rough measure of validity even when used to describe the dense liquid state. It should thus be permissible to use this equation to discuss approximately the occurrence of the gas–liquid phase transformation by the arguments of Sec. 8 · 6.

FERROMAGNETISM

10 · 6 *Interaction between spins*

Consider a solid consisting of N identical atoms arranged in a regular lattice. Each atom has a net electronic spin S and associated magnetic moment $\boldsymbol{\mu}$. Using a notation similar to that of Sec. 7 · 8, the magnetic moment of an atom is then related to its spin by*

$$\boldsymbol{\mu} = g\mu_0 \mathbf{S} \tag{10·6·1}$$

where μ_0 is the Bohr magneton and the g factor is of order unity. In the presence of an externally applied magnetic field H_0 along the z direction, the Hamiltonian $\mathcal{H}_0$ representing the interaction of the atoms with this field is then

$$\mathcal{H}_0 = -g\mu_0 \sum_{j=1}^{N} \mathbf{S}_j \cdot \mathbf{H}_0 = -g\mu_0 H_0 \sum_{j=1}^{N} S_{jz} \tag{10·6·2}$$

In addition, each atom is also assumed to interact with neighboring atoms. This interaction is not just the magnetic dipole-dipole interaction due to the magnetic field produced by one atom at the position of another one. This interaction is in general much too small to produce ferromagnetism. The predominant interaction is usually the so-called "exchange" interaction. This is a quantum-mechanical consequence of the Pauli exclusion principle. Since electrons cannot occupy the same state, two electrons on neighboring atoms which have parallel spin (i.e., which cannot occupy the same orbital state) cannot come too close to each other in space (i.e., cannot occupy the same orbital state); on the other hand, if these electrons have antiparallel spins, they are already in different states, and there is no exclusion-principle restriction on how close they can come to each other. Since different spatial separations of the electrons give rise to different electrostatic interactions between them, this qualitative discussion shows that the *electrostatic* interaction (which can be of the order of 1 ev and can thus be much larger than any magnetic interaction) between two neighboring atoms does also depend on the relative orientations of their spins. This is the origin of the exchange interaction, which for two atoms j and k can be written in the form

$$\mathcal{H}_{jk} = -2J\mathbf{S}_j \cdot \mathbf{S}_k \tag{10·6·3}$$

Here J is a parameter (depending on the separation between the atoms) which measures the strength of the exchange interaction. If $J > 0$, the interaction

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* In Sec. 7 · 8 we used the symbol $\mathbf{J}$ instead of $\mathbf{S}$, but the latter notation is customary in discussions of ferromagnetism; it also avoids confusion with the conventional use of J to designate the exchange energy in (10 · 6 · 3).

energy $\mathcal{H}_{jk}$ is lower when the spins are parallel than when they are antiparallel. The state of lowest energy will then be one which favors *parallel* spin orientation of the atoms, i.e., one which tends to produce ferromagnetism. Note also that, since the exchange interaction depends on the degree to which electrons on the two atoms can overlap so as to occupy approximately the same region in space, J falls off rapidly with increasing separation between atoms; hence the exchange interaction is negligible except when the atoms are sufficiently close to each other. Thus each atom will interact appreciably only with its n nearest neighbor atoms.

Remark Let us show explicitly that the *magnetic* interaction between atoms is far too small to account for ordinary ferromagnetism. Since an atom produces a magnetic field at a distance r of the order of μ_0/r^3, the magnetic interaction of an atom with its n neighboring atoms at a distance r is approximately $(n\mu_0^2/r^3)$. Taking $n = 12$, $\mu_0 \approx 10^{-20}$ ergs gauss^{-1} (the Bohr magneton), and $r = 2 \cdot 10^{-8}$ cm, this gives for the interaction energy 1.5×10^{-16} ergs or, dividing by k, about 1°K. This magnitude of interaction energy might well produce ferromagnetism below 1°K, but certainly not in the region below 1000°K where metallic iron is ferromagnetic!

To simplify the interaction problem, we shall replace (10·6·3) by the simpler functional form

$$\mathcal{H}_{jk} = -2JS_{jz}S_{kz} \tag{10·6·4}$$

This approximate form leaves the essential physical situation intact and avoids the complications introduced by the vector quantities. (The simpler form (10·6·4) is called the "Ising model".)

The Hamiltonian $\mathcal{H}'$ representing the interaction energy between the atoms can then be written in the form

$$\mathcal{H}' = \tfrac{1}{2}\left(-2J \sum_{j=1}^{N} \sum_{k=1}^{n} S_{jz}S_{kz}\right) \tag{10·6·5}$$

where J is the exchange constant for neighboring atoms and the index k refers to atoms in the nearest neighbor shell surrounding the atom j. (The factor $\frac{1}{2}$ is introduced because the interaction between the same two atoms is counted twice in performing the sums).

