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PHENOMENOLOGICAL THEORY OF PHASE TRANSITIONS

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INTRODUCTION TO THE STUDY OF PHASE TRANSITIONS

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Introduction.-

I. Phase transition - General.-Everybody has an intuitive knowledge of the various states (or phases) of matter (solid, liquid, gas...) and of the phase transitions : a small quantitative modification of a "relevant" constraint (in general the temperature) introduces a qualitative change of the physical properties. With our increasing knowledge of the properties of condensed matter, it appeared clearly that this kind of phenomena is very general ; let us mention for example, the magnetic transitions (ferromagnetic - antiferromagnetic - ferrimagnetic transitions towards a paramagnetic state) the order disorder transitions in alloys, the structural transitions (ferroelectric - paraelectric transitions, martensitic transitions...), the paraconductive - superconductive transitions, the metal insulator transitions, the liquid crystal transitions (isotropic-nematic...), the liquid-superfluid transition...

In order to characterize the possible equilibrium states, it is quite natural to define "phase diagrams" which determine the nature of the equilibrium state for given values of the external constraints P_i (temperature, pressure, electric or magnetic field...). The phase diagram defines domains in the parameter space $\{P_i\}$ which are separated by surfaces or lines of singularities. It is then necessary to 1) characterize each of these domains not only qualitatively by the physical properties of the corresponding phase, (metal, insulator, superconductive, ferromagnet...) but also quantitatively by the value of one (or several) "order parameter(s)" determining the peculiar state of the considered system. The definition of this order parameter is obvious in some cases (magnetization for the ferromagnetic paramagnetic transition...) ; it is difficult in other situations and its identification is one of the steps towards the understanding of the transition. For example, the relation between the order parameter of a superconductor and the number of Cooper pairs is not at all obvious and took a long time ; the order parameter for the metal insulator transition is not clear at all...

When we know the order parameter, we have to characterize the nature of the singularities of the thermodynamic potential and of the physical properties ; the surfaces (lines or points) of singularities which appear in the parameter space must be classified from a general point of view to point out the general trends. Several

from Solid State Phase Transformations (19 attempts were done according to the theoretical and experimental knowledge of the considered historical period but, it appearred progressively that these singularities present a surprising "universal" character : the singularities of the thermodynamic potential are often the same for systems which have very different physical properties (for example, structural, magnetic...).

In this introduction, we study qualitatively some elementary phase transitions ; this will allow to exhibit the peculiar characteristic properties of the phase transitions (2). Then, we discuss the methods which are used to solve the problems raised by the study of phase transitions (3) ; we introduce the main models which have been used for these studies (Ising, Heisenberg...) and we show that the same model can a priori represent different physical phase transitions. We discuss the definition of a critical point as a singularity of the thermodynamic potential (5) and finally we present a brief summary of these lectures.

2. Phase transitions : some examples. 2.1- Liquid - Gas transition.- 2.1.1. Equilibrium between several phases.- The equilibrium state of an homogeneous system of N identical particules is determined by the value of two thermodynamic quantities, the volume and the energy for example. It is possible that the system in its thermodynamic equilibrium does not remain homogeneous and becomes separated into several different homogeneous parts. The different states of the system which can coexist in the equilibrium state are defined as the different phases of the considered matter. The equilibrium between these phases (1 and 2 for example) is obtained by requiring 1) the equality of the temperatures ($T_1 = T_2 = T$), 2) the equality of the pressures ($P_1 = P_2 = P$) and 3) the equality of the chemical potentials :

$$\mu_1(T,P) = \mu_2(T,P) \qquad (1)$$

This last condition results from the conservation of the total number of particles ($N = N_1 + N_2$) and from the fact that the free enthalpy G(T,P) is minimum for the equilibrium state $dG = \mu_1\, dN_1 + \mu_2\, dN_2 = 0$). For a given pressure P, the chemical potential of one of the phases (1 for example) is smaller than the order ($\mu_1 < \mu_2$) when $T < T_o$: the phase 1 is then stable whereas 2 is metastable ; for $T = T_o$ both phases have the same molar free enthalpy and for $T > T_o$ the phase 2 becomes stables ; T_o is the temperature for which both phases can coexist (Fig. 1a).

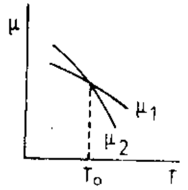


Figure 1a

In a diagram pressure - temperature, the points $T_o(P)$ define a line L which represents the condition (1) ; the points $M = (T,P)$ which are not on this line represent homogeneous states. When we change the external constraints i.e. T,P, the point M which represents the considered system defines a "physical line" in the parameter space and there is phase separation when this line crosses L. Now, if we follow the states of the system in the plane (P,v), the heterogeneous states of the system are represented by a domain of this plane D : the molar volume is - in general - different for both phases($v_1 < v_2$ for example) and a point of D represents a system which has an average molar volume v :

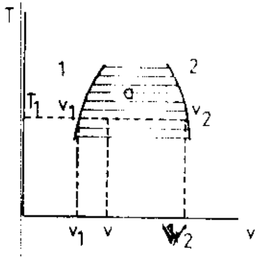


Figure 1b

$$v = x_1 v_1 + x_2 v_2 \qquad (2)$$

$x_1(x_2)$ being the molar fraction of 1(2) ($x_1 + x_2 = 1$). If, as an example, we follow an isothermal variation and if the straight line $T = T_1$ crosses the line L it will appear an heterogenous state with $v_1 < v < v_2$. When we go from one phase to the other ($1 \to 2$) there will be an absorption (or emission) of heat (latent heat $\ell_T = T(s_2 - s_1)$).

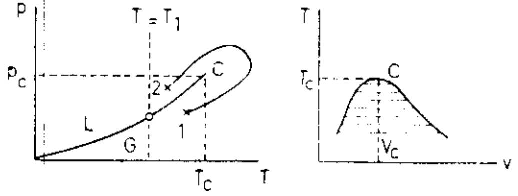


Fig. 1c : Critical point.

2.1.2. Critical point. - The line L can stop at a point (T_c,P_c) called critical point. For $T > T_c$, we can only obtain one phase when we vary P and at $T = T_c$, the difference between both phases disappears ($v_1 = v_2$, $s_1 = s_2$). The diagram (P,v) is then given by the figure 1c. If there is a critical point, we can always go continuously from one phase to another without phase separation : the concept of different phases is then clear only when they coexist.

A critical point can exist only when both phases do not differ qualitatively. For example, if the phases are characterized by different symmetry groups it is impossible to observe a critical point (liquid-solid transition for example). However, if both phases present the same symmetry, a critical point can exist (liquid-gas transition).

When a critical point C exists, it is interesting to study the properties of the system when M is in the neighbourhood of C. Using the definition of C($s_1 \to s_2$, $v_1 \to v_2$ when $T \to T_c$), the stability conditions ($(\partial P/\partial v)_T < 0 \ldots$) and assuming that the critical isotherm is continuous, the critical point is the point for which the isotherm compressibility diverges ($K_T = - 1/v\,(\partial v/\partial P)_T \to \infty$ or $(\partial P/\partial v)_T = 0$). Finally, if we assume that $(\partial v/\partial P)_T$ is an analytic function of v and T for $T \simeq T_c$ and $v \simeq v_c$, we obtain easily the following simple laws for the specific heat and the molar volumes near C (Landau): (Landau-Lifchitz, Statistical Physics).

$$v_1 - v_c = -(v_2 - v_c) \sim (T_c - T)^{1/2} \tag{3a}$$

$$\ell_T \sim T_c - T^{\;1/2} \tag{3b}$$

$$c_p \sim \left[A(T - T_c) + B(v - v_c)^2\right]^{-1} \tag{3c}$$

$$K_T \sim (T - T_c)^{-1} \qquad (T > T_c) \tag{3d}$$

where A and B are constants.

2.1.3. Critical behaviour. - Let us summarize the main experimental features of the liquid-gas transition in relation to the previous results :

1) The liquid-gas transition presents a critical point for which the first derivatives of the thermodynamic potential are continuous ($s_1 = s_2$, $v_1 = v_2$ when $T = T_c$, $P = P_c$):

1a) The isothermal compressibility K_T diverges at $T = T_c$ as : $(T_c - T)^{-\gamma}$ with $\gamma \sim 1$;

1b) The coexistence curve $v_1(T)$, $v_2(T)$ is not a parabola as suggested by (3a) but a cubic : ($v_1(T) - v_c \sim (T_c - T)^{1/3}$).

2) Corresponding states : The isotherms and the coexistence curves are practically the same for a large number of simple systems when we choose reduced variables $t = T/T_c$ and v/v_c.

3) Critical opalescence : the system presents for $T \simeq T_c$ a peculiar "milky" aspect. This results from the diffuse light scattering by droplets the size of which is of the same order of magnitude as the light wave length.

In conclusion, the transition liquid-gas is characterized by a critical point but the predictions of a simple model based on the analycity of $(\partial v/\partial P)_T$ for $T \simeq T_c$ are not satisfied. In the next section, we will precise the concept of critical opalescence the importance of which will be shown to be essential in the following lectures.

2.1.4. Critical opalescence.- The critical opalescence corresponds to a strong small angle light scattering. Let us briefly study the phenomena.

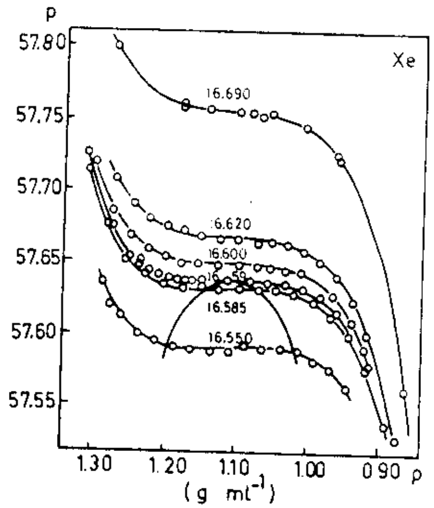


Fig. 2a : Isotherms of xenon in the critical region (from Habgood and Schneider,(1954). Can. J. Chem. 32, 98.

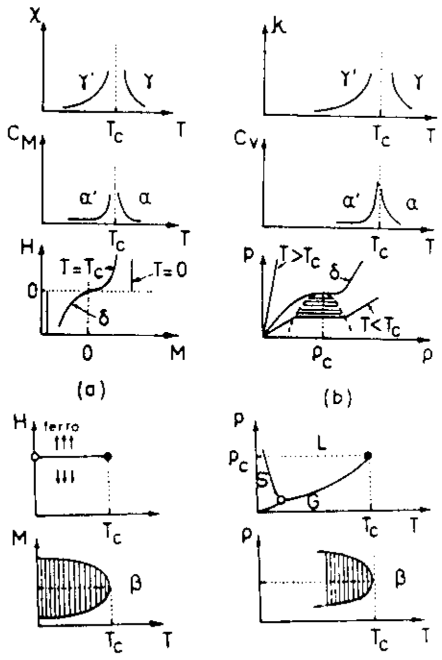


Fig. 2b : Ferromagnets (a) and fluids (b) in the critical region.

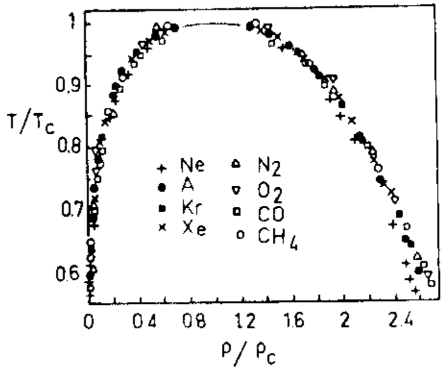


Fig. 2c : Corresponding states (from E.A. Guggenheim, J. Chem. Phys. 13, (1945) 253).

2.1.4.1. Diffuse light scattering. - For a given scattering vector $q(q = k' - k)$ where k and k' are (resp.) the incident (scattered) wave vectors, the diffuse scattered intensity $I(q)$ is proportional to the Fourier transform of the density-density correlation function :

$$\frac{I(q)}{I_o(q)} = \frac{1}{n}\, g(q) \qquad q \neq 0 \tag{4.a}$$

$$g(q) = \int g(r) \, . \, e^{-iqr} \, dr \tag{4b}$$

$$g(r-r') = < (n(r) - n)\, (n(r') - n)> \tag{4c}$$

$n = N/V$ is the density per unit volume ; $I_o(q)$ is the intensity scattered by a random distribution of N particles ; $n(r)$ is the density of particles (per unit volume) for a given configuration and the average $<>$ is an ensemble average over all the configurations of the system in equilibrium with a thermostat (temperature T). Then, $g(r)$ is a measure of the local order i.e. of the correlation between the density $n(r)$ and $n(r')$: if there is no correlation $g(r - r') = <\Delta n(r) \quad \Delta n(r')> = <\Delta n(r)><\Delta n(r')> = 0$ $(\Delta n(r) = n(r)-n)$:

$$g(r - r') = 0 \; (r \neq r') \qquad \text{(disordered system)} \tag{5}$$

since by definition $<n(r)> = n = N/V$.

2.1.4.2. Small angle scattering for $T \simeq T_c$. - To represent the anomalous light scattering for $T \simeq T_c$ it is often useful to represent $I(q,T)^{-1}$ versus q for small q. In this limit $I(q)^{-1}$ can be approximated by a lorentzion :

$$I(q)^{-1} \sim q^2 + \xi^{-2} \qquad (q \to 0) \tag{6}$$

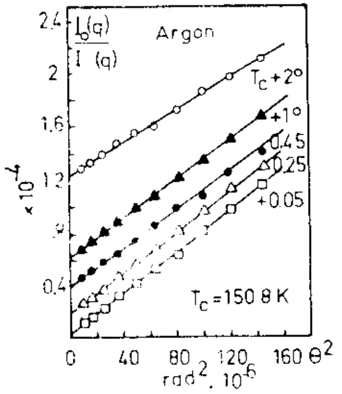
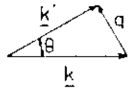


Fig. 3a : Critical diffuse scattering for argon. (from Thomas TE and Schmidt PW, J. Chem. Phys. 39, 1963 2506).



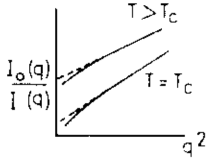


Fig. 3b :Deviations from the law (6) (schematic).

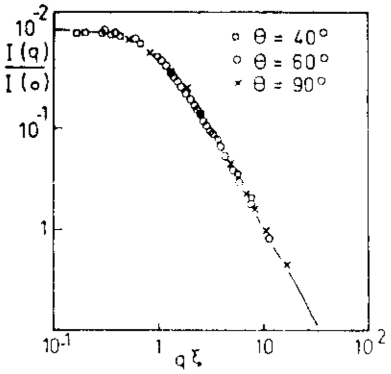


Fig. 3c : Corresponding states for the critical light scattering in a binary liquid.

$\xi(T)$ represents the range of the small angle scattering and $\xi(T)$ (which has the dimension of a length) describes the range of the correlation function g(r). This function can be obtained from (6) by a Fourier transform (cf. 4b) :

$$g(r) \sim \frac{1}{r} \exp - \frac{r}{\xi} \qquad (7)$$

When $T \to T_c$, the correlation length $\xi(T)$ diverges so that we observe a strong small angle scattering. The experimental study of $\xi(T)$ shows that :

$$\xi(T) \sim |T - T_c|^{-\nu} \qquad (8a)$$

and detailed studies show that :

$$g(q) \sim (q\xi)^{-2+\eta} \quad (\eta \neq 0) \text{ for } q\xi >> 1 \qquad (8b)$$

Finally it is possible to verify the existence of "corresponding states" by representing the diffuse scattering versus q and T according to the law (cf. Fig. 3).

$$\frac{I(q)}{I(0)} = f_2(q\xi) \qquad (8c)$$

In conclusion, the small angle scattering shows that the density-density correlation has a range characterized by a correlation length $\xi(T)$ which diverges when $T \to T_c$.

2.2. Binary mixtures. - It is easy to extend the previous results to a system of different particles. The equilibrium conditions are :

$$\mu_i^{\alpha}(T, P, ..., C_j^{\alpha}, ...) = \mu_i^{\beta}(T, P, ..., C_j^{\beta}, ...) \qquad (9)$$

where $c_i^{\alpha} = N_i^{\alpha}/N$ is the concentration of i in the phase α. An equilibrium state of a binary mixture is determined by three quantities, for example T,P and the concentration c of one of the constituents ($0 \leqslant c \leqslant 1$). The equilibrium between two phases is determined by a surface in the parameter space (T,P, μ) ; the equilibrium between three phases is a line (of triple points) in this space and the states with four phases in equilibrium are obtained for isolated points.

In general, the variables T, P and c are preferred. In this space, the equilibrium between two phases is represented by a surface : for given temperature T and pressure P, the intersection of the line ($T = T_0$; $P = P_0$) with this surface determines the concentrations c_α and c_β of the phases in equilibrium. For $c_\alpha < c < c_\beta$, there is phase separation. Usually, the phase diagrams (T,c) are sections of the previous diagrams at constant pressure P. In such a diagram the concentrations of both phases can become equal for some temperature $T_c(P)$ ($c_\alpha(T_c) = c_\beta(T_c)$). This "critical" point can correspond to different physical situations :

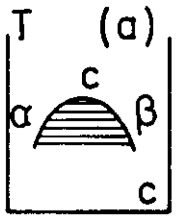


Fig. 4a : Critical point for demixion.

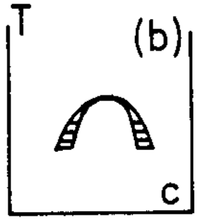


Fig. 4b : Point of equal concentrations.

1) the properties of both phases become identical and we have a critical point the properties of which are similar to those observed for the liquid-gas transitions (Fig. 4a) ;
2) the properties of the phases remain different even when the concentrations are equal : we have a "point of equal concentrations" (Fig. 4b).

When there is a critical point, the phenomena are similar to those we observe for the liquid-gas transitions : the critical point is defined by the condition $\partial\mu/\partial c$ (T,P,c) = 0. Detailed experiments have been done on fluid mixtures ; they showed that the coexistence curve is characterized as previously by a cubic form : $c_\alpha(T) \sim |T_c - T|^{\beta}$, $\beta \simeq 1/3$. Critical opalescence has also been observed, this phenomena is associated to long wave length fluctuations of concentrations ; it can be represented by the same laws as those we discussed in 2.1.4. (Fig. 3.5).

2.3. Binary alloys : order disorder transitions. - 2.3.1. Phase transition and symmetry.- Ordered structures can appear in alloys at "low" temperatures. For "high" temperatures ($T > T_c$) the probability for a site λ to be occupied by an atom A does not depend on the considered site ($c(\lambda) = c$) ; on the contrary, for $T < T_c$ we can observe an ordered phase characterized by a periodic variation of $c(\lambda)$ with λ. In the simplest case, the system remains single phased and the transition is continuous : the concentration $c(\lambda)$ remains constant (and equal to c) for $T > T_c$ but varies continuously when the temperature decreases from T_c ($c(\lambda) \to c$ when $T \to T_c - 0$) to T = 0. This transition presents analogies and differences with the liquid-gas transition : 1) the transition is continuous : the thermodynamic potential G(T,P) and its first derivatives (volume v, entropy s....) are continuous at $T = T_c$ (no latent heat) as previously observed for the liquid-gas transition for $T = T_c$; 2) the transition can also be considered as discontinuous since the symmetry changes when we go from $T_c + 0$ to $T_c - 0$: this was not the case previously since liquid and gas present the same symmetry. The periodicity of the ordered phase is necessarily greater than the periodicity of the disordered phase i.e. the ordered phase has a lower symmetry than the disordered phase. Note finally that for $T < T_c$ the ordered states are identified by the symmetry changes : the new periodicity is obtained from new Bragg lines (superlattice) appearing in the X-ray or neutron diffraction spectrum.

2.3.2. Order disorder transition in β brass.- The first (and simplest) example we consider is the order disorder transition in CuZnβ (Fig. 5). The crystalline lattice is body centered cubic : this lattice results from two simple cubic sublattices (we label α, β). In the disordered state, the A (copper for example) concentration is the same on all the sites ($c_\alpha = c_\beta$). In the ordered state, the symmetry becomes simple cubic (with two atoms per cell) : this change of symmetry comes from the fact that one of the sublattices is occupied preferentially by A atoms, the corresponding concentration being (for c = 1/2) :

$$c_\alpha = \frac{1}{2}(1+\eta) \qquad\qquad c_\beta = \frac{1}{2}(1-\eta) \qquad (10)$$

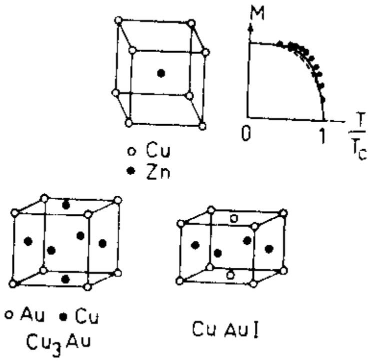


Fig. 5a : Structure, order parameter $\eta(T)$ of β brass (CuZn) (... exp, ——quasichemical method, - - - -MFA) and specific heat $c_v(T)$ (from Nix and Schockley , Rev. Mod. Phys. 10, (1938) 1).

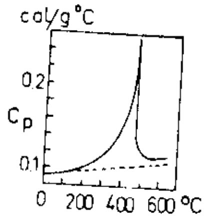


Fig. 5b : Ordered phases in the gold copper system.

For $T < T_c$, the system is characterized qualitatively by the new symmetry and quantitatively by the spatial fluctuation of concentration $\eta(T) = c_\alpha - c_\beta$. The ordered state is characterized by the order parameter $\eta(T)$ which varies from zero ($T = T_c$) to one ($T = 0$) when we go from a disordered ($c_\alpha = c_\beta = 1/2$) to an ordered state ($c_\alpha = 1$, $c_\beta = 0$). For $T < T_c$ the order parameter varies as $\eta(T) \propto |T - T_c|^\beta$ with $\beta \approx 0.3$ and the specific heat presents an anomaly both for $T > T_c$ and for $T < T_c$ (Fig. 5a).

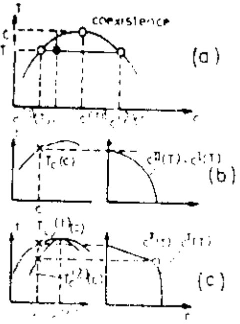


Fig. 5c : Order disorder transitions : a) 2nd order and b) first order transitions.

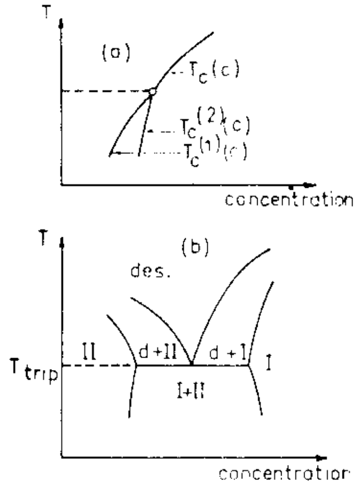


Fig. 5d : Tricritical point.

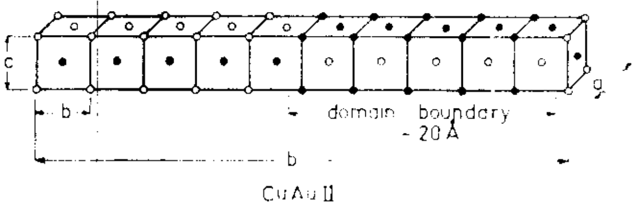


Fig. 5e : Triple point.

2.3.3. Order parameter : CuAu diagram.- The order can be represented by a concentration wave :

$$c(r) = c + A_q \cos(q r + \phi) \qquad (11)$$

characterized by the wave vector q or even by a superposition of such waves :

$$c(\lambda) = c + \frac{1}{2}\left(\sum_q A_q e^{iq\lambda} + A_q^* e^{-iq\lambda}\right) \tag{12}$$

Let us consider as an example the structures observed for the system CuAu, the disordered state being face centred cubic. The system $CuAu_I$ can be represented by a successive stacking of (001) copper and gold planes. The gold concentration can then be written as :

$$c(\lambda) = c + c\eta \cos q_3 \lambda = c\,(1 \pm \eta) \quad (CuAu_I) \tag{13}$$

where $q_3 = [001]\, 2\pi/a$. The superlattice Cu_3Au can be represented by a superposition of three concentration waves :

$$c(\lambda) = c + c_{\eta}\,(\cos q_1\lambda + \cos q_2\,\lambda + \cos q_3\lambda)$$

$$q_1 = [1,0,0]\ \frac{2\Pi}{a},\quad q_2 = [0,1,0]\ \frac{2\Pi}{a},\quad q_3 = [0,0,1]\ \frac{2\Pi}{a} \tag{14}$$

$c(\lambda)$ can have two values on the fcc lattice sites :

$$\begin{cases} c(\lambda) = c + 3\eta c & \text{when } \lambda \text{ is one of the centers of the faces} \\ c(\lambda) = c - \eta c & \text{otherwise} \end{cases} \tag{15}$$

In both cases ((13), (15)) we can also represent the order as follows : 1) consider the fcc lattice as resulting from four simple cubic sublattices ($\alpha = 1, 2, 3, 4$) ; 2) assume that the concentration $c(\lambda)$ depends only on the nature of sublattice α. However, the representation (12) is much more general ; the q vectors are directly determined by the diffraction superlattice lines (X-rays, neutron, electron diffraction). Note that the new period (Fig. 4) can be commensurate or incommensurate with the period of the disordered lattice ; for example in the AuCu system we observe the periodic antiphase $AuCu_{II}$ stable in a small temperature range (30°) around 400°C : the structure of $AuCu_{II}$ can be approximately represented by a regular repetition of two sets of five cells of $AuCu_I$ which are in antiphase with respect to each other.

2.3.4. Conclusion. - The order disorder transitions are characterized qualitatively by a symmetry change. The ordered state is determined by the functions $c(\lambda)$ i.e. i) qualitatively by the q vectors which appear in the expansion of the concentration in periodic concentration waves ; ii) quantitatively by the amplitudes A_q i.e. by the order parameter $\eta c = (\sum_q |A_q|^2)^{1/2}$ which characterize the importance of the concentration fluctuations.

The transition can be continuous ("2nd order") : we discussed qualitatively the properties of this trantition in relation to the liquid gas transition. In the plane (T,c), the temperatures $T_c(c)$ define a line which separates two domains corresponding to single phased ordered ($\eta \neq 0$) and disordered ($\eta = 0$) states. Along this line the transition is continuous and the maximum of this curve $T_c(c)$ - if it exists - has no peculiar physical meaning.

The transition can also be discontinuous (or 1st order), the order parameter going discontinuously from a non zero value $\eta(T_c - 0) \neq 0$ to a zero value $\eta\,(T_c + 0) = 0$. The transition line $T_c(c)$ can present a maximum : in such a case, the line can be splitted in two branches ($T_c^{(1)}(c)$, $T_c^{(2)}(c)$) and both phases coexist for $T_c^{(2)}(c) < T < T_c^{(1)}(c)$. In real cases, the phase diagram can be much more complicated. For example, when we vary the concentration, the first order transition can become a continuous transition at $T_c(c_0)$ (tricritical point) ; we can also observe the coexistence of three phases (two ordered phases and one disordered phase) at the triple point.

2.4. Magnetic transitions. - 2.4.1. Paramagnetic-ferromagnetic transitions. -

2.4.1.1. The first experimental and theoretical studies of magnetic transitions (Faraday, Curie, Weiss...) concerned the simplest case : the system is paramagnetic for $T > T_c$ and becomes ferromagnetic below the Curie temperature T_c (iron, cobalt and nickel...). The ferromagnetic state is characterized by a non zero uniform magnetization M(T) - even without an applied magnetic field H. The magnetization M(T) is a continuous function of T for all values of T ($M(T) \to 0$ when $T \to T_c$) ; more generally, the thermodynamic potential and its first derivatives (M, s, v...) are continuous when T increases from below to above the Curie temperature. However, this transition is also discontinuous since the symmetry (i.e. the set of symmetry operations, which leaves the system invariant, changes discontinuously at $T = T_c$: the symmetry of the ferromagnetic ordered state ($M \neq 0$) is lower than the symmetry of the paramagnetic the order disorder transition observed for the β brass : here, the ordered state is characterized by a (pseudo) vector, the magnetization M, whereas the order disorder transition is characterized by a scalar η. The magnetization is the order parameter related to the paramagnetic ferromagnetic transition. It is an extensive quantity and we will consider in the following sections M as representing the magnetization density per unit volume (or per atom). In practical situations the magnetization is coupled to the lattice variables so that the magnetic state depends on the direction of the magnetization (magnetic anisotropy, easy axis of magnetization...) ; for simplicity, we neglect such effects here ; they do not modify qualitatively the physical picture of the transition in most cases.

2.4.1.2. Critical behaviour (Fig. 6a, c) (experiment). - Let us briefly summarize the magnetic properties of the transition for $T \simeq T_c$ for the simple ferromagnets (Ni, Co, Fe) :

1) For $T < T_c$, the magnetization varies as $|T_c - T|^{\beta}$ with $\beta \simeq 0.3$;
2) The specific heat c_p presents an anomaly for $T \simeq T_c$ (below and above T_c) : it is varying as $(T - T_c)^{-\alpha}$ with $\alpha \simeq 0.1$ (Fig. 6e) ;
3) At $T = T_c$, the magnetic susceptibility $\chi_T = (\partial M/\partial H)_{T,P}$ is divergent and varies as $(T - T_c)^{-\gamma}$ with $\gamma \simeq 1.3$;

4) The critical isotherm (i.e. $M(H,T=T_c)$) varies as $H^{1/\delta}$ with $\delta \simeq 4$;

5) Finally, we observe (by magnetic neutron diffuse scattering) a magnetic critical opalescence i.e. large fluctuations of the magnetization density $\langle |M_q|^2 \rangle$ for small wave vectors q ($q \simeq 0$) (see 2.1.4. for comparison and replace, in equation (4), (5) and (6) the density $\rho(r)$ by the magnetization density $M(r)$).

2.4.1.3. Discussion. -Order parameter and conjugate field. - The critical properties of the previous system are very similar to those we described for the liquid-gas transition : the magnetization M plays the role of the density $\rho - \rho_c$ and the magnetic field H must be compared to the pressure P. In both cases, the order parameter is defined from an extensive variable and the variables ($\rho - \rho_c$, P), (M,H) are "conjugate" in the thermodynamic sense. Among all the intensive variables defining the external constraints the variable H, conjugate to the order parameter M, plays a peculiar role : if the system is submitted to a non zero value of this field H, the order parameter M becomes non zero for $T > T_c$ and the linear response of the system to this field, the susceptibility $\chi = (\partial M/\partial H)_{H=0}$ diverges when $T \to T_c$ (χ, $K_T \to \infty$ when $T \to T_c$). The divergence of this susceptibility is a "premonitory" effect which indicates that the system will support a phase transition for $T = T_c$.

Finally, if we compare these results to the results which are obtained for the order disorder transition we observe a similar behaviour (see(1) and (2)), but the field conjugate to the order parameter η has no physical meaning (see & 2.4.2. for comparison).

2.4.2. Paramagnetic-antiferromagnetic transition.- It is possible that, for $T < T_c$, the ordered state corresponds to an antiferromagnetic arrangement of the moments : the macroscopic magnetization remains zero for all temperatures but the magnetization of each of the lattice sites $m(\lambda)$ is different from zero when $T < T_c$. The magnetization must then vary from site to site. The simplest case corresponds to an antiferromagnet defined from the two sublattices α and β we considered previously for the β brass (2.3.2). The lattice is body centered and the magnetization $m(\lambda)$ is zero (for $H = 0$) on all the lattice sites λ, for $T > T_c$. Below T_c, the magnetization $m(\lambda)$ becomes non zero and the simplest magnetic arrangement to obtain a zero macroscopic magnetization is the following : $m(\lambda) = m_\alpha$ on the α sublattice sites and $m(\lambda) = m_\beta = -m_\alpha$ on the β sites. The symmetry is lowered (from bcc to sc) when the temperature decreases from $T_c + 0$ to $T_c - 0$. The transition can be discontinuous ($m(T) \to m(T_c) \neq 0$ when $T \to T_c - 0$) or continuous ($m(T) \to 0$ when $T \to T_c$). An ordered state is then characterized (see 2.3.2.) by the order parameter $M = m_\alpha - m_\beta$ but, as for the order disorder transitions, the field H conjugate to this parameter has no physical meaning. More precisely, by definition, this field must be coupled to the system by the coupling energy :

$$\langle \mathcal{H}_1 \rangle = -NH(m_\alpha - m_\beta) \qquad (16a)$$

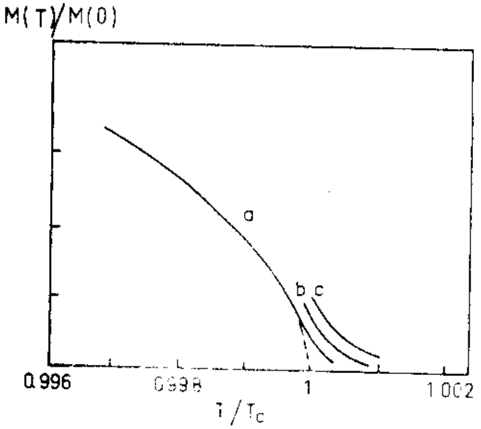


Fig. 6a : Magnetization of $YFeO_3$ ($T < T_c$:
a) H = 38 Oe
b) H = 210 Oe
c) H = 460 Oe
----H = 0.
(from Gorodetsky, G., et al. Sol. St. Comm. 4,(1966) 147.)

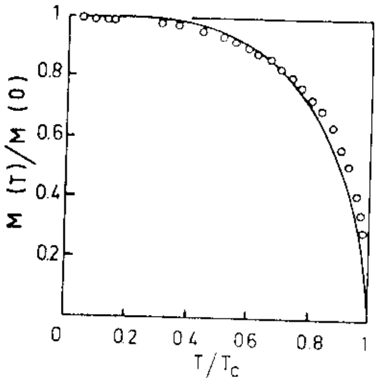


Fig. 6b : Magnetization of nickel versus temperature (from Weiss, P. and Forrer, R., Ann. Phys. (Paris) 5,(1926)153.)

By comparison of this equation with the coupling energy of the system with a space dependent field $H(\lambda)$

$$\langle \mathcal{H}_1 \rangle = -\sum_\lambda m(\lambda) H(\lambda) \qquad (16b)$$

we find that the field conjugate to the order parameter M is a "staggered" field equal to :

$$H(\lambda) = \begin{cases} H \text{ if } & \lambda \in \alpha \\ -H \text{ if } & \lambda \in \beta \end{cases} \qquad (16c)$$

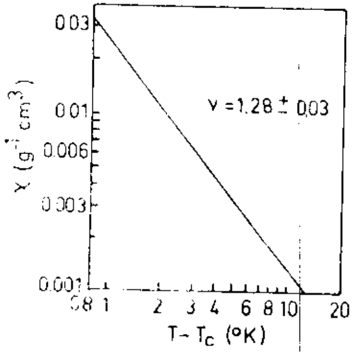


Fig. 6c : Susceptibility of nickel when T ≈ T_c (from Arajs, 1965) J. Appl. Phys. 36, 1136.

