INFLUENCE OF SAMPLE INHOMOGENEITIES ON A SECOND-ORDER PHASE TRANSITION

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It is shown by self-consistent field-theory methods that inhomogeneities in a sample greatly influence the behavior of thermodynamic quantities near the transition point. Thus, the magnitude of the specific-heat "jump" decreases, and the temperature of the maximum specific heat shifts towards lower temperatures. If fluctuations are taken into account, two points, which are nonanalytic in the temperature, may appear. The higher-temperature point is connected with the occurrence of infinitely large regions with a stable ordering parameter η. However, the value of η averaged over the entire sample is zero. The second point is connected with the appearance of a nonzero ordering parameter in the entire sample.

1. A large number of experimental investigations have by now been performed (for example[1,2]) on the measurement of the ordering parameter and of the specific heat near a second-order phase transition point. At temperatures slightly below the maximum point, a "jump" is observed on the specific-heat curve, and is associated with the critical point of the phase transition. Voronel' et al.[1] measured the specific heat of Gd samples of different purity. In the less contaminated samples, a rather sharp "jump" was observed, whereas in the more contaminated samples the "jump" was strongly smeared out. The experiments show also that when the temperature is lowered from the critical point the ordering parameter in inhomogeneous media increases much more slowly than predicted by the theory. A similar picture is observed in investigations of the liquid-vapor critical point[3], namely, addition of impurities broadens the specific-heat curve, and the value of the specific heat at the maximum point decreases. It was assumed in[1,2] that these effects are caused by impurities and by the inhomogeneity of the sample. Theoretical investigations[4,5] in the two-dimensional Ising model show that addition of impurities to a ferromagnet leads to finite values of the specific heat at the transition point.

In the present paper we investigate the influence of inhomogeneities of the medium on the behavior of the thermodynamic quantities near the phase-transition point, within the framework of the phenomenological Landau theory[6], assuming that the inhomogeneity has a characteristic length a which is large compared with the interaction radius r_0 ($a \gg r_0$).

We write down the expansion of the free energy Φ in terms of the ordering parameter η and its derivatives, describing the inhomogeneity by means of the coordinate dependence of the expansion coefficient:

$$\Phi[\eta] = \int [\alpha(\mathbf{r}, T)(T - T_c(\mathbf{r}))\eta^2 + \beta(\mathbf{r}, T)\eta^4 + \gamma(\mathbf{r}, T)(\nabla\eta)^2]\,dV; \quad (1)$$

Here T is the temperature and V is the sample volume over which the integration takes place. In this expansion it is assumed that a volume element that is small compared with the dimension of the inhomogeneities remains isotropic, and consequently there are no terms that are linear or cubic in η, and that the only scalar that depends on the derivatives of η is $(\nabla\eta)^2$.

We assume that the additions to the expansion coefficients, necessitated by the inhomogeneities, are much smaller than the mean values of these coefficients. In this approximation we can regard α, β, and γ as constants and take the inhomogeneity of the medium into account only in $T_c(\mathbf{r}) = T_0 + T_1(\mathbf{r})$, where T_0 is the mean value of the function $T_c(\mathbf{r})$, and $T_1(\mathbf{r}) \ll T_0$,

$$\lim_{V\to\infty} \int_V T_1(\mathbf{r})\,dV = 0.$$

It is meaningful to take into account the influence of the inhomogeneities in the self-consistent field approximation only when the temperature "smearing," which is connected with the inhomogeneities, is much larger than the "smearing" connected with the fluctuations of η. The temperature region where the fluctuations are significant is of the order of $\sim 1/r_0^6$ [7,8], and we shall therefore stipulate fulfillment of the inequality $T_1/T_0 \gg 1/r_0^6$ ($r_0 \gg 1$). The region of applicability of the theory under consideration is ultimately defined by the conditions $1 \gg T_1/T_0 \gg 1/r_0^6$ and $a \gg r_0$.

The problem of the influence of inhomogeneities on the phase transition has much in common with the problem of the statistics of the energy levels of a particle in an inhomogeneous medium[9-11], the only difference being that in our case the equation for η is nonlinear.

The inhomogeneities lead to a decrease or to a vanishing of the "jump" of the specific heat C (an increase in the order of the phase transition), something that can be intuitively understood by recognizing that contributions to C and η are made essentially by those regions where $T < T_c(\mathbf{r})$. If the relative weight of these regions is small, then C and η each contain an additional small factor compared with the expressions in the pure substance.

We note that the influence of the impurities on the phase transition reduces to the occurrence of regions with different impurity concentrations[4], i.e., there appear inhomogeneities that can be described in the same scheme.

