easily checked quantitatively because the actual susceptibility of a metal is made up of a number of contributions among which the above is only one. It is true, however, that alkali metals have a positive susceptibility independent of temperature which is of the order of magnitude (15.24).

15-3. Ferromagnetism; internal field model

A phenomenon which was extremely fruitful for the development of statistical mechanics is ferromagnetism. We call a material ferromagnetic if it is capable of having a magnetic moment in the absence of an applied field. Ferromagnetism is not very widespread among substances in general; the majority of ferromagnets known are alloys or compounds of the elements iron, nickel, cobalt. If a ferromagnet is heated it loses its characteristic properties at a definite temperature, the so-called Curie temperature T_c. Above the Curie point, ferromagnetic materials are paramagnetic, with an enhanced value of the paramagnetic susceptibility. Figure 15.6

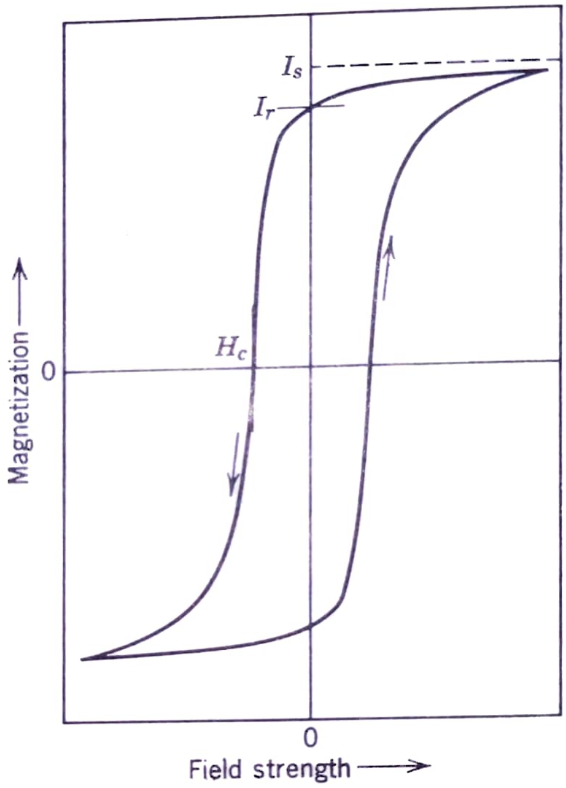

Fig. 15.6. Empirical magnetization curve of a ferromagnetic material; the curve is irreversible, and is roughly characterized by the saturation magnetization I_s, the remanence I_r, and the coercive field H_c.

shows a typical plot of the magnetization as a function of an applied magnetic field for a ferromagnetic material (magnetization curve). It is seen that we deal with a phenomenon showing hysteresis; the magnetization is not a unique function of the field but depends upon past history. In particular, the *remanence* I_r, that is, the magnetization at zero field, depends on the direction in which the specimen was last saturated. Similarly, a finite opposing field, the *coercive field* H_c, is necessary to bring the magnetization to zero. A characteristic aspect is the saturation of the magnetization at a value I_s as the field grows. This aspect is reminiscent of the Langevin curves shown in Fig. 15.3. However, paramagnetism saturates only at very high fields (10,000 oersted) or very low temperatures, while in ferromagnetism the phenomenon occurs in easily accessible ranges of temperature and field. The one element which is truly reminiscent of Langevin's theory is the value of the saturation magnetization, which is essentially the same for paramagnets and ferromagnets.

The interpretation of the mechanism of ferromagnetism has long been handicapped by the obvious nonequilibrium aspect of the phenomenon as commonly observed. The phenomenon as depicted in Fig. 15.6 is nonconservative; in fact, by equation (1.27), the area of the magnetization curve gives directly the amount of energy converted into heat in one hysteresis cycle. The phenomenon contains therefore frictional aspects which are not capable of a direct atomic explanation. Pierre Weiss* took the fundamental step necessary for an understanding by postulating that the atomic nature of ferromagnetism is obscured to us by a structure involving relatively large magnetized blocks, called *domains*. A single domain was supposed to have a magnetization curve of the type shown in Fig. 15.7; the magnetization appears as a definite function of temperature and field. Thermodynamics and statistics are therefore applicable. What distinguishes the curve from the Langevin curve of Fig. 15.1 is the *spontaneous magnetization* which the material possesses at zero field. According to Weiss, those aspects of Fig. 15.6 not reproduced in Fig. 15.7 were to be explained by the assumption of interlocking domains which are spontaneously magnetized but are not free to follow external changes reversibly. This hypothesis of Weiss has been brilliantly verified in the last few years. We shall not try to discuss this aspect here, but shall refer the reader to the appropriate literature.† The atomic aspect of ferromagnetism, represented by Fig. 15.7, is in itself a very interesting problem.

The original hypothesis of Weiss to explain Fig. 15.7 was the hypothesis of an *internal field* proportional to the magnetization. At first sight this

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* P. Weiss. *J. phys.* **6,** 667 (1907).

† C. Kittel and J. K. Galt. "Ferromagnetic domain theory," *Solid State Phys.* **3,** 437 (1956).

seems a reasonable hypothesis because such an effect is known from electrodynamics. Let us therefore modify equation (15.06) by making on the right-hand side the substitution

$$H \rightarrow H + \alpha I \tag{15.25}$$

with α an undetermined number. We get then for the case $j = \frac{1}{2}$, with (15.02) and (15.16)

$$I = \frac{N}{V} \mu \tanh \beta\mu(H + \alpha I) \tag{15.26}$$

The equation of state (15.26) connecting the thermodynamic variables I, H, T, is in qualitative agreement with the facts about ferromagnetism.

