READ: Ch.2 of Khomskii text

SSP I 2019
601

Lecture #2

- How to distinguish various phases.

NB. - A concept of an order parameter
(show in class presentation)

Statement: At finite T, the state of a system is a minimum of of a 'thermodynamic potential Helmholtz or Gibs.

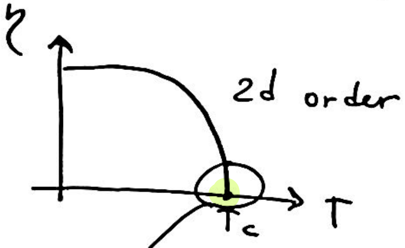
e.g. $F = E - T \cdot S$ → $T \to 0$ $S \to 0$ is unimportant / goes to order

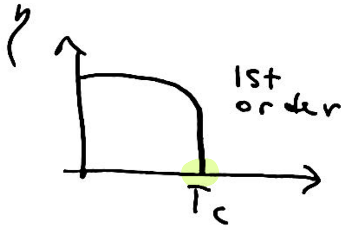
T goes up S ↑

with increasing T, entropy favers disorder.

Order parameter (OP)

OP depends T, P, V, external things like strain, mag. field electric fiels etc.





T_c ≡ critical temperature

around T_c η is small, lets try taillor expansion

Gibs free energy: $\Phi(P,T,\eta) = \Phi_0 + \alpha\eta + A\eta^2 + C\eta^3 + \ldots$

here α, A, C, β are functions of P, T
and hence we can determine them from the condition that

$$\min \Phi \quad \text{for } T > T_c \quad \eta = 0$$
$$\text{for } T < T_c \quad \eta \neq 0$$

$$\Phi = \Phi_0 + \alpha(P,T)\eta + (P,T)\eta^2 + C(P,T)\eta^3 + \underset{(P,T)}{B}\eta^4 + \ldots$$

$\frac{\partial \Phi}{\partial P}$ or $\frac{\partial \Phi}{\partial T} = 0$

What can we say about the expansion coeff.s?

since Φ has to have a minimum the term

$\alpha\eta \rightarrow$ requires $\alpha = 0$ otherwise

as a function of η Φ would always grow,

Next, for $A\eta^2$: we know $\eta = 0$ for $T > T_c$

$\eta \neq 0$ for $T < T_c$

① $A\eta^2$ = is present in the expansion.

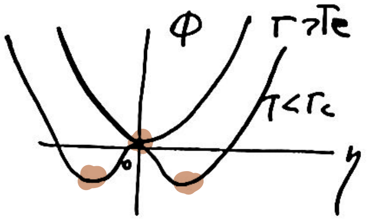
② $A(P,T)\eta^2 \Rightarrow$ $\eta = 0$ for $T > T_c$

$$A(P,T) = \begin{cases} > 0 & T > T_c \\ < 0 & T < T_c \end{cases}$$

the simplest term like this

$$A(P,T) \sim a(T - T_c)$$

we also assume for the moment that $C = 0$ and $B > 0$



$$\Phi = \Phi_0 + A(P,T)\eta^2 + \underset{>0}{B}(P,T)\eta^4 =$$

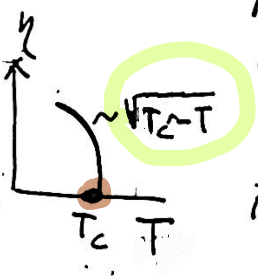
$$\boxed{\Phi = \Phi_0 + a(T - T_c)\eta^2 + B\eta^4}$$

To find out how the or. parameter depends on T

$$\frac{d\Phi}{d\eta} = 0 \rightarrow \cancel{2}a(T - T_c)\cancel{\eta} + \underset{2}{\cancel{4}}B\eta^{\cancel{3}\,2} = 0 \Rightarrow \boxed{\eta^2 = -\frac{a(T - T_c)}{2B}}$$

Here all the coeff. can be a function of P or external parameters:

$a = a(P)$
$B = B(P)$
$T_c = T_c(P)$



For cond. mat. $T_c = T_c(P)$ is the most important.

and $a = B = \text{const}$ in P

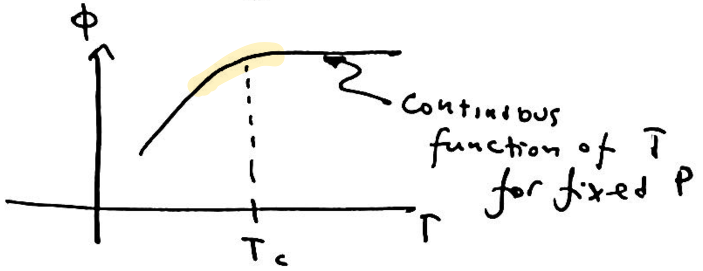
At the equilibrium the free energy:

$$\Phi_{min}\Big|_{T<T_c} = \Phi_0 + A\eta^2 + B\eta^4 = \Phi_0 + A\cdot\frac{a(T - T_c)}{2B} + \frac{\cancel{B}\,a^2(T - T_c)^2}{4B^{\cancel{2}}}$$

$$= \Phi_0 + (-)\frac{a^2(T - T_c)^2}{2B} + \frac{a^2(T - c)^2}{4B} = \Phi_0 - \frac{a^2}{4B}(T - T_c)^2$$

