

I. The Ornstein-Zernike correlation function:

We have seen previously 2 main concrete examples relating thermodynamic averages, their behavior near T_c , and at least at mean-field level we have tried to fill up with physical content the $\alpha, \beta, \gamma, \delta$ critical exponents. However, excepting the study made at Goldstone mode, we do not know much about correlation functions, and we not quite understand why η is defined in a such a strange manner: $G(r) \sim 1/r^{d-2+\eta}$. This gap we try to fill up now by the study of the Ornstein-Zernike correlation function (for which Zernike won Nobel prize.)

1. The Ornstein-Zernike Equation:

Let us consider for simplicity density-density correlations.

We use particle number density:

$$(513) \quad n(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i); \quad N = \text{number of particles, } \vec{r}_i \text{ their position.}$$

The average $\langle n(\vec{r}) \rangle$ is considered as

$$(514) \quad \langle n(\vec{r}) \rangle = \frac{N}{V} = n; \quad (\text{homogenous system})$$

The density-density correlation function is defined as

$$(515) \quad \Gamma(\vec{r}, \vec{r}') = \langle n(\vec{r}) n(\vec{r}') \rangle - \langle n(\vec{r}) \rangle \langle n(\vec{r}') \rangle = \langle n(\vec{r}) n(\vec{r}') \rangle - n^2;$$

In the study of the first term one observes that

$$(516) \quad \langle n(\vec{r}) n(\vec{r}') \rangle = \sum_{i,j=1}^N \langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \rangle = \sum_i \langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_i) \rangle + \sum_{i \neq j} \langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \rangle.$$

In the first term $\delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) = \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_i)$ holds, hence the first term with $i=j$ will be

$$(517) \quad \sum_i \langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_i) \rangle = \delta(\vec{r} - \vec{r}') \sum_i \langle \delta(\vec{r} - \vec{r}_i) \rangle = n \delta(\vec{r} - \vec{r}').$$

The second term, being complicated, $\langle n(\vec{r}) \rangle = n$ will be denoted by:

$$(518) \quad \sum_{i \neq j} \langle \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \rangle = n^2 (G(\vec{r} - \vec{r}') - 1), \quad \text{where } G(\vec{r} - \vec{r}')$$

has a such an argument because of homogeneity and isotropy, and it is an unknown function. Introducing (517, 518) in (515) we finds:

$$(519) \quad \Gamma(\vec{r} - \vec{r}') = n \delta(\vec{r} - \vec{r}') + n^2 G(\vec{r} - \vec{r}')$$

Evidently, from (519) the first term describes the contact part of the correlation function, and $G(\vec{r} - \vec{r}')$ describes the whole distance dependence. Now we Fourier transform the expression by multiplying it with $e^{i\vec{q} \cdot \vec{r}}$ and integrating it $\int \frac{1}{V} d\vec{r}$, and taking \vec{r}' in origine.

$$(520) \quad \frac{1}{V} \int \Gamma(r) e^{-i\vec{q} \cdot \vec{r}} d\vec{r} = \Gamma(\vec{q}); \quad \frac{1}{V} \int \delta(\vec{r}) e^{-i\vec{q} \cdot \vec{r}} d\vec{r} = 1; \quad \frac{1}{V} \int G(\vec{r}) e^{-i\vec{q} \cdot \vec{r}} d\vec{r} = G(\vec{q})$$

and the equation becomes:

(521): $\Gamma(\vec{q}) = n + n^2 G(\vec{q})$

Now let us suppose that we are studying a system in which a phase transition occurs at T_c . Since in this case for $T \rightarrow T_c$ correlations up to $\vec{r} \rightarrow \infty$ occur, and to $\vec{r} \rightarrow \infty$, in the Fourier transformed variable $\vec{q} = \vec{k} \rightarrow 0$ corresponds $\Gamma(\vec{k})$ for $\vec{k} \rightarrow 0$ must diverge, and this can originate only from $G(\vec{k}) \rightarrow \infty$ at $\vec{k} \rightarrow 0$. Hence one has

(522) $G(\vec{k}) \rightarrow \infty$ for $\vec{k} \rightarrow 0$ at $T = T_c$

Furthermore, for T placed far away from T_c , the $G(\vec{k})$ value can be rather small, hence one observes that

(523) $|G(\vec{k})| \in (0, +\infty)$

So the $G(\vec{k})$ function values cover an extremely large domain. Because of this reason is extremely difficult to suppose something realistic about $G(\vec{k})$ in order to advance the problem.

In these circumstances, Ornstein and Zernike came up with an extremely constructive idea. Namely: if $G(\vec{k})$ is unknown and because its values cover a large domain, hence it is hard to approximate let us introduce instead of it another unknown function $C(\vec{k})$ which is such chosen to be much more easy to approximate. This is achieved in such a way, that one chooses the equation which connects $C(\vec{k})$ to $G(\vec{k})$ in a such a form to provide function values for $C(\vec{k})$ in a much restricted region. This equation in \vec{r} space has the form:

(524) $G(\vec{r} - \vec{r}') = C(\vec{r} - \vec{r}') + n \int C(\vec{r} - \vec{r}'') G(\vec{r}'' - \vec{r}') d^3r''$

This is the Ornstein-Zernike equation. As observed, inside the integral is a convolution, hence under Fourier transform one gets