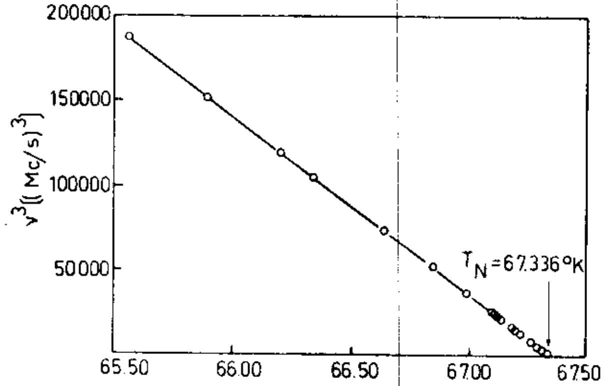


Fig. 6d : Magnetization of a sublattice of MnF_2 when T ≈ T_N : β = 0.33 (from Heller, P., and Benedeck, G.B., Phys. Rev. Lett. 8,(1962)428) from NMR data (M∝ν where ν is the resonance frequency).

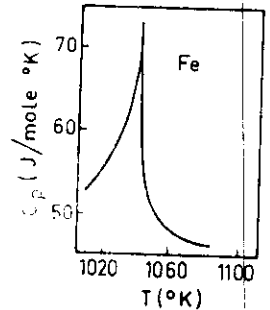


Fig. 6e : Specific heat of iron when T ≈ T_c. (from Lederman, F.L., et al, Phys. Rev. B 9 (1974)2981.)

Practically, such a field cannot be realized so that the susceptibility cannot be measured directly.

2.4.3. Complex magnetic structures - order parameter. More generally, the magnetic order will be characterized by a magnetization density which will be spatially varying according to a single magnetization density wave :

$$m(\lambda) = A_q \cos(q\lambda + \phi) \qquad (17a)$$

or to a superposition of such waves :

$$m(\lambda) = \frac{1}{2}\sum_q \left(A_q e^{iq\lambda} + A_q^{*} e^{-iq\lambda}\right) \qquad (17b)$$

For example, the magnetic structure of bcc chromium is characterized below $T_N \approx 311$ K by a transverse ($q.A_q = 0$) sinusoidal wave (T.A.F. state) ; the wave vector is parallel to [100] and the corresponding wave length decreases continuously from 28a to 21a (a = interatomic distance) when the temperature decrease from 311 K to 123 K. Below 123 K, the wave becomes longitudinal - q and A_q are parallel (L.A.F. state) and its period remains practically constant. The transitions P-TAF, TAF - LAF (P = paramagnetic) are first order transitions but these properties are very sensitive to the impurities : some atomic per cent of impurities (V, Mn...) are sufficient to change this complex antiferromagnetic state into the simple antiferromagnet described in (2.4.2.).

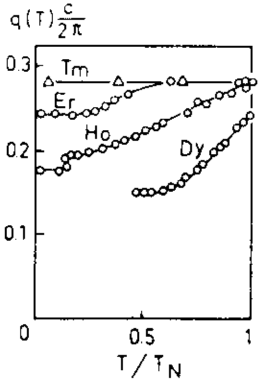


Fig. 7a : Periodicity of the magnetic helix versus temperature for same rare earths (c = periodicity along the hexagonal axis).

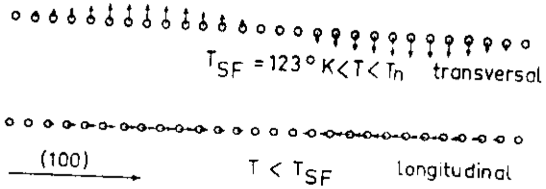


Fig. 7b : Magnetization of chromium.

Another interesting example of complex structures is given by the rare earths for which helicoidal structures are often observed. The lattice symmetry is hexagonal and the transition from the paramagnetic to the helicoidal state is (in general) continuous. The q vector is perpendicular to the hexagonal planes and the moments are perpendicular to a direction $\underline{\Delta}$ which is not necessarily the same as the direction of **q**. Moreover, the periodicity of the magnetic helix varies continuously with temperature (Fig. 7) : the corresponding structures have then (in general) a period which is incommensurate with the period of the crystalline lattice.

2.5. Structural transitions.- From some years, the structural transitions have been extensively studied in relation to ferroelectricity. It has been possible to show that such transitions can be continuous and have the same properties as those we discussed previously. The ordered state has the lowest symmetry and is characterized by the displacement of some atoms relative to the others. For example, in the simple bcc crystal with two s.c. sublattices (§ 2.3.2.) it is possible to imagine that the atoms α are displaced by the same quantity relative to the atoms β ("ferrodistortive" transition) : the symmetry of the ordered system becomes quadratic... In the same way as previously, it is possible to represent an ordered state by one (or several) static displacement waves.

A simple example of such continuous transitions is given by the transition of $SrTiO_3$ from a cubic to a tetragonal state. In the high temperature state the cubic cell is occupied by a titanium atom (at the corners), three oxygen atoms (at the edges) and one strontium atom (at the cube center). Each Sr is then surrounded by an octaedra of oxygen. Below $T_c = 100\,K$, the octaedra are turned around $[001]$ by an angle $\phi(\lambda)$. This angle varies with the crystalline sites λ occupied by titanium (Fig. 8) :

$$\underset{[001]}{\phi(\lambda)} = \phi_q \cos q\lambda \qquad , q = \frac{\Pi}{a} \left[\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right] \tag{18}$$

a being the parameter of the cubic cell. The wave vector related to this distortion wave is parallel to $[111]$; it is such that two neighbouring octaedras are characterized by two opposite values of $\phi(\lambda)$ (antiferrodistortive state).

In the same way, $LaAlO_3$, whose crystalline (perovskite) structure is the same for high temperatures, presents a phase transition from a cubic to a trigonal state when $T_c \simeq 800\,K$. In this case, the octaedras are turned around $[111]$ by an angle $\phi(\lambda)$. This rotation can be considered as the product of three of the previous rotations (18) ($[100] \times [010] \times [101]$) : as previously this transition is antiferrodistortive since two neighbouring octaedras are turned by opposite angles. As for the previous transition, it is possible to study the critical behaviour : the order parameter $\phi(T)$ varies as $|T - T_c|^{\beta}$ with $\beta \simeq 0.33$ when $T \simeq T_c$ (see Fig. 8d).

Finally, let us note that such continuous transitions have also been observed for uni or bidimensional systems (see Gerl's lectures).

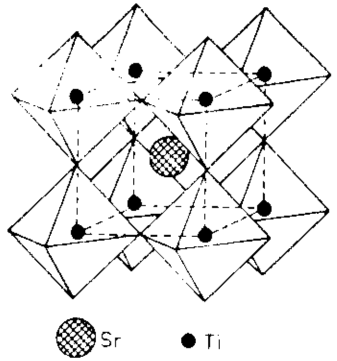


Fig. 8a : Structure of $SrTiO_3$.

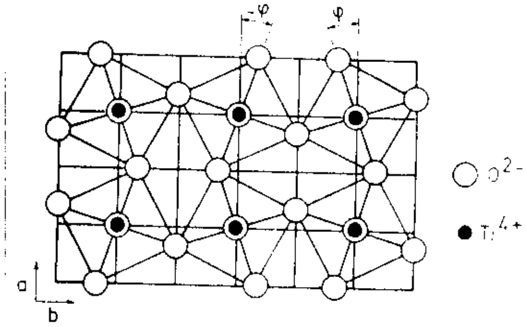


Fig. 8b : Distortion of $SrTiO_3$ for T T_c.

3. Study of the phase transitions methodology. - 3.1. Continuous transitions - General features. - The previous qualitative discussion shows that beyond the variety of the phase transitions, it is possible to exhibit a strong unity. Excluding the discontinuous transitions ("1st order") characterized by a discontinuity of the first derivative of the thermodynamic potential (s, V...), we considered a large number of "continuous" transitions characterized by : 1) a symmetry change at $T = T_c$, one of the phases (the ordered phase) having a lower symmetry than the other ; 2) the continuous variation of the thermodynamic potential and of its first derivatives when we pass through the

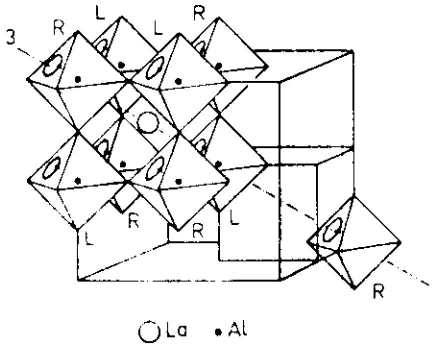


Fig. 8c : Distortion of $LaAlO_3$ for $T < T_c$.

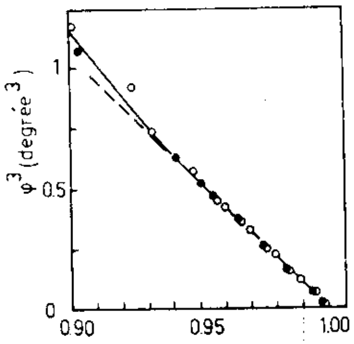


Fig. 8d : Variation of φ (T) with temperature ($\beta = 0.33$) in $SrTiO_3$. (from Müller K.A., et al. in local properties at phase transitions,(1976),ed. by KA Muller, North Holland).

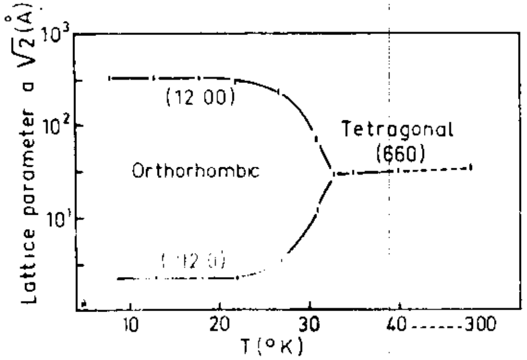


Fig. 8e : Lattice parameter versus temperature for $TbVO_4$ (from Will, G., and Schafer, W., 1971) J. Phys. C 4, 811.

transition temperature ; 3) in the ordered state (i.e. generally for $T < T_c$), an equilibrium state is characterized by the value of an extensive variable M called the "order parameter". This order parameter can be a scalar, a vector or even a tensor... ; it characterizes quantitatively the amount of order and is choosen to be zero (by definition) in the disordered state ; 4) in the "critical region" (i.e. for $T \simeq T_c$) the order parameter, the specific heat... exhibit a singular behaviour and present a non analytic behaviour at $T = T_c$; 5) when $T \to T_c$ the "susceptibility" $\chi = \partial M/\partial H$ i.e. the linear response of the system to the field H conjugate to the order parameter diverges and this divergence for $T \to T_c + 0$ is a "premonitory effect" of the phase transition ; 6) finally, the critical region is characterized by a "critical opalescence" i.e. by large long wave length fluctuations of the order parameter $< |M_q|^2 >$ or by long ranged spatial correlations $< M(o)\, M(r) >$.

It is important to recognize that this class of phase transitions is characterized by this last phenomena. When $T \simeq T_c$, the system is fluctuating between states of similar stability. Then, it appears locally, for $T > T_c$, ordered domains whose size ξ and life time τ increase when $T \to T_c$. The correlation length ξ (T) diverges for a continuous transition whereas it remains finite for a first order transition.

3.2. Problem and methods. - A large number of problems must be solved to understand the physics of the phase transitions. For example : 1) What is the physical origin of such transitions ? ; 2) Is it possible to predict the type ("continuous" or "discontinuous") of a transition ? What is the role of the external constraints ? 3) Is it possible to define precisely an "order parameter" ? 4) Is it possible to precise the singular behaviour of the physical properties in the critical region ? What is the degree of "universality" of such a behaviour ?

As a first step, these problems must be solved qualitatively.

From an experimental point of view, it is necessary to characterize a transition by detailed measurements of the physical properties near T_c which will determine the nature of the singularity of the thermodynamic potential. We need measurements of 1) the thermodynamic quantities 2) and also of the spatial correlations $< M(o)\, M(r) >$ by diffuse (light, X-rays, neutron...) scattering. A transition will be characterized by a set of laws which express the variation of these properties with temperature (C_p(T), S(T), χ(T), ξ(T)...). The comparison of these physical data for different phase transitions (structural, magnetic, order disorder...) will allow to define "universality" classes.

From a theoretical point of view, we can use several approaches according to the "level of approximation" we choose. It is tempting to try to represent as strictly as possible a transition by a microscopic model ; this approach is an "ab initio" determination of the physical properties but 1) it is ambitious : it gives (in principle) too much information for our qualitative purpose and 2) it does not allow to exhibit the "universality " of the critical behaviour. For this reason it is important to develop phenomenological theories based on general assumptions concerning the symmetry.

These theories will allow (in principle !) to classify the transitions, to deduce the conditions which are necessary to obtain continuous transitions, to relate the singularity of the thermodynamic potential at $T = T_c$ to symmetry transformations and to invariance properties.

From a methodological point of view, it will be equally interesting to "build" simplified "microscopic models" which retain the qualitative features and are as simple as possible to be exactly soluble or, at least, analytically and numerically tractable. These models -Ising, Heisenberg, spherical, Pott's... models- are then interesting not only for the applications they can have but also for the qualitative features and exact theorems they allow to discover. We discuss briefly in the next section some of these models.

4. Microscopic models. - The macroscopic system is now assumed to be made of N identical microscopic subsystems λ and the phase transition is a cooperative effect which results from the coupling interaction between the microscopic systems. More precisely, this coupling energy $k_B\theta$ determines the "ordered state" whereas the entropy associated to the disorder induced by the thermostat favors the "disordered" state ; the phase transition comes from the competition between the coupling ($k_B\theta$) and thermal (k_BT) energies, the critical temperature T_c being roughly equal to θ.

4.1. Ising model. - 4.1.1. Definition ; magnetic transitions.- This model has been used extensively to describe the magnetic order. The subsystem λ ("spin" 1/2 for example) can be one of two states (↑ and ↓) whose energies $\varepsilon_\uparrow$, $\varepsilon_\downarrow$ are equal (when there is no applied field). We define the number σ_λ (representing the 2 components of the spin for example) for each system λ : $\sigma_\lambda = +1$ if λ is in the state ↑, $= -1$ otherwise. The coupling energy is then chosen to be as simple as possible : it is assumed to result from pair interactions between "spins". Choosing the origin of the energies so that $\varepsilon_\uparrow = \varepsilon_\downarrow = 0$, the energy of the system may be written as follows (Ising model) :

$$\mathcal{H}(\{\sigma_\lambda\}) = -\frac{1}{2}\sum_{\lambda\neq\mu} v(\lambda-\mu)\,\sigma_\lambda\sigma_\mu - \sum_\lambda \sigma_\lambda H_\lambda \tag{19}$$

H_λ is the (magnetic) field conjugate to σ_λ. The thermodynamic properties of this system will be obtained from the classical relations :

$$F = k_BT \operatorname{Log} Z \tag{20}$$

$$Z = \sum_{\{\sigma_\lambda\}} e^{-\beta\mathcal{H}(\{\sigma_\lambda\})} \tag{21}$$

the sum (21) being defined over all the ("spins") configurations. When $v(\lambda) > 0$, a "spin" ↑ tends to be surrounded by ↑ spins to minimize the coupling energy ; at low temperatures, the system becomes "ferromagnetic" ($\sigma_\lambda = 1\ \forall\lambda$ or $\sigma_\lambda = -1\ \forall\lambda$ when $H_\lambda = 0$) and the coupling energy $k_B\theta = \sum_\mu v(\lambda-\mu)$ is of the order of magnitude of the critical temperature k_BT_c.

4.1.2. Ising model and liquid-gas transition. - This model can also describe a fluid (lattice gas) presenting a liquid-gas transition. In such a case, the degree of freedom associated to each site λ has the following meaning : if $\sigma_\lambda = +1$, the site λ is occupied by an atom A and if $\sigma_\lambda = -1$, this site is unoccupied. Let us now introduce the occupation numbers p_λ :

$$p_\lambda = \frac{1}{2}(1+\sigma_\lambda) = \begin{cases} 1 \text{ if } \lambda \text{ is occupied} \\ 0 \quad \text{otherwise.} \end{cases} \tag{22}$$

If the fluid is in equilibrium with a thermostat, the field conjugate to the density $\rho = 1/N \sum_\lambda p_\lambda$ (N is the number of sites) is the chemical potential μ of the thermostat. The energy of the system $\tilde{\mathcal{H}}$ is then given by :

$$\tilde{\mathcal{H}}(\{p_\lambda\}) = \mathcal{H} - \mu N = -\frac{1}{2}\sum_{\lambda\neq\mu} v(\lambda-\mu)\,p_\lambda p_\mu - \mu\sum_\lambda p_\lambda \tag{23}$$

and the properties of this system (ρ, for example) are calculated using the "grand canonical" ensemble.

4.1.3. Ising model, demixion and order-disorder transitions.- The Ising model can also represent the physics of a binary alloy whose energy $\mathcal{H}$ can be written as a sum of pair interactions $\varepsilon_{ij}(\lambda-\mu)$, $\varepsilon_{ij}(\lambda-\mu)$ being the interaction energy between two atoms i and j in λ and μ. A configuration of the alloy is determined by the set $\{p^i_\lambda\}$ where the occupation numbers p^i_λ are defined (see(22)) by :

$$p^i_\lambda = \begin{cases} 1 \text{ if } \lambda \text{ is occupied by an atom i} \\ 0 \quad \text{otherwise} \end{cases} \tag{24}$$

The energy of the system in equilibrium with the thermostat is given by :

$$\tilde{\mathcal{H}}(\{p^i_\lambda\}) = \mathcal{H} - \sum_i N_i\mu_i = -\frac{1}{2}\sum_{\substack{\lambda\neq\mu\\ i,j}} p^i_\lambda\, p^j_\mu\, \varepsilon_{ij}(\lambda-\mu) - \sum_{i,j} p^i_\lambda\mu_i \tag{25}$$

μ_i(i = A, B) is the chemical potential of the ith constituent.
For a binary alloy and if we assume that all sites λ are occupied ($p^A_\lambda + p^B_\lambda = 1$), an alloy configuration is determined by the numbers $\{p^A_\lambda = p_\lambda\}$ and the energy $\tilde{\mathcal{H}}$ becomes identical to (23) :

$$\tilde{\mathcal{H}}(\{p_\lambda\}) = -\frac{1}{2}\sum_{\lambda\neq\mu} v(\lambda-\mu)\,p_\lambda p_\mu - \sum_\lambda \Delta\mu\, p_\lambda + C \tag{26}$$

C is a constant ; v and $\Delta\mu$ are defined by :

$$v(\lambda-\mu) = \varepsilon_{AA}(\lambda-\mu) + \varepsilon_{BB}(\lambda-\mu) - 2\,\varepsilon_{AB}(\lambda-\mu)$$

$$\Delta\mu = \mu_A - \mu_B + 2\,(\varepsilon_{BB}(0) - \varepsilon_{AB}(0)) \tag{27}$$

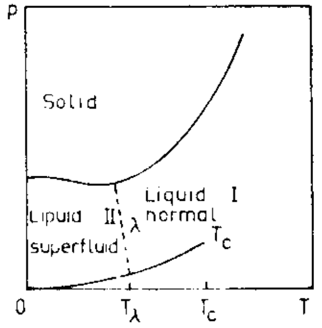


Fig. 9a : Phase diagram of ^{4}He (schematic).

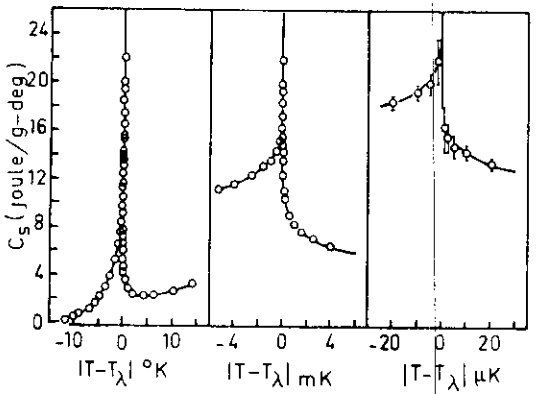


Fig. 9b : Liquid helium : Specific heat when $T \sim T_\lambda$; the transition remains sharp even for $\Delta T \sim 10^{-6}$ K. (from Fairbank, F.W., Proc. Fifth Int. Conf. on Low Temp. Phys. (1937),p. 50, Madison Wiscondin).

be determined by the existence of a singularity of the thermodynamic potential F. However, Z seems to be an analytical function ($T > 0$) since it is a sum of exponentials (see(21)) : at first sight there is no singularity and no phase transition ! This is exact when the number of configurations $\{\sigma_\lambda\}$ is finite : there is no well defined transition for finite systems.

However, in thermodynamics and statistical physics, we are interested by the behaviour of macroscopic systems i.e. by the thermodynamic limit (N, $V \to \infty$, N/V remaining constant) : relations (19) and (20) have been obtained in the thermodynamic limit. When the size of the system (i.e. N) increases, the number of configurations increases exponentially and becomes infinite. The limit of an analytic function is not necessarily analytic so that the phase transitions must be defined mathematically in the thermodynamic limit.

$$\hat{\varepsilon}_{ij}(0) = \sum_{\mu} \varepsilon_{ij}(\lambda - \mu)$$

When $v(\lambda) > 0$, an atom A tends to be surrounded by atoms A and we must observe the demixion at low temperatures. When $v(\lambda) < 0$ an atom A tends to be surrounded by atoms B and we can hope to obtain an ordered structure at low temperatures ; this order depends both on the lattice and on the function $v(\lambda)$. The ferromagnetic (antiferromagnetic) transitions are to be compared (respectively) with the demixion (order-disorder) transitions. If we introduce as previously (see (22)) the quantities $\sigma_\lambda = 2p_\lambda - 1$, the problem (25) is equivalent to an Ising problem with applied magnetic field :

$$\tilde{\mathcal{H}}(\{\sigma_\lambda\}) = -\frac{1}{2} \sum_{\lambda \neq \mu} v(\lambda-\mu)\, \sigma_\lambda \sigma_\mu - (\Delta\mu + \frac{1}{4}\hat{v}(0)) \sum_{\lambda} \sigma_\lambda + C' \qquad (28)$$

C' is a constant.

4.1.4. Ising model and structural transitions. - The Ising model can also represent a structural transition when peculiar atoms can have two possible positions : let us mention for example the ferrodistortive transitions in KH_2PO_4, $NaNO_2$... In the same way, when each **subsystem** λ can be in one of two electronic states and when these states are coupled to the deformations, the corresponding transition can be represented by an Ising model (Jahn-Teller transitions in Vanadium ($DyVO_4$, $TmVO_4$...).

4.1.5. Conclusion. - The Ising model is important because it can represent a transition resulting from the coupling between N subsystems if these subsystems can have two possible states : then, σ_λ will label the spin, the chemical nature, the electronic state, the displacement... of the system λ according to the physical nature of the transition.

4.2. Heisenberg model. - This model has been introduced to describe the ordered magnetic structures and is an extension of the Ising model. We associate a vector S_λ to each subsystem λ and the coupling energy is given by :

$$\mathcal{H} = -\frac{1}{2} \sum_{\lambda \neq \mu} v(\lambda-\mu)\, S_\lambda . S_\mu - \sum_{\lambda} H_\lambda . S_\lambda \qquad (29)$$

The spin S is defined in the "spin" space whose dimension is n : n is the dimensionality of the order parameter. If S is a vector in three dimensional space n = 3 ; if it can only lie in a plane, n = 2 (strong anisotropy)... The Heisenberg model is then characterized by two numbers (n,d) : d is the dimension of the lattice space and n the dimension of the spin space. When $n \to \infty$, we obtain the spherical model : this model is exactly soluble (even when d = 3 !).

5. Phase transition effects. Thermodynamic limit and mathematical definition of a critical point.

- For a given model (the Ising model for example), we must calculate the partition function Z and the free energy F (see (20), (21)). A phase transition will

This can be illustrated by a numerical calculation of F(T) and c_p for an Ising model (square lattice - d = 2 - with interactions $v(\lambda)$ between nearest neighbours). The thermodynamic quantities - the specific heat for example - can be determined from equations (19 and (20) when the system is made of an increasing number of squares (1×1, 2×2, 4×4...). Figure 10 shows that if the specific heat is perfectly regular for the smallest systems (2x2) but an anomaly appears progressively when the size increases, the function $c_p(T)$ remaining regular for all T values when this size remains finite. The singularity appears only in the thermodynamic limit and it has been shown to be logarithmic (Onsager) :

$$c_p \sim \text{Log} \; |T - T_c| \qquad (30)$$

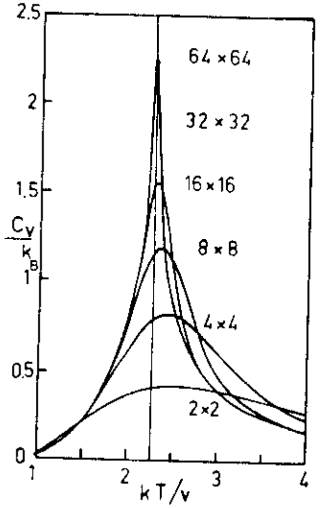


Fig. 10a : Specific heat for n x n Ising squares. (from Ferdinand, A.E., and Fisher, M.E., Phys. Rev. 185,(1969)832).

In conclusion, the phase transitions are defined mathematically by the singularities of the thermodynamic potential for peculiar values of the external constraints (temperature, pressure...) in the thermodynamic limit.

Finally, it is important to recognize that it is difficult to determine experimentally the existence of a transition for T = T_c and the nature of this transition (continuous, discontinuous ?). In some cases, detailed experimental studies have shown that the transition remains well defined for all accessible temperature scales (Fig. 9b) but it is not excluded that defects, impurities... smear out the transition in some cases.

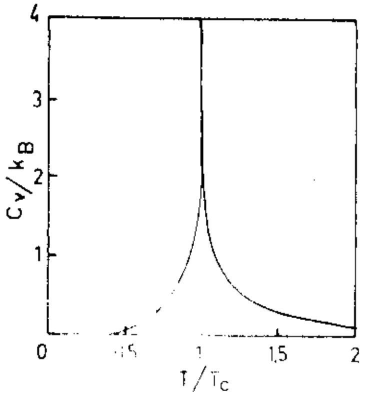


Fig. 10b : Specific heat for a square lattice (from Onsager, L., Phys. Rev. 65,(1944), 117).

6. Conclusion. - The previous analysis allows to : 1) exhibit the main features of the phase transitions, 2) suggest a first classification ("continuous" and "discontinuous" transitions), 3) define the problems we must solve to understand the origin and the properties of these transitions. The following lectures will try to introduce the methods and the concepts without detailed discussions of the peculiar physical situations ; let us now briefly present a summary of these lectures.

In the first chapter, we discuss the phenomenological theory introduced by Landau ; this theory 1) suggests a classification of the phase transitions and defines the order parameter in relation with the symmetry change at T = T_c ; 2) defines some conditions which are necessary to obtain second order transitions and 3) predicts the nature of the singularity of the physical properties (specific heat, susceptibility, order parameter...). This theory uses general symmetry arguments and assumes that the thermodynamic potential presents analytical properties at T = T_c : this last assumption has been shown later to be false, so that the singularities of the physical properties are not correctly predicted by this theory (see chapter 3).

In the second chapter, we study the simplest approximation and model to describe the phase transitions i.e. the mean field approximation (M.F.A.) of the Ising model. We show that the transition we obtain by a M.F.A. has the same features as those obtained by the Landau theory. We show the limitations of this M.F.A., the fluctuations being dominant in the critical region when the space dimensionality is low (d < 4). However, the M.F.A. is practically important since it is the simplest approximation which is always used to obtain a first approach of the phase transition (Bragg Williams for order disorder transitions, B.C.S. method for the superconductors, Van der Waals method for the liquid-gas transitions...).

In chapter 3, we precise the nature of the singularity of the thermodynamic potential for "simple systems". We are mainly interested by the critical region and we show that the thermodynamic potential is a generalized homogeneous function of the temperature and of the field conjugate to the order parameter. We show also that the critical exponents depend mainly on the space and order parameter dimensionalities.

In the last chapter (4) we try to exhibit the sufficient conditions that a system must satisfy to obtain the singular behaviour described in chapter 3. For this, we write the partition function Z as a functional integral (Landau Ginzburg) ; we recover the Landau model as an approximation. Then, we introduce a peculiar group of transformations - the "renormalization group" - which will allow to characterize the critical behaviour ; we show that it is possible to find the singular behaviour of simple systems (see chapter 3) in terms of such transformations (fixed points...). However, we do not discuss the methods which allow, to determine quantitatively the critical exponents, these topics being too specialized for the present introduction. We restrict also our study to the "simple systems" and we do not discuss recent and exciting new developments such as the defects of ordered states, phase transitions in disordered systems...

LANDAU MODEL FOR THE SECOND ORDER PHASE TRANSITIONS

1. Introduction. -1.1. Classification. - As previously mentioned in the introduction, the experimental results obtained for transitions whose physical nature is very different (order disorder, magnetism, liquid helium, structural transitions) showed that the singular behaviour of the thermodynamic potential presents general features. It is then tempting to classify these transitions according to the nature of these singularities. The first attempt has be done by Ehrenfest (1933) : the critical point T_c is a point for which the system presents a discontinuity of the thermodynamic potential or of its derivatives. The 1st order transitions are transitions for which the physical properties related to 1st order derivatives of the thermodynamic potential are discontinuous (entropy Δs, volume Δv if the system is in equilibrium with a thermostat which determines pressure and temperature). The 2nd order transitions are transitions for which there are discontinuities of the physical properties related to the second derivatives of the thermodynamic potential (specific heat at constant pressure c_p, isothermal compressibility K_T...). The first order transitions have a latent heat $\ell_T = T_c \Delta s$ ($\Delta s \neq 0$) whereas the other transitions are such that $\ell_T = 0$ ($\Delta s = 0$). This first classification is interesting because it allows to compare the transitions for different systems (order disorder and magnetism for example) ; however, it has only an historical interest because it assumes that the relevant singularities are discontinuities : this assumption is in agreement with the results of the mean field approximation but later, the experimental studies showed that the nature of the singularity is much more subtle for transitions without latent heat.

Landau (1937) pointed out that the transitions without latent heat ($\ell_T = 0$) are often characterized by : 1) a continuous variation of the properties of the systems and by 2) a discontinuous change of the symmetry. For example, the symmetry changes discontinuously at $T = T_c$ when we consider the order disorder transition of β brass : for $T = T_c + 0$ the system is bcc whereas for $T = T_c - 0$ it becomes simple cubic (with two atoms per cell) and looses a symmetry operation (the translation from a corner to the center of the cubic cell). However, the order parameter (the concentration of a given atom on a given lattice site) changes continuously : this continuous change is -at first sight- the property which characterizes the transitions without latent heat of transitions. The continuous structural transitions are also characterized by a change of symmetry at $T = T_c$ and by a continuous change of the atomic displacements.

Such phase transitions are then characterized both qualitatively by the symmetry change and quantitatively by the value of the order parameter associated to this symmetry change. For the 2nd order phase transitions, the two phase cannot be in equilibrium with each other ; we can only observe the continuous transition from one phase to another. Both phases being identical at the transition temperature T_c, the symmetry of the system at $T = T_c$ must contain all the operations of symmetry and the symmetry must necessarily be lower for the ordered phase i.e. for $T < T_c$[*]. In other words, if G_0 is the symmetry group for $T = T_c$ - i.e. the set of operations of symmetry- rotations, reflexions, translations- for which the crystal remains invariant- the symmetry group remains the same on one side of the transition whereas it becomes $G_1 (G_1 \subset G_0)$ on the other side,some operations of symmetry disappearing for $T < T_c$. When there is a change of symmetry, a necessary condition to observe a second order transition is then that the symmetry of one of the phases (the "ordered phase") is lower than the symmetry of the other (the "disordered phase") i.e. that $G_1 \subset G_0$; this condition is not sufficient as we will show later. On the contrary, there is no similar condition for the 1st order transition.

Note finally that the second order transitions are not accompanied by discontinuities of the thermodynamic potential and of its first derivatives (entropy, energy, volume...) at $T = T_c$. The hysteresis effects corresponding to the coexistence of metastable states with stable states cannot exist for a 2nd order transition since there exists only one state at $T = T_c$.

In conclusion we will consider three types of transitions :

1) The transitions for which the phases have different symmetries ($G_1 \not\subset G_0$, $G_0 \not\subset G_1$) : these transitions are 1st order since it is impossible to go continuously from one phase to the other (polymorphism for example).
2) The transitions for which the symmetry group of the less symmetric phase G_1 is a subgroup of G_0 ($G_1 \subset G_0$). It is then possible to define an order parameter

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[*] Here we assume that the ordered phase exists at low temperature.

associated to this symmetry change (see section 3) and the transition can be of the 2nd order if this order parameter varies continuously across T_c but it can be also a 1st order transition. We will show later some necessary conditions which must be satisfied to have a 2nd order transition.

3) Finally there are some cases where the symmetries of both phases coincide ($G_1 = G_0$) and the transition can be 1st or 2nd order (liquid gas transition) : we can define an order parameter (see the introduction) but it is not related to a symmetry change.

1.2. Landau model for second order transitions. - In this chapter, we study 1) the definition of the order parameter in relation to the symmetry, 2) the conditions which are necessary to observe the 2nd order transition, 3) the properties of the system near the transition temperature T_c. To obtain such properties it is necessary to use simple assumptions about the singularity of the thermodynamic potential G for $T = T_c$. For simplicity, Landau assumes that G is analytic ; we will see that this assumption is not satisfied for most systems and the nature of the singularity of G is described later for simple systems (chapter 3) : this is why the properties, deduced from the analyticety of G, are not correctly predicted by the Landau model. However, the analysis which is related to the symmetry changes i.e. the determination of the order parameter in relation to the irreducible representations of G_0, the conditions which must be satisfied to obtain a 2nd order phase transition seem to remain valid in most cases (chapter 4).

For simplicity, we will present the Landau theory in two steps :

i) We assume the existence of a phase transition characterized by an order parameter M and we show that the analyticety of G determines the properties of the system for $T = T_c$;

ii) the we show how the properties of the phase transitions and the definition of an order parameter can be related to the symmetries of the ordered and disordered phases.