The total Hamiltonian of the atoms is then

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \tag{10·6·6}$$

The problem is to calculate the thermodynamic functions of this system, e.g., its mean magnetic moment $\bar{M}$, as a function of the temperature T and the applied field H_0. The presence of interactions makes this task quite complicated despite the extreme simplicity of (10·6·5). Although the problem has been solved exactly for a two-dimensional array of spins when $H_0 = 0$, the three-dimensional problem is already so difficult that it has up to now defied exact solution. We shall therefore attack the problem by the simplest method of approximation, the molecular-field theory of Pierre Weiss.

10 · 7 *Weiss molecular-field approximation*

Focus attention on a particular atom j, which we shall call the "central atom." The interactions of this atom are described by the Hamiltonian

$$\mathcal{H}_j = -g\mu_0 H_0 S_{jz} - 2JS_{jz} \sum_{k=1}^{n} S_{kz} \tag{10·7·1}$$

The last term represents the interaction of this central atom with its n nearest neighbors. As an approximation we replace the sum over these neighbors by its mean value, i.e., we put

$$2J \overline{\sum_{k=1}^{n} S_{kz}} \equiv g\mu_0 H_m \tag{10·7·2}$$

where H_m is a parameter defined so as to have the dimensions of a magnetic field. It is called the "molecular" or "internal" field and is to be determined in such a way that it leads to a self-consistent solution of the statistical problem. In terms of this parameter (10·7·1) becomes just

$$\mathcal{H}_j = -g\mu_0(H_0 + H_m)S_{jz} \tag{10·7·3}$$

The effect of neighboring atoms has thus simply been replaced by an effective magnetic field H_m. The problem presented by (10·7·3) is just the elementary one of a *single* atom in an external field $(H_0 + H_m)$, a problem discussed in Sec. 7·8. The energy levels of the central jth atom are then

$$E_m = -g\mu_0(H_0 + H_m)m_s, \qquad m_s = -S, (-S+1), \ldots, S \tag{10·7·4}$$

From this one can immediately calculate the mean z component of spin of this atom. One has by (7·8·13)

$$\overline{S_{jz}} = SB_S(\eta) \tag{10·7·5}$$

where

$$\eta \equiv \beta g\mu_0(H_0 + H_m), \qquad \beta \equiv (kT)^{-1} \tag{10·7·6}$$

and $B_S(\eta)$ is the Brillouin function for spin S defined in (7·8·14).

The expression (10·7·5) involves the unknown parameter H_m. To determine it in a self-consistent way, we note that there is nothing which distinguishes the central jth atom from any of its neighboring atoms. Hence any one of these neighboring atoms might equally well have been considered as the central atom of interest and its mean value of $\bar{S}_z$ must also be given by (10·7·5). To obtain self-consistency we must then require that (10·7·2) reduce to

$$2JnSB_S(\eta) = g\mu_0 H_m \tag{10·7·7}$$

Since η is related to H_m by (10·7·6), the condition (10·7·7) is an equation which determines H_m and thus completes the solution of the entire problem. Expressing H_m in terms of η, (10·7·7) becomes

▶
$$B_S(\eta) = \frac{kT}{2nJS}\left(\eta - \frac{g\mu_0 H_0}{kT}\right) \tag{10·7·8}$$

which determines η and thus H_m. In particular, in the absence of external field (10·7·8) becomes,

for $H_0 = 0$,
$$B_S(\eta) = \frac{kT}{2nJS}\eta \tag{10·7·9}$$

The solution of the equations (10·7·8) or (10·7·9) can readily be obtained by drawing on the same graph (as shown in Fig. 10·7·1) both the Brillouin function $y = B_s(\eta)$ and the straight line

$$y = \frac{kT}{2nJS}\left(\eta - \frac{g\mu_0 H_0}{kT}\right)$$

and finding the point of intersection $\eta = \eta'$ of these two curves.

Once the molecular field parameter H_m is determined, the total magnetic moment of the sample is of course known. One has by (10·7·5) simply

$$\bar{M} = g\mu_0 \sum_j \overline{S_{jz}} = Ng\mu_0 S B_S(\eta) \tag{10·7·10}$$

Consider now the case when the external field $H_0 = 0$. It is then always true that $\eta = 0$ is a solution of (10·7·9) so that the molecular field H_m vanishes. But there exists also the possibility of a solution where $\eta \neq 0$ so that H_m