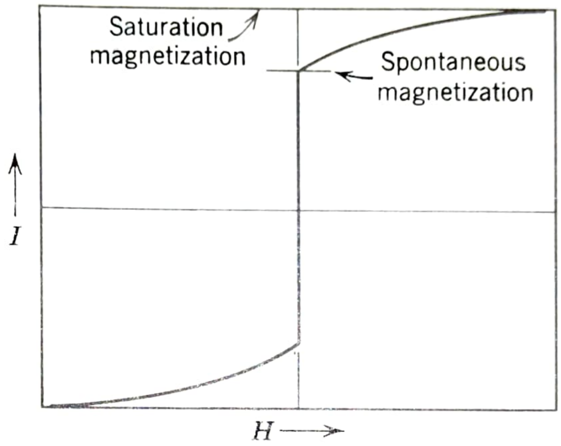

Fig. 15.7. Magnetization curve of a single magnetic domain; the curve is reversible, and differs from the Langevin curves mainly through the presence of a spontaneous magnetization at zero magnetic field.

We shall consider first the fact about spontaneous magnetization. Setting H in (15.26) equal to 0 and solving for T, we get

$$k\,T = \frac{\alpha\,\mu\,I}{\operatorname{arctanh}\left(\dfrac{I\,V}{N\,\mu}\right)} \tag{15.27}$$

The equation yields a T for every I between 0 and $N\mu/V$. When I is almost equal to $N\mu/V$ the denominator is very large and T is correspondingly small. Thereupon as I decreases T increases. However, T does not increase indefinitely because the inverse hyperbolic tangent is always larger than its argument (see Fig. 15.3). We therefore find

$$k\,T < \frac{\alpha\,\mu\,I}{I\,V/N\,\mu} = \frac{\alpha\,N\,\mu^2}{V} = k\,T_c \tag{15.28}$$

When the inequality does not hold, the only solution of (15.27) is $I = 0$. The temperature $T = T_c$ separates therefore a high-temperature region, in which the specimen is paramagnetic, from a low-temperature region, in which it is ferromagnetic. This transition temperature is the Curie temperature discussed earlier. Figure 15.8 shows the spontaneous magnetization versus temperature curve predicted by (15.27) together with empirical results for iron, nickel, cobalt, and magnetite; it is seen that the agreement is close. A particularly interesting aspect of it is the way the magnetization approaches zero near the Curie point. To see this in detail from (15.27), we may assume $I\,V/N\,\mu$ small and expand the arctanh, thus

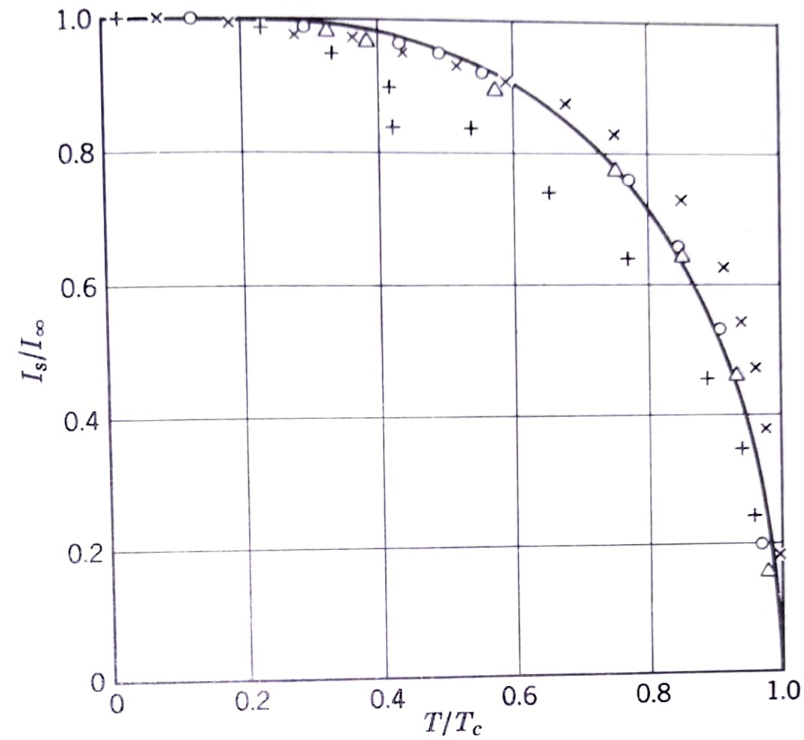

Fig. 15.8. Plot of spontaneous magnetization versus temperature; theoretical two-level internal field curve with experimental points for iron (×), nickel (o), cobalt (Δ), and magnetite (+) (after R. Becker).

$$k\,T \approx \frac{\alpha\,\mu\,I}{\dfrac{I\,V}{N\,\mu} + \dfrac{1}{3}{\dfrac{I\,V}{N\,\mu}}^{3}}$$

or, with the definition (15.28),

$$I \approx \frac{N\,\mu}{V}\sqrt{3}\left(\frac{T_c}{T} - 1\right)^{1/2} \tag{15.29}$$

This is an approach to zero with infinite slope. In addition to the spontaneous magnetization, the internal field theory also predicts correctly the susceptibility of ferromagnetic materials above the Curie temperature. In the paramagnetic range I is small compared to its saturation value, and therefore the tanh in (15.26) is small and can be set equal to its argument; the resultant equation for I is, with (15.28),

$$I = \frac{N\mu^2 H}{Vk(T-T_c)} \tag{15.30}$$

This equation is the *Curie–Weiss law* for the paramagnetic susceptibility of ferromagnetic materials. It differs from the previously derived Curie law only in the replacement of T by $T-T_c$. The Curie–Weiss law is also in good agreement with experiment.

