

## PHENOMENOLOGICAL THEORY OF SECOND-ORDER PHASE TRANSITIONS

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Submitted to JETP editor January 10, 1967

J. Exptl. Theoret. Phys. (U.S.S.R.) **52**, 1688–1706 (June, 1967)

A qualitative description of phase transitions permits one to draw some conclusions regarding the nature of the statistics in the vicinity of the critical point. In the vicinity of the transition all thermodynamic quantities can be expressed in terms of three unknown parameters, provided three assumptions are made: that the temperature fluctuations are uncorrelated, that moments of different magnitudes are uncorrelated, and finally the assumption of space similarity. Singularities are defined by a single parameter. It is shown that in the three-dimensional case the parameter can assume only two values.

**S**ECOND-ORDER phase transitions have been observed and experimentally investigated in ferromagnets and ferroelectrics, in binary alloys and in solutions, in the vicinity of the critical point, and in liquid helium (the  $\lambda$  point). The two-dimensional Ising model and the Kac-Uhlenbeck-Hemmer model have been studied theoretically. Some information has been obtained from computer calculations.

These studies revealed the general features of the behavior of various systems in the transition region. An attempt is therefore made in this paper to obtain all the information about a second-order phase transition in a system with an unknown interaction. It is merely assumed that the interaction radius is finite.

Section 1 describes the phase transition in a sample of finite dimensions. The concept of the phase-transition region is introduced. It is to this region that all the assumptions and conclusions of this paper refer. Outside the phase-transition region the usual methods of statistical physics apply.

The boundaries of the region are determined by the magnitude of the temperature fluctuations (Sec. 2). The physical significance of this magnitude is determined (the thermodynamic theory of fluctuations is not applicable here). A number of arguments are cited favoring the assumption of a gaussian behavior of the temperature fluctuations. This assumption specifies the temperature dependence of the correlation radius, and turns out to be practically equivalent to the well-known law of the logarithmic growth of the specific heat. At the transition point the correlation radius becomes infinite. This circumstance is related to a number of assumptions described in Sec. 3 which are in the final analysis equivalent to the similarity hypothesis.

These two hypotheses exhaust almost completely the content of the phenomenological theory. If in accordance with the meaning of the phase-transition region it is assumed that the nature of the statistics in the phase-transition region does not depend on the temperature, and outside this region it does not depend on the volume, then one can obtain a phenomenological theory described in Sec. 4 which is of course not exact, but simple and complete. Within the framework of this theory only the numerical values of three parameters remain unknown. The nature of the singularities (second-order phase transitions are usually classified by the nature of the singularities) is determined by a single parameter  $n$ .

The presentation of the theory is completed in Sec. 5. The hypothesis of the gaussian nature of the relative fluctuations of the magnetic moment makes it possible to formulate the complete system of equations of the phenomenological theory (the hypothesis of Sec. 4 is now no longer required) and to obtain limits on the possible values of the parameter  $n$ . In the three-dimensional case there are only two possibilities:  $n = 2$  and  $n = 3$ ; in the two-dimensional case  $n$  can assume seven values (2, 3, 4, 5, 6, 7, 8).

For simplicity the entire treatment is carried out for a two-dimensional and three-dimensional Ising model (the magnetic moment of the atom is  $\pm 1$ ) with an arbitrary interaction radius. The possibility of proceeding to a more general case is obvious.

## 1. PICTURE OF THE TRANSITION

We take a ferromagnet as an example of a many-particle system. Let  $m$  be the magnetic moment of the sample (per atom),  $N$  the number of atoms in

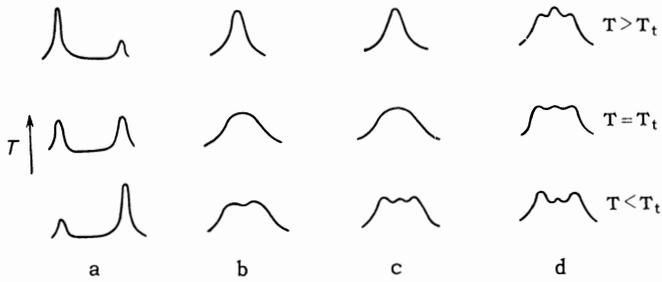


FIG. 1. Change in the distribution of the magnetic moment in the neighborhood of the transition point.

the sample, and  $p(m)$  the probability density for  $m$ . If the dimensions of the sample exceed the radius of action of the forces considerably, then the possible values of  $m$  will concentrate about the maxima of  $p(m)$ . Let  $f_1(m), f_2(m) \dots$  be the free energy per particle (or, more accurately, the thermodynamic potential expressed in terms of  $m$ ) in the neighborhood of the first, second, etc. maximum. If the Gibbs integral is split into a sum of integrals over regions about the configurations which yield the maxima of  $p(m)$ , then the usual arguments of statistical physics yield

$$p(m) = \alpha_1 e^{-Nf_1(m)/kT} + \alpha_2 e^{-Nf_2(m)/kT} + \dots, \quad (1)$$

where the coefficients  $\alpha_1, \alpha_2, \dots$  depend weakly (compared with the exponential) on  $N$  and  $T$ .

For  $N \rightarrow \infty$  the contribution to the sum (1) will only yield a maximum for which the free energy  $f(m)$  is minimal. The contribution of each hump (see Fig. 1a) will change with changing temperature. If there exists a temperature for which the contributions of any two humps turn out to be equal, then this temperature will generally speaking be a first-order transition point.

However, it can occur that some symmetry present in the sample will manifest itself in the symmetry of  $p(m)$  and will lead to the appearance of a series of symmetric and equally varying humps. In this case a sharp change in the nature of the distribution can only be related to a vanishing of the distance between the humps (see Fig. 1b). The corresponding temperature ( $T_t$  in Fig. 1b) can be a second-order transition point. In particular, if one takes for  $f(m)$  a very simple analytic expression consistent with the diagram 1b, then one obtains the phenomenological theory of second-order phase transitions due to Landau.<sup>[1]</sup> The maximum corresponding to the paramagnetic state may also remain below the transition point. This situation is depicted in Fig. 1c. If the equalization of the heights of all the three maxima does not coincide with the vanishing of the distance between the outermost maxima, then we have either a first-order transi-

tion of the type d in Fig. 1, or again a transition of the type b in Fig. 1.

The calculation of first-order transitions is complicated by the existence of two-phase regions and surface tension; however, the independent nature of the motion of each of the two maxima (for unbounded systems) makes it possible to utilize effectively the usual methods of statistical physics.

In first-order phase transition the configurations near each maximum always remain different. In second-order phase transitions there exists a region in which the difference between these configurations lies within the fluctuations and expansion (1) loses its meaning. However, it will be shown that this region has its own simple laws.

In order to define more clearly the boundaries of the region we divide the sample into pieces of dimension  $R$ . Let  $\bar{p}_R(m)$  be the distribution of moments for each such piece. Near the transition point the number of humps  $\bar{p}_R(m)$  (one or two, see Figs. 1 and 2) will depend on the values of  $m$  in neighboring regions and will change, depending on the choice of these values. The fluctuations of  $\bar{p}(m)$  are shown schematically in Fig. 2. In this figure the temperature difference between  $T$  and the transition point  $T_C$  is plotted in dimensionless units  $\tau = (T - T_C)/T_C$  on the ordinate, and the dimension of the piece  $R$  (the volume  $v$ ) on the abscissa. The curves indicate the form of  $\bar{p}(m)$  in various regions. For small  $\tau$  and  $R$  the shape of  $\bar{p}(m)$  is undetermined and the curves oscillate between the extreme values indicated by the dashed curves.

