FLUCTUATIONS OF MAGNETIC MOMENT AND THE SPECIFIC HEAT OF A FERROMAGNET NEAR THE CRITICAL POINT

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(Received April 14, 1976)

The magnetic specific heat near the critical point has been calculated for an isotropic cubic ferromagnet with 1/2 spins. The Helmholtz free energy has been calculated using the constant coupling approximation taking into account the influence of fluctuations of the magnetic moment. The actual inhomogeneous state of the magnetic system is idealized by a model in which the system is divided into N_f equal cells each of which has a volume to the mean volume of a fluctuation. Detailed calculations have been carried out only for temperatures above T_c.

1. Introduction

It is a well known fact that the theoretical temperature dependence of the magnetic specific heat obtained on the grounds of the molecular field approximations does not agree with the experimental data for ferromagnets above the critical point [1]. A tremendous increase in the specific heat is observed when the temperature approaches the critical point while the theoretical results are almost independent of temperature and take on values which are much too small.

The behaviour of specific heat is well predicted by the scaling hypothesis except for temperatures very near the critical point. For reduced temperatures ε of the order 10^{-4} and smaller the scaling law is not obeyed as far as the specific heat is concerned [2].

In theoretical considerations concerning specific heat, a ferromagnet is usually treated as a homogeneous system as far as its magnetization is concerned. On the other hand

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it is known that fluctuations in magnetic moment are responsible for the phenomenon of critical scattering of neutrons near T_c.

We shall show in the following sections of this paper that consideration of fluctuations in magnetic moment leads to temperature dependence of the specific heat which remains in good agreement with the experimental data for temperatures $T \geqslant T_c$.

2. *Fluctuation model of a ferromagnet near the phase transition*

Let us consider a ferromagnetic system of N spins in a paramagnetic phase near the critical temperature. The system in question is inhomogeneous due to fluctuations in the magnetic moment. We replace the actual inhomogeneous state of the system by an idealized model of inhomogeneity in which the system is divided into N_f equal cells in which the magnetic moment differs from the mean one by mean spatial distribution of magnetic moment in a fluctuation. Such a cell following Smoluchowski [3] is treated as a subsystem in a reservoir. The subsystem is very small from a macroscopic point of viev but sufficiently large to apply statistical mechanics to describe the properties of it. The subsystem remains in a nonequilibrium state with respect to the reservoir but we can assume a local equilibrium. In other words, it is generally postulated that all thermodynamic functions of state exist for each cell (subsystem) of the system. The thermodynamic quantities are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities [3, 4].

This physical model of the system near the critical point has been used to derive the equation of state for a fluid system [5]. A similar model has been utilised by Rice [6] in calculating the specific heat of a fluid system.

In such a model the free energy of the system can be expressed by a sum over the free energies of the subsystems. Thus the total change in free energy ΔF of the system due to fluctuations will be equal to the product of the number of fluctuations N_f and the mean value of free energy ΔF_1 of a subsystem

$$\Delta F = N \langle \Delta F_1 \rangle. \tag{1}$$

Equation (1) formally holds for an arbitrary value of N_f connected with the division of the system into subsystems. In the model under discussion only one value of N_f has physical meaning. This value is connected with the most probable number of spins N_1 in the subsystem an can be determined from the condition for a maximum of the probability p of occurrence of a fluctuation

$$\frac{\partial p}{\partial N_1} = 0. \tag{2}$$

The probability distribution function for a subsystem can be expressed by the work necessary to create the fluctuation with a spatial distribution of magnetic moment $\{M_1, M_2, \ldots, M_{N_1}\}$. This work is equal to the change of the proper thermodynamic potential

[7]. Thus the probability distribution function takes the form [8, 10]

$$p(M_1, M_2, \ldots, M_{N_1})dM_1dM_2 \ldots dM_{N_1}$$

$$= \text{const} \exp\left[-\Delta F_1(M_1, M_2, \ldots, M_{N_1})/kT\right]dM_1dM_2 \ldots dM_{N_1}. \tag{3}$$

In order to calculate ΔF_1 an arbitrary phenomenological or microscopic model of a ferromagnet can be applied.