It is interesting that such a successful theory as the internal field theory shows its insufficiency only when the experimental facts are used to estimate α. We get from (15.28)

$$\alpha = \frac{kT_cV}{N\mu^2} \approx \frac{10^{-16} \times 10^3 \times 1}{10^{23} \times 10^{-40}} = 10^4 \tag{15.31}$$

This is in contradiction to electrodynamics, which predicts α's in (15.25) at most equal to 4π. Or, in other words, the observed Curie temperatures, which lie in the neighborhood of 1000°, are much too high if it is assumed that the atomic magnetic dipoles couple through their magnetic interaction.‡

15-4. Ferromagnetism; Ising model

The discovery of the correct nature of the ferromagnetic coupling force came as a by-product of quantum mechanics. Dirac§ showed that the electronic spin and the Pauli exclusion principle combine in such a way as to produce between the spins of two neighboring electrons a coupling of the form

$$\phi = J\,\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 \tag{15.32}$$

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‡ It is interesting that in the related phenomenon of ferroelectricity the conclusion goes the other way. Electric moments are about two orders of magnitude larger (in Gaussian units), and ferroelectric Curie points generally lower than their magnetic analogues. The field constant α thus comes out to be of reasonable order; the internal field hypothesis is therefore right in this case, at least in its basic idea. Of course, the coupling of electric dipoles through their electrostatic interaction has also a local aspect, which is rather more complicated than the ferromagnetic coupling discussed here.

§ P. A. M. Dirac. *Proc. Roy. Soc. A* **123,** 714 (1929). See also any textbook on quantum mechanics.

Here $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are the two spins and J is a function of distance called the *exchange energy* or *exchange coupling*. It can be of either sign. If the wave functions of the two electrons interpenetrate substantially, the exchange energy is of the same order as the electrostatic interaction, but at larger distances it falls off exponentially as the wave functions themselves. We may therefore think of J as being of electrostatic order, but only acting between close neighbors. Heisenberg‖ was the first to realize that this exchange energy J, if of negative sign, offers a natural explanation for the phenomenon of ferromagnetism. For a local coupling of spins of the form (15.32), strung throughout a crystalline material, will tend to align spins to form a large resultant; in atoms, this effect is well known as *Hund's rule* and arises from just this cause.

We have today only partial answers concerning a set of spins coupled by exchange coupling. For some purposes approximate answers may be obtained by the use of approximate methods. There is one question of principle, however, which needs a straightforward answer, and that is whether the spontaneous magnetization and the Curie point phenomenon, as exhibited in Fig. 15.8, are in fact consequences of the interaction (15.32). A transition of the Curie point type, in which a system passes through a continuity of intermediate states, yet exhibits a discontinuity in some temperature derivatives at a temperature T_c, is called a *second-order phase transition*. The question whether a coupling between neighbors, strung over large distances, can entail such second-order phase changes is a question of principle which statistics must answer by yes or no. This is the reason for the intense interest in this type of system on the part of workers in statistical mechanics.

At the present time, the question raised in the preceding paragraph cannot be answered mathematically for the full exchange interaction (15.32). There is, however, a simplified form of the exchange interaction, the so-called *Ising model*, for which far-reaching answers have been obtained. We shall therefore turn to this model for further discussion.

The Ising model is essentially a truncated exchange hamiltonian. It replaces $\sigma_{1x}\,\sigma_{2x} + \sigma_{1y}\,\sigma_{2y} + \sigma_{1z}\,\sigma_{2z}$ by $\sigma_{1z}\,\sigma_{2z}$ only; this is qualitatively plausible because, if the quantization is along the z direction, only this part is diagonal, and the expectation values of the other operators are zero. In addition, in its simpler aspects, the Ising problem needs no quantum mechanics for its discussion, because all variables of the truncated hamiltonian commute. The quantum variable σ_z thus becomes a classical scalar σ capable of two values, $+1$ and -1. A network of such scalar spins is

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‖ W. Heisenberg. *Z. Physik* **49**, 619 (1928).

thus assumed to stretch through the crystal, forming a coupled system. The magnetic enthalpy of the model is thus taken as

$$E = -\tfrac{1}{2}\sum_{i,k} J_{ik}\,\sigma_i\,\sigma_k - \mu\,H\sum_i \sigma_i \tag{15.33}$$

where each summation runs over all spins. The magnitude of the interaction constants J_{ik} is almost always chosen so as to leave only adjacent pairs in the first sum. In fact, in some forms of the model there is just one coupling constant linking all neighbors. Expression (15.33) then takes the form

$$E = -J\sum_{\langle i,k\rangle} \sigma_i\,\sigma_k - \mu\,H\sum_i \sigma_i \tag{15.34}$$

Here the summation $\sum_{\langle i,k\rangle}$ runs over all pairs of direct neighbors. The suppression of the x and y components of spin in the Ising model produces consequences which one must keep in mind to interpret the results of the model reasonably. In the first place, it deprives magnetism of its angular momentum aspect and thus falsifies its dynamics. It is, furthermore, incorrect at low temperature, as we shall see later. It appears, however, that there is no essential defect in the model at and above the Curie point, where the statistical count of states assumes preponderant importance; this count is right in the model. We may therefore presume that the cooperative aspect of an exchange coupled network is similar to the one resulting from the truncated expressions (15.33) and (15.34).