2. The ordering parameter η is determined by minimizing the functional (1), and the corresponding equation is

$$\gamma\Delta\eta = \alpha(T - T_c(\mathbf{r}))\eta + 2\beta\eta^3. \quad (2)$$

In our theory, η changes over macroscopic distances, and η and η' can be regarded as continuous.

We shall prove that if $T_c(r)$ is an analytic function (as will be assumed throughout), then the ordering parameter either vanishes identically in the entire sample, or vanishes nowhere. For simplicity we consider the case of a one-dimensional distribution of the inhomogeneities (the generalization to the three-dimensional case is trivial).

Let η vanish at the point x_0. If $\eta'(x_0) = 0$ at the same point, then, differentiating (2), we can show that the derivative of η with respect to x, of any order, also vanishes at the point x_0, i.e., $\eta \equiv 0$. If $\eta'(x_0) \neq 0$, then we can construct a function $\tilde{\eta}(x)$, continuous with a continuous first derivative, such that $\Phi[\tilde{\eta}] < \Phi[\eta]$ and $\tilde{\eta}$ does not vanish anywhere. We introduce $\tilde{\eta}_1 = |\eta|$. It is seen from (1) that $\Phi[\eta] = \Phi[\tilde{\eta}_1]$. In a small vicinity of x_0 $(x_0 - \epsilon, x_0 + \epsilon)$, we write $\eta(x) = \eta'(x_0)(x - x_0)$. We define $\tilde{\eta}$ in such a way that $\tilde{\eta} = \tilde{\eta}_1$ throughout with the exception of the vicinity of x_0, and in this vicinity we put

$$\tilde{\eta} = \frac{\eta'(x_0)}{2}\varepsilon + \frac{\eta'(x_0)}{2\varepsilon}(x - x_0)^2.$$

It is easy to verify that $\tilde{\eta}$ and $\tilde{\eta}'$ are continuous and the equality $\Phi[\eta] = \Phi[\tilde{\eta}]$ is satisfied upon integration over all of space, with the exception of the vicinity of x_0. Upon integration over the vicinity of x_0, the values of the functionals (1) are respectively equal to

$$\Phi[\eta] = 2\gamma\eta'^2(x_0)\varepsilon, \quad \Phi[\tilde{\eta}] = {}^2/_3\gamma\eta'^2(x_0)\varepsilon,$$

i.e., $\Phi[\tilde{\eta}] < \Phi[\eta]$, q.e.d.

3. We shall consider henceforth the one-dimensional case. The main result, however, can be readily generalized to include the three-dimensional case.

In the spatial region $\tau > 0$ $(\tau = T_c(x) - P)$ we have the estimate $\gamma\eta'' \sim \gamma\eta/a^2$. In the temperature region $\tau \sim T_1$ we obtain $\gamma\eta''/\alpha\tau\eta \sim \gamma/a^2\alpha T_1 = \delta$. Taking into consideration the expression for the correlation radius $r_c^2(T - \tilde{T}) = \gamma/\alpha|T - \tilde{T}|$ ($\tilde{T}$—critical point), we obtain the estimate $\delta \sim r_c^2(T_1)/a^2$. We consider first the case $\delta \ll 1$, i.e., $r_c \ll a$.

In the zeroth approximation $-\alpha\tau\eta_{(0)} + 2\beta\eta_{(0)}^3 = 0$ and

$$\eta_{(0)}^2 = \alpha\tau / 2\beta. \tag{3a}$$

In the first approximation in δ we have

$$\eta_{(1)} = \frac{\gamma}{4\sqrt{2\alpha\beta}}\frac{1}{\tau^{5/2}}\left(\tau\frac{d^2T_1}{dx^2} - \frac{1}{2}\left(\frac{dT_1}{dx}\right)^2\right). \tag{3b}$$

If $\tau \gtrsim T_1$ we have

$$\eta_{(1)} / \eta_{(0)} \lesssim \gamma / \alpha T_1 a^2 = \delta \ll 1,$$

i.e., formulas (3a) and (3b) are valid. These expressions, however, are not valid near the points x_0 at which $\tau(x_0) = 0$. If x_0 is not an extremum point of τ $(\tau'_x(x_0) \neq 0)$, then the limits of applicability of (3a) and (3b) are given by the inequality

$$\frac{\gamma}{\alpha\tau^3}\frac{T_1'^2}{a^2} = \delta\frac{T_1^3}{\tau^3} \ll 1.$$