(525) $G(\vec{k}) = C(\vec{k}) + n C(\vec{k}) G(\vec{k})$; hence

(526) $C(\vec{k}) = \frac{G(\vec{k})}{1 + n G(\vec{k})}$

Now one sees that $|C(\vec{k})| \in (0, \frac{1}{n})$ so a tiny region, because if $G(\vec{k}) \rightarrow 0 \Rightarrow C(\vec{k}) \rightarrow 0$, but if $G(\vec{k}) \rightarrow \infty \Rightarrow C(\vec{k}) \rightarrow \frac{1}{n}$. Since according to (522) G diverges at $\vec{k} \rightarrow 0$, it results that

(527) $C(\vec{k} \rightarrow 0) = \frac{1}{n}$

But now one observes, that the $\vec{k} = 0$ Fourier component means the average of the starting function in \vec{r} space. Indeed

(528) $C(\vec{k}) = \frac{1}{V} \int C(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d^3r \Rightarrow C(\vec{k} = 0) = \frac{1}{V} \int C(\vec{r}) d^3r = \langle C(\vec{r}) \rangle$

This means that the average of $C(\vec{r})$ is (see (527)):

(529) $\langle C(\vec{r}) \rangle = \frac{1}{n}$; small number

This means that from physical point of view $C(\vec{r})$ describes short range correlations. Often is said that these are "direct" correlations, namely the correlations of the particle with its nearest-neighbor neighborhood. Usually the range of $C(\vec{r})$ is roughly the range of $U(\vec{r})$ the interaction potential. And since in many-body systems the screening is extremely strong, and $U(\vec{r})$ is

is of short-range type, it results that $C(\vec{r})$ is also of short-range type.

2. The $C(\vec{r})$ direct correlation function:

Based on the above information, the following image can be constructed about the Ornstein-Zernike correlations: it considers the correlation function $G(\vec{r})$ (hence also $\Gamma(\vec{r})$) to be built up from a concatenation (succession) of short-range correlations. So explicit long range contributions are not present in it. But long-range correlation exists, built up exclusively from the succession of short-range correlations (see Fig. 34). From the point of view of the information transmission from A to B (B is placed at high distance from A) this looks like a row of persons A, A_1, A_2, \dots, A_n, B , each of this communicating only with his nearest neighbor. If the long-range correlation appears indeed in this manner, one says today, that the correlation is of Ornstein-Zernike type.



Fig 34.

each of this communicating only with his nearest neighbor. If the long-range correlation appears indeed in this manner, one says today, that the correlation is of Ornstein-Zernike type.

Approximating $C(\vec{r})$:

Since the $C(\vec{r})$ function values are placed on a small domain, namely $k(\vec{r}) \in (0, \frac{1}{\lambda})$ it is easy to make approximations for it. $C(\vec{r})$ takes its maximum value at $\vec{r}=0$, so in order to have an image about its behavior, one can take the Taylor expansion of $C(\vec{r})$ around $\vec{r}=0$, and to stop in this expansion at a relatively small order (note that the emerging terms in the expansion are smaller and smaller if the expansion order increases).

$$(530) \quad C(\vec{r}) = \frac{1}{V} \int C(\vec{r}') e^{-i\vec{k} \cdot \vec{r}'} d^3r' = C(0) + \vec{k} \frac{\partial C(\vec{r})}{\partial \vec{r}} \Big|_{\vec{r}=0} + \vec{k}^2 \frac{1}{2!} \frac{\partial^2 C(\vec{r})}{\partial \vec{r}^2} + \dots$$

$$= C(0) + \vec{k} C_1(n,T) + \vec{k}^2 C_2(n,T) + \dots$$

where

$$(531) \quad C_l(n,T) = \frac{1}{l!} \frac{\partial^l C(\vec{r})}{\partial \vec{r}^l} \Big|_{\vec{r}=0} ; \quad \frac{\partial}{\partial \vec{r}} = \nabla_{\vec{r}}$$

From the other hand, in $C(\vec{r})$, the different \vec{r} orders of the expansion can be understood to appear from the Taylor expansion of $e^{-i\vec{k} \cdot \vec{r}}$ under the integral in (530)

$$(532) \quad e^{-i\vec{k} \cdot \vec{r}} = 1 + (-i\vec{k} \cdot \vec{r}) + \frac{1}{2!} (-i\vec{k} \cdot \vec{r})^2 + \dots$$

Hence:

$$(533) \quad C_l(n,T) \vec{k}^l = \frac{1}{V} \int C(\vec{r}') \frac{1}{l!} (-i\vec{k} \cdot \vec{r}')^l \left[\underbrace{\sin \theta d\theta d\varphi r^2 dr}_{d^3r \text{ in polar coordinates}} \right]$$

Fixing the z axis along the \vec{k} direction (note that \vec{k} is fixed for the integral in (533)), taking into account that $\vec{k} \cdot \vec{r} = kr \cos \theta$, taking isotropic systems, hence $C(\vec{r}) = C(|\vec{r}|) = C(r)$; $r = |\vec{r}|$, one observes that for odd value of l one has an odd r function under the integral which is integrated on a symmetric domain, so $C_{2m+1} = 0$, one obtains

$$(534) \quad C_{2m}(n,T) = \frac{1}{(2m)!} \frac{1}{V} \int C(r) [-i k r \cos \theta]^{2m} \sin \theta d\theta d\varphi r^2 dr ; m \geq 1,$$

$$C_{2m+1}(n,T) = 0, \quad C_0 = C(0) = \frac{1}{\rho}$$

Since $C(\vec{r})$ is of short-range type, the integrals from C_{2m} in (534) do not diverge, hence the leading order contribution in $C(\vec{r})$ after $C(0)$ in (530) will be the κ^2 term. Note that $C_2; m=1$, because of $(-i)^2 = -1$ will be negative, consequently, we can write:

$$(535) \quad C(\vec{r}) = C(0) + \kappa^2 C_2(n, T) = C_0(n, T) + \kappa^2 C_2(n, T)$$