The first thing to do in a discussion of the Ising model is to simplify it still further so as to yield an approximate derivation of the Weiss theory. In this approximate derivation we treat the plus spins and minus spins as two chemical species. Let N_+ be the number of plus spins and N_- the number of minus spins, and define their concentrations by the customary relations

$$c_+ = \frac{N_+}{N_+ + N_-} = \frac{N_+}{N} \tag{15.35a}$$

$$c_- = \frac{N_-}{N} = 1 - c_+ \tag{15.35b}$$

If we consider these concentrations fixed but the distribution of the spins random, then the entropy of the arrangement is given by equation (5.66) for the entropy of mixture:

$$S = -N\,k\,(c_+ \ln c_+ + c_- \ln c_-) \tag{15.36}$$

To estimate the energy, we limit ourselves to the case for which there is only one nearest neighbor interaction J. The assumption of a random arrangement of spins implies then that the relative abundances of $++$, $--$, and $+-$ neighbor pairs have their random values, that is, are as c_+^2, c_-^2 and $2c_+ c_-$, respectively. If we insert this into the energy expression (15.34) we get

$$E = -\tfrac{1}{2} z N J (c_+^2 + c_-^2 - 2 c_+ c_-) - N \mu H (c_+ - c_-) \quad (15.37)$$

Here z is the number of nearest neighbors of any given spin (two for a linear array, four for a two-dimensional square net, six for a simple cubic lattice, eight for a body-centered cubic lattice, etc.). To simplify further, let us introduce the total magnetic moment M as a variable through the substitutions

$$c_+ = \tfrac{1}{2}\left(1 + \frac{M}{N\mu}\right) \quad (15.38a)$$

$$c_- = \tfrac{1}{2}\left(1 - \frac{M}{N\mu}\right) \quad (15.38b)$$

We then get for E

$$E = -\frac{1}{2}\frac{z J M^2}{N \mu^2} - M H \quad (15.39)$$

and for S, from (15.36),

$$S = N k \left\{\ln 2 - \tfrac{1}{2}\left(1 - \frac{M}{N\mu}\right) \ln\left(1 - \frac{M}{N\mu}\right) - \tfrac{1}{2}\left(1 + \frac{M}{N\mu}\right) \ln\left(1 + \frac{M}{N\mu}\right)\right\} \quad (15.40)$$

Now we introduce the free energy Φ at constant field

$$\Phi = U - T S - H M = E - T S \quad (15.41)$$

It is the free energy entering on the right-hand side of (8.38). By (8.39), it has the property of being a minimum for fixed temperature and fixed magnetic field. If, therefore, we succeed in approximating this quantity for a given physical situation, and if we find the approximation contains one or more undetermined parameters describing the internal state of the system, then we must dispose of them in accordance with the Second Law, and make Φ a minimum with respect to these parameters. In the present instance, we have one such parameter M; we must dispose of it by demanding that

$$\left(\frac{\partial \Phi}{\partial M}\right)_{H,T} = 0 \quad (15.42)$$

This yields, after some rearrangement of terms,

$$\frac{M}{N\mu} = \tanh \frac{\mu}{k T}\left(H + \frac{z J M}{N \mu^2}\right) \quad (15.43)$$

We recognize in (15.43) equation (15.26) previously derived, with a physical interpretation for the "internal field constant" α:

$$\alpha = \frac{z\,J}{N\,\mu^2/V} \tag{15.44}$$

Since N/V is the number of spins per unit volume, it is of the order $1/r^3$, where r is the distance between neighboring spins; the denominator of (15.44) is thus of the order of the magnetic interaction energy μ^2/r^3 of two neighboring spins, which is roughly 10^{-16} erg. The numerator, on the other hand, is the exchange coupling, which is more like an electrostatic quantity; this means that it may rise toward 10^{-12} erg. The large magnitude of α is thus explained, and the "internal field" idea reduced to a more rational set of assumptions. With the reduction of α to fundamental constants, quantities derived from it are also so reduced. We shall note here only the new expression for the Curie temperature T_c which replaces (15.28), namely,

$$\frac{z\,J}{k\,T_c} = 1 \tag{15.45}$$

According to the Weiss internal field theory, the Curie point transition is characterized, not only by the magnetic effects just discussed, but also by a characteristic thermal behavior. This thermal behavior is worth discussing here because it is indicative of cooperative phenomena in general. Viewed from this point of view, paramagnetism and ferromagnetism deal with the same ordering process, first without, then with, cooperative action. The modification of the thermal behavior as a consequence of this action is then of basic interest. Part of this modification can be predicted from equation (7.44), which is valid for structural transformation in general. The coupling makes the enthalpy change larger, while the entropy change stays the same. The transformation is thereby shifted into a higher temperature range. However, this is not the most striking change. To see the modification we eliminate M between (15.39) and (15.43), setting $H = 0$. The result is

$$\frac{k\,T}{J} = z\,\frac{\sqrt{-\dfrac{2E}{zNJ}}}{\operatorname{arctanh}\sqrt{-\dfrac{2E}{zNJ}}} \tag{15.46}$$

Differentiation of T with respect to E yields the heat capacity curve shown in Fig. 15.9. It is seen that the curve has a discontinuity at the Curie point: the specific heat rises to a maximum and thereupon goes discontinuously to zero. Yet, at the same time, the change is not as abrupt as for normal phase changes, where two forms of different material properties coexist at one temperature. In other words, we have reproduced the features of a second-order phase change.

