

I. The van der Waals gas.

In the previous lecture I was mentioning that in the field of the mean-field theory, van der Waals received Nobel prize. In fact he received the Nobel prize for its theory describing real gases, but this theory is in fact a mean-field theory. For us it represents interest because I can exemplify in a concrete case how critical exponents can be deduced in the critical region placed around the critical point of a first order phase transition, where the order parameter notion cannot be defined.

1. Ideal gas.

A classical ideal gas is a gas of classical objects (molecules) without interaction between the components. Then the Hamiltonian (now the Hamilton function $H = T + V$, $V = 0$, since we are in classical physics) contains only the kinetic energy contributions:

(417) $H = \sum_{i=1}^N \frac{p_i^2}{2m}$; $N =$ nr. of particles in the system.

Hence the partition function, (note that we are in the classical phase space depending on \vec{r}_i, \vec{p}_i variables)

(418) $Z_0 = \frac{1}{N!} \left[\int d^3p_i \int d^3r_i e^{-\beta \frac{p_i^2}{2m}} \right]^N = \text{Tr} e^{-\beta H}$; Lower index 0 means ideal gas.

Now the p integrals mean

(419) $\int d^3p_i e^{-\frac{\beta p_i^2}{2m}} = \int_{-\infty}^{+\infty} dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} = \chi^3$

where $\chi = \int_{-\infty}^{+\infty} dp_x e^{-a p_x^2} = \sqrt{\frac{\pi}{a}}$; $a = \frac{\beta}{2m}$; since this is a standard Gaussian integral

Then, from Z in (418) $\int d^3r_i = V =$ the volume remains, hence

(420) $Z_0 = \frac{1}{N!} \frac{V^N}{\chi^{3N}}$

The partition function gives the thermodynamic potential via $\Phi_0 = -k_B T \ln Z_0$, then one has

(421) $\Phi_0 = -k_B T \ln \left[\frac{1}{N!} \frac{V^N}{\chi^{3N}} \right]$

Now (we are in canonical system with N fixed, describing the system with the free energy)

(422) $P = -\frac{\partial \Phi_0}{\partial V} = +k_B T \frac{N V^{N-1}}{V^N} = N k_B T \frac{1}{V}$, from where (equilibrium equat. of stat)

(423) $\boxed{PV = N k_B T} = \frac{N}{N_A} \underbrace{(k_B N_A)}_R T = n R T$ the ideal gas law is

obtained where R is the universal gas constant, N_A is the Avogadro's number $n = N/N_A$ is the molar concentration. This system do not has phase transitions, it has only the disordered gas phase. This model considers particles without dimension.

2. The van der Waals gas:

A) Partition function:

a.) However, we know that the particles have their own volume (let us denote this volume by b). Then, in fact the volume in which the particles can move, and they have it at disposal is
 (424) $V' = (V - Nb)$ = the real volume at disposal;

b.) From the other hand, the particles interact as well. So in fact, instead of the Hamiltonian (417) one has for a real gas

$$(425) H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j);$$

Let us deduce now the equation of state. To incorporate a.) we must introduce in Z_0 the $V' = V - Nb$, so one has

$$(426) \text{ in } Z_0: V \rightarrow V' = V - Nb; \text{ at the end of the calculation.}$$

Now the interaction should be incorporated. For this again the partition function must be calculated

$$\begin{aligned} Z &= \frac{1}{N!} \left[\int \left(\prod_{i=1}^N d^3 p_i \right) \int \left(\prod_{i=1}^N d^3 r_i \right) \exp \left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m} \right] \exp \left[-\beta \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right] \right] = \\ (427) &= \frac{1}{N!} \left[\int \left(\prod_{i=1}^N d^3 p_i \right) \exp \left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m} \right] \right] \left[\int \left(\prod_{i=1}^N d^3 r_i \right) \exp \left[-\beta \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right] \right] = \\ &= \frac{1}{N!} \left[\int d^3 p_i e^{-\beta \frac{p_i^2}{2m}} \right]^N \left[\int \left(\prod_{i=1}^N d^3 r_i \right) \left\{ 1 - \beta \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right\} \right]; \end{aligned}$$

where in the last steps we have taken into account that the inter-particle interaction is small, hence $e^{-x} \approx 1 - x$ has been employed.