2. Landau model and properties of a phase transition. - 2.1. Introduction. - First we assume that the system is characterized in the ordered state by a scalar order parameter M (magnetization for a ferromagnetic transition, long range order parameter for an order disorder transition...) ; G(T,P,M) is the thermodynamic potential of the equilibrium state obtained for fixed values of the constraints T,P,M. If we apply an external field H_0, the equilibrium value for the order parameter M is obtained minimizing the potential $\tilde{G} = G - MH_0$.

$$\frac{\partial \tilde{G}}{\partial M} = 0 \qquad\qquad \frac{\partial^2 \tilde{G}}{\partial M^2} > 0 \qquad (1.1)$$

For a second order transition, $M \to 0$ when $T \to T_c - 0$. Then following Landau, we assume that the potential G(T,P,M) is analytic at $T = T_c$. More precisely :

i) we assume that we can expand G(T,P,M) in successive powers of M when $M \to 0$:

$$G(T,P,M) = G^{o}(T,P) + \alpha M + A(T,P)\frac{M^2}{2} + B(T,P)\frac{M^3}{3} + C(T,P)\frac{M^4}{4} + D(T,P)\frac{M^5}{5} + E(T,P)\frac{M^6}{6} + \ldots \qquad (1.2)$$

G_o (T,P) being the thermodynamic potential for $T > T_c$;

ii) we assume that the coefficients (α, A, B, C,...) are continuous functions of T,P... at $T = T_c$.

In some cases the expansion (1.2) can be simplified by symmetry considerations ; for example, if G(T,P,M) is invariant by the change $M \to -M$, the odd powers of M disappear from (1.2). Moreover, it is easy to show that, if the ordered and disordered states are characterized by different symmetry groups, $\alpha = 0$ (see section 3). We will consider only such transitions in this chapter.

The previous assumptions seem "a priori" to be natural. However, they are not at all obvious since T_c is a singular point for the thermodynamic potential ; we will show that they imply a critical behaviour which is different from those which are experimentally observed.

2.2. Relative stability of the ordered and disordered states 1st and second order transition.- Form (1.1) the disordered state (M = 0) is stable only if :

$$A(T) > 0 \qquad\qquad , T > T_c \qquad (1.3)$$

The critical temperature T_c is the temperature for which the disordered state becomes unstable relative to the ordered state ($M \neq 0$). Moreover, for a second order transition, M must increase continuously from zero when T decreases from T_c ; in such a case we must have : i) $A(T_c) = 0$ ($M = 0$ at $T = T_c$), ii) $A(T < T_c) < 0$ for $T < T_c$ (instability of the disordered state). If A(T) is analytic for $T = T_c$ these conditions require the following expression for A :

$$A(T) = a(T - T_c) + 0((T - T_c)^2),\ a > 0 \qquad (1.4)$$

The condition (1.3) is a necessary condition to insure that the disordered state is stable but it is not sufficient to insure that it is the most stable. For example, if for $T > T_c$, B is negative ($B < 0$) and if we neglect the higher order terms of (1.2) ($C = D = \ldots 0$), the states for which $M > -3\,A/2B$ are more stable than the disordered state (Fig. 1.1.a) :

$$G\left(M > -\frac{3A}{2B}\right) < G\,(M=0) \qquad (1.5)$$

To obtain the new equilibrium state, it is then necessary to consider one (at least) of the higher order terms of (1.2) : otherwise, G(M) would decrease continuously for increasing values of M ($M > -3A/2B$) ; we must keep (at least) the higher order terms of G up to the first one which is positive. Let us assume for simplicity that C is positive and neglect its temperature variation since we consider only the critical region ($T \simeq T_c$). The thermodynamic potential is then characterized at $T = T_c$ by two minima : the most stable state corresponds to $M(T_c) \neq 0$ so that for this temperature the equilibrium state is ordered. The system remains ordered for all the temperatures $T < T_0$ such that the minimum of $G(M)$ for $M \neq 0$ is more stable than the disordered state. T_0 is then defined by the conditions :

$$\begin{cases} G(M=0, T_0) = G(M(T_0), T_0) \qquad M(T_0) \neq 0 \\ \dfrac{\partial G}{\partial M} \; (M(T_0)) = 0 \end{cases} \tag{1.6}$$

Using (1.2) these conditions become :

$$\begin{cases} A(T_0) + \dfrac{2B}{3} \; M(T_0) + \dfrac{C}{2} \; M(T_0)^2 = 0 & (1.7a) \\ A(T_0) + BM(T_0) + C\, M(T_0)^2 = 0 & (1.7b) \end{cases}$$

and substracting (1.7a) from (1.7b) we obtain the value of $M(T_0)$:

$$M(T_0) = - \frac{2B}{3C} \tag{1.8}$$

The temperature T_0 is then obtained from (1.8) and one of the equation (1.7). If we assume that the expansion (1.4) remains valid, T_0 is given by :

$$T_0 = T_c + \frac{2B^2}{9\,Ca} > T_c \tag{1.9}$$

For $T > T_0$, the most stable state is disordered but for $T < T_0$ the ordered state corresponding to the second minimum of G becomes more stable : the order appears discontinuously (see(1.8)) and the first order transition has a critical temperature T_0 larger than T_c. We obtain the same result when B is positive.

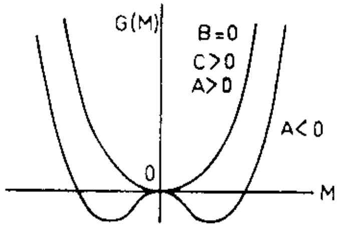
The previous discussion shows that <u>a necessary condition to obtain a second order</u> transition is that the third order term of the Landau expansion (1.2) is zero :

$$B = 0$$

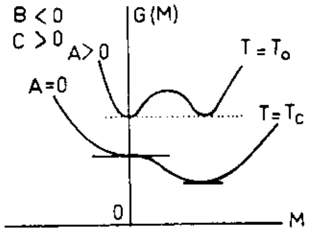
In the same way, we will show that C must be non negative to obtain a second order transition (see section 2.3.).

For some systems the coefficient B can be shown to be zero from symmetry considerations : for magnetic transitions the order parameter is the magnetization and the free energy is invariant by the change $M \to -M$: in such a case, all the odd terms of the expansion (1.2) disappear and the transition can be a 2nd order transition. For the order-disorder transition (β brass, cf introduction), the change $M \to -M$ exchanges the sublattices α, β and does not change the thermodynamic potential : the order disorder transition Cu Zn can be a 2nd order transition. On the contrary for the Au Cu and Au_3Cu structures we described in the introduction such a symmetry does not exist and a 2nd order transition cannot appear in this Landau theory.

2.3. <u>Physical meanning of A - susceptibility</u>. - The physical meaning of A is simple. Let us assume that we apply to the system an external field H_0 (magnetic field for a para-ferromagnetic transition, electric field for a para-ferroelectric transition...) coupled to the order parameter M. The equilibrium state is obtained by the minimization of $\tilde{G} = G - MH_0$ i.e. by :



<u>Fig. 1.1a</u> : Thermodynamic potential when $T \simeq T_c$ (2nd order transition).



<u>Fig. 1.1.b</u> : Thermodynamic potential when $T \simeq T_0$ (1st order transition).

$$\begin{aligned} &\frac{\partial G}{\partial M} - H_0 = 0 \qquad && AM + B\,M^2 + \ldots = H_0 \\ &\frac{\partial^2 G}{\partial M^2} > 0 \qquad && A + 2\,BM + \ldots > 0 \end{aligned} \tag{1.10}$$

For small fields H_0 (linear approximation) and $T > T_c$, the order parameter which is induced by H_0 is given by :

$$AM = H_0 \text{ or } M = \chi\, H_0 \qquad \text{with} \qquad \chi = A^{-1} \tag{1.11}$$

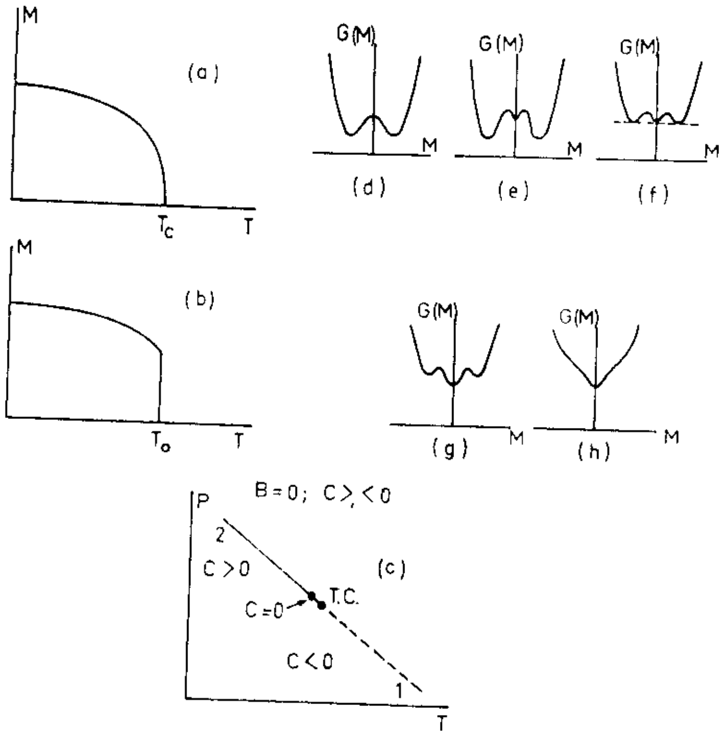


Fig. 1.1.c : a) second order transition, b) 1st order transition, c) continuous transition from a 1st to a 2nd order transition (TC : tricritical point), d) to h) thermodynamic potential versus temperature : d) $T < T_c$; e) $T_c < T < T_c^1$; f) $T = T_c^1$; g) $T_c^1 < T < T_o$; h) $T < T_o$.

The susceptibility X-i.e. the value of the order parameter per unit applied field is equal to the inverse of the coefficient A. For the critical temperature T_c of a second order transition the susceptibility diverges. Assuming that the condition (1.4) is satisfied, we obtain a Curie-Weiss law for the susceptibility :

$$X(T) = \frac{C_{cw}}{T - T_c} \qquad C_{cw} = a^{-1} \tag{1.12}$$

2.4. 2nd order transition : ordered state and critical behaviour for C > 0 (Fig.1.1.b). - The ordered state ($T < T_c$) is obtained when we keep (at least) the higher order terms of G up to the first one which gives a positive contribution to G. Let us assume for simplicity that C > 0 and neglect the variation of C with T since we consider only the critical region ($T \simeq T_c$). The case C < 0 will be considered in the next section.

The equilibrium is obtained for $T < T_c$ and $H_o = 0$ from :

$$\left\{ \begin{array}{ll} \frac{\partial G}{\partial M} = A M + CM^3 = 0 & (1.13a) \\ \frac{\partial^2 G}{\partial M^2} = A + 3 CM^2 > 0 & (1.13b) \end{array} \right.$$

(1.13a) has three solutions :

$$M = 0 , \qquad M^{(\pm)} = \pm \left(\frac{a}{C T_c}\right)^{1/2} (T_c - T)^{1/2} \tag{1.14}$$

but (1.13b) is not satisfied by the solution corresponding to the disordered state : in conclusion, we obtain a second order transition ($M \neq 0$, $T < T_c$) at $T = T_c$ when (1.2) (1.3) and C > 0 are satisfied.

When we apply a field H_o coupled to the order parameter, the equilibrium is determined by :

$$A(T)\,M + C(T)\,M^3 = H_o \tag{1.15}$$

and the critical isotherm is given by :

$$H_o = C(T_c)\,M^3 \tag{1.16}$$

The entropy of the ordered state is (see (1.2))

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{\partial G^o}{\partial T}\right)_p - \left(\frac{\partial G}{\partial M}\right)\left(\frac{\partial M}{\partial T}\right)_p \tag{1.17}$$

When $H_o = 0$ and $T \simeq T_c$ we obtain :

$$\left\{ \begin{array}{lll} S = S_o & , T > T_c & (1.18a) \\ S = S_o - a\frac{M^2}{2} = S_o - \frac{a^2}{2C(T_c)}\,(T_c - T) & , T < T_c & (1.18b) \end{array} \right.$$

S_o being the entropy of the disordered state : the entropy decreases linearly with T from the value S_o. For this reason the specific heat has a jump at $T = T_c$ in such a model :

$$\left\{ \begin{array}{lll} C_p = C_{p_o} = T\left(\frac{\partial S_o}{\partial T}\right)_p & T > T_c & (1.19a) \\ C_p = C_{p_o} + \frac{a^2 T_c}{C(T_c)} + O(T - T_c) & T < T_c & (1.19b) \end{array} \right.$$

2.5. First order transition for $C(T_c) < 0$ (Fig. 1.1.c). - When C(T) is negative, we must consider at least the next higher order term of (1.2) since otherwise G(M) would be negative for $M^2 > 2A/C$ and decrease continuously when M increases. We assume -for simplicity- that only even power terms of M appear in (1.2) and that $E > 0$. The extremum of G is then obtained by the condition ($H_o = 0$) :

$$\left[a(T-T_c) + CM^2 + EM^4\right] M = 0 \qquad (1.20)$$

This equation has the following solutions :

$$M = 0 \qquad (1.21a)$$

$$M = \pm \left\{ -\frac{C}{2E}\left[1 + \left(1 - \frac{4aE}{C^2}(T-T_c)\right)^{1/2}\right]\right\}^{1/2} \qquad (1.21b)$$

$$M = \pm \left\{ -\frac{C}{2E}\left[1 - \left(1 - \frac{4aE}{C^2}(T-T_c)\right)^{1/2}\right]\right\}^{1/2} \qquad (1.21c)$$

From (1.21) the extremum (1.21b) exists only when $T < T_o$ whereas the extremum (1.21a) exists for $T_c < T < T_o$ where :

$$T_o = T_c + \frac{1}{4}\frac{C^2}{aE} > T_c \qquad (1.22)$$

It is easy to show that (1.21c) corresponds to a maximum of the free energy so that we do not consider it. When we apply a magnetic field (1.10) becomes :

$$A(T)M + C(T)M^3 + E(T)M^5 = H_o \qquad (1.23)$$

and the susceptibility defined as previously by :

$$\chi = \left(\frac{\partial M}{\partial H_o}\right)_P (H_o = 0) \qquad (1.24)$$

is given by :

$$\chi^{-1} = A(T) + 3C(T)M^2 + 5E(T)M^4 \qquad (1.25)$$

In the ordered phase (1.21b) the susceptibility is then expressed as :

$$\chi^{-1} = \frac{C}{E}\left[1 - \frac{4aE}{C^2}(T-T_c)\right)^{1/2}\left\{1 + \left(1 - \frac{4aE}{C^2}(T-T_c)\right)\right\}\Big]^{1/2} \qquad (1.26)$$

The divergence of the susceptibility is obtained at $T = T_o$: the temperatures for which the ordered ($T < T_o$)and disordered phase ($T > T_c$) are stable do not coincide. When the temperature increases, the ordered phase becomes more stable (for $T < T_o$) than the disordered phase but for $T_c < T < T_o$ the disordered phase remains (meta) stable.
The transition between ordered and disordered states is then characterized by the plots

of G(T,P,M) when we vary the temperature (Fig. 1.1.c). We can then consider the following situations obtained for increasing temperatures :

1) For $T < T_c$, G represents two minima $\pm M_o$ corresponding to the possible states of stable equilibrium ;
2) For $T_c < T < T_c^1$, a third extremum appears for $M \neq 0$ (see(1.21c)) but it corresponds to an unstable equilibrium ;
3) For $T = T_c^1$, the disordered state $M = 0$ becomes degenerate with the ordered stable state (1.21b). The temperature T_c^1 is given by :

$$T_c^1 = T_o + \frac{3}{16}\frac{C^2}{aE} \qquad (1.27)$$

and represents the critical temperature for a first order transition : when T varies from $T = T_c^1 - 0$ to $T = T_c^1 + 0$ the value of M changes discontinuously from $\left[-3/4\, C/E\right]^{1/2}$ to zero, the susceptibility remaining finite ;
4) For $T_c^1 < T < T_o$, the disordered state is the most stable equilibrium state whereas the ordered state is metastable ;
5) Finally, for $T > T_o$, the metastable ordered states disappear.

2.6. From a 2nd order to a first order transition : tricritical point. - Let us now consider the case $C = 0$. The equilibrium states are determined by the condition :

$$\left[a(T-T_c) + EM^4\right] M = 0 \qquad (1.28)$$

The order parameter varies as :

$$M(r) = \frac{a}{E(T_c)}(T_c - T)^{1/4} \qquad (1.29)$$

when $T < T_c$ and the susceptibility varies according to a Curie Weiss law :

$$\begin{cases} \chi = \dfrac{1}{a(T-T_c)} & T > T_c \\ \lambda = \dfrac{1}{4a(T-T_c)} & T < T_c \end{cases} \qquad (1.30)$$

For a given system, the Landau coefficients A, C... vary with the external constraints (the pressure P for example) and it can happen that the variation of P changes the sign of the Landau coefficients ; for example, $C(P) > 0$ for $P > P_o$ and $C(P) \leqslant 0$ for $P < P_o$: in such a case we will observe a progressive evolution from a first order to a second order transition when the pressure increases. In the plane (T,P), we can define a line which represents the set of critical temperatures $T_c(P)$. This line can be separated in two parts by the tricritical point (T_c^o, P_o) defined by $C(T_c^o, P_o) = 0$: for $P < P_o$ the temperatures $T_c(P)$ are the critical temperatures for first order transitions whereas the points T_c for $P > P_o$ represent second order phase transitions.

2.7. Discussion : Landau critical exponents. - The general assumptions we considered previously allowed i) to define conditions on the Landau coefficients which are necessary to obtain second order phase transitions ; ii) to determine the properties of the system for $T \simeq T_c$. It is possible to characterize qualitatively the singularities of the physical properties of the system by critical exponents ; the results of a Landau theory are summarized as follows for a typical second order transition (see §.2.4.) :

for $T > T_c$ $\quad C_p \sim (T - T_c)^{-\alpha}$ with $\alpha = 0$ $\quad \chi \sim (T - T_c)^{-\gamma}$ with $\gamma = 1$ (1.31)

at $T = T_c$ $\quad H_0 \sim M^{\delta}$ with $\delta = 3$ (1.32)

for $T < T_c$ $\quad C_p \sim (T_c - T)^{-\alpha'}$ with $\alpha' = \alpha = 0$ $\quad \chi \sim (T_c - T)^{-\gamma'}$ with $\gamma' = \gamma = 1$ $\quad M \sim (T_c - T)^{\beta}$ with $\beta = 1/2$ (1.33)

3. Second order phase transition with a symmetry change. - We consider the transitions which are characterized by i) a continuous variation of the properties of the system when $T \simeq T_c$; ii) a discontinuous variation of the symmetry at $T = T_c$. This discontinuity is defined by the symmetry groups G_0 and G_1 corresponding (resp.) to the high and low symmetry phases ($G_1 \subset G_0$). Let us recall here that the symmetry group of a system (in a given state) is the set of the symmetry operations which leave invariant the state of the considered system. This state is characterized by one (or several) function(s) which determine the spatial variation of the physical properties the symmetry of which is changed at $T = T_c$. For example, a "magnetic" system will be characterized by the magnetization density m(r) (per unit volume), a system which will present "electric" transitions will be characterized by the electric polarization density **P**(r), a structural transition will be characterized by the atomic displacement u (r), an order disorder transition of a binary system will be characterized by the spatial variation of the concentration c(r) of one of its constituents... This density (m (r), P(r), u(r), c(r)...) can be a scalar, a pseudo vector or even a tensor. For simplicity, we will assume here that this function we note M(r) is a scalar ; the generalization is obvious. (see 3.6).

The Landau conditions for a second order phase transition (see §2.3) determine 1) new conditions concerning the nature of the symmetries G_1 which can appear after such a transition ; 2) the definition of the order parameter M and the Landau expansion of the thermodynamic potential in successive powers of M(r).

2.1. Symmetry change and function M(r). - An equilibrium state is characterized by the function M(r). Near T_c we can write :

$$M(r) = M_0(r) + \delta M(r) \qquad (1.34)$$

where $M_0(r)$ is the part of M(r) which presents the symmetry of G_0 for $T > T_c$

$$\delta M(r) = 0 \qquad \text{for } T \geq T_c \qquad (1.35)$$

δM(r) is the part of M(r) which determines the symmetry group G_1 of the low symmetry phase (δM(r) ≠ 0 for $T < T_c$). The symmetry operations $T \in G_0$ (translations, rotations, reflexions...) change the density M(r) into a new density TM(r) defined by :

$$TM(Tr) = M(r) \qquad \text{or} \qquad TM(r) = M(T^{-1}r) \qquad (1.36)$$

By definition of G_0, $TM_0(r) = M_0(r)$ $\forall T \in G_0$ but δM(r) is not invariant by all the operations of G_0. From group theory it can be shown that an arbitrary function δM(r) can always be represented as a linear combination of basis functions $\phi_i^{(n)}(r)$ which transform according to :

$$T\phi_i^{(n)}(r) = \sum_j D_{ji}^{(n)}(T)\,\phi_j^{(n)}(r) \qquad (1.37)$$

The functions $\{\phi_i^{(n)}\}$ ($i = 1, 2 \dots d_n$) are the basis functions of an irreducible representation (n) of the group G_0 ; the matrices $D_{ji}^{(n)}(T)$ define the corresponding irreducible representations ; n labels the representation and i one of the functions of the representation n. Among all the $\phi_i^{(n)}$ there is always one of them which is invariant by all the operations $T \in G_0$; it defines the representation "identity" of G_0 and is noted M_0. (see the book by Cornwell for example). δM(r) can be written as :

$$\delta M(r) = \sum_{(n)\,i}{}' \; C_i^{(n)}\,\phi_i^{(n)}(r) \qquad (1.38)$$

where the summation is extended over all the representations (except the representation identity) since δM(r) is not invariant by all the operations $T \in G_0$. M(r) and δM(r) being real we can choose $\phi_i^{(n)}(r)$ as real functions (if $\phi_i^{(n)}(r)$ are not real they will appear only through the combinations $\phi_i^{(n)} + \phi_i^{(n)*}$).

3.2. Thermodynamic potential. - The thermodynamic potential G(T,P,δM(r)) is a function of the external constraints and a functional of the density δM(r) i.e. a function of the coefficients $C_i^{(n)}$ determining the state of the system :

$$G(T,P,\delta M(r)) = G(T,P,\dots C_i^{(n)}\dots) \qquad (1.39)$$

The coefficients $C_i^{(n)}$ which characterize the equilibrium state are determined by the minimization of G ; they are equal to zero for $T > T_c$ (so that δM(r) = 0) but one of them -at least- must be non zero for $T < T_c$. To obtain a second order phase transition at $T = T_c$ all the coefficients $C_i^{(n)}$ must vanish when $T - T_c \to 0$ since δM(r) → 0 when $T - T_c \to 0$. As previously (see §.2), it is then useful to expand $G(T,P,C_i^{(n)})$ in successive powers of $C_i^{(n)}$ when we are interested by the critical properties for $T \simeq T_c$ but it is important to use the symmetry properties. The coefficients $C_i^{(n)}$ are transformed by $T \in G_o$ in the same way as the basis functions $\phi_i^{(n)}$*; moreover, the thermodynamic potential $G(T,P,C_i^{(n)})$ is a scalar so that it must be invariant by the operations $T \in G_o$. The expansion of G in successive powers of $C_i^{(n)}$ will then only contain linear, quadratic, cubic... invariants built from $C_i^{(n)}$ $(i : 1, 2 \dots d_n)$ for the representations (n) which determine the low symmetry phase. Then we can use two general results :

i) there is no linear invariant built from $C_i^{(n)}$ i.e. no linear combination of the $C_i^{(n)}$ $(i : 1, 2, \dots d_n)$ invariant by the operations $T \varepsilon G_o$: otherwise, the representation (n) would contain the representation identity and it would be either the representation identity itself or reducible - which is impossible.

ii) there is only one quadratic invariant for each representation n : it is a quadratic form of the coefficients $C_i^{(n)}$ which reduces to $A_i^{(n)} \Sigma_i C_i^{(n)2}$.

Finally the thermodynamic potential can be written as follows :

$$G(T,P) = G^o(T,P) + \sum_n A^{(n)} \sum_i C_i^{(n)^2} + \dots \qquad (1.40)$$

3.3. Second order transition - order parameter. - For $T > T_c$, the coefficients $A^{(n)}(T,P)$ must be positive to insure the stability of the disordered state. To obtain a transition at $T = T_c$, one -at least- of the coefficients $A^{(n)}$ must change of sign at $T = T_c$; T_c is then the largest temperature for which one of the coefficients $A^{(n_o)}$ is zero. Except for peculiar cases, only one coefficient is zero and for $T = T_c$

$$\left\{ \begin{array}{l} \delta M(r) = \sum_i C_i^{(n_o)} \phi_i^{(n_o)}(r) \\ A^{(n_o)}(T_c,P) = 0 \end{array} \right. \qquad (1.41)$$

The "order parameter" related to the transition is the set of the d_{n_o} coefficients $\{C_i^{(n_o)}\}$ which determine the state for $T < T_c$; it is transformed by $T \varepsilon G_o$ as the set of the basis functions of the irreducible representation n_o of G_o. The dimension of the order parameter is then (by definition) the dimension of the irreducible representation n_o. It is easy to show that the operations T for which $\delta M(r)$ is invariant is a subgroup G_1 of G_o.

$$* \; T\,\delta M(r) = \sum_{i,(n)}{}' C_i^{(n)} T \phi_i^{(n)}(r) = \sum_{i,j,(n)}{}' C_i^{(n)} D_{ji}^{(n)}(T) \; \phi_j^{(n)}(r)$$

$$= \sum_{j\,(n)} TC_j^{(n)} \phi_j^{(n)}(r) \quad \text{(definition of } TC_j^{(n)}\text{)}$$

$$\text{Then} \quad TC_j^{(n)} = \sum_i D_{ji}^{(n)}(T)\, C_i^{(n)} \qquad \text{(see eq. 1.37)}$$

3.4. Landau expansion of the thermodynamic potential. - Let us now suppress the index n_o in the expansion of G for $T < T_c$. It is natural to define the quantities γ_i and M by :

$$M^2 = \sum_i C_i^2 \qquad \gamma_i = \frac{C_i}{M} \qquad (1.42)$$

so that the thermodynamic potential becomes :

$$G(T,P,M, \gamma_i) = G^o(T,P) + \frac{A(T,P)M^2}{2} + \sum_\alpha B_\alpha(T,P)\, f_\alpha^{(3)}(\gamma)\frac{M^3}{3} + \sum_\alpha C_\alpha(T,P)\, f_\alpha^{(4)}(\gamma)\frac{M^4}{4} + \dots \qquad (1.43)$$

$f_\alpha^{(3)}, f_\alpha^{(4)} \dots$ are the invariants of third fourth ... order obtained from the coefficients γ_i. As discussed in section 2.3 the transition is determined by $A(T_c) = 0$. This transition will be a 2nd order transition only if : i) the third order terms are zero (§2), ii) the fourth order terms are positive. The first condition will be satisfied if the symmetry symmetry of G_1 is such that it is impossible to form third order invariants with $C_i^{(n)}$ (§2). If this condition is satisfied G(T,P) can be written as :

$$G(T,P) = G^o(T,P) + A(T,P)\frac{M^2}{2} + \sum_\alpha C_\alpha(T,P)\, f_\alpha^{(4)}(\gamma)\frac{M^4}{4} + \dots \qquad (1.44)$$

The equilibrium will be determined by minimizing G with first respect to γ_i and second with respect to M.

4. Application : order disorder transitions in binary alloys. - 4.1. Introduction. -In a binary alloy, the density M(r) is determined by the occupation numbers p_λ (see section 2 of the introduction).

$$M(r) = \sum_\lambda p_\lambda \; M_A(r-\lambda) + (1 - p_\lambda)\, M_B(r-\lambda) \qquad (1.45a)$$

It is the superposition of the densities characteristic of the A and B atoms ($M_A(r-\lambda)$ and $M_B(r-\lambda)$ respectively) distributed over the sites λ of a perfect lattice with one atom per cell. Here, we are only interested by the transitions which come from different atomic distributions ; an ordered state is then characterized by the local concentration $c_\lambda = \langle p_\lambda \rangle$ on each site λ or by its deviation from its average value c :

$$M_\lambda = c_\lambda - c \qquad (1.45b)$$

In the disordered state $M_\lambda = 0$ for all sites λ. From the Landau assumption, the thermodynamic potential can be written as :

$$G(T,P,\{M_\lambda\}) = G^o(T,P) + \frac{1}{2}\sum_{\lambda,\mu} A(\lambda,\mu) M_\lambda M_\mu + \frac{1}{3}\sum_{\lambda\mu\rho} B(\lambda,\mu,\rho) M_\lambda M_\mu M_\rho + \dots \qquad (1.46)$$

The coefficients A, B... are only dependent on the relative distances between $\lambda, \mu, \rho \dots$ ($A(\lambda, \mu) = A(\lambda - \mu)$, $B(\lambda, \mu, \rho) = B(\lambda - \rho, \mu\lambda - \rho)$...) since these quantities are characteristic of the disordered state. We can use this property -characteristic of the translational invariance of the perfect lattice- and introduce the Fourier components M_q of M_λ :

$$\left\{ \begin{array}{l} M_q = \frac{1}{\sqrt{N}} \sum\limits_{\lambda} e^{-iq\lambda} M_\lambda \\ M_\lambda = \frac{1}{\sqrt{N}} \sum\limits_{q} e^{iq\lambda} M_q \end{array} \right. \tag{1.47}$$

Note that $M_q = M_q^*$ since M_λ is real and G_o includes the inversion. An ordered state is then characterized by the set of Fourier components $\{M_q\}$ and the thermodynamic potential becomes (see(1.46) (1.47)) :

$$G(T,P,\{M_q\}) = G^o(T,P) + \frac{1}{2} \sum_q A(q) \, |M_q|^2 + \frac{1}{3} \sum_{q_1,q_2} B(q_1,q_2) M_{q_1} M_{q_2} M_{(q_1+q_2)} + \dots \tag{1.48}$$

with

$$\left\{ \begin{array}{l} A(q) = \sum\limits_{\lambda} A(\lambda) \; e^{-iq\lambda} \\ B(q_1, q_2) = \sum\limits_{\lambda,\mu} B(\lambda \, \mu) \, e^{iq_1\lambda} \; e^{-iq_2\mu} \end{array} \right. \tag{1.49}$$

At first sight the expression (1.48) is similar to the canonical form (1.40) : we used the translational invariance to diagonalize the second order term in (1.46). We will discuss in the next section the relation between this transformation and the symmetry properties. Let us now recall here that the disordered state will be stable for all temperatures T for which $A(q) > 0 (\forall q)$; it becomes unstable when one (at least) of the coefficients A(q) is negative. When the temperature T decreases A(q) becomes zero for the first time for a wave vector q_c such that :

$$\left\{ \begin{array}{lll} A(q_c, T_c) = 0 & & A(q_c, T_c) < A(q, T_c) \\ A(q,T) \;>\; 0 & \forall q, \quad T > T_c & \end{array} \right. \tag{1.50}$$

T_c is a priori the critical temperature -if the transition is a second order transition. At this point we must consider two situations we discuss now in sections 4.2. and 4.3.

4.2. Modulated structures. - When q_c is incommensurate with the reciprocal lattice vectors, the ordered crystal has a translational symmetry which is completely different from the symmetry of the disordered lattice ; we are not in a situation which is described by Landau ($G_i \not\subset G_o$). Note that the concentration can be modulated with a wave vector which varies continuously with the temperature and is determined by the minimum of the thermodynamic potential. These modulated structures are discussed in other lectures (see the lectures by Gerl and Pouget) and will not be considered here. Let us note only that it is possible to "block" an incommensurate structure by external perturbations (pressure...), the periodicity becoming commensurate with the original lattice. From the previous discussion, the incommensurate transition is a first order transition ($G_1 \not\subset G_o$).

4.3. Superlattices whose periods are commensurate with the period of the original lattice. - In this case, the transition can be studied by the classical Landau arguments. To study the conditions we have to satisfy to obtain a second order transition, we have to expand M_λ and $G(T,P\{M_\lambda\})$ according to the irreducible representations of G_o (see section 3). The expansion of the [illegible] concentrations M_λ according to their Fourier components M_q (1.47) can be shown to be an expansion of the type (1.38) : the function M_λ is a superposition of functions $M_q(\lambda) = e^{iq\lambda}$ which transform according to the basis functions of irreducible representations of G_o. Let us verify now this point.

If $T_R \in G_o$ is a translation (vector R) :

$$T_R \, e^{iqR} = e^{-iqR} e^{iqR} \Rightarrow T_R M_q(\lambda) = e^{-iqR} M_q(\lambda) \tag{1.51}$$

If $T \in G_o$ is a rotation $|R$

$$|R \, e^{iqR} = {}^{iq|R^{-1}r} = e^{i|Rqr} \Longrightarrow |R \, M_q(\lambda) = M_{|Rq}(\lambda) \tag{1.52}$$

we used $|Rq \; |Rr = qr$.

The functions $M_{|Rq}(r)$ ($|R \in G_o$) are then transformed into each other by the symmetry operations $T \in G_o$: they form a representation of the group G_o (1.37).

Let us consider now the set of s different vectors $q_1 = q, q_2, \dots q_i, \dots q_s$ such that $Rq_i = q + K$ (where K is a reciprocal lattice vector) *: this set is called the star of q. The set of the operations $|R$ which leave invariant the vector q will be called the group of vector q. From the previous discussion, the representation of G_o are labelled by the vector q and assuming that the ordered state is characterized by only one of these representations, we can write M_λ as follows :

$$\left\{ \begin{array}{l} M_{qi} = M\gamma_i \qquad \sum\limits_{i=1}^{s} |\gamma_i|^2 = 1 \\ M_\lambda = \frac{M}{2} \sum\limits_{j=1}^{s} (\gamma_j \, e^{iq_j\lambda} + \gamma_j^* \, e^{-iq_j\lambda}) \end{array} \right. \tag{1.53}$$

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* Two vectors which differ only by a reciprocal lattice vector K are considered to be identical since they define the same set of values of $M_q(\lambda)$ for all sites.

The previous expansion was performed assuming that there is only one atom per cell. If there are several atoms per cell, the basis functions of the irreducible representations of G_o can be shown to be Bloch functions :

$$\left\{\begin{array}{l} M_q(r) = u_q(r)\, e^{iqr} \\ u_q(r) = u_q(r+\lambda) \end{array}\right. \tag{1.54}$$

For a wave vector q, there are -in general- several functions $u_q(r)$ (noted $u_q^{\alpha}(r)$) : these functions transform into each other by the operations of the group of vector q : they form a representation of G_o called "small representation".

4.4. Landau conditions for commensurate structures. - We can now summarize the Landau conditions which are necessary to obtain a second order phase transition : 1) $G_1 \subset G_o$, G_1 being a subgroup of G_o ; 2) only one irreducible representation of G_o defines the symmetry of the ordered state ; 3) there is no third order term in the expansion of G ; 4) according to the crystalline system, q_c has the following values :

$$q_c = 0 \qquad q_c = \frac{K}{2},\ \frac{K}{3} \text{ or } \frac{K}{4} \tag{1.55}$$

where K is a reciprocal lattice vector of the disordered phase.

We discussed previously the conditions 1) 2) 3).

The third condition can also be written as follows :

C 3 : the transition is a first order transition if there are three vectors q_1, q_2, q_3 of the star of q such that $q_1 + q_2 + q_3 = 0$ (if such vectors exist, they will give a third order term in (1.48)!).

