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Internal energy versus moment for ferromagnets and pyroelectrics

P. J. Grout and N. H. March
Department of Physics, The Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2BZ, United Kingdom
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Since the internal energy E is a monotonically increasing function of the temperature T, the moment $M(T)$ can be expressed as a function of internal energy E. The corresponding form of $E(M)$ is focused on in this paper. For ferromagnets, the two-dimensional Ising model is used to obtain the exact form of $E(M)$ and this is discussed both near $T=0$ and near the critical temperature T_c. In three dimensions, we are *only* able to discuss the forms of $E(M)$ near $T=0$ and $T=T_c$. For low temperatures, spin-wave theory readily yields the result that, for *insulating* ferromagnets, $\Delta E = E - E(0)$ is proportional to $(\Delta M)^{5/3}$ with $\Delta M = M(0) - M(T)$ while for the metallic case $\Delta E \propto (\Delta M)^{4/3}$. Though the theory is much less complete than for ferromagnets, some results are very briefly discussed for pyroelectrics.

I. INTRODUCTION

The present paper is concerned with exploring the relationship between the internal energy $E(T)$ and the moment M in systems such as ferromagnets and pyroelectrics. Because the first-principles theory of pyroelectricity is still lacking the emphasis is predominantly on ferromagnets, with some brief comments on pyroelectrics.

The reason for such a relationship between $E(T)$ and the moment M can be simply stated as follows: $E(T)$ is accessible by experiment, say via the specific heat c_v. Since c_v is positive, E is a monotonically increasing function of T. Consequently, we can formally express T uniquely as $T(E)$. Then we can rewrite the moment $M(T)$ as a function of the internal energy E. It is such a discussion in the (E,M) plane that is the focal point of this paper.

Though naturally we are concerned basically with three-dimensional systems, we shall make the above considerations precise by starting with the two-dimensional Ising model, for which we have the exact Onsager solution.

II. INTERNAL ENERGY VERSUS MOMENT FOR FERROMAGNETS

A. Two-dimensional Ising model

The exact results of the two-dimensional Ising model can be summarized as follows[1]: If J measures the strength of the exchange interaction, the internal energy $E(T)$ is given by

$$E(T) = -J\coth 2K\,[1 + (2/\pi)(2\tanh^2 2K - 1)K_1(m)]\,, \tag{2.1}$$

where

$$m = 2\sinh 2K/\cosh^2 2K, \quad K = J/k_BT \tag{2.2}$$

and $K_1(m)$ is the complete elliptic integral of the first kind.

Also, the magnetization M is given in terms of its zero-temperature value $M(0)$ by

$$M(T) = \begin{cases} M(0)(1-\operatorname{csch}^4 2K)^{1/8}, & T < T_c \\ 0, & T > T_c \end{cases}. \tag{2.3}$$

It will be convenient at first to work with the reduced magnetization $\sigma = M(T)/M(0)$. In the present case it is simplest to eliminate T in favor of E by using Eq. (2.3) in (2.1).

Then we find straightforwardly that

$$\begin{aligned} E(M) &= E(\sigma) \\ &= -J[1+(1-\sigma^8)^{1/2}]^{1/2} \\ &\quad \times (1 + (2/\pi)\{2[1+(1-\sigma^8)^{1/2}]^{-1} - 1\}K_1(m)). \end{aligned} \tag{2.4}$$

Here m is given in terms of σ by

$$m = 2(1-\sigma^8)^{1/4}/[(1-\sigma^8)^{1/2}+1]. \tag{2.5}$$

Evidently then Eqs. (2.4) and (2.5) give precise expressions to the philosophy outlined above. The form of the relation for E as a function of $\Delta = 1 - \sigma$ is plotted in Fig. 1.