Now according to (419) one has

$$(428) \left\{ \int d^3 p_i \exp \left[-\beta \frac{p_i^2}{2m} \right] \right\}^N = \frac{1}{\lambda^{3N}} = \frac{V^N}{\lambda^{3N}} \cdot \frac{1}{V^N}$$

$$Z = \underbrace{\left[\frac{1}{N!} \frac{V^N}{\lambda^{3N}} \right]}_{Z_0} \cdot \left[\int \left(\prod_{i=1}^N \frac{d^3 r_i}{V} \right) \left(1 - \beta \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right) \right] \Rightarrow$$

$$(429) Z = Z_0 \cdot \left[\int \left(\prod_{i=1}^N \frac{d^3 r_i}{V} \right) \left(1 - \beta \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right) \right]$$

Since $\int \frac{d^3 r_i}{V} = 1$, from (429) one finds

$$(430) Z = Z_0 \left[1 - \beta \int \left(\prod_{i=1}^N \frac{d^3 r_i}{V} \right) \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \right];$$

In order to continue, we must calculate the remaining integral in (430). In order to do that we use a mean-field approximation, in which we consider that each particle feels exactly the same mean-field. In this case

$$(431) \sum_{i \neq j} U(\vec{r}_i, \vec{r}_j) \rightarrow \frac{N(N-1)}{2} U(\vec{r}_1, \vec{r}_2)$$

where $\frac{N(N-1)}{2}$ represents the number of pairs which can be made from N objects, i.e. combination of N objects on 2 places. In this manner $N-2$ integrals can be effectuated in (430) providing 1, and we find:

$$Z = Z_0 \left[1 - \beta \frac{N(N-1)}{2} \int \frac{d^3 \vec{r}_2}{V} \int \frac{d^3 \vec{r}_1}{V} U(\vec{r}_1, \vec{r}_2) \right]; \quad (432)$$

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In treating the last integral, from the starting variables \vec{r}_1, \vec{r}_2 we turn to relative coordinates (distance \vec{r} , and center of mass \vec{R})

$$(433) \quad \vec{r} = \vec{r}_1 - \vec{r}_2, \quad \vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}; \quad \frac{1}{2} \int \frac{d^3 \vec{r}_2}{V} \int \frac{d^3 \vec{r}_1}{V} \rightarrow \int \frac{d^3 \vec{R}}{V} \int \frac{d^3 \vec{r}}{V}$$

and this is possible because

$$(434) \quad U(\vec{r}_1, \vec{r}_2) = U(|\vec{r}_1 - \vec{r}_2|) = U(r); \quad r = |\vec{r}|$$

because of the system isotropy. Consequently one remains

with $\int \frac{d^3 \vec{R}}{V} \int \frac{d^3 \vec{r}}{V} U(r) = \int \frac{d^3 \vec{r}}{V} U(r); \quad \int \frac{d^3 \vec{R}}{V} = 1$; Hence, taking into account that because of $N \gg 1$, $N(N-1) \cong N^2$, one obtains

$$Z = Z_0 \left[1 - \beta \frac{N^2}{V} \int d^3 \vec{r} U(r) \right]; \quad (436).$$

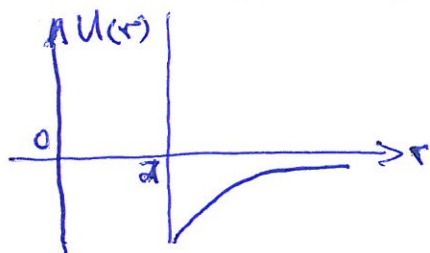


Fig 31.

Taking a hard wall (or hard sphere) potential for simplicity, a = minimum interparticle distance \approx particle diameter, one has

$$\int \frac{d^3 \vec{r}}{V} U(r) = -a; \quad a > 0 \quad (437)$$

which is "attractive" (i.e. minus sign).

Hence one has

$$(438) \quad Z = Z_0 \left[1 + \beta a \frac{N^2}{V} \right] = Z_0 \cdot Z_1; \quad Z_1 = 1 + \beta a \frac{N^2}{V}$$

where Z_0 is given by the kinetic part of the Hamilton function and Z_1 by its interaction part ($H = T + V$). The Z_0 term is taken from (420) but with the specification (426), namely $V \rightarrow V'$. Consequently:

$$(439) \quad Z = \left[\frac{1}{N!} \cdot \frac{(V - bN)^N}{\lambda^{3N}} \right] \left[1 + \beta a \frac{N^2}{V} \right]; \quad \text{This is the partition function of the van der Waals gas.}$$

B) Thermodynamic potential:

One knows that $\phi = -k_B T \ln Z$, hence:

$$(440) \quad \phi = -k_B T \ln \left[\frac{1}{N!} \cdot \frac{(V - bN)^N}{\lambda^{3N}} \right] - k_B T \ln \left(1 + \beta a \frac{N^2}{V} \right); \quad \lambda = \sqrt{\frac{\beta}{2\pi m}}$$

Because of $\ln(1+x) \approx x$, last term becomes (a is a small number):

$$(441) \quad \phi = -k_B T \ln \left[\frac{1}{N!} \cdot \frac{(V - bN)^N}{\lambda^{3N}} \right] - a \frac{N^2}{V}; \quad \text{This is the thermodynamic potential (exactly free energy) of the van der Waals gas.}$$