3. Magnetic free energy of a subsystem

To calculate the free energy of the subsystem we assume the Heisenberg model of an isotropic cubic ferromagnet with 1/2 spins. The thermodynamic properties of the subsystem of N_1 spins have been derived by utilizing the constant coupling approximation [9] in which a system can be described by the properties of a representative pair of spins. The spatial distribution of the magnetic moment of a fluctuation treated as a subsystem has been taken into account by introducing an inhomogeneous molecular field into the effective Hamiltonian for a pair of spins [10]. In this approximation the free energy ΔF_1 can be expressed as follows

$$\Delta F_1 = \tfrac{1}{2} \sum_{R=1}^{N_1} \sum_{\alpha=1}^{z} \Delta F_{R,R+\alpha}, \tag{4}$$

where $\Delta F_{R,R+\alpha}$ is related to a pair of spins at $\boldsymbol{R}$, $\boldsymbol{R}+\boldsymbol{\alpha}$ lattice sites and z denotes the number of nearest neighbours. It is convenient to replace the summation over $\boldsymbol{R}$ by integration over the volume of a fluctuation. Thus

$$\Delta F_1 = \frac{1}{2v} \int_{V_1} d^3\boldsymbol{r} \Delta F[b(\boldsymbol{r})], \tag{5}$$

where $b(\boldsymbol{r})$ denotes the spatial distribution of the molecular field in a fluctuation and v is the volume per unit atom in a crystal lattice. The free energy $\Delta F[b(\boldsymbol{r})]$ of a cluster of $z+1$ spins with central spin at $\boldsymbol{r}$ has been obtained by expanding $\Delta F_{R,R+\alpha}$ into a Taylor series with respect to the values of molecular field at $\boldsymbol{R}$ and $\boldsymbol{R}+\boldsymbol{\alpha}$ in the following form [11, 12]

$$\Delta F[b(\boldsymbol{r}] = B_1[b(\boldsymbol{r})]^2 + B_2[\nabla^2 b(\boldsymbol{r})]\, b(\boldsymbol{r})$$

$$+ B_3[\nabla b(\boldsymbol{r})]^2 + B_4[b(\boldsymbol{r})]^2\, [\nabla b(\boldsymbol{r})]^2 + B_5[b(\boldsymbol{r})]^4 + B_6[b(\boldsymbol{r})]^3\, \nabla^2 b(\boldsymbol{r}). \tag{6}$$

The coefficients B obtained in the constant coupling approximation have the form

$$B_1 = \tfrac{1}{4}\beta^{-1} z\gamma^2 u_2, \quad B_2 = \tfrac{1}{4}\beta^{-1}a^2\gamma^2 u_2, \quad B_3 = \tfrac{1}{8}\beta^{-1}a^2\gamma^2(u_2+u_3),$$

$$B_4 = \tfrac{1}{32}\beta^{-1}a^2\gamma^4(u_4+6u_5), \quad B_5 = \tfrac{1}{16}\beta^{-1}z\gamma^4 u_5, \quad B_6 = \tfrac{1}{8}\beta^{-1}a^2\gamma^4 u_5, \tag{7}$$

where

$$u_2 = \eta^2 - (z-4)/z, \quad u_3 = (2\beta J)^{-1}(3+\eta^2)(1-\eta^2), \quad u_4 = u_3[8(z-1)/z - 3(3+\eta^2)],$$

$$u_5 = \tfrac{1}{4}(3+\eta^2)^2(\eta^2-3) + \tfrac{4}{3}(7-\eta^4)(z-1)/z, \tag{8}$$

$\gamma = \dfrac{4\mu\beta}{3+\eta^2}$, $\eta = \exp(-\beta J)$. $\beta = 1/kT$, and where μ denotes the Bohr magneton and where μ denotes the Bohr magneton, J — exchange constant, a — lattice constant.