The number of humps becomes stable only for sufficiently large pieces for which one can neglect the surface energy. The dashed lines in Fig. 2 indicate the points at which the number of humps becomes definite.

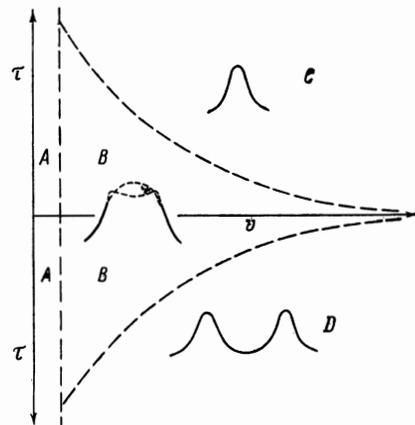


FIG. 2. The neighborhood of the transition point. Regions with identical physical phenomena.

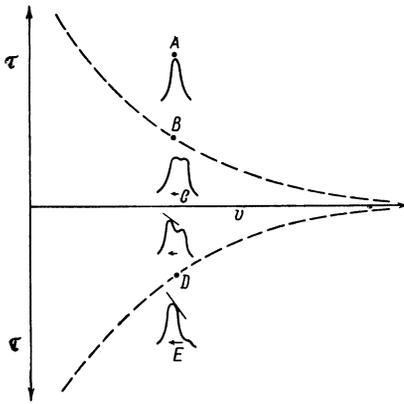


FIG. 3. The magnitude of the spontaneous moment in the neighborhood of the transition.

Instead of the instantaneous value  $\bar{p}(m)$ , one can take  $p(m)$ —the average over all the configurations of the surroundings. For the convenience of the discussion we divide the vicinity of the transition into the regions shown in Fig. 2. Above the transition point and for sufficiently large samples (region C) the possible values of  $m$  concentrate about  $m = 0$ . Below the transition point, also for sufficiently large  $R$  (region D), the maxima of  $p(m)$  correspond to the possible values of the spontaneous magnetic moment (there are two in the figure). In the intermediate region B the fluctuations of the moment exceed the distance between the maxima. Region A corresponds to samples with dimensions smaller than  $l$ —the radius of the interaction between the spins.

In order to exclude summation over the directions of the spontaneous moment, we place the magnetic substance in an external magnetic field, sufficiently small so as not to change the distribution in a finite region, but sufficiently large to prevent a change in the sign of the spontaneous moment of the entire sample. Let us introduce the following notation:  $m_0$  is the value of the specific spontaneous moment,  $v$  is the volume of part of the sample,  $V$  is the volume of the entire sample,  $H$  is the external field, and  $T$  is the temperature. The condition formulated above means that

$$vm_0H \ll kT \ll Vm_0H. \quad (2)$$

For  $V/v \rightarrow \infty$  there always exist for any real magnetic substance fields which satisfy both inequalities. Under these conditions the evolution of the distribution will have the form shown in Fig. 3. The horizontal arrows indicate the magnitude of the spontaneous moment. The thin slanting lines show the value of the factor  $\exp(-mH_0/kT)$  where  $H_0$  is the average field produced by the neighboring regions.

It is seen from this diagram that at the points A and E the values of the average moment  $m_0$  will simultaneously also be the values of the most probable moment. In other words, these values of the average moment will be stable, small perturba-

At the point C, on the other hand, the value of the average moment  $m_0$  corresponds to its least probable value. This means that turning on the field results in rotation of the pieces and rapid increase in the average moment from a value of zero to the value denoted in Fig. 3 by a horizontal arrow. The points B and D are the boundaries of the regions having various properties which have been described above. At those points  $\partial^2 f / \partial m^2 = 0$  for  $m = m_0$ , whereas  $\partial^2 f / \partial m^2 > 0$  for  $m = m_0$  (stability) at the points A and E, and  $\partial^2 f / \partial m^2 < 0$  for  $m = m_0$  (instability) at the point C.

The transition region can therefore be defined as follows; We place the system in an external field  $H$  satisfying condition (2). We choose any bounded region of volume  $v$ , set the value of the total moment  $mv$  of the region, and average (with a Gibbs weighting) over all remaining parameters of the system. The distribution  $p(m)$  calculated in this way is expressed in the form

$$p(m) = e^{-vf(m)}. \quad (3)$$

Simultaneous fulfillment of the conditions

$$\partial f / \partial m = 0, \quad \partial^2 f / \partial m^2 = 0, \quad (4)$$

will yield an equation for determining the boundaries of the phase transition in the given region  $v$ .

We note that the picture described above assumes the existence of two possible definitions of the spontaneous moment: the moment indicated on Fig. 3 by a horizontal arrow and the usual spontaneous moment. Outside the transition region both definitions coincide. Within the region the moments differ and can in various phenomena play a different role. Although  $p_v(m)$  has been defined for a finite region, it is not an analytic function of  $\tau$ . Indeed, the specific heat

$$\frac{\partial^2}{\partial \tau^2} \ln \int p_v(m) dm,$$

becomes, as is well known, infinite for  $\tau \rightarrow 0$ .

The presence of two humps means that a homogeneous state with a moment equal to the average value of the moment will be relatively improbable and unstable. If we were to prepare such a state by some means, then during the following instant the system would split, first into small domains with opposite spin directions, followed by the appearance of larger regions, and we would obtain a hierarchy of dimensions, the fluctuations of the mo-

ment not being smooth functions even on a large scale.

The dimension of the region of phase transition can be related to the magnitude of the correlation radius  $R_C$ . The concentration of the values of the moment about  $m = 0$  (region C) can occur only for  $R > R_C$  when the number of independent regions equal to  $R^3/R_C^3$  is large. For this very reason the dimension  $R$  of the region D is larger than  $R'_C$ —the correlation radius for deviations of the moment from the average value. In the region B the dimension of the sample  $R$  is less than the correlation radius.

## 2. MAGNITUDE OF THE TRANSITION REGION AND THE CORRELATION RADIUS

The phase-transition region is shown in Figs. 2 and 3 in terms of the variables  $\tau = (T - T_C)/T_C$  and  $R$ —the dimension of the sample. This is the region in which the nature of the statistics is the same as in the direct vicinity of  $\tau = 0$ . If we were to specify a definite value of  $\tau$  and change  $R$ , then the distribution of the magnetic moment would change sharply in passing through the value  $R$  equal to the dimension of the unordered regions for  $T < T_C$ . Therefore the boundary of the region can be specified by the condition  $R = R_C(\tau)$ .

If we specify the dimension of the sample  $R$  and change the temperature  $\tau$ , then because of the finiteness of the sample the phase transition will turn out to be smeared out over some range of temperatures. The singularities of the thermodynamic quantities at  $\tau = 0$  are due to a rapid increase in the number of degrees of freedom connected with long-wave fluctuations. The smearing for finite  $R$  occurs because of the absence of a contribution from degrees of freedom with a wavelength larger than  $R$ . For  $R = R_C(\tau)$  the dimensions of the fluctuations become equal to the dimensions of the sample and on further decrease of  $\tau$  new degrees of freedom do not appear. For the boundary of the phase-transition region we again obtain the condition  $R = R_C(\tau)$ .

In this section we estimate the magnitude of the temperature smearing  $\Delta\tau$  as a function  $\Delta\tau(R)$  of the dimensions of the region  $R$ . As has been shown above, for a given  $\tau$  the correlation radius  $R_C$  is equal to that value of  $R$  for which  $\tau = \Delta\tau$ . Therefore  $R_C$  is obtained from the condition  $\Delta\tau(R_C) = \tau$ .