The entropy easily can be calculated from here since $S = -\frac{\partial \phi}{\partial T}$. But for this we have to introduce the λ value explicitly. One has

$$(441) \quad \frac{1}{\lambda^{3N}} = (2\pi m k_B T)^{\frac{3N}{2}}$$

Hence the explicit form of ϕ becomes:

(442): $\Phi = -k_B T \ln \left[\frac{1}{N!} (V-bN)^N (2\pi m k_B T)^{\frac{3N}{2}} \right] - a \frac{N^2}{V}$; $m = \text{particle mass}$ -4-
 Consequently:

(443): $S = -\frac{\partial \Phi}{\partial T} = k_B \ln \left[\frac{1}{N!} (V-bN)^N (2\pi m k_B T)^{\frac{3N}{2}} \right] + \frac{3N}{2} k_B$; Then for TS we have:

(444): $TS = \underbrace{\left\{ T k_B \ln \left[\frac{1}{N!} (V-bN)^N (2\pi m k_B T)^{\frac{3N}{2}} \right] + a \frac{N^2}{V} \right\}}_{-\Phi} - a \frac{N^2}{V} + \frac{3N}{2} k_B T$

consequently:

(445) $TS = -\Phi - a \frac{N^2}{V} + \frac{3}{2} N k_B T$

Now because $U = \Phi + TS$; (Φ is here $F = U - TS$, the free energy) one obtains for the internal energy U

(446) $U = \frac{3}{2} N k_B T - a \frac{N^2}{V}$; This is the internal energy of the van der Waals gas.

C.) The specific heat.

As can be seen from (446) the internal energy, in its T dependence is as for ideal gas. Only a small V -dependent term signals the presence of the interaction, and b does not enter in the expression. We are going to see below that this small term what huge changes in the physical properties produces.

Once one has U , the specific heat can be calculated. Since $C = \frac{\partial U}{\partial T}$, one finds:

(447) $C = \frac{3}{2} N k_B = C_V$; (since V is constant here) is as in the case of the ideal gas. Since T dependence is no more present in (447) it results that the critical exponent α of the specific heat is zero. So

(448) $\alpha = 0$

D.) The equation of state.

Now we should use (422): $P = -\frac{\partial \Phi}{\partial V}$ for (441). By a derivation one finds:

(449): $P = N k_B T \frac{1}{V-bN} - a \frac{N^2}{V^2}$

This written in the form

(450) $\left(P + a \frac{N^2}{V^2} \right) (V-bN) = N k_B T$

This equation represents the van der Waals equation of states.

(450) was deduced in the PhD dissertation of van der Waals. After publication, Maxwell lauded him in a Nature publication. We also know that van der Waals in his Nobel lecture thanked to Laplace for the idea that the pressure is reduced (see (449)) by a factor proportional to density square given by the intermolecular attraction.

Then it seems that in fact the $a \frac{N^2}{V^2} = aS^2$ term originates from Laplace. -5-

6.) Physical interpretation:

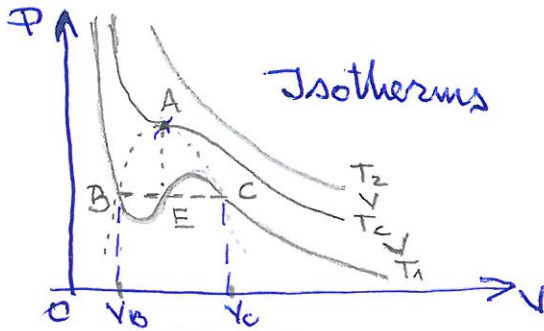


Fig 32.

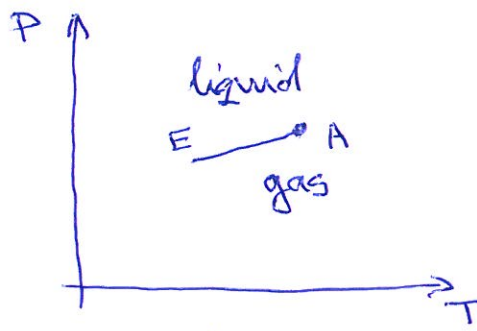


Fig 33.

