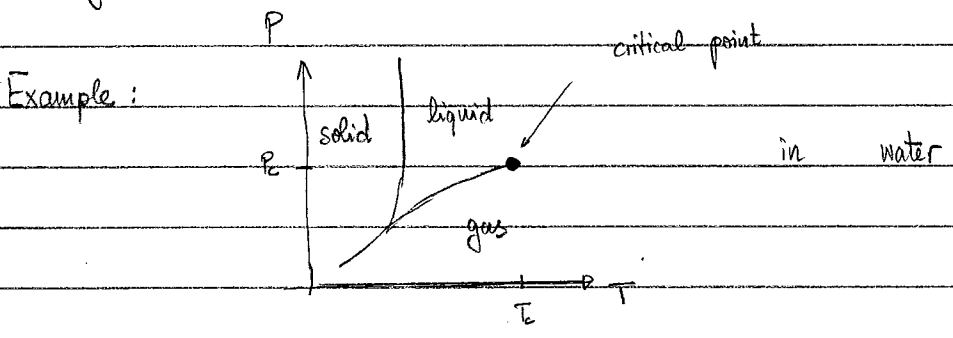


9) PHASE TRANSITION

Physically a phase transition is a point in parameter space, where the physical properties of a many-particle system undergo a sudden change.



Mathematically a phase transition is a point in parameter space where the free energy $F = -kT \ln Z$, $Z = \sum_{\text{microstates } \Gamma} e^{-E(\Gamma)/kT}$

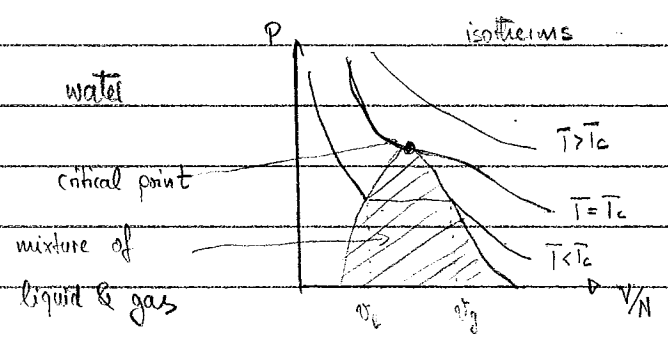
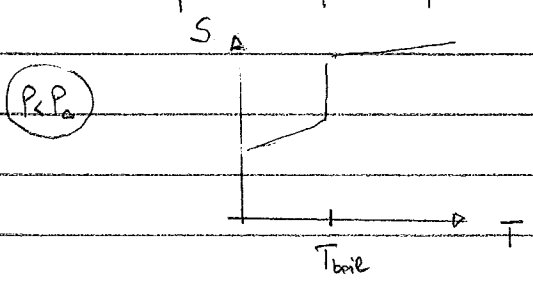
becomes a nonanalytic function of one of its parameters (i.e. F or some of its derivatives become singular/discontinuous) in the thermodynamic limit (particle # to infinity).

For a finite system F is always analytic because $\omega > Z > 0$ ($\Rightarrow F$ cannot be singular) and e.g. $\frac{\partial Z}{\partial T} = \sum_{\Gamma} \frac{E(\Gamma)}{kT^2} e^{-E(\Gamma)/kT}$ convergent sum of analytic fns

Phase transitions are usually divided into two categories:

- (1) First order phase transitions: these are phase transitions where the free energy is continuous, but a first derivative is discontinuous. At the transition there is phase coexistence

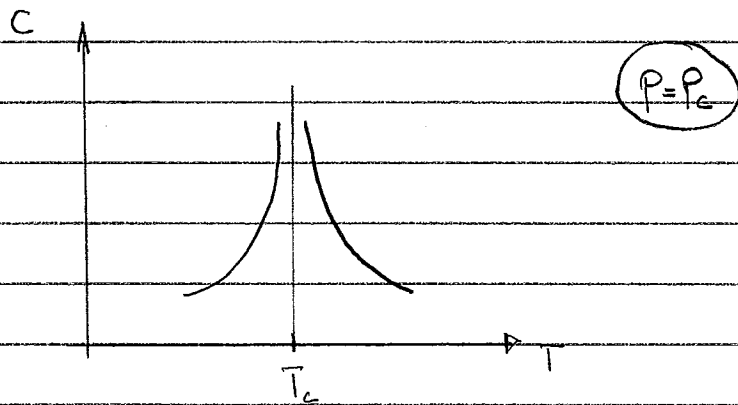
Example: liquid-vapour transition in water



