SSP I 2017
601

Lecture #2

- How to distinguish various phases.

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

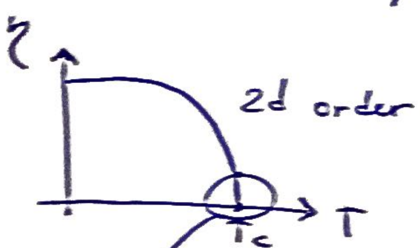
<u>Statement:</u> At finite T, the state of a system is a <u>minimum</u> of of a thermodynamic potential Helmholz or Gibs.

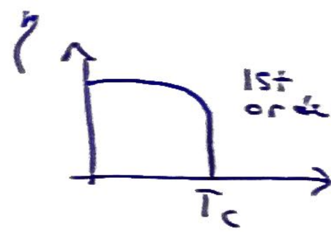
e.g. $F = E - T \cdot S$ → $T \to 0 \Rightarrow S \to$ is unimportant goes to order
⇒ T goes up $S \uparrow$

with increasing T, entropy favors <u>disorder</u>.

Order parameter (OP)

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





$T_c \equiv$ <u>critical</u> temperature

around T_c η is small, lets try tailor 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

$\min \Phi$ for $T > T_c$ $\eta = 0$
for $T < T_c$ $\eta \neq 0$

$\Phi = \Phi_0 + \alpha(P,T)\eta + A(P,T)\eta^2 + C(P,T)\eta^3 + \frac{5}{[illegible]}\eta^4 + \ldots$

$\frac{\partial \Phi}{\partial \eta}$ 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.

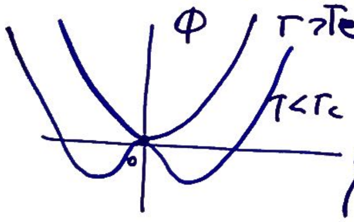
② $A(P,T)\eta^2 \Rightarrow$ $\eta = 0$ for $T > T_c$

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

the simplest term like this

$$A(P,T) = a(T - T_c)$$

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



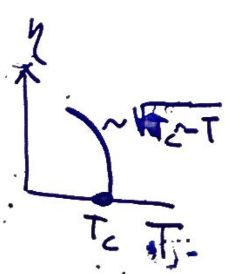
$$\Phi = \Phi_0 + A(P,T)\eta^2 + \underset{>0}{B}(P,T)\eta^4 =$$

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

To find out how the or. parameter depends on T

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

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 = $ const in P

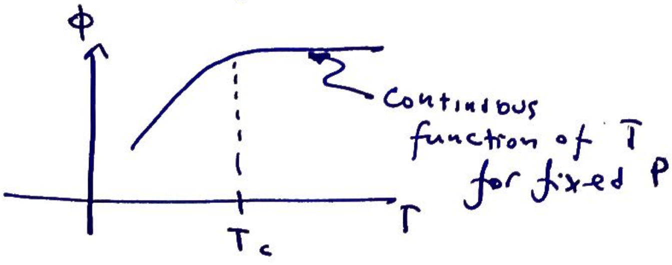
At the equilibrium the free energy:

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

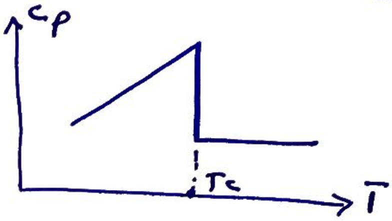
$$= \Phi_0 + (-)\frac{a^2(T-T_c)^2}{2B} + \cancel{B}\frac{a^2(T-c)^2}{4B} = \Phi_0 - \frac{a^2}{4B}(T-T_c)^2$$

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

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



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



★ **Homework:** 1) Derive c_p behavior at the 2d 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:

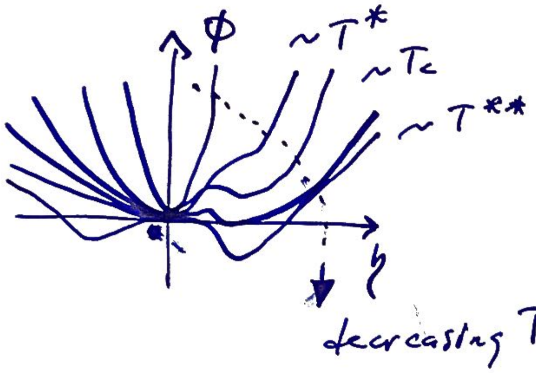
2). e.g. $S_{ord} = \int^{T_c} S(T)\, dT$

(SEE SEPARATE PDF)

Weak 1^{st} order phase transition.

In the Gibbs energy definition we have ignored $C\eta^3$ term. This term is generally 0 by symmetry. e.g. in FM $M(\bar{r})$ $M(-\bar{r}) = M(r)$ $\Rightarrow$ for this kind of systems there should be only even terms.

Let's assume however that $C\eta^3 \neq 0$

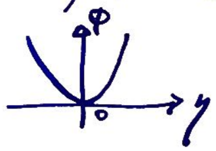


Lets study the case when $C < 0$

① $\Phi = \Phi_0 + A\eta^2 + B\eta^4 + C\eta^3 + \dots$

if A is large > C

we get one minimum.



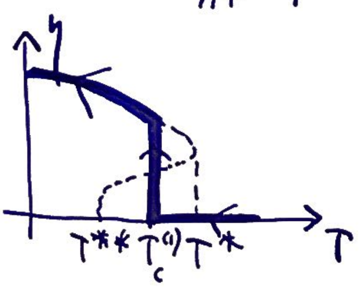
② T goes down A ↓

B and C play more important role.

