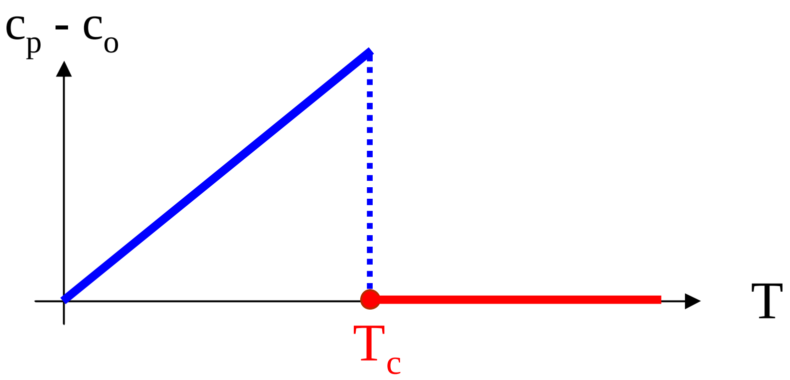
No Latent Heat: $T_c \Delta S = 0$

Landau Theory

• Second Order Phase Transitions

✓ Specific heat :

$$c_p = T\frac{\partial S}{\partial T} = -T\frac{\partial^2 \Phi}{\partial T^2} = \begin{cases} c_o & T \geq T_c \\ \dfrac{a^2 T}{2B} & T < T_c \end{cases}$$



Landau Theory

•Second Order Phase Transitions

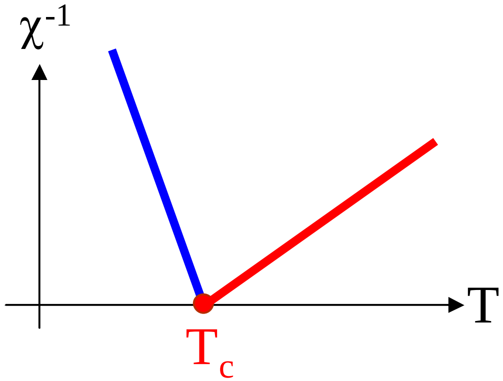
✓ Susceptibility : $\chi = \dfrac{\partial \eta}{\partial \mathrm{h}}$ $\qquad \chi^{-1} = \dfrac{\partial \mathrm{h}}{\partial \eta}$

$$\Phi_{\mathrm{h}}(\eta) \approx \Phi_{\mathrm{o}} + \frac{1}{2}\mathrm{A}\cdot\eta^2 + \frac{1}{4}\mathrm{B}\cdot\eta^4 - \mathrm{h}\eta$$

$$\left.\frac{\partial \Phi_{\mathrm{h}}(\eta)}{\partial \eta}\right|_{\mathrm{eq}} = 0 = \frac{\partial \Phi_{\mathrm{h}=0}(\eta)}{\partial \eta} - \mathrm{h}$$

$$\chi^{-1} = \frac{\partial \mathrm{h}}{\partial \eta} = \frac{\partial^2 \Phi_{\mathrm{h}=0}(\eta)}{\partial \eta^2}$$

$$\chi^{-1} = \mathrm{A} + 3\mathrm{B}\eta_{\mathrm{o}}^2 = \begin{cases} \mathrm{A} = a(\mathrm{T} - \mathrm{T_c}) & \mathbf{T \geq T_c} \\ -2\mathrm{A} = 2a(\mathrm{T_c} - \mathrm{T}) & \mathbf{T < T_c} \end{cases}$$