The subsequent discussions, like most of the other conclusions of this paper, are not rigorous proofs but merely arguments favoring certain assumptions. We shall therefore present three variants of one and the same argument:

a) One can make use of the relations of thermodynamic theory of fluctuations, but the temperature must be defined in terms of the values of the parameter  $\lambda$  for which the correlation radius  $R_\lambda$  is limited to several interatomic distances. Only in this case will the distribution of values of the parameter  $\lambda$  uniquely determine the temperature field. As the  $\lambda$  parameter one can apparently take arbitrary configurations of  $k$  spins  $\sigma(\mathbf{r}_k)$  ( $\sigma$  is the moment and  $\mathbf{r}_k$  is the coordinate of the atom) if all the spins lie within a small region and satisfy the conditions:

$$\sum_k \sigma(\mathbf{r}_k) = 0, \quad \sum_k \mathbf{r}_k \sigma(\mathbf{r}_k) = 0.$$

Let us calculate, for example, the correlation of the quantities  $\sigma_{k+1} - 2\sigma_k + \sigma_{k-1} \approx \partial^2 \sigma_k / \partial k^2$ . If  $G(\mathbf{r}) = \overline{\sigma_k \sigma_l}$  is the correlation of two spins, then the correlation

$$\frac{\overline{\partial^2 \sigma_k \partial^2 \sigma_l}}{\partial k^2 \partial l^2} = \frac{\partial^4 G(r)}{\partial r^4} \quad (5)$$

However slow the decrease of the function  $G(r)$  for  $\tau = 0$ , the correlation length

$$4\pi \int \frac{\partial^4 G}{\partial r^4} r^3 dr$$

is finite, and will therefore be cut off at atomic distances (there are no other parameters). Thus the overwhelming majority of independent parameters characterizing any small region will not be correlated with the same parameters of another region.

The temperature fluctuations inside  $R_\lambda$  will be  $(\Delta\tau)^2 = (\partial\lambda/\partial\tau)^{-2} (\Delta\lambda)^2$ . The temperature fluctuations in the entire sample are obtained by dividing this expression by the number of independent regions  $v/v_\lambda$ ; we obtain

$$(\Delta\tau)^2 = a/v, \quad a = v_\lambda (\partial\lambda/\partial\tau)^{-2} (\Delta\lambda)^2. \quad (6)$$

The values entering in  $a$  are assumed to refer to a small region and are not correlated with neighboring values. In an infinite sample they will be the same as in a granule of volume  $v_\lambda$  and can therefore have no singularities for  $\tau \rightarrow 0$ . In other words,  $a$  does not depend on  $\tau$  and  $R$  and is a constant.

b) No singularities of thermodynamic quantities can be observed in a finite sample, even if only because of the fluctuations of these quantities. Therefore all singularities are connected with larger scales. But these scales have comparatively few degrees of freedom (the density of states is proportional to the square of the wave number). If there are singularities of the magnetization or specific heat, then this means that long-wave vibra-

tions make the largest contribution to these quantities. But the temperature fluctuations in a system of independent or weakly coupled degrees of freedom will be the same ( $\approx T$ ) for any degree of freedom; this follows from the Gibbs distribution. The contribution of long-wave vibrations will in this case be negligibly small. The fluctuations of the average temperature will be inversely proportional to the number of degrees of freedom, i.e., to  $R^3$ , and we shall again obtain (6).

We note that in a system consisting of independent degrees of freedom there can be no phase transition; therefore the long-wave fluctuations must be coupled. However, one might expect that the temperature fluctuations per degree of freedom will not change appreciably on this account and the contribution of long-wave fluctuations will be small, as before.

The following hypothesis that the smearing temperature remains constant becomes thus likely; the (temperature) width of the transition region coincides with the magnitude of the temperature fluctuations, and these fluctuations do not change when the sample is split into a large number of interacting parts.

We have not defined here the concept of temperature fluctuations, but the formulation does not depend on this definition. The meaning of the hypothesis is that long-range correlations do not affect the temperature smearing.

As was shown at the beginning of this section, at the boundary of the transition region the distance to the transition point is equal to the magnitude of the temperature smearing ( $\tau = \Delta\tau$ ), and the dimension of the sample  $R$  is close to the correlation radius  $R_C$  ( $R = R_C$ ). Substituting these two relations in (6), we obtain expressions for the volume of the correlation region  $v_c$ :

$$\tau^2 = a/v_c. \quad (7)$$

An exact formulation of the temperature smearing hypothesis is: the boundaries of the transition region defined by the conditions  $\partial f_V/\partial m = \partial^2 f_V/\partial m^2 = 0$  (see Sec. 1) are described by the dependence  $\tau^2 v = a$ .

We note that the conclusion described above is not exact, although it yields the right result. Equation (6) is valid inside the phase-transition region, and outside this region it coincides with the corresponding formula of the thermodynamic theory of fluctuations; however, the magnitude and meaning of the constants in these two formulas are different [for details see c) below].

As will be shown in the next section, the hypothesis proposed above is practically equivalent to the

well-known law of the logarithmic increase of the specific heat in the vicinity of the critical point. This equivalence can be explained with the aid of the following simple considerations. The temperature smearing  $\Delta\tau$  is connected with the fluctuations of the total magnetic moment  $M$  by the relation

$$\overline{(\Delta\tau)^2} = (\partial M/\partial\tau)^{-2} \overline{M^2}.$$

According to the thermodynamic theory of fluctuations  $\overline{M^2} = kT_C \partial M/\partial H$  ( $H$  is the magnetic field,  $T_C$ —the Curie point, and  $k$ —the Boltzmann constant). Making use of the well-known thermodynamic identity

$$C_H - C_M = T(\partial M/\partial T)^2 (\partial M/\partial H)^{-1},$$

we obtain:

$$\overline{(\Delta\tau)^2} = k/(C_H - C_M).$$

Here  $C_M$  and  $C_H$  are total heat capacities, not the specific heats. Constant  $a$  means that the difference between the specific heats  $C_{H=0} - C_{M=0}$  for  $\tau > 0$  and  $v < v_c$  is constant. But  $C_{H=0}$  is the heat capacity of a sample with constant spontaneous magnetic moment, and  $C_{M=0}$  is the heat capacity of a sample consisting of two halves with opposite directions of the spontaneous moment (the surface energy prevents further division). One can therefore expect that  $C_{M=0}$  is equal to  $C_{H=0}$  for a sample of half the volume. The fact that  $a$  is constant means that the dependence of  $C_{H=0}(v)$  on the volume  $v$  satisfies the relation

$$c(v) - c(v/2) = a = \text{const.} \quad (8)$$

Applying this relation to  $v/2$ ,  $v/2^2$ , etc.  $n$  times, we obtain;  $c(v) = an + c(v/2^n)$ . Or, assuming  $v = 2^n v_0$ , where  $v_0$  is a small constant volume, and expressing  $n$  in terms of  $v$ , we find that

$$c(v) = a \log_2 \frac{v}{v_0} + c(v_0).$$

We note that this argument is similar to the method employed by Buckingham<sup>[2]</sup> in his discussions. The increase of the heat capacity on increasing the volume  $v$  will stabilize at  $v$  equal to double the volume of the correlation sphere  $v_c$ , since for  $v > 2v_c$  and  $\tau > 0$  in the state with  $H = 0$  there is no spontaneous moment (we assume that in the regions  $v_c$  the spontaneous moments are not zero, but are independent and  $c_{H=0} - c_{M=0} = c(v) - c(v/2) = 0$ ). Denoting the specific heat of an infinite sample by  $c$ , we obtain

$$c = c(2v_c) = a \log_2 \frac{2v_c}{v_0} + c(v_0).$$

Substituting here the value of the correlation radius  $R_C$  from (7), we find finally:

$$c = A \ln \tau + B_+, \quad \tau > 0, \quad (9)$$

where  $A$  and  $B_+$  are constants (do not depend on  $\tau$ ).

