Second order phase transitions

- Order parameter
- Free energy
- Critical behavior
- Phase transitions in external field
- Landau functional
- Fluctuations of the order parameter
- Ginzburg number
- Critical region

Phase transitions

Phenomenological definition: two phases

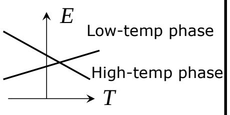
Energy is always continuous at the transition point

1st order: First energy derivatives are discontinuous
2nd order: First derivatives are continuous; second derivatives are discontinuous

(according to this definition, also 3rd order or even fractional order transitions are possible!)

More intuitive understanding

1st order phase transition: two phases
(example: liquid-gas transition)



2nd order phase transition: two phases with different symmetry

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Second order phase transitions

2nd order phase transition: two phases with different symmetry

Spontaneous symmetry breaking

Examples:

- Structure phase transitions: space symmetry group
- Pyroelectricity: Inversion symmetry
- Magnetism: Time-reversal symmetry
- Superconductivity: Gauge invariance

Mathematical description: symmetry groups

Low-symmetry phase: group $\mathbf{L}$
High-symmetry phase: group $\mathbf{H}$

2nd order phase transition: $\mathbf{L}$ is a subgroup of $\mathbf{H}$

Otherwise: 1st order phase transition

Order parameter

How do we characterize the spontaneous symmetry breaking?

Order parameter *η* – a quantity characterizing the transition

$\eta = 0$ high-symmetry phase
$\eta \neq 0$ low-symmetry phase

Examples:

- Structural phase transition – atomic displacement (real vector or scalar)
- Ferromagnetic (Curie) transition – magnetization (vector)
- Superconducting phase transition – complex scalar
- Transitions in liquid crystals - tensor

At the transition point the order parameter is continuous; the derivative must be discontinuous

Singularities in the thermodynamic properties

Landau functional

Next to the transition point: the order parameter is small

Phenomenological theory!

We can expand the free energy in terms of the order parameter

$$\boxed{F[\eta] = F_0 + F_1\eta + F_2\eta^2 + F_3\eta^3 + F_4\eta^4 + \text{higher order } -Vh\eta}$$

Irrelevant

Always vanishes from symmetry arguments (for Curie transition: energy is a scalar and can not contain the first power of a vector)

Usually vanishes from symmetry arguments ; if not, corresponds to a critical point (1st order phase transition)

At each temperature, the order parameter *η* is determined from the minimization of the free energy.

Landau functional

$$\boxed{F[\eta] = F_2\eta^2 + F_4\eta^4 + \text{higher order } -Vh\eta}$$

Usually not needed

V - volume

External field term
For Curie transition:
$-\vec{h}\vec{h}_0$

Let us forget for a moment about the external field and determine the temperature dependence of the coefficients.

F_4 -must be positive at all temperatures (otherwise no equilibrium order parameter): can take it temperature independent

$$\boxed{F_4 = bV/4, b > 0}$$

F_2 -must vanish at the transition temperature

$$\boxed{F_2 = a\tau V/2, a > 0}$$

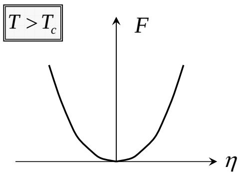
$$\boxed{\tau = \frac{T - T_c}{T_c}}$$

Landau functional

$$\boxed{F[\eta]/V=\frac{a\tau}{2}\eta^2+\frac{b}{4}\eta^4}$$

Only one phase exists at each temperature!

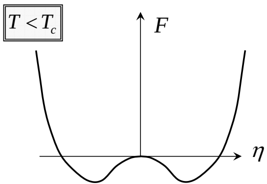
$\boxed{T>T_c}$



The only minimum:
$\eta=0$

High-symmetry phase

$\boxed{T<T_c}$



Two minima: $\eta=\pm\sqrt{-a\tau/b}$

Symmetry broken!!