The distribution of the molecular field $b(r)$ can be determined by means of the variational principle. The method has been formulated in [10]. Application of this method to the problem in question leads to the differential equation for the distribution of the magnetic moment in the following form [12]

$$\Delta M - K_1^2 M - K_3 M^3 - K_5 M(\nabla M)^2 = 0 \tag{9}$$

with

$$K_1^2 = 2za^{-2}\frac{u_2}{u_3-u_2}, \quad K_3 = (\mu a)^{-2} z \frac{u_5}{u_3-u_2}, \quad K_5 = \mu^{-2}\tfrac{1}{4}\frac{6u_5-u_4}{u_3-u_2}. \tag{10}$$

In writing equation (9), the following relation [12] between magnetic moment and molecular field has been used

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

Equation (9) has been obtained by neglecting all terms higher than the fourth order in the expansion (6). When equation (9) is derived neglecting terms higher than the second order in the thermodynamic potential, one obtains a solution for the distribution of magnetic moment with spherical symmetry as follows

$$M(r) = \text{const}\,\frac{\exp(-K_1 r)}{r}. \tag{11}$$

One of the possible approximate solutions of the nonlinear equation (9) with spherical symmetry has the form [13]

$$M(r) = \mu A \exp(-Kr) \tag{12}$$

where

$$K^2 = \frac{K_1^2 + \frac{1}{2}K_3(\mu A)^2}{3[1-\frac{1}{2}K_5(\mu A)^2]} \tag{13}$$

and A denotes the mean value of the magnetic moment (in Bohr magnetons) at the origin and can take values from 0 to 1.

Substituting relation (6) into expression (5), then using the distributions of magnetic moment (11) or (12) and integrating over r we obtain correspondingly in the linear approximation of equation (9),

$$\Delta F_1^{(l)} = \frac{\pi}{4}(v\beta)^{-1}v^2a^3(\mu A)^2(\mu_3+u_2)\,[K_1a+v^{-1}] \tag{14}$$

and in the nonlinear approximation

$$\Delta F_1^{(n)} = \frac{\pi}{16}(v\beta)^{-1}a^3(\mu A)^2(Ka)^{-1}\{(u_3-u_2)\,[1+(K_1a)^2(Ka)^{-2}] + \tfrac{1}{32}(\mu A)^2(u_4+2u_5[z(aK)^{-2}-3])\}, \tag{15}$$

where (va) is the distance between the nearest neighbour spins. In order to obtain formulae (14) and (15) the integral in (5) has been calculated in the limit $V_1 \to \infty$ on the assumption that these integrals converge rapidly because of the form of the solutions (11) and (12). The last assumption is not correct for the linear approximation for temperatures near T_c. This point will be discussed in Section 6.

4. Mean number of fluctuations

It results from our physical model that the mean number of fluctuations N_f is equal to the ratio of all spins N to the mean number of spins N_1 in the fluctuation. Thus to calculate the mean number of fluctuations we use the general condition (2). To simplify the calculations we consider the problem in the approximation of homogeneous fluctuations. In this approximation the change of free energy due to the existence of a fluctuation has the form

$$\Delta F_1(M) = \tfrac{1}{2}N_1[W^{(2)}(T)M^2+W^{(4)}(T)M^4], \tag{16}$$

where

$$W^{(2)}(T) = (4\mu^2\beta)^{-1}zu_2, \qquad W^{(4)}(T) = (16\mu^2\beta)^{-1}zu_5.$$

In order to apply formula (2) one should know the analitical form of the normalization constant

$$(\text{const})^{-1} = \int_{-\infty}^{+\infty} \exp\,[-\Delta F_1(M)/kT]dM. \tag{17}$$

When calculations are carried out neglecting terms higher than the second order in the thermodynamic potential (16), the probability distribution function has the form

$$p^{(l)} = \left(\frac{N_1W^{(2)}}{2\pi kT}\right)^{1/2} \exp\left[-\frac{1}{2kT}N_1W^{(2)}M^2\right] \tag{18}$$

and

$$N_1^{(l)}(T) = \frac{kT}{M^2W^{(2)}(T)}. \tag{19}$$

In this approximation the mean number of fluctuations is expressed in the form

$$N_f^{(1)} = N(kT)^{-1}(\mu A)^2 W^{(2)}(T). \tag{20}$$

Integral (17) cannot be expressed in a form convenient for further calculation when the thermodynamic potential is given in the form (16). Therefore in the nonlinear approximation, we try to find an approximate value of N_f. To do this, we replace $\frac{1}{2}N_1 W^{(4)}M^4$ by $\frac{1}{2}N_1 W^{(4)}\tilde{M}^2 M^2$. Thus

$$(\text{const})^{-1} = \int_{-\infty}^{+\infty} \exp\left\{-\frac{1}{2kT} N_1[W^{(2)}M^2 + W^{(4)}M^4]\right\} dM$$

$$\to \int_{-\infty}^{+\infty} \exp\left\{-\frac{1}{2kT} N_1[W^{(2)}M^2 + W^{(4)}\tilde{M}^2 M^2]\right\} dM.$$

