Mem. Fac. Lit. & Sci., Shimane Univ., Nat. Sci., 4, pp. 62–70,
1 text-fig., March 15, 1971

Theory of Equilibrium Static Phenomena Near Critical Points

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(Received October 2, 1970)

The theory of static critical phenomena in systems at equlibrium is discussed. The nature of the classical phenomenological theory of Landau is explained. Critical point exponents β, γ, γ', δ,... obtained from the Landau theory differ from the results of the theory for Ising model and experimental results. Statistical evaluation of the order parameter is obtained by taking into account the fluctuation. Then the correlation effect is considered. These approaches make implicit use of the assumption that the free energy if expandable in power series in the order parameter. From the calculation of spatial fluctuation and long range correlation effect the validity of the Landau theory is discussed.

§ 1. Introduction

Change of phase—the boiling of water, the melting of iron—is a striking phenomena in matter. In many cases the properties of various phases seem quite dissimilar and separate, and transitions between them are abrupt. As the temperature is raised the properties of a liquid and the vapor in equilibrium become more and more similar until, at a particular temperature, the differences vanishes. The state at this temperature is the critical point. At room temperature iron has the spontaneous magnetization in the absence of magnetic field. As the temperature is raised this magnetization diminishes and suddenly disappears at a temperature of 770°C. This state of iron is called the Curie point. Similar phenomena are observed in many cases: Nêel point in antiferromagnetism, λ-point in liquid helium 4, and so on.

All these phenomena have in common that at a definite transition point a substance gains or loses all at once. In this respect they differ from the first order phase transitions, melting, evaporation, sublimation, in which the physical change is not sudden but take place by a small portion of the substance from one state to another.

More formally those transitions in which one or more first derivatives of the relevant thermodynamic potential change discontinuously as a function of their variables may be first order transitions. For a fluid it is appropriate to consider the Gibbs free energy G as a function of p and T; the specific volume $V=(\partial G/\partial p)_T$ and the entropy $S=-(\partial G/\partial \mathrm{H})_p$ are discontinuous across the vapor pressure curve. In a ferromagnet the equilibrium magnetization $M=-(\partial F/\partial H)_T$ where F is the Helmholtz free energy and H the magnetic field, changes abruptly st the field passes through zero when T is less than T_C.

On the other hand, transitions in which the first derivatives of the thermodynamic potential remain continuous while only higher order derivatives such as the compressibility, the specific heat or the susceptibility are divergent or change discontinuously at the transition point may conveniently be termed second order transitions (due to Ehrenfest) or continuous transitions. It is for such transitions we use the term critical point.

There are quite marked similarities between apparently very distinct phase transitions. Theoretical and experimental questions have much in common for all critical points. They are attested by the fact that they have been treated by very similar models and theories. These models and theories are based on the idea that phase transitions and critical points are brought about through the mutual cooperative interactions of many particles. The essential similarity of the early theory for the cooperative phenomena, the van der Waal theory of the liquid-vapor critical point, Curie-Weiss theory of ferromagnetism, the Bragg-Williams and Bethe theory of order disorder phenomena give an excellent qualitative picture of critical phenomena, but fail more and more seriously in their quantitative predictions as the critical point is reached. Their ultimate inadequcy is demonstrated with Onsager's[1] exact solution of the two dimensional Ising model of ferromagnetism.

§ 2. Thermodynamical Theory on the Second Order Phase Transitions —— The Landau Theory

The important theoretical concept for the second order phase transition is the order parameter[2] P. The parameter is a numerical measure of ordering built up in the vicinity of the critical point. For example, in a ferromagnetic crystal with an easy axis of magnetization along the z direction, a suitable order parameter P is the statistically averaged z component of magnetization $M(\boldsymbol{r})$ at the point $\boldsymbol{r}$. The order parameter may vanish above the critical point, but it must be nonzero in the region below T_c and approches zero cotinuously as $T \rightarrow T_c$ from below.

A relatively simple phenomenological theory, which is useful to understand general behavior near critical point, was provided by Landau[3] who has taken into account the spatial fluctuation of the order parameter P. Although the theory does not agree with experimental observations very close to the critical point, it serves to realize a qualitative behavior except in the vicinity of critical point.