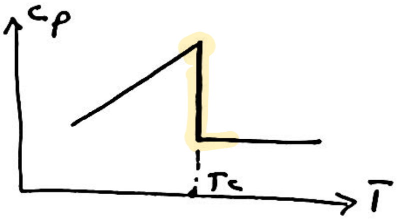
and $\Phi = \Phi_0$ for $T > T_c$

$$\Phi_{min} = \begin{cases} \Phi_0 - \frac{a^2}{4B}(T-T_c)^2 & T<T_c \\ \Phi_0 & T>T_c \end{cases}$$



continuous function of T for fixed P

but $\frac{\partial \Phi}{\partial T}$ has a kink at T_c!.



★ Homework: 1) ~~Derive c_p behavior at the 2^d order phase transition temperature.~~

~~Given $c_p = T\left(\frac{\partial s}{\partial T}\right)_p$; $s = -\left(\frac{\partial \Phi}{\partial T}\right)_p$~~

~~$\eta^2 = \frac{a}{2B}(T_c - T)$, $\Phi_{min} = \Phi_0 - \frac{a^2}{4B}(T_c-T)^2$~~

~~Comment on~~

~~Assume $S = 1/2$, calculate total entropy in the ordered phase:~~

2). ~~e.g. $S_{ord} = \int^{T_c} S(T)\, dT$~~

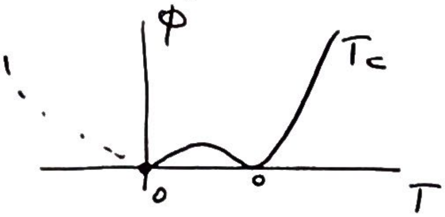
(SEE SEPARATE PDF)

THIS HOMEWORK WILL BE POSTED AS PDF

General Rules:

① if you include the cubic term $\sim \eta^3$ you always end up with 1st order transitions.

② in this case T_c is <u>not the singular minimum</u> of Φ but the point where two minima have equal energy.



③ T^* and T^{**} are <u>the singular points</u>

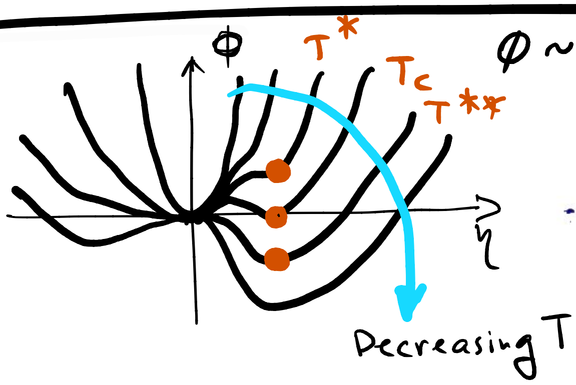
④ Thermodynamic quantities e.g. C_p or C_v will not diverge at T_c but will diverge at T^* and T^{**}

limit of overcooling

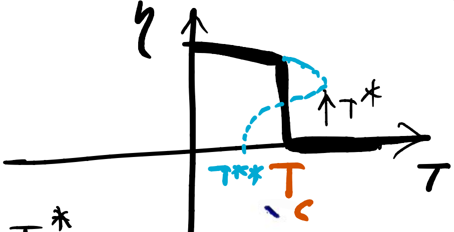
limit of overheating

A Cool example of 1st order ph. transition.

SEE NEXT PAGE



$\Phi \sim A\eta^2 - C\eta^3 + B\eta^4$

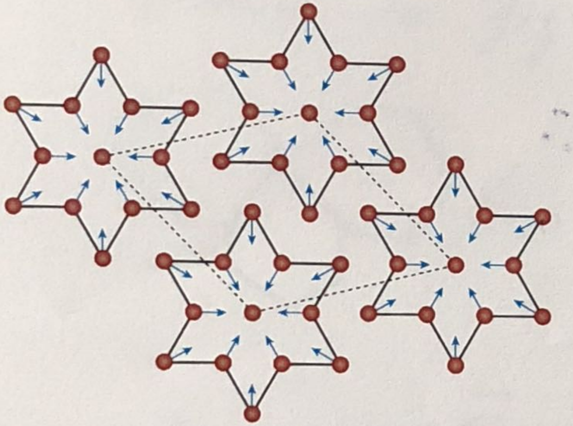


①, Between T^* and T_c $A>0$ and $C<0$

② if we wait long enough the system will jump from $\eta=0$ to $\eta\neq 0 \Rightarrow$ 1st order but then $A<0$. no $\eta=0$ state.