The equation describes a gas-liquid phase transition. Isotherms are presented in Fig 32. At low temperatures (T_1) in the right side of the C point ($V > V_c$), the volume changes with pressure, so this is a compressible system, hence a gas. But below the B point huge pressure changes cause little volume change, so now the system is almost incompressible, hence is a liquid. The BEC portion of the curve is unphysical. In reality here one has the horizontal line \overline{BC} . In this region the liquid and gas there are in contact at equilibrium, and at constant temperature and pressure the gas (point C) transforms in liquid (point B) and meantime a volume change occurs $\Delta V = V_c - V_b$, hence this is a first order phase transition in the Ehrenfest's scheme. The position of the \overline{BC} line can be found by the Maxwell's construction: namely;

Between the \overline{BC} line and van der Waals curve there are two areas in the left and right side of the point E. Since we are placed in the (P,V) diagram, these areas represent works of opposite sign. Since external energy is not needed to push the system from C to B, it results that these areas should be the same. Hence, the $P_B = P_C$ value corresponding to the isotherm T_1 can be found by

$$(451) \quad P_B(V_c - V_B) = \int_B^C P(T_1, V) dV; \quad \text{This is the Maxwell's construction procedure.}$$

Latent heat: From $C \rightarrow B$ gas to liquid transformation the volume changes, but as seen in (446), even if P, T are constant, the internal energy changes

$$(452) \quad U(B) - U(C) = -a \frac{N^2}{V_B} + a \frac{N^2}{V_C} = aN^2 \left(\frac{1}{V_C} - \frac{1}{V_B} \right) = aN^2 \frac{V_B - V_C}{(V_B V_C)^2} < 0$$

consequently:

$$(453) \quad U(B) < U(C); \quad \text{The difference, as latent heat is given to the environment.}$$

Seen from (443) the entropy S since it is a monotonic and increasing function of the volume, at $C \rightarrow B$ decreases as well, hence the liquid is a phase which is more ordered than the gas. Meantime all the time (i.e. in each point on the curve) the thermodynamic potential (441) remains continuous.

The critical isotherme:

If now increase the temperature, and arrive to $T = T_c$ one reaches the critical isotherme which in the point A leads to the almost incompressible phase. If we plot the EA curve in (P, T) diagram (see Fig 33) we obtain the phase separation line in the phase diagram, separating the gas phase from the liquid phase. This line terminates in the A point. This is the critical point of the first order phase transition that one has.

(454) A point (Fig 32, 33) = critical point

This is because for $T > T_c$ (example $T = T_2$ in Fig 32), now only one phase exists, namely the gas. Note that on the critical isotherme, on the A point both the first and second derivatives of $P = P(V)$ function are zero

$$(455) \quad \frac{\partial P}{\partial V} = 0; \quad \frac{\partial^2 P}{\partial V^2} = 0; \quad T = T_c; \quad V = V_c; \quad P = P_c; \quad (\text{the A point coordinates})$$

If $T \gg T_c$, then in (450) $P \gg a \frac{N^2}{V^2}$; $V \gg bN$, and (450) turns into

$$(456) \quad PV = NK_B T \quad \text{ideal gas (which describes only a gas phase.)}$$

Universality: (i.e. reduced form of the equation of states).

The first sign for universality (as a collection of many different systems that behave in the same way) is coming also from the van der Waals equation. This is seen from the fact that the equation can be recast (i.e. transformed) into an invariant form without the material constants a, b , applicable to all real-gas - fluid systems.

But in order to see that let us deduce first the coordinates T_c, P_c, V_c of the point A (the critical point). For 3 parameters 3 equations are needed, and these are the derivatives (455) and the equation (450) itself. Then one has:

$$1) \quad \frac{\partial P}{\partial V} = - \frac{NK_B T}{(V - bN)^2} + 2a \frac{N^2}{V^3} = 0;$$

$$2) \quad \frac{\partial^2 P}{\partial V^2} = + 2 \frac{NK_B T}{(V - bN)^3} - 6a \frac{N^2}{V^4} = 0; \quad (457)$$

$$3) \quad P = \frac{NK_B T}{V - bN} - a \frac{N^2}{V^2};$$

where the V, P, T solutions will provide V_c, P_c, T_c .

The first two equations become

$$(458) \quad \left. \begin{aligned} 2a \frac{N^2}{V_c^3} &= \frac{NK_B T_c}{(V_c - bN)^2} \\ 6a \frac{N^2}{V_c^4} &= \frac{2NK_B T_c}{(V_c - bN)^3} \end{aligned} \right\} \Rightarrow \text{dividing them one obtains} \quad \frac{V_c}{3} = \frac{V_c - bN}{2} \Rightarrow V_c = 3bN;$$

Now this result introduced in the first equation gives:

$$(459) \quad 2a \frac{N^2}{(3bN)^3} = \frac{NK_B T_c}{(2bN)^2} \Rightarrow \frac{2a}{27b^3 N} = \frac{K_B T_c}{4b^2 N} \Rightarrow K_B T_c = \frac{8a}{27b};$$

All these results introduced in the third equation of (457) gives

$$(460) \quad P_c = \frac{N}{2bN} \cdot \frac{8a}{27b} - \frac{a}{9b^2} = \frac{a}{b^2} \left[\frac{4}{27} - \frac{1}{9} \right] = \frac{a}{27b^2} \Rightarrow P_c = \frac{a}{27b^2}$$