(ii) SECOND ORDER PHASE TRANSITIONS:

These are characterized by a divergence in one of the higher derivatives ("susceptibilities") of the free energy

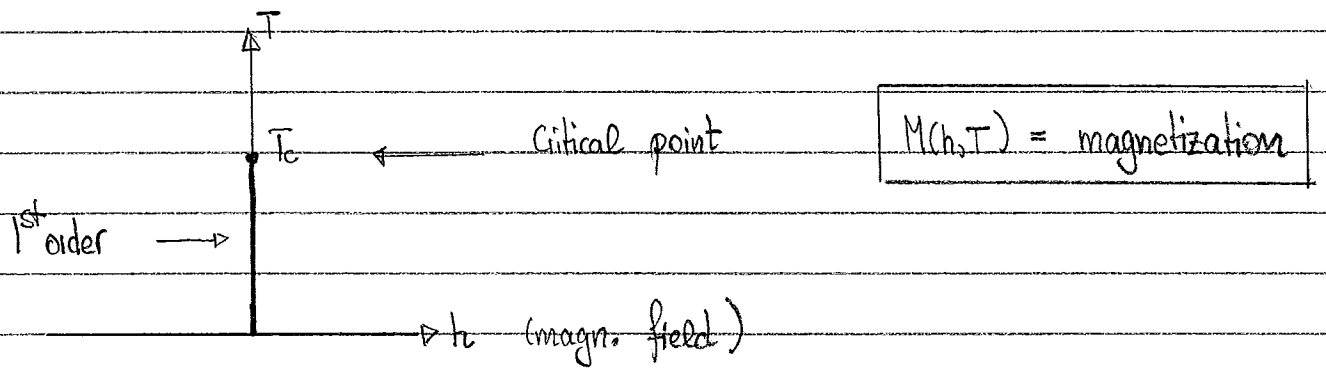
Example: the critical point in the liquid-gas transition



CRITICAL BEHAVIOUR

Close to a critical point thermodynamic functions display power-law behaviours characterized by critical exponents

EXAMPLE: PARAMAGNET \rightarrow FERROMAGNET transition in Fe or Ni



At $T < T_c$ the magnetization per site in zero field is nonzero

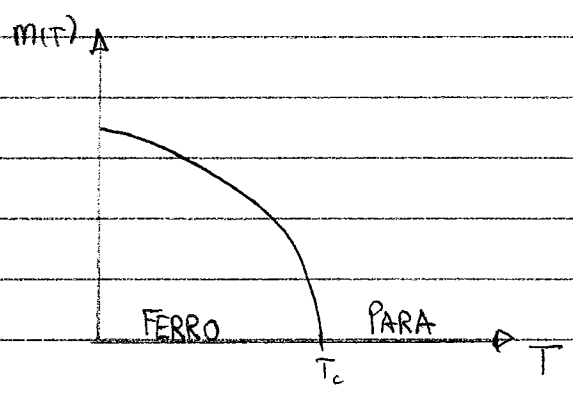
① ORDER PARAMETER

This is a thermodyn. function that is different in the various phases and can be used to characterize the transition

$$m(T) = \lim_{h \rightarrow 0} \frac{1}{V} M(h, T)$$

$T \approx T_c$

$$m(T) \propto \begin{cases} 0 & T > T_c \\ |t|^\beta & T < T_c \end{cases} \quad t = \frac{T - T_c}{T_c}$$



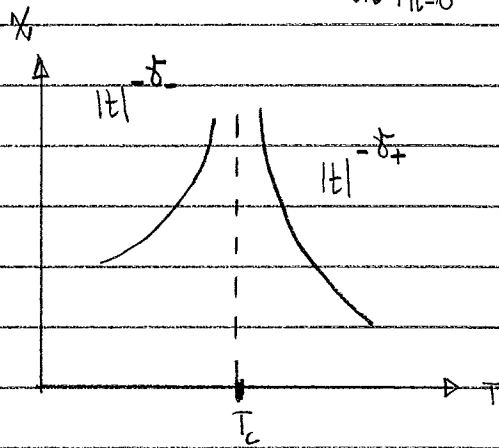
β is a critical exponent

2

SUSCEPTIBILITIES

AT THE CRITICAL point the system is very sensitive to external perturbations. The singularity in the response of the order parameter to a field "conjugate" to it is characterized by a critical exponent δ .

