# SMOLUCHOWSKI-TYPE TREATMENT OF FLUCTUATIONS IN FERROMAGNETS AT THE CRITICAL POINT

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The differential equation determining the spin correlation function in ferromagnets, for temperatures above or at the critical $T_c$, is derived with the accuracy to the third order terms. These nonlinear terms play a decisive role in the interval of temperatures $T$, approximately given by the condition $|T-T_c|/T_c < 10^{-4}$.

This follows from the fact that they are practically independent on temperature, while the linear term proportional to $K_1^2$ vanishes at $T_c$. The approach of Smoluchowski in his critical opalescence theory is thus extended to cover the correlation function. The numerical solution of the nonlinear equation is approximated analytically by the spin correlation of the form $A \exp[-\delta(|x|+|y|+|z|)]$, strikingly confirmed by the neutron critical scattering experiment in the ferroelectric $BaTiO_3$. The various approximate forms of the cross-section for a monocrystal and a polycrystal, following from this correlation, are discussed with respect to the temperature shift of the (main) maximum of scattering.

## 1. Introduction

The importance of fluctuations in magnetic moment in the critical region follows from their relation with the correlation function between spins. The space-time dependence of critical correlations is expressible through the space-time dependence of critical fluctuations. A justified description of the behaviour of critical correlation of spins is attained *via* the derivation of the differential equation which the correlation function should obey. In the static case, which we shall treat here, the equations for the magnetic moment distribution in space and the space dependence of the correlation function are equivalent.

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What is true for the magnetic moment distribution is also true for the correlation function between spins.

In the contemporary literature, when the correlation function is derived as a solution of a differential equation, the latter is a linear one, corresponding to the original Ornstein and Zernike approximation. In the classic critical opalescence theory of Smoluchowski [1, 2] the intensity of scattering at the critical point itself, is determined by the fourth order term in the series into which the thermodynamic potential has been expanded. It is just there, where the series expansion has been introduced for the first time. This approach was accepted by Einstein [3] in his extension of Smoluchowski's theory. The second order phase transition theory of Landau serves itself also with the fourth order term in the series expansion of the potential. This fourth order term will be shown to correspond to a nonlinear term in the differential equation for the correlation function. This nonlinear term is accompanied by another one, of the same order of magnitude (and the same sign when appearing in the equation), connected with the spatial inhomogeneity of the magnetic moment. The importance of these two nonlinear terms in the equation for the correlation function (spatial dependence of magnetic moment) stems from the fact that they are practically independent on temperature, while the linear term containing the Ornstein -Zernike parameter $K_1^2$ changes with temperature like $(T_0 - T_c)^\gamma$ ($\gamma$ being the critical exponent). Thus in the immediate vicinity of the critical point, which will appear to be determined by the condition $(T_0 - T_c)/T_c < 10^{-4}$ the parameter $K_1^2$ loses importance in determining the correlation function. The nonlinear terms lead to a correlation function of finite range at the critical point. The calculations will be done for temperatures above the critical point only, although a similar result is expected to hold when temperature approaches $T_c$ from below. The conclusion concerning the limited role of the parameter $K_1^2$ determines the limits of application of the scaling theory to temperatures outside the border given by $(T_0 - T_c)/T_c = 10^{-4}$. It follows from our theory that the transmission of neutrons at the critical point has a finite value, contrary to the unphysical consequence of the infinite transmission in the linear approximation. This result corresponds exactly to Smoluchowski's expression for the critical opalescence cross-section which at the critical point, although quite large, remains finite.

It is worthwhile to comment on the validity of our approximate model of ferromagnet. We shall use the constant coupling approximation which has been shown to give quite a good description of a ferromagnet at high temperatures, failing only at low temperatures [4]. Thus the temperature behaviour of the higher order terms in the thermodynamic potential need not arise doubts.

## 2. The thermodynamic potential

Our approach to the calculation of the spin correlation function has been formulated in [5]. It is based on:

1. Treating a fluctuation in a thermodynamic variable, e. g. magnetic moment, as a subsystem in a reservoir in the sense of Gibbs, which enables the determination to be made of the average spatial distribution of this magnetic moment within the subsystem.

2. Postulating the relation between the spin correlation function and this distribution in the magnetic moment in the form[1]

$$\langle \hat{S}_0^z(0)\hat{S}_r(0)\rangle = M^z(0)M^z(\vec{r}) \tag{2.1}$$

where $M(\vec{r})$ denotes the average magnetic moment in a small volume centred at $\vec{r}$ which, eventually, may be reduced to the volume per one spin.

The distribution in the magnetic moment is determined by the variational principle, which states that for the subsystem in local equilibrium, the increase in the thermodynamic potential (equal to the work neccessary for creating a fluctuation) is maximal subject to some physically imposed boundary conditions, for the magnetic moment in question.

It has been shown previously [5, 7] that the form of thermodynamic potential depends on the choice of the intensive variable coupled with the magnetic moment $M$. Thus it may be either the external field $B_{ex}$ or the local field $B_{ex}+B_m$, ($B_m$ denotes the molecular field), and that the resulting linear differential equations are of different types.

The calculation will be limited to temperatures above or at $T_c$, and to a vanishing external field. The Heisenberg model of cubic ferromagnet with spin $s = \frac{1}{2}$ at the lattice site will be assumed. In the constant coupling approximation, the thermodynamic properties of a subsystem of $N_1$ spins are expressed in the terms of the properties of a pair of nearest neighbour spins. For a pair of spins situated at the lattice sites $\vec{r}, \vec{r}+\vec{\alpha}$, the internal energy is determined by

$$E_{r,r+\alpha} = \mathrm{Tr}\,\varrho^{(2)}H^{(2)} = \sum_{v=0}^{3} f_v H_{vv}^{(2)} \tag{2.2}$$

where $\varrho^{(2)}$ is the density operator for a pair of spins

$$\varrho^{(2)} = e^{-\beta\mathscr{H}_e}(\mathrm{Tr}\,e^{-\beta\mathscr{H}_e})^{-1}, \quad \beta = (kT_0)^{-1} \tag{2.3}$$

$$\mathscr{H}_e = -2J\vec{S}_r \cdot \vec{S}_{r+\alpha} - 2\mu(b_r S_r^z + b_{r+\alpha}S_{r+\alpha}^z) \tag{2.4}$$

$J$ being the exchange integral and $b_r$ the fluctuation in the molecular field and where $H^{(2)}$ is the Hamiltonian of the pair of spins

$$H^{(2)} = -2J\vec{S}_r \cdot \vec{S}_{r+\alpha} - 2\mu B_{ex}z^{-1}(S_r^z + S_{r+\alpha}^z) \tag{2.5}$$

while $H_{vv}^{(2)}$ denote its eigenvalues, and $z$ the number of nearest neighbours of a spin, while

$$f_v = e^{-\beta\varepsilon_v}(\sum_{v=0}^{3} e^{-\beta\varepsilon_v})^{-1} \tag{2.6}$$

and where finally the $\varepsilon_v$ denote the eigenvalues of the Hamiltonian $\mathscr{H}_e$ in the singlet and triplet states of the pair of spins:

$$\varepsilon_0 = \tfrac{1}{2}J + (J^2 + (\mu\delta b)^2)^{\frac{1}{2}}$$
$$\varepsilon_1 = \tfrac{1}{2}J - (J^2 + (\mu\delta b)^2)^{\frac{1}{2}}$$
$$\varepsilon_2 = -\tfrac{1}{2}J - \mu\sum b$$
$$\varepsilon_3 = -\tfrac{1}{2}J + \mu\sum b \tag{2.7}$$