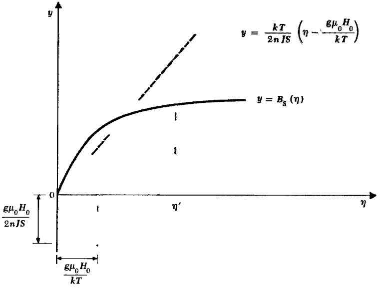

Fig. 10·7·1 Graphical solution of Eq. (10·7·8) determining the molecular field H_m corresponding to the intersection of the curves at $\eta = \eta'$. The dashed straight line corresponds to the case where the external field $H_0 = 0$.

assumes a finite value; correspondingly, there exists then a magnetic moment given by (10 · 7 · 10). The presence of such spontaneous magnetization in the absence of an external field is, of course, the distinguishing characteristic of ferromagnetism. To have such a solution where $\eta \neq 0$ it is necessary that the curves in Fig. 10 · 7 · 1 intersect at a point $\eta \neq 0$ when both curves start out at the origin. The condition for this to occur is that the initial slope of the curve $y = B_S(\eta)$ is larger than that of the straight line, i.e., that

$$\left[\frac{dB_S}{d\eta}\right]_{\eta=0} > \frac{kT}{2nJS} \tag{10·7·11}$$

But when $\eta \ll 1$, B_S assumes the simple form given by (7 · 8 · 19)

$$B_S(\eta) \approx \tfrac{1}{3}(S+1)\eta \tag{10·7·12}$$

Hence (10 · 7 · 11) becomes

$$\frac{1}{3}(S+1) > \frac{kT}{2nJS}$$

or

$$T < T_c$$

where

▶ $$kT_c \equiv \frac{2nJS(S+1)}{3} \tag{10·7·13}$$

Thus there exists the possibility of ferromagnetism below a certain critical temperature T_c, called the "Curie temperature," given in terms of J by (10 · 7 · 13). This ferromagnetic state where all spins can exploit their mutual exchange energy by being preferentially aligned parallel to each other has lower free energy than the state where $\eta = H_m = 0$. At temperatures below T_c the ferromagnetic state is therefore the stable one.*

As the temperature T is decreased below T_c, the slope of the dashed straight line in Fig. 10 · 7 · 1 decreases so that it intersects the curve $y = B_S(\eta)$ at increasingly large values of η corresponding to increasingly large values of y. For $T \to 0$, the intersection occurs for $\eta \to \infty$ where $B_S(\eta) \to 1$; then (10 · 7 · 10) gives $\bar{M} \to Ng\mu_0 S$, the magnetic moment when all spins are aligned completely parallel. For all these temperatures one can, of course, use (10 · 7 · 10) to compute $\bar{M}(T)$ corresponding to the various values of η. One then obtains a curve of the general shape shown in Fig. 10 · 7 · 2.

Finally we investigate the magnetic susceptibility of the solid in the presence of a small external field at temperatures *above* the Curie temperature

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* This does not mean that a macroscopic sample in zero external field necessarily has a net magnetic moment. To minimize the energy stored in the magnetic field, the sample tends to become subdivided into many domains, each magnetized along a definite direction, but with these directions differing from one domain to another. (See C. Kittel, "Introduction to Solid State Physics," 2d ed., chap. 15, John Wiley & Sons, Inc., New York, 1956.) Our discussion thus applies to a single domain.

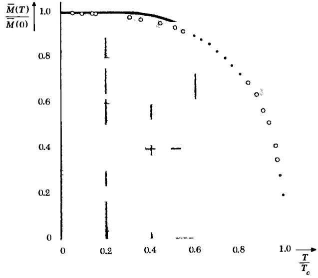

Fig. 10·7·2 Spontaneous magnetization $\bar{M}$ of a ferromagnet as a function of temperature T in zero external magnetic field. The curve is based on the molecular field theory of (10·7·10) and (10·7·9) with $S = \frac{1}{2}$. The points indicate experimental values for nickel (measured by P. Weiss and R. Forrer, Ann. Phys., vol. 5, p. 153 (1926)).

(10·7·13). Then we are in a region where η in Fig. 10·7·1 is small. Thus one can use the approximation (10·7·12) to write the general consistency condition (10·7·8) in the form

$$\frac{1}{3}(S+1)\eta = \frac{kT}{2nJS}\left(\eta - \frac{g\mu_0 H_0}{kT}\right)$$

Solving this for η gives, using the quantity kT_c defined in (10·7·13),

$$\eta = \frac{g\mu_0 H_0}{k(T - T_c)} \tag{10·7·14}$$

Thus (10·7·10) yields

$$\bar{M} = \tfrac{1}{3}Ng\mu_0 S(S+1)\eta$$

so that

▶ $$\chi \equiv \frac{\bar{M}}{H_0} = \frac{Ng^2\mu_0{}^2 S(S+1)}{3k(T - T_c)} \tag{10·7·15}$$

is the magnetic susceptibility of N atoms. This is called the Curie-Weiss law. It differs from Curie's law (7·8·22) by the presence of the parameter T_c in the denominator. Thus χ in (10·7·15) becomes infinite when $T \to T_c$, i.e., at the Curie temperature where the substance becomes ferromagnetic.