Low-symmetry phase

Singularities

$$\boxed{F[\eta]/V=\frac{a\tau}{2}\eta^2+\frac{b}{4}\eta^4}$$

Consider $T<T_c$

Order parameter: $\boxed{\eta\propto\sqrt{T_c-T}}$

Free energy: $\boxed{F/V=-\frac{(a\tau)^2}{4b}\propto(T_c-T)^2}$

Entropy: $\boxed{S=-\partial F/\partial T\propto T_c-T}$ - continuous at the transition point

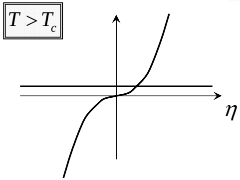
Specific heat: $\boxed{C=T\partial S/\partial T}$ - jumps at the transition point

External field

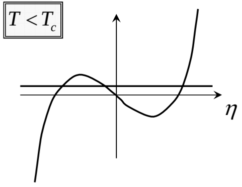
$$\boxed{F[\eta]/V=\frac{a\tau}{2}\eta^2+\frac{b}{4}\eta^4-h\eta}$$

Equation for the minimum: $\boxed{a\tau\eta+b\eta^3=h}$

$\boxed{T>T_c}$



$\boxed{T<T_c}$



One solution $\boxed{T=T_c\Rightarrow\eta=(h/b)^{1/3}}$

Three solutions: two stable, one unstable

External field

$$\boxed{F[\eta]/V=\frac{a\tau}{2}\eta^2+\frac{b}{4}\eta^4-h\eta}$$

Succeptibility: $\boxed{\begin{array}{l}T=T_c\Rightarrow\eta=(h/b)^{1/3}\\ \chi=\partial\eta/\partial h\propto\left|T_c-T\right|^{-1}\end{array}}$

The transition is "smeared" – for any value of the field the order parameter is nonzero.
This is because the field lowers the symmetry of the high-symmetry phase.

Typical scale of the field: when one has three solutions

$$\boxed{h_c=\frac{2}{3}\frac{\left(a\left|\tau\right|\right)^{3/2}}{(3b)^{1/2}}}$$

Intermediate summary

We found a number of critical exponents

Order parameter: $\boxed{\begin{array}{l}h=0\Rightarrow\eta\propto(T_c-T)^{1/2}\\ T=T_c\Rightarrow\eta\propto h^{1/3}\end{array}}$

Specific heat: $\boxed{C=const}$

Succeptibility: $\boxed{\chi\propto\left|T_c-T\right|^{-1}}$

The problem: often not confirmed by exact solutions, numerical studies or experiments

Reason: fluctuations of the order parameter not taken into account in the mean-field approach

Landau functional

Order parameter fluctuations: $\boxed{\eta(\vec r)}$

Assume that only long-wavelength fluctuations are important

$$\boxed{F[\eta]=\int d^3\vec r\left[\frac{c}{2}\left(\vec\nabla\eta\right)^2+\frac{a\tau}{2}\eta^2+\frac{b}{4}\eta^4-h\eta\right]}$$

Fluctuation term: higher order gradients are less important

If fluctuations are small, we can linearize the functional around the uniform solution η_0 $\boxed{\eta(\vec r)=\eta_0+\Delta\eta(\vec r)}$

Quadratic: $\boxed{\Delta F[\eta]=\frac{1}{2}\int d^3\vec r\left[c\left(\vec\nabla\Delta\eta\right)^2+a\tau\left(\Delta\eta\right)^2+3b\eta_0^2\left(\Delta\eta\right)^2\right]}$

Order parameter fluctuations

$$\Delta F[\eta]=\frac{1}{2}\int d^3\vec{r}\left[c\left(\vec{\nabla}\Delta\eta\right)^2+a\tau\left(\Delta\eta\right)^2+3b\eta_0^2\left(\Delta\eta\right)^2\right]$$

Expand in Fourier series: $\Delta\eta(\vec{r})=\frac{1}{\sqrt{V}}\sum_{\vec{k}}\eta_{\vec{k}}e^{i\vec{k}\vec{r}}$

$$\Delta F[\eta]=\sum_k\left(a\tau+3b\eta_0^2+ck^2\right)\left|\eta_k\right|^2$$

This is a contribution of a particular fluctuation.

What is the contribution of all fluctuations to the free energy?