Writing down τ near x_0 in the form

$$\tau = \frac{dT_1(x_0)}{dx}(x - x_0),$$

we obtain a limitation on the spatial region of applicability of these formulas

$$(x - x_0)^3 / a^3 \gg \delta. \tag{4}$$

We now consider the spatial region $\tau < 0$. If we neglect the correlation of the ordering parameter of the regions with $\tau < 0$ and $\tau > 0$, then, recognizing that the integrand in (1) is non-negative, we get $\eta = 0$. It is therefore natural to assume that the ordering parameter is small, to neglect the last term in (2), and to solve the simplified equation in the quasiclassical approximation. As a result we have

$$\eta = \frac{D}{|\tau|^{1/4}}\exp\left\{\pm\int_{x_0}\sqrt{\frac{\alpha}{\gamma}|\tau|}\,dx\right\}. \tag{5}$$

The sign in (5) should be chosen such as to make the solution attenuate in the interior of the region $\tau < 0$. Since

$$\int_{x_0}^{x}\sqrt{\frac{\alpha}{\gamma}|\tau|}\,dx \sim \sqrt{\frac{\alpha}{\gamma}T_1(x - x_0)} \sim \frac{x - x_0}{r_c},$$

i.e., the characteristic length of variation of η $(\sim r_c)$ is much smaller than the dimension of the inhomogeneity a, and the quasiclassical method is applicable. The spatial limits of applicability of formula (5), as well as of (3), are given by the inequality (4).

Let us "join together" the solutions in the regions $\tau > 0$ and $\tau < 0$. We expand the functions $\eta(x)$ and $\tau(x)$ near x_0 in a Taylor series:

$$\eta(x) = A + B(x - x_0) + c(x - x_0)^2, \quad \tau(x) = \frac{dT_1(x_0)}{dx}(x - x_0). \tag{6}$$

From (2) we get $c = (\beta/\gamma)A^3$. Let x_1 be the point for which the conditions $\tau(x_1) > 0$ and $(x_1 - x_0)^3/a^3 \sim \delta$ are satisfied. Then

$$A \sim \sqrt{\frac{\alpha}{\beta}}\tau^{1/2}(x_1) \sim \sqrt{\frac{\alpha}{\beta}}\left(\frac{T_1}{a}\cdot a\delta^{1/3}\right)^{1/2} \sim \eta\delta^{1/6},$$

where η is the order of magnitude of the ordering parameter in the region $\tau > 0$. We can analogously "join together" formulas (5) and (6), obtaining thereby the estimate

$$D \sim \eta T_1^{1/4}\delta^{1/4}. \tag{7}$$

If $(x - x_0)^3/a^3 \lesssim \delta$, then all the terms in (6) are of the same order of magnitude, and this series is suitable for the estimates obtained above.

Finally, let us consider Eq. (2) in the spatial region near the point of maximum τ (the point x_{max}). It is seen from (3a) and (3b) that the condition for applicability of these formulas is given by the inequality $\delta T_1^2/\tau_{max}^2(T) \ll 1$, where $\tau_{max}(T) \equiv \tau(x_{max})$. Inasmuch as the length ΔX of the region where $\tau > 0$ is determined by the estimate

$$\Delta x^2 \sim \tau_{max} / T_1'' \sim \tau_{max}a^2 / T_1,$$

the inequality given above has a simple physical meaning:

$$r_c^2(\tau_{max}(T)) / \Delta x^2 \ll 1.$$

If Δx is bounded from above at each given temperature T by a quantity the order of $a\sqrt{\tau_{max}/T_1}$ (the distribution of T_c cannot have fluctuations that lead to anomalously large regions with positive τ), then it can be shown, by elementary estimates of the terms of formula (1), that when $r_c(\tau_{max}) \gg \Delta x$ the condition for the minimum of (1) ensures that $\eta \equiv 0$. Thus, the critical temperature can be obtained from the condition $r_c(\tau_{max}) \sim \Delta x$, i.e.,

$$\tilde{T} = T_0 + T_1(x_{max}) - k\delta^{1/2}T_1, \quad k \sim 1. \tag{8}$$

4. Let us calculate the mean values of the ordering parameter and of the specific heat $\bar{\eta}$ and $\bar{C}$, neglecting the exponentially small contribution of the regions with $\tau < 0$, using the formulas

$$\bar{\eta} = \lim_{L\to\infty} \int_{\tau>0} \left(\frac{\alpha}{2\beta}\right)^{1/2} \tau^{1/2} dx, \quad \bar{C} = -T\alpha \lim_{L\to\infty} \int_{\tau>0} \frac{\partial \eta^2}{\partial T} dx = \frac{T\alpha^2}{2\beta} \lim_{L\to\infty} \int_{\tau>0} dx, \tag{9}$$

where L is the length of the sample. The integration in (9) is carried out only over regions where $\tau > 0$.