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[1] Relation (2.1) corresponds to one version of the static scaling hypothesis [6].

with

$$\delta b = b_{r+\alpha} - b_r, \qquad \sum b = b_{r+\alpha} + b_r.$$

The free energy of a pair of spins is given by

$$F_{r,r+\alpha} = E_{r,r+\alpha} - T_0 S_{r,r+\alpha} \tag{2.8}$$

where $S_{r,r+\alpha}$ denotes the entropy

$$S_{r,r+\alpha} = -k\left[\sum_{\nu=0}^{3} f_\nu \ln f_\nu + \frac{z-1}{z} \ln\left\{4\frac{(1-S^*)^{S^*-1}}{(1+S^*)^{S^*+1}}\right\}\right] =$$

$$= -k\left[\sum_{\nu=0}^{3} f_\nu \ln f_\nu + (z-1)\ln g_{r,r+\alpha}(S^*)\right] \tag{2.9}$$

$$S^* = f_1 - f_3. \tag{2.10}$$

Writing

$$f'_\nu = e^{-\beta \varepsilon_\nu}, \qquad \sum_{\nu=0}^{3} f'_\nu = Z_e \tag{2.11}$$

we have

$$f_\nu = f'_\nu Z_e^{-1} \tag{2.12}$$

and the free energy takes a form more convenient for further calculations:

$$F_{r,r+\alpha} = \beta^{-1}\ln Z_e^{-1} + \beta^{-1}(z-1)\ln g_{r,r+\alpha}(S^*) + Z_e^{-1}\sum_{\nu=0}^{3} f'_\nu(H_{\nu\nu}^{(2)} - \varepsilon_\nu). \tag{2.13}$$

For the other pair of variables, namely $B_{ex} + B_m$, $M$, the corresponding free energy $\Phi_{r,r+\alpha}$ is obtained by replacing in (2.8) the internal energy $E_{r,r+\alpha}$ with

$$U_{r,r+\alpha} = \sum_{\nu=0}^{3} f_\nu \varepsilon_\nu \tag{2.14}$$

which results in

$$\Phi_{r,r+\alpha} = \beta^{-1}\ln Z_e^{-1} + \beta^{-1}\ln g_{r,r+\alpha}(S^*). \tag{2.15}$$

## 3. The differential equation

In order to derive the differential equation for the fluctuation in the molecular field $b(\vec{r})$ (which will be subsequently expressed in the terms of the fluctuation in magnetic moment) we shall expand the potential $F_{r,r+\alpha}$ in a series with respect to $\delta b$ and $\sum b$ with the accuracy to fourth order terms. The next order terms in $\delta b$ are in the sixth power, and those in $\sum b$ are also in the sixth power, since the uneven powers in $\sum b$ which appear in the expansions of the $f_\nu$ cancel out in the expressions for $Z_e$ and $\ln g(S^*)$. Even the fourth order terms in $\delta b$ could be rejected at once since in the following they will be shown to contribute to the differential equation terms of higher order than the remaining

ones. The leading higher order terms in the differential equation stem from the powers of $\sum b$ in the potential. The term $(\sum b)^6$ contributes to the differential equation a term proportional to $b^5$ with the coefficient by an order of magnitude smaller than the term proportional to $b^3$ which is brought about by $(\sum b)^4$ in the potential. This indicates the fast convergence of the expansion.

Our procedure corresponds with the approach of Smoluchowski [1, 2] in his theory of critical opalescence where the free energy was expanded in a series with respect to the fluctuation in volume (or density) of the subsystem, with an accuracy up to the fourth order term (proportional to $\partial^3 P/\partial V^3$), which does not vanish at the critical point. The difference is that Smoluchowski did not account for the mean spatial inhomogeneity in the fluctuation, and treated the subsystem as a whole.

We now proceed to the expansion of $F_{r,r+\alpha}$. For the $f_v'$ of (2.11) we find the following expressions

$$f_0' = \eta^{3/2}[1 - 2\beta J x^2 + 2\beta J(1+\beta J)x^4]$$
$$f_1' = \eta^{-1/2}[1 + y + \tfrac{1}{2}y^2 + \tfrac{1}{6}y^3 + \tfrac{1}{24}y^4]$$
$$f_2' = \eta^{-1/2}[1 + 2\beta J x^2 - 2\beta J(1-\beta J)x^4]$$
$$f_3' = \eta^{-1/2}[1 - y + \tfrac{1}{2}y^2 - \tfrac{1}{6}y^3 + \tfrac{1}{24}y^4] \tag{3.1}$$

with

$$x = \frac{\mu\delta b}{2J}, \quad y = \beta\mu\sum b, \quad \eta = \exp(-\beta J) \tag{3.2}$$

and correspondingly

$$\beta^{-1}Z_e^{-1} = \beta^{-1}\eta^{1/2}a_1^{-1}(1 + a_1^{-2}a_2^2 + a_1^{-2}y^4 +$$
$$+ 2a_1^{-2}a_2y^2 - a_1^{-1}a_2 - a_1^{-1}a_3 - a_1^{-1}y^2 - \tfrac{1}{12}a_1^{-1}y^4) \tag{3.3}$$

with

$$a_1 = 3 + \eta^2$$
$$a_2 = 2\beta J(1-\eta^2)x^2$$
$$a_3 = 2\beta J[(\eta^2-1) + \beta J(1+\eta^2)]x^4. \tag{3.4}$$

Further on we find that

$$\ln g_{r,r+\alpha}(S^*) = z^{-1}[\ln 4 - (S^*)^2 + \tfrac{1}{6}(S^*)^4] \tag{3.5}$$
$$S^* = 2a_1^{-1}[y - a_1^{-1}a_2y + (\tfrac{1}{6} - a_1^{-1})y^3] \tag{3.6}$$

so that we have

$$\beta^{-1}(z-1)\ln g_{r,r+\alpha}(S^*) =$$
$$= \beta^{-1}\frac{z-1}{z}\{\ln 4 - 4a_1^{-2}[y^2 - 2a_1^{-1}a_2y^2 +$$
$$+ (\tfrac{1}{3} - 2a_1^{-1} + \tfrac{2}{3}a_1^{-2})y^4]\}. \tag{3.7}$$

Finally, calculating

$$H_{00}^{(2)} - \varepsilon_0 = -4Jx^2 + 8Jx^4$$

$$H_{11}^{(2)} - \varepsilon_1 = \beta^{-1}y$$

$$H_{22}^{(2)} - \varepsilon_2 = 4Jx^2 - 8Jx^4$$

$$H_{33}^{(2)} - \varepsilon_3 = -\beta^{-1}y \tag{3.8}$$

we find for the last term on the r.h.s. of (2.13) the expression

$$\beta Z_e^{-1} \sum_{\nu=0}^{3} f'_\nu(H_{\nu\nu}^{(2)} - \varepsilon_\nu) =$$

$$= 4Ja_1^{-1}\beta(1-\eta^2)x^2 + 2a_1^{-1}y^2 +$$

$$+ (\tfrac{1}{3}a_1 - 2)a_1^{-2}y^4 - 8Ja_1^{-2}\beta(1-\eta^2)x^2y^2 \tag{3.9}$$

where the terms proportional to $x^4$ have been already omitted. Adding up the expressions (3.3), (3.7) and (3.9) we find for the increase in the free energy due to fluctuations in the molecular field the expression

$$\Delta F_{r,r+\alpha} = A \left(\sum b\right)^2 + B(\delta b)^2 + C \left(\sum b\right)^2 (\delta b)^2 + D \left(\sum b\right)^4 \tag{3.10}$$

with

$$A = \mu^2\beta^2(3+\eta^2)^{-2}\left(\eta^2 - \frac{z-4}{z}\right)$$

$$B = \mu^2\beta^2(3+\eta^2)^{-2}(2\beta J)^{-1}(3 - 2\eta^2 - \eta^4)$$

$$C = \mu^4\beta^4(3+\eta^2)^4(1-\eta^2)(3+\eta^2)(2\beta J)^{-1}\left(8\frac{z-1}{z} - 3(3+\eta^2)\right)$$

$$D = \mu^4\beta^4(3+\eta^2)^4\left[\tfrac{1}{4}(3+\eta^2)^2(\eta^2-3) + \tfrac{4}{3}\frac{z-1}{z}(7-\eta^4)\right]. \tag{3.11}$$

In these formulae the terms proportional to $(\delta b)^4$ have been omitted since they contribute higher order terms to the differential equation than the ones left.