Now instead of the P, V, T variables of (450) we introduce the reduced variables -7-

$$(461) \quad \bar{P} = \frac{P}{P_c}; \quad \bar{V} = \frac{V}{V_c}; \quad \bar{T} = \frac{T}{T_c} \Rightarrow P = \bar{P}P_c; \quad V = \bar{V}V_c; \quad T = \bar{T}T_c$$

and we introduce them into the (450) equation of states:

$$(462) \quad \left[\bar{P}P_c + a \frac{N^2}{(\bar{V}V_c)^2} \right] [\bar{V}V_c - bN] = NK_B \bar{T}T_c; \quad \text{here we now divide by } P_c, bN, \text{ obtaining}$$

$$(463) \quad \left[\bar{P} + \frac{1}{\bar{V}^2} \frac{aN^2}{P_c V_c^2} \right] \left[\bar{V} \frac{V_c}{N b} - 1 \right] = \frac{K_B T_c}{b P_c} \bar{T}; \quad \text{The obtained three coefficients are as follows}$$

$$(464) \quad a \frac{N^2}{P_c V_c^2} = \frac{aN^2}{27b^2 \cdot (3Nb)^2} = 3; \quad \frac{V_c}{Nb} = \frac{3Nb}{Nb} = 3; \quad \frac{K_B T_c}{b P_c} = \frac{8a}{27b} = 8$$

Hence, the universal (i.e. reduced) form of the van der Waals equation of states becomes:

$$(465) \quad \left(\bar{P} + \frac{3}{\bar{V}^2} \right) (3\bar{V} - 1) = 8\bar{T}$$

Note that this equation do not contains material constants hence is valid for all real-gas-fluid systems.

The possibility to write an equation like (465) showed that many different systems presenting a phase transition and building up together a class of materials, can be described together with the same equation not containing material specific constants. This is the precursor of the universality.

E.) Critical exponents:

As was mentioned in Lecture 6, the region around the critical point A is a critical region where the scaling laws hold, and based on mathematical analogies (see (276), (277)):

$$(466) \quad t = \frac{T - T_c}{T_c}; \quad \Delta \sim \beta - \beta_c; \quad h \sim P - P_c$$

hence one considers below

$$t = \frac{T - T_c}{T_c} = \bar{T} - 1 \Rightarrow \bar{T} = t + 1$$

$$(467) \quad \Delta = \frac{\beta - \beta_c}{\beta_c} = \frac{\beta}{\beta_c} - 1 = \frac{m}{m} - 1 = \frac{V_c}{V} - 1 = \frac{1}{\bar{V}} - 1 \Rightarrow \bar{V} = \frac{1}{1 + \Delta}$$

$$h = \frac{P - P_c}{P_c} = \bar{P} - 1 \Rightarrow \bar{P} = 1 + h$$

So now we have the t, h, Δ values which can be used in deducing critical exponents (α already known from (468))

The β critical exponent:

The β critical exponent is defined as $\Delta \sim |t|^\beta, h=0$. The peculiar aspect here is that one must has $h=0 \Rightarrow P=P_c$, so in Fig 32 we must be exclusively on the horizontal line crossing point A, the critical point, which is the $\bar{P}=P_c$ line in the figure. But on this line (457-1) holds, hence one must to place ourselves on this line. From (457-1) we find:

$$(468) \quad 2a \frac{N^2}{V^3} = \frac{Nk_B T}{(V-bN)^2} \Rightarrow \frac{2aN}{V^3} = \frac{k_B T}{(V-bN)^2} ;$$

First we must write (468) in reduced form, i.e. with \bar{V}, \bar{T} variables. For this we use (461), namely $T = \bar{T} T_c; V = \bar{V} V_c$, obtaining:

$$(469) \quad \frac{2aN}{(\bar{V}V_c)^3} = \frac{k_B \bar{T} T_c}{(\bar{V}V_c - bN)^2} \Rightarrow \frac{1}{\bar{V}^3} = \frac{V_c^3}{2aN} \cdot \frac{T_c k_B}{V_c^2} \cdot \frac{\bar{T}}{(\bar{V} - \frac{bN}{V_c})^2} ;$$

Since from (458, 459) $V_c = 3Nb, k_B T_c = \frac{8a}{27b}$, we find

$$(470) \quad \frac{V_c k_B T_c}{2aN} = \frac{3Nb \cdot \frac{8a}{27b}}{2Na \cdot 27b} = \frac{4}{9} ; \quad \frac{bN}{V_c} = \frac{1}{3} ;$$

So the reduced form of the law on $P = P_c$ line is

$$(471) \quad \frac{1}{\bar{V}^3} = \frac{4}{9} \frac{\bar{T}}{(\bar{V} - \frac{1}{3})^2} \Rightarrow \frac{1}{\bar{V}^3} = \frac{4\bar{T}}{(3\bar{V} - 1)^2} \Rightarrow \boxed{\frac{(3\bar{V} - 1)^2}{\bar{V}^3} = 4\bar{T}}$$