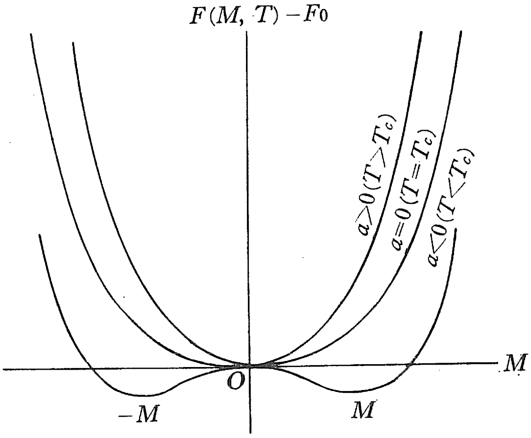
A dominant characteristic of the critical phenomena is the large increase of the microscopic fluctuations in the vicinity of critical point. The fluctuation of magnetization, energy can reach effectively macroscopic magnitudes, and correspondingly, the second thermodynamic derivatives (specific heats, susceptibilities, etc.)

The continuity of the change of state for a second order phase transition is expressed mathematically by the fact that near a transition point order parameter, say, magnetization M can take arbitrary small values. In the following description, we prefer magnetization of a ferromagnet as the order parameter. Considering now the neighborhood of a transition point, it would seem reasonable to expand the free energy per unit volume of a ferromagnet in a power series in the magnetization :

$$F(M, T) = F_0 + a(T)M^2 + b(T)M^4 + \dots \qquad (1)$$

The first term F_0 represents the free energy which would exist were it not for magnetization. Direct spin-spin interaction produce the remaining term in F. Because these interactions do not change when we change the sign of M, these terms contain no odd terms. This is the origin of the term M^2 and M^4 in Eq. (1).

As regards the coefficients a of the second order term, it is easy to see that it vanishes at the transition point. Indeed, for the disordered phase the minimum of F must correspond to the value $M=0$; this obviously requires $a>0$. Conversely, on the other side of transition point, in the ordered phase, the equilibrium state (for the minimum of F) must correspond to nonzero value of M; this is only possible for $a<0$. Figure shows the form of the function F for $a \gtreqless 0$. Being positive on one side of the transition point and negative on the other, $a(T)$ must vanish at the point itself :



$$a(T_c)=0. \tag{2}$$

But for the transition itself to be a stable state, i. e., for F to be a minimum there as a function of M (at $M=0$), it is necessary that the third order term must also vanish at this point, and fourth order term must be positive :

$$b(T_c)>0. \tag{3}$$

Being positive at the transition point, the coefficient b is, of course, also positive in its neighborhood. The transition point is determined by Eq. (2). Near the transition point we can write

$$a(T)=a'(T-T_c), \tag{4}$$

where $a'=\left.\frac{\partial a}{\partial T}\right|_{T=T_c}$ is a constant.

The dependence of M on temperature near T_c in the ordered phase is determined by the condition that F should be a minimum as a function of M. Equating the derivative $\partial F/\partial M$ to zero,

we obtain

$$M(a+2bM^2)=0,$$

whence

$$M=0 \quad \text{and} \quad M^2=-\frac{a}{2b}=\frac{a'}{2b}(T_c-T). \tag{5}$$

(the solution $M=0$ corresponds to the disordered phase.)

Hence near T_c the system can produce large scale fluctuations in M with relatively little coast in free energy which if fourth order in M.

We now follow the thread of the Landau theory and derive the relations between the critical phenomena.

First consider the temperature dependence of magnetization M at zero magnetic field. According to Eq. (5) the magnetization just below T_c is proportional to $(T_c-T)^{1/2}$. We shall obtain and use several results of this type. we define a critical index β by the condition that the order parameter go to zero as $(T_c-T)^{\beta}$. We have just known that in the Landau theory $\beta=\frac{1}{2}$.

To continue the discussion of critical exponents, we insert the interaction $-MH$ between the magnetization and the applied magnetic field H — assumed parallel to the easy axis z — to F, and minimize the free energy, we obtain

$$M(2a+4bM^2)=H. \tag{6}$$

At $T=T_c$, then $a=0$ so that

$$M=(H/4b)^{1/3}. \tag{7}$$

Another critical exponent δ is defined as $M\sim H^{\delta}$ and hence $\delta=\frac{1}{3}$.

The susceptibility $\chi=(\partial M/\partial H)_T$ is obtained by differentiating Eq. (6) with respect to H. At zero magnetic field, the resulting susceptibility may be evaluated as

$$\chi=\begin{cases}\dfrac{1}{2a}=\dfrac{1}{2a'(T-T_c)} & \text{for } T>T_c,\\[2ex] -\dfrac{1}{4a}=\dfrac{1}{4a'(T_c-T)} & \text{for } T<T_c,\end{cases} \tag{8}$$

which is just the Curie-Weiss law. The magnetic susceptibility is seen to diverge both above and below T_c as $\chi\sim(T-T_c)^{-\gamma}$ for $T>T_c$; $\chi\sim(T_c-T)^{-\gamma'}$ for $T<T_c$ and hence $\gamma=\gamma'=1$.