Probability of a fluctuation: $\exp\left(-\Delta F[\eta]/k_BT\right)$

Specific heat

Fluctuation contribution to the partition function:

$$Z_{fl}=\sum_{\text{all fluct.}}\exp\left(-\Delta F[\eta]/k_BT\right)$$

Mathematically: an integral over a field

It is best expressed in Fourier representation:

$$Z_{fl}=\prod_k d\,\mathrm{Re}\,\eta_k d\,\mathrm{Im}\,\eta_k\exp\left(-\Delta F[\eta]/k_BT\right)$$

$$\sum_k\ldots=\frac{1}{V}\int\frac{d^3\vec{k}}{(2\pi)^3}$$

Fluctuation contribution to the free energy: $F_{fl}=-k_BT\ln Z_{fl}$

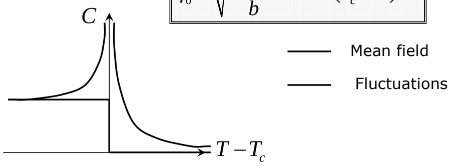
Result for the specific heat: $C=\frac{Va^2}{16\pi c^{3/2}}\frac{1}{\sqrt{a\tau+3b\eta_0^2}}$

Specific heat

$$C=\frac{Va^2}{16\pi c^{3/2}}\frac{1}{\sqrt{a\tau+3b\eta_0^2}}$$

High symmetry phase: $\eta_0=0\Rightarrow C\propto(T-T_c)^{-1/2}$

Low-symmetry phase: $\eta_0=\sqrt{-\frac{a\tau}{b}}\Rightarrow C\propto(T_c-T)^{-1/2}$



Ginzburg number

We have assumed that fluctuations are small. How good is this assumption?

Compare fluctuation correction to the specific heat to the mean field value:

$$C_{MF}=\frac{a^2}{2bT_c}V \qquad C=\frac{Va^2}{16\pi c^{3/2}}\frac{1}{\sqrt{2|a\tau|}}$$

Not too close to the transition!

Need $G\ll1!$

$$G\equiv\frac{b^2T_c^2}{ac^3}\ll|\tau|\ll1$$

Ginzburg number

Otherwise we can not expand in powers of the order parameter!

Ginzburg number

$G=\frac{b^2T_c^2}{ac^3}$ Let us express it in more intuitive terms.

Two spatial scales

r_0 -distance between the particles (formally: the fluctuation of the order parameter at this scale is the same as the order parameter itself

$$F/V\sim k_BT_cr_0^{-3}\sim a\eta^2\sim b\eta^4$$

$$r_0\sim(bT_c/a^2)^{1/3}$$

r_c -correlation radius (distance at which the order parameter fluctuations are correlated)

$$c\eta^2r_c^{-2}\sim a\eta^2 \qquad r_0\sim\sqrt{c/a}$$

$G=\left(\frac{r_0}{r_c}\right)^6$ Large fluctuations mean $r_0\sim r_c$

Critical region: Landau theory does not apply

Critical region

$G=\left(\frac{r_0}{r_c}\right)^6$ Numbers depend on the microscopic details of the system

- Superconductors: $G\sim10^{-4}$ In practice, can not be achieved
- Magnetic systems: $G\sim0.1$ Critical region important!

What can we say about the critical region?

$$r_c\propto|T-T_c|^{-1/2}\to\infty$$

But r_0 also grows and faster than r_c : they become equal at the edge of the critical region

D=4: there is a systematic expansion in r_0/r_c all the way to the transition point.

Wilson ’75: 4 – ε expansion: can extrapolate down to D=3!!

Critical region

What if we can not use 4 – ε expansion?

Scaling hypothesis!

There is only one spatial scale characterizing the fluctuations: $r_0 \sim r_c$

All physical laws stay the same at any scale.

Mathematically: if we rescale the length $r \to r / u$

all the relations stay the same (do not depend on *u*) upon
the power-law rescaling

$\tau \to \tau u^{\delta_\tau}, \eta \to \eta u^{\delta_\eta}, h \to he^{\delta_h}$ (Renormalization group procedure)

Provides the values of critical indices (different from Landau theory)