Using now (525) we have

$$(536) \quad G(\vec{r}) = \frac{C(\vec{r})}{1 - n C(\vec{r})}, \text{ then from (521), the complete correlation function } \Gamma(\vec{r}) \text{ becomes:}$$

$$(537) \quad \Gamma(\vec{r}) = n + n^2 G(\vec{r}) = n + \frac{n^2 C(\vec{r})}{1 - n C(\vec{r})} = \frac{n}{1 - n C(\vec{r})}$$

Now using (535) and taking into account that $C_2 = -|C_2|$, i.e.

$$(538) \quad C(\vec{r}) = C_0(n, T) - \kappa^2 |C_2(n, T)|,$$

for the full correlation function $\Gamma(\vec{r})$ from (537) one finds:

$$(539) \quad \Gamma(\vec{r}) = \frac{n}{1 - n [C_0(n, T) - \kappa^2 |C_2(n, T)|]} = \frac{n}{\frac{1 - n C_0(n, T)}{n |C_2(n, T)|^{-1}} + \kappa^2}$$

where $C_0(n, T) = C(0)$ as seen from (535).

Denoting by:

$$(540) \quad a^2(n, T) = \frac{1 - n C_0(n, T)}{n |C_2(n, T)|^{-1}}; \text{ note that } C_0(n, T) \leq \frac{1}{n}$$

one observes that for $T \rightarrow T_c$, one has $C_0(n, T) = C(0) = \frac{1}{n}$, hence

$$(541) \quad \lim_{T \rightarrow T_c} a(n, T) = 0; \text{ Denoting by } Q = |C_2(n, T)|^{-1} = \text{constant at } T_c \text{ the numerator in (539), one obtains}$$

$$(542) \quad \Gamma(\vec{r}) = \frac{Q}{a^2 + \kappa^2} \quad \begin{array}{l} a=0 \text{ if } T=T_c \\ Q = \text{constant around } T_c, \text{ and nonzero.} \end{array}$$

The obtained correlation function in (542) is the Ornstein-Zernike correlation function.

Interpretation of the result:

If we analyze the critical exponent η , it is defined as $\Gamma(\vec{r}) \sim \frac{1}{r^{d-2+\eta}}$, $t=0$, (i.e. $T=T_c$). However, we have shown the Fourier transform of the function $1/r^{d-2+\eta}$ (see Lecture 6, Goldstone modes, Eq (331)) that Hence one has at the definition of η :

$$(543) \quad \Gamma(\vec{r}) \sim \frac{1}{r^{d-2+\eta}} \Rightarrow \Gamma(\vec{r}) \sim \frac{1}{\kappa^{2-\eta}}; t=0$$

In the light of (542), taking into account that (541) holds and $a=0$ for $t=0$, the Ornstein-Zernike correlation function gives

$$(544) \quad \Gamma(\vec{r}) \sim \frac{1}{\kappa^2}; t=0 \Rightarrow \eta=0,$$

Hence for the Ornstein-Zernike correlation function one has

$$(546) \quad \boxed{\eta=0}$$

Now it is possible to understand why we define the critical exponent as $\Gamma(\vec{k}) \sim \frac{1}{\epsilon^{d-2+\eta}}$. The reason is that in this scheme, $\eta=0$ means Ornstein-Zernike behavior. And if one has $\eta \neq 0$, one automatically knows that the behavior is not of Ornstein-Zernike type. Furthermore, the magnitude of η shows how far we are placed from the Ornstein-Zernike behavior.

Critical opalescence:

The critical opalescence is a phenomenon which occurs in a critical region (i.e. $\epsilon \rightarrow \infty$) when we approach T_c , and the system is a transparent gas or liquid. As the critical point is approached the density fluctuations increase, become of the size comparable to the wavelength of light [700nm (red) \rightarrow 400nm (violet)] and the light is scattered. This causes the normally transparent system to appear cloudy. This phenomenon is the critical opalescence. If the system is a mixture, at and around T_c , the components separate by the strong fluctuations, and the phenomenon of the critical opalescence becomes more easy to be observed.

At the mathematical level this is connected to the fact that the scattering amplitude is directly related to the pair correlation function $\Gamma(\vec{k})$. Indeed the scattering amplitude $I(\vec{k})$ (where $\vec{k} = \vec{k}_s - \vec{k}_i$, \vec{k}_i and \vec{k}_s being the incident and scattered wave vectors)

$$(547) \quad I(\vec{k}) = \left\langle \left| \sum_{j=1}^N a_j(\vec{k}) \right|^2 \right\rangle$$

where $a_j(\vec{k})$ is the amplitude of the scattered light from the j -th particle. Now the scattering from two different particles, say 1 and j , has a phase difference:

$$(548) \quad a_j(\vec{k}) = a_1(\vec{k}) e^{-i\vec{k} \cdot (\vec{r}_j - \vec{r}_1)}$$

hence, taking the origine in \vec{r}_1 , one has

$$(549) \quad I(\vec{k}) \sim \left\langle \left| \sum_{j=1}^N e^{-i\vec{k} \cdot \vec{r}_j} \right|^2 \right\rangle = \left\langle \sum_{i=1}^N e^{-i\vec{k} \cdot \vec{r}_i} \sum_{j=1}^N e^{+i\vec{k} \cdot \vec{r}_j} \right\rangle = \left\langle \sum_{ij} e^{-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle$$