Having verified that a certain type of approximate treatment of the Ising model will yield the Weiss internal field theory and the second-order phase change associated with it, we must go on to verify whether these results are a consequence of the model or of the approximations used in evaluating its properties. For many years this distinction was not properly appreciated. It is true that we deal with approximations in either case: in one case we deal with a model which is only an approximate image of reality; in the other we derive a result which is only an approximate consequence of the theory. However, there is a world of difference between the two cases. In the approximate evaluation of a theory we simply make mistakes; that is, we depart from logic. We hope the departure is small. But when we get striking results, such as those shown in Figs. 15.8 and 15.9, then it is possible that they are a consequence of our mistakes;

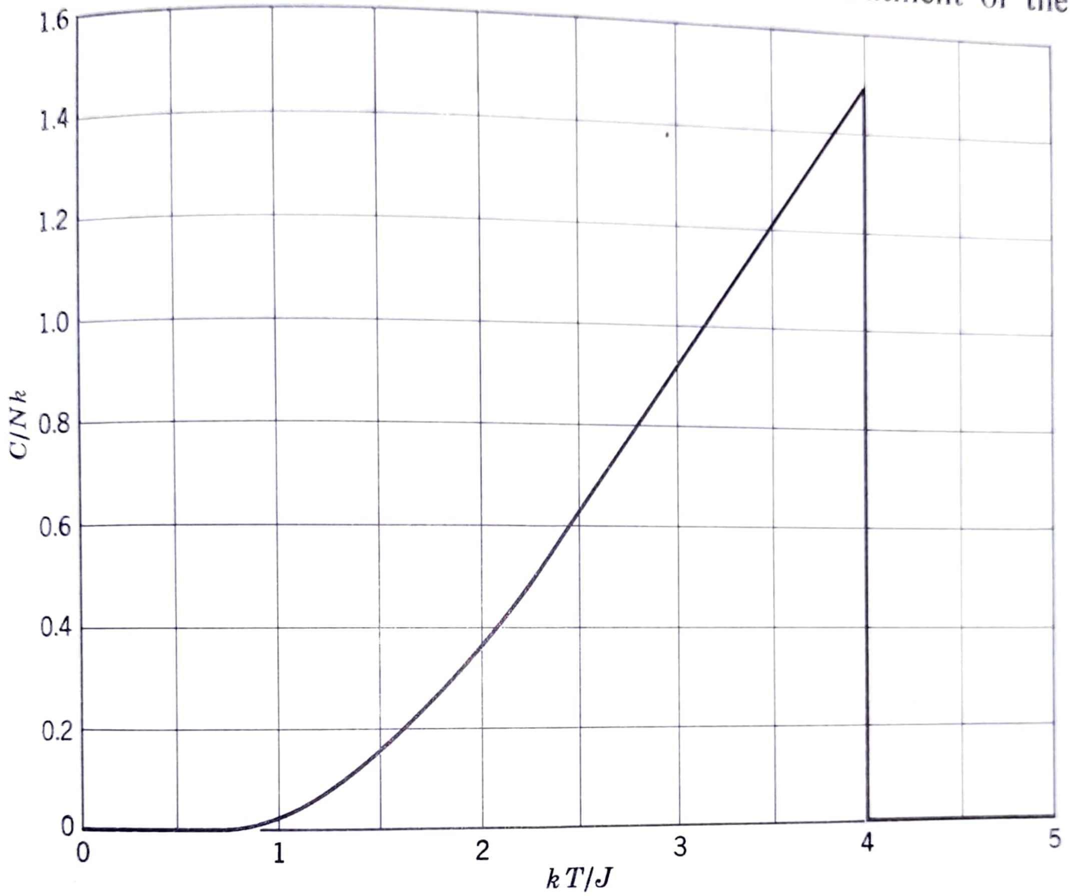

Fig. 15.9. Heat capacity at constant field versus temperature in the internal field theory of ferromagnetism; comparison of this curve with Fig. 15.4 shows the effect of a cooperative coupling.

the results are then worthless and prove nothing. If, on the other hand, we adopt an internally consistent model which admittedly does not correspond exactly to anything in nature, and if we evaluate conscientiously the properties of that model, striking results of the type mentioned are of value. We know then that there is an interacting system which exhibits second-order phase changes according to the known laws of physics, and that perhaps experimentally observed systems are not too far removed from our model system.

It is this kind of reason which has led physicists to investigate seriously the Ising model. Second-order phase changes are tricky: by equation (4.19), erratic changes in the specific heat imply erratic changes in the fluctuations of the system. Even today the nature of these fluctuations near the critical temperature is poorly understood. But the Ising model has at least shown that second-order phase changes can arise as a consequence of the known laws of physics. This is the reason why this model is worth studying in detail.

Careful investigation of the Ising model means construction of its partition function. Since we want to investigate its properties in the presence of a magnetic field, the partition function will be of the type $F^\star$ discussed in Section 8-2. Anticipating this later need, we wrote down the necessary relations at that time. The "energy" in the Boltzmann exponent is the quantity (8.37), which we usually call magnetic enthalpy for clarity. Fortunately it is also the energy discussed in (15.33) and (15.34); it differs from U in that it also contains the potential energy in the applied field H. For this type of energy the partition function $F^\star$ equals

$$F^\star = \sum_{\sigma_i = \pm 1} \exp\left[\beta J \sum_{\langle i,k\rangle} \sigma_i \sigma_k + \beta \mu H \sum_i \sigma_i\right] \tag{15.47}$$

Here $\sum_i$ goes over all spins, $\sum_{\langle i,k\rangle}$ over all pairs of direct neighbors, and $\sum_{\sigma_i=\pm 1}$ over the 2^N combinations ± 1 of the N spins. We verify that we get from $F^\star$ by differentiation

$$E = -\left(\frac{\partial \ln F^\star}{\partial \beta}\right)_H \tag{15.48}$$

and

$$M = \frac{1}{\beta}\left(\frac{\partial \ln F^\star}{\partial H}\right)_\beta \tag{15.49}$$

These relations were already written down in (8.39). It was shown in (8.38) that the partition function $F^\star$ is associated with the "magnetic free energy" $A - \mathbf{H} \cdot \mathbf{M}$.