The final thermodynamic properties in the specific heat at zero magnetic field is given by thermodynamics as

$$C_H=-T\frac{\partial^2 F}{\partial T^2}\bigg|_{H=0} \tag{9}$$

But, at $H=0$, we can use Eq. (5) to find

$$F=\begin{cases}F_0 & \text{for } T>T_c,\\[1ex] F_0-\dfrac{a^2}{4b} & \text{for } T<T_c.\end{cases} \tag{10}$$

The extra term in the free energy below T_c produces a constant term in specific heat. Thus, there is a discontinuity of amount

$$\Delta C=\frac{a'^2}{2b}T_c, \tag{11}$$

The Landau theory does not work for Ising models, that is, the theoretical study of Ising model has obtained the values of all the critical indices. Other theoretical[4] and experimental[5] studies on the critical exponents differ with those from the Landau theory. We have seen above that The Landau theory neglects fluctuations, hence it has the range of validity.

§ 3. Statistical Averages of Magnetization

The free energy F of a ferromagnet can be assumed to depend on the magnetization for no external field as in Eq. (1) and from Eq. (4)

$$F = F_0 + a'(T-T_c)M^2 + b\,M^4 \tag{12}$$

for temperature T near the Curie temperature T_c ; a′ and b are positive and approximately temperature-independent.

We derive the temperature dependence of average magnetization $M(T)$.

The probability of observing a magnetic moment density between M and $M+dM$ is proportional to exp $(-F/kT)\,dM$. Thus the most probable magnetization M_0 is the one for which $F(M, T)$ has a minimum as a function of M. When we neglect the effect of fluctuations, the average magnetization

$$M = \int M\mathrm{e\,xp}\,(-F/kT)dM \Big/ \int \exp\,(-F/kT)\,dM \tag{13}$$

is equal to M_0. This is because the distribution function $\exp(-F/kT)$ is large in the neighborhood of M_0. From the condition that $F(M, T)$ be a minimum, we find

$$M_0 = \begin{cases} \left[\dfrac{a'}{2b}(T_c-T)\right]^{1/2} & \text{for } T < T_c \\ 0 & \text{for } T > T_c \end{cases} \tag{14}$$

as in Eq. (5)

Next, to obtain an estimate of the fluctuations on the calculation $\langle M\rangle$, we consider the difference $\langle M\rangle - M_0$ for two cases.

(a) Introduce a dimensionless parameter u for $T<T_c$ by

$$M = M_0 + \left[\frac{kT}{2a'(T_c-T)}\right]^{1/2} u, \tag{15}$$

where

$$M_0 = \left[\frac{a'}{2b}(T_c-T)\right]^{1/2}. \tag{17}$$

Then, expanding $F(M, T)$ about the value M_0, we find

$$F = F_0 - \frac{a'^2}{4b}(T_c-T)^2 + kT\left(u^2 + \frac{u^3}{A} + \frac{u^4}{4A^2}\right), \tag{16}$$

with

$$A = [a'^2(T_c-T)^2/bkT]^{1/2}. \tag{17}$$

With this new variable, we find for the fractional fluctuation from Eq. (13),

$$\frac{\langle M\rangle - M_0}{M_0} = \frac{\int_{-A}^{\infty} u \exp[-(u^2+u^3/A+u^4/4A^2)]\, du}{\int_{-A}^{\infty} \exp[-(u^2+u^3/A+u^4/4A^2)]\, du}. \tag{18}$$

Exact evaluation of these integrals would be impossible. However, in the limit $A \gg 1$, we have, to the first order in $1/A$, that

$$\int_{-A}^{\infty} u \exp\left[-\left(u^2+\frac{u^3}{A}+\frac{u^4}{4A^2}\right)\right] du \approx -\frac{1}{A}\int_{-A}^{\infty} u^4 \exp(-u^2) du \approx -\frac{1}{A}\int_{-\infty}^{\infty} u^4 \exp(-u^2) du. \tag{19}$$

Thus, in this limit $A \gg 1$, we obtain

$$\frac{\langle M\rangle - M_0}{M_0} \approx \frac{-\int_{-\infty}^{\infty} u^4 \exp(-u^2) du}{A^2 \int_{-\infty}^{\infty} \exp(-u^2) du} = -\frac{3}{4A^2} = -\frac{3bkT}{4a'^2(T_c-T)^2} \tag{20}$$