The next step consists in passing to the continuous variable $\vec{r}$ and in expanding $\sum b$ and $\delta b$ in Taylor series. When this has been done, one finds the following relations

$$\left(\sum b\right)^2 = 4b^2 + \left(\frac{\partial b}{\partial \vec{r}} \cdot d\vec{r}\right)^2 + 2b\,\frac{\partial^2 b}{\partial \vec{r}^2}(d\vec{r})^2$$

$$(\delta b)^2 = \left(\frac{\partial b}{\partial \vec{r}} \cdot d\vec{r}\right)^2$$

$$\left(\sum b\right)^2(\delta b)^2 = 4b^2\left(\frac{\partial b}{\partial \vec{r}} \cdot d\vec{r}\right)^2$$

$$\left(\sum b\right)^4 = 16b^4 + 24b^2\left(\frac{\partial b}{\partial \vec{r}} \cdot d\vec{r}\right)^2 + 16b^3\left(\frac{\partial^2 b}{\partial \vec{r}^2}(d\vec{r})^2\right). \tag{3.12}$$

On the r.h.s. of the relations (3.12) only these terms have been retained, which will contribute to the differential equation terms of magnitude not exceeding the third order. In order to take into account the cubic lattice structure, we have to take a sum over the $z$ pairs to which a spin belongs, and we find

$$\sum_{\alpha=1}^{z} (\delta b)^2 = 2a^2(\nabla b)^2$$

$$\sum_{\alpha=1}^{z} (\textstyle\sum b)^2 = 4zb^2 + 2a^2(\nabla b)^2 + 4a^2 b \Delta b$$

$$\sum_{\alpha=1}^{z} (\textstyle\sum b)^2(\delta b)^2 = 8a^2 b^2(\nabla b)^2$$

$$\sum_{\alpha=1}^{z} (\textstyle\sum b)^4 = 16zb^4 + 48a^2 b^2(\nabla b)^2 + 32a^2 b^2 \Delta b \tag{3.13}$$

where $a$ denotes the lattice constant. After having inserted the expressions (3.13) into the free energy formula (3.10) summed over the $z$ pairs, denoted by $\Delta F_z$, we may subject it to the variational procedure. We find for the corresponding terms in the Euler equation the expressions

$$\frac{d\Delta F_z}{db} = 8zAb + 4a^2 A \Delta b + 64zDb^3 +$$

$$+ 16(C+6D)a^2 b(\nabla b)^2$$

$$-\sum_{i=x,y,z} \frac{d}{dx_i} \frac{d\Delta F_z}{d\left(\dfrac{\partial b}{\partial x_i}\right)} = -4a^2 A \Delta b - 4a^2 B \Delta b -$$

$$- 32a^2(C+6D)b(\nabla b)^2$$

$$\sum_{i=x,y,z} \frac{d^2}{dx_i^2} \frac{d\Delta F_z}{d\left(\dfrac{\partial^2 b}{\partial x_i^2}\right)} = 4a^2 A \Delta b + 192a^2 Db(\nabla b)^2. \tag{3.14}$$

By the relation between the molecular field $b$ and the magnetic moment[2] $M$

$$b(\vec{r}) = \frac{3+\eta^2}{4\mu^2\beta} M(\vec{r}) \tag{3.15}$$

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[2] Note the difference between the magnetic moment $M$ at the lattice site $\vec{r}$ and the magnetic moment $m$ of a spin treated as a member of one of the $z$ pairs to which it belongs. The relation between them is $M = zm$ [4, 5].

we replace the variable $b$ by $M$ and adding the terms on the r.h.s. of (3.14), we obtain the differential equation for the spatial dependence of magnetic moment in the fluctuation in the form:

$$\Delta M - K_1^2 M - K_3 M^3 - K_3 v M (\nabla M)^2 = 0 \tag{3.16}$$

with

$$K_1^2 = \frac{2z}{a^2} \frac{\left(\eta^2 - \dfrac{z-4}{z}\right)}{\left(\dfrac{z-4}{z} - \eta^2 + (2\beta J)^{-1}(3 - \eta^2 - \eta^4)\right)} \tag{3.17}$$

$$K_3 = \frac{z}{a^2 \mu^2} \frac{\left(\dfrac{4}{3}\dfrac{z-1}{z}(7 - \eta^4) - \dfrac{1}{4}(3 + \eta^2)^2(3 - \eta^2)\right)}{\left((2\beta J)^{-1}(3 - 2\eta^2 - \eta^4) + \dfrac{z-4}{z} - \eta^2\right)} \tag{3.18}$$

$$K_3 v = \frac{\left(8\dfrac{z-1}{z}(7 - \eta^4) - \dfrac{3}{2}(3 - \eta^2)(3 + \eta^2)^2 + (2\beta J)^{-1}\left(3\eta^2 + \dfrac{z+8}{z}\right)(3 - 2\eta^2 - \eta^4)\right)}{4\mu^2\left((2\beta J)^{-1}(3 - 2\eta^2 - \eta^4) + \dfrac{z-4}{z} - \eta^2\right)} . \tag{3.19}$$

The first two terms on the l.h.s. of (3.16) represent the Ornstein-Zernike equation for the correlation function. The importance of the two third order terms rests in their qualitatively different dependence on temperature than $K_1^2 M$. The coefficients $K_3$ and $K_3 v$ change
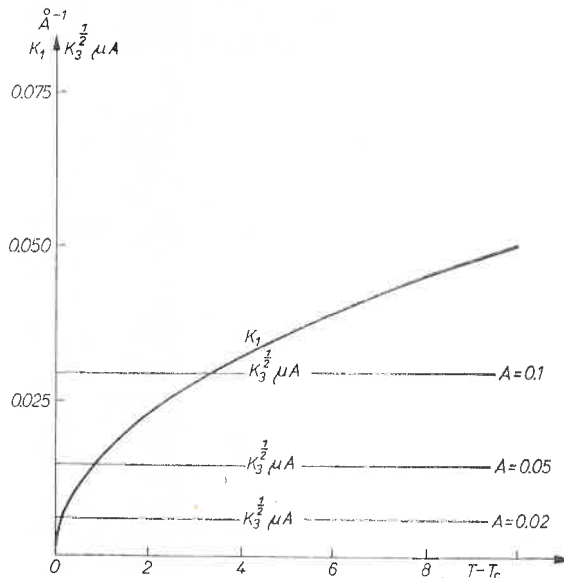


Fig. 1. Comparison of parameters $K_1$ and $\sqrt{K_3}\,\mu A$ in their dependence on temperature, for certain values of $A$

very slowly with temperature and in the interval of several tens of degrees above $T_c$ may be treated as constant and equal to their values at $T_c$. For the b.c.c. lattice ($z = 8$) one finds

$$K_3(T_c) = 0.714a^{-2}\mu^{-2}$$

$$K_3(T_c)\nu(T_c) = 1.008\mu^{-2}.$$

On the contrary $K_1^2$ is close to $T_c$ proportional to $(T-T_c)$ in our approximation (Fig. 1). Thus in the immediate vicinity of the critical point, $K_1^2$ cannot play any role in determining the behaviour of the correlation function.