L2

TaS_2



Tc ?

Tc ?

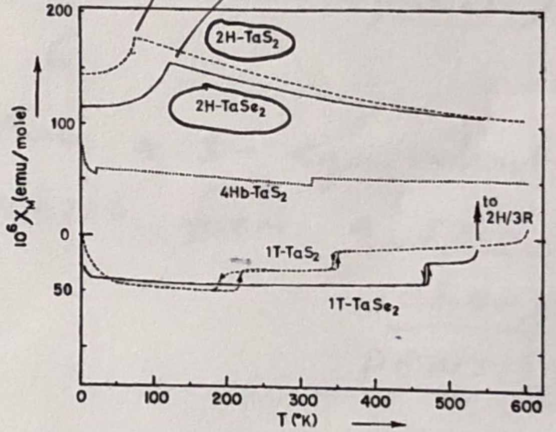
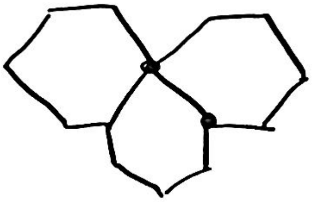


Fig. 2. The molar magnetic susceptibility (χ_M) versus temperature (T) for TaS_2 and T_c with different lattice structures. The background diamagnetic term has not been subtracted. The data are taken from ref. 3.

So how do we describe the order parameter in this system?

① we include every possible term allowed by symmetry

i.e. on triangular (hexagonal) lattice shown in fig. 6



there a 3-equivalent vectors which form a spin or SDW
charge CDW
DENSITY WAVE

$\eta_n = \eta e^{i\bar{Q}_n\cdot\bar{r}}$

$n = 1, 2, 3$

so that $\bar{Q}_1 + \bar{Q}_2 + \bar{Q}_3 = 0$

Then we can form a new invariant in the Gibbs free energy, i.e.

$$C\eta_1\cdot\eta_2\cdot\eta_3 = C\eta^3 e^{i\underbrace{(\bar{Q}_1+\bar{Q}_2+\bar{Q}_3)}_{=0}\cdot\bar{r}} =$$

$= C\eta^3$ ← this term will cause the 1st order phase transition found in

TaS_2 or TaSe

as shown in fig. on page 6 L2

Q: what do you think about crystallization or melting?
is it a 1st or 2d order phase transition?

L2 (two) Cont'd

Another possibility of getting 1st order.

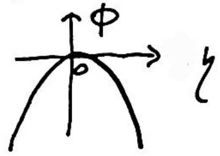
Assume that there are no odd terms η^3, η^5 etc

$$\Phi = A(P,T)\eta^2 + B(P,T)\eta^4 =$$

$$= a(T-T_c)\eta^2 + \underset{>0}{B(P,T)}\eta^4$$

Assume that at some value of P the coeff. B is <0

so $T<T_c$ both η^2 and η^4 <0

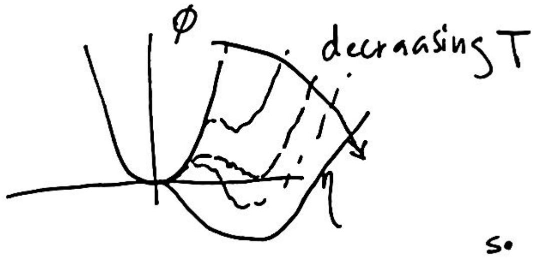


, so this system is unstable.

We need to stabilize the system, we add up

$$\Phi = \ldots\ldots + \underset{>0}{D}\eta^6$$

For $D>0$ and $T>T_c$ where $A>0$ and very small, $B<0$



near T_c $a(T-T_c)$ is small

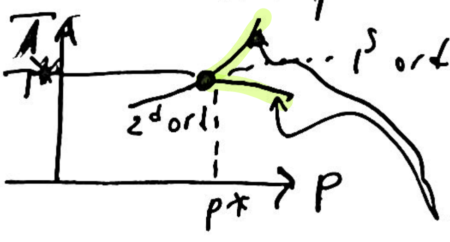
$-B\eta^4$ is large enough

so we may end up with 2 minima

or the 1st order phase transition.

Note however if $B(P,T)>0$ then we will have a "regular" 2d order phase tr.

Thus if at some pressure P^* $B(P^*,T)$ changes sign we will have 2d to 1st order transition. This point is called the tricritical point



lines of overheating and overcooling.