B. Behavior near T_c

While we have in Eqs. (2.4) and (2.5) the behavior of E for all σ between 0 and 1, it is of interest in what follows to discuss the form of $E(\sigma)$ around T_c, when $M(T)$, and therefore σ, tends to zero. We can either develop the above equations for this case, or we can note the well-established results for (a) the logarithmic singularity in c_v, i.e.,

$$c_v \sim \ln(T_c - T)\,, \tag{2.6}$$

and (b) the behavior of σ,

$$\sigma \propto (T_c - T)^{1/8}. \tag{2.7}$$

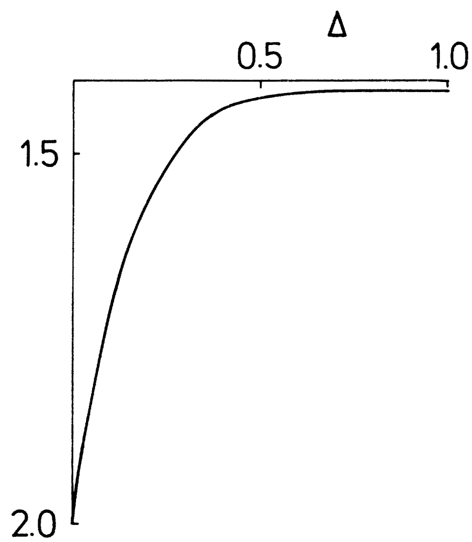

FIG. 1. Plot of internal energy E/J vs $1-\sigma=\Delta$, where σ is the reduced magnetization. This is the exact result of the two-dimensional Ising model. Note the slope of this curve is finite at $\Delta=0$ (Ref. 2).

Now

$$\frac{\partial E}{\partial T}=\frac{\partial E}{\partial \sigma}\frac{\partial \sigma}{\partial T}\sim\frac{\partial E}{\partial \sigma}\frac{1}{8\sigma^7}, \tag{2.8}$$

and since $\partial E/\partial T$ is given by (2.6) it is straightforward to verify that

$$E(T)-E(T_c)\sim 8\sigma^8\ln\sigma-\sigma^8. \tag{2.9}$$

In Fig. 1, we actually have plotted $E(M)$ as a function of $\Delta=1-\sigma$.

All these results are exact for the two-dimensional Ising model. Naturally, in three dimensions, we have no exact solutions,but for the limiting cases of low temperatures and of T near T_c we can again make precise statements for ferromagnets.

III. THREE-DIMENSIONAL FERROMAGNETS

A. Ferromagnets

1. Insulating ferromagnets

In this case at low temperatures the well-established spin-wave theory gives us the results we desire. Since the spin-wave energy is proportional to k^2, at long wavelengths, in contrast to the linear k dependence of the energy of the acoustic phonons, the specific heat in an insulating ferromagnet is dominated by the spin-wave excitations. Thus we can write

$$c_v \propto T^{3/2}+\text{(higher-order terms)}. \tag{3.1}$$

Hence the departure of the internal energy from $E(0)$, its zero-temperature value, is given by

$$\Delta E=E(T)-E(0)$$
$$=\text{const}\,T^{5/2}+\text{(higher-order terms)}. \tag{3.2}$$

The magnetization follows the Bloch $T^{3/2}$ law, and consequently we can write the reduced magnetization as

$$\sigma=1-M(T)/M(0)$$
$$=\text{const}\,T^{3/2}+\text{(higher-order terms)}. \tag{3.3}$$

From Eq. (3.2), at sufficiently low temperatures, $T(E)\propto(\Delta E)^{2/5}$. This together with Eq. (3.3) gives

$$\Delta E=\text{const}\,(\Delta M)^{5/3}+\text{(higher-order terms in }\Delta M), \tag{3.4}$$

where $\Delta M=M(0)-M(T)$. This is the desired result for insulating ferromagnets.