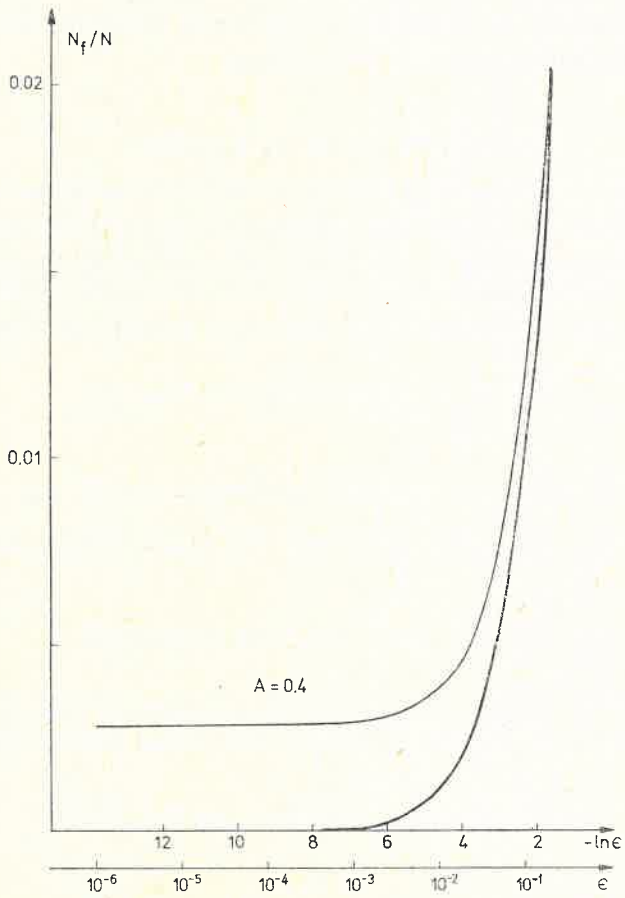

Fig. 1. Temperature dependence of the mean number of fluctuations per spin. The upper curve represents the nonlinear approximation (formula (22)). The lower curve is obtained on the basis of formula (20)

To estimate the value of $\tilde{M}^2$ we consider that $W^{(2)}(T \to T_c) \to 0$. At the critical point we have

$$(\tilde{M}^2)^2 = \frac{2^5 \pi^2 k T_c}{\Gamma^4(\frac{1}{4}) W^{(4)}(T_c) N_1(T_c)}. \tag{21}$$

Eventually, we obtain the following expression for N_f in the nonlinear approximation

$$N_f^{(n)} \simeq N(kT)^{-1}(\mu A)^2 [W^{(2)}(T) + 2W^{(4)}(T)\mu^2 A^2]. \tag{22(}$$

The temperature dependence of $N_f^{(l)}$ and $N_f^{(n)}$) for the amplitude $A = 0.4$ is plotted in Fig. 1.

5. *Discussion*

In order to calculate the specific heat one should apply the thermodynamic relation

$$\Delta C = -T \frac{\partial^2}{\partial T^2} (\Delta F)$$

where ΔF is given by formula (1). Substituting equations (14) and (20) or equations (15) and (22) we obtain expressions for the specific heat in the linear and nonlinear approximation. The numerical calculations have been performed in both approximations. In the linear approximation of the differential equation (9) the specific heat obeys the scaling law. When higher order terms in the thermodynamic potential are taken into account, the specific heat has a finite value at T_c and is a linear function of ln ε when not too near T_c. The specific heat calculated from a nonlinear approximation for two values of the amplitude A is plotted as a function of temperature in Fig. 2.