For our magnet $\chi_{\pm}(T) = \left. \frac{\partial}{\partial h} \right|_{h=0} \frac{1}{V} M(h, T) \propto |t|^{-\delta_{\pm}}$

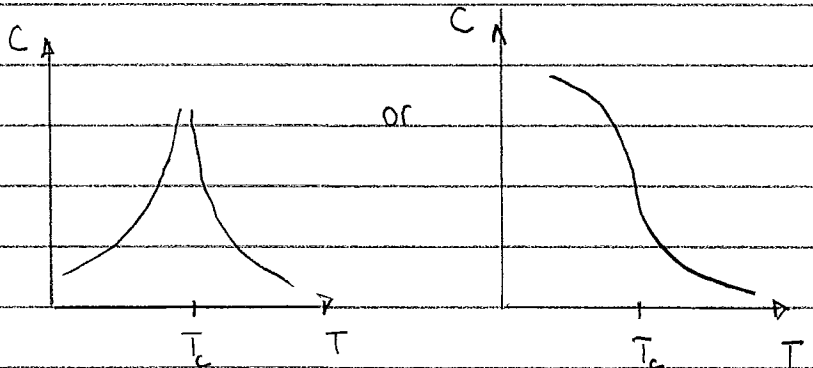


3

HEAT CAPACITY

$$C(T) \equiv -T \frac{\partial^2 F}{\partial T^2} \propto \begin{cases} A_+ |t|^{-\alpha_+} \\ A_- |t|^{-\alpha_-} \end{cases}$$

This may look like



depending on the signs of A_{\pm}

"UNIVERSALITY:"

The critical exponents are insensitive to microscopic details of the system under consideration and are characteristic of the critical point. A consequence of this is that completely different systems can exhibit the same critical behaviour.

9.2

LANDAU THEORY OF PHASE TRANSITIONS

This is a general approach to phase transitions that

(i) is phenomenological in nature and deals only with macroscopic quantities

(ii) applies only to the neighbourhood of a critical point, where the order parameter is small

STEP 1: Identify the order parameter(s) characterizing the transition

STEP 2: Form a "coarse-grained" order parameter density $\phi(\vec{r})$.
Think of this as a magnetic moment density, averaged over atomic distances. This is a continuum field.

STEP 3: Write the partition function as a path integral

$$Z = \int \mathcal{D}\phi(\vec{r}) e^{-\int d^D r F[\phi, h]}$$

where $F[\phi]$ is the (unknown) free energy density of the system we are considering and h some external field that couples to the order parameter field (i.e. a "source"), i.e. $\left. \frac{\delta F}{\delta \phi} \right|_{\phi=0} = -h$

STEP 4: We know that by construction $\phi(\vec{r})$ is small close to our critical point \Rightarrow we can expand F around $\phi = 0$:

$F[\phi] \approx \text{const} - h\phi + \alpha_2 \phi^2 + \alpha_3 \phi^3 + \alpha_4 \phi^4 + \dots$ $+ \frac{1}{2} \nabla \phi ^2 + \dots$
--

Here the coefficient of $|\nabla \phi|^2$ is fixed to be $\frac{1}{2}$ by convention (this fixes a scale for ϕ)

Here we have assumed that ϕ is real, but in general it could be complex and have several components.

The coefficients α_n are a priori all functions of temperature.

STEP 5: Use symmetries and the fact that we are interested in the vicinity of a critical point to constrain the α_n .