The study of $F^\star$ for cases of physical interest is an extremely hard problem. Its difficulty resides in the fact that, if one wishes to evaluate it for the purpose of investigating phase transitions, one cannot assume the number of cooperating units to be finite. For in this latter case (15.47) consists of a finite sum of terms without temperature singularity; this makes the sum likewise nonsingular. All interesting results are therefore obtained by examination of the Nth root of $F^\star$ in the limit that N goes to infinity. The difficulties of a limiting process are therefore superimposed upon the combinatorial difficulty of evaluating (15.47).

Some further thought along the same lines shows that even an infinite Ising model cannot show ferromagnetism as long as it is infinite in one dimension only. For ferromagnetism means a spontaneous magnetization, which in turn means long-range order among the spins without an applied field. Suppose that we have such an ordered arrangement of N Ising spins with all spins parallel. Then we can upset it by introducing a single break in it, that is, introducing the energy $2J$ at one point as shown in Fig. 15.10. Since this break can be made at any of N positions (where $N + 1$ is the number of members of the linear chain), the entropy gain is $k \ln N$. The free energy change is therefore

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Fig. 15.10. Destruction of order in a linear array of spins; one single reverse coupling is sufficient to destroy long-range order.

$$\Delta\Phi = 2J - kT \ln N$$

Since we have to consider $\Delta\Phi$ in the limit of infinite N, there is no temperature, however small, sufficient to prevent destruction of long-range order, because Φ is always lower for the disordered state.

The same argument was developed by Peierls[¶] to prove the contrary for a square net of Ising spins: such a net is ferromagnetic. For this purpose an estimate must be made of the number of ways in which a border of L segments separating + and − spins can be laid in a square net. Such a border is shown in Fig. 15.11. The number of ways in which such a border can be laid determines the entropy, and the length of the border determines the energy. The result of the investigation is that the entropy, as well as the energy, varies as the first power of the length of such a border. A temperature can therefore be found which is sufficiently low so that the

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[¶] R. Peierls. *Proc. Cambridge Phil. Soc.* **32,** 477 (1936).

energy overpowers the entropy in the expression $E - TS$. The stable state is then one not containing such a border if the temperature is sufficiently low.

The chapter following this one gives the derivation of the system partition function for the rectangular Ising net without magnetic field, that is, a two-dimensional array of spins having the value ± 1 and having an interaction $-J_1 \sigma \sigma'$ between neighbors in the rows and an interaction $-J_2 \sigma \sigma'$ between neighbors in the columns. There are several derivations known, but they all make use of advanced algebraic methods which have no easily discerned relationship to physical reasoning. We shall therefore separate the algebra from the physical discussion and take over the results (16.62), (16.63), and (16.67) from the next chapter. To avoid extraneous complications we shall restrict the detailed discussion to the case $J_1 = J_2$, with a few observations concerning the more general case.

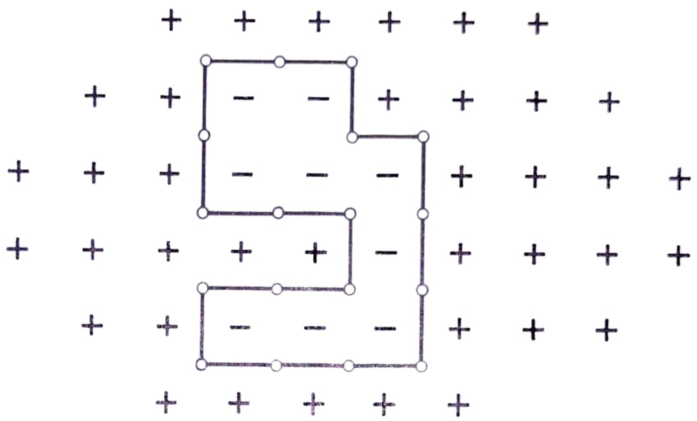

Fig. 15.11. Introduction of reverse orientation into the square Ising net: it is now necessary to maintain a border of high energy.

As worked out in Chapter 16, the square net of Ising spins has a partition function F which equals

$$F = f^N \tag{15.50}$$

where N is the total number of spins, and f is given by

$$\ln f = \ln(2 \cosh 2\beta J) + \frac{1}{\pi} \int_0^{\frac{1}{2}\pi} \ln \left\{ \frac{1 + (1 - \kappa^2 \sin^2 \omega)^{\frac{1}{2}}}{2} \right\} d\omega \tag{15.51}$$

with

$$\kappa = \frac{2 \sinh 2 \beta J}{\cosh^2 2 \beta J} \tag{15.52}$$

The parameter κ is zero at small temperature, rising to a maximum of unity at a temperature at which

$$\sinh \frac{2J}{kT_c} = 1 \tag{15.53a}$$

or

$$\frac{J}{kT_c} = 0.4407 \tag{15.53b}$$

Then κ returns to zero at high temperature. This means that the integral in (15.51) vanishes for both very low and very high temperatures. The rough outline of the behavior of f is therefore contained in the first term; however the second term has an effect at intermediate temperatures.