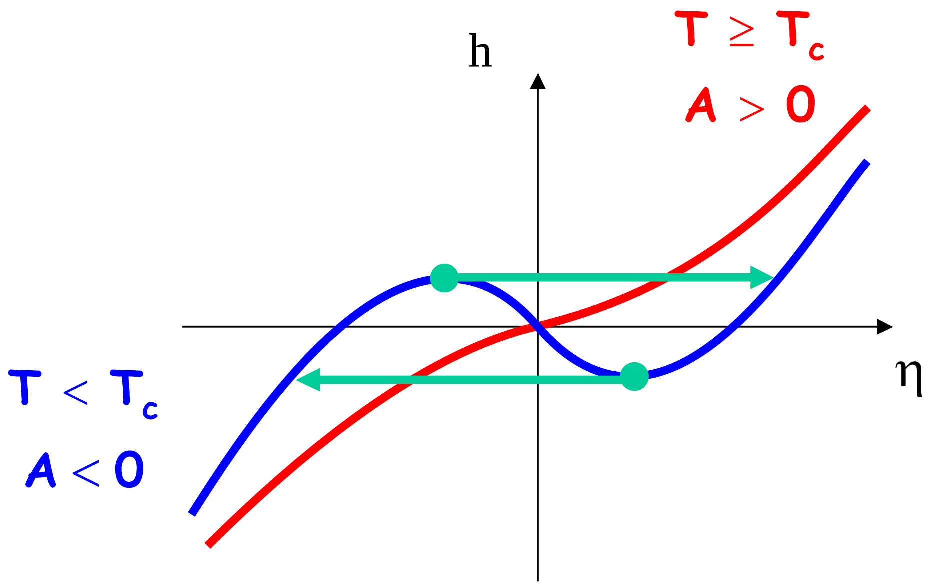


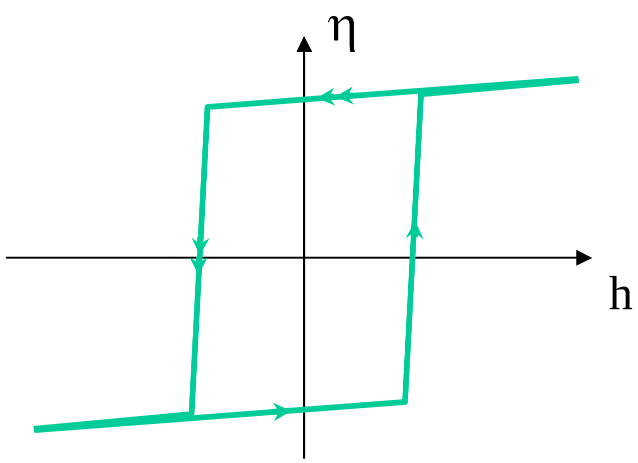
Curie law

Landau Theory

•Second Order Phase Transitions

✓ field hysteresis : $$h = \frac{\partial \Phi_{h=0}(\eta)}{\partial \eta} = A\eta + B\eta^3$$





Landau Theory

•Second Order Phase Transitions **SUMMARY**

- ✓ One critical temperature T_c
- ✓ No discontinuity of Φ, η, S (no latent heat) at T_c
- ✓ Jump of C_p at T_c
- ✓ Divergence of ξ and χ at T_c
- ✓ Field hysteresis

Landau Theory

•First Order Phase Transitions:

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

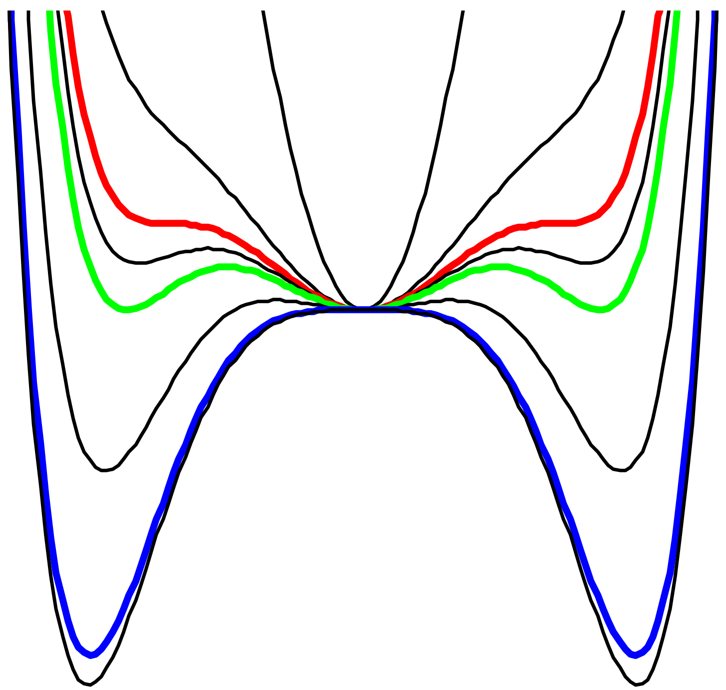
$C > 0$	$A = a\cdot(T - T_c)$ $a > 0$	$B < 0$
$\Phi(\eta) \underset{\eta\to\infty}{\to} \infty$	$\eta_o \neq 0$ at $T < T_c$	$\neq$ from 2nd order