(i) If we truncate our expansion at order ϕ^4 then we must have $\alpha_4 > 0$ for thermodynamic stability (if $\alpha_4 < 0$ then $F[\phi]$ is unbounded from below and can become infinitely negative)

(ii) If we know that our system is invariant under some symmetry operation, e.g.

$$\phi \rightarrow -\phi$$

then $F[\phi]$ must respect this symmetry. A ferromagnet has this symmetry in absence of a magnetic field because of time-reversal invariance.

$$\Rightarrow \text{in this case } \alpha_3 = 0$$

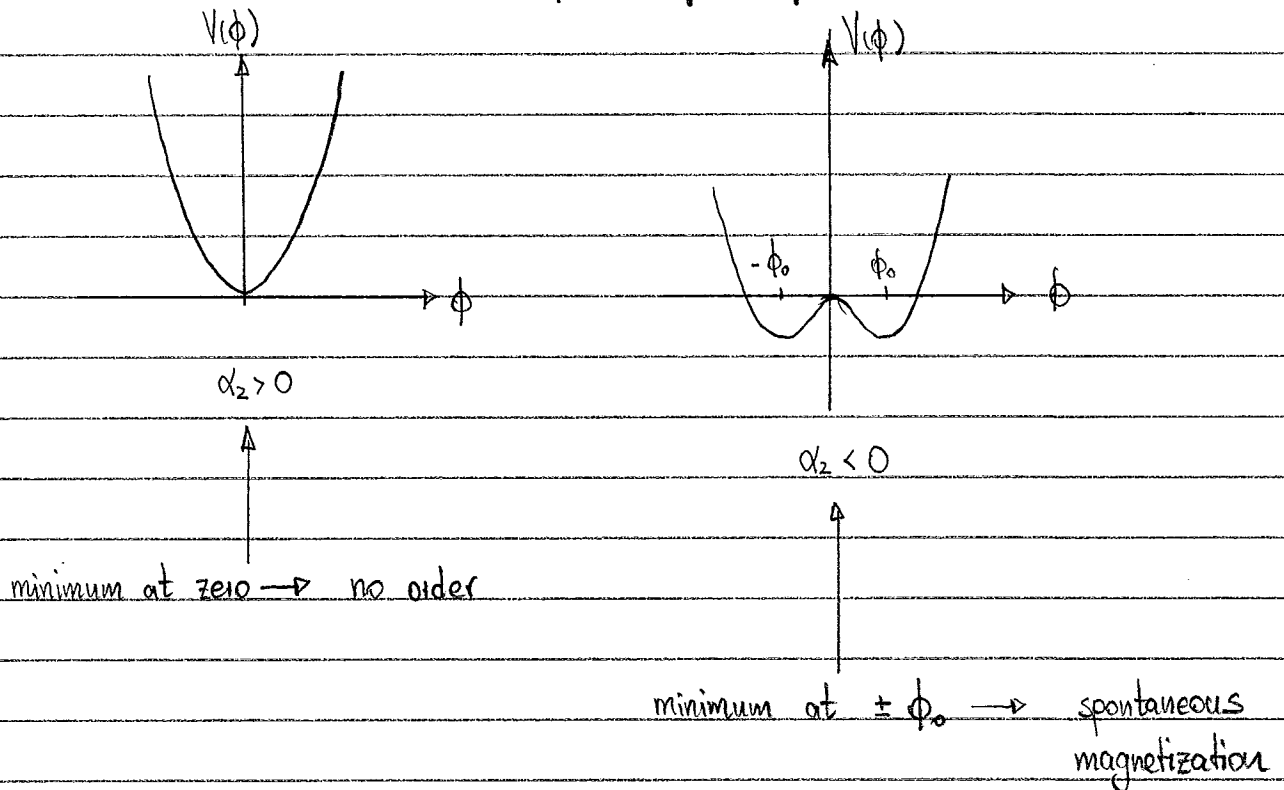
(iii) Consider $F[\phi] = \frac{1}{2} |\nabla\phi|^2 + \alpha_2 \phi^2 + \alpha_4 \phi^4$.