Below the transition point ( $\tau < 0$ ) all arguments refer to the deviation of the moment from its average value  $m_0$  equal to the value of the spontaneous moment (per atom) of an infinite sample. Therefore, instead of  $c_{M=0}$  one must take everywhere  $c_{M=m_0}$ . In addition, the equality  $c_{H=0} = c_{M=m_0}$  will occur for  $v \approx v_c$ . Therefore relation (8) will cease to hold for  $v = v_c$ , and not for  $v \approx 2v_c$  as in the case  $\tau > 0$ . Instead of (9), we obtain

$$c = A \ln |\tau| + B_-, \quad \tau < 0, \quad (10)$$

where  $A$  and  $B_-$  are constants (do not depend on  $\tau$ ), and  $B_+ - B_- = A$ .

This conclusion takes into account the specific characteristics of the phase transition, but takes no account of the existence of a nonzero average magnetic moment. In order to allow for the interaction of distant regions by means of the average magnetic moment, one can use self-consistent field type methods (the Bragg-Williams or Curie-Weiss methods) or Landau's theory. These methods yield for the jump in the specific-heat values which are several times larger than that calculated above [ $A$  in (10) can be taken from experiment] and of opposite sign.

Thus the observed jump of the specific heat consists of two differing parts of opposite sign. In particular, the jump can vanish, as in the two-dimensional Ising model where the Kramers-Wannier symmetry ensures the symmetry of the specific-heat peak.

c) In statistical physics the temperature is defined as the Gibbs distribution parameter. Equilibrium systems are Gibbs distributions, and there are therefore no temperature fluctuations in such systems.

However, any real equilibrium is only approximate; therefore, we make use actually of the concept of the local temperature defined without allowance for the interaction of the system with the surroundings. The local temperature can be meaningful, for example, in a case when the temperature of different regions of the sample is different, but for sufficiently small volumes the equilibrium dependence of the parameters on the temperature is preserved.

Taking into account the different corresponding relaxation times, we can also in the equilibrium case relate part of the fluctuations with a change of the "temperature" of a small region. Here, as in the thermodynamic theory of fluctuations,<sup>[1]</sup> it is

natural to assume that the relationship between the local value of the parameters and the local "temperature" coincides with the temperature dependence of the mean values of these parameters. In particular, if one defines the temperature in terms of the energy of the system, then one obtains for the magnitude of the temperature fluctuations<sup>[1]</sup>

$$\overline{(\Delta\tau)^2} = \frac{k}{c_v} \frac{1}{v}, \quad (11)$$

where  $v$  is the volume of the region and  $c_v$  is the specific heat.

In the vicinity of the transition point there exists for sufficiently large regions (but outside the region of applicability of the thermodynamic theory of fluctuations) an uncertainty in the value of the local temperature which is considerably greater than (11) and related to the indefinite nature of the concept of the "temperature of a small region" in the case when this region interacts intensively with the surroundings. Neglecting the interaction, we introduce an error of the order of

$$\overline{(\Delta\tau)^2} = \frac{(kT)^2}{(\Delta E_{\text{int}})^2} = \frac{k}{c_{\text{int}} v}, \quad (12)$$

where  $E_{\text{int}}$  is the interaction energy and  $c_{\text{int}}$  is the specific heat connected with this energy. In deriving (11) and (12) use is made of the Gibbs distribution; neglecting the interaction energy, we cannot reconstruct the Gibbs distribution from the distribution of the parameters within the region with an accuracy greater than (12).

Within the phase transition region the interaction of a small portion of the sample with the surroundings can be described as follows. The surroundings determine the direction of the spontaneous moment and the choice of the maximum of the double-humped distribution shown in Fig. 3. The interaction energy is connected with the deviations of the moment from the most probable value in the vicinity of this maximum. Since the vibrations close to one maximum give the regular part of the specific heat, it can be expected that  $c_{\text{int}}$  tends to a constant for  $v \rightarrow \infty$ , unlike  $c_v$  in (11) which is related to jumps between the humps.

Dividing the region into halves, we obtain from the relation

$$E(2v) = 2E(v) + E_{\text{int}}$$

for the specific heats ( $E_{\text{int}}$  is the energy of one half in the uniform field produced by the other half; therefore  $E_{\text{int}} \sim v$ )

$$c(2v) - c(v) \approx c_{\text{int}} = \text{const.} \quad (13)$$

From this relation we obtain, as in the previous

subsection, a logarithmic dependence of  $c_V$  on  $v$ .

The exponent in expression (7) has been obtained by Widom,<sup>[3]</sup> Pokrovskii and Patashinskiĭ,<sup>[4]</sup> and Kadanoff<sup>[5]</sup> from the assumption of the logarithmic nature of the specific-heat divergence. They also assumed that the Essam-Fisher-Widom<sup>[6]</sup> relations are valid and made use of similarity concepts. Calculations have also been carried out<sup>[7]</sup> of the temperature dependence of the correlation radius which are close to the method used in this paper.

In this connection we note that the main result of this work as far as the  $v_C(\tau)$  dependence is concerned consists of two theses: first—that the coefficient  $a$  in (7) contains no logarithmic and similar weak divergences, second—that relation (7) follows to some extent from the general properties of many-particle systems, and it is therefore logically simpler to consider it primary rather than derive it from the logarithmic behavior of the specific heat and the relations of<sup>[4, 5, 7]</sup>

The content of this section includes the main conclusions which can be reached on the basis of the hypothesis that the temperature smearing is constant, without additional assumptions. These conclusions—the exponents in the power relations of the correlation length and partly the specific heats—do not depend on any micro- or macroscopic characteristics of the material and differ in this respect from the results which will be obtained in the following sections.

### 3. NATURE OF THE STATISTICS IN THE VICINITY OF THE CRITICAL POINT AND THE CORRELATION FUNCTION

For  $\tau \rightarrow 0$  the correlation radius  $R_C$  becomes infinite. There appears an unbounded hierarchy of scales. Under these conditions one can expect that for distances  $R$  much larger than the interaction radius and much smaller than  $R_C$  the nature of the statistics does not depend on the choice of scale—a similarity region appears. The insensitivity of the correlation function to a choice of scale can only be assured by a power dependence on  $R$ . The similarity hypothesis can be justified to some extent, the nature of the considerations depending considerably on the method of introducing the similarity. The derivation of the power dependence of the correlation function will also differ. We shall cite three variants of this derivation.

a) In the Kolmogorov theory of turbulence<sup>[8]</sup> (the connection between the theory of turbulence and the problem of the phase transition was pointed out by Patashinskiĭ and Pokrovskii<sup>[9]</sup>) the accepted picture is of an energy flux from large to small

scales via intermediate scales. On the whole coupling of large scales is accomplished only by means of a scale-independent constant—the energy flux. For small scales—on the boundary of the turbulence region—the energy flux vanishes.