$T > T_1$: $\eta_o = 0$ stable

$T_1 > T > T_o$: $\eta_o = 0$ stable
$\eta_o \neq 0$ metastable

$T_o > T > T_c$: $\eta_o = 0$ metastable
$\eta_o \neq 0$ stable

$T_c > T$: $\eta_o \neq 0$ stable



Landau Theory

•First Order Phase Transitions:

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

$C > 0$ $\quad A = a\cdot(T - T_c)$ $\quad B < 0$

$a > 0$

$T > T_1$: η_o=0 stable

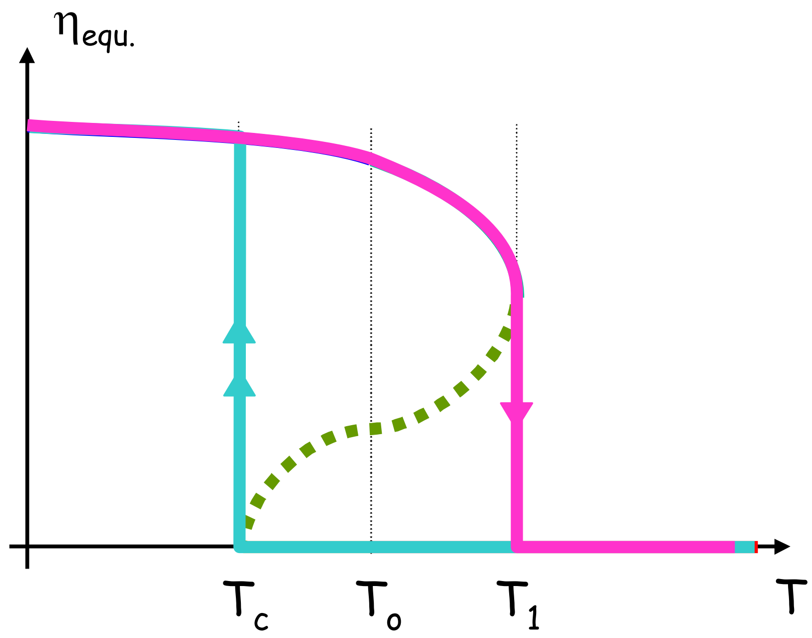
$T_1 > T > T_o$: η_o=0 stable

$\eta_o \neq 0$ metastable

$T_o > T > T_c$: η_o=0 metastable

$\eta_o \neq 0$ stable

$T_c > T$: $\eta_o \neq 0$ stable



Thermal hysteresis

Landau Theory

•First Order Phase Transitions:

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

$C > 0$ $\qquad A = a\cdot(T - T_c)$ $\qquad B < 0$

$a > 0$

✓ Steady state :

$$\left.\frac{\partial\Phi}{\partial\eta}\right|_{\eta_o} = \eta_o\cdot\left(A + B\eta_o^2 + C\eta_o^4\right) = 0$$

T ≥ T$_c$ $\qquad \eta_o = 0$

T < T$_c$ $\qquad \eta_o \neq 0$

$$\eta_o^2 = \frac{-B + \sqrt{B^2 - 4AC}}{2C} \overset{?}{>} 0$$

$$\Rightarrow B^2 - 4AC > 0$$

limit when $B^2 - 4AC = 0 \Rightarrow$ $T_1 = T_c + \frac{B^2}{4aC}$

$$\eta_o^2(T_1) = \frac{|B|}{2C}$$

$$\eta_o^2(T_c) = \frac{|B|}{C}$$

Landau Theory

•First Order Phase Transitions:

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

$C > 0$ $\qquad A = a\cdot(T - T_c)$, $a > 0$ $\qquad B < 0$

✓ Steady state : T = T_o

$$\frac{\partial\Phi}{\partial\eta} = \eta_o\cdot\left(A + B\eta_o^2 + C\eta_o^4\right) = 0$$

$$\Phi - \Phi_o = \eta_o^2\cdot\left(\frac{1}{2}A + \frac{1}{4}B\eta_o^2 + \frac{1}{6}C\eta_o^4\right) = 0$$

$$\Rightarrow \frac{1}{2}B\eta_o^2 + \frac{2}{3}C\eta_o^4 = 0$$

$$\eta_o^2(T_o) = \frac{3|B|}{4C} \quad \Rightarrow \quad T_o = T_c + \frac{3}{4}\cdot\frac{B^2}{4aC}$$