We introduce the function $\rho(T_1)dT_1$, which describes the distribution of the probability of the quantity T_1 and the temperature interval dT_1 on a segment of length $\sim a$, with a normalization condition

$$\int_{-\infty}^{\infty} \rho(T_1)dT_1 = 1.$$

Using this function, we can rewrite (9) in the form

$$\bar{\eta} = \left(\frac{\alpha}{2\beta}\right)^{1/2} \int_{T-T_0}^{\infty} (T_0 + T_1 - T)^{1/2} \rho(T_1)dT_1, \quad \bar{C} = \frac{T\alpha^2}{2\beta} \int_{T-T_0}^{\infty} \rho(T_1)dT_1. \tag{10}$$

Let us carry out the calculations for several forms of the distribution function $\rho(T_1)$.

a) Gaussian distribution function

$$\rho(T_1) = \frac{1}{\sqrt{2\pi}\, t} \exp\left\{-\frac{T_1^2}{2t^2}\right\}$$

(the conditions for the applicability of formulas (10) are of the form $1 \gg t/T_0 \gg 1/r_0^6$, $\delta \sim \gamma/\alpha t a^2 \ll 1$, and $|T - T_0| \ll T_0$). From (10) we can easily obtain asymptotic expressions in different limiting cases:

I. $$\bar{\eta} = \frac{1}{4}\left(\frac{\alpha}{2\beta}\right)^{1/2} \frac{t^2}{(T-T_0)^{3/2}} \exp\left\{-\frac{(T-T_0)^2}{2t^2}\right\}\left(1 - \frac{15}{8}\frac{t^2}{(T-T_0)^2}\right),$$

$$\bar{C} = \frac{\alpha^2 T}{2\beta} \frac{1}{\sqrt{2\pi}} \exp\left\{-\frac{(T-T_0)^2}{2t^2}\right\} \frac{t}{T-T_0}, \tag{11a}$$

when $T - T_0 \gg t$, $T > T_0$;

II. $$\bar{\eta} = \frac{t^{1/2}}{2^{3/4}\pi^{1/2}}\left(\frac{\alpha}{2\beta}\right)^{1/2}\left[\Gamma\left(\frac{3}{4}\right) - \sqrt{2}\,\Gamma\left(\frac{5}{4}\right)\frac{T-T_0}{t}\right],$$

$$\bar{C} = \frac{\alpha^2 T}{2\beta}\left[\frac{1}{2} - \frac{T-T_0}{\sqrt{2\pi}\, t}\right], \tag{11b}$$

when $|T - T_0| \ll t$;

III. $$\bar{\eta} = \left(\frac{\alpha}{2\beta}\right)^{1/2} (T_0 - T)^{1/2}\left(1 - \frac{1}{4}\frac{t^2}{(T-T_0)^2}\right),$$

$$\bar{C} = \frac{\alpha^2 T}{2\beta}\left(1 - \frac{1}{\sqrt{2\pi}}\exp\left\{-\frac{(T-T_0)^2}{2t^2}\right\}\frac{t}{T_0 - T}\right), \tag{11c}$$

when $|T - T_0| \gg t$, $T < T_0$.

It is seen from (11) that the maximum of the specific heat shifts from the point T_0 towards lower temperatures. The maximum value of the specific heat in an inhomogeneous medium decreases with increasing amplitude of the inhomogeneity t.

We note that in our case T_1 is not bounded. Therefore, at any temperature T there is a region with dimension $\sim a$, characterized by such a T_1 that $r_c^2 \sim \gamma/\alpha T_1 \ll a$, and consequently formulas (3a) and (3b) are valid. According to Sec. 2, the parameter η will differ from zero in the entire sample, i.e., there is no critical point.

b) We now consider the case when T_1 is bounded from above by the quantity T_{1max} in the temperature region close to $T_0 + T_{1max}$, so that $\rho(T_1)$ can be represented in the form

$$\rho(T_1) \approx \frac{\rho^{(n)}(T_{1\,max})}{n!}(T_1 - T_{1\,max})^n. \tag{12}$$

In the temperature interval $\tau_{max}^2/T_1^2 \gg \delta$ (the correlation radius $r_c^2 \sim \gamma/\alpha(T_0 + T_{1max} - T)$ is much smaller than the average length of the region with positive τ in the vicinity of x_{max}) we have

$$\bar{\eta} = \left(\frac{\alpha}{2\beta}\right)^{1/2} \frac{1}{n!}\rho^{(n)}(T_{1\,max}) \int_{T-T_0}^{T_{1\,max}} (T_0 + T_1 - T)^{1/2}(T_1 - T_{1\,max})^n dT_1$$
$$= \frac{2^{n+1}}{(2n+3)!!}\left(\frac{\alpha}{2\beta}\right)^{1/2} |\rho^{(n)}(T_{1\,max})|\, \tau_{max}^{n+3/2},$$
$$\bar{C} = \frac{\alpha^2 T}{2\beta}\frac{|\rho^{(n)}(T_{1\,max})|}{(n+1)!}\tau_{max}^{n+1}. \tag{13}$$