## 4. The case of the local magnetic field as an intensive variable

The approximations and calculations are in this case analogous to those of the previous chapter. We therefore write down only the final result. Applying the variational procedure to the increase of the thermodynamic potential $\Phi$ given by (2.15) one finds the following equation for the spatial dependence of magnetic moment in the fluctuation:

$$\Delta M + K_2^2 M + K_4 M^3 + K_6 M(\nabla M)^2 = 0 \tag{4.1}$$

with the following values of the coefficients:

$$K_2^2 = \frac{2z}{a^2} \frac{\left(3+\eta^2+4\frac{z-1}{z}\right)}{\left((2\beta J)^{-1}(3-2\eta^2-\eta^4)-\eta^2-\frac{7z-4}{z}\right)} \tag{4.2}$$

$$K_4 = \frac{z}{6a^2\mu^2} \frac{\left(\frac{1}{2}(3+\eta^2)(9-\eta^4)+8\frac{z-1}{z}(7-\eta^4)\right)}{\left((2\beta J)^{-1}(3-2\eta^2-\eta^4)-\eta^2-\frac{7z-4}{z}\right)} \tag{4.3}$$

$$K_6 = \frac{\left(\frac{1}{2}(3+\eta^2)(9-\eta^4)+8\frac{z-1}{z}(7-\eta^4)-(2\beta J)^{-1}(3-2\eta^2-\eta^4)\left(11-\eta^2-\frac{8}{z}\right)\right)}{4\mu^2\left((2\beta J)^{-1}(3-2\eta^2-\eta^4)-\eta^2-\frac{7z-4}{z}\right)} \tag{4.4}$$

Since $K_2$ is practically temperature independent, the nonlinear terms remain always much smaller than the linear ones, and the linear approximation proves to be sufficient for the local field and magnetic moment variables.

## 5. Numerical solution of the nonlinear equation

While looking for the numerical solution of equation (3.16) we have been guided by our earlier approach of [8], where we have introduced the solution of the Ornstein-Zernike equation for a cubic lattice of the form

$$g(x, y, z) = A \exp\left[ -\frac{K_1}{\sqrt{3}} (|x| + |y| + |z|) \right] \qquad (5.1)$$

where $x$, $y$, $z$ refer to the crystalline axes in the cubic lattice. This solution fulfills the demand of reflecting the crystal lattice symmetry, a feature which the correlation function should obviously have. Radial symmetry can enter only at large distances or in the case of poly-crystals. For the body centred and face centred cubic lattices the direction of the preferred directions is not unique, since they may be chosen either along the edges of the cubic or so as to point to the nearest neighbours of the spin at the origin. For the present we shall not discuss the latter possibility. The form (5.1) of the correlation function has found already a striking experimental verification in the neutron critical scattering in the ferroelectric $BaTiO_3$, which has approximately cubic symmetry [9]. The constant intensity curves in Fig. 5 of that paper, follow exactly from the correlation (5.1). While rewritten in terms of the variable

$$\xi = |x| + |y| + |z| \qquad (5.2)$$

the equation (3.16) takes the form

$$3 \frac{d^2 M}{d\xi^2} - K_1^2 M - K_3 M^3 - 3K_3 v M \left(\frac{dM}{d\xi}\right)^2 = 0. \qquad (5.3)$$
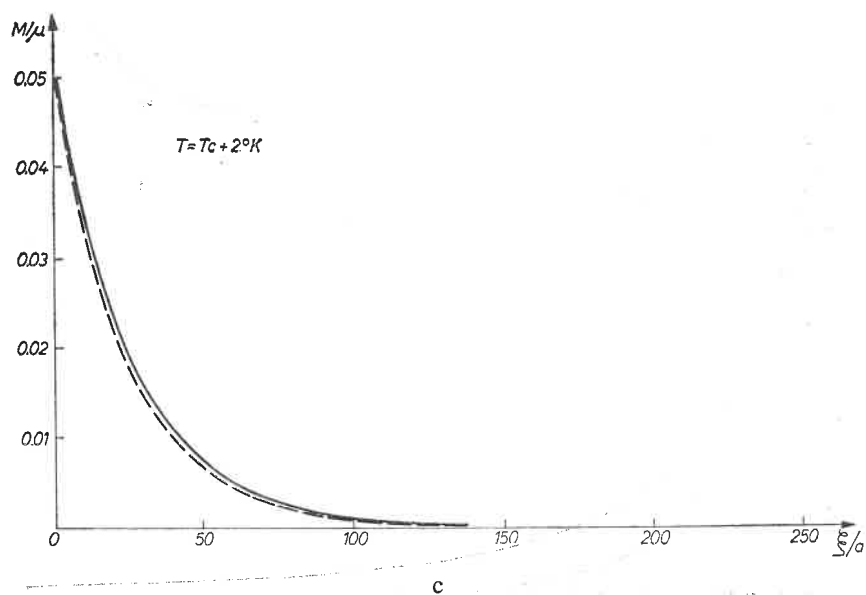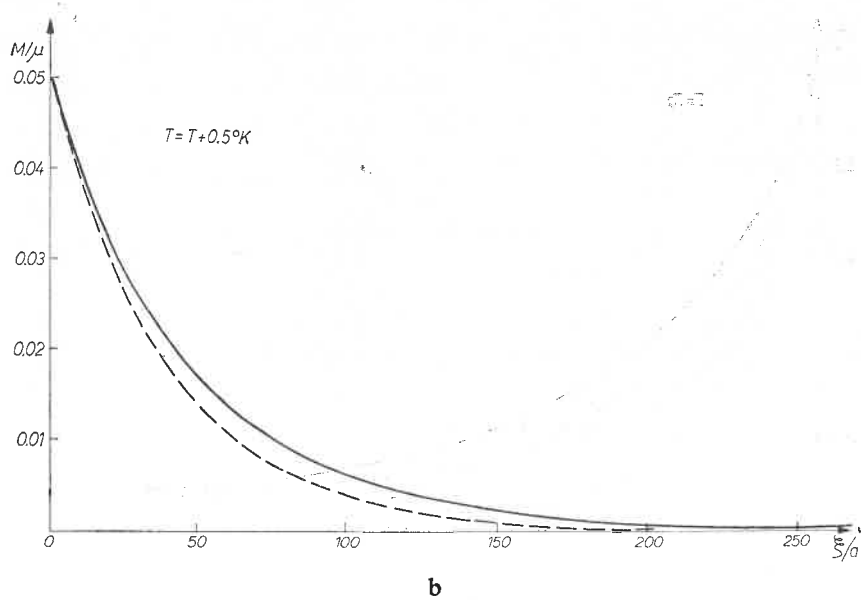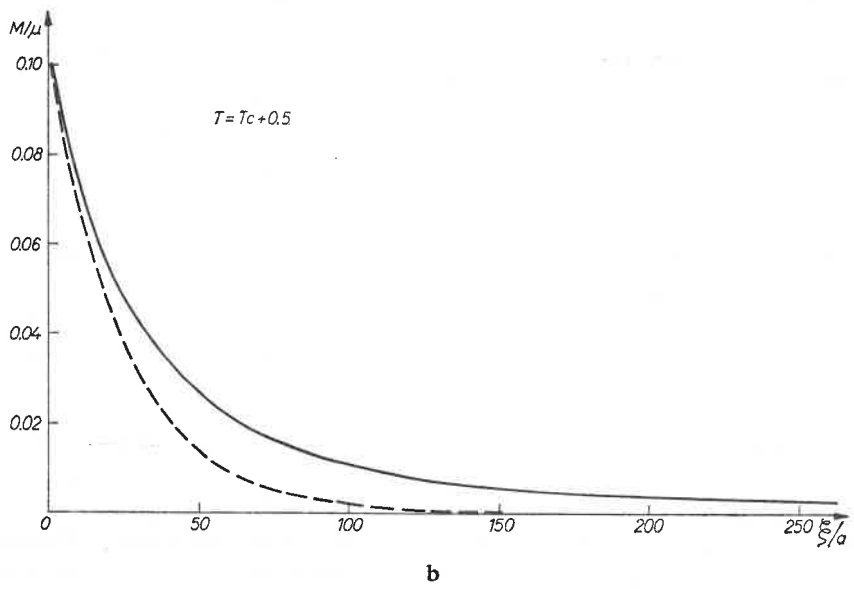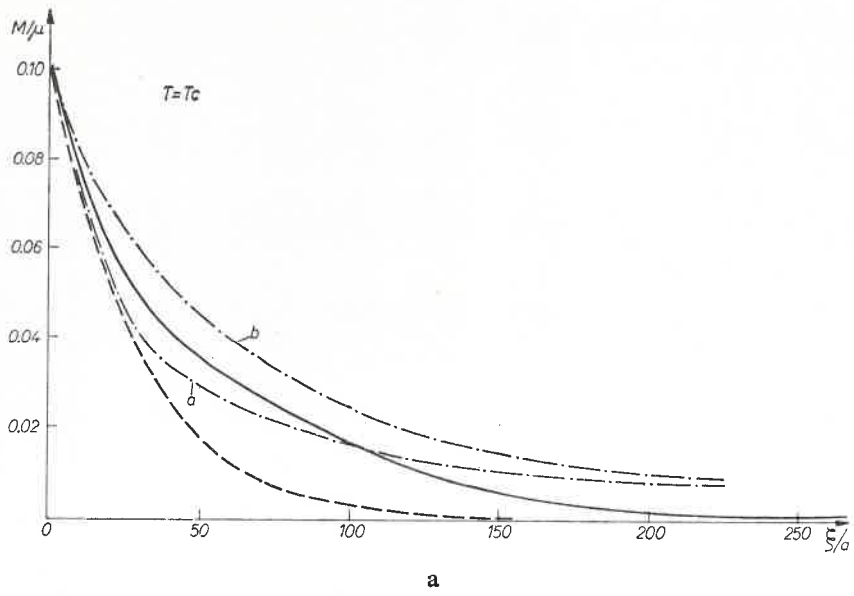