In the region of a phase transition there is an analogous constant—the part of the heat capacity which is connected with the interaction energy, or the change in the specific heat when the volume of the system is doubled. The dimension of this constant is that of the free energy  $f$  divided by  $\tau^2$ , and the dimension of  $\tau^2$  is according to (1)  $[v]^{-1}$ . If the free energy (more accurately, its dimension) is of the form  $f \approx bm^{2n}$ , then we obtain for the correlation  $G(r) = \overline{m_1 m_r}$

$$\overline{[m_1 m_r]} = [f/\tau^2]^{1/n} [r]^{-1/n}$$

and consequently

$$G(r) \approx b/v^{1/n}; \quad (14)$$

$v = 4\pi r^3/3$  for the three-dimensional case,  $v = \pi r^2$  in the two-dimensional case, and  $b$  is a constant.

b) The power dependence (14) can also be obtained directly from similarity considerations. Let, for example, on increasing the scale by a factor of  $K$ , i.e., on increasing the distances between spins from  $r_0$  to  $Kr_0$ , the correlation between these spins decrease by a factor of  $L$ ; that is,

$$G(Kr_0) = G(r_0)/L. \quad (15)$$

Using Kadanoff's considerations,<sup>[5]</sup> one can show that for  $r_0 \rightarrow \infty$  the quantity  $L$  tends to a finite limit. We divide the sample into regions of dimension  $r_0$  and denote the spontaneous moment of the region by  $m_0$  and the direction of the spontaneous moment of the region  $K$  by  $\sigma_K = \pm 1$ . The correlation  $G(r_0)$  is close to  $m^2$  (see Sec. 4) and  $L$  is expressed in terms of the correlations  $\overline{\sigma_K \sigma_{K'}}$ . However large  $r_0$ , the responsibility for the singularities as  $\tau \rightarrow 0$  lies with the Ising model made up of the  $\sigma_K$ . For this reason the parameters of this model always lie in the phase-transition region, and  $\overline{\sigma_K \sigma_{K'}}$  cannot vanish for close regions.

If  $L$  is independent of  $r_0$ , then an  $n$ -fold application of (15) yields  $G(K^n r_0) = G(r_0)/L^n$ . Setting  $K^n r_0 = r$ , we obtain

$$G(r) = \frac{b}{r^{2\beta}}, \quad b = r_0^{2\beta} G(r_0), \quad 2\beta = \frac{\ln L}{\ln K}. \quad (16)$$

Expression (16) for the exponent  $2\beta$  has been obtained with the aid of analogous considerations in Khinchin's book<sup>[10]</sup> and in the work of Novikov and Stuart.<sup>[11]</sup>

c) For large systems one usually assumes the existence of a limiting value of the specific free

energy  $f(m)$  as a function of the specific moment  $m$ . It is correspondingly assumed that there exists a limiting distribution  $p(m) = \exp[-vf(m)]$ . It is assumed that for  $R \rightarrow \infty$  the quantity  $p(m)$  retains its form, i.e., the function  $p(m/\Delta)$  where  $\Delta = (m^2) = (\overline{m^2})^{1/2}$  has a limit. This means that  $vf[m/\Delta(v)]$  does not depend on  $v$ . Differentiating, we obtain  $f - vf'm\Delta'/\Delta^2 = 0$ . For a given  $R$  the solution is of the form

$$f = cm^{2n}, \quad (17)$$

where  $c$  is a constant, and  $2n = \Delta/v\Delta'$ . The expression for  $n$  yields an equation for  $\Delta$  whose solution is of the form  $\Delta^2 = \overline{m^2}$ )

$$\overline{m^2} = b'/v^{1/n}, \quad (18)$$

where  $b'$  is a constant.

Making use of relation (23) derived in Sec. 4, we obtain for the correlation the expression (14) with

$$b = (1 - 1/n)b'. \quad (19)$$

We note that the distribution satisfying the above requirements of the limiting behavior in the theory of probability is called stable (see, for instance, [12]).

#### 4. SIMPLEST VARIANT OF THE PHENOMENOLOGICAL THEORY

This section contains considerations in the spirit of [4-7]. However, use of (7) makes it possible not only to amplify the Essam-Fisher-Widom relations, [6] but also to construct a complete albeit not a rigorous theory.

a) Spontaneous magnetic moment. Let  $\sigma_k$  be the magnetic moment of the  $k$ -th atom. Below the transition point there appears for each atom a non-zero average magnetic moment  $m_0$ . The quantity  $\sigma_k$  can be represented in the form of a sum of  $m_0$  and a random deviation  $\Delta_k$ , i.e., one can set  $\sigma_k = m_0 + \Delta_k$ . The average value of  $\Delta_k$  is zero, and the average value of the product  $\overline{\Delta_k \Delta_l}$  for two atoms  $k$  and  $l$  decreases with increasing distance between the atoms and vanishes when this distance exceeds the correlation radius  $R_c$ . The vanishing of  $\overline{\Delta_k \Delta_l}$  for  $|\mathbf{r}_k - \mathbf{r}_l| > r_c$  means that

$$\overline{\sigma_k \sigma_l} = m_0^2 + \overline{\Delta_k \Delta_l} = m_0^2 \text{ for } |\mathbf{r}_k - \mathbf{r}_l| > r_c. \quad (20)$$

On the left-hand side we have the correlation function; therefore  $m_0^2 = G(r_c)$ . Let us take for  $G(r)$  expression (14), and making use of (7) express  $r_c$  in terms of  $\tau$ . We obtain

$$m_0 = (b^{1/2}/a^{1/n})\tau^{1/n}. \quad (21)$$

b) Fluctuations of the magnetic moment and the correlation function. Let us calculate the mean square of the total moment  $M$  of part of the ferromagnet—a circle of radius  $R$  in the two-dimensional case, or a sphere of radius  $R$  in the three-dimensional case:

$$\overline{M^2} = \sum_{k,l} \overline{\sigma_k \sigma_l} = \sum_{k,l} G(\mathbf{r}_k - \mathbf{r}_l).$$

The sum is taken over all  $\mathbf{r}_k$  and  $\mathbf{r}_l$  within the circle or the sphere. For regions smaller than  $R_c$  we find approximately ( $v$  is the volume of the sphere or the area of the circle)

$$M^2 = 4\pi v \int_0^R G(r) r^2 dr \text{ in the three-dimensional case}$$

$$M^2 = 2\pi v \int_0^R G(r) r dr \text{ in the two-dimensional case.} \quad (22)$$

Differentiating (22) with respect to  $R$  and setting  $M = mv$ , we find

$$G(r) = \frac{1}{3r^2} \frac{\partial(\overline{m^2} r^3)}{\partial r} \text{ in the three-dimensional case,}$$

$$G(r) = \frac{1}{2r} \frac{\partial(\overline{m^2} r^2)}{\partial r} \text{ in the two-dimensional case.} \quad (23)$$

Calculating  $\overline{m^2}$  from the distribution

$$p(m) = e^{-vm^{2n}}$$

and substituting in (23), we obtain the connection between the constant  $b$  of relation (14) and the constant  $c$  of (17):

$$b = \left(1 - \frac{1}{n}\right) \frac{\Gamma(3/2n)}{\Gamma(1/2n)} \left(\frac{1}{c}\right)^{1/n}. \quad (24)$$

c) Susceptibility. From the definition of the susceptibility  $\chi$  ( $v_c$  is the volume of the correlation sphere) we have above  $T_c$

$$\chi_+ = \int \overline{\sigma(0)\sigma(\mathbf{r})} d^3r = v_c \overline{m^2} \Big|_{r=r_c}. \quad (25)$$

Below  $T_c$  we have for a state with a given direction of the spontaneous moment  $m_0$

$$\begin{aligned} \chi_- &= \int [\overline{\sigma(0) - m_0}][\overline{\sigma(\mathbf{r}) - m_0}] d^3r \\ &= v_c (\overline{m^2} \Big|_{r=r_c} - m_0^2). \end{aligned} \quad (26)$$

The value of  $\overline{m^2}$  for  $r = r_c$  is obtained from (19), (20), and (7), and for  $m_0$  we take expression (9). For  $v_c = R_c^3$  we obtain:

$$\chi_+ = \left[ \frac{ba^{1-1/n}}{1-1/n} \right] \frac{1}{\tau^{2-2/n}}, \quad \chi_- = \frac{1}{n} \left[ \frac{ba^{1-1/n}}{1-1/n} \right] \frac{1}{\tau^{2-2/n}}. \quad (27)$$