2. Metallic ferromagnets

The above results depend solely on collective magnetic excitations. We now consider the case of the metallic ferromagnet where other excitations are involved. In these materials at sufficiently low temperatures the specific heat is dominated not by the contribution from the spin-wave excitations but by that from the conduction electrons. This contribution is proportional to T and hence the internal energy ΔE is given by

$$\Delta E\propto T^2+\text{(higher-order terms)}. \tag{3.5}$$

The magnetization, however, is still given by the Bloch $T^{3/2}$ law,[3] and therefore, since from (3.5) it follows that $T(E)\propto(\Delta E)^{1/2}$, we get from (3.1) a result different from that of the insulating ferromagnet, that at low temperatures (small ΔM)

$$\Delta E=\text{const}\,(\Delta M)^{4/3}+\text{(higher-order terms in }\Delta M). \tag{3.6}$$

We note that in the (E,M) plane both for insulating and for metallic ferromagnets the internal energy approaches its zero-temperature limit with zero slope.

B. Critical behavior of ferromagnets

In terms of the usual critical indices, we can write the specific heat c as

$$c\propto(T_c-T)^{-\alpha} \tag{3.7}$$

and the magnetization as

$$M\propto(T_c-T)^{\beta} \tag{3.8}$$

sufficiently near the critical temperature. Thus the approach of E to its value $E(T_c)$ at the critical point is given by

$$E-E(T_c)\propto(T_c-T)^{1-\alpha} \tag{3.9}$$

and hence

$$E - E(T_c) \propto M^{(1-\alpha)/\beta} \tag{3.10}$$

While in molecular-field theory we have $\alpha = 0$, $\beta = \frac{1}{2}$, β in practice seems near $\frac{1}{3}$, while $\alpha \sim 0.1$ or 0.2. Therefore E approaches its value $E(T_c)$ at T_c with zero slope, as also is the case in molecular-field theory.

Though the exponents α and β may turn out to be different for insulating ferromagnets on the one hand, with short-range exchange interactions, and for metallic ferromagnets on the other, with longer-range Rudermann-Kittel-Kasuya-Yosida exchange forces, the arguments of this section make it quite clear that in three-dimensional ferromagnets the internal energy E as a function of moment M approaches its values $E(T_c)$ and $E(0)$ with zero slope. This is the most important qualitative conclusion we reach here for ferromagnets, whether insulators or metals.

IV. COMMENTS RELATED TO PYROELECTRICS

Though the first-principles theory is much less well developed than for ferromagnets, we feel it is of some interest to comment finally on the relevance of the above approach to pyroelectrics. For these materials a satisfactory phenomenological argument exists for the rigid-ion model.[4] This yields

$$\Delta E \propto \Delta M . \tag{4.1}$$

Thus the assumption of rigid ions leads to a cusp at $\Delta M = 0$. From the above conclusions for ferromagnets we anticipate that a proper treatment of the electronic deformability as the ions move will remove this cusp and lead to zero slope. The arguments of the present paper strongly suggest that in pyroelectrics

$$\Delta E \propto (\Delta M)^{n+1}, \quad \text{with } n > 0 . \tag{4.2}$$

Thermodynamic inequalities[4] yield $n \leq 1$. With $c_v \propto T^3$ at low temperatures, the pyroelectric coefficient $d(\Delta M)/dT \propto T^{4/(n+1)-1}$. If $n > 0$, the primary pyroelectric coefficient always dominates the secondary one, which is proportional to T^3, at sufficiently low temperatures.

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[1]See, for example, J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1974), Pt. A, p. 132.

[2]Dr. J. Stephenson has drawn our attention to the fact that for any Ising lattice the low-temperature expansions of $\Delta E[= E(T) - E(0)]$ and $\Delta[= M(0) - M(T)]$ lead to $\Delta E \propto \Delta$, for small Δ. See, *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Chap. 6.

[3]Of course, Stoner excitations contribute a higher-order term proportional to T^2.

[4]P. J. Grout, N. H. March, and T. L. Thorp, J. Phys. C 8, 2167 (1975).