But

$$(550) \quad \frac{1}{V} \int d^3r \frac{1}{V} \int d^3r' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) = e^{-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)}, \text{ hence}$$

$$(551) \quad I(\vec{k}) \sim \frac{1}{V} \int d^3r \int d^3r' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \left\langle \sum_{ij=1}^N \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle$$

From (515, 513) it result now that

$$(552) \quad \left\langle \sum_{ij} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle = \Gamma(\vec{r} - \vec{r}') + n^2; \text{ consequently}$$

$$(553) \quad I(\vec{k}) \sim \frac{1}{V} \int d^3r \frac{1}{V} \int d^3r' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} [\Gamma(\vec{r} - \vec{r}') + n^2] = \frac{1}{V} \int d^3r e^{-i\vec{k} \cdot \vec{r}} \Gamma(\vec{r}) + n^2 \delta(\vec{k})$$

where \vec{r}_1 has been taken into origine. Hence excepting $\vec{k} = 0$ (here gives the last term contributions) $\Gamma(\vec{k})$

$$(554) \quad I(\vec{k}) \sim \Gamma(\vec{k}); \vec{k} \neq 0$$

where (554), excepting $\vec{k} = 0$, holds for arbitrary small \vec{k} . Hence, if $\Gamma(\vec{k})$ increases, the scattering amplitude $I(\vec{k})$ increases as well, and around the critical point opalescence occurs.

About the η value.

Measurements (hence in 3D) provide the following η values: in liquid-vapour systems: $\eta = 0.042$; fluid mixtures: 0.038 ; lattices $\eta = 0.036$; (Monte Carlo: $\eta = 0.036$). Consequently, the best mean-field value of the critical exponents is $\eta = 0$.

II. The Landau theory of phase transitions. (Landau: Nobel prize winner)

It was the first theory that aimed a general description of continuous phase transitions. One starts by expecting to obtain more than mean field, since the deduction of the Ginzburg-Landau thermodynamic potential, at least at first view seems rigorous.

What we use for the deduction is the Ginzburg-Landau thermodynamic potential.

1. Critical exponents of the first group of scaling laws:

(see point 5.) of Lecture 5): $\alpha, \beta, \gamma, \delta$

For the start, one needs the Ginzburg-Landau thermodynamic potential for homogeneous system, eq. (152)

$$(152) \quad \phi = \phi_0 + A(p,T) \Delta^2 + B(p,T) \Delta^4 - h \Delta; \quad \text{where } A(p,T) \begin{cases} > 0; T > T_c \\ = 0; T = T_c \\ < 0; T < T_c \end{cases}$$

hence
(555) $A \sim t = \frac{T - T_c}{T_c}$; $B > 0$; (see (149));

The critical exponent β :

At $\Delta \neq 0$, $\frac{\partial \phi}{\partial \Delta} = 0$ must hold. Hence from (152) we find:

$$(556) \quad 2A(p,T) \Delta + 4B(p,T) \Delta^3 - h = 0$$

For β one has $h = 0$, and since $\Delta \neq 0$ one simplifies by Δ :

$$(557) \quad 2A(p,T) \Delta + 4B(p,T) \Delta^3 = 0 \Rightarrow 2A(p,T) = -4B(p,T) \Delta^2$$

consequently, because (555): $A \sim t$, one obtains (for $T < T_c, t < 0$)

$$(558) \quad \Delta^2 = -\frac{A(p,T)}{2B(p,T)} \sim -t = |t| \Rightarrow \Delta^2 \sim |t|; \Delta \sim |t|^{1/2}$$

and since $\Delta \sim |t|^\beta, h = 0$ defines the β critical exponent, one has

$$(559) \quad \boxed{\beta = \frac{1}{2}}$$

The critical exponent γ :

One turns back to (556) and calculate the h derivative of the expression, taking into account that $\chi = \frac{\partial \Delta}{\partial h}$. We find:

$$(560) \quad 2A(p,T) \chi + 12B(p,T) \Delta^2 \chi = 1$$

But $A(p,T) \sim t$, and from (559) also $\Delta^2 \sim t$ hence

$$(561) \quad \chi = \frac{1}{2A(p,T) + 12B(p,T) \Delta^2} \sim \frac{1}{t} \Rightarrow \chi \sim t^{-1}$$

Because γ is defined as $\chi \sim t^{-\gamma}, h \rightarrow 0$, one obtains

$$(562) \quad \boxed{\gamma = 1}$$

Now the critical exponent δ comes:

The critical exponent δ :

We turn back to (556) and take into consideration that $\Delta \sim h^{1/\delta}$, $t=0$. Consequently we put $t=0$ in (556), and since $A \sim t$, it results that $A(p,T) = 0$. Hence (556) becomes

$$(563) \quad \Delta^3 = \frac{h}{4B(p,T)} \Rightarrow \Delta^3 \sim h \Rightarrow \Delta \sim h^{1/3} \Rightarrow \delta = 3$$

consequently:

$$(564) \quad \boxed{\delta = 3} \text{ holds.}$$

The critical exponent α .