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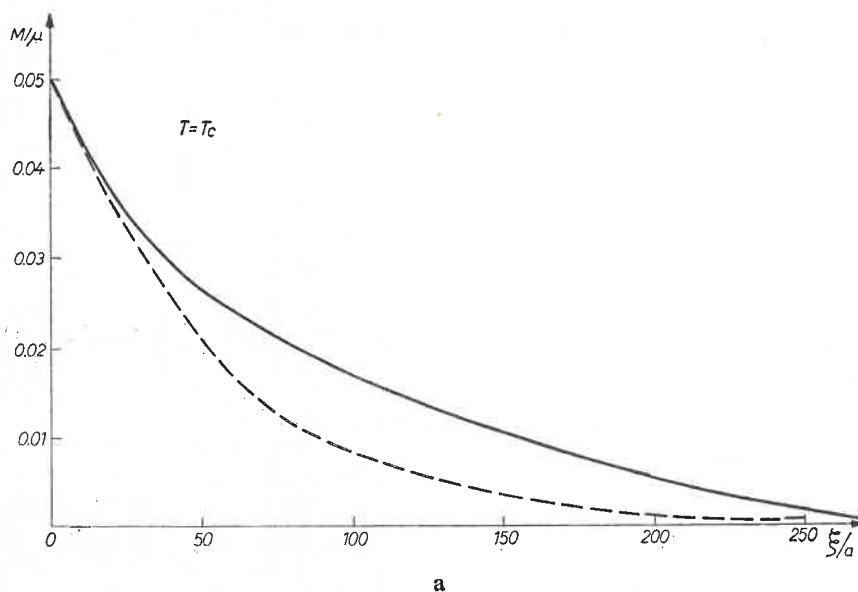
Fig. 2a, b, c. Numerical solution (——) of equation (5.3) together with the exponential approximation (— — — —) given by formula (6.1), for $A = 0.05$ and $T = T_c, T_c + 0.5°$ and $T_c + 2°$
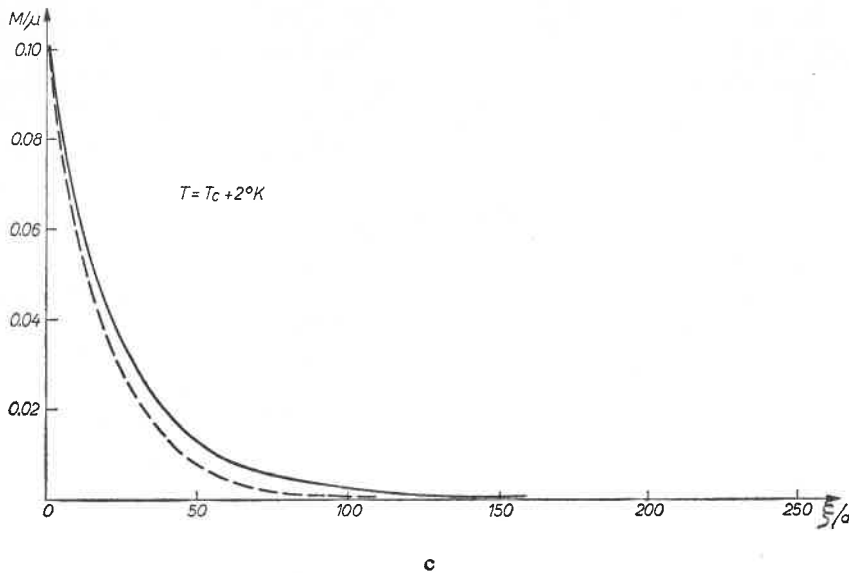
a



b

Fig. 3a, b, c. Numerical solution (———) of equation (5.3), together with the exponential approximation (– – – –) and the hyperbolic approximation (– · – · – · –), for $A = 0.1$, and $T = T_c$, $T_c + 0.5°$ and $T_c + 2°$

Its numerical solution has been found by the Runge-Kutta method, for the boundary conditions $M(0) = $ const, $M(\infty) = 0$. There is only one value of the derivative $dM/d\xi$ at $\xi = 0$ which ensures a solution which fulfills the imposed boundary conditions. The value $M(0) = A\mu$ of magnetic moment at the centre is a parameter which may be varied within the limits $0 \leqslant A\mu \leqslant \mu$. The behaviour of the numerical solutions for two values of the amplitude $A$ is shown in Fig. 2a, b, c, 3a, b, c. Let us notice that the nonlinear terms in the equation (3.16) are important only from $T_c$ up to a few degrees above $T_c$ (for iron the interval is $(T_c, T_c + 2°)$). For higher temperatures the term with $K_1^2$ dominates the behaviour of the correlation function.