(b) Define a second parameter v for $T > T_c$ by

$$M = \left[\frac{kT}{a'(T-T_c)}\right]^{1/2} v; \tag{21}$$

then

$$F = F_0 + kT\left(v^2 + \frac{v^4}{A^2}\right), \tag{22}$$

and hence, we find for the fluctuation

$$\langle M\rangle = \left[\frac{kT}{a'(T-T_c)}\right]^{1/2} \frac{\int_0^{\infty} v \exp[-(v^2+v^4/A)]\, dv}{\int_0^{\infty} \exp[-(v^2+v^4/A^2)]\, dv}, \tag{23}$$

where A is defined in Eq. (17). In the limti $A \gg 1$, we obtain

$$\langle M\rangle \approx \left[\frac{kT}{\pi a'(T-T_c)}\right]^{1/2}. \tag{24}$$

In the presence of a magnetic field H, we add a term $-MH$ to F. Thus the average magnetization above Curie temperature is given by

$$\langle M(H)\rangle = \left[\frac{kT}{a'(T-T_c)}\right]^{1/2} \frac{\int_0^{\infty} v \exp\{-(v^2+vH/[kTa'(T-T^c)^{1/2}\}\, dv}{\int_0^{\infty} \exp(-v^2) dv}, \tag{25}$$

where terms of order $1/A \ll 1$ have been neglected. Thus to first order in H,

$$\langle M(H)\rangle = \frac{H}{2a'(T-T_c)} \qquad \text{(Curie-Weiss law).} \tag{26}$$

The susceptibility is given by

$$\chi = \left.\frac{\partial\langle M\rangle}{\partial H}\right|_{H=0} = \frac{1}{2a'(T-T_c)}. \tag{27}$$

This result have already been obtained from thermodynamics in Eq. (8). The Landau theory neglects fluctuations. The magnetization fluctuate considerably in actual ferromagnet. However, some of these fluctuations may be removed by averaging the order parameter over a suitable region. For the Landau theory to work well, fluctuations in the magnetization must be small in comparison with the magnetization itself. We have then,

$$M_0 - \langle M\rangle \ll M_0. \tag{28}$$

This necessary condition becomes from Eq. (20) near T_c

$$\frac{36kT_c}{4a'^2(T_c-T)^2} \ll 1, \tag{29}$$

so that the Landau theory could only be correct if

$$|\varepsilon| = \left|\frac{T-T_c}{T_c}\right| \gg \left(\frac{3K}{8\Delta C}\right)^{1/2}, \tag{30}$$

where ΔC is the jump in the heat capacity per unit volume predicted by the Landau theory in Eq. (11).

§ 4. Critical Fluctuations and Long-Range Correlations

Next consider correlation of fluctuations in the magnetization. The fluctuation in the magnetization $M(r)$ is given by $[M(r) - \langle M(r)\rangle]$. The point to be studied is how the deviation of M from its average at one point in the material coupled to the similar fluctuations in the neighboring region. The mathematical description of this correlation is given by the correlation function

$$f(r, r') = [M(r) - \langle M(r)\rangle][M(r') - \langle M(r')\rangle] \tag{31}$$

and the susceptibility is given by

$$\chi = (kT)^{-1}\int f(r, r')dr'. \tag{32}$$

There are useful correlation function expressions for thermodynamic derivatives. For example, if $E(r)$ is the energy density, the specific heat at fixed H is given by

$$C_H = \int \langle [E(r) - \langle E(r)\rangle][E(r') - \langle E(r')\rangle]\rangle\, dr' \tag{33}$$

To calculate the correlation function (31) we follow the style in the text by Landau and Lifshitz[3]. We may write the total free energy of the body as the integral

$$F_t = \int F\,dV,$$

taken over the total volume of the body, where F denotes as yet the free energy per unit volume. Let $\langle F\rangle$ be the average value of F, constant throughout the body. As a result of fluctuation F become, together with the magnetization, a quantity which changes from point to point of the body and

$$\varDelta F_t = \int (F-\langle F\rangle)\,dV. \qquad (34)$$

We expand $F-\langle F\rangle$ in power of $M-\langle M\rangle$ at constant temperature. The first term in the expansion is proportional to $M-\langle M\rangle$, and vanishes on integration over the volume, owing to the relation $\int M\,dV = \int \langle M\rangle dV$, The second order term is of the form $a(M-\langle M\rangle)^2$, where the positive coefficient a vanish at the critical point and is small near to it. The coefficient of the third order term is also small near the critical point, so that one ought to take the fourth order terms into account.