At T^* appears 2^d minimum = the metastable state.

This means that at this T^*

If we wait long enough Temp. will jump to the state with $\eta \neq 0$



, or. we end-up with 1^s order ph.trans.

by the way $\eta = 0$ = disordered phase.

T^* and T^{**}

↑ overheating ↑ overcooling

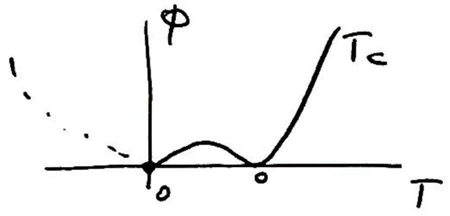
those points are called SPINODAL PO[illegible]

They determine maximum of hysteresis

General Rules:

① if you include the cubic term $\sim\eta^3$ you always end up with 1^{st} 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~~ overheating

A Cool example of 1st order ph. transition

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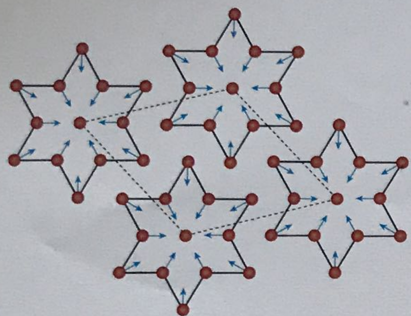
TaS_2



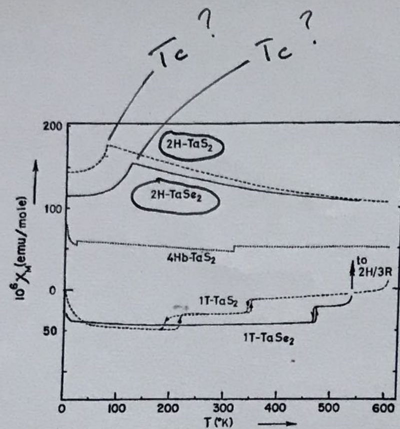


Fig. 2. The molar magnetic susceptibility (χ_M) versus temperature (T) for TaS_2 and T_c with different lattice structures. The background diamagnetic term has not been subtracted. The data are taken from ref. 3.

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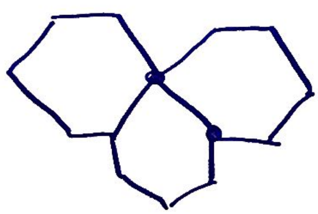
So how do we describe the order parameter in this system?

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 Gibs 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 2nd order phase transition?

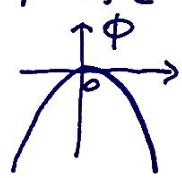
Another possibility of getting 1^{st} order.

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 $\eta^4 < 0$

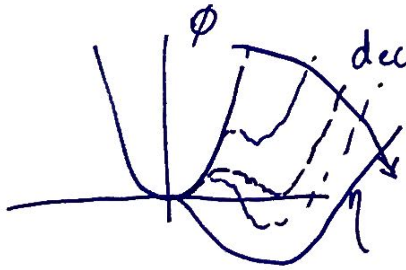


, so this system is unstable.

We need to stabilize the system, we add up

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

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



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

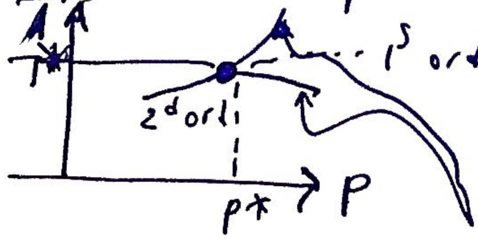
$-B\eta^4$ is large enough

so we may end up with 2 minima

or the 1^{st} order phase transition.

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

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



lines of overheating and overcooling.

Interaction with other degrees of freedom

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

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

elastic energy

coupling between distortion u and magnetic order parameter

Findin min:

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

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

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

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

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

< 0

For those who care!

What if the order parameter is complex?

Superconductivity for pedestrians.

In transitioning to superconductivity the broken 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!

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

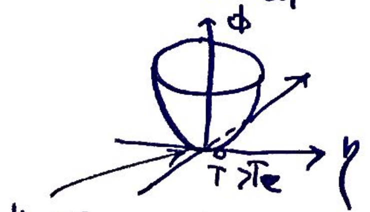
$$= \Phi_0 + a(T-T_c)\eta_0^2 + B\eta_0^4 \Rightarrow$$

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

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

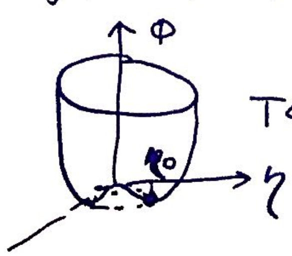
$$\eta_0 = \left[\frac{a(T-T_c)}{2B}\right]^{1/2}, \; T < T_c$$

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



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

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



T<Tc

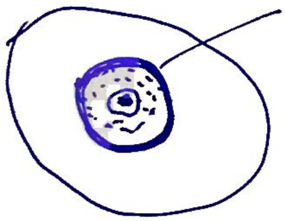
$\Rightarrow$ the symmetry is broken!

$\eta = \eta_0 e^{i\theta}$, 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:



~~⇒~~ 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:
$\Delta N \cdot \Delta\theta \sim 1$.