The best way to investigate the result more closely is to compute the energy E by (15.48). If we maintain the distinction between the two terms in (15.51) we get E in the form

$$E = -2NJ \tanh 2\beta J - NJ \frac{\sinh^2 2\beta J - 1}{\sinh 2\beta J \cosh 2\beta J} \left\{\frac{2}{\pi} K(\kappa) - 1\right\} \tag{15.54}$$

where $K(\kappa)$ is the complete elliptic integral of the first kind. At first sight the statement that the first term gives roughly the behavior of the system seems even more appropriate for E than it was for f. For now the second term vanishes three times: at high and at low temperature (because of the vanishing of the curly bracket), and at the critical point defined by (15.53) [because of the vanishing factor $(\sinh^2 2\beta J - 1)$]. This rough result is not unexpected. The first term in (15.54) is the result (16.14) for a one-dimensional Ising chain, with an obvious doubling of the exchange interaction J for the two dimensions. However, the influence of the second term is now more apparent. $K(\kappa)$, the complete elliptic integral of the first kind, has a logarithmic infinity at the critical point for which $\kappa = 1$. Consequently the entire second term behaves as $(T-T_c) \ln |T-T_c|$ in the immediate neighborhood of T_c. The slope of the energy curve is therefore infinite at $T = T_c$, and the heat capacity is also infinite. Away from the critical point the second term has a typically "cooperative" influence. When the first term is strongly negative the correction is also negative; on the other hand, when the first term approaches zero the correction is positive and brings the result still closer to zero. Figure 15.12 shows the two energy versus temperature curves in heavy and dotted outline.

This is perhaps the right moment to refer back to the internal field approximation, which gave for the Curie point the result (15.45). In the language of equation (15.53) this means for the square net

$$\frac{J}{k\,T_c} = 0.25$$

This is not in very good agreement with (15.53). Even more disappointing is the energy versus temperature curve as a whole, which is shown for comparison in Fig. 15.12 as the curve in light outline. In addition to misplacing the Curie point the internal field theory misinterprets its significance. It yields zero energy, that is, complete randomness, at the Curie temperature, while in reality 70 % of the total coupling is still present. This is due to short-range alignment of neighboring spins. This alignment predominantly determines the energy, even if the sample as a whole has no resultant spin. The same discrepancy is shown in Fig. 15.13 in a comparison of the two heat capacity curves.

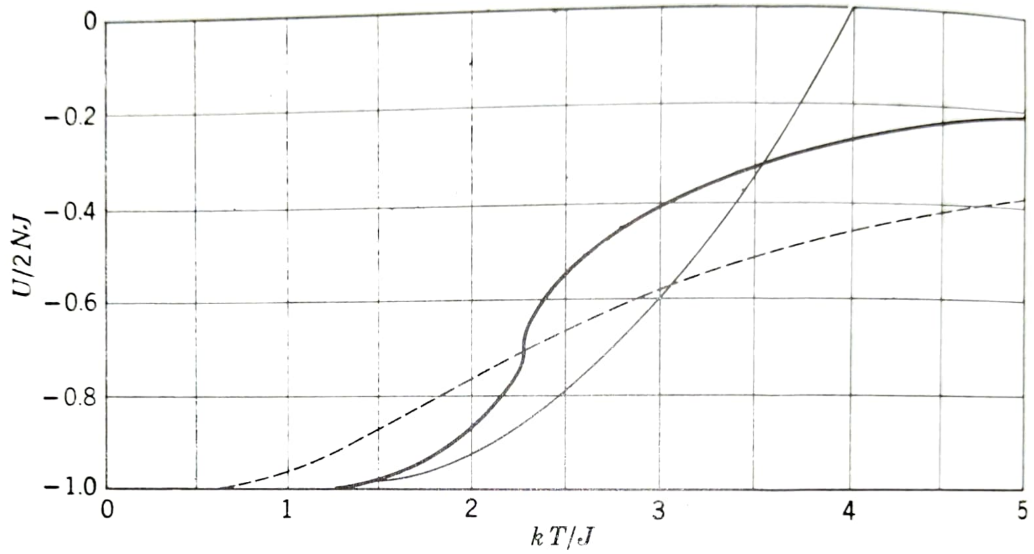

Fig. 15.12. Energy versus temperature for the Ising square net. The exact curve is shown in heavy outline, the "internal field" curve in light outline, and the equivalent one-dimensional curve dashed.

The behavior of the two-dimensional Ising model as a function of the magnetic field is not known at this time, the mathematics having been found intractable. We have therefore no good evidence about the validity of the Curie–Weiss law (15.30) in a theoretically consistent model. Yang** did succeed in computing the spontaneous magnetization. It is zero above the Curie point and below it has the value

$$M = N\mu\left[\frac{\cosh^2 2\beta J}{\sinh^4 2\beta J}(\sinh^2 2\beta J - 1)\right]^{1/8} \qquad (15.55)$$