Now we introduce here from (467) $\bar{T} = t+1; \bar{V} = \frac{1}{1+\Delta}$ obtaining

$$(472) \quad \left(\frac{2-\Delta}{1+\Delta}\right)^2 (1+\Delta)^3 = 4(t+1) \Rightarrow \left(1 - \frac{\Delta}{2}\right)^2 (1+\Delta) = t+1$$

Effectuating the product in the left side, one obtains

$$(473) \quad \left(1 - 2 \cdot \frac{\Delta}{2} + \frac{\Delta^2}{4}\right) + \left(\Delta - \Delta^2 + \frac{\Delta^3}{4}\right) = t+1$$

↳ neglected because it is of high order

From here we obtain:

$$(474) \quad -\frac{3}{4}\Delta^2 = t \Rightarrow \Delta^2 \sim |t| \Rightarrow \Delta \sim |t|^{1/2}$$

hence one has

$$(475) \quad \boxed{\beta = \frac{1}{2}}$$

The critical exponents γ, δ .

For these critical exponents is not present $h=0$, only $h \rightarrow 0$. Hence the full equation of states (465), where we introduce from (476) $\bar{T} = t+1, \bar{P} = h+1; \bar{V} = \frac{1}{1+\Delta}$ obtaining

$$(477) \quad (h+1+3(1+\Delta)^2) \left(\frac{3}{1+\Delta} - 1\right) = 8(t+1); \text{ without any approximation.}$$

From here $\left(\frac{3}{1+\Delta} - 1\right) = \frac{2-\Delta}{1+\Delta} = 2 \frac{1-\frac{\Delta}{2}}{1+\Delta}$, hence from (468) we find

$$(478) \quad \boxed{[h+1+3(1+\Delta)^2] \left[1 - \frac{\Delta}{2}\right] = 4(t+1)(\Delta+1);}$$

This is the van der Waals equation written in the variables t, h, Δ . If we effectuate the product, we obtain

$$(479) \quad h \left(1 - \frac{\Delta}{2}\right) + [4+6\Delta+3\Delta^2] \left[1 - \frac{\Delta}{2}\right] = 4(1+t+\Delta+t\Delta)$$

which becomes

$$(480) \ln\left(1 - \frac{\Delta}{2}\right) + \underline{\underline{4 + 6\Delta + 3\Delta^2}} + \underline{\underline{-2\Delta - 3\Delta^2 - \frac{3}{2}\Delta^3}} = \underline{\underline{4}} + \underline{\underline{4\Delta}} + 4t + 4t\Delta$$

in which the underlined terms cancel out. We find from (471):

$$(481) \boxed{\ln\left(1 - \frac{\Delta}{2}\right) - \frac{3}{2}\Delta^3 = 4(1 + \Delta)t}$$

Since starting from (465) approximations have not been made, this becomes the simplest form of the van der Waals equation in "critical" t, h, Δ variables, which however is valid for the whole P, T, V domain.

The δ value:

Since in the definition of Δ one has $\Delta \sim h^{1/3}$, $t=0$, introducing $t=0$ (this means that we are placed on the critical line $T=T_c$ in Fig 32) the following relation hold

$$(482) \ln\left(1 - \frac{\Delta}{2}\right) = \frac{3}{2}\Delta^3; \quad \text{This is the most simple form of the critical line of the van der Waals equation}$$

Now if we consider $\Delta \rightarrow 0$ one has

$$(483) \Delta^3 \sim h \Rightarrow \Delta \sim h^{1/3} \Rightarrow \delta = 3$$

Hence one has

$$(484) \boxed{\delta = 3}$$

in the case of the van der Waals gas.

The γ value:

The definition of γ is $\gamma = \frac{\partial \Delta}{\partial h} \sim t^{-\gamma}$, $h \rightarrow 0$. Then, according to this relation we calculate γ from (481). By a derivation in function of h we obtain:

$$(485) \left(1 - \frac{\Delta}{2}\right) - \frac{h}{2}x - \frac{9}{2}\Delta^2 x = 4xt$$

Now we take $h \rightarrow 0$ and obtain

$$(486) \left(1 - \frac{\Delta}{2}\right) = \left(4t + \frac{9}{2}\Delta^2\right)x$$

But we know from (474) that for small Δ , $\Delta^2 \approx -\frac{3}{4}t$, consequently one has

$$(487) \left(1 - \frac{\Delta}{2}\right) = \left(4 - \frac{27}{8}\right)tx = \frac{5}{8}tx$$

since $\Delta \rightarrow 0$, $1 - \frac{\Delta}{2} \approx 1$, hence we find

$$tx \approx 1 \Rightarrow x \sim t^{-1} \Rightarrow \gamma = 1.$$

Hence we obtain for the van der Waals gas

$$(488) \boxed{\gamma = 1}$$

Now collecting all results related to critical exponents we have the following list: (see (468), (475), (484), (488)):

(489) $\alpha = 0, \beta = \frac{1}{2}, \gamma = 1, \delta = 3$

which are typical mean-field type of critical exponents. Hence it can be seen that indeed, the van der Waals description represents a mean field type of description.