L2 (two)

Interaction with other degrees of freedom

Suppose we want to study how strain ε or pressure P affects a magnetic phase transition.

bulk modulus
$b = \Delta P / \Delta V/V$
$b_{steel} = 160 \times 10^9 \frac{N}{m^2}$
$b_{H_2O} = 2.2 \times 10^9 \frac{N}{m^2}$
$\frac{1}{b}$ = compressibility

$$\Phi = a(T-T_c)\eta^2 + B\eta^4 + \frac{bu^2}{2} + \lambda\eta^2 \cdot u$$

elastic energy

coupling between distortion u and magnetic order parameter

Findin min:

$$\frac{d\Phi}{du} = \cancelto{0}{a(T-T_c)\eta^2} + \cancelto{0}{B\eta^4} + bu + \lambda\eta^2 = 0$$

$$\Rightarrow \quad u_{min} = -\frac{\lambda\eta^2}{b}$$

$$\Phi(u_{min}) = a(T-T_c)\eta^2 + B\eta^4 + \frac{\cancel{b}}{2}\frac{\lambda^2\eta^4}{b^{\cancel{2}}} + \lambda\eta^2\left(-\frac{\lambda\eta^2}{b}\right) = a(T-T_c)\eta^2 + \left(B - \frac{\lambda^2}{2B}\right)\eta^4$$

now if coupling to the lattice, e.g. magnetoelastic coupling is strong, or lattice compressibility is large, i.e. bulk modulus b is small $\Rightarrow$

$$\underset{<0}{\left(B - \frac{\lambda^2}{2b}\right)}\eta^4 \Rightarrow$$ 2d order turns into 1st orde phase transition

NB. thing which are difficult to compress has a large bulk modulus, b but small compressibility $1/b$

L2

For those who care!

What if the order parameter is complex?

Superconductivity for pedestrians.

In transitioning to superconductivity the brooken symmetry is the gage symmetry.

① in the superconducting state the macroscopic wafe function is the complex order parameter, e.g.

$$\eta = \eta_0 e^{i\theta} \quad , \eta_0 \text{ and } \theta \text{ are real}$$

Now we can write down Φ!

$$\Phi = \Phi_0 + \underset{a(T-T_c)}{A}|\eta|^2 + \underset{>0}{B}|\eta|^4 + \dots =$$

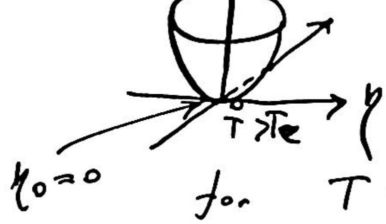
$$= \Phi_0 + a(T-T_c)\eta_0^2 + B\eta_0^4 \Rightarrow$$

$$\frac{d\Phi}{d\eta_0} = a(T-T_c)\cdot 2\eta_0 + 4B\eta^3 = 0 \Rightarrow \left(a(T-T_c) + 2B\eta_0^2\right). \quad \eta_0 = 0$$

or $\eta_0 = 0$ for $T > T_c$

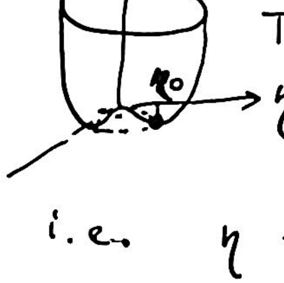
$$\eta_0 = \left[\frac{a(T-T_c)}{2B}\right]^{1/2}, T < T_c$$

For the normal state of a superconductor when $T > T_c$ $\Phi = \Phi_0$ and gage symmetry is preserved



or $\begin{cases} \eta_0 = 0 \\ \text{and thus } \theta \text{ can take any value} \end{cases}$

for $T < T_0$ $\eta_0 = \left(\frac{a(T-T_c)}{2B}\right)^{1/2}$ and θ is fixed $\Rightarrow$ $\Rightarrow$ the symmetry is broken!

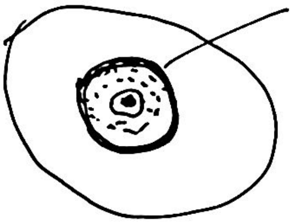


$\eta = \eta_0 e^{i\theta}$, however the system can moved inside the "mexican hat"

i.e. $\eta \rightarrow \eta' = e^{i\theta'}\cdot\eta$ the set of all rotations in the complex plane U(1)

So it seems that even in the superconducting phase we have gage symmetry in the ordered phase. i.e $\theta \to \theta'$ but with the same energy. All those orderer states are degenerate in energy.

Topview:



minumum of the "mexican" hat = = circle

every point on the circle is a possible state.

When the symmetry is spontaneously broken the system choses a specific η^* and θ^*.

__physical picture__:

Just below T_c only a small number of electons codense into Cooper pairs with specific θ. When $T = 0K$ max number of N condens. so N and θ are conjugate: or: $\Delta N \cdot \Delta\theta \sim 1$,