In the second limiting case, $\tau_{max}^2/T_1^2 \ll \delta$, the main contributions to $\bar{\eta}$ and $\bar{C}$ are made by regions with $\tau > 0$ and with length l much larger than the average length of such regions ($\Delta x \sim a\sqrt{\tau_{max}/T_1}$) (fluctuations in the distribution of T_1 over the sample have low probability). On the other hand, in regions with length on the order of $a\sqrt{\tau_{max}/T_1}$, the values of η, according to the estimate, coincide with the limiting values, which in accordance with (5) are exponentially small. The length l is estimated from the condition $l \sim r_c(\tau_{max}) \sim (\gamma/\alpha\tau_{max})^{1/2}$, and the probability of having a region with $\tau > 0$ and with dimension l is estimated by the formula

$$\left[\frac{1}{n!}\rho^{(n)}(T_{1\,max}) \int_{T-T_0}^{T_{1\,max}} (T_1 - T_{1\,max})^n dT_1\right]^{(r_c/a)^3} \sim \tau_{max}^{A_1},$$
$$A_1 = (n+1)\left[\left(\frac{\gamma}{\alpha\tau_{max}}\right)^{1/2}\frac{1}{a}\right]^3 = (n+1)\left(\delta\frac{T_1}{\tau_{max}}\right)^{3/2}. \tag{14}$$

Hence

$$\bar{\eta} \sim \tau_{max}^{A_1 + 1/2}, \quad \bar{C} \sim \tau_{max}^{A_1+1}.$$

The transition point $\tilde{T}$ coincides with the maximum value T_c, i.e.,

$$\tilde{T} = T_0 + T_{1max}. \tag{15}$$

Thus, if T_1 is bounded from above, then the specific heat and all its derivatives are continuous. Similar results are obtained for a ferromagnet diluted by impurities in the two-dimensional Ising model[4].

5. In Secs. 3 and 4 we have considered the case $\delta \ll 1$ ($r_c(T_1) \ll a$). Let us consider now the opposite limiting case, $\delta \gg 1$ ($r_c(T_1) \gg a$). We represent η in the form

$$\eta(x) = \eta_0 + \eta_1(x), \tag{16}$$

$$\eta_0 = \lim_{L\to\infty} \frac{1}{2L}\int_{-L}^{L} \eta(x)dx. \tag{17}$$

The value of η at a certain specified point in space is determined by the integral properties of $T_c(x)$ in the vicinity of this point (radius of the vicinity $r_c \gg a$). In the zeroth approximation, the inhomogeneities are averaged over regions with dimension $\sim r_c$, and it can be assumed that $\eta \approx \eta_0$. In the first approximation, account is taken of $\eta_1(x)$ ($\eta_1 \ll \eta_0$). Averaging Eq. (2), rewritten in the form

$$\gamma\eta_1'' = \alpha(T - T_0 - T_1(x))\eta_0 + \alpha(T - T_0)\eta_1 - \alpha T_1\eta_1 + 2\beta(\eta_0^3 + 3\eta_0^2\eta_1 + 3\eta_0\eta_1^2 + \eta_1^3), \tag{18}$$

over the entire volume of the sample, we obtain

$$\alpha(T - T_0)\eta_0 - \alpha\overline{T_1(x)\eta_1(x)} + 2\beta\eta_0^3 + 6\beta\eta_0\overline{\eta_1^2} = 0. \tag{19}$$

Subtracting (19) from (18) we get

$$\gamma\eta_1'' = -\alpha T_1(x)\eta_0 + \alpha(T - T_0)\eta_1 - \alpha(T_1(x)\eta_1(x) - \overline{T_1(x)\eta_1(x)}) + 6\beta\eta_0^2\eta_1 + 3\beta\eta_0(\eta_1^2 - \overline{\eta_1^2}) + \beta\eta_1^3. \tag{20}$$

Using the condition $\eta_1 \ll \eta_0$, we get from (19) and (20) in the zeroth approximation

$$\alpha(T - T_0)\eta_0 - \alpha\overline{T_1(x)\eta_1(x)} + 2\beta\eta_0^3 = 0, \tag{21a}$$

$$\gamma\eta_1'' = -\alpha T_1(x)\eta_0 + \alpha(T - T_0)\eta_1 + 6\beta\eta_0^2\eta_1. \tag{21b}$$