The last condition expresses the fact that $A(q, T_c)$ is extremum by symmetry for the vector q_i of the star of q_c. We will not discuss this condition in detail. The analysis of Lifchitz shows that in most cases the Bravais lattice is doubled. However, in the centred lattices (cubic, tetragonal and orthorhombic) and the face centred lattice some lattice periods can be multiplied by four. The main results of Lifchitz are reproduced in the book by Krivoglaz.

4.5. Conclusion. - We discussed the Landau theory for a scalar order parameter and mainly for order disorder transitions. However, for magnetic and structural transitions the order parameter is a vector so that the symmetry is determined not only by the spatial symmetry but also by the symmetry in the order parameter space. The generalization is obvious : it is sufficient to consider each component $\delta M_\alpha(r)$ of the order parameter, to expand it according to (1.38) and to consider the thermodynamic potential as a function of the coefficients $C^{(n)}_{i\alpha}$; we do not discuss this point here.

The Landau theory allowed to find some conditions which are necessarily satisfied when a second order transition occurs. It assumes that the thermodynamic potential is analytic at $T = T_c$ so that we can have a priori some doubt about the results obtained with this theory. However, we can think that the arguments which are only related to the symmetry remain valid : we will discuss this point in chapter 4.

ISING MODEL MEAN FIELD APPROXIMATION

1. Introduction. - In this chapter, we study : 1) the properties of a second order phase transition obtained from the Ising model, 2) the principle and the results of the mean field approximation (MFA) applied to such a model. The system we study is made of N identical subsystems λ sitting on the sites of a perfect lattice. Each of these subsystems λ can be in one of two different states ; the energies of these states are assumed to be the same in the absence of an external field ; the value of this energy is chosen to be the origin of the energy scale and the two possible states of the system are characterized by an index σ_λ which is equal either to +1 or -1. Finally the N systems λ are coupled so that the total energy corresponding to a configuration $\{\sigma_1 \ldots \sigma_\lambda \ldots \sigma_N\} = \{\sigma_\lambda\}$ is given by :

$$\mathcal{H}(\{\sigma_\lambda\}) = -\frac{1}{2}\sum_{\lambda \neq \mu} v(\lambda-\mu)\,\sigma_\lambda\sigma_\mu - \sum_\lambda H_{o\lambda}\,\sigma_\lambda \tag{2.1}$$

The first term of (2.1) is the coupling energy whereas the second term represents the coupling of each of the subsystems λ with the external field $H_{o\lambda}$. We noted previously (see the Introduction) that this model can represent a magnetic trantition, an order-disorder transition... For simplicity we will often call each subsystem λ a "spin" but the following considerations are generally valid.

The transition results from a competition between the order introduced by the coupling energy and the disorder introduced by the thermal energy given by the thermostat with which the system is in equilibrium. For simplicity, we shall essentially consider the peculiar case for which the interactions $v(\lambda)$ are all positive ; the ground state ($T = 0$ K, $H_o = 0$) of the system is then ferromagnetic in order to minimize the coupling energy :

$$\begin{array}{ll} T = 0K, \quad \sigma_\lambda = 1 \ \forall\ \lambda & \text{when } v(\lambda) > 0 \quad \forall \\ \qquad \text{or } \sigma_\lambda = -1 \ \forall\ \lambda & \end{array} \tag{2.2}$$

The coupling energy is then equal to :

$$\mathcal{H}(\{\pm 1\}) = -N\tilde{v}(o)/2 \tag{2.3a}$$

where $\tilde{v}(o)$ is defined by :

$$\tilde{v}(o) = \sum_{\lambda \neq o} v(\lambda) \tag{2.3b}$$

The transition will occur when the thermal energy k_BT_c will be roughly equal to the coupling energy i.e. when :

$$v(o) \sim k_BT_c \qquad (2.4)$$

We will study first the nature of this "ferromagnetic-paramagnetic" transition in the mean field approximation ; we will consider later the general case corresponding to positive and negative values of $v(\lambda)$ in order to show the possible existence of modulated structures the period of which can be incommensurate with the lattice period.

The mean field approximation neglects the spin correlations which necessarily occur from the interactions $v(\lambda)$. We estimate the importance of these correlations in the simplest approximation (RPA) and we show that these correlations become essential for d dimensional systems ($d < 4$) when $T = T_c$; from a simple (Ginzburg Landau) criterion we estimate the temperature range for which the correlations are essential to describe thermodynamic properties (critical region).

2. Mean field approximation. 2.1. Principle of the M.F.A.. - Keeping only the terms $\mathcal{H}$ (2.1) which are dependent on σ_λ:

$$\mathcal{H}_\lambda = -\sigma_\lambda\ H_\lambda \qquad (2.5)$$

$$H_\lambda = H_{o\lambda} + \sum_{\mu\neq\lambda} v(\lambda-\mu)\,\sigma_\mu \qquad (2.6)$$

it is easy to see that each spin σ_λ experiences a field H_λ which results from the external field $H_{o\lambda}$ and from the interactions $v(\lambda-\mu)$. The total field H_λ depends on the values of all other spins $\sigma_\mu\ (\mu\neq\lambda)$. The mean field approximation neglects the fluctuations of H_λ relative to its thermal average value $\langle H_\lambda\rangle$. For the calculation of the thermodynamic properties, each subsystem λ is then considered as an isolated system in the field $\langle H_\lambda\rangle$:

$$\langle H_\lambda\rangle = H_{o\lambda} + \sum_{\mu\neq\lambda} v(\lambda-\mu)\langle\sigma_\mu\rangle \qquad (2.7)$$

the correlation between the movements of neighbouring spins is then neglected. The difficult problem of N interacting subsystems is replaced by the much easier problem of N identical subsystems in the mean field of the others ; we discuss later the validity of this method (see section 8).

It is interesting to compare the exact form of the internal energy

$$\langle\mathcal{H}\rangle = -\frac{1}{2}\sum_{\lambda\neq\mu} v(\lambda-\mu)\langle\sigma_\lambda\sigma_\mu\rangle - \sum_\lambda H_{o\lambda}\langle\sigma_\lambda\rangle \qquad (2.8)$$

to its approximate value $\langle\mathcal{H}\rangle_{MFA}$ obtained in the M.F.A. :

$$\langle\mathcal{H}\rangle_{MFA} = -\frac{1}{2}\sum_{\lambda\neq\mu} v(\lambda-\mu)\langle\sigma_\lambda\rangle\langle\sigma_\mu\rangle - \sum_\lambda H_{o\lambda}\langle\sigma_\lambda\rangle \qquad (2.9)$$

This last equation can be obtained as follows : i) the average energy of each spin σ_λ in the field $\langle H_\lambda\rangle$ is $\langle\mathcal{H}_\lambda\rangle = -\langle\sigma_\lambda\rangle\langle H_\lambda\rangle$;
ii) however, the total energy $\langle\mathcal{H}\rangle_{MFA}$ is not equal to the sum of these energies

$$\langle\mathcal{H}\rangle_{MFA} \neq \sum_\lambda \langle\mathcal{H}_\lambda\rangle \qquad (2.10)$$

since this sum takes into account twice the interactions between the spins σ_λ and σ_μ (first in $\langle\mathcal{H}_\lambda\rangle$ and second in $\langle\mathcal{H}_\mu\rangle$); to obtain $\langle\mathcal{H}\rangle_{MFA}$ we must then divide by two the coupling energies which appear in the r.h.s. of (2.10) in order to recover equation (2.9).

2.2 Spin correlations - correlation function. - The MFA neglects the spin correlations ; the comparison between (2.9) and (2.8) is consistent with the fact that the correlation function $g(\lambda-\mu)$ defined by :

$$g(\lambda-\mu) = \langle\sigma_\lambda\sigma_\mu\rangle - \langle\sigma_\lambda\rangle\langle\sigma_\mu\rangle \qquad (2.11)$$

is zero in the mean field approximation :

$$g_{MFA}(\lambda)=0 \quad \text{or} \quad \langle\sigma_\lambda\sigma_\mu\rangle_{MFA} = \langle\sigma_\lambda\rangle_{MFA}\langle\sigma_\mu\rangle_{MFA},\ \lambda\neq\mu \qquad (2.12)$$

The function $g(\lambda)$ represents the "memory" that the system has in μ from the spin state in λ. For example, in the paramagnetic state ($\langle\sigma_\lambda\rangle = 0$, $H_{o\lambda} = 0$) :

$$g(\lambda-\mu) = \langle\sigma_\mu\rangle_{\sigma_\lambda=+1} - \langle\sigma_\mu\rangle_{\sigma_\lambda=-1} = 2\langle\sigma_\mu\rangle_{\sigma_\lambda=+1} \qquad (2.13)$$

$\langle\sigma_\mu\rangle_{\sigma_\lambda=\pm1}$ represents the value of σ_μ averaged over all the configurations for which $\sigma_\lambda = \pm1$; the last equality of (2.13) results from the fact that both spin directions are equivalent when $H_{o\lambda} = 0$. When the spin states are randomly distributed, there is no correlation between the values of σ_λ and σ_μ $(\lambda\neq\mu)$; the average value of σ_μ is then independent on the state of the λth spin and :

$$g(\lambda-\mu) = 0\ (\lambda\neq\mu) \quad \text{random distribution of spins} \qquad (2.14)$$

The MFA assumes such a random distribution of spins but, in an equilibrium state, the spins are never randomly distributed for non zero pair interactions $v(\lambda-\mu)$: there is a local order between neighbouring spins. This can easily be understood from the following qualitative argument. Let us assume for example that $v(\lambda-\mu)= v$ is positive when λ and μ are two nearest neighbours and zero otherwise ; the field that the μth spin experiences from its local environment when $\sigma_\lambda = \pm 1$ is then mainly due to the λth spin and is equal to $\pm$ v. In the high temperature limit, the probability for the spin μ to be in the state $\pm$ 1 is then given by :

$$P_\pm = \frac{e^{\pm v/k_B T}}{e^{v/k_B T} + e^{-v/k_B T}} \simeq \frac{1}{2} \left(1 \pm \frac{v}{k_B T}\right), \quad v << k_B T \tag{2.15}$$

and the correlation function between two neighbouring spins is given by :

$$g(\lambda-\mu) = 2 \; \langle\sigma_\mu\rangle_{\sigma_\lambda = +1} = 2\left[P_+ - P_-\right] \sim \frac{2v}{k_B T} \tag{2.16}$$

If the spin λ is in a given direction ($\sigma_\lambda = +1$ for example) the neighbouring spins will be mostly in the same direction when $v > 0$: this local order is measured by $g(\lambda-\mu)$ (2.16). It decreases when the temperature increases and when the distance $|\lambda-\mu|$ increases. The critical temperature T_c being roughly given by :

$$k_B T_c = V(o) \simeq Z v \tag{2.17}$$

where Z is the coordination number of the considered lattice ; the local order for nearest neighbours is given by $g \simeq 2/Z$ at $T = T_c$. Qualitatively, the system has not lost all its coupling energy for $T > T_c$ as assumed by the MFA since it keeps an energy roughly given by $\langle \mathcal{H} \rangle \sim N/2 \; Z \, v \, g \sim N \, v \quad 1/Z \, k_B T_c$.
It is then important to estimate the quantitative and qualitative effect of the SRO on the thermodynamic properties ; quantitatively the MFA is not sufficient to obtain reliable results ; for example, it overestimates the transition temperature T_c which must be computed using more sophisticated methods (Kikuchi's method : see for example, Bocquet's lectures) taking into account local order. Qualitatively, the thermodynamic behaviour is not correctly represented by the MFA. For example, even when the nature of the LRO and of the phase transition is correctly predicted by the MFA, this approximation cannot represent the thermodynamic behaviour in the critical region $\left[T_c - \Delta T, T_c + \Delta T\right]$ for which the contribution of the spin correlation will be shown to be dominant.

2.3. MFA and variational method : (see Appendix 1).- We used the simplest presentation of the MFA. However, this approximation can be obtained by a variational method. It is a priori reasonable to approximate the free energy by the free energy of a set of independent spins λ submitted to fields :

$$H_\lambda = \sum_\mu v(\lambda-\mu)\,\overline{\sigma}_\mu + H_{o\lambda} \tag{2.18a}$$

the quantities $\overline{\sigma}_\mu$ are to be determined a posteriori. It is easy to calculate the free energy of each of these systems and to show that the free energy F_m deduced from the MFA i.e. from the choice :

$$\overline{\sigma}_\mu = \langle\sigma_\mu\rangle \tag{2.18b}$$

is the best free energy consistent with the assumption (2.18a). We show this theorem in the appendix 1.

3. Ferromagnetic-paramagnetic transition in the MFA.- The MFA replaces N interacting systems by N independent systems in the field $\langle H_\lambda \rangle$ (cf.(2.7)) and in equilibrium with a thermostat. Let us briefly recall the properties of an isolated spin, define the self consistent mean field equations (& 3.1) and study the conditions for the existence of a ferromagnetic phase.

3.1. Self consistent equations. - The coupling energy of an isolated spin σ_λ with an external field H is given by :

$$h(\sigma_\lambda) = - H \, \sigma_\lambda \tag{2.19}$$

The thermal average of σ_λ when the spin is in equilibrium with a thermostat (temperature T) is given by the Boltzmann statistics :

$$\langle\sigma_\lambda\rangle = \frac{(1)\,e^{\beta H} + (-1)\,e^{-\beta H}}{e^{\beta H} + e^{-\beta h}} = \text{th} \; \beta H \;\left(\beta = \frac{1}{k_B T}\right) \tag{2.20}$$

When the field H is very small, $\langle\sigma_\lambda\rangle$ is proportional to the applied field H :

$$\langle\sigma_\lambda\rangle = \beta H \qquad (\beta H << 1) \qquad \text{(Curie Law)} \tag{2.21}$$

(low field and high temperature limits).
When the field is very large $\langle\sigma_\lambda\rangle$ saturates i.e. $\langle\sigma_\lambda\rangle \to 1$ (high field and low temperature limits $\beta H >> 1$).
The equations (2.7) and (2.20) must be solved self consistently : the system of N non linear equations has in general several solutions and the physical solution will be the solution which will minimize the free energy. The spin - spin interactions determine the low temperature ordered spin structures ($\langle\sigma_\lambda\rangle \neq 0$ for $H_{o\lambda} = 0$) which are destroyed by thermal disordering when the temperature increases. When the ordered state has a simple symmetry, the solution of the system (2.7), (2.20) is simple : this is the case when the ordered state is ferromagnetic, the N equations corresponding to the N spins λ becoming identical.

3.2. Ferromagnetic-paramagnetic transition. - In the MFA, it is easy to determine the ordered structure which can appear when we decrease the temperature from $T = \infty$. In the present section, we consider only the ferromagnetic structure the general case being considered later (see section 5).

We assume that the interactions $v(\lambda)$ are positive so that at low temperatures all the spins are parallel, the ordering energy being :

$$\mathcal{H}(\{\sigma_\lambda = 1\}) = -\frac{N}{2}\tilde{v}(o) \qquad (H_o = 0) \tag{2.22}$$

where

$$\tilde{v}(q) = \sum_\lambda v(\lambda)\, e^{iq\lambda} \tag{2.23}$$

From (2.7) and (2.20) the condition of appearance of ferromagnetism (i.e. $\langle\sigma_\lambda\rangle = \langle\sigma\rangle \neq 0$ when $H_o = 0$) is given by :

$$\langle\sigma\rangle = \text{th}\ \beta\tilde{v}(o)\langle\sigma\rangle \tag{2.24}$$

For $T > T_c$, where T_c is the transition temperature (Fig. 2.1.a) defined by :

$$k_B T_c = \tilde{v}(o) \tag{2.25}$$

only the disordered solution ($\langle\sigma\rangle = 0$) is in agreement with (2.24). However for $T < T_c$, there are two other solutions $\pm\langle\sigma\rangle_o \neq 0$; these solutions $\pm\langle\sigma\rangle_o$ tend to zero when $T \to T_c$ and they will be shown to be the most stable (see section 4.4). The MFA then predicts a second order transition between ordered ($T < T_c$) and disordered phases ($T > T_c$). We study the properties of these transitions for all possible lattices in the next section.

4. Properties of the paramagnetic ferromagnetic transition in the MFA. -

4.1. Order parameter (magnetization) for $T < T_c$ ($H_o = 0$). - $\langle\sigma\rangle$ is varying as :

$$\langle\sigma\rangle = (T_c - T)^\beta \qquad \beta = \frac{1}{2} \tag{2.26}$$

(2.26) can easily be shown by expanding (2.24) for small $\langle\sigma\rangle$; we obtain :

$$\langle\sigma\rangle = \sqrt{3}\left(\frac{T_c - T}{T}\right)^{1/2} \tag{2.27}$$

4.2. Susceptibility for $T > T_c$. - When we apply an uniform ($H_{o\lambda} = H_o \ \forall\lambda$) external field to the system, a "ferromagnetic" order of the spins appears even for $T > T_c$: the uniform field is coupled to the order parameter $\langle\sigma_\lambda\rangle = \langle\sigma\rangle$ and, by definition, the (linear) susceptibility is given by :

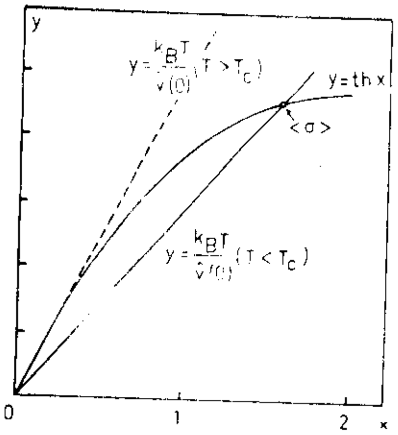


Fig. 2.1.a : Graphical determination of the ordered state for $T < T_c$ in the MFA.

$$\chi = \left.\frac{d\langle\sigma\rangle}{dH_o}\right|_{H_o = 0} \tag{2.28}$$

For isolated spins the susceptibility χ^o is given by (see eq. (2.21)) :

$$\chi^o = \beta = \frac{1}{k_B T} \qquad \text{(Curie law)} \tag{2.29}$$

For interacting spins in the MFA, the susceptibility χ is obtained from the expansion of the self consistent equation :

$$\langle\sigma\rangle = \text{th}\ \beta\langle H\rangle = \text{th}\ \beta(H_o + \tilde{v}(o)\langle\sigma\rangle) \tag{2.30}$$

In the low field limit ($\beta H \ll 1$) :

$$\langle\sigma\rangle = \chi^o(H_o + \tilde{v}(o)\langle\sigma\rangle) = \chi H_o \tag{2.31}$$

The susceptibility for interacting spins, χ, becomes a function of the susceptibility for non interacting spins, χ^o. χ is given by :

$$\chi = \frac{\chi^o}{1 - \tilde{v}(o)\chi^o} \tag{2.32}$$

or, more precisely by the Curie-Weiss law :

$$\chi = \frac{1}{k_B(T - T_c)} \tag{2.33}$$

For $T > T_c$ and when $T \rightarrow T_c$, the susceptibility is then varying as :

$$\chi \sim |T - T_c|^{-\gamma} \qquad \gamma = 1 \tag{2.34}$$

It is easy to show that the susceptibility χ is varying like (2.34) for $T < T_c$.

4.3. <u>Critical isotherm : ($T = T_c$)</u>. - At $T = T_c$, the self consistent equation (2.31) becomes :

$$(3\,\beta_c H_0)^{1/3} = \beta_c H_0 + \cdots \qquad \left(\beta_c = \frac{1}{k_B T_c}\right) \tag{2.35}$$

The order parameter is then varying as $H_0^{1/3}$ at $T = T_c$, i.e.

$$\langle\sigma\rangle \sim H_0^{\;1/\delta} \qquad \delta = 3 \tag{2.36}$$

4.4. <u>Free energy</u>. - <u>Qualitatively</u>, the transition results from the competition between the ordering energy (introduced by the spin-spin couplings) and the disordering thermal energy. The ordering energy is maximum at T = 0K (2.22) and decreases with $\langle\sigma\rangle$ when T increases ; on the other hand, the entropy is zero at T = 0K and increases up to $N k_B$ Log 2 when T increases.

<u>Quantitatively</u>, the energy $\langle\mathcal{H}\rangle$ and the entropy S can easily be obtained in the MFA i.e. neglecting the spin-spin correlations. From (3.9) the energy is given by (for $H_0 = 0$) :

$$\langle\mathcal{H}\rangle_{MFA} = -\frac{N}{2}\,\varphi(o)\,\langle\sigma\rangle^2 \qquad (H_0 = 0) \tag{2.37}$$

The entropy is given by :

$$S = k_B \,\mathrm{Log}\, W \tag{2.38}$$

where W is the number of different configurations consistent with the order parameter $\langle\sigma\rangle$. In the MFA, the spin-spin correlations are neglected so that W is the number of ways to put <u>at random</u> N_+ spins in the state +1 and N_- spins in the state -1 on the N lattice sites :

$$W_{MFA} = \frac{N!}{N_+!\,N_-!} \tag{2.39}$$

The number of systems in the state +1 (-1), N_+(N_-), is related to $\langle\sigma\rangle$ by :

$$\left\{\begin{array}{l} N = N_+ + N_- \\ \langle\sigma\rangle = \dfrac{N_+ - N_-}{N_+ + N_-} \end{array}\right. \quad \text{i.e.} \quad \begin{array}{l} N_+ = \dfrac{N}{2}(1 + \langle\sigma\rangle) \\ N_- = \dfrac{N}{2}(1 - \langle\sigma\rangle) \end{array} \tag{2.40}$$

In the thermodynamic limit ($N \rightarrow \infty$) and using the Stirling formula, the entropy becomes :

$$S_{MFA} = -N_i k_B \left\{ \frac{1+\langle\sigma\rangle}{2}\,\mathrm{Log}\left(\frac{1+\langle\sigma\rangle}{2}\right) + \frac{1-\langle\sigma\rangle}{2}\,\mathrm{Log}\left(\frac{1-\langle\sigma\rangle}{2}\right)\right\} \tag{2.41}$$

As predicted on physical grounds (2.41) shows that the entropy increases from zero to its maximum value $S_{max} = N k_B$ Log 2 when T increases from zero. However, the maximum value is reached when $T = T_c$ in the MFA since we neglect the local order (i.e. spin-spin correlations) in this approximation.

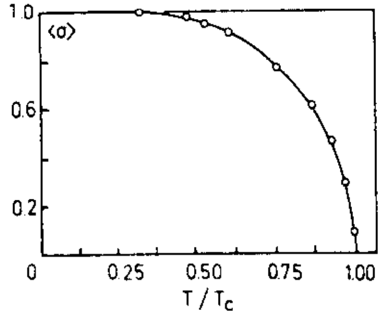
The free energy $F = \langle\mathcal{H}\rangle - TS$ is obtained in the MFA from (2.37) and (2.41). F is a function of $\langle\sigma\rangle$ and the equilibrium value for $\langle\sigma\rangle$ can be obtained either from the previous discussion (see section 3.2) or from the condition :

$$\frac{dF}{d\langle\sigma\rangle} = 0 \quad \text{(equilibrium)} \tag{2.42}$$

The solution corresponding to the stable equilibrium is obtained by requiring that the free energy is minimum :

$$\frac{d^2F}{d\langle\sigma\rangle^2} > 0 \qquad \text{(stability)} \tag{2.43}$$

The condition (2.42) is equivalent to (2.24) ; this can easily be shown from (2.37) and (2.41). The condition (2.43) is satisfied for the solution $\langle\sigma\rangle = 0$ when $T > T_c$ whereas it is only satisfied for the solutions $\pm\langle\sigma\rangle_0 \neq 0$ for $T < T_c$. The shape of the curves $F(\langle\sigma\rangle)$ is shown in figure 2.1.b ; in the next section, we verify these results when $T = T_c$.



<u>Fig. 2.1.b</u> : Order parameter versus temperature.

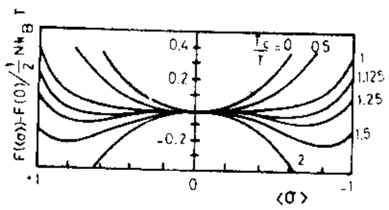


Fig. 2.1.c : Free energy versus $<\sigma>$ for various temperatures (MFA).

4.5. Landau expansion of the free energy when $T \simeq T_c$. - When $T \sim T_c$ i.e. $<\sigma> \simeq 0$, the free energy can be expanded in successive powers of the order parameter. From (2.41) the entropy is equal to :

$$S_{MFA} = Nk_B \,\mathrm{Log}\, 2 - \frac{Nk_B}{2}\left(<\sigma>^2 + \frac{<\sigma>^4}{6} + \ldots\right) \qquad (2.44)$$

whereas the free energy (see eq. (2.37)) is given by :

$$F_{MFA}(<\sigma>) = - N k_B \,\mathrm{Log}\, 2 + \frac{N}{2}(k_BT - \hat{v}(0))<\sigma>^2 + \frac{N k_B T}{12}<\sigma>^4 + \ldots \qquad (2.45)$$

When $T \simeq T_c$, equation (2.43) is the (Landau) expansion for the free energy in the MFA :

$$\frac{F(T,v)}{N} = \frac{A(T)}{2}<\sigma>^2 + \frac{C(T)}{4}<\sigma>^4 + \ldots \qquad (2.46)$$

The Landau coefficients A(T) and C(T) are given by :

$$\begin{cases} A(T) = k_B(T - T_c) \\ \\ C(T) = k_BT/3 \end{cases} \qquad (2.47)$$

and satisfy the conditions we discussed previously to obtain a second order phase transition (see chapter 1).

4.6. Specific heat coefficient. - The specific heat :

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v \qquad (2.48)$$

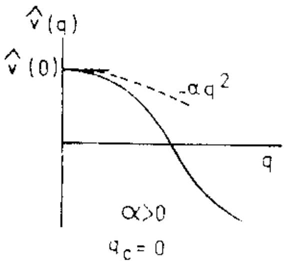


Fig. 2. 2.a : $\hat{v}(q)$ when the ordered state is "ferromagnetic" ($q_c = 0$).

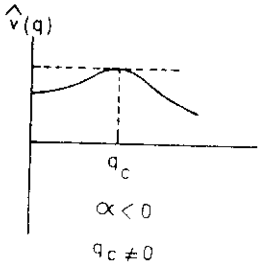


Fig. 2.2.b : $\hat{v}(q)$ when the ordered state presents a modulated structure ($q_c \neq 0$).

introduced by the spin ordering is given by (2.41) and (2.24). As we neglect spin correlations for $T > T_c$, the entropy is constant for $T > T_c$ and the corresponding specific heat is zero. It is given by :

$$C_v = \begin{cases} 0 & T > T_c \\ \frac{3 N k_B}{2} & T \leq T_c \end{cases} \qquad (2.49)$$

and has a simple jump at $T = T_c$ as shown by the Landau theory.

4.7. Conclusion. - The properties of the transition we obtain in the MFA are those we deduced from the Landau phenomenological theory ; the coefficients A(T), C(T)... which appear in this theory are clearly related to the coupling coefficients v( ). Note finally that the properties we found are independent of the dimension d of the system ; they are summarized in figure 3.

5. Modulated structures in the MFA. - 5.1. Modulated structures. - In the previous section, we assumed, for simplicity, that the interactions v( ) are positive so that the stable state at T = 0K is obviously ferromagnetic :

$$\langle\sigma_\lambda\rangle = \langle\sigma\rangle \quad \forall\lambda \quad \begin{matrix}(H_o = 0)\\ (v(\lambda) > 0)\end{matrix} \qquad T < T_c \tag{2.50}$$

For this reason we did not consider solutions $\langle\sigma_\lambda\rangle$ which are inhomogeneous. However, in general, the interactions can be positive or negative and they can "a priori" oscillate with distance. According to the nature of interactions and of the lattice, the ground state can be ferromagnetic, antiferromagnetic (with two sublattices in the simplest case) or much more complex. When the lattice is perfect and when all the spins are identical, it is possible "a priori", from symmetry considerations, to obtain simple modulated structures :

$$\langle\sigma_\lambda\rangle = A_{qo}\cos(q_o\lambda + \phi) \tag{2.51}$$

the period $2\pi/|q_o|$ can be incommensurate with the lattice periodicity. It is interesting to determine the conditions for which such modulated structures can appear. We will determine these conditions in the MFA as previously. We introduce the Fourier transforms of the coupling constants v (λ) and of the spin variables σ_λ :

$$\begin{cases} \tilde{v}(q) = \sum\limits_\lambda v(\lambda)\, e^{iq\lambda} \\ \sigma_q = \dfrac{1}{\sqrt{N}} \sum\limits_\lambda e^{iq\lambda}\sigma_\lambda \end{cases} \tag{2.52}$$

The spin configurations are determined by the N numbers $\{\sigma_\lambda\}$ ($\lambda = 1, 2,\dots N$) ; they are also determined by the numbers $\{\sigma_{qi}\}$ ($i = 1, 2,\dots N$) where the q_i are in the first Brillouin zone and are given by :

$$q_i = \sum_{\alpha=1}^{d} \frac{P_\alpha}{N_\alpha} A_\alpha , \quad i = (P_1,\dots P_\alpha \dots P_d) \tag{2.53}$$

In (2.53) N_α is the number of crystalline sites in the direction α of the lattice basis vector $\underline{a}_\alpha$, $\underline{A}_\alpha$ is the lattice reciprocal vector corresponding to $\underline{a}_\alpha$ ($\underline{A}_\alpha \cdot \underline{a}_\beta = 2\pi\ \delta_{\alpha\beta}$) and P_α is an integer.

From (2.52) and applying the relation :

$$\frac{1}{N} \sum_\lambda e^{iq\lambda} = \begin{cases} 0 & \text{if } q \neq 0 \\ N & \text{if } q = 0 \end{cases} \tag{2.54}$$

it is easy to show that :

$$\sigma_\lambda = \frac{1}{\sqrt{N}} \sum_q{}' \, e^{iq\lambda}\, \sigma_q \tag{2.55}$$

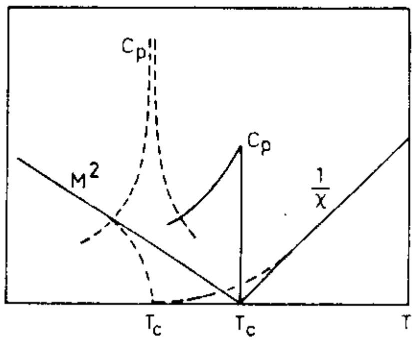


Fig. 2.3. : Phase transitions :
——— MFA,
- - - - - - exact results : d = 3 for short range interactions v(λ) (schematic)

the sum Σ'_q being extended to the q vectors of the first Brillouin zone. The energy $\mathcal{H}$ (see section 3.1) can then be written as :

$$\mathcal{H}(\{\sigma_q\}) = -\frac{1}{2} \sum_q{}' \, v(q)\, \sigma_q\, \sigma_{-q} \tag{2.56}$$

In the MFA, we replace $\langle\sigma_\lambda\sigma_\mu\rangle$ by $\langle\sigma_\lambda\rangle\langle\sigma_\mu\rangle$ ($\lambda \neq \mu$) or $\langle\sigma_q\,\sigma_{-q}\rangle$ by $\langle\sigma_q\rangle\langle\sigma_{-q}\rangle$ and the internal energy is given by :

$$\langle\mathcal{H}\rangle_{MFA} = -\frac{1}{2} \sum_q{}' \, \tilde{v}(q) \langle\sigma_q\rangle\langle\sigma_{-q}\rangle = -\frac{1}{2} \sum_q{}' \, \tilde{v}(q)\, |\langle\sigma_q\rangle|^2 \tag{2.57}$$

In the last equation (2.57) we used the fact that the lattice is assumed here, for simplicity, to have an inversion symmetry so that :

$$\sigma_q = \sigma^*_{-q} \qquad , \quad \tilde{v}(q) = \tilde{v}(-q) \tag{2.58}$$

The modulated structures (2.51) correspond to (see eq. (2.52)) :

$$\langle\sigma_q\rangle = \frac{A_{qo}}{2} \sqrt{N}\, (\delta_{q\,qo} + \delta_{q-q_o}) \tag{2.59a}$$

and the energy (2.57) can then be written as :

$$\langle\mathcal{H}\rangle_{MFA} = -\frac{N}{2}\, \tilde{v}(q_o)\, A_{q_o}^2 \tag{2.59b}$$

Among the set of all the modulated structures (2.51), the most stable are those for which $\tilde{v}(q_o)$ is maximum. They are obtained for the vectors q_c such that (see fig. 2.2.) :

$$\tilde{v}(q) \leq \tilde{v}(q_c) \tag{2.60}$$

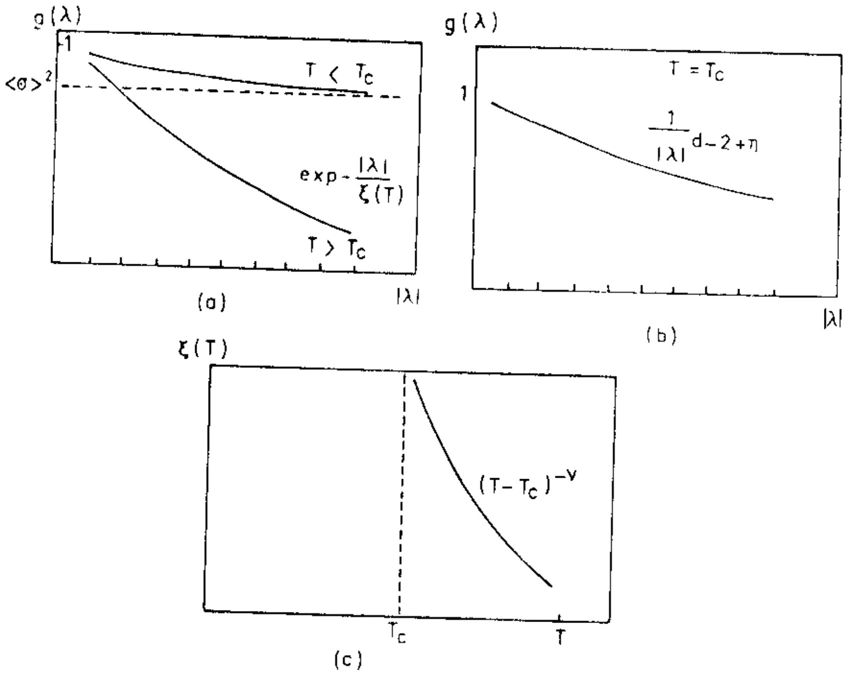


Fig. 2.4 : correlation function g(λ) and correlation length ξ(T) when $T \simeq T_c$ (schematic).

If $\tilde{v}(q)$ decreases for increasing $|q|$ values, the ferromagnetic solution will be the most stable but if $\tilde{v}(q)$ is maximum for some q_c value ($q_c \neq 0$) in the Brillouin zone, the most stable solution will be modulated with a period incommensurate with the lattice period : the periodicity of the ordered state is then determined by the nature of the spin-spin interactions.