For the α definition one has $C \sim E^{-\alpha}$, $h=0$, hence for $\phi(h=0)$ from (152) we determine first the T dependence:

$$(565) \quad \phi = \phi_0 + A(p,T)\Delta^2 + B(p,T)\Delta^4$$

$$\text{Since } A(p,T) \sim t; \Delta^2 \sim t \Rightarrow$$

$$(566) \quad \phi \sim t^2; \text{ But } C = -T \frac{\partial^2 \phi}{\partial T^2} \Rightarrow C \text{ becomes a continuous function of } T, \text{ hence}$$

$$(567) \quad \boxed{\alpha = 0}$$

As seen: $\alpha=0, \beta=\frac{1}{2}, \gamma=1, \delta=3$ are the mean-field critical exponents.

2. Critical exponents of the second group of scaling laws:

(see point 6.) of Lecture 5.): M, ν

Now one expects that perhaps here one achieves an advancement in comparison to mean-field. In order to see this, we must use the Ginzburg-Landau thermodynamic potential in inhomogeneous case (153, 155) Lecture 4.

$$(568) \quad \bar{\phi} = \bar{\phi}_0(\vec{r}) + A(p,T)\Delta^2(\vec{r}) + B(p,T)\Delta^4(\vec{r}) + g(p,T)(\nabla\Delta(\vec{r}))^2 - h\Delta(\vec{r})$$

$$\phi = \frac{1}{V} \int \bar{\phi}(\vec{r}) d^d r; \quad B(p,T) > 0; \quad g(p,T) > 0; \quad A(p,T) \sim t$$

Again ϕ must be in its minimum for the $\Delta(\vec{r})$ which is achieved, but now $\Delta(\vec{r})$ is not a parameter, but a function hence the derivative becomes here a variation ($\Delta(\vec{r}) + \delta\Delta(\vec{r})$) produces a $\delta\phi$ variation of ϕ .

Hence:

$$(569) \quad \delta\phi = \frac{1}{V} \int d^d r [2A(p,T)\Delta(\vec{r})\delta\Delta(\vec{r}) + 4B(p,T)\Delta^3(\vec{r})\delta\Delta(\vec{r}) - h\delta\Delta(\vec{r}) +$$

$$+ 2g(p,T)\nabla\Delta(\vec{r})\cdot(\nabla\delta\Delta(\vec{r}))]; \text{ As seen, the variation rules are similar to the derivation rules.}$$

Now the last term is partially integrated

$$(570) \quad \int \nabla dU = \int \nabla U|_{\text{surface}} - \int U dV; \text{ one has}$$

$$(571) \quad \nabla = \nabla\Delta(\vec{r}) \Rightarrow dV = \nabla^2\Delta(\vec{r}) d^d r; \text{ hence}$$

$$dU = \nabla(\delta\Delta(\vec{r})) d^d r \Rightarrow U = \delta\Delta(\vec{r})$$

$$(572) \quad \int (\nabla\Delta(\vec{r}))\cdot(\nabla\delta\Delta(\vec{r})) d^d r = (\nabla\Delta(\vec{r}))\cdot(\delta\Delta(\vec{r}))|_{\text{surface}} - \int (\nabla^2\Delta(\vec{r}))\delta\Delta(\vec{r}) d^d r$$

Since on the surface which encloses the volume in the thermodynamic limit, physical quantities have no physical meaning, the second term remains only in the right side of (572). Consequently:

$$(573) \int (\nabla \Delta(\vec{r})) (\nabla S \Delta(\vec{r})) d^d r = - \int (\nabla^2 \Delta(\vec{r})) S \Delta(\vec{r}) d^d r$$

Reintroducing (573) into (569) we find

$$(574) S \phi = \frac{1}{V} \int d^d r [2A(P,T) \Delta(\vec{r}) + 4B(P,T) \Delta^3(\vec{r}) - h - 2g(P,T) \nabla^2 \Delta(\vec{r})] S \Delta(\vec{r})$$

But for the minimum we should have $S \phi = 0$, and this to be possible (since should occur at all temperatures

$$(575) 2A(P,T) \Delta(\vec{r}) + 4B(P,T) \Delta^3(\vec{r}) - 2g(P,T) \nabla^2 \Delta(\vec{r}) = h(\vec{r})$$

must be satisfied. Comparing (575) with the equation which provides the minimum ϕ in the homogeneous case (556), we see that excepting the third term is practically the same. Taking $\Delta(\vec{r}) = \Delta = \text{constant}$, we indeed reobtain from (575) the relation (556). Now the main difference is that (556) was an algebraic equation, and (575) is a differential equation.