The ratio of the susceptibilities depends on  $n$  only:

$$\chi_-/\chi_+ = 1/n. \tag{28}$$

In deriving (27) it was assumed that within the phase-transition region the correlation  $G(r)$  does not depend on  $\tau$ , while outside it  $G(r) = 0$  for  $\tau > 0$  and  $G(r) = G(r_c)$  for  $\tau < 0$ . This indicates an asymmetry between  $m$  for  $\tau > 0$  and  $m - m_0$  for  $\tau < 0$ , and as a result a different susceptibility above and below  $T_c$ .

d) Specific heat. The results of preceding sections make it possible to estimate the magnitude of the partition function. We divide the sample into regions of volume  $v_c$  where  $v_c$  is the volume of the correlation region. Let  $m$  be the magnetic moment of the region (calculated per spin),  $f(m)$  the specific free energy of the region, and  $v$  the volume of the sample. The values of the moment in various regions can be considered independent; therefore the partition function is

$$Z = \left[ \int e^{-v_c f(m)} d(v_c m) \right]^{v/v_c}. \tag{29}$$

For sufficiently small  $m$  above  $T_c$  the free energy  $f_+ = m^2/2\chi_+$ .

Below  $T_c$  there will in addition be the interaction energy of the average moment of the region and the spontaneous moment of the sample  $m_0^2/\chi_+$  ( $m_0$  increases from zero and we have therefore taken the high-temperature susceptibility). The total energy will be

$$f_-(m) = (m - m_0)^2/2\chi_- - m_0^2/\chi_+.$$

The energy is determined with an accuracy up to a constant, but this constant has no singularities in  $\tau$  since for  $m \neq 0$  there is no phase transition.

Substituting in (17) the expressions for  $f_+(m)$  and  $f_-(m)$ , we obtain for the specific free energy:

$$f_+ = -\frac{2a}{\tau^2} \ln[\pi k T_c v_c \chi_+], \quad f_- = -\frac{\tau^2}{2a} \ln[\pi k T_c v_c \chi_-] - \frac{m_0^2}{\chi_+} \tag{30}$$

Using (7), (21), and (27), we find an expression for the specific heat  $c$  (the plus and minus signs refer to  $\tau > 0$  and  $\tau < 0$  respectively):

$$c = A \ln \tau + B_+, \tag{31}$$

$$A = \frac{2(2n-1)}{na}, \quad B_+ = \frac{1}{na} + \frac{1}{a} \ln \left[ \frac{\pi k T_c b a^2}{(1-1/n)a^{1/n}} \right],$$

$$B_- = B_+ + \frac{2-2/n}{a} - \frac{1}{a} \ln n.$$

The relative jump in the specific heat

$$\frac{B_- - B_+}{A} = \frac{n}{2(2n-1)} \left[ 2 - \frac{2}{n} - \ln n \right] \tag{32}$$

depends only on  $n$ . The jump consists of two

parts—the energy gain  $m_0^2/\chi_+$  and on entropy loss  $\ln(\chi_-/\chi_+)^{1/2}$  equal to the logarithmic ratio of the spreads of the moments above and below  $T_c$ . For  $n \approx 8$  the jump vanishes and becomes negative with further increase in  $n$ .

Formula (30) establishes the connection between the specific heat and the susceptibility and confirms the assumptions of [13, 14] concerning their close values.

e) The total system of equations. Let us write out the relations of the preceding Sections. We denote the volume of a region of radius  $r$  by  $v$ .

The correlation of the deviations of the moment from its average value  $m_0$  is:

$$G(r) = \frac{b}{v^{1/n}} - m_0^2, \quad v < v_c, \tag{33}$$

$$G(r) = 0, \quad v > v_c. \tag{34}$$

The susceptibility is:

$$\chi = v \left[ \frac{b}{(1-1/n)v^{1/n}} - m_0^2 \right], \quad v < v_c, \tag{35}$$

$$\chi = v_c \left[ \frac{b}{(1-1/n)v_c^{1/n}} - m_0^2 \right], \quad v > v_c. \tag{36}$$

The free energy per unit volume is:

$$f = \frac{1}{2v} \ln(\pi k T \chi v) + \frac{m_0^2}{\chi_+}, \quad v < v_c, \tag{37}$$

$$f = \frac{1}{2v_c} \ln(\pi k T \chi_+ v_c) + \frac{m_0^2}{\chi_+}, \quad v > v_c, \tag{38}$$

For  $v > v_c$  the quantity  $m_0$  is determined by expression (21); therefore for  $v > v_c$  relations (33)–(38) and (21) provide a complete description of the properties of a system with given constants  $a$ ,  $b$ , and  $n$ . For  $v < v_c$  the quantity  $m_0$  coincides in its meaning with the spontaneous moment introduced in Sec. 1 and marked in Fig. 3 by horizontal arrows. However, the assumptions of the preceding sections are insufficient for determining its value. The simplest additional assumption is the following: for sufficiently small  $\tau$  on lowering the temperature from the upper limit of the transition region the moment increases equally for arbitrary  $v$ . This means that to determine  $m_0$  at any point  $(v, \tau)$  one must take the temperature separation from the upper limit  $(a^{1/2}/v^{1/2} - \tau)$  and ascertain for what  $v$  this separation becomes the width of the transition region. For this  $v$  the sought moment will be equal to the spontaneous moment at the lower limit given by relation (21). Finally, we obtain

$$m_0(v, \tau) \xrightarrow{\tau \rightarrow 0} \frac{b^{1/2}}{a^{1/2n}} \left[ \frac{1}{2} \left( \frac{a^{1/2}}{v^{1/2}} - \tau \right) \right]^{1/n}. \tag{39}$$

Actually, for finite  $v$  there is always a region where the moment increases proportionally to  $(a^{1/2}/v^{1/2} - \tau)^{1/2}$ , since here  $f(m)$  can be expanded

in series and one can use Landau's theory. The assumption formulated above means that asymptotically for  $\tau \rightarrow 0$  one can neglect the contribution of this region (for  $n \neq 2$ ).

Relation (39) is not used in this paper, but for sufficiently large  $v$  the system of equations (33)–(39) provides a complete description of the magnetic substance.

f) Free energy. Let us place the sample in a magnetic field  $H$ . A moment  $\chi H$  will now be added to the spontaneous moment  $m_0$ . The entire discussion and all conclusions which referred to deviations from  $m_0$  remain unchanged for deviations of the moment from the average value  $m_0 + \chi H$ . Therefore, to describe the system in the external field one need only replace in Eqs. (33)–(39)  $m_0$  by  $m_0 + \chi H$ .

The volume of the correlation sphere is determined from the condition

$$b^{1/2}/v_c^{1/2n} = m_0 + \chi H. \tag{40}$$

When  $\chi H \gg m_0$ , then  $v_c = (b^{1/2}/\chi H)^{2n}$ . Substituting this expression in (36), we obtain

$$\chi = \frac{b}{1 - 1/n} \left( \frac{b^{1/2}}{\chi H} \right)^{2n-2}. \tag{A}$$

Expressing  $\chi$  in terms of  $H$ , we find for  $m = \chi H$  the equation of state:

$$m = \frac{b^{n/(2n-1)}}{(1 - 1/n)^{2n-1}} H^{1/(2n-1)}. \tag{41}$$

If, on the other hand,  $\chi H \ll m_0$ , then we obtain directly from (30) for the singular part of the specific heat  $2a^{-1} \ln v^{-1/2n}$ :

$$c_H \approx \frac{2(2n-1)}{a} \ln \left( \tau^{1/n} + \frac{a^{1/n}}{b^{1/2}} \chi_{\pm} H \right). \tag{42}$$

Since  $\chi_+ \neq \chi_-$ , the halves of the lambda curve will be distorted differently. In a magnetic field there appears an additional quantity  $\Delta$  to the jump in the specific heat; according to (42)

$$\Delta = \frac{2(2n-1)}{a} \ln \frac{\tau^{1/n} + (a^{1/2n}/b^{1/2}) \chi_+ H}{\tau^{1/n} + (a^{1/2n}/b^{1/2}) \chi_- H}.$$

For  $H = 0$  this additional quantity is equal to zero, but  $\partial\Delta/\partial H$  becomes infinite for  $H = 0$  and  $\tau = 0$  in accordance with the results of [15, 16].