Landau Theory

•First Order Phase Transitions:

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

$C > 0$ $\quad A = a\cdot(T - T_c)$, $a > 0$ $\quad B < 0$

✓ Entropy : T = T_o

$$S = -\frac{\partial\Phi}{\partial T} = S_o - \frac{\partial}{\partial T}\left(\frac{1}{2}A\eta_o^2 + \frac{1}{4}B\eta_o^4 + \frac{1}{6}C\eta_o^6\right)$$

A and η^2 depend on T !

$$-S + S_o = \frac{1}{2}\eta_o^2\frac{\partial A}{\partial T} + \frac{1}{2}\underbrace{\left(A + B\eta_o^2 + C\eta_o^4\right)}_{=0}\frac{\partial\eta_o^2}{\partial T}$$

Latent heat $\quad T_o\cdot\Delta S\big|_{T_o} = \frac{3}{8}\frac{aB}{C}T_o \neq 0$

Landau Theory

•First Order Phase Transitions:

$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

$$C > 0 \qquad A = a\cdot(T - T_c) \quad a > 0 \qquad B < 0$$

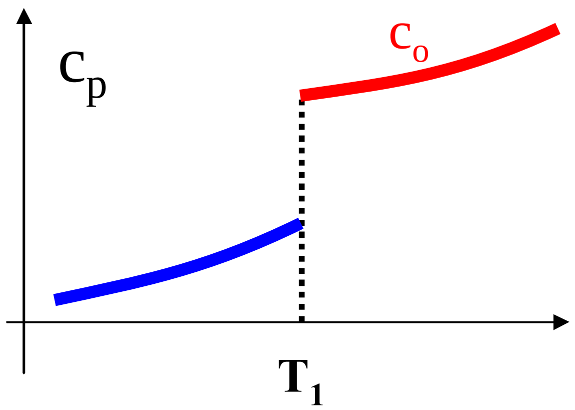
✓ Specific heat : T < T_1

$$S - S_o = -\frac{1}{2}\eta_o^2\frac{\partial A}{\partial T}$$

$$c_p - c_o = -\frac{1}{2}\frac{\partial A}{\partial T}\cdot\frac{\partial\eta_o^2}{\partial T} - \underbrace{\frac{1}{2}\eta_o^2\frac{\partial^2 A}{\partial T^2}}_{=0}$$

$$\eta_o^2 = \frac{|B| + \sqrt{B^2 - 4AC}}{2C}$$

$$c_p - c_o = -\frac{1}{2}\frac{\partial A}{\partial T}\cdot\frac{\partial\eta_o^2}{\partial T} = \frac{-a^2}{2|B|}\cdot\frac{1}{\sqrt{1 - \frac{4aC}{|B|^2}(T - T_c)}}$$



Landau Theory

•First Order Phase Transitions:

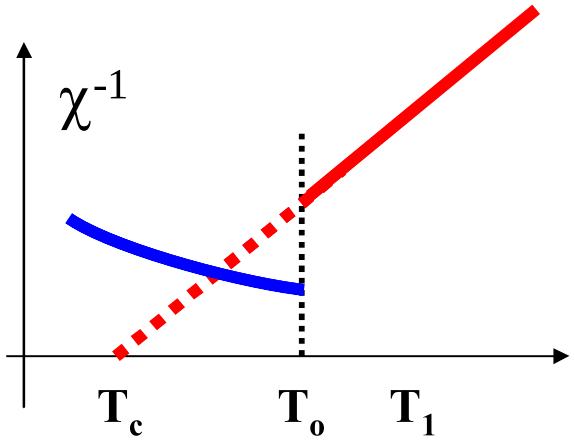
$$\Phi_h(\eta) \approx \Phi_o + \frac{1}{2}A\cdot\eta^2 + \frac{1}{4}B\cdot\eta^4 + \frac{1}{6}C\cdot\eta^6$$