It is then possible to study the transition from a modulated structure to a paramagnetic state as it has been done previously for the ferromagnetic-paramagnetic transition. In the next sections we summarize briefly such a study. We define the corresponding susceptibility χ (q) and we briefly summarize the properties of the transition and the variation of the free energy versus $<\sigma_q>$. Finally we determine the condition of instability of the paramagnetic state versus a modulated structure when the temperature decreases and we determine the corresponding critical temperature T_c (see section 5.4). The principles of such considerations are exactly the same as previously, but they will be useful later for the study of spin-spin correlations and of the validity of the MFA.

5.2. Local susceptibility for $T > T_c$.- The values of $<\sigma_\lambda>$ are given by the self consistent condition :

$$<\sigma_\lambda> = \text{th}\,\beta(H_{o\lambda} + \sum_\mu v(\lambda-\mu)<\sigma_\mu>) \tag{2.61a}$$

In the high temperature and low field $<H_\lambda>$ limit, we can linearize the previous equations :

$$<\sigma_\lambda> = \beta\,(H_{o\lambda} + \sum_\mu v(\lambda-\mu)<\sigma_\lambda>) \tag{2.61b}$$

The external field $H_{o\mu}$ acting on the site μ induces a local order around this site μ whose value is (by definition) $<\sigma_\lambda> = \chi(\lambda-\mu)\,H_{o\mu}$. The local susceptibility $\chi(\lambda-\mu)$ is only dependent on λ- μ when the system is invariant by the lattice translations. In the linear approximation, $<\sigma_\lambda>$ results from the linear superposition of the effects induced by all the fields $H_{o\mu}$:

$$<\sigma_\lambda> = \sum_\mu \chi(\lambda-\mu)\,H_{o\mu} \tag{2.62a}$$

Fourier transforming (2.62) we obtain :

$$<\sigma_q> = \frac{1}{N}\sum_{\lambda,\mu} \chi(\lambda-\mu)\,e^{-iq(\lambda-\mu)}\,H_{o\mu}\,e^{-iq\mu} \tag{2.62b}$$

i.e.

$$<\sigma_q> = \chi(q)\,H_{oq} \tag{2.63a}$$

with the definition

$$\begin{cases} H_{oq} = \dfrac{1}{\sqrt{N}} \sum_\lambda H_{o\lambda}\, e^{-iq\lambda} \\ \chi(q) = \sum_\lambda \chi_{o\lambda}\, e^{-iq\lambda} \end{cases} \tag{2.63b}$$

5.3. Local susceptibility in the MFA. - From the expansion of equation (2.61b) we can determine the local susceptibility of interacting spins, χ, from the susceptibility of non interacting spins, χ^o, in the same way as we obtained the uniform susceptibility χ from χ^o in §.4.2. From (2.61b) the susceptibility $\chi^o(\lambda-\mu)$ of non interacting spins (v = 0) is given by :

$$\chi^o_{\lambda\mu} = \chi^o(\lambda-\mu) = \chi^o\,\delta_{\lambda\mu} \tag{2.64}$$

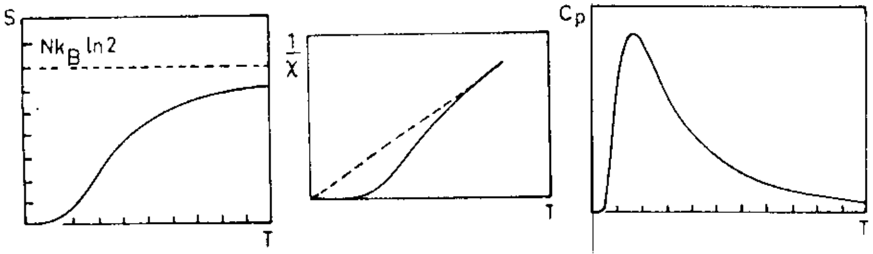


Fig. 2.5 : Specific heat, entropy and susceptibility in an Ising model ($d = 1$) (schematic).

the magnetization $\langle\sigma_\lambda\rangle$ is only modified by the external field $H_{o\lambda}$ which is applied on the site λ. This is no longer true when the spins are interacting ($v \neq 0$). Multiplying (2.61b) by $e^{-iq\lambda}/\sqrt{N}$ and summing over all the lattice vectors λ we obtain :

$$\langle\sigma_q\rangle = \beta\,(H_{oq} + \vartheta(q)\langle\sigma_q\rangle) \qquad (2.65)$$

This equation is the extension of equation (2.31) obtained for the uniform susceptibility.

The q dependent susceptibility $\chi(q)$ defined by (2.63b) is then given by :

$$\chi(q) = \frac{\chi^\circ}{1 - \vartheta(q)\,\chi^\circ} = \frac{1}{k_B(T - T_q)} \qquad (2.66)$$

with

$$k_B T_q = \vartheta(q) \qquad (2.67)$$

When the temperature decreases from infinity, the susceptibility diverges for the first time for the temperature T_{qc} defined by (2.60) i.e. for the vector q_c for which the instability of the disordered state appears first.

5.4. Free energy in the MFA. - The free energy of the ordered state can be obtained in the same way as in the uniform case. The energy $\langle\mathcal{H}\rangle$ is given by (2.57) and the entropy is obtained by a generalization of (2.41) :

$$S_{MFA} = k_B \sum_\lambda \left\{ \frac{1-\langle\sigma\lambda\rangle}{2} \operatorname{Log} \frac{1-\langle\sigma\lambda\rangle}{2} + \frac{1+\langle\sigma\lambda\rangle}{2} \operatorname{Log} \frac{1+\langle\sigma\lambda\rangle}{2} \right\} \qquad (2.68)$$

In the same way as in section 4.4. it is possible to obtain the mean field solution i.e. (2.60) from the condition :

$$\frac{dF}{dA_q}(q_c) = 0 \qquad (2.69a)$$

Using the classical relation (see eq. (2.54) and 2.55)) :

$$\sum_\lambda \langle\sigma_\lambda\rangle^2 = \sum_q |\langle\sigma_q\rangle|^2 \qquad (2.71)$$

the free energy F is given by :

$$F(T,V,\langle\sigma_q\rangle) = +\frac{1}{2} \sum_q (\vartheta(q) - k_B T)|\langle\sigma_q\rangle|^2 + 0(|\langle\sigma_q\rangle|^4) \qquad (2.72)$$

From the value we obtained for $\chi(q)$ (2.66), the Landau expansion of F can be written as :

$$F(T,v,\langle\sigma_q\rangle) = \frac{1}{2} \sum_q{}' \frac{|\langle\sigma_q\rangle|^2}{\chi(q)} + \ldots = \frac{1}{2} \sum_q{}' A(q)\,|\langle\sigma_q\rangle|^2 + \ldots \qquad (2.73)$$

From (2.73) we recognize that : i) the inverse susceptibility is the second derivative of F relative to $\langle\sigma_q\rangle$; ii) the Landau coefficient A(q) associated to $\langle\sigma_q\rangle$ is :

$$A(q) = \chi(q)^{-1} = k_B(T - T_q) \qquad (2.74)$$

and changes its sign for $T = T_q$. When the temperature decreases, the paramagnetic solution becomes unstable for the temperature

$$T_c = T_{qc} \qquad (2.75)$$

and for $T < T_c$, the ordered state (2.51) is more stable than the paramagnetic solution. The value of the order parameter A_{qc} can then be obtained from the equations (2.61) or, for $T \leq T_c$, by expanding F up to the fourth order. This expansion allows to obtain the properties of the solution near the critical temperature T_c i.e. the exponents β, γ, δ and α we defined previously for the order parameter, the susceptibility, the critical isotherm and the specific heat : it is easy to show that they are the same as those we obtained for the ferromagnetic-paramagnetic transition.

6. Relation between local susceptibilities, fluctuations and correlations. - 6.1. Fluctuations and correlations. - For simplicity, we will consider only the high temperature phase for which $\langle\sigma_q\rangle = 0$. The extension of the following results to the low temperature phase is straightforward.

The spin fluctuations in the equilibrium state are characterized by the function g(q) defined by :

$$g(q) = \langle\sigma_q\,\sigma_{-q}\rangle_o - |\langle\sigma_q\rangle_o|^2 \qquad (2.76a)$$

the thermal average $< >_o$ being taken for an equilibrium state without applied field ($H_o = 0$). This function g(q) is the Fourier transform of the correlation function g(λ) we defined previously. Let us now show this relation <u>for $T > T_c$</u> : from (2.52), g(q) is given by :

$$<\sigma_q \sigma_{-q}>_o = \frac{1}{N} \sum_{\lambda\mu} <\sigma_\lambda \sigma_\mu>_o e^{-iq(\lambda-\mu)} \qquad (2.76b)$$

the system being invariant by the lattice translations when $H_{o\lambda} = 0$, $<\sigma_\lambda \sigma_\mu>_o = g(\lambda-\mu)$ is dependent on $|\lambda - \mu|$ and we obtain :

$$g(q) = \sum_\lambda <\sigma_0 \sigma_\lambda>_o e^{-iq\lambda} = \sum_\lambda g(\lambda)\, e^{-iq\lambda} \qquad (2.77)$$

The relation between the correlation function g(λ) and the spectrum of fluctuations of wave vector q, g(q), can be also written by Fourier transforming (2.77) as follows :

$$g(\lambda) = \frac{1}{N} \sum_q{}' g(q)\, e^{iq\lambda} \qquad (2.78)$$

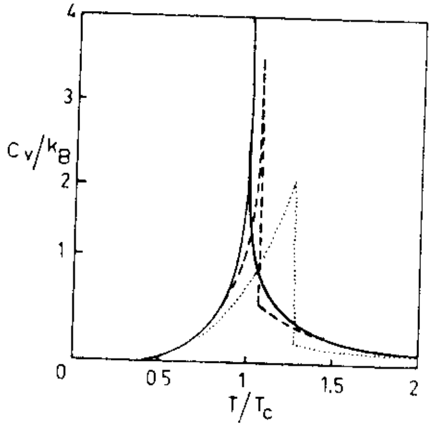


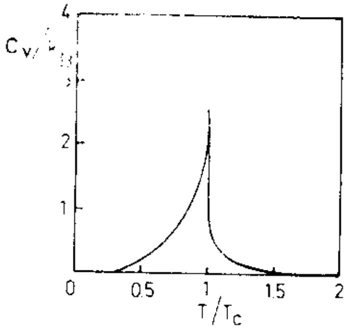
Fig. 2.6.a : Specific heat of an Ising model (d = 2) (from Domb,(1960)).
—— exact (Onsager)
··· Bethe
---- Kikuchi.

6.2. <u>Fluctuations and susceptibility</u>. - The local susceptibilities χ(λ) and the correlation function g(λ) are related by an exact theorem the validity of which is independent of the approximations used to calculate these quantities (fluctuation - dissipation theorem). We consider here only its classical version : the correlation function g(q) for the equilibrium state (without field) is proportional to the linear response to an applied field H_{oq} with the same periodicity :

$$g(q) = <\sigma_q \sigma_{-q}>_o = k_B T \; \chi(q) \qquad (2.79)$$

To demonstrate this relation we note the thermal average of σ, $<\sigma>$ (or $<\sigma>_o$) when the system is submitted to a non zero (or to a zero) applied field respectively. The energy of the spin system coupled to an external field H_o, such that $H_{oq'} = H_{oq}\,\delta_{qq'}$ is given by :

$$\mathcal{H} = \mathcal{H}_o - H_{oq}\,\sigma_{-q} \qquad (2.80)$$



<u>Fig. 2.6b</u> : Specific heat of a 3d Ising model for a fcc lattice (from Domb,(1960), Adv. in Phys. <u>9</u>, 149).

The partition function Z is then :

$$Z = \sum_{\{\sigma_q\}} e^{-\beta\mathcal{H}(\{\sigma_q\})} \qquad (2.81)$$

the summation being taken over all the possible spin configurations (each configuration is determined by the numbers $\{\sigma_q\}$ $(q = ...q_j...)$. By definition the thermal average of σ_q, $<\sigma_q>$ is given by

$$<\sigma_q> = \frac{\sum_{\{\sigma_{q'}\}} \sigma_q e^{-\beta\mathcal{H}(\{\sigma_{q'}\})}}{\sum_{\{\sigma_{q'}\}} e^{-\beta\mathcal{H}(\{\sigma_{q'}\})}} \qquad (2.82)$$

Without applied field, $\mathcal{H} = \mathcal{H}_o$, $Z = Z_o$ and $<\sigma_q>_o = 0$ for $T > T_c$. For a non zero applied, $H_{oq'} = \delta_{qq'} H_{oq}$, we can obtain $<\sigma_q>$ from an expansion of (2.82) in successive powers of H_o. Keeping only the first order terms, we obtain the linear susceptibility χ(q) defined by (2.63a) :

$$<\sigma_q> = \chi(q)\, H_{oq} = \frac{\sum_{\{\sigma_{q'}\}} e^{-\beta\mathcal{H}_o(\{\sigma_{q'}\})}\,[1 + \beta H_{oq}\sigma_{-q} + \dots]\,\sigma_q}{Z_o(1 + \dots)} \qquad (2.83)$$

From the definition of $<\sigma_q \, \sigma_{-q}>_o$:

$$<\sigma_q \sigma_{-q}>_o = \frac{1}{Z_o} \sum_{\{\sigma_{q'}\}} e^{-\beta \mathcal{H}_o(\{\sigma_{q'}\})} \sigma_q \sigma_{-q} \qquad (2.84)$$

and using the fact that $<\sigma_q>_o = 0$ for $T > T_c$ we obtain (2.79). This demonstration can be easily extended to the temperature range $0 < T < T_c$.

7. Correlation function near the critical temperature. - 7.1. Introduction. - The MFA neglects the spin correlations ($g_{MFA}(\lambda) = 0 \ \forall \lambda \neq 0$). However, it is easy to show that, usually, these correlations are strong when $T \simeq T_c$ (see section 2.2) ; moreover, they become long ranged so that the validity of the MFA we examine later is a priori dubious when $T \simeq T_c$ (see section 8). In this section we obtain an estimation of $g(\lambda)$ from (2.79) and from the MF value of $\chi(q)$ (cf. (2.66)). This procedure is not consistent since the correlation function $g(q)$ is calculated from an expansion of the susceptibility $\chi(q)$ which neglects such correlations. It is however valid to examine qualitatively the order of magnitude of the correlations and to verify if they are not qualitatively important to describe the second order transition. In order to understand physically the assumptions of such a procedure, it is interesting to recover the corresponding value of $g(q)$ i.e. (see eq. (2.65) and (2.79)) :

$$g(q) = k_B T \, \chi(q) = \frac{k_B T}{k_B T - \tilde{v}(q)} \qquad (2.85)$$

from an extension of the mean field equations. Let us now examine this point.

By definition, $g(\lambda)$ can be written (for $T > T_c$) in the following way :

$$g(\lambda) = \frac{1}{2} \left[<\sigma_\lambda>_+ - <\sigma_\lambda>_- \right] \qquad (2.86)$$

The spin 0 has the probability 1/2 to be in the state +1 ; if it is in this state, it polarizes the neighbours λ which are then characterized by a non zero average value of σ_λ, $<\sigma_\lambda>_+$ (conditional average). In the same way, if the spin 0 is in the state -1 (probability 1/2) the average value of σ_λ is $<\sigma_\lambda>_-$. Without applied field, both spin directions are equivalent so that $<\sigma_\lambda>_- = - <\sigma_\lambda>_+$ and :

$$g(\lambda) = <\sigma_\lambda>_+ \qquad (2.87)$$

$<\sigma_\lambda>_+$ can be estimated if we assume that the spin λ is submitted to the field induced by the spin 0, $v(\lambda)$, and to the average field induced by the other spins (for which nothing is known).

$$<\sigma_\lambda>_+ = \text{th} \, \beta \Big(v(\lambda) + \sum_{\rho \neq 0} v(\lambda - \rho) <\sigma_\rho>_+\Big) \qquad (2.88)$$

- This estimation is an extension of the MFA since it neglects the correlations between the spin λ and the other spins ρ which are not at the origin ($\rho \neq 0$). In the linear approximation :

$$g(\lambda) = \beta \, v(\lambda) + \beta \sum_{\rho \neq 0} v(\lambda - \rho) \, g(\rho) \quad \lambda, \rho \neq 0 \qquad (2.89)$$

This equation can be solved by a Fourier transformation :

$$\tilde{g}(q) = \sum_{\lambda \neq 0} g(\lambda) \, e^{-iq\lambda} = \beta \, \tilde{v}(q) + \beta \, \tilde{v}(q) \, \tilde{g}(q) \qquad (2.90)$$

In the l.h.s. of (2.90) we neglected the restriction $\rho \neq 0$; it is easy to see that this correction is not qualitatively important. g and $\tilde{g}$ are related by a simple relation : by definition $g(0) = <\sigma_o^2> = 1$ and :

$$g(q) = 1 + \tilde{g}(q) \qquad (2.91)$$

It is then trivial to recover (2.85) from (2.90) and (2.91). Finally note that it is possible to obtain by the same methods the correlation functions for $T < T_{q_c}$; in a ferromagnetic state $g(q)$ is given by :

$$g(q) = \frac{1 - <\sigma>^2}{1 - \beta \, \tilde{v}(q) \, (1 - <\sigma>^2)} \qquad (T < T_c) \qquad (2.92)$$

7.2. Correlation function for $T \simeq T_c$. - The previous form of $g(q)$ (2.85) (2.92)) presents a singularity when $T \simeq T_c$ and $q = q_c$. Let us now study the singular behaviour of $g(\lambda)$ near the transition temperature. For simplicity, we consider only the ferromagnetic transition ($q_c = 0$) but the results obtained for $q_c \neq 0$ would be qualitatively similar. We study the spatial dependence of $g(\lambda)$: i) at $T = T_c$ and later ii) for $T \neq T_c$.

7.2.1. Correlation function at $T = T_c$ (Fig. 4.b). - When $\tilde{v}(q)$ is a "regular" function fo all q values in the Brillouin zone, the asymptotic form of $g(\lambda)$ ($|\lambda| \to \infty$) is determine by the values of $g(q)$ and of $\tilde{v}(q)$ (2.85) for $q \simeq 0$. It is then useful to keep only the first terms of its expansion, for $q \simeq 0$, in (2.78). $\tilde{v}(q)$ can then be written as follows :

$$\tilde{v}(q) = \sum_\lambda{}' \, v(\lambda) \, e^{iq\lambda} \simeq \tilde{v}(o) + \sum_\lambda iq\lambda v(\lambda) + \Big(-\frac{(q\lambda)^2}{2} v(\lambda) + \ldots\Big) \qquad (2.93)$$

Using (2.58), the linear term of (2.93) is zero and if the symmetry is cubic (2.93) becomes :

$$\begin{aligned} \tilde{v}(q) &= \tilde{v}(o) - \alpha q^2 + \ldots \\ \alpha &= \frac{1}{3} \sum_\lambda |\lambda|^2 v(\lambda) \end{aligned} \qquad (2.94)$$

We keep this simple form for (2.93), the anisotropy of the expansion being not essential for the qualitative results we want to discuss here.

From (2.78) and (2.94) the correlation function becomes :

$$g(\lambda, T_c) \sim \int dq^d \, \frac{e^{iq\lambda}}{q^2} \qquad (2.95)$$

where d is the dimension of the considered lattice. Introducing a dimensionless vector $x = q\,|\lambda|$ and the unit vector $\hat\lambda$ ($\lambda = |\lambda|\,\hat\lambda$) we obtain :

$$g(\lambda, T_c) \sim \int \frac{dx^d}{|\lambda|^d} \, \frac{e^{ix\hat\lambda}}{q^2} \sim \frac{1}{|\lambda|^{d-2}} \int dx^d \, \frac{e^{ix\hat\lambda}}{x^2} \qquad (2.96)$$

At $T = T_c$ the correlation function $g(\lambda, T_c)$ is decreasing slowly as a power of the distance $|\lambda|$:

$$g(T_c, \lambda) = \frac{1}{|\lambda|^{d-2+\eta}} \qquad \eta = 0 \qquad (2.97)$$

The parameter η which is introduced experimentally is zero in the approximation we use here for $g(\lambda)$.

7.2.2. Correlation function when $T \simeq T_c$ (Fig. 4a). - For $T > T_c$, the correlation function can be written as : (see eq. (2.85) and (2.94))

$$g(q) = \frac{k_B T}{\alpha\,(q^2 + 1/\xi^2)} \qquad (2.98)$$

where the "correlation length" ξ determines the range of the correlation function. In the approximation we consider here, $\xi \to \infty$ when $T \to T_c$ as (Fig. 4.c) :

$$\xi(T) \sim |T - T_c|^{-\nu} \qquad \nu = 1/2 \qquad (2.99a)$$

More precisely :

$$\xi(T) = \sqrt{\frac{\alpha}{k_B}} \, (T - T_c)^{-1/2} \qquad (2.99b)$$

The spatial dependence of the correlation function when $T \simeq T_c$ can then be otained by Fourier transforming g(q). For example when d = 3 we obtain :

$$g(\lambda) \sim \frac{e^{-|\lambda|/\xi(T)}}{|\lambda|} \qquad (d = 3) \qquad (2.100)$$

Similar results are easily obtained from (2.92) for $T < T_c$.

7.2.3. Discussion. When $T \to T_c$, the importance of the spin fluctuations (or correlations) becomes larger and larger. For $T \neq T_c$, the correlation function decreases exponentially with the distance $|\lambda|$ and its range is small when we are far from the transition

temperature. However, near the critical temperature, the importance of the fluctuations becomes qualitatively and quantitatively important. At $T = T_c$ the correlation length $\xi(T)$ diverges and the correlation function decreases as a power of $|\lambda|$. Note that short range interactions $v(\lambda)$ (limited to the nearest neighbours for example) induce long range correlations at $T = T_c$. The detailed variation of the spin interactions $v(\lambda)$ with $|\lambda|$ does not determine the correlation function when $T = T_c$: here $g(\lambda, T_c)$ is only determined by the lattice dimension d.

However, as previously mentioned, the calculation of $g(\lambda)$ we presented in this section is not self-consistent and we suspect "a priori" the validity of such results. Let us only mention here that the qualitative features we obtained for $g(\lambda)$ for $T \simeq T_c$ are well predicted when the transition is a 2nd order transition ($\xi(T)$ diverges at $T = T_c$) but, the detailed form of the correlation function is not correct. For simple systems we will represent the correlation function when $T \simeq T_c$ as follows :

$$\begin{cases} g(|\lambda|, T) = \dfrac{1}{|\lambda|^{d-2+\eta}} \, f_1\!\left(\dfrac{|\lambda|}{\xi}\right) & (2.101a) \\ \xi(T) \sim |T_c - T|^{-\nu} & (2.101b) \end{cases}$$

The variation of the spin-spin correlations for $T \simeq T_c$ is then characterized by two indices η and ν and by the function $f_1(x)$. Using the previous approximation we obtain :

$$\eta = 0, \nu = 1/2 \qquad , \qquad f_1(x) = e^{-x} \qquad (2.102a)$$

In reciprocal space, using the same transformation as previously (see (2.96)), the Fourier transform of (2.101) is given by :

$$g(q, T) = \frac{1}{q^{2-\eta}} \, f_2(q\,\xi) \qquad (2.102b)$$

8. Validity of the M.F.A. Ginzburg - Landau criterion. - 8.1. Specific heat when $T \simeq T_c$. - It is interesting to estimate the specific heat and the internal energy for $T \simeq T_c$. For such an estimation, we can use the approximate form we obtained for the correlations in the previous section. Such a calculation will allow to understand qualitatively the role of the correlations when $T \simeq T_c$. These correlations will change qualitatively the properties of the transition for d < 4 (see section 8.2).

From equations (2.36) and (2.85) the internal energy, which is directly related to the correlation function, is given by :

$$\langle \mathcal{H} \rangle = -\frac{1}{2} \, \frac{V}{8\pi^3} \int dq^d \, \frac{\tilde v(q) \; k_B T}{k_B T - \tilde v(q)} \qquad (2.103)$$

where the integral must be taken over the first Brillouin zone. The singularity for $T > T_c$ is determined by the expansion of g(q) when $q \simeq 0$:

$$\langle \mathcal{H} \rangle = -\frac{1}{2} \frac{V}{8\pi^3} \frac{k_B T}{\alpha} \int dq^d \frac{1}{q^2 + \xi^{-2}} \tag{2.104}$$

and the specific heat for $T > T_c$ is given by :

$$c_v = \left(\frac{\partial \langle \mathcal{H} \rangle}{\partial T}\right)_v = -\frac{1}{2} \frac{V}{8\pi^3 \alpha} \int \frac{dq^d}{q^2 + \xi^{-2}} + \frac{V}{8\pi^3} \frac{1}{2} \int \frac{dq^d}{(q^2 + \xi^{-2})^2} \tag{2.105}$$

When $T = T_c$, $\xi^{-2} = 0$ and we must integrate in a space of dimension d, q^{-2} and q^{-4}. Since $dq^d = \Omega_d q^{d-1} dq$, we must calculate $\int dq/q^n$ with $n = 3-d$ and $5-d$. The integrals diverge for $q = \infty$ and for $q = 0$ for two reasons :

i) The divergence for $q = \infty$ is artificial : it comes from the fact that we expanded $\varphi(q)$ in (2.103) (see (2.94)) but this expansion is not valid for $q = \infty$; the estimation (2.105) allows only to determine the $q \simeq 0$ contribution to the specific heat when we replace the upper limit of the integrals by a cut off $q_o \simeq 2\pi/\lambda_o$ (where λ_o is the range of the spin couplings).

ii) The integral $\int_0^{q_o} dq/q^{5-d}$ diverges for $d < 4$ and this divergence is essential : it comes from the fact that the correlation length diverges at $T = T_c$. In other words, the specific heat remains finite when $T \simeq T_c$ for $d > 4$, but for $d < 4$, the specific heat is divergent. It is interesting to determine the nature of this singularity. With $|q| = x\xi^{-1}$ we obtain :

$$\int_o^{q_o} \frac{q^{d-1} dq}{(q^2 + \xi^{-2})^2} = \xi^{4-d} \int_o^{q_o \xi} \frac{x^{d-1} dx}{(x^2 + 1)^2} \tag{2.106a}$$

When $T \to T_c$, $q_o \xi \to \infty$ and the specific heat becomes for $d < 4$:

$$c_v \sim \xi(T)^{4-d} = N\mathcal{B}(T - T_c)^{d-4/2} \qquad \mathcal{B} \sim \alpha^{-d/2} \tag{2.106b}$$

In the same way, when d=4, it can be shown that :

$$c_v \sim \mathrm{Log}\,|T - T_c| \tag{2.106c}$$

Finally note that the integral $\int_o^{q_o} dq/q^{3-d}$ is also divergent for $d < 2$ but the corresponding divergence is less important than the previous one : $c_v \sim \xi^{d-2} \sim |T - T_c|^{d-2/2}$.

The results obtained in the MFA. When $T \simeq T_c$ are those we obtained previously from the Landau theory : the critical behaviour is characterized by the same critical exponents (α, β ...). The MFA neglects the spin-spin correlations (or the spin fluctuations). An estimate of these fluctuations shows that they are qualitatively important in a critical region ($T_c - \Delta T$, $T_c + \Delta T$), the width of this region becoming larger when the range of the spin-spin couplings becomes smaller.

For temperatures which are not in the critical region, the MFA can represent qualitatively the physical trends by an interpolation between the ordered and disordered states. However, even from a qualitative point of view this MFA leads often to wrong results. First, it predicts the existence of a transition for all values of d ; however, it is easy to show that when d = 1 (linear chain) there is no phase transition for $T_c \neq 0$ when the spin couplings are short ranged (see Fig. 5 and appendix 2). In shuch a case, the general behaviour of the physical properties (specific heat, susceptibility...) is not qualitatively reproduced by the MFA. Moreover, when $v(\lambda)$ is not always positive the ordered state when $d > 1$ is not always exactly predicted by the MFA : some general theorems allow to determine the nature of the ordered state for $T = 0$K for pair interactions $v(\lambda)$ going up to the fourth nearest neighbours. Finally, the order of the transition (2nd or 1st) is not even correctly predicted in a number of cases.

Quantitatively it is possible to develop more sophisticated MFA to study the phase transition in the Ising model (Bethe, Kikuchi...). These methods allow to obtain a better agreement with the exact results far from T_c when they are available ; however, they do not change the critical behaviour we discussed previously. In these lectures we do not discuss the analytical (high temperature expansions...) and numerical methods which allow to obtain more precise informations on the phase transitions in the Ising model (see the book by Domb and Green).

8.2. Discussion - Landau Ginzburg-criterion. - For $d < 4$, we have shown the existence of an inconsistency since the corrections to the MFA modify qualitatively these results : the jump of specific heat is replaced by a divergence. A similar calculation can be done for the ordered phase (cf. (2.92)). The specific heat results both from i) the contribution of the Landau theory, ii) the contribution of the fluctuations of σ around its average value. For $d < 4$, the contribution of these fluctuations is dominant when $T \simeq T_c$ and the MFA has no longer any meaning in this critical region $[T_c - \Delta T, T_c + \Delta T]$. The Landau theory (or MFA) will be valid when the temperature is out of this region. An order of magnitude of ΔT is obtained when the two contributions to the specific heat are of the same order of magnitude i.e. when (see eq. (2.49) and (2.106)) :

$$\frac{3 k_B}{2} \sim \mathcal{B} \, |T - T_c|^{(d-4)/2} \tag{2.107}$$

The coefficient β depends both on d and on the range of the pair interactions $v(\lambda)$ (see (2.94)). When the interactions are short ranged (for example $v(\lambda) \sim v(0) \exp - |\lambda|/\lambda_0$ where λ_0 is the range of the interactions), the coefficient α varies as λ_0^{d+2} and the critical region is given by :

$$|\Delta T| \sim \lambda_0^{-d(d+2)/4-d} \tag{2.108}$$

When the range of the spin interactions λ_0 is large, the critical region is small ; it can even be so small that the experimental behaviour seems to be governed by the MFA! (superconductivity for example).

9. Conclusion : validity of the MFA. - In this chapter we discussed the results obtained in the MFA ; the importance of this approximation comes from its simplicity. Moreover, it can be applied as a first approximation to explain phase transitions the physical nature of which is different (Van der Waals for the liquid gas, B.C.S. for the superconductor metal, Bragg Williams for the order disorder, molecular field for the magnetic transitions...).

APPENDIX 1

MFA AND VARIATIONAL METHOD : We show that the MFA results from a variational principle (see section 1) and we apply it to the Ising model (see section 2).

1. Variational principle. - (Bogoliubov inequality). The calculation of the thermodynamic potential F(T,V) of a system whose hamiltonian is $\mathcal{H}$:

$$F(T,V) = -k_B T \operatorname{Log} Z \qquad Z = \sum_{\{\sigma_\lambda\}} e^{-\beta\mathcal{H}} \tag{A.1}$$

is in general impossible so that we try to obtain the best approximation for F from a soluble hamiltonian. We note $\mathcal{H}_0$ the hamiltonian of a system for which it is possible to determine exactly the free energy F_0 :

$$F_0(T,V) = -k_B T \operatorname{Log} Z_0 \qquad Z_0 = \sum_{\{\sigma_\lambda\}} e^{-\beta\mathcal{H}_0} \tag{A.2}$$

It is then possible to show the following inequality :

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \tag{A.3}$$

$$\langle \mathcal{H} - \mathcal{H}_0 \rangle_0 = \sum_{\{\sigma_\lambda\}} (\mathcal{H} - \mathcal{H}_0)\, e^{-\beta\mathcal{H}_0} \Big/ \sum_{\{\sigma_\lambda\}} e^{-\beta\mathcal{H}_0} \tag{A.4}$$

Then, among the hamiltonians $\mathcal{H}_0(x)$ of a set depending of the continuous parameter x and chosen to represent reasonably -from physical arguments- the free energy, the best hamiltonian $\mathcal{H}_0(x)$ is obtained when $F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$ is minimum i.e. when :

$$\frac{d}{dx}\left(F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0\right)\Big|_{x=x_0} = 0 \text{ and } \frac{d^2}{dx^2}\left(F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0\right) > 0 \tag{A.5}$$

The inequality A-3 is shown in section 3 of this appendix.

2. Application of the variational principle to the Ising model. - Let us choose as soluble hamiltonians $\mathcal{H}_0$ the hamiltonians of independent particles in an external field :

$$\begin{cases} \mathcal{H}_0 = \sum_\lambda h_0(\lambda) \\ h_0(\lambda) = -\sum_\mu v(\lambda-\mu)\, \overline{\sigma_\mu}\, \sigma_\lambda + \frac{1}{2} \sum_{\lambda,\mu} v(\lambda-\mu)\, \overline{\sigma_\lambda}\, \overline{\sigma_\mu} \end{cases} \tag{A.6}$$

$\mathcal{H}_0(\overline{\sigma_\lambda})$ depends on the parameters $\overline{\sigma_\lambda}$ (external field) we must determine by the previous variational principle. We will show that the best approximation for the field acting on the λth system :

$$H_\lambda = \sum_\mu v(\lambda-\mu)\, \overline{\sigma_\mu} \tag{A.7}$$

is the average field $\langle H_\lambda \rangle$ we introduced in the MFA i.e. the field (4.7) with :

$$\overline{\sigma_\mu} = \langle \sigma_\mu \rangle \tag{A.8}$$

For simplicity, let us only consider here the ferromagnetic paramagnetic transition and assume that all the $\overline{\sigma_\lambda}$ are equal : $\overline{\sigma_\lambda} = x$. The free energy F_0 is then given by :

$$F_0 = -N k_B T \operatorname{Log}\left(e^{\beta v(0)x} + e^{-\beta v(0)x}\right) + N \frac{v(0)}{2} x^2 \tag{A.9}$$

$\mathcal{H} - \mathcal{H}_0$ can be written in the following form (see (A.6)) :

$$\mathcal{H} - \mathcal{H}_0 = -\frac{1}{2} \sum_{\lambda\mu} v(\lambda-\mu)\,(\sigma_\lambda - \overline{\sigma_\lambda})(\sigma_\mu - \overline{\sigma_\mu}) \tag{A.10}$$

and its average value is (from (A.6)) :

$$\langle \mathcal{H} - \mathcal{H}_0 \rangle_0 = -N \frac{v(0)}{2} \langle (\sigma - x)^2 \rangle_0 \tag{A.11}$$

The condition (A.5) becomes (see (A.9) (A.11)) :

$$\left\{ \begin{aligned} \frac{\partial F_o}{\partial x} &= N\, v(o)x - N\, v(o)\, \mathrm{th}\, \frac{v(o)}{k_B T} && \text{(A.12a)} \\ \frac{\partial \langle \mathcal{H} - \mathcal{H}_o \rangle_o}{\partial x} &= - N v(o)\ \langle \sigma - x \rangle_o \left[\frac{d\langle \sigma \rangle_o}{dx} - 1 \right] && \text{(A.12b)} \end{aligned} \right.$$

The condition (A.5) can then easily be written, using (A.12) and (A.6), as follows :

$$x = \langle \sigma \rangle_o = \mathrm{th}\ \frac{v(o)x}{k_B T} \qquad \text{(A.13)}$$

It is then equivalent to the mean field self-consistent equation (2.24).