## 6. Approximate exponential solution

For discussing the properties of the solution of the nonlinear equation it is convenient to compare the numerical solution with a solution of the form (5.1), namely

$$M(x, y, z) = \mu A \exp\left(-\delta(|x| + |y| + |z|)\right) \tag{6.1}$$

where the amplitude $A$ remains a parameter which may be varied within the limits $0 \leqslant A \leqslant 1$, and $\delta$ is determined by the formula

$$\delta = C\left[\frac{K_1^2 + K_3\mu^2 A^2}{3(1 - K_3 v\mu^2 A^2)}\right]^{\frac{1}{2}} \tag{6.2}$$

where $C$ is a temperature dependent parameter determined numerically, (Fig. 4). The correlation function of the form (6.1) leads to the cross-section for neutron scattering

which covers the experimental data for all the values of the ratio $q/\delta$ at all temperatures $T \geqslant T_c$ [10]. The numerical solution and the solution (6.1) have been compared in Fig. 2, 3 for some values of temperature and of the amplitude $A$. The parameter $C$ has been chosen so as to minimize the difference of the integrals of the numerical and analytical solutions. The approximation (6.1) to the numerical solution is rather poor quite close to $T_c$ and a better one may be found (*vide* the next chapter), however, it is preferable from the point of view of facilitating a qualitative discussion of the properties of the cross-section, as has been already done, [10]. The formula (6.2) for the inverse formal correlation range enables one to evaluate the interval of temperatures within which the term with $K_1^2$ in the differential equation may be neglected as compared with the nonlinear terms. The intervals of temperature where $K_1^2$ is of the same order of magnitude as $K_3\mu^2A^2$ or by an order of magnitude smaller may be read off from Fig. 1, and the condition $|T-T_c|/T_c < 10^{-4}$ for the decisive role of the nonlinear terms may thus be deduced. The formal correlation range $\delta^{-1}$ is finite at the critical point, leading to finite transmission and removing the unphysical result of infinite transmission of the conventional theory. This deficiency of the Ornstein-Zernike cross-section was the subject of Placzek's investigation [11], who tried to remove it by taking into account the dimensions of the scattering system. However, his cross-section formula calculated for unit volume depends on the volume (through the radius $R$) of the scattering system which is not satisfying. Our result corresponds with that of Smoluchowski in the critical opalescence theory [1].

## 7. Temperature shift of the main maximum of scattering

The condition for the temperature shift is given by

$$\frac{d}{dT}\left(\frac{d\sigma}{d\Omega}\right) = 0. \tag{7.1}$$

We shall discuss the consequences of the condition for monocrystals and polycrystals. In both the cases we shall neglect the temperature dependence of the amplitude $A$, which makes our conclusions approximate, but only in a quantitative sense. At constant $A$ condition (7.1) transforms to

$$\frac{d}{d\delta}\left(\frac{d\sigma}{d\Omega}\right) = 0. \tag{7.2}$$

Monocrystals. We shall discuss the magnitude of the shift depending on the direction of the scattering vector $\vec{q} = \vec{k} - \vec{k}_0$. When the form factor and the constant terms are omitted, the cross-section following from the correlation (6.1) has the form [8]:

$$\frac{d\sigma}{d\Omega} = \frac{A\delta^3}{(\delta^2 + q_x^2)\,(\delta^2 + q_y^2)\,(\delta^2 + q_z^2)}. \tag{7.3}$$

For $\vec{q}$ parallel to one of the cubic axes, say, to [001], the cross-section (7.3) reduces to

$$\frac{d\sigma}{d\Omega} = \frac{A}{\delta(\delta^2 + q^2)} .$$ (7.4)

Application of the condition (7.2) to this cross-section ($A$ = constans), leads to no shift. The interpretation should be that the shift is small, if detectable at all.

For $\vec{q}$ in the direction [110] the cross-section (7.3) reduces to

$$\frac{d\sigma}{d\Omega} = \frac{A\delta}{(\delta^2 + \frac{1}{2}q^2)^2}$$ (7.5)

and the application of the condition (7.2) leads to the relation determining the position of the maximum on the temperature axis:

$$\delta^2 = \tfrac{1}{2}q^2$$ (7.6)

or with the expression (6.2) for $\delta$ to the relation

$$K_1^2 = p_0 q^2 - p_1$$ (7.7)

$$p_0 = \frac{3}{2C^2} (1 - K_3 \nu \mu^2 A^2)$$

$$p_1 = K_3 \mu^2 A^2.$$

The equation (7.7) has no solution for $q^2 < p_1/p_0$, which means that for such $q$ the maximum appears at $T = T_c$, that is at the boundary of the interval in which the cross-section is defined. This means no shift for too small $q$ values. The limiting value of $q$ at which the shift starts depends on the value of the parameters $A$ and $C$. As may be seen from Fig. 4, the parameter $C$ is practically constant when temperature exceeds $T_c$ by a few
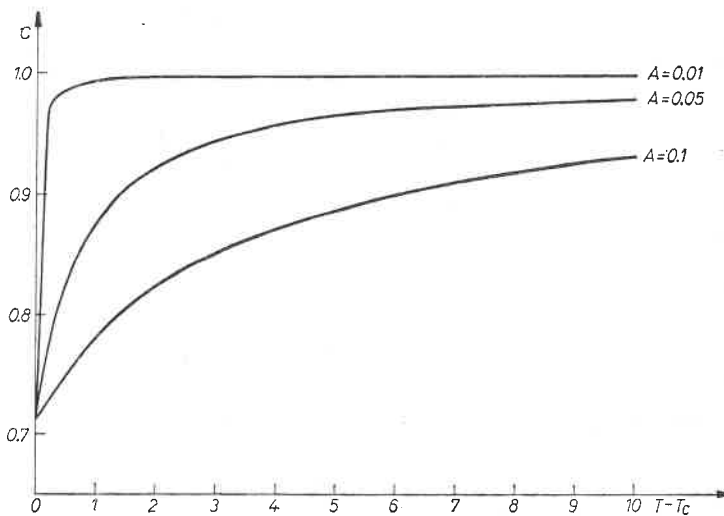