Solving the second linear equation of (20) with respect to η_1, we obtain

$$\eta_1 = \frac{\alpha\eta_0}{2\gamma\lambda}\left(-e^{\lambda x}\int_{x_1}^{x} T_1(y)e^{-\lambda y}dy + e^{-\lambda x}\int_{x_2}^{x} T_1(y)e^{\lambda y}dy\right), \tag{22a}$$

$$\lambda = \sqrt{\frac{\alpha(T - T_0) + 6\beta\eta_0^2}{\gamma}}. \tag{22b}$$

If $\rho(T_1)$ is a homogeneous function (independent of x), then

$$\overline{T_1\eta_1} = -\frac{\alpha\eta_0}{2\gamma\lambda}\lim_{L\to\infty}\frac{1}{2L}\left(\int_{-L}^{L} dx\int_{x-x_1}^{0} G(z)e^{\lambda z}dz + \int_{-L}^{L} dx\int_{x_2-x}^{0} G(z)e^{\lambda z}dz\right)$$

$$= \frac{\alpha\eta_0}{\gamma\lambda}\lim_{L\to\infty}\frac{1}{2L}\int_{-L}^{L} d\xi\int_0^{\xi} G(z)e^{\lambda z}dz, \tag{23}$$

where $G(|x - y|) = \overline{T_1(x)T_1(y)}$.

We shall assume that $G(z) \to 0$ at $z \gg a$ more rapidly than $e^{-\mu z}$, where μ is an arbitrary positive constant, i.e., the characteristic region of integration in (23) with respect to ξ is $\sim L \gg a$, and therefore

$$S = \int_0^{\xi} G(z)e^{\lambda z}dz = \int_0^{\infty} G(z)e^{\lambda z}dz.$$

In this integral

$$\lambda z \sim \sqrt{\frac{\alpha(T - T_0) + 6\beta\eta_0^2}{\gamma}}\,a \lessapprox \sqrt{\frac{\alpha T_1}{\gamma}}\,a = \frac{1}{\delta} \ll 1.$$

Using this small parameter, we write

$$S = \int_0^{\infty} G(z)dz, \quad \overline{T_1\eta_1} = \frac{\alpha\eta_0}{\gamma\lambda}S. \tag{24}$$

Substituting (24) in (21a) and using (22b), we obtain an equation for the determination of η_0 below the critical point:

$$24\beta^3\eta_0^6 + 28\alpha\beta^2(T - T_0)\eta_0^4 + 10\alpha^2\beta(T - T_0)^2\eta_0^2 + \alpha^3(T - T_0)^3 - \alpha^4S/\gamma = 0. \tag{25}$$

We obtain the critical point from (25) by putting $\eta_0 = 0$:

$$\tilde{T}_c = T_0 + \tilde{T}_1, \tilde{T}_1 = \left(\frac{\alpha}{\gamma}S^2\right)^{1/3} \sim \left(\frac{\alpha}{\gamma}T_1^4a^2\right)^{1/3} \sim \frac{T_1}{\delta^{1/3}} \ll T_1. \tag{26}$$

Thus, the critical point lies above T_0.

Elementary manipulations enable us to find η_0 and C:

$$\eta_0^2 = \frac{3\alpha}{10\beta}(\tilde{T}_c - T)\left(1 + \frac{16}{100}\frac{\tilde{T}_c - T}{\tilde{T}_1}\right), \tag{27}$$

$$C = \frac{3\alpha^2}{10\beta}T\left(1 + \frac{16}{100}\frac{\tilde{T}_c - T}{\tilde{T}_1}\right), \quad \frac{\tilde{T}_c - T}{\tilde{T}_1} \ll 1;$$

$$\eta_0^2 = \frac{\alpha}{2\beta}(T_0 - T)\left[1 + \left(\frac{\alpha}{2\gamma}\right)^{1/2}\frac{S}{(T_0 - T)^{3/2}}\right],$$

$$C = \frac{\alpha^2T}{2\beta}\left[1 - \frac{1}{2}\left(\frac{\alpha}{2\gamma}\right)^{1/2}\frac{S}{(T_0 - T)^{3/2}}\right], \quad \frac{\tilde{T}_c - T}{\tilde{T}_c} \gg 1. \tag{28}$$

From (27) and (28) we see that when the temperature is decreased from the critical point, the value of the specific heat after the "jump" continues to increase. Let us estimate η_1 by means of formula (22a) in the region $T - T_0 \lessgtr T_1$. Taking into account the inequality $\lambda a \ll 1$, we can regard $\exp(\pm\lambda x)$ as a smooth function compared with $T_1(x)$. Integrating (22a) by parts, we obtain

$$\eta_1 \sim \frac{\alpha\eta_0}{\gamma}T_1a^2, \qquad \frac{\eta_1}{\eta_0} \sim \frac{\alpha}{\gamma}T_1a^2 = \frac{1}{\delta} \ll 1$$

in accordance with the initial assumption.