Summary about mean-field, its validity:

We have studied 2 concrete systems before, obtaining the mean-field critical exponent values. As a summary relating mean-field we have to remember the following:

Instead to treat during the description the interaction between each particle as it is, in mean-field when we describe the interaction of an arbitrary i th particle, one considers that the other particles together build up a mean-field, and our particle i (as all particles) interacts with it. In this manner, in fact, the description is reduced to a one-particle type of description. Since the interaction of the i th particle with equally placed nearest-neighbors approximates rather well an interaction with a mean-field (average field), and if the dimensionality increases, it means that the number of nearest neighbors increases, it results that the mean-field description becomes good in higher dimensions (above the upper critical dimension, see lecture 2 pg 9.). For $d \rightarrow \infty$ it becomes exact (in infinite dimensions), at least this was proved rigorously for localized degrees of freedom (localized spins).

A mean-field approximation when is effectuated, not depends on the dimension d , and practically neglects all correlation effects. I note that mean-field type of treatment could become of much more higher quality when long-range forces are present.

The validity of the mean-field theory can be rigorously expressed, and what we find in this manner is called Ginzburg-criterion: If Δ denotes the order parameter, then the mean-field treatment becomes valid when the fluctuations in the order parameter ($\delta\Delta$) are much less than the actual value of the order parameter (Δ):

(490) $\langle\langle (\delta\Delta)^2 \rangle\rangle \ll \langle\langle X^2 \rangle\rangle_{T \rightarrow T_c}$; second average is space average, the first is thermodynamic one.

Since mean-field is used in the trial to deduce some ordering, one takes the $T \rightarrow T_c$ limit in its expression. More precisely

(491) $\langle \delta\Delta(\vec{r}_i) \delta\Delta(\vec{r}_j) \rangle = G(\vec{r} = \vec{r}_i - \vec{r}_j)$
 $\langle X(\vec{r}) \rangle = \Delta(\vec{r})$; (X averaged gives Δ , eg. $X = \text{spin}$, $\Delta = \text{magnetization}$)

Then (490) reads

(492) $\int_V d^d r G(r) \ll \int_V d^d r \Delta^2(r)$; The calculations must be made at $T \rightarrow T_c$ and $V = \mathbb{Z}^d$ (so the extension in one direction must be comparable to the correlation length.)

For the study of the left hand side the fluctuation-dissipation theorem is needed, which we deduce now here: -11-

Fluctuation-dissipation result:

Let $\hat{H} = -\bar{\mu} H \sum_i S_i^z$; $\bar{\mu} = g\mu_B$; $\hat{H} \parallel (0z)$ spin system in magnetic field, the inter spin interaction does not matters (i.e.: can be or cannot be, is the same). Let $M = \bar{\mu} \langle \sum_i S_i^z \rangle$ the magnetization. The $\langle \dots \rangle$ means thermodynamic average:

(493) $Z = \text{Tr} e^{-\beta \hat{H}}$; $\langle A \rangle = \frac{1}{Z} \text{Tr} (A e^{-\beta \hat{H}})$; A = arbitrary

If one calculates M; and then $\chi = \frac{\partial M}{\partial H}$, one finds:

(494) $M = \bar{\mu} \frac{1}{Z} \text{Tr} [\sum_i S_i^z e^{-\beta \hat{H}}]$, and

(495) $\chi = \bar{\mu} \left[\left(\frac{1}{Z} \frac{\partial Z}{\partial H} \right) \text{Tr} [\sum_i S_i^z e^{-\beta \hat{H}}] + \frac{1}{Z} \text{Tr} [\sum_i S_i^z \left(\frac{\partial e^{-\beta \hat{H}}}{\partial H} \right)] \right]$; But

(496) $\frac{\partial}{\partial H} e^{-\beta \hat{H}} = \frac{\partial}{\partial H} e^{\beta \bar{\mu} H \sum_i S_i^z} = \beta \bar{\mu} \sum_i S_i^z e^{-\beta \hat{H}}$; and similarly

(497) $\frac{\partial Z}{\partial H} = \frac{\partial}{\partial H} \text{Tr} e^{-\beta \hat{H}} = \text{Tr} \left[\frac{\partial}{\partial H} e^{-\beta \hat{H}} \right] = \beta \bar{\mu} \text{Tr} [\sum_i S_i^z e^{-\beta \hat{H}}]$;