As $Z = \int \mathcal{D}\phi e^{-S[\phi]} e^{-\int d^d r F[\phi]}$ the vicinity of the minimum

of F will contribute most to Z . We will see in a moment that this minimum corresponds to \vec{r} -independent order parameters. In order to understand the nature of

the phase transition we therefore can simply look at the minima of the potential

$$V(\phi) = \alpha_2 \phi^2 + \alpha_4 \phi^4$$



\Rightarrow The phase transition corresponds to α_2 changing sign at T_c

So for $T \approx T_c$ we have (by Taylor expanding)

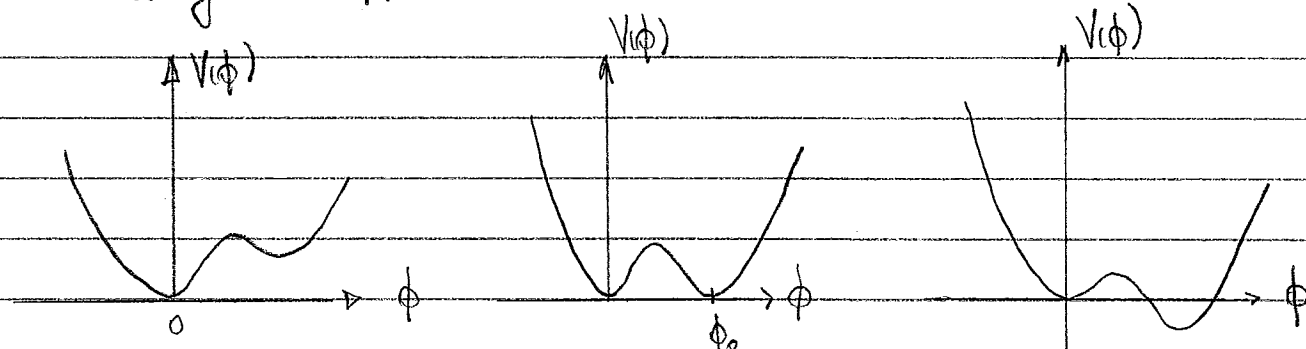
$\alpha_2 = At + \mathcal{O}(t^2)$	$t = \frac{T - T_c}{T_c}, A > 0$
------------------------------------	----------------------------------

Note: α_4 is also t -dependent but $\alpha_4(t) = \alpha_4(0) + \dots$
 where $\alpha_4(0) > 0$ always dominates.

(iv) If we have $\alpha_3 < 0$ the phase transition is generically 1st order

$$F[\phi] = \frac{1}{2} |\nabla\phi|^2 + \underbrace{\alpha_2\phi^2 + \alpha_3\phi^3 + \alpha_4\phi^4}_{V(\phi)}$$

The minima of F are obtained by \vec{r} -independent fields
→ can understand the nature of the transition by looking at $V(\phi)$



$\alpha_2 > 0$

$\alpha_3 < 0, \alpha_4 > 0$

minimum at $\phi = 0 \Rightarrow$ no order

α_2 smaller

$\phi \neq 0$

order

order parameter jumps
from $\phi = 0$ to $\phi = \phi_0$

9.2.1.

MEAN-FIELD THEORY

In general the Landau field theory is still difficult to analyze \Rightarrow make further approximations

A saddle-point approximation takes into account the most likely configuration $\phi(\vec{r})$ (i.e. the configuration that minimizes $F[\phi]$)

$$\frac{\delta F[\phi, h]}{\delta \phi(\vec{r})} = 0$$

$$\rightarrow \boxed{-\vec{\nabla}^2 \phi(\vec{r}) + 2\alpha_2 \phi(\vec{r}) + 4\alpha_4 \phi^3(\vec{r}) - h = 0} \quad (*)$$

For $h=0$ the \vec{r} -independent solutions to (*) are

$$\phi = 0 \quad \text{and} \quad \phi = \pm \sqrt{-\frac{\alpha_2}{2\alpha_4}}$$

* $\phi(\vec{r}) = 0$ is the minimum of F for $\alpha_2 > 0$ ($T > T_c$)
because it minimizes both $V(\phi) = \alpha_2 \phi^2 + \alpha_4 \phi^4 \geq 0$
and $|\vec{\nabla} \phi|^2 \geq 0$

This corresponds to the disordered (high temperature) phase.

* $\phi(\vec{r}) = \pm \sqrt{-\frac{\alpha_2}{2\alpha_4}}$ is the minimum for $\alpha_2 < 0$ ($T < T_c$)

because it minimizes both $V(\phi)$ and $|\vec{\nabla} \phi|^2 \geq 0$.

This corresponds to the ordered (low temperature) phase.