6. Let us estimate the influence of fluctuations on the ordering parameter η and on the specific heat of the substance. The fluctuation length can have two scales, a and r_c. We estimate first the role of fluctuations with characteristic length r_c in the case when $r_c(T_1) \ll a$. According to[8], these fluctuations (in first approximation in the parameter $r_0^{-3}\tau^{-1/2}T_0^{1/2}$) yield, accurate to an inessential numerical factor, the following correction to the specific heat:

$$C_1 \sim \frac{\alpha^2T_0^{3/2}}{\beta r_0^3}\int\frac{\rho(T_1)dT_1}{\sqrt{|T - T_0 - T_1|}}. \tag{29}$$

In the case of a Gaussian function $\rho(T_1)$ this contribution turns out to be appreciable when $T - T_0 \gg t$, $T > T_0$, and is of the form

$$C_1 \sim \frac{\alpha^2T_0^{3/2}}{\beta r_0^3}\frac{t}{\sqrt{T - T_0}}. \tag{30}$$

The second approximation contains an additional small factor

$$T_0^{1/2}/r_0^3|T - T_0|^{1/2} \ll T_0^{1/2}/r_0^3t^{1/2} \ll 1$$

and can be disregarded.

The divergences of higher order of perturbation theory, in the integration with respect to T_1 at the point $T_1 = T - T_0$ ($T_1 < T_{1max}$, $\eta \neq 0$) are eliminated by the existence of an effective magnetic field in the zeroth approximation.

In the cases described by formulas (13) and (14), the correction to the specific heat, due to the fluctuations in the region $T > T_c$, is of the form (30), where t is replaced by T_1, and the contribution from the region $T < T_c$ is estimated by the expression

$$C_1 \sim T_c\overline{C}/r_0^3\sqrt{|T - \tilde{T}|}, \tag{31}$$

where $\overline{C}$ is determined by formula (14).

The condition for the applicability of the theory of the self-consistent field has the usual form

$$T_0/r_0^3\sqrt{|T - \tilde{T}|} \ll 1. \tag{32}$$

Formula (14) can be generalized to include the case when the inequality (32) is not satisfied, provided we know the dependence of r_c on $T - \tilde{T}$ in the homogeneous substance. Let $r_c = b/\tau_{max}^p$, $p > 0$. Then a reasoning similar to that used in the derivation of (14) yields the singular part of the specific heat in the form

$$\bar{C} \sim \tau_{max}^{B_1}, \qquad B_1 = (n+1)(b/a\tau_{max}^{p})^3. \tag{33}$$

The case $r_c(T_1) \gg a$ in the zeroth approximation (in $1/\delta$) can be regarded as homogeneous, and therefore the corrections necessitated in the theory by the fluctuations of the parameter η and the region of applicability of the theory are of the same order of magnitude as in[7,8].

Let us estimate now, in the case $r_c(T_1) \ll a$, the probability of the change of the sign of the ordering parameter η in one spatial region with $\tau > 0$. We shall use the formula $w \sim \exp(-R_{min}/T)$ ([6], Sec. 144), where R_{min} is the minimum work necessary to realize the given fluctuation. It is easy to see that the work will be minimal if the change of the sign and of the magnitude of η occurs in a spatial region $T > T_c$ of thickness r_c, where η has a minimal absolute magnitude. In the remaining region, where the fluctuation took place, η reverses sign, but does not change its absolute magnitude.

The order of R_{min} can be estimated from the formula

$$R_{min} \sim \gamma \int (\nabla\eta)^2 dV \sim \gamma\left(\frac{\eta}{r_c}\right)^2 V_1 \sim L_1^2 \exp\left\{-g\frac{a_1}{r_c}\right\}, \tag{34}$$

where $V_1 \sim L_1^2 r_c$ is the volume of the region in which η differs in absolute magnitude from the values corresponding to the true minimum of Φ, L_1 is the average linear dimension of the region with $\tau > 0$, g is a constant of the order of unity, and a_1 is the average distance between the regions with $\tau > 0$. The latter expression of (34) contains all the most significant factors.

In (34), L_1, a_1, and r_c are functions of the temperature. When the temperature changes from values $T_0 + T_{1max}$ to $T_0 - T_{1max}$, the average linear dimension L_1 of the region changes from values of the order of a to infinity, and $r_c(T) \to a_1(T)$. This leads to $R_{min} \ll T_0$ near the temperature $T_0 + T_{1max}$ and $R_{min} \gg T_0$ near $T_0 - T_{1max}$. The concrete temperature dependence of L_1, a_1, and r_c, and consequently also of R_{min}, is determined by the function $\rho(T_1)$.