3. Demonstration of the Bogoliubov inequality. - Let us introduce for $0 < \lambda < 1$ a set of hamiltonians $\mathcal{H}(\lambda)$ defined by :

$$\mathcal{H}(\lambda) = \mathcal{H}_o + \lambda\ V \qquad \text{(A.14)}$$

Then :

$$\mathcal{H}(o) = \mathcal{H}_o \quad , \quad \mathcal{H}(1) = \mathcal{H} \qquad \text{(A.15)}$$

To each $\mathcal{H}(\lambda)$, we can associate a free energy $F(\lambda)$ (see (A.1)). From the definitions (A.1) and (A.14) we obtain :

$$F(\lambda) = - k_B T\ \mathrm{Log} \quad \Sigma_{\{\sigma_\lambda\}} e^{-\beta(\mathcal{H}_o + \lambda V)} \qquad \text{(A.16)}$$

$$\frac{dF}{d\lambda}(\lambda) = \langle V \rangle_\lambda = \frac{1}{Z(\lambda)} \quad \Sigma_{\{\sigma_\lambda\}} e^{-\beta \mathcal{H}(\lambda)} \qquad \text{(A.17)}$$

$$\frac{d^2F}{d\lambda^2}(\lambda) = - \langle (V - \langle V \rangle_\lambda)^2 \rangle < 0 \qquad \text{(A.18)}$$

The inequality (A.3) is obtained from the relation :

$$F(1) - F(o) = F - F_o \leqslant \frac{d^2F}{d\lambda^2}(\lambda = o) \times (1 - 0) \leqslant 0 \qquad \text{(A.19)}$$

which can be written :

$$F \leqslant F_o + \langle V \rangle_o = F_o + \langle \mathcal{H} - \mathcal{H}_o \rangle_o \qquad \text{(A.20)}$$

APPENDIX 2

ISING MODEL FOR d = 1

We show here that an Ising model for d = 1 and with interactions between nearest neighbours has no transition for $T \neq 0K$. Let us assume that there is no applied field H_o so that the energy for a given spin configuration $\{\sigma_1, \sigma_2 \dots \sigma_n\}$ is :

$$\mathcal{H}(\{\sigma_\lambda\}) = - v(\sigma_1\sigma_2 - \sigma_2\sigma_3 + \dots + \sigma_{N-1}\sigma_N) \qquad \text{(A.2.1.)}$$

The partition function Z can be written as follows :

$$Z_N = \Sigma_{\{\sigma_\lambda\}} e^{\beta v(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \dots + \sigma_{N-1}\sigma_N)} \qquad \text{(A.2.2.)}$$

Let us split from (A.2.2.) the contributions of the Nth spin to Z_N :

$$Z_N = Z_{N-1}(e^{\beta v \sigma_{N-1}} + e^{-\beta v \sigma_{N-1}}) = 2\mathrm{Ch}\ \beta v\ Z_{N-1} \qquad \text{(A.2.3.)}$$

By an iterative process we obtain :

$$F_N = - k_B T\ \mathrm{Log}\ [2^N \mathrm{Ch}\ \beta v)^{N-1}] \qquad \text{(A.2.4.)}$$

In the thermodynamic limit ($N \to \infty$) F_N becomes :

$$F = - N k_B T\ \mathrm{Log}\ 2\mathrm{Ch}\ \beta v \qquad \text{(A.2.5.)}$$

From this expression, it is easy to calculate the entropy and the specific heat and to show that all these functions are regular. Note however that c_v presents a maximum when $k_B T \sim v$ recalling the result obtained by the MFA.

1. Introduction. - In this chapter we precise the nature of the singularity of the thermodynamic potential associated to the second order phase transitions of "simple" systems. The determination of this singularity results from a large number of theoretical and experimental studies which tried to determine the general features of the critical phenomena. From these studies, it has been possible to exhibit the important ("relevant") parameters which determine the thermodynamic potential for $T \simeq T_c$. These parameters depend only of general properties related to the symmetry (space and order parameter dimensionalities) of "simple" systems ; this peculiar property of critical phenomena allows to relate systems whose physical nature is very different. In this chapter, we define the nature of the singular part of the thermodynamic potential G(T,P) and we precise the parameters which determine qualitatively this behaviour ; we do not try to determine quantitatively the physical properties of such systems. In the next chapter, we will justify the singularity of G(T,P) we describe here.

One of the first discrepancies between the exact behaviour and the results of the Landau theory for $T \simeq T_c$ appeared when the Ising model for d = 2 has been solved exactly (Onsager 1944) : for such a system, the specific heat c_v presents a logarithmic singularity for $T \simeq T_c$ ($c_v \sim \mathrm{Log}\,|T - T_c|$), the order parameter varies as $|T-T_c|^{1/8}$ and the susceptibility diverges as $|T-T_c|^{-7/4}$. Later, detailed experiments allowed to precise the behaviour of the specific heat, the susceptibility... near $T = T_c$; this behaviour has been characterized by power laws $|T_c - T|^{\phi}$, the corresponding exponents ϕ being the "critical exponents". It appeared quickly that these exponents are real numbers related by relations called "scaling laws" ; then it became clear that these relations (first inequalities and later equalities !) can be derived from a peculiar form of the thermodynamic potential - this potential being a "generalized" homogeneous function. Such an "homogeneity" property can then be -as usual- derived from a scaling hypothesis and by a dimension analysis. The scaling hypothesis assumes that the long range spin correlation near T_c determines the singular behaviour of G(T, P) : to obtain this singular behaviour, it is sufficient to assume that i) the correlation function decreases with some power law at $T = T_c$; ii) the scale of the phenomena at a temperature T is determined by only one length, the correlation length $\xi(T)$ which diverges at $T = T_c$.

In this chapter, we define the critical exponents and summarize the main scaling laws. Then, we define the singular part of the thermodynamic potential as a generalized homogeneous function ; we show that this assumption is consistent with the scaling laws and can be deduced from the scaling hypothesis.

2. Critical exponents - scaling laws. - The behaviour of the physical properties when $T \simeq T_c$ is characterized by power laws t^{ϕ} where $t = |T - T_c|$; we introduced these exponents when we discussed the Landau theory and the MFA. Let us recall here their definitions :

order parameter for $T < T_c$:	$M(T) \sim t^{\beta}$
specific heat C_p :	$C_p \sim t^{-\alpha}$
susceptibility χ :	$\chi \sim t^{-\gamma}$
critical isotherm H(M), $T = T_c$:	$H \sim M^{\delta}$
correlation function at $T = T_c$, $g(r, T_c)$:	$g(r, T_c) \sim 1/|r|^{d-2+\eta}$
correlation length $\xi(T)$:	$\xi(T) \sim t^{-\nu}$

Let us note that a physical quantity $\phi(t)$ varies as t^{ϕ} for $t \to 0$ when $\phi(t)/t^{\phi} \to C \neq 0$ where C is a constant. When there is a logarithmic singularity, we will say that it corresponds to $\phi = 0$ (since $\mathrm{Log}\, t/t^{\phi} \to \infty$ when $\phi > 0$ and $\mathrm{Log}\, t/t^{\phi} \to 0$ when $\phi < 0$).
In these lectures we do not distinguish the exponents for $T > T_c$ (α, γ, ν...) and for $T < T_c$ (α', γ', ν'...) since the experiments seem to show that they are equal for "simple" systems.
The six critical exponents we defined previously are related by the four following independent scaling laws :

$$\alpha + 2\beta + \gamma = 2 \qquad \text{(Rushbrooke)} \ (\geq) \ (3.1)$$

$$\gamma = \beta(\delta - 1) \qquad \text{(Widom)} \ (\geq) \ (3.2)$$

$$\gamma = \nu(2 - \eta) \qquad \text{(Fisher)} \ (\leq) \ (3.3)$$

$$d\nu = 2 - \alpha \qquad \text{(Josephson)} \ (\geq) \ (3.4)$$

These laws were first shown to be inequalities (see for example the book by Stanley), the nature of the inequalities being precised in the previous equations (3.1, 4). The critical behaviour of the simple systems is then determined only by two independent critical exponents. Finally note that among all the scaling laws, only the last one is explicitly dependent of the dimensionality d.
The relations (3.1, 4) are satisfied when exact results can be obtained ; for example, the exponents of the Ising model when d = 2 are given by :

$$\alpha = 0 \quad \beta = 1/8 \quad \gamma = 7/4 \quad \delta = 15 \quad \eta = 1/4 \quad \nu = 1$$

Moreover, the numerical methods allow to evaluate these coefficients for simple models (Heisenberg...) and the results obtained by such methods are also in agreement with the previous laws (see table I).

Critical exponents

	d	n	α	β	γ	δ	η	ν
Ising	2	1	0	0.125	1.75	15.04	0.25	1
Heisenberg	2	3			2.5 0.1			
Ising	3	1	0.11	0.31	1.25	5	0.03	0.64
X Y	3	2	-0.07	0.35	1.32	4.8	0.03	0.67
Heisenberg	3	3	-0.12	0.37	1.39	4.8	0.03	0.71
Spherical	3	∞	-1	0.5	2	5	0	1

3. Homogeneity laws. - The singularities, we characterized previously by the critical exponents and the scaling laws, can be deduced from a peculiar form of the thermodynamic potential G and of the correlation function g : if we assume that these functions G and g are generalized homogeneous functions (homogeneity assumption), the relations between the critical exponents are recovered.

Let us first recall the definition of such generalized homogeneous functions : a function ϕ (x, y, z...) of n real variables x,y,z... is homogeneous with degrees α, β, γ... if, for each λ real, we have either :

$$\phi(\lambda x^{\alpha}, \lambda y^{\beta}, \lambda z^{\gamma}, \ldots) = \lambda\,\phi(x,y,z,\ldots) \tag{3.5a}$$

or :

$$\phi(x,y,z,\ldots) = x^{a}\ \psi\left(\frac{y}{x^{\phi_y}}, \frac{z}{x^{\phi_z}}, \ldots\right) \tag{3.5b}$$

The equation (3.5b) is equivalent to (3.5a) ; it can be deduced from (3.5a) choosing $\lambda = x^{-1/\alpha}$; a, ϕ_y, ϕ_z... are then given by :

$$a = -1/\alpha\ , \quad \phi_y = \beta/\alpha\ , \quad \phi_z = \gamma/\alpha\ , \ldots \tag{3.5c}$$

and :

$$\psi(z, t, \ldots) = \phi(1, z, t, \ldots) \tag{3.5d}$$

The definition (3.5) is a simple generalization of the classical definition of homogeneous functions (we recover if $\alpha = \beta = \gamma \ldots 1$). We now examine the behaviour of the thermodynamic potential (subsection (3.1)) and of the correlation function we can deduce from this assumption (subsection (3.2)).

3.1. Thermodynamic potential. - The homogeneity hypothesis applied to the thermodynamic potential G, $G(T,H,p) = G_r(T, H, p) + G_s(T, H, p)$ assumes that the singular part $G_s(T, H, p \ldots)$ is a function (3.5) where x = t, Y = H, z = p,... In this section we consider only the dependence of $G_s(t,H)$ with the temperature and the field H coupled to the order parameter M. As shown previously (section 2) two critical indices are then sufficient to determine the critical behaviour so that the homogeneity hypothesis characterized by the degrees associated to t and H (or by a and ϕ_H) determines completely the critical behaviour. The exponents a, ϕ_H will be chosen in order that the critical behaviour is characterized by the usual exponents : we will verify below that $a = \alpha - 2$ and $\phi_H = \beta\delta$; the thermodynamic potential can then be written in the following form :

$$G(T, p, H) = G_r(T, p) + t^{2-\alpha} f\left(\frac{H}{t^{\beta\delta}}\right) \tag{3.5e}$$

This expression is only valid in the critical region i.e. when $t \to 0$ and $H \to 0$. From (3.5e), the order parameter M and the susceptibility are then varying as :

$$M = \frac{\partial G}{\partial H}(t,H) \simeq t^{2-\alpha-\beta\delta}\, g\left(\frac{H}{t^{\beta\delta}}\right) \tag{3.6}$$

$$\chi = \frac{\partial M}{\partial H} \sim t^{2-\alpha-2\beta\delta}\, h\left(\frac{H}{t^{\beta\delta}}\right) \tag{3.7}$$

the function g and h being the first and second derivatives of the function f.

Let us now show that this choice of the coefficients a and ϕ_H is consistent with the usual definition of the critical indices :

i) specific heat : (H = 0)

$$C_p(H=0) = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p \sim f(o)\, t^{-\alpha} \tag{3.8}$$

The coefficient α in (3.5e) is then consistent with the usual definition.

ii) order parameter ($T < T_c$, H = 0) (see eq. (3.6))

$$M(t) \sim t^{2-\alpha-\phi_H} \Longrightarrow \beta = 2-\alpha-\phi_H \tag{3.9}$$

iii) susceptibility ($T > T_c$) (see eq. (3.7))

$$\chi(t) \sim t^{2-\alpha-2\phi_H} \Longrightarrow \gamma = 2\,\phi_H + \alpha - 2 \tag{3.10}$$

iv) <u>scaling law</u> (3.1). - Eliminating ϕ_H from (3.9) and (3.10) we obtain (3.1)

v) <u>critical isotherm</u> : this isotherm is obtained from (3.6) when $t = 0$, $H \neq 0$. From (3.6), $g(y)$ must vary as $y^{1/\delta}$ in order to recover the classical meaning of the exponent δ :

$$H \sim M^{\delta} \ (T = T_c) \Longrightarrow g(y) \sim y^{1/\delta} \tag{3.11}$$

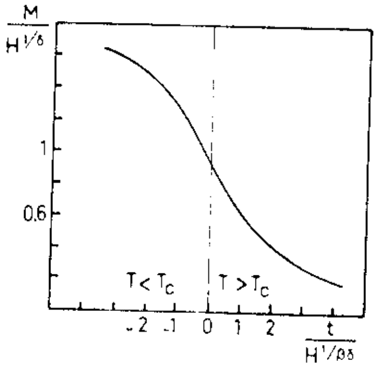
When $t \to 0$ in (3.6) the t dependence must not introduce a singularity ; this requires using (3.9) :

$$t^{2-\alpha-\phi_H} \left(t^{-\phi_H}\right)^{1/\delta} \sim t^{o} \Longrightarrow \phi_H = \beta\delta \tag{3.12}$$

vi) <u>Widom's relation</u> : eliminating ϕ_H and α between (3.9), (3.10) and (3.12) we recover (3.2).

vii) <u>Conclusion</u> : In conclusion, we have shown that the assumption (3.5e) is consistent with the usual definition of the critical indices and with the scaling laws (3.1), (3.2) ; the other scaling laws can only be obtained if the homogeneity hypothesis is applied to the correlation function. Finally, we must mention that the assumption (3.5e) can be verified for soluble models (spherical model, Ising model for d = 2...) and from numerical and experimental studies. It is often easier to represent the state equation M(t,H) using the reduced coordinates :

$$m = \frac{M}{t^{\beta}} \qquad h = \frac{H}{t^{\beta\delta}} \tag{3.6b}$$



<u>Fig. 3.1.</u> : Reduced magnetization of $CrBr_3$ (schematic) : $M/H^{1/\delta} = \psi\,(t/H^{\beta\delta})$

All the curves M(t, H) when $T \sim T_c$ are then represented by an unique curve m(h) which summarizes the variation of the order parameter when $t \to 0$ (Fig. 3.1). This is a generalization of the classical law of corresponding states (see introduction).

3.2. <u>Correlation function</u>. - The homogeneity hypothesis for the correlation function g(t,r) requires the following form :

$$g(r,t) = \frac{1}{r^{d-2+\eta}} \ f_1(r/\xi) \tag{3.13}$$

where the correlation length $\xi \sim t^{-\nu}$ determines the scale of the phenomena when $T \sim T_c$. The critical behaviour of g is determined by two critical indices η and ν. These indices are then related to the other indices deduced from G(t,H). We show now that (3.13) determines the Fisher relation (3.3). (3.13) is equivalent to the relation :

$$\Gamma(q,t) = \frac{1}{q^{2-\eta}} \ f_2(q\xi) \tag{3.14}$$

as easily shown by Fourier transforming (3.13) when t = 0 in the same way as in chapter 2. From the fluctuation dissipation theorem (chapter 2, (2.79)), the uniform susceptibility becomes :

$$\chi(q = 0) = \chi = k\,T\,g(0,t) \tag{3.15a}$$

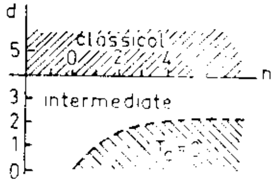
and varies as $t^{-\gamma}$ (by definition of γ). In order to obtain a finite value for χ, it is then necessary that :

$$f_2(x) \sim x^{2-\eta} \qquad (x \to 0) \tag{3.15b}$$

and, from (3.14), we obtain :

$$t^{-\gamma} \sim \lim_{q \to 0} g(q,t) \sim \xi^{2-\eta} \sim t^{-\nu(2-\eta)} \tag{3.16}$$

Comparing the first and last relations of (3.16) we obtain Fisher's relation (3.3).



<u>Fig. 3.2</u> : Critical behaviour versus n and d (from G. Toulouse and P. Pfeuty, 1975, Introduction au Groupe de Renormalisation, P.U.G., Grenoble)).

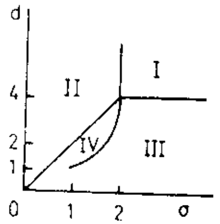


Fig. 3.3. Critical behaviour versus d and σ.
I : classical regime (short range)
II : classical regime (long range)
III : non trivial regime (short range)
IV : non trivial regime (long range). (from G. Toulouse and P. Pfeuty).

4. Scale transformations and homogeneity hypothesis. -It is possible to obtain the previous forms for $G_s(t, H)$ and $g(r,t)$ from the following assumptions : 1) the spatial scale of the critical phenomena is determed at a given temperature by only one length, the correlation length $\xi \sim t^{-\nu}$, which diverges at $t = 0$; 2) the correlation function decreases as a power law at $t = 0$. (3.5e) and (3.13) can then be obtained from these assumptions by a scaling transformation. If we multiply the unit of length by s, the measure of the distance between two points r is divided by s, $r' = r/s$; the thermodynamic potential per unit volume $G'(t,H)$ is then multiplied by s^d :

$$G'(t,H) = s^d\, G(t, H) \qquad (3.17a)$$

and the correlation length becomes $\xi' = \xi/s$. From assumption 1), the thermodynamic potential G is the potential corresponding to the temperature t' :

$$\xi' = \xi/s \sim \frac{t^{-\nu}}{s} = t'^{-\nu} \Longrightarrow t' = s^{1/\nu}\, t \qquad (3.18)$$

Then we obtain from (3.17), (3.18) the relation :

$$G'(t,0) = G(s^{1/\nu} t, 0) = s^d G(t, 0) \qquad (3.17b)$$

After this scaling transformation, the order parameter M(r) becomes M'(r') and the correlation function becomes :

$$g'(t,r') = < M'(0)\, M'(r') > \qquad (3.19)$$

At $T = T_c$ it is invariant by this scaling transformation ($g'(0,r') = g(0,r)$) since, from 1) ξ is not modified by this transformation : it remains infinite !. This invariance is satisfied when :

$$M'(r') = s^{\frac{d-2+\eta}{2}}\, M(r) \qquad (3.20)$$

i.e. when :

$$g(o,r) \sim \frac{1}{r^{d-2+\eta}} \qquad \text{(assumption (2))} \qquad (3.21)$$

We can obtain the law of transformation of the field H from its coupling energy between the order parameter ($M'H' = s^d MH$) which is transformed as G :

$$H' = s^{\frac{d-2+\eta}{2}}\, H \qquad (3.22)$$

After the scaling transformation the thermodynamic potential becomes (see eq. (3.17) and (3.22)) :

$$G'(t,H) = s^d G(t,H) = G(s^{1/\nu} t, s^{\frac{d+2-\eta}{2}} H) \qquad (3.23)$$

If we choose $s = t^{-\nu}$ we obtain :

$$G\left(1, \frac{H}{t^{\frac{\nu(d+2-\eta)}{2}}}\right) = t^{-\nu d}\, G(t, H) \qquad (3.24)$$

This expression shows that G(t, H) is a generalized homogeneous function the critical indices of which are determined by η and ν. Applying (3.8) to calculate the specific heat and using the definition of the index α we obtain relation (3.4) :

$\nu d = 2 - \alpha$ (3.4) Josephson

Using the same method, the correlation function becomes, (cf. equation (3.19) and (3.20)) :

$$g'(t,r',H) = s^{d-2+\eta}\, g(t,r,H) = g\left(s^{1/\nu} t, \frac{r}{s}, s^{\frac{d+2-\eta}{2}} H\right) \qquad (3.25)$$

When H = 0 and using s = r, we obtain :

$$g(t,r,0) = \frac{1}{r^{d-2+\eta}}\, g\left(\left(\frac{r}{t^{-\gamma}}\right)^{1/\nu}, 1, 0\right) = \frac{1}{r^{d-2+\eta}}\, f_1(r/t^{-\gamma}) \qquad (3.26)$$

and we recover the form we used in the previous section for g(t,r)(see (3.13)). Then we can deduce Fisher's relation (3.3) as in section 3.2 . Finally we obtain the scaling laws (3.1) and (3.2) as in section 3.1 with $\phi_H = \nu(d + 2 - \eta)/2$: the homogeneity relations (3.24), (3.26) deduced from the scaling assumption are then equivalent to the homogeneity assumption we introduced in section 3.1 and 3.2. The scaling assumption and the scaling transformations determine relations (3.1) to (3.4) : for this reason these relations are called <u>scaling laws</u>.

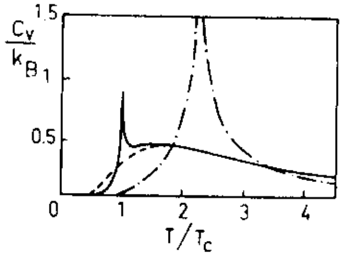


Fig. 3.4. : — specific heat of a linear chain (Ising d = 1)
·— specific heat of a square lattice (Ising d = 2)
—— specific heat of a rectangular lattice.
(Ising d = 2)
$v_{//} = 1/100\ v_{\perp}$ (from Onsager, L., Phys. Rev. 65, (1944), 117).

5. Critical behaviour of the "simple" systems. - As mentioned in the introduction, a large set of systems (called "simple") present a singularity characterized by (3.5). We must now try to determine the parameters which govern the critical indices. The numerical and experimental results obtained for some simple models (Ising, Heisenberg, spherical... models) throw some light on this point : the critical indices depend on : i) the space dimension d ; ii) the order parameter dimension n and iii) the range of the "spin" couplings (long or short range couplings). We examine the importance of these parameters in the next section.

5.1. Dimension d. - In the previous chapters we pointed out that the space dimension d plays an important role in the determination of the properties of phase transitions. First, we have shown that the fluctuations become qualitatively important only for $d < 4$; hence we can hope that the critical indices are given by their classical (i.e. Landau) values for $d > 4$. Moreover, we have shown that if the space dimension is too small ($d = 1$ for the Ising model) phase transitions become impossible (for $T \neq 0K$) when the spin couplings are short ranged.

It can be thought -at first slight- that it is not physically interesting to consider d as a continuous variable ($0 \leq d \leq \infty$) and to calculate the exponents as a function of d. However, note first that the values d = 1, 2, 3 present a physical interest. All the physical systems crystallize in the three dimensional space (d = 3) but it is possible that this system can be represented by a set of weakly coupled atomic lines (or planes) : more precisely, the interactions between the atoms of each line (or plane) $v_{//}$ can be much larger than the interactions between atoms of different lines (planes) $v_{\perp}$ ($v_{//} \gg v_{\perp}$).

When $v_{//} \gg k_B T \gg v_{\perp}$, we can observe "a priori" an ordered structure among the atoms of the same line (plane) but there is no order between the atoms of the different lines (planes). The system is characterized by d = 1 (or d = 2). This discussion is illustrated in figure 3.4 : this figure shows the result obtained for a two dimensional

Ising model for which $v_{//}/v_{\perp}$ can take several values. We obtain Onsager's result for d = 2 when $v_{//}/v_{\perp} = 1$ whereas we obtain the result corresponding to a linear chain when $v_{//}/v_{\perp} = 0$ or ∞ (see Fig. 3.2 for comparison).

5.2. Order parameter dimension n. - The role of n is illustrated by the results obtained for the Ising (n = 1), XY (n = 2), Heisenberg (n = 3) and spherical ($n = \infty$) models (see table 1). For a given dimension d, the exponents can vary strongly with n : for example, α decreases and changes its sign when n increases.

Let us recall here that n is the dimension of the irreducible representation of the symmetry group G_0 which determines the phase transition ; n can then take very different values according to the considered case. For example :

- n = 1, corresponds to the liquid gas, order disorder, some structural transitions (see introduction),
- n = 2, corresponds to the magnetic ordering of systems having a plane of easy magnetization, the superconductor -metal transition, the nematic- smectic A transition in liquid crystals, the Peierls structural transition for d = 1 systems...,
- n = 3, corresponds to the magnetic transitions represented by the Heisenberg model...

When the unit cell does not change during the transition, it is sufficient to consider the point group and $n \leq 3$; on the contrary, when the cell is doubled in one direction (at least) it is then necessary to consider the representations of the space group whose dimension n can be larger (n = 4 for the structural transition in NbO_2).

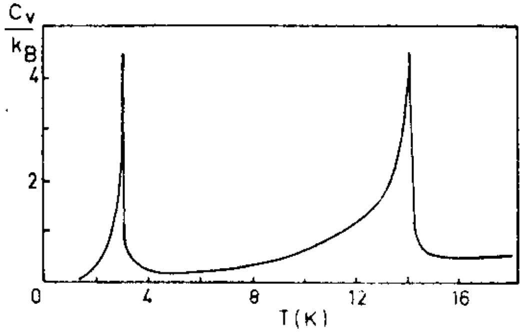
5.3. Range of (pair) interactions. In chapter 2, we showed for the Ising model that the range of the spin couplings determines the width of the critical region : the results of the MFA become exact when the range of the spin couplings become infinite ($v(\lambda) = v/N$) and for all d values we obtain $T_c > 0$. Then, for d = 1, n = 1 a transition from the regime $T_c = 0\ K$ to a regime $T_c > 0$ must exist when the range of the interactions increases. If we characterize the asymptotic behaviour of $v(r)$ ($r \to \infty$) by the law :

$$v(r) \sim A/r^{d+\sigma} \qquad \sigma > 0 \tag{3.27}$$

it is possible to show that, for $\sigma > 1$, there is no longer a phase transition with non zero T_c : the line $\sigma = 1$ separates the region for which $T_c \neq 0K$ from the region for which $T_c = 0K$ (Fig. 3.3).

The range of the interactions plays an essential role to determine the nature of the transition and their properties ; the experimental observation of classical exponents when d = 3 can be for example the indication of the existence of long range interactions (elastic for example as suggested for the system PdH (Fig. 3.5).

5.4. Simple system. - We have shown the importance of the role of n, d and σ in the determination of the critical behaviour. Other quantities can be important to



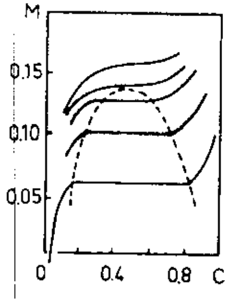


Fig. 3.5. : demixion in PdH systems : chemical potential versus hydrogen concentration (from G.Alefeld, Phys. Stat. Sol. 32, 1969, 67).

determine this behaviour. Let us mention for example : i) the anisotropy of the "spin" couplings (dipolar interactions) ; ii) the anisotropy in the order parameter space ; iii) the anisotropy in the real space ; iv) the existence of a coupling of the order parameter with other degrees of freedom (magnetoelastic couplings...). In this chapter, we considered only isotropic simple systems for which the critical behaviour is represented by an (unique) order parameter (dimension n) and is induced by isotropic and short range couplings. Their critical indices will depend only on n and d and the critical behaviour is shown in figure 3.2. All these systems define a universality class for which the critical behaviour is determined regardless of the physical nature of the transitions. Our task is now to understand the origin of this surprising universality of the critical behaviour.

INTRODUCTION TO THE STUDY OF THE GINSBURG - LANDAU - WILSON MODEL.

1. Introduction. - 1.1. Method. - The fluctuation are qualitatively important in the critical region for most of the real systems : they determine the critical behaviour and can even change the nature of the phase transition. It is then necessary to develop new methods which will take account of these fluctuations and which will allow to 1) understand the physical origin of the homogeneity laws and of the universality of the critical exponents 2) calculate these exponents. In this chapter, we introduce the "renormalization group" methods in a simple way and we show that they allow to characterize qualitatively (nature of the homogeneous functions) and quantitatively qualitatively (value of the critical exponents) the critical behaviour.

These methods define a set of transformations (R_s) which relate the state μ of a system of a peculiar class (for example an Ising model with interactions between nearest neighbours v, the thermodynamic potential of which is determined by $K = v/T$) to another state ' of a system of the same class (characterized by v' or of $K'=v'/T$). The R_s will be defined as "complex dilatation" and the critical point T_c will be related to a

fixed point μ^* for these transformations i.e. a point invariant by all the operations $R_s : \mu^* = R_s \mu^*$; the critical exponents will be determined by the properties of R_s when μ is in the neighbourhood of μ^* (i.e. when $T \simeq T_c$). Qualitatively, it can seem obvious that the critical temperature must be related to an invariant point : the system is invariant by a dilatation at $T = T_c$(ξ remains infinite !) and this invariance is broken when $T \neq T_c$. In order to precise the nature of the operations R_s and their role, we present in the Appendix 1 a detailed discussion of the physical argument first developed by Kadanoff (1966).

1.2. Summary. - First we recall the description of a macroscopic system by blocks (2) and we extend the Landau theory to a system which has an order parameter M(r) varying with r : the results we obtain in this section are essentially those we obtained for modulated structures in the MFA (chapter 2). In the present study we must take full account of the fluctuations to represent the critical behaviour : for this reason we write the partition function as a "functional integral" (4). We introduce the simplest possible model to study the role of fluctuations i.e. the Landau -ginzburg model ; we discuss this model for an isotropic system with short range interactions. The partition function Z is then the sum of the contributions $\exp -\beta\mathcal{H}(\{M(r)\})$ of the states with order parameter M(r) : in the Ginzburg- Landau formulation, the so-called "hamiltonian" $\mathcal{H}(\{M(r)\})$ has the classical Landau form :

$$\mathcal{H}(\{M(r)\}) = \frac{r}{2} M(r)^2 + \frac{u}{4} (M(r)^2)^2 + \ldots + \frac{c}{2} |\nabla M(r)|^2$$

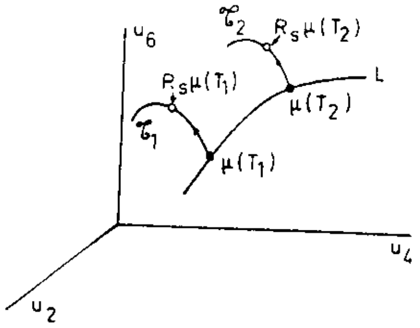


Fig. 4.a. : Parameter space, physical line L and renormalization lines $\mathcal{C}_1$, $\mathcal{C}_2$.

and a state of this system is then determined by the set of coefficients $\mu = (r, u, \ldots c)$.

This model is the simplest possible ; nevertheless, it is not possible to obtain exact solutions for Z and F ! If we neglect all terms of $\mathcal{H}$ except the first and the last ones, we obtain the gaussian model which is soluble (section 5) but which is not physically correct (the low temperature phase is not defined !). If we consider only the contributions of the distributions M(r) = M which are independent of r, we obtain the MFA (section 6) which is not sufficient in the critical region. It is then necessary to take account of at least the three first terms of $\mathcal{F}$ to obtain a non trivial answer. An exact solution of this model is only possible in some peculiar cases ($d = 1$, $n = \infty$ ...) we do not consider here.

In the second part of this chapter, we do not try to determine quantitatively Z by analytical methods but we will investigate the properties of the systems represented by $\mathcal{F}(\{M(r)\})$ relative to the operations of the renormalization group. The elementary operations R_s are defined in the real space and in the reciprocal space (see section 7); we show how the thermodynamic potential F and the correlation function $\langle M(o)M(r)\rangle$ are transformed by R_s. An operation R_s relates a point $\mu(r, u,...c)$ of the parameter space to another point of this space : $\mu' = R_s\mu$. The critical behaviour is then shown to be determined by the neighbourhood of a peculiar fixed point $\mu^* = R_s\mu^*$ (section 8). We apply this proposition to the gaussian model (section 9) and we show that the fixed point for the gaussian model determines the critical behaviour of the simple systems for $d > 4$. We discuss the case $d < 4$ and we show that the critical behaviour of these systems is governed by another fixed point the coordinates of which $(r^*, u^* ...)$ can be determined by an expansion in successive powers of $\varepsilon = 4-d$. Finally we discuss the general validity of the renormalization group method.

2. Blocks. - It is necessary to take account of the correlations which are neglected in the Landau model. However, we are only interested here by the critical region for which the correlations are long ranged ($\xi \gg a$, a = interatomic distance). For this reason we introduce a representation of the system which is valid when we are interested by phenomena the scale of which is large as compared to the interatomic distance ($b \gg a$) but small as compared to the correlation length ξ ($b \ll \xi$). ξ determines, for a given temperature, the scale of the critical phenomena (see chapter 3). In such a representation, the fine (atomic) structure is no longer relevant and we can use a continuous description of the system : the order parameter M(r) is then represented by a continuous function which is, as usual, a density per unit volume (of magnetization, polarization...). This procedure is the same as classically used in electrodynamics of continuous media - see for example the definitions of the charge density, $\rho(r)$, the current density $j(r)$... ; these quantities are only meaningful for scales large as compared to the distance between charges but small as compared to the scale of the physical phenomena we study. In the present case, M(r) is assumed to be real and the thermodynamic potential is "a priori" a function of all the values that the order parameter M(r) can have for all the points r. More precisely, we consider the system as resulting from blocks centred on r_i ($i = 1,...\mathcal{N}$) and of size b (volume $v = b^d$) such that $a \ll b \ll \xi$. The state of the system can then be characterized only by the set of values $\{M(r_i)\}$ of the order parameter of each of the blocks (total magnetization, polarization... of each of the blocks") but the variation of the order parameter on a smaller scale can be thought to be irrelevant for our purpose. With such an assumption and for each scale b, we can then, in principle, represent the partition function Z and the thermodynamic potential by a function of all the possible values of the densities $M_i = M(r_i)/v$; this expression will be shown in section 4. We can use the continuous limit ($\mathcal{N} \to \infty$) and represent mathematically Z as a functional integral but, for practical reasons (i.e. for those who are not familiar with such a formalism) we will use only the discrete block representations : Z is then an integral ($\mathcal{N}$uple) over the variables M_i. In this chapter we use, as a first step, the block representation to extend the Landau model for ordered states characterized by space dependent order parameters. Then, we take into account the fluctuations and discuss the mathematical description of Z and F.