The effect of impurities and inhomogeneities can be taken into account to a first approximation by introducing an effective magnetic field produced by these defects. The distortion of the lambda curve will be similar to (42) and will also be asymmetric.

Knowing the  $f(H)$  dependence, one can find the free energy for a given magnetic moment. Without dwelling on the derivation, we note that for  $R \gg R_c$  and  $m \ll m_0$

$$f(m) = a_n m^{2n} + a_{n-1} \tau^{2/n} m^{2n-2} + a_{n-2} \tau^{4/n} m^{2n-4} + \dots + a_1 \tau^{2-2/n} m^2 + f_0(\tau).$$

Here  $\alpha_S$  are coefficients which depend on  $a$  and  $b$ , and  $\alpha_S \sim a^{S/n}/ab^S$ . Or, since  $m_0 \sim \tau^{1/n}$  and  $m \ll m_0$ , we have

$$f(m) = f_0(\tau) + \alpha \tau^{2-2/n} m^2 + \beta \tau^{2-4/n} m^4,$$

where  $\alpha$  and  $\beta$  are some coefficients. For  $n = 2$  we obtain the well-known Landau expansion.<sup>[11]</sup> For  $n = 3$  we have an expansion proposed by Mama-ladze<sup>[17]</sup> for the neighborhood of the  $\lambda$  point of He<sup>4</sup>. For the transition of helium to the superfluid state the mathematical analog of  $m^2$  will apparently be the square of the absolute value of the wave function of the ground state.<sup>[18]</sup>

For an antiferromagnet each sublattice will have its own Eqs. (33)–(39). We shall then obtain two or several systems of the type (33)–(39) coupled with each other.

g) Other variants of the theory. This section contains the simplest variant of the theory which apparently reproduces correctly the main features of the transition while permitting one at the same time to obtain explicit expressions for the thermodynamic quantities. It is interesting that the entire theory is set up without making use of expression (17) for  $f(m)$ . If, on the other hand, one takes this expression to be basic, then one obtains somewhat less transparent (the integrals cannot be obtained in explicit form) but more accurate and logically simpler variants of the theory.

For example, assuming that (17) is fulfilled for deviations of the moment from the average value  $\pm m_0$ , we take

$$f(m) = \frac{c}{2} \left( \frac{m - m_0}{\Delta} \right)^{2n} + \frac{c}{2} \left( \frac{m + m_0}{\Delta} \right)^{2n}.$$

For the susceptibility we obtain

$$\chi = \frac{\int (m - m_0)^2 \exp \{-1/2 v_c c [(m - m_0)^{2n} + (m + m_0)^{2n}]\} dm}{\int \exp \{-1/2 v_c c [(m - m_0)^{2n} + (m + m_0)^{2n}]\} dm}$$

and for the specific free energy

$$f = \frac{1}{v_c} \ln \left\{ \int \exp \left\{ -\frac{v_c c}{2} [(m - m_0)^{2n} + (m + m_0)^{2n}] \right\} dm \right\}.$$

Here  $m_0$  is given by expression (21). Generally one need not use expression (14) for the correlation and consider  $m_0(\tau)$  to be an unknown function. This function can be determined from the condition  $|m| = m_0$  for  $v = v_c$  or from any other condition giving the lower boundary of the transition.

The approximate nature of the calculations which have been carried out is obvious. For example, it

has been assumed that for  $R < R_c$  the correlation function does not depend on the temperature and vanishes jump-wise for  $R = R_c$ . But the singularities of the thermodynamic quantities increase with increasing  $R$  and reach a maximum precisely at the point  $R = R_c$ .

However, because of their simplicity and clarity, this calculation and system of hypotheses are of interest independently of the existence of an exact theory.

## 5. THE INDEPENDENCE OF LARGE-SCALE FLUCTUATIONS

The relations of the preceding section practically determine the form of  $f(m)$ ; however, there remains an arbitrariness which results in a small error in the susceptibility and specific heat. Certain details of the behavior of the system in an external magnetic field also remain unexplained.

The hypothesis of the independence of large-scale fluctuations formulated in this section removes this arbitrariness. This hypothesis makes it possible to obtain an equation that describes the evolution of the distribution when the volume of the region changes (for large  $v$ ). With the aid of the hypothesis that the temperature smearing is constant we can relate the volume dependence with the temperature dependence. In the end there appears a system of equations which makes it possible, starting from (17), to describe the entire vicinity of the transition without resorting to atomic scales.

The appearance near the transition point of a broad spectrum of scales allows one to assume that fluctuations of differing scales (differing in the sense of a different nature of the distribution) are to a large degree independent. At the transition point the correlations decrease with distance both in  $x$  and  $p$  space, and the distribution of the moment  $p(m)$  tends with increasing scale to its limiting value (17). This means that there are changes of scale which are sufficiently small for  $p(m)$  to change little, but sufficiently large for the moments of the corresponding regions to be weakly correlated.

a) The independence of relative fluctuations. For  $v \rightarrow \infty$  the value of the specific free energy is the result of averaging over small-scale fluctuations. The averaging procedure can be described by the relation

$$f_\infty(m) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{h=1}^N f_v(m_h) = \int f_v(m') p_v(m', m) dm', \quad (43)$$

where  $p_v(m', m)$  is the probability of finding in a system with moment  $m$  within a volume  $v$  a moment  $m'$ .

The assumption that relative fluctuations are independent means that in sufficiently large regions the values  $m' - m$  do not depend on  $m$  and consist of a large number of independent deviations (within a single volume  $v$ ), i.e., they have a gaussian distribution

$$p_v(m', m) = (\pi \overline{m_v^2})^{-1/2} \exp\{- (m' - m)^2 / \overline{m_v^2}\}. \quad (44)$$

According to the stipulation the dispersion does not depend on  $m$ , and for  $m = 0$  it is obviously equal to the average value of  $m^2$  within the volume  $v$ .

Substituting (5) in (4), we obtain for  $f_v(m)$  the equation

$$\partial f_v / \partial \overline{m_v^2} = -\frac{1}{2} \partial^2 f_v / \partial m^2. \quad (45)$$

For  $v \rightarrow \infty$  the quantity  $\overline{m_v^2} \rightarrow 0$  and the gaussian nature of the distribution (44) signifies the absence of a phase transition in a sample with a given  $m$ . One can, on the contrary, require the absence of a phase transition and from this condition derive (44).

The solution of this equation with the initial condition (17) for integer  $n$  is:

$$f(m) = c \sum_{s=0}^n (-1)^s C_{2n}^{2s} (2s-1)!! m^{2n-2s} \left(\frac{\overline{m^2}}{2}\right)^s. \quad (46)$$

Since

$$\overline{m^2} = \int m^2 e^{-v f(m)} dm = \overline{m^2} \int y^2 \exp\{-v(\overline{m^2})^n \varphi(y)\} dy, \quad (47)$$

where

$$\varphi(y) = c \sum_{s=0}^n (-1)^s C_{2n}^{2s} (2s-1)!! \frac{y^{2n-2s}}{2^s},$$

then condition

$$\int y^2 \exp\{-v(\overline{m^2})^n \varphi(y)\} dy = 1$$

yields

$$\overline{m^2} = b' / v^{1/n}, \quad (48)$$

where  $b'$  is a constant determined from the relation

$$\int y^2 \exp\{- (b')^n \varphi(y)\} dy = 1. \quad (49)$$

An expression has thus been obtained for the dependence of the specific free energy on the volume at the transition point

$$f(m) = c \left\{ \frac{a_0}{v} + (-1)^{n-1} \frac{a_1 m^2}{v^{1-1/n}} + (-1)^{n-2} \frac{a_2 m^4}{v^{1-2/n}} + \dots + m^{2n} \right\}, \quad (50)$$

where  $a_s$  are numerical coefficients which depend on  $n$  and are given by the relations (46)–(49).