CRITICAL EXPONENTS IN THE SADDLE-POINT (MEAN-FIELD) APPROXIMATION

(i) For $t < 0$ we have ($\alpha_2 = At$) for the order parameter

$$\phi_0 = \pm \sqrt{\frac{A}{2\alpha_4} |t|}^{1/2}$$

\Rightarrow the critical exponent $\beta = 1/2$

(ii) Differentiating (*) with respect to h gives

$$2\alpha_2 \frac{\partial \phi}{\partial h} + 12\alpha_4 \frac{\partial \phi}{\partial h} \phi^2 = 1$$

(where we assume \vec{r} -indep. solutions ϕ)

$$\Rightarrow \chi = \frac{\partial \phi}{\partial h} = \frac{1}{2\alpha_2 + 12\alpha_4 \phi^2} \quad \text{magnetic susceptibility}$$

Using that $\alpha_2 = At$ and $\phi_0^2 = \frac{A}{2\alpha_4} |t|$

$$\Rightarrow \chi = \begin{cases} \frac{1}{2At} & t > 0 \\ \frac{1}{4A|t|} & t < 0 \end{cases} \Rightarrow \gamma_{\pm} = 1$$

(iii) Heat capacity $C(T, h=0) = -T \frac{\partial^2 F}{\partial T^2}$

Using $\phi \approx \begin{cases} 0 & t > 0 \\ \phi_0 & t < 0 \end{cases}$ we have $F \approx \begin{cases} 0 & t > 0 \\ -\frac{A^2 t^2}{4\alpha_4} & t < 0 \end{cases}$

$$\Rightarrow C(T, h=0) \approx \begin{cases} 0 & t > 0 \\ \frac{A^2 T_c}{2\alpha_4} & t < 0 \end{cases}$$

This has a finite jump at $T_c \Rightarrow$ the critical exponent

$$\alpha = 0$$

The final exponent we want to determine is the correlation length exponent ν . It is defined by

$$\langle \phi(\vec{r}) \phi_{(0)} \rangle \sim e^{-|\vec{r}|/\xi} \quad \text{for } |\vec{r}| \rightarrow \infty$$

where the correlation length $\xi \propto |t|^{-\nu}$

typically diverges at the critical point.

We take $F = \frac{1}{2} |\nabla \phi|^2 + \alpha_2 \phi^2 + \alpha_4 \phi^4$ and determine ν in the Gaussian approximation

(i) disordered phase $t > 0$: here $\alpha_2 > 0$ and we drop the ϕ^4 term.

$$\rightarrow \langle \phi(\vec{r}) \phi_{(0)} \rangle = \frac{1}{N} \int \mathcal{D}\phi \phi(\vec{r}) \phi_{(0)} e^{-\int d^D \vec{r} \left[\frac{1}{2} |\nabla \phi|^2 + \alpha_2 \phi^2 \right]}$$

Trick: make h \vec{r} -dependent and use it as a source:

$$\rightarrow \langle \phi(\vec{r}) \phi_{(0)} \rangle = \frac{1}{N} \frac{\delta}{\delta h(\vec{r})} \frac{\delta}{\delta h_{(0)}} \Big|_{h=0} \int \mathcal{D}\phi e^{-\int d^D \vec{r} \left[\frac{1}{2} |\nabla \phi|^2 + \alpha_2 \phi^2 - h(\vec{r}) \phi(\vec{r}) \right]}$$

FOURIER TRANSFORM: $\phi(\vec{r}) = \int \frac{d^D \vec{p}}{(2\pi)^D} e^{-i\vec{p} \cdot \vec{r}} \tilde{\phi}(\vec{p})$

$$\rightarrow \int d^D \vec{r} F[\phi(\vec{r}), h(\vec{r})] = \int \frac{d^D \vec{p}}{(2\pi)^D} \left[\left(\frac{\vec{p}^2}{2} + \alpha_2 \right) \tilde{\phi}(\vec{p}) \tilde{\phi}(-\vec{p}) - \tilde{h}(\vec{p}) \tilde{\phi}(-\vec{p}) \right] \equiv \Gamma$$