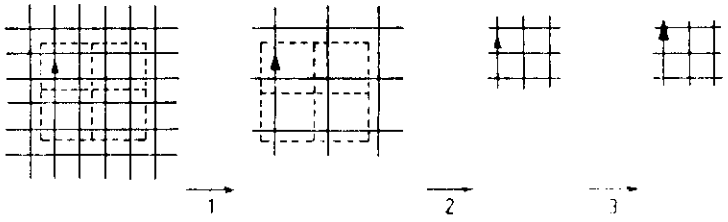


Fig. 4.2. : Renormalization group : each operation R_s results from 1) a partial integration 2) a change of unit length, 3) a renormalization of M.

3. Extension of the Landau model. - 3.1. Introduction. - In this section, we extend the assumptions of the classical Landau model to the case of an ordered state the order parameter M(r) of which is space dependent ; for simplicity, we assume here that this order parameter is a scalar (n = 1).

As previously (see section 2 of chapter 1) we assume that : i) it is possible to define a thermodynamic potential for each configuration $\{M_i\}$, $G(T,p,\{M_i\})$; ii) this potential is analytic and can be expanded in successive powers of all the variables $\{M_i\}$, T, p ; iii) the equilibrium state is obtained by a minimization of this potential with respect to the variables $\{M_i\}$.

Let us now precise these steps :

i) expansion of the thermodynamic potential : The Landau thermodynamic potential can be expanded as follows (in the discrete case) :

$$G(T,p,\{M_i\}) = G^o(T,p) + \frac{1}{2}\sum_{i,j} a_{ij} M_i M_j + \frac{1}{3}\sum_{i,j,k} b_{ijk} M_i M_j M_k + ... \qquad (4.1a)$$

In the continuous limit, these sums become integrals and (4.1a) can be written as follows :

$$G(T,p,\{M(r)\}) = G^o(T,p) + \frac{1}{2}\int a(r,r') M(r) M(r')\, dr\, dr' + \frac{1}{3}\int b(r,r',r'') \times M(r) M(r') M(r'')\, dr\, dr'\, dr'' + ... \qquad (4.1b)$$

The coefficients a, b, c... are T and p dependent ; they are determined by the disordered state (they are obviously independent of M(r)!). We will assume for simplicity that this state is homogeneous and isotropic ; the coefficients a, b, c... are then only dependent on the relative distance between the points r, r', r''... :

$$\begin{cases} a(r,r') = a(r-r') \\ b(r,r',r'') = b(r-r', r-r'') \end{cases} \tag{4.2}$$

ii) equilibrium state : The equilibrium is obtained by the minimization of G. G is extremum when the following condition is satisfied (discrete case and zero external field (see eq. (4.1a) :

$$\frac{\delta G}{\delta M_i} = 0 \Leftrightarrow \sum_j a_{ij} M_j + \sum_{j,k} b_{ijk} M_j M_k + \dots = 0 \tag{4.3a}$$

In the continuous limit, this condition is equivalent to :

$$\frac{\delta G}{\delta M(r)} = 0 \Leftrightarrow \frac{\delta G}{\delta M(r)} \equiv \int a(r-r') M(r')\, dr' + \int b(r-r', r-r'') M(r') M(r'')\, dr'\, dr'' + \dots = 0 \tag{4.3b}$$

$\frac{G}{A(r)}$ is the "functional derivative" of G({M(r)}).

For a non zero applied field $H_o(r)$ the thermodynamic potential becomes :

$$\tilde{G} = G - \int M(r) H_o(r)\, dr \tag{4.4}$$

and the condition to obtain an extremum of G is :

$$\frac{\delta \tilde{G}}{\delta M(r)} = 0 \quad \Leftrightarrow \quad \frac{\delta G}{\delta M(r)} = H_o(r) \tag{4.5}$$

iii) Fourier transformation : When the disordered state is homogeneous, it is useful to Fourier transform the previous equations. The ordered state is then characterized by the Fourier components $\{M_q\}$ of the order parameter $\{M(r)\}$:

$$\begin{aligned} M_q &= \frac{1}{\sqrt{V}} \int M(r)\, e^{-iqr}\, dr \\ M(r) &= \frac{1}{\sqrt{V}} \sum_q M_q\, e^{iqr} \end{aligned} \tag{4.6}$$

The thermodynamic potential is then a functional of M_q. Using the properties of the Fourier transforms (see chapter 2) we obtain :

$$\int a(r-r') M(r) M(r')\, dr\, dr' = \sum_q \hat{a}(q) M_q M_{-q} \tag{4.7a}$$

$$\int b(r-r'', r'-r'') M(r) M(r') M(r'')\, dr\, dr'\, dr'' = \sum_{q,q'} \hat{b}(q,q') M_q M_{q'} M_{-q-q'} \tag{4.7b}$$

with the definitions :

$$\begin{cases} \hat{a}(q) = \int a(r)\, e^{iqr}\, dr \\ \hat{b}(q,q') = \int b(r,r')\, e^{iqr}\, e^{iq'r'}\, dr\, dr' \\ ---- \end{cases} \tag{4.8}$$

and the thermodynamic potential becomes (see eq. (4.1) and (4.7)) :

$$\begin{aligned} G(T,p, \{M_q\}) = G^o(T,p) &+ \frac{1}{2} \sum_q \hat{a}(q) M_q M_{-q} + \frac{1}{3} \sum_{q,q'} \hat{b}(q,q') M_q M_{q'} M_{-q-q'} \\ &+ \frac{1}{4} \sum_{q,q',q''} \hat{c}(q,q',q'') M_q M_{q'} M_{q''} M_{-q-q'-q''} + \dots \end{aligned} \tag{4.9}$$

The thermodynamic potential $\tilde{G}$(4.4) is obtained from (4.9) and from the relation :

$$\int H_o(r) M(r)\, dr = \sum_q H_o(q) M_{-q} \tag{4.10}$$

with the definition :

$$H_o(q) = \frac{1}{\sqrt{V}} \int H_o(r)\, e^{-iqr} dr \tag{4.11}$$

Using this form for the Landau expansion, we examine now i) the instability of the disordered state (section 3.2,), ii) the general form of the correlation function and iii) the expression of G in the macroscopic limit (q →0) (section 3.4).

3.2. Instability of the disordered state physical meaning of $\hat{a}(q)$. - The disordered state becomes unstable if (at least) one of the coefficients $\hat{a}(q)$ - i.e. $\hat{a}(q_c)$- becomes negative for $T < T_c$; a sufficient condition for this instability is :

$$\hat{a}(q_c, T_c) = 0, \quad \hat{a}(q, T > T_c) > 0 \; \forall q \tag{4.12}$$

If the disordered state is stable for $T > T_c$, both $\hat{a}(q,T)$ ($\forall q$, $T > T_c$) and the quartic term are always positive. The coefficient $\hat{a}(q)$ has a simple physical meaning - which is the generalization of (1.11). The equilibrium state is obtained from the condition (see (4.5), (4.9) and (4.10)) :

$$\frac{\partial \tilde{G}}{\partial M_q} = 0 \quad \Longleftrightarrow \quad \frac{\partial G}{\partial M_q} = H_o(q) \tag{4.13}$$

In the linear approximation we obtain :

$$H_o(q) = \hat{a}(q)\, M_q \tag{4.14}$$

and $\hat{a}(q)$ is the q dependent susceptibility we defined in chapter 2 ; if we apply an external field $H_o(r) = 1/\sqrt{V}\, e^{iqr} H_o(q)$ in the disordered state, the order parameter $M(r) = 1/\sqrt{V} M_q e^{iqr}$ has the same periodicity as the applied field in the linear approximation ; this order is proportional to the applied field $H_o(q)$, the coefficient of proportionality being the susceptibility $\chi(q)$:

$$M_q = \chi(q)\, H_o(q) \qquad (4.15)$$

and (see (4.14) and (4.15)) :

$$\chi(q) = \hat{a}(q)^{-1} \qquad (4.16)$$

when $T > T_c$, $\chi(q)$ is positive and when $T \to T_c$, $\chi(q_c, T) \to \infty$ (when $T \to T_c$, $\hat{a}(q_c) \to 0$ (see (4.12)). In the next section, we restrict our discussion to the case of a transition for which $q_c = 0$ (ferro-para transitions).

3.3. Correlation function for $T > T_c$. - It is possible to have an estimation of the correlation function from the Landau expansion ; the results obtained are then qualitatively the same as those obtained in MFA. For this reason we summarize briefly the method used to obtain the correlation function. This function is defined by :

$$g(r - r') = \langle M(r)\, M(r') \rangle_o \qquad T > T_c \; (\langle M(r) \rangle_o = 0) \qquad (4.17)$$

The thermal average $\langle\ \rangle_o$ is taken over the equilibrium (canonical) distribution (for $H_o = 0$). The Fourier transform of $g(r)$:

$$g(q) = \int g(r)\, e^{-iqr}\, dr \qquad (4.18)$$

is related directly to the fluctuations of M_q in the equilibrium state :

$$g(q) = \langle M_q M_{-q} \rangle_o \qquad (4.19)$$

The susceptibility $\chi(q)$ is itself related to the correlation function $g(q)$ by (2.79) :

$$\langle M_q M_{-q} \rangle_o = k_B T\, \chi(q) \qquad (4.20)$$

$g(q)$ is then given by :

$$g(q) = \frac{k_B T}{\hat{a}(q)} \qquad (4.21)$$

We are interested in the asymptotic behaviour of $g(r)$ $(r \to \infty)$ and of $g(q)$ $(q \to 0)$. It is then sufficient to expand $\hat{a}(q)$ in the successive powers of q for $|q| \to 0$:

$$\hat{a}(q) = \hat{a}(o) + k q^2 \qquad (4.22)$$

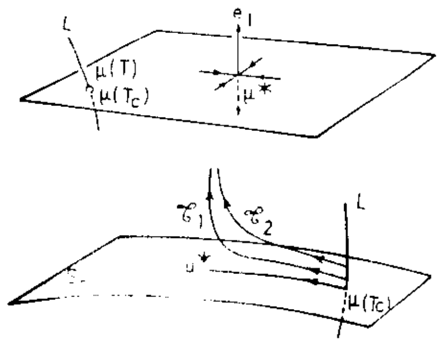


Fig. 4.3 : The fixed point μ^* is unstable relative to t_1.

Note that from (4.12) $\hat{a}(q)$ increases with $|q|$ since we assumed that the first value of q, q_c for which the instability appears is $q_c = 0$. For a second order transition :

$$\hat{a}(o, T_c) = 0 \qquad (4.23)$$

and, assuming that $\hat{a}(0,T)$ is an analytic function of T ;

$$\hat{a}(o, T_c) = a(T - T_c) \qquad \text{when } T \to T_c \; (a > 0) \qquad (4.24)$$

The correlation function (4.21) can then be written as follows :

$$g(q) = \frac{k_B T}{\hat{a}(o) + kq^2} \qquad (4.25)$$

We recover the formula previously obtained in the MFA ; $g(r)$ is then varying as :

$$g(r) \sim e^{-r/\xi}/r \qquad (d=3) \qquad (4.26)$$

where $\xi(T) \sim (T - T_c)^{-1/2}$. The critical fluctuations become dominant when $T \to T_c$; their contribution to the specific heat is significant in the critical region for $d < 4$ (see chapter 2) and the Landau approximation is no longer valid when $T \to T_c$.

3.4. Thermodynamic potential for $q \to 0$. - In the $q \to 0$ limit, we can expand the coefficient $\hat{a}(q)$ (eq. (4.22)) and replace the coefficients $b(q,q')$, $c(q,q',q'')$... by their values for $q = q' - q'' = 0$: A, B, C ; we obtain the following expression for $G(T,P \{M_q\})$:

$$G(T,p,\{M_q\}) = G^o(T,p) + \frac{A}{2}\sum_q M_q M_{-q} + \frac{B}{4}\sum_{q,q'} M_q M_{q'} M_{-q-q'} + \\ + \dots + k\, \Sigma_q M_q M_{-q} q^2 \qquad (4.27)$$

In the real space $G(T,p\ \{M(r)\})$ becomes (Fourier transforming (4.27)) :

$$G(T,p,\{M(r)\}) = G^o(T,p) + \frac{A}{2}\int M(r)^2\,dr + \frac{B}{3}\int M(r)^3\,dr + \dots + \frac{k}{2}\int |\nabla M(r)|^2\,dr \tag{4.28}$$

4. Ginzburg Landau model. - 4.1. Introduction. - We must obtain a mathematical expression for the thermodynamic potential G which takes full account of the fluctuations. We will consider only here a ferro - para transition and we will then assume that the relevant fluctuations are those for which $q \simeq 0$. A macroscopic description of the states of the system by the density $M(r)$ (or by the block densities M_i) (see section 2) is then sufficient. But, do not use the Landau assumptions. We define the simplest possible model (§4.3) whose singular behaviour for $T \to T_c$ will be studied in the next sections.

4.2. Partition function - functional integral. - The free energy $F(T,V)$ is related to the partition function Z by the well-known relation :

$$F = -k_B\, T \operatorname{Log} Z$$
$$Z = \sum_n e^{-\beta E_n} \tag{4.29}$$

The sum is extended to all the possible states n. For example, in the Ising model : (see chapter 2) :

$$\mathcal{H} = -\frac{1}{2}\sum_{\lambda \neq \mu} v(\lambda-\mu)\,\sigma_\lambda\sigma_\mu \tag{4.30}$$

the partition function becomes :

$$Z = \Sigma_{\{\sigma_\lambda\}}\, e^{-\beta\mathcal{H}(\{\sigma_\lambda\})} \tag{4.31}$$

the sum being extended to all the "spin" configurations $(\{\sigma_\lambda = \pm 1\})$.

In the macroscopic limit, and for a given scale b, of the system is determined by the values of the densities $M_i (i = 1, 2 \dots \mathcal{N})$ defined for all the blocks ($\omega = b^d$ $\xi \gg b \gg a$). For an Ising model, M_i is given by $M_i = 1/\omega\Sigma_{\lambda\epsilon(i)}\sigma_\lambda$, the summation being extended over all the sites λ of the ith block. It is then physically useful to write Z as follows. We split the summation in two parts : i) first we sum over all the possible spin configurations for which the $\mathcal{N}$ densities M_i are given ; ii) then, we sum over all the states corresponding to different values of the M_i. By definition, the result of the first step will be noted $e^{-\beta\ (\{M_i\})}$ and Z is given by :

$$Z = \sum_{\{M_i\}} e^{-\beta\mathcal{F}(\{M_i\})}$$

$\mathcal{F}(\{M_i\})$ is the "free energy" associated to the configurations for which the M_i are fixed. We can also introduce the energy $E(\{M_i\})$ associated to these configurations ; it is defined by :

$$e^{-\beta\mathcal{F}(\{M_i\})} = e^{-\beta E(\{M_i\})}\ \omega(\{M_i\}) \tag{4.33}$$

where $\omega(\{M_i\})$ is the number of different states corresponding to the same distribution of M_i. The entropy associated to these configurations is :

$$S(\{M_i\}) = k_B \operatorname{Log}\ \omega(\{M_i\}) \tag{4.34}$$

and the "free energy" $\mathcal{F}$ is given as usually by :

$$\mathcal{F}(\{M_i\}) = E(\{M_i\}) - T\,S(\{M_i\}) \tag{4.35}$$

The partition function Z can be written exactly (for each scale b) as an integral ($\mathcal{N}$uple) :

$$Z_{\mathcal{N}} = \int \prod_{i=1} dM_i\ e^{-\beta\mathcal{F}(\{M_i\})} \tag{4.36}$$

In the continuous limit ($\mathcal{N} \to \infty$), $\mathcal{F}(\{M(r)\})$ is a "functional" of $M(r)$ and Z is a "functional" integral :

$$Z = \int \mathcal{D}M(r)\, e^{-\beta\mathcal{F}(\{M(r)\})} \tag{4.37a}$$

the mathematical meaning of which is given by $Z = \lim Z_{\mathcal{N}}\ \ \mathcal{N} \to \infty$

The density probability for a given "configuration" $M(r)$ is then given by :

$$\mathcal{P}(\{M(r)\}) = e^{-\beta\mathcal{F}(\{M(r)\})}/Z \tag{4.37b}$$

The previous mathematical expressions (4.36), (4.37) have a simple physical meaning : we replace the summation over all the possible microscopic spin configurations by a summation over the possible order functionsM(r).

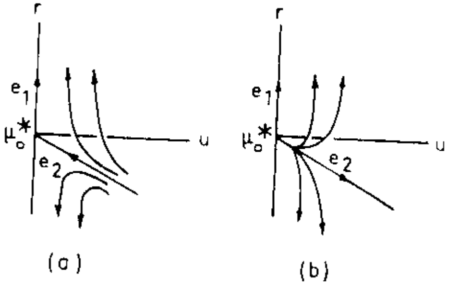


Fig. 4.4. : Stability of the gaussian fixed point a) d > 4 ; b) d < 4.

4.3. Ginzburg Landau model for $\tilde{\mathcal{F}}(\{M\})$. - The determination of the thermodynamic potential (4.29) requires the calculation of : i) the function $\tilde{\mathcal{F}}(\{M\})$ for each microscopic hamiltonian $\mathcal{H}$ - (4.30), for example, in the Ising case - ; ii) the functional integral (4.37). $\tilde{\mathcal{F}}_b(\{M\})$ can be - at least in principle obtained for each length b "step by step" : starting from the initial Ising model, we can define blocks of b^d microscopic cells (b = 2, 3, 4....), define the densities $M_i = 1/b^d \sum_{\lambda \in i} \sigma_\lambda$, calculate $\tilde{\mathcal{F}}_b(\{M_i\})$(b = 2, 3...) from its definition. This procedure is appropriate in some simple cases (Ising model for d = 2...) but it is in general difficult to use. In these lectures we will use the simplest "reasonable" function $\tilde{\mathcal{F}}(\{M_i\})$. This function will be obtained by phenomenological considerations similar to those we used to develop the Landau model ; this is "a priori" sufficient for our purpose since we can think that, if it is necessary to take into account the fluctuations (to evaluate the functional integral (4.37)), the detailed (quantitative) expression of $\tilde{\mathcal{F}}(\{M\})$ is not important for the study of the critical phenomena (universality of the critical exponents). Finally $\tilde{\mathcal{F}}(\{M\})$ must be chosen so that we recover the classical Landau results when we neglect the fluctuations of M(r) from its equilibrium value $\langle M(r) \rangle$.

The transition results from a cooperative effect i.e. from coupling between the blocks. The simplest form for $\tilde{\mathcal{F}}$ can be written as follows :

$$\tilde{\mathcal{F}}(\{M_i\}) = \sum_i \tilde{\mathcal{F}}_1(M_i) + \frac{1}{2}\sum_{i \neq j} \tilde{\mathcal{F}}_2(M_i, M_j) \tag{4.38}$$

it results from the "free energy" of each of the blocks $\tilde{\mathcal{F}}_1$ and of the pair interactions $\tilde{\mathcal{F}}_2(M_i, M_j)$. Let us examine the simplest assumptions we can use for $\tilde{\mathcal{F}}_1$ and $\tilde{\mathcal{F}}_2$.

4.3.1. $\tilde{\mathcal{F}}_1(M)$. - We will represent $\tilde{\mathcal{F}}_1$ by its expansion in successive powers of M ; this expansion will have the general form, consistent with the symmetry, we introduced for the study of the Landau model (see chapter 1, eq. (1.43)). If we consider a simple homogeneous isotropic system characterized by a scalar order parameter and presenting the symmetry $M \to -M$ we obtain :

$$\beta \tilde{\mathcal{F}}_1(M) = u_o + u_2 \frac{M^2}{2} + u_4 \frac{M^4}{4} + \dots \tag{4.39a}$$

with
$$u_2 = a(T - T_c) \qquad (a > 0) \tag{4.39b}$$

If the dimension of the order parameter is n, M^2 and M^4 in the expansion (4.39) are defined in terms of the components M_α of M by :

$$M^2 = \sum_{\alpha=1}^{n} M_\alpha^2 \tag{4.40}$$

$$M^{2p} = (M^2)^p \tag{4.41}$$

4.3.2 Couplings $\tilde{\mathcal{F}}_2(M_i,M_j)$ [illegible] increases when the order parameter varies from block to block ($M_i \neq M_j$) ; the simplest analytical form for $\tilde{\mathcal{F}}_2$ is then given by :

$$\beta \tilde{\mathcal{F}}_2(M_i M_j) = \frac{k_{ij}}{2} \frac{1}{b^2} (M_i - M_j)^2 \qquad k_{ij} > 0 \tag{4.42a}$$

For short range couplings it will be sufficient to consider the pair interactions between neighbouring blocks. For long range couplings we can assume that the coefficients k_{ij} decrease as power laws (see chapter 3, section 5.3) :

$$k_{ij} = \frac{k}{|r_i - r_j|^{d+\sigma}} \tag{4.42 b}$$

4.3.3. Summary : Ginzburg Landau model for an isotropic system with short range couplings. - In the following sections we will assume that $\tilde{\mathcal{F}}(\{M_i\})$ is given in the discrete case (see (4.28) for comparison) by :

$$\beta \tilde{\mathcal{F}}(\{M_i\}) = \mathcal{N} u_o + \frac{u_2}{2} \sum_i M_i^2 + \frac{u_4}{4} \sum_i M_i^4 + \dots + \frac{c}{2} \frac{1}{b^2} \sum_{i,j}{}' (M_i - M_j)^2 \tag{4.43}$$

The summation $\sum_{ij}'$ in the last term of (4.43) ranges over neighbouring blocks i.
In the continuous limit $\tilde{\mathcal{F}}(\{M(r)\})$ becomes :

$$\beta \tilde{\mathcal{F}}(\{M(r)\}) = \int dr^d \left[u_o + \frac{u_2}{2} M(r)^2 + \frac{u_4}{4} M(r)^4 + \dots + \frac{c}{2} (\nabla M(r))^2\right] \tag{4.44}$$

with the definition :

$$(\nabla M(r))^2 = \sum_{i=1}^{d} \sum_{\alpha=1}^{n} \left(\frac{\partial M_\alpha}{\partial x_i}\right)^2 \tag{4.45}$$

An equilibrium state of the system is then determined by the set of parameters (u_{2n}, c) and by external constrainst (T,p). This simple form for $(\{M(r)\})$ allows to recover the classical Landau results (section 3) when we neglect the fluctuations of M(r) (see section 6).

4.4. Ginzburg Landau model in the reciprocal space. - It is possible to define another -equivalent- representation of Z in terms of the Fourier coefficients of M(r), M_q. For a given scale $b \sim \Lambda^{-1}$, the relevant Fourier components M_q are those for which $q < \Lambda$. We introduce as previously the free energy $\mathcal{F}_\Lambda(\{M_q\})$ which is defined as follows :

$$e^{-\beta \mathcal{F}_\Lambda(\{M_q\})} \tag{4.46}$$

represents the contribution to the partition function of all the configurations for which the $M_q (q < \Lambda)$ have fixed values. The partition function Z is then :

$$Z = \int \prod_{q<\Lambda} d M_q \; e^{-\beta \mathcal{F}_\Lambda(\{M_q\})} \tag{4.47}$$

and

$$\mathcal{P}(\{M_q\}) = \frac{1}{Z} e^{-\beta \mathcal{F}_\Lambda(\{M_q\})} \tag{4.48}$$

is the probability of the configurations for which the Fourier components $M_q (q < \Lambda)$ are fixed.

$\mathcal{F}_\Lambda(\{M_q\})$ is a "free energy" which has the same physical meaning as $\mathcal{F}_b(\{M_i\})$: qualitatively, this description is accurate for scales larger than $b = 2\pi/\Lambda$ The simplest form for $\mathcal{F}(\{M_q\})$ is obtained using the same arguments as previously ; for isotropic systems with short range couplings we have (see (4.27) for comparison) :

$$\beta \mathcal{F}(\{M_q\}) = u_0 \mathcal{V} + \frac{1}{2} \sum_{q<1} (u_2 + cq^2) M_q M_{-q} + \frac{1}{V} \sum_{q,q',q''<\Lambda} u_4 M_q M_{q'} M_{q''} M_{-q-q'-q''} \tag{4.49}$$

4.5. Parameter space (Fig. 4.1). - We have defined a class of systems represented by (4.44) or (4.49). Each equilibrium state of a system of this class is determined by the values of $u_2(T)$, $u_4(T)$... It will be useful to represent this state by a point $\mu(T)$ whose coordinates are $(u_2, u_4, u_6 ...)$. When the temperature T varies, the point $\mu(T)$ defines a "physical" line in the parameter space. This line cuts the critical surface defined in the parameter space as the locus of all critical points $\mu(T_c)$. Finally note that we will use the classical notation :

$$u_2 = r \qquad\qquad u_4 = u$$

4.6. Conclusion. - We have introduced a simple model for $\mathcal{F}(M)$ which represents phenomenologically the isotropic systems with short range interactions. The previous considerations can be extended to more complicated situations. As an example, if there is an isotropy in the order parameter space, $\mathcal{F}$ is no longer a function of M^2 and we must replace $u_2 M^2$ by $\sum_\alpha u_{2\alpha} M_\alpha^2$ (quadratic anisotropy), $u_4 M^4$ by $u_4 M^4 + V \sum_\alpha M_\alpha^4$ (cubic anisotropy)... In the same way, if the system is anisotropic, we must introduce different coupling terms c_i $(i = 1, ... d)$.

For a given system, the coefficients (u_{2n}, c) are determined by the microscopic hamiltonian $\mathcal{H}$. In this chapter, we do not try to determine them but we want to determine the qualitative features of the thermodynamic potential we obtain from (4.29), (4.36) and (4.43) (or (4.47) and (4.49)).

5. Gaussian model. - This model is obtained from (4.43) or (4.49) neglecting the terms u_{2p}, $(p > 1)$:

$$\mathcal{F}'(\{M_q\}) = \frac{1}{2} \sum_{q<\Lambda} (r + q^2) M_q^2 \tag{4.50}$$

The calculation of Z is then trivial since the integrals corresponding to the different M_q become independent :

$$Z = \prod_{q<\Lambda} \int d M_q \; e^{-(r+q^2)\frac{M_q^2}{2}} = \prod_{q<\Lambda} \left(\frac{2}{\pi} \;\; \frac{1}{r+q^2} \right)^{1/2} \tag{4.51}$$

and the free energy becomes :

$$F = F_r + k_B T \sum_{q<\Lambda} \mathrm{Log}\,(r + q^2) \tag{4.52}$$

F_r being the regular part of F. For $T > T_c$, the integral defining Z has a physical meaning $(r > 0)$. When $r < 0$, a positive quartic term $(u_4 > 0)$ is necessary to insure the convergence of the integral : the low temperature phase has no physical meaning in this Gaussian model. The specific heat is obtained from (4.52) :

$$c_v = - T \left(\frac{\partial^2 F}{\partial T^2}\right)_v \sim \int_0^\Lambda \frac{q^{d-1}\, dq}{(r + q^2)^2} \tag{4.53}$$

We find the same expression and critical index α as discussed previously (see chapter 2, section 8) for the Ising model :

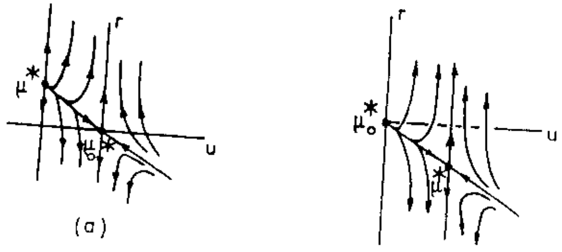
$$\alpha = 0 \;\; (d > 4) \qquad\qquad \alpha = \frac{4-d}{2} \quad (d < 4) \tag{4.54}$$

The correlation function is given by :

$$g(q) = \langle |M_q|^2 \rangle_0 = \frac{1}{Z} \int \prod_{q'<\Lambda} dM_{q'} \; e^{-\sum_{q'} (r+q'^2)\frac{M_q^2}{2}} M_q^2 \sim \frac{1}{r+q^2} \tag{4.55}$$

and has the same dependence as that obtained in the Landau model (see (4.25)) ; the exponents of the Gaussian model are then classical :

$$\gamma = 1 \qquad\qquad \nu = 1/2 \qquad\qquad \eta = 0$$



(a) (b)

Fig. 4.5. : Stability of the fixed points for d ≃ 4, a) d > 4 ; b) d < 4.

In conclusion, in order to describe accurately the critical behaviour, which is experimentally observed, we have to take account of the coupling between fluctuations ($u_4 \neq 0,\dots$).

6. MFA and Landau's model. - 6.1. The MFA assumes that among all the configurations M(r) which contribute to Z, one of them is <u>dominant</u> in the thermodynamic limit i.e. the most probable. If such a configuration exists, it corresponds to an uniform distribution M(r) = M. With such an assumption, we replace the functional integral by the term exp $-\beta\tilde{\mathcal{F}}(\bar{M})$ where $\tilde{\mathcal{F}}(\bar{M})$ minimizes $\tilde{\mathcal{F}}(M)$ (to maximize $\mathcal{P}$ - cf(4.37)) :

$$\frac{\partial\tilde{\mathcal{F}}}{\partial M}(\bar{M}) = 0 \qquad \frac{\partial^2\tilde{\mathcal{F}}}{\partial M^2}(\bar{M}) > 0 \tag{4.56}$$

The free energy F is then equal to $\tilde{\mathcal{F}}(\bar{M})$.

$$Z = e^{-\beta\tilde{\mathcal{F}}(\bar{M})} \implies F = \tilde{\mathcal{F}}(\bar{M}) \tag{4.57}$$

and using (4.4), we recover the Landau expansion with $A = u_2(\ = r)\ C = u_4\dots$

6.2. - The previous M.F. results are exact if we neglect the spatial variations of M(r) in (4.36) ; in such a case $e^{-\beta\tilde{\mathcal{F}}(M)}$ becomes :

$$e^{-\beta\tilde{\mathcal{F}}(\{M\})} = e^{-\beta\mathcal{N}\tilde{\mathcal{F}}_1(M)} \tag{4.58}$$

and presents a maximum for $M = \bar{M}$ (see chapter 1, section 2) :

$$\begin{cases} \tilde{\mathcal{F}}_1(M) = \tilde{\mathcal{F}}_1(\bar{M}) + \dfrac{(M-\bar{M})^2}{2}\,\tilde{\mathcal{F}}''_1(\bar{M}) & (4.59)\\ e^{-\beta\tilde{\mathcal{F}}(\{M\})} = e^{-\beta\tilde{\mathcal{F}}_1(\bar{M})}\,e^{-\mathcal{N}\tilde{\mathcal{F}}''_1(\bar{M})\,(M-\bar{M})^2/2} & (4.60)\end{cases}$$

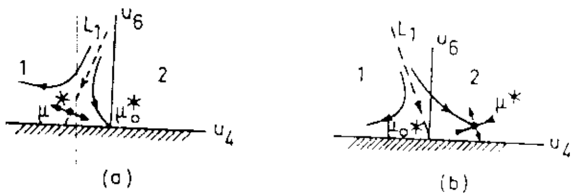
In the limit $\mathcal{N}\to\infty$, $e^{-\beta\tilde{\mathcal{F}}(M)}$ is a Gaussian the width of which is zero.

$$\Delta = \frac{1}{\sqrt{\mathcal{N}\beta\tilde{\mathcal{F}}''_1(\bar{M})}} \sim 0\left(\frac{1}{\sqrt{\mathcal{N}}}\right)$$

The configuration $M = \bar{M}$ is then (infinitely) most probable than the others : $\mathcal{P}(\bar{M}) \sim \sqrt{\mathcal{N}}$.
We obtain for Z and F the results of a MFA (see (4.57)) :

$$\begin{cases} \displaystyle\int e^{-\beta\tilde{\mathcal{F}}(\{M\})}dM = e^{-\mathcal{N}\beta\tilde{\mathcal{F}}_1(\bar{M})}\int e^{-(M-\bar{M})^2/2\Delta^2}\,dM & (4.61)\\ F = F_0 + \mathcal{N}\tilde{\mathcal{F}}_1(\bar{M}) & (4.62)\end{cases}$$

6.3. However, the MFA is no longer valid when we allow spatial fluctuations for M(r) (except for couplings k_{ij} independent of the distance) and the contribution of these fluctuations become dominant when $T \to T_c$. It is then tempting to take into account the spatial fluctuations M(r) in the vicinity of the M.F. solution $M(r) = \bar{M}$ and neglect the couplings $u_4\dots$ We do not reproduce such calculations since we would get results similar to those of the Gaussian model. In conclusion, a relevant model for the phase transition must take into account -at least- the terms u_2, u_4 and c.



(a) (b)

Fig. 4.6. : The domain of attraction of the fixed points μ_0 for d > 4 and μ^* for d < 4 is limited in the plane (u_4, u_6) by the line L_1.

7. Renormalization group - definition and properties. - 7.1. <u>Definition (reciprocal space).</u> - A "renormalization" group is a set of transformations R_s in the parameter space :

$$\mu' = R_s\mu$$

R_s is defined for each real value of s (s > 1) ; $\mu' = \{u'_{2p}\}$ is determined from $\mu = \{u_{2p}\}$ by the transformation :

$$e^{-\beta\tilde{\mathcal{F}}_1(R_s\mu,\{M_q\})} = \prod_{s^{-1}q\ [illegible]}\int dM_q\, e^{[illegible]\,(\mu,\{M_q\})} \quad M_q \to s\,M_{sq} \tag{4.63}$$

After a partial integration over the variables $M_q(\Lambda/s < q < \Lambda)$, we replace M_q by $\lambda_s M_{sq}$ and obtain a function of the variables M_q $(q < \Lambda)$ but the number of these variables has been divided by s^d by the partial integration. Then, we write this result in the canonical form (4.49) $\exp - \beta\tilde{\mathcal{H}}(\mu', \{M_q\})$. The factor λ_s which renormalizes the order parameter is then chosen in order that the coefficient of q^2 in (4.49) remains the same i.e. $c=c'=1$. Let us now describe this transformation which is performed in three steps :

i) partial integration : we first integrate over all the variables $\Lambda/s < q < \Lambda$: the new "free energy" $\tilde{\mathcal{H}}(\mu')$ can only describe the phenomena which vary over distances $r > b = 2\pi s/\Lambda$: this step is a scaling transformation.

ii) cut off : The previous quantity depends on all the M_q for $q < \Lambda/s$; we must change the unit of length to obtain the same cut off after the transformation : this is obtained by taking a unit of length s times larger. After this transformation $r \to r/s$, $q \to sq$ and $\Lambda/s \to \Lambda$.

iii) renormalization : Finally, we replace M_{sq} by $\lambda_s M_{sq}$ and we choose this renormalization factor such as $c'=c$: this choice insures that the coupling between blocks keeps the same weight before and after the transformation.