Our aim was to show that fluctuations should be taken into account in calculations of the specific heat near the critical point. The results obtained for a ferromagnet above the Curie temperature confirm the important role of fluctuations in the critical region as far as the physical properties of a system are concerned. The significance of fluctuations is evident even if calculations are carried out in a rough approximation.

In order to examine the influence of fluctuations on the specific heat several simplifying mathematical and physical assumptions have been made. The division of a system into N_f cells equal to the mean volume of a fluctuation is an idealization of a real system. However, it does not seem possible to describe a real inhomogeneous system due to the fluctuations in any other way.

To calculate the mean number of fluctuations we assumed a homogeneous space distribution of magnetic moment in a fluctuation. The calculations of N_f are, at least in principle, possible in the model of inhomogeneous fluctuations. However, it would involve real mathematical difficulties. In general, when an inhomogeneous fluctuation is replaced by a homogeneous fluctuation their amplitudes need not be the same. The numerical calculations have been performed for several values of the amplitude A treated as a parameter

of the theory independent on temperature. In these calculations we took the same value of the amplitude in the expression for free energy of inhomogeneous fluctuation and for determination of the mean number of fluctuations in homogeneous fluctuation model. Such an assumption can change the final results quantitatively but does not influence the temperature dependence of the specific heat.

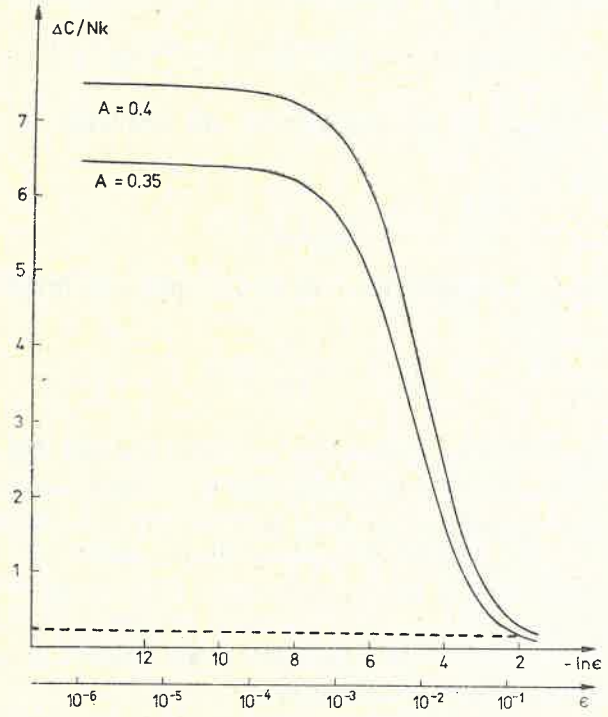

Fig. 2. Magnetic specific heat as the function of ln ε. The upper curves represent the increment of the specific heat due to fluctuations calculated by a nonlinear approximation. The specific heat for a homogeneous system obtained by means of constant coupling approximation is given by the dashed line

In calculating the free energy of a fluctuation, the summation over N_1 spins (Eq. (4)) was replaced by the integral over the volume of the fluctuation (Eq. (5)). This integral has been calculated in the limits $(0, \infty)$. Such an approximation is justified only if the integral converges rapidly. The last approximation is the reason why the linear approximation cannot be extrapolated to the immediate vicinity of the critical point. The upper limit $+\infty$ of the integral in Eq. (5) should be replaced by the radius of a fluctuation.

Another approximation is associated with the calculation of the normalization constant (Eq. (17)) necessary to determine the mean number of fluctuations. From the physical point of view, the set of possible values M is limited by $\pm g\mu S$. Again, integration of the probability distribution function between the limits $\pm\infty$ is justified except when near T_c, when the probability distribution function is not very sharp and does not converge rapidly. The choice of $\pm\infty$ as the limits in Eq. (17) leads to an error in determining the mean number

of fluctuations, but because of the temperature independence of these limits, this does not influence the temperature dependence of the specific heat.

Fitting the numerical results with experimental data for specific heat is possible by proper choice of the value of the parameter A which has a sense of the amplitude of a fluctuation at its center. However, because of the approximations discussed above the value of A corresponding to the best fit cannot be treated as a real value of the amplitude.

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