The quantity  $f(m)$  for a portion of the sample of volume  $v$  should be close to the specific free en-

ergy of a sample of volume  $v$ . But in the latter instance the Gibbs integral contains a finite number of sums; therefore  $f(m)$  can be expanded in series in powers of  $m$ . For noninteger  $n$  we obtain, instead of (46), an infinite series expressed as an integral of  $m^{2n}$  with a diffuse kernel. One sees readily that in this case  $f(m)$  does not expand in a Taylor series in powers of  $m$ . Therefore  $n$  must be an integer.

Other limitations on the possible values of  $n$  can be obtained from the usual expression for the interaction energy of long-wave fluctuations.<sup>[11]</sup>

$$\int (\nabla m_\omega)^2 dx = N \int_0^\omega k^2 a_k^2 d\omega \quad A$$

[ $N$  is the total number of degrees of freedom and  $a_k$  is the Fourier harmonic of  $m(x)$ ]. The average energy per degree of freedom in the long-wave region

$$\frac{1}{\omega} \int_0^\omega k^2 a_k^2 d\omega$$

for  $a_k^2 = \overline{dm_\omega^2}/d\omega$  and  $m_\omega^2 \sim \omega^{1/n}$  will in the three-dimensional case be proportional to  $k^{3/n-1}$  and becomes infinite for small  $k$ , if  $n > 3$ . Inasmuch as it was shown above that  $n$  should be an integer, there remain in the three-dimensional case only two alternatives:  $n = 2$  and  $n = 3$ . This result has been obtained in a somewhat different way by Fixman;<sup>[19]</sup> such a possibility was indicated by A. Z. Patashinskiĭ (private communication). In a space with a number of dimensions larger than three (the fourth dimension can, in particular, be the time) the only admissible value is  $n = 2$ .

In the two-dimensional case the only limitation can be the requirement that the specific heat increase in a transition to a more ordered phase.<sup>[11]</sup> Indeed, it follows from (30) that for finite  $v$  the heat of fusion is proportional to  $\tau \Delta c$  where  $\Delta c$  is the specific heat jump and  $\tau \sim v^{-1/2}$ . But the heat of fusion is always positive; consequently the jump  $\Delta c$  should also be positive. Equation (32) shows that for a uniaxial magnetic substance an increase in the specific heat is only obtained for  $n \leq 8$ . Thus seven values of  $n$  are possible in the two-dimensional case: 2, 3, 4, 5, 6, 7, and 8.

For sufficiently large  $n$  it turns out that not only is the interaction energy infinite but also the contribution to the energy that appears when one fixes the direction of one of the spins. This can be shown using the following considerations of Fixman.<sup>[19]</sup> On fixing the spin there appears in the magnetic substance at the origin a magnetic moment  $m(x) = G(x) \sim R^{-3/n}$ . The energy of the long-wave fluctuations will change by  $(\partial G/\partial x)^2 d^3x$ . This quantity

is proportional to  $R^{1-6/n}$  and becomes infinite for  $n > 6$ .

b) Strengthening of the temperature smearing hypothesis. For regions smaller than the correlation radius, the value of the free energy depends on the configuration of neighboring regions, but it can be assumed that the effect of the neighbors will in a first approximation reduce to a smearing of the temperature. In other words, we shall assume that for a state with an accurately defined temperature the specific free energy is by definition equal to its limiting value for  $v \rightarrow \infty$ , and the actual free energy is due to a temperature spread which is unavoidable for a sample of finite dimensions. From considerations presented in Sec. 2 it follows that the temperature smearing will be gaussian with a spread  $(\Delta\tau)^2 = a/v$ . This means that the average value of the free energy will be

$$f(\tau, v) = \left(\frac{v}{2\pi a}\right)^{1/2} \int f(\tau', \infty) \exp\left\{-\frac{(\tau - \tau')^2}{2a} v\right\} d\tau', \quad (51)$$

or ( $\omega = 1/v$ ):

$$\frac{\partial f}{\partial \omega} = \frac{a}{2} \frac{\partial^2 f}{\partial \tau^2}. \quad (52)$$

This relation, in conjunction with (50), makes it possible by using relatively simple calculations to obtain from (17) the main results of Sec. 4.

c) Calculation of the thermodynamic quantities. The free energy  $f(m; \omega, \tau)$  is sought in the form

$$f(m, \omega, \tau) = a_0 + a_1 m^2 + a_2 m^4 + a_3 m^6 + \dots$$

For  $\omega \neq 0$  (finite volume)  $f_0$  is expressed in terms of the Gibbs integral over a finite number of degrees; therefore  $f_0$  can be expanded in  $\tau$  under the integral sign. This means that the coefficients  $a_k$  can be sought in the form

$$a_k = a_k^{(0)} + a_k^{(1)} \tau + a_k^{(2)} \tau^2 + \dots$$

Equation (20) permits one to express all  $a_1^{(i)}$  in terms of  $a_1^{(0)}$  and  $a_1^{(1)}$ . The coefficient  $a_1^{(0)}$  is given by expression (50), and the coefficient  $a_1^{(1)}$  can be found from condition (7) at the upper boundary of the transition region, i.e., from the condition

$$a_1(\omega, \tau) = 0, \text{ for } \tau^2 = a\omega \text{ and } \tau > 0.$$

Having solved Eq. (45) with the boundary condition

$$\frac{\partial f}{\partial m} \Big|_{m=0} = 0, \quad \frac{\partial^2 f}{\partial m^2} \Big|_{m=0} = a_1(\omega, \tau),$$

we find  $f(m, \overline{m^2})$ . Substituting this solution in relation (8), we obtain an expression for determining  $\overline{m^2}$ . The value of  $m_0$  will be obtained from the con-

dition  $\partial^2 f / \partial m^2 \Big|_{m=m_0} = 0$  at the lower boundary of the transition region.

Solution of these equations will yield the value of  $f(m)$  which should be substituted in (29) and an expression for the  $m_0(\tau)$  dependence which had been practically postulated by relation (39). Knowledge of this dependence makes it possible to close the system of equations (33)–(39) (formulated in Sec. 3) for finding the free energy in an external magnetic field or for a given magnetic moment.

In conclusion we note that in accordance with the ideas of item c) of Sec. 2, the quantity  $a$  in (52) should only be constant along the lines  $v\tau^2 = \text{const}$ , but cannot remain constant for arbitrary temperatures. Nor can relation (44) be universal, since  $\frac{m^2}{m_v^2} \sim (\partial^2 f / \partial m^2)^{-1}$  depends on  $m$  also for large  $m$ . However, it follows from (50) that for  $m^2 < m_v^2$  (i.e., for the overwhelming majority of the  $m$ )  $\frac{m^2}{m_v^2} \sim (\partial^2 f / \partial m^2)_{\text{max}}^{-1}$  and depends weakly on  $m$ .

I thank A. I. Larkin, V. L. Pokrovskii, G. M. Eliashberg, and M. Sh. Gitterman for useful advice and criticism.

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