Fig. 4. Dependence of parameter $C$ in the exponential approximation of the correlation function on temperature, for amplitude $A$ equal to 0.01, 0.05 and 0.1
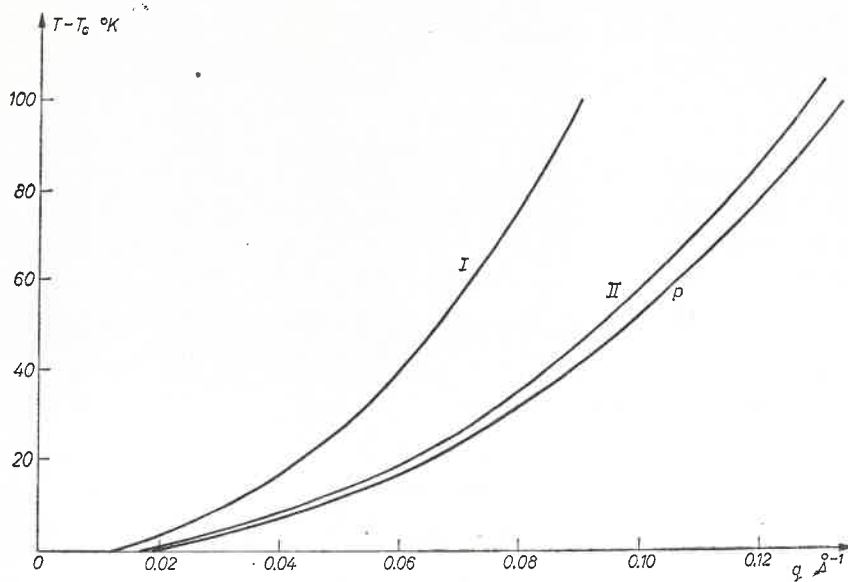
Fig. 5. Dependence of the temperature shift of the (main) maximum of scattering on the scattering vector $q$. Curves $I$ and $II$ correspond to $q$ parallel to the directions [110] and [111] respectively. Curve $p$ represents the shift in polycrystals
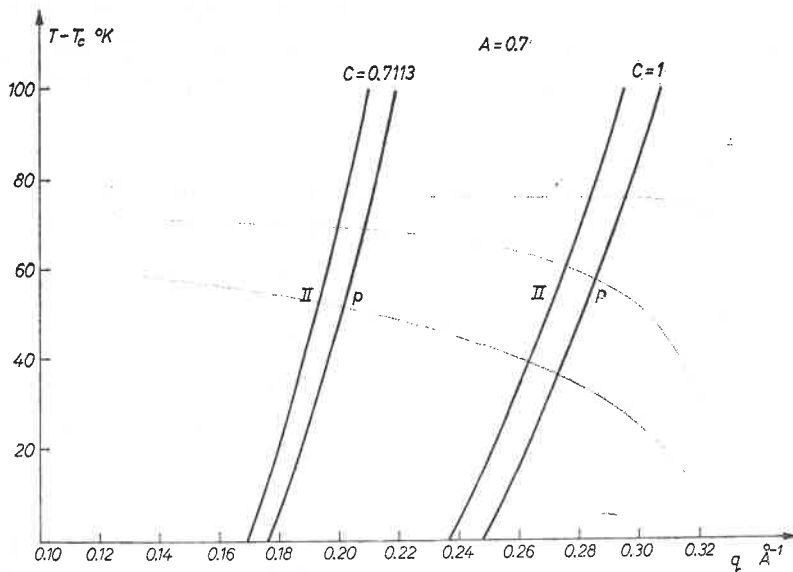


Fig. 6. Dependence of the temperature shift of the (main) maximum of scattering on scattering vector $q$ for a large value of the amplitude $A = 0.7$. Curves $II$ and $p$ represent the shift for $q$ parallel to the direction [111] in a monocrystal, and in a polycrystal. These curves have been calculated with the help of the exponential correlation (6.1) with $C$ equal to the limiting values: 0.711 and 1

degrees, so that what remains in this case is only the dependence on $A$. Since the parabola (7.7):

$$K_1^2 = f(q^2)$$

starts from below the $q$ axis, the dependence of the shift on $q$ is stronger than $q^2$. As a matter of fact, the magnitude of the slope of the curve is influenced by the value of $A$ through the term $p_1/p_0$, which determines the point of intersection of the parabola with the $q$ axis.

For $\vec{q}$ in the direction [111], we find

$$\frac{d\sigma}{d\Omega} = \frac{A\delta^3}{(\delta^2 + \frac{1}{3}q^2)^3} \tag{7.8}$$

and condition (7.2) leads to the relation

$$\delta^2 = q^2$$

or

$$K_1^2 = p_0'q^2 - p_1' \tag{7.9}$$

$$p_0' = \frac{3}{C^2}(1 - K_3\nu\mu^2 A^2)$$

$$p_1' = K_3\mu^2 A^2$$

with a similar meaning as before. Some examples of the magnitude of the shift according to formulae (7.7) and (7.9) are represented in Figs 5, 6.

Polycrystals. The cross-section is obtained from the formula (7.3) after averaging over the directions of the scattering vector $\vec{q}$, and has apart from the form factor and constant terms the form:

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}A\delta \frac{\text{arctg}(\sqrt{1+2p}/p) + \text{arctg}(1/\sqrt{1+2p})}{(1+3p)\sqrt{1+2p}}$$

$$p = \delta^2/q^2. \tag{7.10}$$

The condition (7.2) is now rewritten as

$$\frac{d}{dp}\left(\frac{d\sigma}{d\Omega}\right) = 0. \tag{7.11}$$

The value of $p = p_{max}$ determining the maximum has to be found numerically. Equating this value of $p$ to $\delta^2/q^2$ we get the relation for the shift in the same form as that for monocrystals

$$\delta^2 = p_{max} q^2. \tag{7.12}$$

## 8. Another approximate solution

This has the form

$$M(x, y, z) = \frac{A}{1+B\xi} \tag{8.1}$$

for $K_1^2 \to 0$, that means $T \approx T_c$. Insertion of the solution (8.1) into the equation (4.3) leads to the expression for $B$ as a function of $A$, for two limiting cases, (a) when $\xi \to 0$, and (b) when $\xi \to \infty$. For the case (a) one finds

$$B^{(a)} = \frac{\mu A \sqrt{K_3}}{\sqrt{6 - 3K_3 \nu \mu^2 A^2}} \tag{8.2}$$

while for the case (b):

$$B^{(b)} = \tfrac{1}{6} \mu A \sqrt{K_3}. \tag{8.3}$$

For $A \ll 1$ the difference between the two expressions for $B$ is small, however, for $A \to 1$, the approximate expression of the case (a) is better, because the function (8.1) with $B^{(a)}$ coincides with the numerical solutions for a larger interval of $\xi$ values than with $B^{(b)}$. For $z = 8$ one finds for the ratio $B^{(a)}/B^{(b)}$ the inequality

$$1 < \frac{B^{(a)}}{B^{(b)}} < \sqrt{2} \tag{8.4}$$

where the l.h.s. corresponds to $A = 0$, and the r.h.s. to $A = 1$. The function (8.1) approximates the numerical solution the better, the smaller is the amplitude $A$.

## 9. Radial symmetry solution

For radial symmetry the equation (3.16) takes the form

$$\frac{d^2 M}{dr^2} + \frac{2}{r} \frac{dM}{dr} - K_1^2 M - K_3 M^3 - K_3 \nu M \left(\frac{dM}{dr}\right)^2 = 0. \tag{9.1}$$

We lay upon the solution the demand of being finite for $r \to 0$, and of disappearing for $r \to \infty$. These demands may be met only in the case of joining together two solutions $M_1$, $M_2$ at an intermediate point $0 < r < \infty$. To this end we have chosen the point $r = a$, "$a$" being the lattice constant.