7.2. Definition (real space). - The corresponding definition in the real space is :

$$e^{-\beta\tilde{\mathcal{H}}(R_s\mu, \{M(r)\})} = \left[e^{-\beta K_s \tilde{\mathcal{H}}(\mu, \{M(r)\})} \right]_{M(r) \to \lambda'_s M(r/s)} \qquad (4.64)$$

1) The operation K_s ("partial integration") allows to change the scale from b to sb : after this transformation the system is characterized by the centers r of the new blocks made of s^d blocks of size $\omega = b^d$. A state of the considered system is then determined by the values $M(r)$ of the order parameters of the new blocks ; $M(r)$ is the average value of order parameters of the s^d "old" blocks ; $\exp -\beta K_s \tilde{\mathcal{H}}(\mu, M(r))$ is the contribution to the partition function of the states having fixed values of $\{M(r)\}$ and the partition function is given by :

$$Z = \int \prod_r dM_r \; e^{-\beta K_s \tilde{\mathcal{H}}(\mu, \{M_r\})} \qquad (4.65)$$

The integral (4.65) is taken over all the new blocks (volume $(sb)^d$). The operation K_s decreases the spatial resolution.

2) Then, we multiply the unit of length by $s (r \to r/s)$ so that the measure of each block becomes b.

3) Finally, we renormalize the order parameter associated to each "new" block by multiplying it by a constant λ'_s.

Thus, after the steps 2) and 3) we replace $M(r)$ by :

$$M(r) \to \lambda'_s M(r/s) \qquad (4.66)$$

The result can be written in the Ginzburg Landau canonical form (4.43) ; the coefficient λ'_s is chosen so that $c = c' = 1$

7.3. Product $R_s R_{s'}$ - semi group. - We can define the product of two operations R_s, $R_{s'}$ by the simple succession of these opetations :

$$R_s R_{s'} \mu = R_s(R_{s'} \mu) \qquad (4.67a)$$

This operation is associative and the set of transformations R_s has a neutral element $(R_1 \mu = \mu)$. $\{R_s\}$ is then a semi-group ; it is not a group because the inverse of R_s does not exist (we loose information by a scaling transformation !).

Finally, it is equivalent to do the transformation $R_{ss'}$ in one or two steps $[R_s R_{s'}]$:

$$R_{ss'} = R_s R_{s'} \qquad (4.67b)$$

This condition is only satisfied if λ_s varies as s^y :

$$\lambda_s = s^y \qquad (4.68)$$

This is easily verified from the definition (4.63) since (4.67b) is satisfied only if the functional equation $\lambda_{ss'} = \lambda_s \lambda_{s'}$ is itself satified.

7.4. Renormalization group and Gaussian model. - As an illustration, we apply the previous definition of R_s to the gaussian model : $(u_4 = 0, n = 1)$. In the present case, the first step (partial integration) is trivial because there is no coupling between the different variables M_q :

$$\int \prod_{\frac{\Lambda}{s} < q < \Lambda} dM_q \; e^{-\sum_{q<\Lambda} (r + q^2) \frac{M_q^2}{2}} = \prod_{\frac{\Lambda}{s} < q < \Lambda} \left(\frac{2M}{r + q^2} \right)^{1/2} e^{-\sum_{q<\Lambda/s} (r + q^2) \frac{M_q}{2}} \qquad (4.69a)$$

The second and third steps replace the argument of the exponential in the rhs of (4.69a) by :

$$\frac{1}{2} \sum_{q < \frac{\Lambda}{s}} (r + q^2) s^{2y} M_{sq}^2 = \frac{1}{2} \sum_{q<\Lambda} (rs^{2y} + s^{2(y-1)} q^2) M_q^2/2 \qquad (4.69b)$$

The rhs of (4.69b) defines $\tilde{\mathcal{H}}(\mu', \{M_q\})$ in the canonical form and the new coefficients $\{u'_{2p}\}$, c' are given by :

$$r' = r s^{2y}, \; u'_{2p} = 0 \; (p > 1) \quad c' = s^{2(y-1)} \qquad (4.69c)$$

The renormalization of the order parameter is determined in order to insure that $c' = 1$; this requires :

$$y = 1 \qquad (4.69d)$$

In conclusion, (see (4.69c) and (4.69d)) we have shown that an operation of the renormalization group transforms a state of a Gaussian model into another state of the same model :

$$R_s(r,o,o...) = (rs^2, o, o,...) \qquad (4.69e)$$

7.5 Renormalization group - correlation function and free energy. - It is important to relate the free energy perunit volume and the correlation function to the distributions of probabilities $\mathcal{P}, \mathcal{P}'$ defined (resp.) by μ and μ' : this will allow to relate the critical behaviour to the operations of the renormalization group. For the correlation function we show in this section that :

$$g(q,\mu) = \lambda_s^2 \; g(sq, R_s\mu) \qquad (4.70a)$$

For the free energy density, we will not give the demonstration of the intuitive relation (R_s is a complex dilatation) :

$$F(R_s\mu) = s^d F(\mu) \qquad (4.70b)$$

The complete demonstration of (4.70b) is given in the book by Ma. Let us now establish (4.70a) :

For $q<\Lambda$, we can write $g(q,\mu)$ as follows :

$$g(q,\mu) = \int \prod_{q'<\Lambda} dM_{q'} \mathcal{P}(\mu,\{M_{q'}\}) \, |M_q|^2 \qquad (4.70c)$$

where $\mathcal{P}(\mu,\{M_{q'}\})$ is the probability for the system in the state μ to have a distribution of order parameters characterized by $\{M_{q'}\}$ $(q'<\Lambda$, see (4.47b)).

We first integrate over the variables $\Lambda/s < q' < \Lambda$ and define a new probability distribution $\mathcal{P}_1(\{M_{q'}\}(q' < \Lambda/s)$

$$\begin{aligned} g(q,\mu) &= \int \prod_{q'<\frac{\Lambda}{s}} dM_{q'} \mathcal{P}_1(\mu,\{M_{q'}\}) \, |M_q|^2 \\ \mathcal{P}_1(\mu,\{M_q\}) &= \int \prod_{\frac{\Lambda}{s}<q<\Lambda} dM_{q'} \, \mathcal{P}(\mu,\{M_{q'}\}) \end{aligned} \qquad (4.71)$$

This probability $\mathcal{P}_1$ is sufficient to determine the properties which vary on a scale $q'<\Lambda/s$. Now we can change the variables ($q' = sq''$) and define the probability $\mathcal{P}_2(\{M_{q''}\}) = \mathcal{P}_1(\{M_{sq''}\})$:

$$g(q,\mu) = \int \prod_{q'<\Lambda} dM_{q'} \, \mathcal{P}_2(\mu,\{M_{q'}\}) \, |M_{sq}|^2 \qquad (4.72)$$

Finally we renormalize the order parameter defining the new probability $\mathcal{P}'(\{M_{q'}\})$ by :

$$\left\{ \begin{aligned} &\mathcal{P}'(\{M'_{q'}\}) \prod_{q<\Lambda} dM'_q = \mathcal{P}_2(\{M_q\}) \prod_{q<\Lambda} dM_q && (4.73a) \\ &M_q = \lambda_s M'_q && (4.73b) \end{aligned} \right.$$

and we obtain for $g(q,\mu)$:

$$g(q,\mu) = \int \prod_{q} dM'_q \, \mathcal{P}'(\mu,\{M'_q\}) \, |M'_{sq}|^2 \, \lambda_s^2 \qquad (4.73c)$$

The operations we defined previously $(\mathcal{P} \to \mathcal{P}_1 \to \mathcal{P}_2 \to \mathcal{P}')$ are the same as those introduced in the definition of the renormalization group and :

$$\mathcal{P}'(\mu, \{M_q\}) = \mathcal{P}(R_s\mu, \{M_q\}) \qquad (4.74)$$

hence (4.73c) and (4.74) prove (4.70a).

8. Fixed point and its neighbourhood. - 8.1. Some definitions. - Renormalization lines (Fig. 4.1) : Starting from μ, the set of points $\mu' = R_s\mu$ obtained when s increases from one to infinity defines a renormalization line in the parameter space.

Fixed point : A fixed point μ^* is a point of the parameter space which remains invariant by all the operations of the renormalization group :

$$R_s\mu^* = \mu^* \quad (\forall s > 1) \qquad (4.74)$$

Domain of attraction of a fixed point : We can associate to each point μ^* the set of points μ which are on the renormalization lines which go towards μ^* when $s\to\infty$:

$$\lim_{s\to\infty} R_s\mu = \mu^* \qquad (4.75)$$

This set defines the "domain of attraction" of the fixed point μ^*.

8.2. Neighbourhood of a fixed point. - The properties of the neighbourhood of μ^* will determine the critical properties. If $\mu = \mu^* + \delta\mu$ is a point of this neighbourhood such as $\delta\mu = \{(\delta u_{2n})\}$ is assumed to be small, we can linearize the effect of R_s :

[illegible] $+ 0(\delta\mu^2)$ (4.76)

The operations R_s define in this limit a linear transformation R^L_s which can be represented by a matrix ; for example if we keep only the quadratic and quartic terms of $\mathcal{H}(u_{2p} = u'_{2p} = 0 \; p > 2)$, we obtain :

$$\begin{pmatrix} \delta r' \\ \delta u' \end{pmatrix} = \begin{pmatrix} R^L_{s\,11} & R^L_{s12} \\ R^L_{s21} & R^L_{s22} \end{pmatrix} \begin{pmatrix} \delta r \\ \delta u \end{pmatrix} \tag{4.77}$$

It is then useful to diagonalize this matrix and to define local axis in the parameter space : these axes are defined by unit vectors e_i which satisfy the relation :

$$R^L_s\ e_i = \lambda_i\, e_i \tag{4.78a}$$

From (4.67) the coefficient λ_i is then necessarily equal to some power of s. We define the exponent y_i through the relation :

$$\lambda_i = S^{yi}\ , \qquad\qquad R^L_s\ e_i = s^{yi}\ e_i \tag{4.78b}$$

A point in the neighbourhood of μ^* is then determined by its components in the local coordinates :

$$\delta\mu = \sum_i\ t_i\, e_i \tag{4.79}$$

and the effect of R_s on $\delta\mu$ will be given by :

$$R^L_s\ \delta\mu = \sum_i\ s^{yi}\, t_i\, e_i \tag{4.80}$$

The "free energy" density in the neighbourhood of μ^* :

$$\mathcal{F}(\mu, \{M_q\}) = \widetilde{\mathcal{F}}(\mu^*, \{M_q\}) + \sum_i\ \frac{1}{2i}\,\delta u_{2i}\, M^{2i} + \frac{1}{2}\sum_q q^2 M_q{}^2 \tag{4.81}$$

can then be written, using (4.79) in terms of t_i :

$$\widetilde{\mathcal{F}}(\mu, \{M_q\}) = \widetilde{\mathcal{F}}(\mu^*, \{M_q\}) + \sum_i t_i\ \theta_i(M) + \frac{1}{2}\sum_q\ q^2 M_q{}^2 \tag{4.82}$$

The scaling variables t_i are obtained from (4.79) as linear combination of the δu_{2i} ($\delta u_{2i} = \Sigma A_{ij}\, t_j$) and the $\theta_i(M) = \sum_j A_{ij}\, M^{2i}$ are the *scaling fields*.

Relevant variables, irrelevant variables. - From (4.80), $R_s\ \delta\mu$ is obtained from $\delta\mu$ by multiplying its local coordinates by s^{yi}. The effect of R_s is then qualitatively different according to the sign of y_i : when $y_i > 0$, the renormalization line associated to a point μ on the ith local axis ($\delta\mu = t_i e_i$) goes away from μ^* ($s^{yi} \to \infty$ when $s \to \infty$) whereas it goes towards μ^* when $y_i < 0$ ($s^{yi} \to 0$ when $s \to \infty$ $y_i < 0$). A scaling variable is *relevant* when $y_i > 0$. It is *irrelevant* when $y_i < 0$ and it is *marginal* for $y_i = 0$. In the following we will choose the scaling variables so that :

$$y_1 \geqslant y_2 \geqslant \ldots \geqslant y_n \geqslant \ldots \tag{4.83}$$

Stability, unstability. - When $y_i > 0$, the fixed point is said to be *unstable* relative to t_i ; for $y_i < 0$, it is said to be stable.

8.3. *Neighbourhood of a fixed point and critical exponents.* - Let us consider the class of systems represented by (4.44), (4.49) ; each system is represented by a point $\mu(T)$ in the parameter space ; the locus of all the critical points for all these systems defines the critical surface S_c in the parameter space. Let us now show the following proposition which relates the neighbourhood of a fixed point to the critical behaviour of a simple system : a class of systems characterized by a fixed point μ^* unstable relative to only one scaling variable $t_1 = a(T - T_c)$ has, at $T = T_c$ the same singular behaviour of the thermodynamic potential and the correlation function as experimentally observed for simple systems (see chapter 3).

Let us first note that the assumption $t_1 = a(T - T_c)$ requires that the domain of attraction of μ^* is a part of the critical surface ; starting from a point $\mu(T)$ ($T = T_c$), the renormalization line will be characterized by points which go towards μ^* in all the directions ($i > 1$, $y_i < 0$) *except one* (e_1) (Fig. 4.3).

1) Correlation function : When $T = T_c$ we obtain from (4.79),(4.80) :

$$\begin{aligned} \mu(T_c) &= \sum_{i>1}\ t_i\ e_i \\ g(q, \mu(T_c)) &= s^{2y}\, g(sq, \mu^* + \sum_{i>1}\ s^{yi}\, e_i t_i) \end{aligned} \tag{4.84}$$

We choose $s = \Lambda/2q > 1$ and obtain :

$$g(q, \mu(T_c)) = q^{-2y} \left(\frac{\Lambda}{2}\right)^{2y} g\left(\frac{\Lambda}{2}, \mu^* + \sum_{i>1} \left(\frac{\Lambda}{2q}\right)^{2y}\ e_i\right) \tag{4.85}$$

In the limit of small wave vectors ($q \to 0$) the correlation function becomes :

$$g(q, \mu(T_c)) = q^{-2y}\, g\left(\frac{\Lambda}{2}, \mu^*\right) + \ldots \tag{4.86}$$

and the exponent y for the renormalization of the order parameter is then necessarily related to η (see es. (3.14)) by :

$$y = 1 - \eta/2 \tag{4.87}$$

When $T \simeq T_c$ we obtain from (4.79), (4.80) :

$$g(q, \mu) = s^{2-\eta}\, g(sq,\ \mu^* + t_1 s^{y_1} e_i + \sum_{i>1} t_i s^{y_i} e_i) \tag{4.88}$$

This relation is satisfied for all real $s > 1$; choosing

$$s = t_1^{-1/y_1} \tag{4.89}$$

we introduce the "correlation length" $\xi(T)$ defined by :

$$\xi(T) = a^{-1/y_1} (T - T_c)^{-1/y_1} \tag{4.90}$$

When $s \to \infty$ $(T \to T_c)$ equation (4.88) becomes :

$$g(q,\mu(T)) = \frac{1}{q^{2-\eta}}\, (q\,\xi)^{2-\eta}\ g(q\xi\ ,\ \mu^* + e_i) \tag{4.91}$$

The behaviour of $g(q,\mu(T))$ is then similar to the behaviour we described in chapter 3 (see equation (3.14)) if :

$$\nu = \frac{1}{y_1}\ ,\ (q\,\xi)^{2-\eta}\, g(q\,\xi\ ,\ \mu^* + e_i) = f_2(q\xi) \tag{4.92}$$

Note that we can obtain corrections to the critical regime by an expansion of (4.84) and (4.88) in successive powers of $(T - T_c)$ i.e. taking into account the irrelevant variables.

2) Free energy : The free energy $F(\mu)$ is related to $F(R_s\mu)$ by (4.70b) i.e. by :

$$F(\mu^* + t_1 s^{y_1} e_1 + \sum_{i>1} t_i\, s^{y_i} e_i) = s^d\ F(\mu^* + \sum_i t_i\, e_i) \tag{4.94}$$

when $\mu(T)$ is in the neighbourhood of the fixed point μ^*. Choosing s as in equation (4.89) we obtain when $s \to \infty$:

$$F(\mu(T)) = t_1^{-d/y_1}\ F(\mu^* + e_i) \sim |T - T_c|^{-d/y_1} \tag{4.95}$$

The critical index α is then given by :

$$2 - \alpha = \frac{d}{y_1} \tag{4.96}$$

and we obtain from (4.92) the Josephson scaling law (3.4).

In order to obtain the other exponents, we have to take into account the effect of a filed H coupled to the other parameter M ; we do not discuss this point in these lectures (see book by Ma for example).

In conclusion, the critical behaviour is determined by the exponents y and y_1 which are related to the exponents η and ν by equations (4.87) and (4.92).

9. Application : stability of the Gaussian fixed point. - We apply the previous results to the study of the fixed point of the Gaussian model and we show the peculiar role played by the dimension d = 4 for the stability of this fixed point.

If we consider the Gaussian model, the parameter space is reduced to the axis $r > 0$ and the fixed point μ^* is the origin $r = 0$.

From (4.69) this point is unstable but we cannot define a low temperature phase for this model (see section 5) ; for this reason it is necessary to introduce (at least) the quartic term $(u_4 > 0)$. Let us now assume that $\mathscr{H}(M)$ has only quadratic and quartic terms $(u_2 = r,\ u_4 = u,\ u_{2n} = 0\ n > 2)$: is this model able to describe the phase transition of a "simple" system ? We apply the previous proposition (section 8.3) to answer this question.

The space parameter $\mu = (r,u)$ has now two dimensions and the origin $\mu^* = (0, 0)$ is always a fixed point called the Gaussian fixed point ; it is then essential to study the stability of this point and to know if its neighbourhood govers the critical behaviour of such systems. If $\mu(r,u)$ is in the neighbourhood of μ^* it is easy (but tedious) to calculate the coordinates of $R_s^L\mu$ -keeping only the terms proportional to r and u. We obtain y = 2 and (see the book by Ma) :

$$\begin{cases} r' = s^2\,(r + u\,B(1 - s^{2-d})) + O(u^2) \\ u' = s^{4-d}\ u + O\ (u^2) \end{cases} \tag{4.97a}$$

B is a real number defined by :

$$B = (n + 1/2)\ \frac{\Lambda^{d-2}}{d-2}\ \ 2^{-d+1}\ \pi^{-d/2} / \Gamma(\frac{d}{2}) \tag{4.97b}$$

The matrix R_s^L defined by (4.97)

$$R_s^L = \begin{pmatrix} s^2 & (s^2 - s^{4-d})B \\ 0 & s^{d-4} \end{pmatrix} \tag{4.98}$$

is easily diagonalized ; the local axes e_1 and e_2 are given by :

$$e_1 = (1, 0)\ ,\qquad e_2 = \frac{1}{\sqrt{1 + B^2}}(-B, 1) \tag{4.99}$$

and the corresponding eigenvalues are :

$$s^2 \qquad\qquad s^{4-d} \tag{4.100}$$

$$\text{i.e. } R_s^L e_1 = s^2 e_1 , \qquad\qquad R_s^L e_2 = s^{4-d} e_2 \tag{4.101}$$

We have to distinguish two situations :

1) <u>$d > 4$</u> : μ_o^* is unstable relative to t_1 ($y_1 = 2 > 0$) but it is stable relative to t_2 ($y_2 = 4 - d < 0$) : the singularities of the system are determined by (see section 8.3) :

$$\nu = \frac{1}{y_1} = \frac{1}{2} \qquad\qquad \eta = 0 \tag{4.102}$$

2) <u>$d < 4$</u> : μ_o^* is unstable relative to the variables t_1 and t_2(y_1, $y_2 > 0$) and the renormalization lines go away from μ_o^* : it is then necessary to look for the existence of another ficed point.

10. Critical behaviour near d = 4. - We try to obtain the fixed points when d = 3 and to identify the point which governs the critical behaviour. The physical case d = 3 is difficult to solve directly and we use another approach : the integrals which define Z can be defined for all real values of d and it is then possible to expand the expressions for Z... in successive powers of $\varepsilon = 4-d$. We hope that the behaviour and the exponents can then be obtained by such an expansion ($\varepsilon = 1$!) when d = 3. The expansion in successive powers of ε is easier than the direct calculation and it is useful because the fixed point μ^* which determines the critical behaviour will be shown to be in the neighbourhood of μ_o^*($\mu^* \to \mu_o^*$ when $d \to 4$) : it is then sufficient to expand as previously $R_s \mu$ in successive powers of (r, u). We discuss qualitatively this case since it illustrates the method of the renormalization group.

If we use the same method as in section 9 and if we keep in $R_s\mu$ the second order terms (i.e. those proportional to r^2 and u^2) we obtain -after a tedious calculation- two fixed points μ_o^* and μ^* whose coordinates and exponents y_1, y_2 are given by :

$$\begin{aligned} &\mu_o^* = (0, 0) ; \quad y_1 = 2 , \quad y_2 = \varepsilon \\ &\mu_o^* = \left(\frac{n+2}{2(n+8)}\varepsilon , \frac{\varepsilon}{16(n+8)} \right) ; y_1 = 2 - \frac{n+2}{n+8}\varepsilon , y_2 = - \varepsilon \end{aligned} \tag{4.103}$$

This expansion is valid when [illegible] since the new fixed point μ^* remains in the neighbourhood of μ_o^*. The values of y_1 and y_2 show that we must distinguish two cases :

1) <u>$d > 4$</u> : The Gaussian fixed point μ_o^* is stable with respect to t_2 whereas μ^* is unstable : the Gaussian fixed point determines the critical behaviour (see section 9).

2) <u>$d < 4$</u> : The "non trivial" fixed point μ^* is stable with respect to t_2 whereas the Gaussian point μ_o^* is unstable : the fixed point μ^* determines the critical behaviour.

When d increases from a values d> 4 to a value d< 4, the two fixed points μ_o^* and μ^* exchange their stability and the nature of the critical behaviour is modified. The geometry of the renormalization lines is shown in figure 4.5 and the critical exponents are given for d 4 by (see (4.103)) :

$$\begin{aligned} &\alpha = \frac{4-n}{2(n+8)}\varepsilon , \quad \beta = \frac{1}{2} - \frac{3\varepsilon}{2(n+8)}, \gamma = 1 + \frac{(n+2)\varepsilon}{2(n+8)} \\ &\delta = 3 + \varepsilon , \quad \eta = 0 , \quad \nu = \frac{1}{2} + \frac{(n+2)\varepsilon}{4(n+8)} \end{aligned} \tag{4.104}$$

It is possible to extend these calculations up to ε^3 and to use sophistivated methods to determine the critical exponents when d = 3 from the above results[*].The results we obtain for example for the Ising model (n = 1, d = 3) with the previous method (keeping terms up to ε^2) are in excellent agreement with numerical results. Note that the exponents are only dependent on n and d (universality).

In the previous theory, we did not take into account the terms u_{2p}, p > 2 in the expansion of $\tilde{\mathcal{H}}(M)$; $u = u_4$ must then be positive for reasons of convergence. It is then possible to ask : 1) what is the importance of the terms u_6, u_8 ? 2) what occurs when the Landau theory predicts a first order transition ($u_4 < 0$, $u_6 > 0$ for example) ?. The answer to these questions is relatively simple. For $d = 4 - \varepsilon$, it is easy to show that the fixed point μ^* remains in the neighbourhood of μ_o^* ($u_4^* \sim \varepsilon$ $u_6^* \sim \varepsilon^2$...) and the expansion in successive powers of ε remains meaningful. When we take into account u_6, we can define two fixed points μ_o^* and μ^* (as previously). The first one is unstable with respect to only one variable r(T - T_c) (μ_o^* for d > 4, μ^* for d < 4) ; however, the domain of attraction of these points is limited in the plane (u_4, u_6) (Fig. 4.6). It is then possible to define two types of systems if we consider the possible values of u_4 and u_6 : 1) if μ(T) is in the domain of attraction of μ_o^* (d > 4) or μ^*(d < 4) the transition has the same behaviour as previously ; 2) if μ (T) is not in these regions , the renormalization line goes to infinity and it is impossible to say something about the phase transition in these systems : in such a case - by analogy with the Landau results (see chapter 1) - we can think that the system presents a <u>first order transition</u>.

11. Conclusion. - The method we discussed for simple homogeneous, isotropic systems with short range interactions allows to characterize the critical behaviour by the neighbourhood of fixed points unstable with respect to (only) one relevant variable (the

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[*] A detailed examination of the series $\alpha(\varepsilon)$, $\beta(\varepsilon)$... shows that they are divergent but it is possible to use classical mathematical techniques (Borel transformations) to replace these series by convergent algorithms ; it is then possible to obtain the critical exponents with a reasonable accuracy.

temperature). If the representative point of the system in the parameter space $\mu(T)$ is in the domain of attraction of such a fixed point, the system presents a second order phase transition and the critical exponents can be calculated from the dimensions of the 1) real space (d), 2) order parameter space (n). When the renormalization line of $\mu(T)$ goes to infinity, the transition is "probably" a first order (discontinuous) transition.

This method can be generalized when the system is anisotropic (in real space, in the order parameter space) and when there are external fields. These external fields can be either without qualitative importance for the critical behaviour or they can change qualitatively the critical behaviour (relevant fields !) or even suppress the transition (field coupled to the order parameter for example). When there are several fields P_i we observe the competition between several critical transitions with a "cross over" between these behaviours. Such cross over can be explained phenomenologically from the homogeneity assumption (see Appendix 2) ; it corresponds in the renormalization group method to an exchange of stability of the fixed points corresponding to the different critical behaviours.

Finally, note that we did not discuss the role of the fluctuations on the nature (order) of the transition and on the predictions of the Landau model (see chapter 1). These predictions seem to be verified in most cases ;note however that there are exceptions - for example the condition $B \neq 0$ does not always mean that there must be a first order transition.

APPENDIX 1

The model of Kadanoff : Definition of R_s. -Let us consider as an example an Ising model defined on a square lattice with parameter a ; we assume that the pair interactions are equal to v between two nearest neighbours and zero otherwise.

A state of equilibrium is characterized by the value of $k = \beta v$. ξ is by definition the correlation length when we take the lattice parameter as the unit length ($\xi \gg 1$, $T \to T_c$) ; it is a function of k, $\xi(k)$ to be determined. The idea comes from the fact that the spins are strongly correlated in the volume $(\xi a)^d$ (here $d = 2$) large as compared to the cell volume a^d and which becomes infinite when $T = T_c$. The elementary operation $k_1 = R_2(k)$ defines a new Ising model (characterized by k_1) from the initial model. The definition of R_2 results from three operations and two assumptions.

1. Partial integrations. - We group the spins of the initial lattice by blocks (size 2a x 2a) and assume that the correlations between neighbouring spins are so strong that it works as if each block can have only two states $\sigma_i = \pm 1$ (i is the label of the block) : the number of degrees of freedom is reduced.

2. Renormalization. - An equilibrium state of the system is then characterized by the coupling between blocks. We assume that these couplings keep the Ising form and that they are still limited to the first nearest neighbours. These interactions v_1(or $k_1 = \beta v_1(T)$) are obviously not equal to the initial interactions. An equilibrium state of the system is now represented by an equilibrium state of a new Ising model built on a lattice 2a x 2a and characterized by the interaction $k_1 = \beta v_1$. k_1 is determined by k :

$$k_1 = f(k) \qquad (1)$$

and we can assume that the function f(k) is analytic even for $k = k_c (T = T_c)$ since it is a local quantity (only the macroscopic quantities can present singularities in the thermodynamic limit). The measure of the correlation length - with a unit length 2a - is $\xi(k_1)$.

3. Dilatation. - The lattice parameter of the "new" Ising model being 2a, we change the unit length in order to compare the final and the initial Ising models. Multiplying the unit length by two, the lattice become identical and the correlation length becomes $\xi(k)/2$. The same equilibrium state is then represented by two Ising models and the correlation length being obviously the same, we have :

$$\xi(k_1) = \xi(k)/2 \qquad (2)$$

In the same way :

$$F(k_1) = 2^d F(k) \qquad (3)$$

Comments. - Let us briefly comment on the previous definition. The essential difficulty to describe the behaviour of a macroscopic system when $T \to T_c$ comes from the fact that we must take into account the correlations between a large number of particles (those which are in a volume $\xi^d \gg 1$). In practice we can calculate the effect of the correlations between two or three particles but, the calculation is hopeless when $T \to T_c$! To solve this problem, it is sufficient to relate systems with different correlation lengths : if we can solve the problem for small correlation lengths $\xi/s \sim a$ and if we know the transformation which allows to pass from ξ/a to $\xi/s \gg 1$) then we have solved our problem ! The operations of the renormalization group are such operations.

Wen we have defined R_2, we can obtain R_s by iteraction ($s = 2^n$) defining blocks of 2^d, 4^d... n^d spins. Note that the existence of R_2 is probable but must be proved. For example, the role of the interactions between 2d, 3d... nth neighbours, between clusters of 3, 4... different spins is not necessarily negligible in the renormalization procedure as has been assumed previously.

4. Renormalization goup and critical behaviour. - Let us now show that if R_2 exists and if k_c is invariant under the operations $R_s (k_c = f(k_c))$ i.e. is a "fixed point" k^* then the correlation length ξ does not have a regular behaviour when $T \to T_c$, this behaviour

being determined by $f(k)$ when $k \simeq k_c$.

$k = k_c$ requires that $\xi(k_c) = \infty$ (see(2)). When $k \simeq k_c$:

$$f(k) = f(k_c) + \lambda(k - k_i) + 0((k - k_c)^2) \quad \lambda = f'(k_c) \tag{4}$$

(2) and (4) have then the following solution :

$$\xi(k) \sim (k - k_c)^{-\nu} \tag{5}$$

with

$$\frac{\xi(f(k))}{\xi(k)} = \left(\frac{f(k) - k_c}{k - k_c}\right)^{-\nu} \tag{6}$$

From (1) and (4) this equation becomes :

$$\lambda^{-\nu} = \frac{1}{2} \tag{7}$$

The exponent ν is then determined by the behaviour of $f(k)$ when $k \simeq k_c$:

$$\nu = \frac{\text{Log } 2}{\text{Log } \lambda} \tag{8}$$

The important point here is to understand how the non analytical behaviour of ξ appeared when we considered the neighbourhood of μ^* !

APPENDIX 2

External perturbations : cross over between two critical behaviours : Let us assume that the system is perturbed by an external field P (the pressure for example). We can assume a priori that the correlation function and the thermodynamic potential keep the same homogeneous form :

$$G(t, H, P,\ldots) \sim t^{2-\alpha} f\left(\frac{H}{t^{\phi_H}}, \frac{P}{t^{\phi_P}}, \ldots\right)$$

$$g(t, r, H, P,\ldots) \sim \frac{1}{r^{d-2+\eta}} f_1\left(\frac{r}{t^{-\nu}}, \frac{H}{t^{\phi_H}}, \frac{P}{t^{\phi_P}}, \ldots\right)$$

In the critical region the scaling variable P is replaced by P/t^{ϕ_p} and we have to consider two situations :

1) $\phi_p < 0$: the external field is irrelevant : when $t \to 0$, $P/t^{\phi_p} \to 0$ and the critical behaviour is the same as the critical behaviour without field ($P = 0$) ;

2) $\phi_p > 0$: the external field is relevant (H is a relevant field $\phi_H > 0$!) and introduces a qualitative change of the critical behaviour : when $P \ll t^{\phi_p}$ the behaviour remains the same as described without field ($P = 0$) but when $P > t^{\phi_p}$ the perturbation becomes significant. There will be a cross over from the initial critical behaviour to another one when $t^* \sim p^{1/\phi p}$. When $t \to 0$, the critical behaviour will be determined by another fixed point (or there will no longer be any phase transition).

A good example of this cross over between two critical behaviours is given by the spatial anisotropy. Let us assume that the system is made of weakly coupled chains : the interchain ($c_\perp$) is much smaller than the interchain $c_{/\!/}$ couplings ($c_{/\!/} \gg c_\perp$). At high temperature, we will observe 1) a behaviour characteristic of a $d = 1$ system ; 2) a $d = 3$ 2nd order phase transition at low temperature (Fig. 3.4). The fixed point $d = 1$ is unstable with respect to the interchain coupling : the stable fixed point is the point corresponding to $d = 3$.

References

The list of references given below is not intended to be exhaustive but rather to give some basic references about the different subjects involved in these lectures. Detailed references can be found in the books and reviews listed below.

INTRODUCTION.

Stanley, M.E., Introduction to phase transitions and critical phenomena, Clarendon Press (1971).

Critical phenomena, Course LI (International School of Physics Enrico Fermi), Academic Press (1971).

Local properties at phase transitions, Course LIX (International School of Physics Enrico Fermi), North Holland (1976).

Feynmann, R.P., Statistical mechanics : a set of lectures, Benjamin (1974).

Blinc, R. and Zeks, B., Soft modes in ferroelectrics and antiferroelectrics, North Holland (1974).

Kincaid, J.M. and Cohen, E.G.D., Phys. Rep. 22, (1975) 58.

Wheatley, J.C., Rev. Mod. Phys. 47, (1975) 415.

De Gennes, P.G., The Physics of Liquid Crystals, Clarendon Press (1974)

Krivoglaz, M.A. and Smirnov, A.A., The theory of order-disorder in Alloys, Mac Donald, London (1964).

Kachaturyan, A.G., Phys. Stat. Sol. (b) 60 9 (1973) ; Order Disorder Transformations, ed. H. Warlimont P. 114, Springer Verlag (1974).

LANDAU MODEL FOR THE SECOND ORDER PHASE TRANSITIONS

Landau, L. and Lifchitz, E., Physique Statistique, Editions Mir, Moscou (1967).

Kadanoff, L.P., Gotze, W., Hamblen, D., Hecht, R., Lewis, E.A.S., Palciauskas, V.V., Rayl, M., Swift, J., Aspnes, D., and Kane, J., Rev. Mod. Phys. 39, (1967) 395.

Boccara, N., Symétries brisées, Herman (1976).

Cornwell, J.F., Group Theory and Electronic Energy bands in Solids, North Holland (1969).

ISING MODEL : MEAN FIELD APPROXIMATION

Brout, R., Phase Transitions, Benjamin (1965).

Thompson, C.J., Mathematical Statistical Mechanics, Mac Millan (1972).

Onsager, L., Phys. Rev. 65, (1944) 117.

CRITICAL PHENOMENA and INTRODUCTION TO THE STUDY OF THE GINZBURG - LANDAU - WILSON MODEL.

Toulouse, G. Pfeuty, P., Introduction au groupe de renormalization et à ses applications,Presses Universitaires de Grenoble, (1975).

Domb and Green, Phase transitions and critical phenomena, Vol. 1 to 6, Academic Press.

Ma, S.K., Modern theory of critical phenomena, Benjamin (1976)

Wilson, R.G. Kogut, J., Phys. Rep. 12 C, (1974) 2.

Kadanoff, L.P., Physics 2, (1966) 263.

Fisher, M.E., Rev. Mod. Phys. 46, (1974) 597.

Solyom, J., Adv. Phys. 28, (1979) 201.

Parisi, G., Brezin, E., Phys. Rep. 49, (1979) 221.