Now from (575) we calculate the non-local susceptibility

$$(576) \chi(\vec{r}, \vec{r}') = \frac{\delta \Delta(\vec{r})}{\delta h(\vec{r}')} ; \text{ This shows how } \Delta \text{ reacts to the order parameter at point } \vec{r}, \text{ to an external field applied at point } \vec{r}'.$$

From (575) we find:

$$(577) 2A(P,T) \chi(\vec{r}, \vec{r}') + 12B(P,T) \Delta^2(\vec{r}) \chi(\vec{r}, \vec{r}') - 2g(P,T) \nabla^2 \chi(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$$

which means the differential equation:

$$(578) [2A(P,T) + 12B(P,T) \Delta^2(\vec{r}) - 2g(P,T) \nabla^2] \chi(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$$

But using now the fluctuation-dissipation result (502) from the previous lecture:

$$\chi(\vec{r}, \vec{r}') = \frac{1}{k_B T} G(\vec{r}, \vec{r}') ; \text{ where } G(\vec{r}, \vec{r}') \text{ is the pair correlation function. Taking isotropic system, one has } G(\vec{r}, \vec{r}') = G(|\vec{r} - \vec{r}'|), \text{ and (578) becomes of the form:}$$

$$(579): [2A(P,T) + 12B(P,T) \Delta^2(\vec{r}) - 2g(P,T) \nabla^2] G(\vec{r} - \vec{r}') = k_B T \delta(\vec{r} - \vec{r}')$$

Now, because \vec{r}' is fixed in (579), we take the origine in \vec{r}' . Furthermore, to be valid our result for all types of Δ 's, we move in the disordered state ($\Delta(\vec{r}) = 0$), but close to T_c . In this manner, the equation for the pair correlation function of the Landau theory becomes:

$$(580) [A(P,T) - g(P,T) \nabla_r^2] G(\vec{r}) = \frac{k_B T}{2} \delta(\vec{r}).$$

We can transform the differential equation (580) in algebraic equation by a Fourier transform. For this one, takes

$$(581) G(\vec{r}) = \int \frac{d^d k}{(2\pi)^d} G(\vec{k}) e^{i\vec{k} \cdot \vec{r}} ; \quad \delta(\vec{r}) = \int \frac{d^d k}{(2\pi)^d} e^{i\vec{k} \cdot \vec{r}} ; \quad \nabla_r e^{i\vec{k} \cdot \vec{r}} = i\vec{k} e^{i\vec{k} \cdot \vec{r}} ;$$

$$\nabla_r^2 e^{i\vec{k} \cdot \vec{r}} = (i\vec{k})^2 e^{i\vec{k} \cdot \vec{r}} = -k^2 e^{i\vec{k} \cdot \vec{r}} ; \text{ we obtain hence by introducing the results (581) to (580) the following relation:}$$

$$(582) \int \frac{d^d k}{(2\pi)^d} e^{i\vec{k}\cdot\vec{r}} \left[(A(p,T) + k^2 g(p,T)) G(\vec{k}) - \frac{k_B T}{z} \right] = 0$$

From where, since (582) must be satisfied for all \vec{r} , one obtains

$$(583) G(\vec{k}) = \frac{k_B T}{z} \cdot \frac{1}{A(p,T) + k^2 g(p,T)}$$

Since always $g(p,T) > 0$, one denotes

$$(584) a^2(p,T) = \frac{A(p,T)}{g(p,T)}; \lim_{t \rightarrow 0} A(p,T) = 0 \text{ (since } A(p,T) \sim t)$$

Furthermore

$$(585) Q = \frac{k_B T}{2g(p,T)}; \lim_{t \rightarrow 0} Q = \frac{k_B T_c}{2g(p,T_c)} = \text{constant}$$

hence one has around T_c a correlation function

$$(586) G(\vec{k}) = \frac{Q}{a^2(p,T) + k^2}; a^2 \sim t; \text{ which is exactly the Ornstein-Zernike correlation function (542)}$$

Hence for η , (546) applies, hence

$$(587) \boxed{\eta = 0} \text{ in the Landau theory.}$$

The ν critical exponent:

The expression of the obtained correlation function is in fact of the form

$$(588) G(\vec{k}) \sim \frac{1}{X^2 + k^2}; \text{ where } X^2 = a^2 \sim t; t > 0 \text{ since } T > T_c$$

The Fourier transform of this function is of the form

$$(589) G(r^2) \sim \frac{1}{r^{\frac{d-1}{2}}} e^{-Xr}; \text{ Here the leading } r \text{ dependence is given by } e^{-Xr} = e^{-\frac{r}{\xi}}; \text{ where the correlation length } \xi:$$

$$(590) \xi = \frac{1}{X} \sim \frac{1}{\sqrt{t}} \Rightarrow \xi \sim t^{-1/2}$$

Since ν is defined as $\xi \sim t^{-\nu}$, one concludes that

$$(591) \boxed{\nu = \frac{1}{2}} \text{ for the Landau theory of phase transitions.}$$

The summary of all critical exponents of the Landau theory of phase transitions (see below (567), and (587), (591)) provides

$$(592) \alpha = 0; \beta = \frac{1}{2}; \gamma = 1; \delta = 3; \eta = 0; \nu = \frac{1}{2}$$

As seen, these are the mean-field critical exponents (see (410) from Lecture 7.). Consequently:

$$(593) \boxed{\text{The Landau theory of phase transitions is a mean-field theory.}}$$

Now let us check how scaling laws are satisfied with the mean-field critical exponents:

First group of scaling laws: (Lecture 5, (232)):

Wilson: $\gamma = \beta(\delta-1) \Rightarrow 1 = \frac{1}{2}(3-1) \Rightarrow 1=1; \checkmark$
Griffiths: $\alpha + \beta(\delta+1) = 2 \Rightarrow 0 + \frac{1}{2} \cdot 4 = 2 \Rightarrow 2=2; \checkmark$
Rushbrooke: $\alpha + 2\beta + \gamma = 2 \Rightarrow 0 + 2 \cdot \frac{1}{2} + 1 = 2 \Rightarrow 2=2; \checkmark$

(594)

This means that the Landau theory is thermodynamically consistent. It perfectly satisfies the first group of scaling laws.