Experimentally the Curie-Weiss law is well obeyed at temperatures well

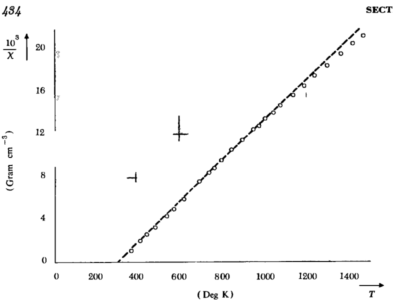

Fig. 10·7·3 Plot of χ^{-1} versus T per gram of gadolinium metal above its Curie temperature. The curve is (except for some slight departures at high temperatures) a straight line, in accord with what would be expected from the Curie-Weiss law (10·7·15). The intercept of the line with the temperature axis gives $T_c = 310°K$. The metal becomes ferromagnetic below 289°K. (Experimental data of S. Arajs and R. V. Colvin, J. Appl. Phys., vol. 32 (suppl.), p. 336 (1961).)

above the Curie temperature. It is, however, not true that the temperature T_c occurring in (10·7·15) is exactly the same as the Curie temperature at which the substance becomes ferromagnetic. Furthermore, the shape of the magnetization curve calculated by the Weiss molecular-field theory in Fig. 10·7·2 is quantitatively not quite correct. One of the most serious discrepancies of the present theory concerns the behavior of the specific heat at the Curie temperature in zero external field. Experimentally, the specific heat has a very sharp discontinuity at that temperature, whereas the theory just discussed predicts a much less abrupt change. The existence of these discrepancies is not surprising in view of the drastic approximations used in this simple theory which replaced all spins by some average effective field and neglected the existence of any correlated fluctuations in the orientations of different spins. The simple theory is, nevertheless, remarkably successful in exhibiting all the main features of ferromagnetism. Needless to say, more refined approximation methods have been devised which improve agreement with experiment considerably.*

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* One of the simplest of these, the so-called Bethe-Peierls-Weiss approximation (the Weiss involved here being a different person from Pierre Weiss, who introduced the concept of the molecular field), is a straightforward generalization of the method used in this section. It simply treats a central atom *and* its nearest neighbors exactly and replaces all the *other* atoms by an effective molecular field. See P. R. Weiss, *Phys. Rev.*, vol. 74, p. 1493 (1948).

SUGGESTIONS FOR SUPPLEMENTARY READING

Solids

C. Kittel: "Introduction to Solid State Physics," 2d ed., chaps. 5 and 6, John Wiley & Sons, Inc., New York, 1956.

J. F. Lee, F. W. Sears, and D. L. Turcotte: "Statistical Thermodynamics," chap. 12, Addison-Wesley Publishing Company, Reading, Mass., 1963.

R. Becker: "Theorie der Wärme," chap. 5, Springer-Verlag, Berlin, 1955. (In German.)

M. Blackman: "The Specific Heats of Solids," in "Handbuch der Physik," vol. 7/1, pp. 325–382, Springer-Verlag, Berlin, 1955. (In English.)

(The last two references give more detailed discussions of lattice vibrations.)

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Ferromagnetism

C. Kittel: "Introduction to Solid State Physics," 2d ed., chap. 15, John Wiley & Sons, Inc., New York, 1956. (A simple discussion, including domain formation.)

G. H. Wannier: "Elements of Solid State Theory," chap. 4, Cambridge University Press, 1959. (The Ising model and other cooperative phenomena.)

P. R. Weiss: *Phys. Rev.*, vol. 74, p. 1493 (1948). (Improved approximation method for treatment of ferromagnetism.)

R. Brout: "Phase Transitions," W. A. Benjamin, Inc., New York, 1965. (A general discussion of types of cooperative behavior leading to various kinds of phase transformations.)

PROBLEMS

10.1 For the quantized lattice waves (phonons) discussed in connection with the Debye theory of specific heats, the frequency ω of a propagating wave is related to its wave vector $\boldsymbol{\kappa}$ by $\omega = c\kappa$, where $\kappa = |\boldsymbol{\kappa}|$ and c is the velocity of sound. On the other hand, in a ferromagnetic solid at low temperatures quantized waves of magnetization (spin waves) have their frequency ω related to their wave number κ according to $\omega = A\kappa^2$, where A is a constant. At low temperatures, find the temperature dependence of the heat capacity due to such spin waves.

10.2 Use the Debye approximation to find the following thermodynamic functions of a solid as a function of the absolute temperature T:

(*a*) ln Z, where Z is the partition function
(*b*) the mean energy $\bar{E}$
(*c*) the entropy S