Now redefine fields: $\tilde{\Psi}(\vec{p}) = \tilde{\phi}(\vec{p}) - \frac{\tilde{h}(\vec{p})}{\vec{p}^2 + 2\alpha_2}$

$$\begin{aligned} \text{Then } \tilde{\Psi}(\vec{p}) \tilde{\Psi}(-\vec{p}) &= \tilde{\phi}(\vec{p}) \tilde{\phi}(-\vec{p}) - \frac{\tilde{\phi}(\vec{p}) \tilde{h}(-\vec{p})}{\vec{p}^2 + 2\alpha_2} - \frac{\tilde{\phi}(-\vec{p}) \tilde{h}(\vec{p})}{\vec{p}^2 + 2\alpha_2} \\ &\quad + \frac{\tilde{h}(\vec{p}) \tilde{h}(-\vec{p})}{(\vec{p}^2 + 2\alpha_2)^2} \end{aligned}$$

This allows us to rewrite

$$\Gamma = \int \frac{d^D \vec{p}}{(2\pi)^D} \left\{ \tilde{\varphi}(\vec{p}) \tilde{\varphi}(-\vec{p}) \left(\frac{\vec{p}^2}{2} + \alpha_2 \right) - \frac{1}{2} \frac{\tilde{h}(\vec{p}) \tilde{h}(-\vec{p})}{\vec{p}^2 + 2\alpha_2} \right\}$$

As the field redefinition is a "constant shift" we have

$$\mathcal{D}\phi \equiv \mathcal{D}\varphi$$

Hence our generating functional is

$$Z[h] = \int \mathcal{D}\tilde{\varphi} e^{-\int \frac{d^D \vec{p}}{(2\pi)^D} \tilde{\varphi}(\vec{p}) \tilde{\varphi}(-\vec{p}) \left(\frac{\vec{p}^2}{2} + \alpha_2 \right)} \\ \times e^{\frac{1}{2} \int \frac{d^D \vec{p}}{(2\pi)^D} \frac{\tilde{h}(\vec{p}) \tilde{h}(-\vec{p})}{\vec{p}^2 + 2\alpha_2}}$$

But the 1st factor is the h -independent constant N !

Fourier transforming back $\tilde{h}(\vec{p}) = \int d^D \vec{r} e^{i\vec{p}\cdot\vec{r}} h(\vec{r})$ gives

$$Z[h] = N e^{\frac{1}{2} \int d^D \vec{r} d^D \vec{r}' h(\vec{r}) h(\vec{r}') G(\vec{r}, \vec{r}')}$$

$$G(\vec{r}, \vec{r}') = \int \frac{d^D \vec{p}}{(2\pi)^D} e^{i\vec{p}\cdot(\vec{r}-\vec{r}')} \frac{1}{\vec{p}^2 + 2\alpha_2}$$

$$\text{Thus } \langle \phi(\vec{r}) \phi(\vec{0}) \rangle = \frac{\delta}{\delta h(\vec{r})} \frac{\delta}{\delta h(\vec{0})} \Big|_{h=0} Z[h]$$

$$\equiv G(\vec{r}) \propto \frac{e^{-|\vec{r}| \sqrt{2\alpha_2}}}{|\vec{r}|^{\frac{D-1}{2}}} \quad \text{for } |\vec{r}| \rightarrow \infty$$

which gives

$$\xi \equiv \frac{1}{\sqrt{2\alpha_2}} \propto \frac{1}{|\vec{r}|^{1/2}} \quad \text{i.e. } \nu = \frac{1}{2}$$

(ii) In the ordered phase $t < 0$ we expand $F[\phi]$

around the minimum at $\phi_0 = \sqrt{\frac{-\alpha_2}{2\alpha_4}}$:

$$V(\phi) = \alpha_2 \phi^2 + \alpha_4 \phi^4 \approx \alpha_2 \phi_0^2 + \alpha_4 \phi_0^4 + \frac{1}{2} (2\alpha_2 + 12\alpha_4 \phi_0^2) (\phi - \phi_0)^2 + \dots$$

Drop the constant and define

$$\delta\phi \equiv \phi - \phi_0$$

$$\text{Then } F[\delta\phi] \approx \left[\frac{1}{2} |\vec{\nabla} \delta\phi|^2 + \tilde{\alpha}_2 (\delta\phi)^2 \right]$$

$$\tilde{\alpha}_2 = -2\alpha_2 > 0 \quad (\text{recall that } t < 0)$$

Copying the calculation in the ordered phase gives

$$\langle \delta\phi(\vec{r}) \delta\phi(0) \rangle \sim \frac{e^{-|\vec{r}| \sqrt{-4\alpha_2}}}{|\vec{r}|^{\frac{D-1}{2}}}$$

and $\xi \sim \frac{1}{|t|^{1/2}}$ as well.