Second group of scaling laws: (Lecture 5: (255)):

Fisher: $(2-\eta) \nu = \gamma \Rightarrow (2-0) \frac{1}{2} = 1 \Rightarrow 1=1; \checkmark$

Josephson: $2-\alpha = \nu d \Rightarrow 2-0 = \frac{1}{2} d \Rightarrow$ true for $d=4$

(595)

First Buckingham-Gunton: $2-\eta = d \frac{\delta-1}{\delta+1} \Rightarrow 2-0 = d \frac{2}{4} \Rightarrow$ true for $d=4$

Second Buckingham-Gunton: $2-\eta = d \frac{\gamma}{2\beta+\gamma} \Rightarrow 2-0 = d \frac{1}{2 \cdot \frac{1}{2} + 1} \Rightarrow$ true for $d=4$

Since it becomes to be good in $d=4$ and not for the real world $d=3$ it means that is not the absolute theory of the phase transitions. Indeed as we know from the previous lectures, is practically a mean-field type of theory.

Where is the mistake in the deduction of the Landau theory?

Based on the Onsager's solution of the 2D Ising model, we know that: the statement that ((143), Lecture 4)

(596): $A(p,T) > 0; T > T_c; \text{ is a correct statement}$
 $A(p,T) < 0; T < T_c;$

But from (596) does not results that then $A(p, T=T_c) = 0$.
Actually in the 2D Ising case a logarithmic divergence occurs at $T=T_c$ of the form

(597) $A(p,T) \sim \text{sign}(T-T_c) \ln|T-T_c|;$

From this one concludes that in order to develop the theory of phase transitions, we have find a better theoretical description. This is given by the renormalization group.

Before going further, I would like to mention some developments of the Landau theory

Developments based on Landau theory:

a.) Cubic invariants: sometimes for some groups also cubic invariants are possible to be constructed. In this case

(598) $\phi = \phi_0 + A(p,T)\Delta^2 + C(p,T)\Delta^3 + B(p,T)\Delta^4 + \dots$

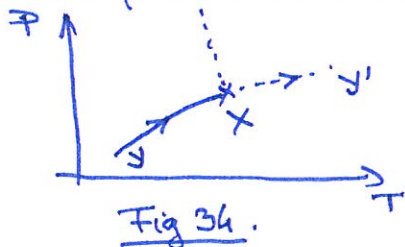
occurs, and the stability of the ordered phase requires

(599) $C(p_c, T_c) = 0$. (stability just around T_c).

Hence, with $A(p_c, T_c) = 0$ at T_c , one has 2 equations at the transition, which instead a transition line, provide only 1 transition point. Such case can occur at the intersection of first order transition lines, where the intersection point means only a continuous transition.

b.) Critical point of a continuous phase transition :

If $B(p,T) = 0$ occurs, the continuous transition turns in a first order phase transition (see Fig 34), point X. This is in fact a triple point called "tricritical", where $\gamma \rightarrow X$ is a continuous phase transition, while $X \rightarrow \gamma'$ is a first order phase transition line. The point X is also called the critical point of the continuous transition $\gamma - X$. At this point at $t=0$ both $A(p,T)$ and $B(p,T)$ become zero. Because of this fact a sixth order term is also included in ϕ which becomes



(560) $\phi = \phi_0 + A\Delta^2 + B\Delta^4 + F\Delta^6$
 providing the critical exponents (see Anex 1)

(561) $\alpha = \frac{1}{2}, \beta = \frac{1}{4}; \gamma = 1, \delta = 5, \nu = \frac{1}{2}, \eta = 0$

During deduction $A \neq 0, B \neq 0$ is used. This critical exponents satisfy the first group of scaling laws, while the second group of scaling laws provide $d=3$. Hence around the critical point of the continuous phase transition, the Landau theory has a better quality than usual.

c.) Trial for Δ^6 in ϕ :

Based on the previous success

(562) $\phi = \phi_0 + A\Delta^2 + F\Delta^6$

has been also explored, taking $F > 0$ always. It provides the exponents:

(563) $\alpha = 0; \beta = \frac{1}{4}; \gamma = 1; \delta = 5$

which however not satisfy the Rushbrooke $(\alpha + 2\beta + \gamma = 2)$ equality hence is not a consistent theory.

Let us consider the thermodynamic potential

(A.1.1) $\phi = \phi_0 + A\Delta^2 + B\Delta^4 + E\Delta^5 + F\Delta^6$
 where $A > 0, B < 0, F > 0$. Because of the minimum of ϕ , we must have $\frac{\partial \phi}{\partial \Delta} = 0, \frac{\partial^2 \phi}{\partial \Delta^2} > 0$, hence

(A.1.2) $\frac{\partial \phi}{\partial \Delta} = 2A\Delta + 4B\Delta^3 + 5E\Delta^4 + 6F\Delta^5 = 0 \Rightarrow$ (since $\Delta \neq 0$ in the ordered phase)
 $2A + 4B\Delta^2 + 5E\Delta^3 + 6F\Delta^4 = 0$

The second derivative becomes:

(A.1.3) $\frac{\partial^2 \phi}{\partial \Delta^2} = 2A + 12B\Delta^2 + 20E\Delta^3 + 30F\Delta^4 > 0$