Reintroducing all results to (495) one finds

(498) $\chi = \beta \bar{\mu}^2 \left\{ \underbrace{\left[\frac{1}{Z} \text{Tr} (\sum_i S_i^z e^{-\beta \hat{H}}) \right]}_{\sum_j \langle S_j^z \rangle} \right\} \left[\underbrace{\left[\frac{1}{Z} \text{Tr} (\sum_i S_i^z e^{-\beta \hat{H}}) \right]}_{\sum_i \langle S_i^z \rangle} \right] + \underbrace{\frac{1}{Z} \text{Tr} (\sum_{ij} S_i^z S_j^z e^{-\beta \hat{H}})}_{\sum_{ij} \langle S_i^z S_j^z \rangle} \right\}$

consequently

(499) $\chi = \beta \bar{\mu}^2 \sum_{ij} [\langle S_i^z S_j^z \rangle - \langle S_i^z \rangle \langle S_j^z \rangle]$; But $M_i = \bar{\mu} S_i^z$ is the magnetic moment per site.

Hence:

(500) $\chi = \frac{1}{k_B T} \sum_{ij} \underbrace{[\langle M_i M_j \rangle - \langle M_i \rangle \langle M_j \rangle]}_{G(i,j): \text{the correlation function.}}$ Then

(501) $\chi = \frac{1}{k_B T} \sum_{ij} G(i,j) = \sum_{ij} \chi(i,j)$; $\chi(i,j)$ = nonlocal susceptibility.

Consequently:

(502) $\chi(i,j) = \frac{1}{k_B T} G(i,j)$; This is the fluctuation-dissipation result.

If $G(\vec{r}_i, \vec{r}_j) = G(\vec{r} = \vec{r}_i - \vec{r}_j)$ then, (501) (first equality) becomes

(503) $\chi = \frac{1}{k_B T} \sum_{\vec{r}} G(\vec{r})$; which, if \vec{r} is continuous: $\sum_{\vec{r}} \Rightarrow \int_V G(\vec{r}) d\vec{r}$, and

(504) $\chi = \frac{1}{k_B T} \int_V d\vec{r} G(\vec{r})$; where the volume V is the whole volume at the disposal of the system.

Study of the Ginsburg criterion:

Now we use (504) in the left side of (492) and finds:

(505): $\int_V d\vec{r} G(\vec{r}) = k_B T \chi$; Since one are placed around T_c , so $T \rightarrow T_c$ holds, $\chi \sim |t|^{-\gamma} \Rightarrow \chi = C_1 |t|^{-\gamma}$, $C_1 = \text{a constant}$, one obtains:

(506) $\int d^d r G(\vec{r}) = [C_1 k_B T_c] \cdot |t|^{-\delta}$

Similarly, since $\Delta \sim |t|^\beta \Rightarrow \Delta(\vec{r}) = C_2 |t|^\beta$; and, since $\chi \sim \xi^d$, one has

(507) $\int d^d r \Delta^2(\vec{r}) = C_2 \xi^d |t|^{2\beta}$; where C_2 is also a constant.

Furthermore $\xi \sim |t|^{-\nu}$, hence $\xi = C_3 |t|^{-\nu}$, C_3 being also a constant.

Now from (482, 506, 507), by taking

(508) $\int d^d r \Delta^2(r) = C_2 C_3 |t|^{2\beta - 2\nu d}$; one finds for the Ginzburg criterion:

(509) $[C_1 k_B T_c] |t|^{-\delta} \ll C_2 C_3 |t|^{2\beta - 2\nu d}$; hence

(510) $|t|^{4d - \delta - 2\beta} \ll \frac{C_2 C_3}{C_1} \frac{1}{k_B T_c}$; where C_1, C_2, C_3 are all $O(1)$

This expression is written usually as follows: $\frac{C_2 C_3}{C_1} = C$ of $O(1)$, then

(511) $4d - \delta - 2\beta = 4 \left[d - \frac{\delta + 2\beta}{4} \right] = 4(d - d_c)$; $d_c = \frac{\delta + 2\beta}{4}$ = upper critical dimension.
and one obtains for the Ginzburg criterion:

(512) $|t|^{4(d - d_c)} \ll \frac{C}{(k_B T_c)}$; $d_c = \frac{\delta + 2\beta}{4}$; C is of order unity.
 d_c = upper critical dimension.

In this expression $|t| \ll 1$ holds.

Observations:

- 1° For a mean-field description $\delta = 1$; $\beta = \frac{1}{2}$; $\nu = \frac{1}{2} \Rightarrow d_c = 4$. So for $d > 4$, the small number in the left side is taken at positive power, so (512) is usually satisfied.
- 2° For $d < 4$, the left side appears with negative power, so almost diverges, hence the mean-field gives usually a poor result. But often we use it since provides a rapid "first view" analyzes possibility.
- 3° For $d = 4$, the value of T_c and C also matters in several cases. But about $d = 4$ we discuss more when we analyze the Landau theory of phase transitions.