$\langle \delta\phi \delta\phi \rangle$ is the connected correlator :

$$= \langle (\phi(\vec{r}) - \phi_0)(\phi(0) - \phi_0) \rangle = \underbrace{\langle \phi(\vec{r}) \phi(0) \rangle}_{\phi_0} - \underbrace{\langle \phi(\vec{r}) \rangle}_{\phi_0} \phi_0 - \underbrace{\langle \phi(0) \rangle}_{\phi_0} \phi_0 + \phi_0^2$$

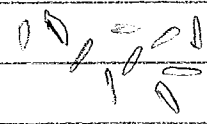
9.2.4

Other Examples of Phase Transitions

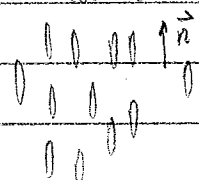
(1) ISOTROPIC - NEMATIC TRANSITION IN LIQUID CRYSTALS

liquid crystals are fluids of rod-like molecules

High temperatures : - centers of mass randomly distributed
- rods are randomly oriented



Low temperatures : in the nematic phase the rods spontaneously align along a common axis



What is the order parameter?

Associate a unit vector $\vec{n}(\vec{r})$ with a molecule at \vec{r} . How about taking $\langle \vec{n}(\vec{r}) \rangle$ as our order parameter? No good as the molecules are invariant under inversion $\vec{n} \rightarrow -\vec{n}$. Try something quadratic in n_i , e.g. $\langle n_i n_j \rangle$. But this is non-zero even for randomly oriented molecules:

$\vec{n} = \begin{pmatrix} \sin\theta \cos\phi \\ \sin\theta \sin\phi \\ \cos\theta \end{pmatrix}$ for a single molecule

$\langle n_i n_j \rangle = \frac{1}{4\pi} \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin\theta n_i n_j = \frac{1}{3} \delta_{ij}$

→ use $Q_{ij} = \langle n_i n_j \rangle - \frac{1}{3} \delta_{ij}$

This is zero at high T, but if the molecules are aligned in the z-direction $\vec{n} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

$Q = \begin{pmatrix} -1/3 & & \\ & -1/3 & \\ & & 2/3 \end{pmatrix}$

Now that we have an order parameter, how do we find the free energy?

The high- T phase (and therefore F) is invariant under rotations of molecules i.e. under

$$a \rightarrow R a R^T$$

$$\Rightarrow \text{by } \boxed{F[a] = \alpha_2 \text{Tr}[a^2] + \alpha_3 \text{Tr}[a^3] + \alpha_4 (\text{Tr}[a^2])^2 + \dots}$$

The presence of a cubic term suggests that the transition is 1st order, as is indeed observed experimentally.

(2) SUPERFLUID TRANSITION IN WEAKLY INTERACTING BOSONS

Recall the 2nd quantized form of the Hamiltonian

$$H = \int d\vec{r} \left\{ \frac{\hbar^2}{2m} \nabla^2 c(\vec{r}) + \frac{u}{2} c^\dagger(\vec{r}) c^\dagger(\vec{r}) c(\vec{r}) c(\vec{r}) \right\}$$

In the superfluid phase we have

$$\langle c(\vec{p}=0) \rangle \propto \sqrt{N_0} \Rightarrow c(\vec{r}) = \frac{1}{\Omega^{3/2}} \int e^{-i\vec{p}\cdot\vec{r}} c(\vec{p}) \text{ has a}$$

$\langle \cdot \rangle$ expectation value in the superfluid phase, i.e.

$\psi(\vec{r}) = \langle c(\vec{r}) \rangle \neq 0$ in the superfluid phase. Then

$$\boxed{F[\psi] = \int d\vec{r} \left\{ \frac{\hbar^2}{2m} |\nabla\psi|^2 + V(\vec{r}) |\psi(\vec{r})|^2 + \frac{u}{2} |\psi|^4 \right\}}$$

where we have allowed for an external potential $V(\vec{r})$. Note that ψ is a complex order parameter.