Extracting (A.1.2) from (A.1.3) we find

(A.1.4) $8B\Delta^2 + 15E\Delta^3 + 24F\Delta^4 > 0 \Rightarrow 8B + 15E\Delta + 24F\Delta^2 > 0$
 which provides the roots in between which the inequality is not satisfied as:

(A.1.5) $\Delta_{1,2} = \frac{1}{48F} [-15E \pm \sqrt{(15E)^2 - 32 \cdot 24BF}]$

Since $B < 0, F > 0$ in the ordered phase, the roots become equal at $E = 0$ which becomes the condition of stability $\frac{\partial^2 \phi}{\partial \Delta^2} > 0$ and $\frac{\partial \phi}{\partial \Delta} = 0$. Hence we obtain

(A.1.6) $\phi = \phi_0 + A\Delta^2 + B\Delta^4 + F\Delta^6$

Now $\frac{\partial \phi}{\partial \Delta} = 2A\Delta + 4B\Delta^3 + 6F\Delta^5 = 0 \Rightarrow 2A + 4B\Delta^2 + 6F\Delta^4 = 0$

(A.1.8) $\Delta_{1,2}^2 = \frac{1}{6F} [-2B \pm \sqrt{4B^2 - 12FA}]$; $A < 0; B < 0 \Rightarrow$ only one positive (hence physical) solution exists, namely

(A.1.9) $\Delta = \left[\frac{1}{6F} (-2B + \sqrt{4B^2 - 12FA}) \right]^{1/2}$, hence, since $t > t^2 \Rightarrow \sqrt{t} > t$

β : \wedge

(A.1.10) $\Delta \sim \left[\frac{1}{6F} (-B + \sqrt{4B^2 - 12FA}) \right]^{1/2} \sim \left[\frac{1}{6F} \sqrt{4B^2} \right]^{1/2} \Rightarrow \Delta \sim (\sqrt{|B|})^{1/2} = |B|^{1/4}$

This can be seen also from the fact that since $A > 0, B < 0$
 $A + 2B\Delta^2 + 6F\Delta^4 = 0 \Rightarrow t(1 + 2\Delta^2) + 6F\Delta^4 = 0 \Rightarrow \Delta^4 \sim |t|, \Delta \sim |t|^{1/4}$

Hence (A.1.11): $\beta = \frac{1}{4}$

γ : From (A.1.6) with field

(A.1.12) $\phi = \phi_0 + A\Delta^2 + B\Delta^4 + F\Delta^6 - h\Delta$

(A.1.13) $\frac{\partial \phi}{\partial \Delta} = 2A\Delta + 4B\Delta^3 + 6F\Delta^5 - h = 0$; $x = \frac{\partial \Delta}{\partial h}$, hence

(A.1.14): $2Ax + 12B\Delta^2 x + 30F\Delta^4 x = 1$; since $t \rightarrow 0$

(A.1.15): $2Ax \sim 1 \Rightarrow x \sim \frac{1}{A} = t^{-1} \Rightarrow \gamma = 1$

Hence

(A.1.16) $\boxed{\gamma = 1}$

s:

From (A.1.13) one has

(A.1.17) $2A\Delta + 4B\Delta^3 + 6F\Delta^5 = h$; Ant, Bnt

But $t=0$ for S , hence

(A.1.18) $6F\Delta^5 = h \Rightarrow \Delta \sim h^{1/5} \Rightarrow \boxed{s=5}$

α :

From (A.1.1) and $\Delta \sim t^{1/4} \Rightarrow \phi \sim t^{5/4} = |t|^{3/2}$ (A.1.19)

Hence $S = -\frac{\partial \phi}{\partial t} \sim |t|^{1/2}$; $C \sim \frac{\partial S}{\partial t} \sim |t|^{-1/2}$; $C \sim |t|^{-\alpha} \Rightarrow \alpha = \frac{1}{2}$; (A.1.20), i.e

(A.1.21) $\boxed{\alpha = \frac{1}{2}}$

The $\nu = \frac{1}{2}$, $\eta = 0$ values from the correlation function remain the same.

check of the scaling laws:

Widom: $\gamma = \beta(s-1) \Rightarrow 1 = \frac{1}{4} \cdot 4 \checkmark$

Griffiths: $\alpha + \beta(s+1) = 2 \Rightarrow \frac{1}{2} + \frac{1}{4} \cdot 6 = 2 \Rightarrow \frac{1}{2} + \frac{3}{2} = 2 \Rightarrow 2 = 2 \checkmark$

Rushbrooke: $\alpha + 2\beta + \gamma = 2 \Rightarrow \frac{1}{2} + 2 \cdot \frac{1}{4} + 1 = 2 \Rightarrow 2 = 2 \checkmark$

Fisher: $(2-\eta)\nu = \gamma \Rightarrow (2-0)\frac{1}{2} = 1 \Rightarrow 1 = 1 \checkmark$

Josephson: $2-\alpha = \nu d \Rightarrow 2 - \frac{1}{2} = \frac{1}{2} d \Rightarrow \frac{3}{2} = \frac{d}{2} \Rightarrow d = 3 \checkmark$

First B-G: $2-\eta = d \frac{s-1}{s+1} \Rightarrow 2-0 = d \frac{4}{6} \Rightarrow d = 3 \checkmark$

Second B-G: $2-\eta = d \frac{\gamma}{2\beta+\gamma} \Rightarrow 2-0 = d \frac{1}{\frac{2}{4}+1} \Rightarrow 2 = d \frac{4}{6} \Rightarrow d = 3 \checkmark$