This is, as to the order of magnitude, the smallest distance from the centre of the fluctuation which has a physical meaning. Numerical solutions of the equation (9.1) presented in Fig. 7 have been determined with the assumptions

$$M_1(r = a) = A, \quad (dM_1/dr)_{r=0} = 0 \tag{9.2}$$

where $M_1(r)$ denotes the solution for $0 \leqslant r \leqslant a$ and the conditions

$$M_2(r = a) = M_1(r = a), \quad (dM_2/dr)_{r=a} = -M_2(a)(1 + K_1 a) \tag{9.3}$$
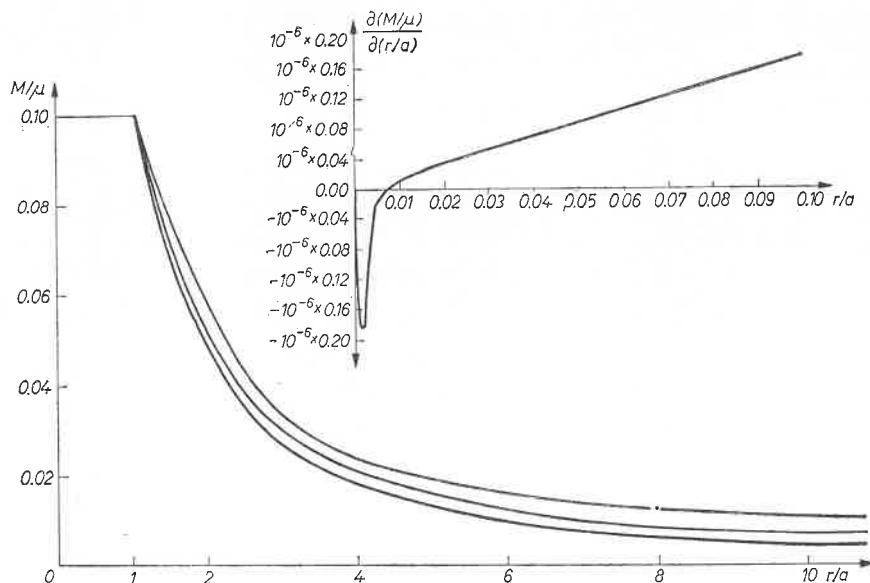
Fig. 7. Numerical solution of the equation (9.1) in the spherical symmetry approximation, for $A = 0.1$. The inset shows the behaviour of the derivative $dM/dr$ for small values of $r/a$, where $a$ denotes the cubic lattice constant

TABLE I

A comparison of values for the numerical solution and the Ornstein-Zernike function

| r/a \ M/μ | $T_c$ | | $T_c+0.5$ | | $T_c+2$ | |
|---|---|---|---|---|---|---|
| | Eq. (9.1) | Eq. (9.4) | Eq. (9.1) | Eq. (9.4) | Eq. (9.1) | Eq. (9.4) |
| | ×100 | ×100 | ×1000 | ×1000 | ×1000 | ×1000 |
| 1.00 | 10.00000 | 10.00000 | 100.00000 | 100.00000 | 100.00000 | 100.00000 |
| 6.00 | 1.66730 | 1.66670 | 14.18000 | 14.17400 | 12.06700 | 12.06000 |
| 11.00 | 0.90989 | 0.90910 | 6.58110 | 6.57350 | 4.76460 | 4.75690 |
| 16.00 | 0.62586 | 0.65010 | 3.85090 | 3.84260 | 2.37370 | 2.36480 |
| 21.00 | 0.47708 | 0.47620 | 2.49820 | 2.48930 | 1.31310 | 1.30290 |
| 26.00 | 0.38553 | 0.38462 | 1.71890 | 1.70950 | 0.77282 | 0.76094 |
| 31.00 | 0.32352 | 0.32258 | 1.22910 | 1.21910 | 0.47557 | 0.46149 |
| 36.00 | 0.27873 | 0.27778 | 0.90318 | 0.89261 | 0.30432 | 0.28736 |
| 41.00 | 0.24486 | 0.24391 | 0.67769 | 0.66640 | 0.20316 | 0.18245 |
| 46.00 | 0.21836 | 0.21739 | 0.51715 | 0.50503 | 0.14319 | 0.11759 |
| 51.00 | 0.19705 | 0.19608 | 0.40039 | 0.38731 | 0.10868 | 0.07665 |

the latter ensuring that the solutions can be, in the interval $a \leqslant r < \infty$, approximated by the Ornstein-Zernike function. A comparison of values for the numerical solution and the Ornstein-Zernike function is represented in Table I. A good approximation the numer-

ical solution is therefore

$$M(r) = A; \quad 0 \leqslant r \leqslant a$$

$$M(r) = A \frac{a}{r} \exp[-K_1(r-a)]; \quad a \leqslant r < \infty. \tag{9.4}$$

The analytic solution near the origin may be represented by the series

$$M(r) = A \left(1 + \alpha_1 \left(\frac{r}{a}\right) + \alpha_2 \left(\frac{r}{a}\right)^2 + \ldots\right). \tag{9.5}$$

Substituting it into the equation (9.1) we find that

$$\alpha_1 = 0$$

$$\alpha_2 = \tfrac{1}{6}(K_3 A^2 + (K_1 a)^2) \tag{9.6}$$

thus demonstrating the character of the analytic solution finite at the origin.

The scattering cross-section calculated with the correlation function (9.4) has the form:

$$\frac{d\sigma}{d\Omega} = \frac{4\pi A}{q^2} \left(\frac{\sin qa}{q} - a \cos qa\right) +$$

$$+ \frac{4\pi A}{q} \frac{1}{K_1^2 + q^2} e^{-K_1 a}[K_1 \sin qa + q \cos qa]. \tag{9.7}$$

This cross-section leads to the shift of the maximum of scattering to temperatures higher than $T_c$, depending on the value of the scattering vector. The condition for the maximum of scattering applied to (9.7) leads to the following equation, which determines the temperature at which the maximum of scattering appears as a function of $q$:

$$K_1^3 + K_1^2 \left(q \operatorname{ctg} qa + \frac{1}{a}\right) + K_1 \left(\frac{2q}{a} \operatorname{ctg} qa + q^2\right) +$$

$$+ q^3 \operatorname{ctg} qa - \frac{q^2}{a} = 0. \tag{9.8}$$

In order to prove only the existence of the shift, without determining its magnitude, it suffices to observe that a solution with $K_1 \geqslant 0$, that means with $T_{max} \geqslant T_c$, is possible only on condition that

$$\operatorname{ctg} qa \leqslant \frac{1}{qa} \tag{9.9}$$

$$0 \leqslant \frac{1}{qa} < \pi.$$

The sign of equality in (9.9) corresponds to $q = 0$, and means that the shift begins already for $q = 0$, a feature which is not confirmed by experiment. It is always possible to find solutions $K_1 > 0$ for $q > 0$ which generally means the existence of the shift.

## *10. Conclusions*

The results of this investigation prove the importance of the nonlinear terms in the equation determining the correlation function, for the description of the immediate vicinity of the critical point. Our argument represents an extension of Smoluchowski's in his critical opalescence theory. The fourth order term in the series expansion of the free energy was used by Smoluchowski in the aim of obtaining finite scattering at the critical point. This argument has been abandoned since the papers of Ornstein and Zernike appeared on account of the introduction of correlation between volume elements so small as to contain in the course of time one or no molecule. We have shown that these correlation effects also do depend on the fourth order terms in the expansion of the thermodynamic potential, when the temperature of the system is close enough to the critical one. It is expected, and the work presently in progress confirmes this expectation, that for gases near the critical point, the role of the fourth order terms in the series expansion of the thermo-dynamic potential is exactly the same as for ferromagnets. The theory of critical indices loses its validity close to $T_c$, *i.e.* for $|T-T_c|/T_c < 10^{-4}$ because the isothermal susceptibility does not enter into the description of fluctuations in the system in this interval of temperature.

The usefullness of our exponential approximation to the solution of the nonlinear differential equation is worth underlining both in the view that it yields all the types of experimentally verified cross-sections (except for the lateral maxima), and in the view of its confirmation by the measurements in the ferroelectric $BaTiO_3$.

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