Let us describe qualitatively the effects resulting from the interaction between the different regions in which $l > 0$. The Hamiltonian of such a system can be written in the form

$$H = R_{min}\sum_{i,k}\sigma_i\sigma_k, \tag{35}$$

where R_{min} is determined by formula (34) and $\sigma_i = \pm 1$, depending on the sign of the ordering parameter in the region; the summation in (35) is carried out over the numbers of the nearest regions.

Using the Bragg-Williams method, we obtain an equation for the determination of the relative number of regions with positive and negative signs of the ordering parameter:

$$X = \mathrm{th}(g_1 R_{min} X/T), \tag{36}$$

where $X = (2N_+ - N)/N$, N and N_+ are respectively the total number of regions and the number of regions with positive η, and g_1 is a constant on the order of unity.

From (36) we get an equation for the determination of the critical point $\tilde{T}_1$, below which a nonzero value (averaged over the volume of the sample) is obtained for the ordering parameter

$$g_1\frac{R_{min}(\tilde{T}_1)}{T_0} = 1. \tag{37}$$

From (36) we obtain the following values of X:

$$X = 0 \quad \text{if } T > \tilde{T}_1,$$
$$X^2 = \frac{3}{g_1^2}\frac{R'_{min}(\tilde{T}_1)}{T_0}(\tilde{T}_1 - T) \quad \text{if } \tilde{T}_1 > T, \frac{\tilde{T}_1 - T}{\tilde{T}_1} \ll 1,$$
$$X^2 = 1 - 2\exp\left\{-2g_1\frac{R_{min}(T)}{T_0}\right\} \quad \text{if } \frac{R_{min}(T)}{T_0} \gg 1. \tag{38}$$

The values of $\bar{\eta}$ calculated from formulas (11), (13), and (14), with allowance for the considered fluctuations, have the significance of average values (over a region with dimension L_1) of the ordering parameter.

The ordering parameter $\bar{\bar{\eta}}$ averaged over the dimensions of the sample is determined from the formula

$$\bar{\bar{\eta}} = \eta X. \tag{39}$$

The correction to the specific heat C_2, necessitated by allowance for the interaction of different regions, is given by

$$C_2 = -\frac{T_0}{2L_1^3}\frac{dX}{dT}\ln\frac{1+X}{1-X}. \tag{40}$$

From (40) we obtain the value of the "jump" of the specific heat at the critical point $\tilde{T}_1$:

$$\Delta C_2 = \frac{3}{2g_1^2}\frac{R'_{min}(\tilde{T}_1)}{L_1^3}. \tag{41}$$

Using the estimate $R'_{min}(\tilde{T}_1) \sim T_0/T_1$, we get

$$\Delta C_2 \sim \frac{T_0}{T_1 L_1^3} \lesssim \frac{r_c^2(T_1)}{a^2 L_1} \sim \frac{\delta}{L_1} \ll 1,$$

and therefore the "jump" ΔC_2 of the specific heat in an inhomogeneous medium is smaller than the jump of the specific heat in the pure substance by a factor δ/L_1.

Thus, in the case when $r_c(T_1) \ll a$, there can exist two point that are not analytic in the temperature, a higher one connected with the occurrence of unlimited regions with $\tau > 0$, and a lower one in which the ordering parameter averaged over the entire sample differs from zero. Both singularities resulting in this case are quite weak.

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[1] A. V. Voronel', S. R. Garber, L. P. Simkina, and I. A. Chashkina, Zh. Eksp. Teor. Fiz. 49, 429 (1965) [Sov. Phys.-JETP 22, 301 (1966)].

[2] B. A. Strukov, S. A. Taraskin and V. A. Koptsik, Zh. Eksp. Teor. Fiz. 51, 1037 (1966) [Sov. Phys.-JETP 24, 692 (1967)].

[3] Yu. R. Chashkin, V. G. Gorbunova, and A. V. Voronel', Zh. Eksp. Teor. Fiz. 49, 433 (1965) [Sov. Phys.-JETP 22, 304 (1966)].

[4] M. A. Mikulinskiĭ, Zh. Eksp. Teor. Fiz. 53, 1071 (1967) [Sov. Phys.-JETP 26, 637 (1968)].

[5] A. A. Lushnikov, Phys. Lett. 27A, 158 (1968).

[6] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, Nauka, 1964 [Statistical Physics, Addison-Wesley, 1958].