The point is that we have to consider the inhomogeneous magnetization. Then, the expansion of F may contain not only the different power of magnetization itself, but also its spatial derivatives of various orders. Since the body is isotropic, the first derivatives can only enter into the expansion of the magnetization as the scalar combination $(\varDelta M)^2$, and the second as the combination $\varDelta M$ (where $\varDelta$ is the Laplacian operator). The integral of the term of the form const. $\varDelta M$ over the volume transforms into an integral over the surface of the body, irrelevant surface effect, while integral of the term $M\varDelta M$ transforms into the integral of $(\varDelta M)^2$. Thus we can assume

$$F-\langle F\rangle a(M-\langle M\rangle)^2+c(\varDelta M)^2, \qquad (35)$$

where c is a positive constant due to the exchange interaction ; the constant need by no means vanish at the critical point and hence is not small near it.

The study of fluctuations of the Fourier components of the magnetization near the critical point is of much greater interest. If we expand $M-\langle M\rangle$ as a Fourier series in the volume V of the body, it takes the form

$$M-\langle M\rangle = \sum_{\mathbf{k}} M_{\mathbf{k}} \exp(i\boldsymbol{kr}) \qquad (36)$$

where the components of the wave vector $\boldsymbol{k}$ take positive and negative values, and the coefficients

$$M_{\mathbf{k}} = \frac{1}{V}\int (M-\langle M\rangle)\exp(i\boldsymbol{kr})\,dV$$

are connected by the relation

$$M_{-\mathbf{k}} = M_{\mathbf{k}}^*$$

which follows from the reality of $M-\langle M\rangle$. Substituting Eq. (36) into Eq. (35) and integrating over the volume we get

$$\Delta F_t = V \sum_{\mathbf{k}} (a+ck^2) M_{\mathbf{k}} M_{\mathbf{k}}^* . \tag{37}$$

Each of the terms of this sum involves only one of the $M_{\mathbf{k}}$: hence the the fluctuations of the different $M_{\mathbf{k}}$ are statistically independent. $M_{\mathbf{k}} M_{\mathbf{k}}^* = |M_{\mathbf{k}}|^2$ enters twice into Eq. (37) from $\pm \boldsymbol{k}$. so that the probability distribution for the fluctuation of the magnetization may be given by the Boltzmann factor $\exp[-2V(a+ck^2)|M_{\mathbf{k}}|^2/kT]$. Hence we obtain the required mean sqare fluctuation

$$\langle M_{\mathbf{k}} M_{\mathbf{k}}^* \rangle = \frac{kT}{2V(a+ck^2)} \tag{38}$$

Note that this formula holds only for values of wave vector $\boldsymbol{k}$ which are not too large, because the expansion (35) contains only the lower spatial derivatives of the coordinate. Thus in the limit $k \to 0$ Eq. (38) coincide with Eq. (32), for $2a = 1/\chi$. Now that as $T \to T_c$ $1/\chi$ approaches to zero, the right side of Eq. (38) is inversely proportional to k^2 : This implies that the long wave length fluctuation of the magnetization increase unusually large with tending to T_c. These macroscopic fluctuation—critical fluctuation would be the origin for the many sort of singularities associated with the second order phse transition. This is, indeed, equivalent to the appearance macroscopic long range correlations. To recognize the situation, by means of an inverse Fourier transformation to Eq. (38), we find

$$\langle [M(\boldsymbol{r}) - \langle M(\boldsymbol{r}) \rangle][M(\boldsymbol{r}') - \langle M(\boldsymbol{r}') \rangle] \rangle = \frac{1}{V^2} \sum_{\mathbf{k}} \langle M_{\mathbf{k}} M_{-\mathbf{k}} \rangle \exp[-i\boldsymbol{k}(\boldsymbol{r}-\boldsymbol{r}')]$$

$$= \frac{kT}{8\pi c} \frac{\exp(-|\boldsymbol{r}-\boldsymbol{r}'|/\xi)}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{39}$$

where $\xi = \sqrt{c/a} = \sqrt{2c\chi}$ is a measure for the range of correlation :

$$\xi = \begin{cases} \left[\dfrac{c}{a'(T-T_c)} \right]^{1/2} & \text{for } T > T_c, \\ \left[\dfrac{c}{2a'(T_c-T)} \right]^{1/2} & \text{for } T < T_c. \end{cases} \tag{40}$$

As $T \to T_c$ χ grew up exceedingly, the coherent length $\xi(\sim\sqrt{\chi})$ extend gradually, and finelly the long-range correlation of macroscopic scale will appear.

Correlation function (40) is also calculated by other method and a criterion for the validity of the Landau theory has been given in the paper by Kadanoff *et al*[6].

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