$C > 0$ $\quad A = a\cdot(T - T_c)$, $a > 0$ $\quad B < 0$

✓ Susceptibility : $\chi^{-1} = \frac{\partial^2\phi}{\partial T^2} = A + 3B\eta_o^2 + 5C\eta_o^4$

$T > T_o: \quad \chi^{-1} = a\cdot(T - T_c)$ $\qquad$ ***η_o= stable until T down to T_o***

$$\begin{cases} T < T_o: \quad \chi^{-1} = a\cdot(T - T_c) + 3B\eta_o^2 + 5C\eta_o^4 \\ \eta_o^2 = \frac{|B| + \sqrt{B^2 - 4aC(T - T_c)}}{2C} \end{cases}$$



Landau Theory

•First Order Phase Transitions **SUMMARY**

- ✓ Existence of metastable phases
- ✓ Temperature domain ($T_c \leftrightarrow T_1$) for coexistence of high and low temperature phases
- ✓ at T_o ($T_c < T_o < T_1$) both high and low teperature phases are stable
- ✓ Temperature hysteresis
- ✓ Discontinuity of η, Φ, S (latent heat), C_p, χ at T_c

•Tricritical point

In the formalism of first order phase transitions, it can happen that B parameter changes sign under the effect of an external field. Then there is a point, which is called tricritical point, where B=0. The Landau expansion then takes the following form:

$$\Phi\ (\eta) \approx \Phi_o + \frac{1}{2} A \cdot \eta^2 + \frac{1}{6} C \cdot \eta^6$$

✓ Equilibrium conditions :

$$\left.\frac{\partial \Phi}{\partial \eta}\right|_{\eta_o} = \eta_o \cdot \left(A + C\eta_o^4\right) = 0 \quad \Rightarrow \quad \begin{cases} \eta_o = 0 \\ \eta_o^4 = -\dfrac{A}{C} \end{cases}$$

$$\left.\frac{\partial^2 \Phi}{\partial \eta^2}\right|_{\eta_o} = \left(A + 5C\eta_o^4\right) = 0 \quad \Rightarrow \quad \begin{cases} A \quad \text{pour} \quad \eta_o = 0 \\ -4A \quad \text{pour} \quad \eta_o^4 = -\dfrac{A}{C} \end{cases} \quad \Rightarrow \quad \begin{cases} > 0 \quad \text{pour} \quad T > T_c \\ > 0 \quad \text{pour} \quad T < T_c \end{cases}$$

•Tricritical point

✓ Potential :

$$\Delta\Phi = \Phi - \Phi_o = \frac{1}{2}A\eta_o^2 + \frac{1}{6}C\eta_o^6$$

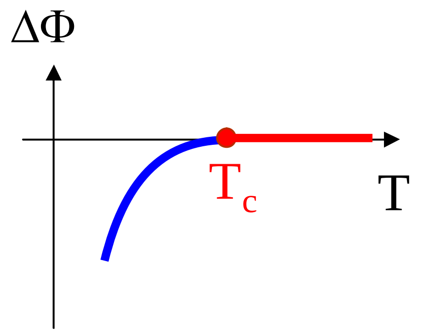
T>Tc: η=0

$$\Delta\Phi = 0$$

T>Tc: η≠0

$$\Delta\Phi = \frac{1}{2}A\left(\frac{-A}{C}\right)^{1/2} + \frac{1}{6}C\left(\frac{-A}{C}\right)^{3/2}$$

$$\Delta\Phi = -\frac{1}{3}\cdot\frac{a^{3/2}}{C^{1/2}}\cdot\left|T - Tc\right|^{3/2}$$



Landau Theory

- Tricritical point

✓ Entropy :

$$S = -\frac{\partial \Phi}{\partial T} = S_o - \frac{\partial}{\partial T}\left(\frac{1}{2}A\eta_o^2 + \frac{1}{6}C\eta_o^6\right)$$

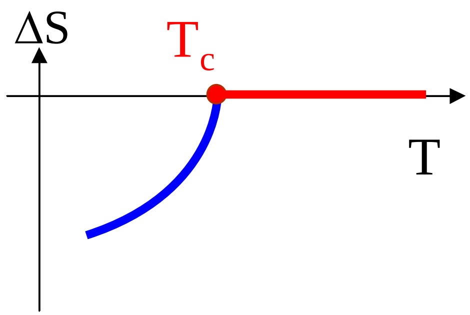
A and η^2 depend on T !