** C. M. Yang. *Phys. Rev.* **85,** 809 (1952).

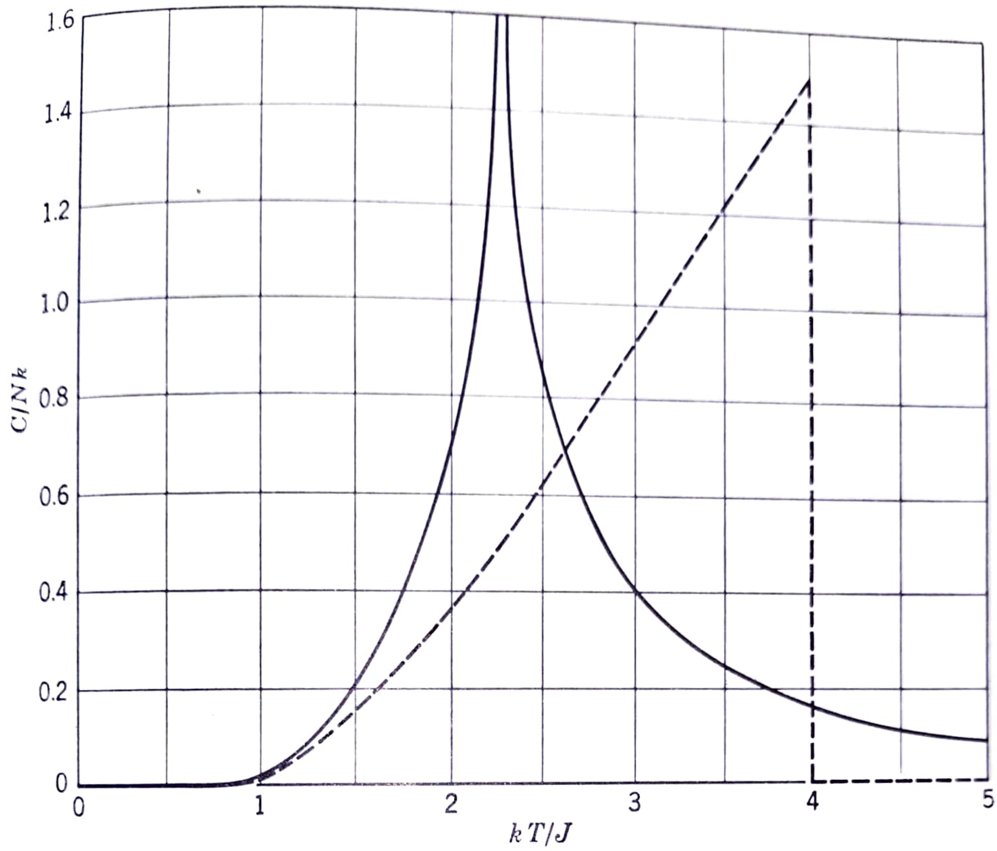

Fig. 15.13. Exact and internal field plots for the heat capacity of the Ising square net versus temperature.

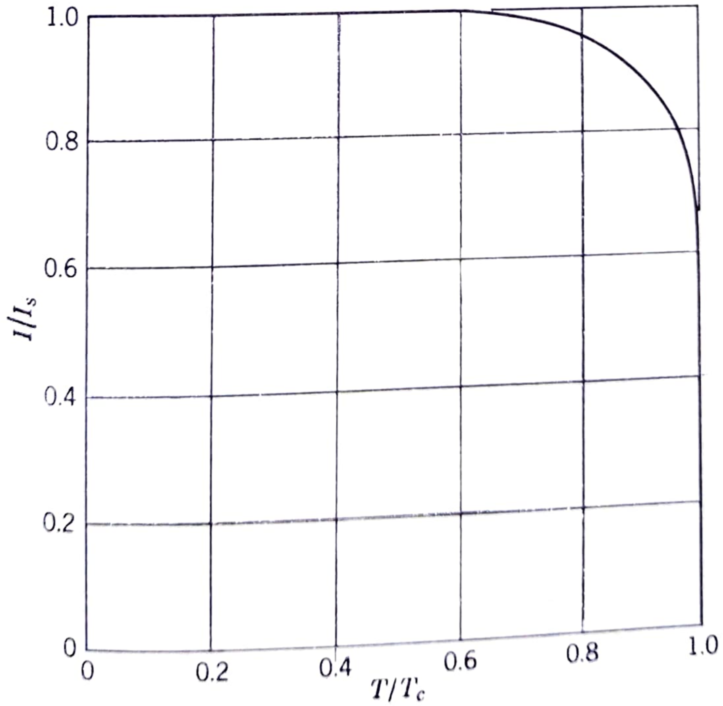

Fig. 15.14. Spontaneous magnetization versus temperature for the Ising square net.

So the magnetization does indeed vanish at the Curie point with vertical slope, as expected; but in detail, discrepancies with the internal field model are again strong. As seen in Fig. 15.14, the $\frac{1}{8}$ power in (15.55) leads to an extremely sharp drop of the magnetic moment very close to the Curie point. This is a result which does not agree with either the internal field theory or most experimental results, as illustrated in Fig. 15.8. We shall have occasion to discuss this deficiency when dealing with the theory of spin waves.

By presenting only the internal field model and exact results for the Ising model we have of course not given an adequate picture of the field. Very sophisticated approximations can be devised which make the numerical disagreement between the approximation and the exact theory very small. The three-dimensional Ising model has not been solved analytically, and there is little hope that it ever will be. We must therefore draw the best possible conclusion from the available evidence for three dimensions. The evidence is that the specific heat is also infinite at the Curie point, perhaps with a law which is not logarithmic. Also the power law in the drop-off of the spontaneous magnetization at the Curie point seems to be more than 1/8, which is encouraging. At present, hope for further progress is almost entirely based on the powerful numerical computing techniques which are now becoming available to us.

*15-5. Spin wave theory of magnetization

If we consider how difficult the problem is of making reliable statistical computations at or near the Curie point, we would be pretty foolhardy to use a formula such as (15.53) for an empirical determination of the exchange coupling in an actual material. The situation is in this respect very similar to the case for gases: the critical point is too severe a disturbance of the perfect gas to teach us much about intermolcular forces. We must look for a weaker disturbance. In Chapter 12 we turned to the Joule–Thomson effect or the second virial coefficient. In ferromagnets we find this kind of effect in the low-temperature behavior of the spontaneous magnetization.

In an almost saturated sample, the only excitation recognized by the Ising model is the reversal of an individual spin with the breaking of the corresponding bonds. In modern parlance we would call this a particle excitation. These excitations are expensive energy-wise and lead to a decrease of the spontaneous magnetization with increasing temperature as $1 - \exp[-\alpha/T]$. Bloch†† first showed that a localized system of spins

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†† F. Bloch. *Z. Physik* **61,** 206 (1930).