$$\Delta S = S - S_o = -\frac{1}{2}\eta_o^2\frac{\partial A}{\partial T} - \frac{1}{2}\left(A + C\eta_o^4\right)\frac{\partial \eta_o^2}{\partial T}$$

T>Tc: η=0 $\Delta S = 0$

T>Tc: η≠0 $\Delta S = -\frac{1}{2}\eta_o^2\frac{\partial A}{\partial T} - \frac{1}{2}\left(A + C\left(\frac{-A}{C}\right)\right)\frac{\partial \eta_o^2}{\partial T}$

$$\Delta S = -\frac{1}{2}\eta_o^2\frac{\partial A}{\partial T} = -\frac{1}{2}\cdot\frac{a^{3/2}}{C^{1/2}}\cdot\left|T_c - T\right|^{1/2}$$



Landau Theory

•Tricritical point

✓ Specific heat :

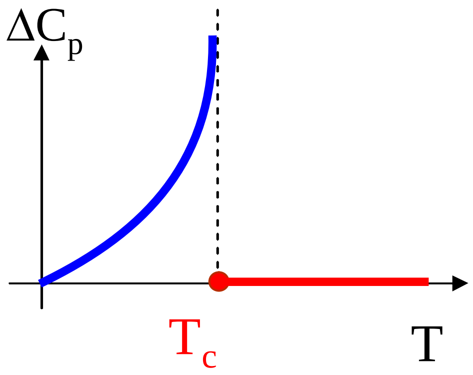
$$\Delta Cp = T \cdot \frac{\partial \Delta S}{\partial T} = T \cdot \frac{\partial}{\partial T}\left(-\frac{1}{2}\eta_o^2 \frac{\partial A}{\partial T} \right)$$

$$\Delta Cp = -\frac{1}{2} T \cdot \left\{ \frac{\partial \eta_o^2}{\partial T} \cdot \frac{\partial A}{\partial T} + \eta_o^2 \cdot \frac{\partial^2 A}{\partial T^2} \right\}$$

T>Tc: η=0 $\Delta Cp = 0$

T>Tc: η≠0 $\Delta Cp = -\frac{1}{2} T \cdot \left\{ \frac{1}{2}\left(\eta_o^4\right)^{-1/2} \cdot \frac{\partial \eta_o^4}{\partial T} \cdot a + 0 \right\}$

$$\Delta Cp = \frac{1}{4} \cdot \frac{a^{3/2}}{C^{1/2}} \cdot T \cdot \left| T - T_c \right|^{-1/2}$$

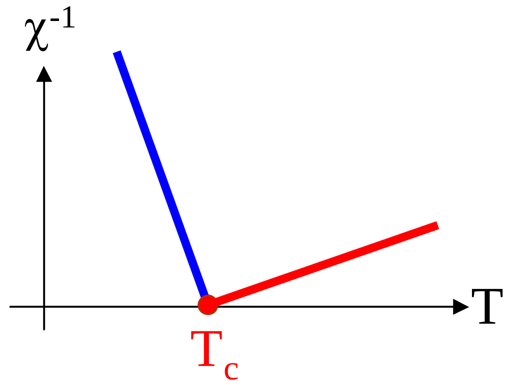


Landau Theory

•Tricritical point

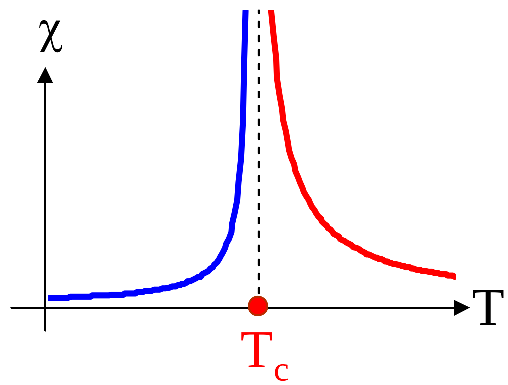
✓ Susceptibility :

$$\chi^{-1} = \frac{\partial^2 \phi}{\partial T^2} = A + 5C\eta_o^4$$



T>Tc: η=0

$$\chi^{-1} = A = a \cdot |T - Tc|$$



T>Tc: η≠0

$$\chi^{-1} = -4A = 4a \cdot |T - Tc|$$