

differing only in the sign of η . At the point of continuous transition (O in Fig. 69) all three phases become identical.

In more complex cases two or more curves of phase transition of the first kind (e.g. two in Fig. 69b) touch at the point of continuous transition. Phase I has the highest symmetry, phases II and III a lower symmetry, phases IV and V another lower symmetry, these pairs of phases differing only in the sign of η .

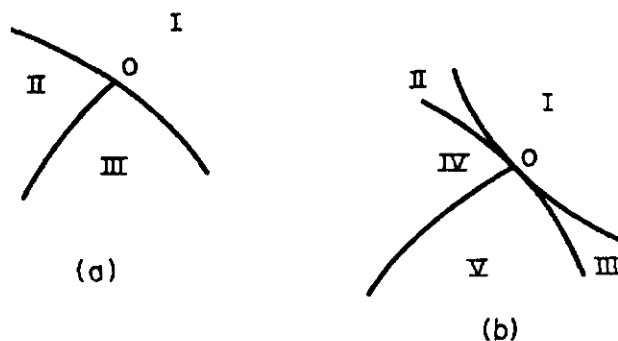


FIG. 69

§ 151. Phase transitions of the second kind in a two-dimensional lattice

The impossibility of a general theoretical determination of the critical indices lends especial interest to a simple model which allows an exact analytical solution of the problem of phase transitions of the second kind. This is a two-dimensional lattice model, for which the phase-transition problem was first solved by L. Onsager (1944).[†]

The model considered is a plane square lattice having N points, at each of which is a "dipole" with its axis perpendicular to the lattice plane. The dipole can have two opposite orientations, so that the total number of possible configurations of the dipoles in the lattice is 2^N .[‡] To describe the various configurations we proceed as follows. To each lattice point (with integral coordinates k, l) we assign a variable σ_{kl} which takes two values ± 1 , corresponding to the two possible orientations of the dipole. If we take into account only the interaction between adjoining dipoles, the energy of the configuration may be written

$$E(\sigma) = -J \sum_{k,l=1}^L (\sigma_{kl}\sigma_{k,l+1} + \sigma_{kl}\sigma_{k+1,l}), \quad (151.1)$$

[†] The original method used by Onsager was extremely complex. Later, various authors simplified the solution. The method described below (which in part makes use of certain ideas in the method of M. Kac and J. C. Ward (1952)) is due to N. V. Vdovichenko (1964).

[‡] This model is known as the *Ising model*; it was in fact first used by W. Lenz (1920) and was studied by E. Ising (1925) for the one-dimensional case (in which there is no phase transition).

where L is the number of points in a lattice line, the lattice being regarded as a large square, and $N = L^2$.† The parameter $J (> 0)$ determines the energy of interaction of a pair of adjoining dipoles, which is $-J$ and $+J$ for like and unlike orientations of the two dipoles respectively. Then the configuration with the least energy is the “completely polarised” (ordered) configuration, in which all the dipoles are oriented in the same direction. This configuration is reached at absolute zero; as the temperature increases, the degree of ordering decreases, becoming zero at the transition point, when the two orientations of each dipole become equally probable.

The determination of the thermodynamic quantities requires the calculation of the partition function

$$Z = \sum_{(\sigma)} e^{-E(\sigma)/T} = \sum_{(\sigma)} \exp \left\{ \theta \sum_{k,l} (\sigma_{kl}\sigma_{k,l+1} + \sigma_{kl}\sigma_{k+1,l}) \right\}, \quad (151.2)$$

taken over all the 2^N possible configurations ($\theta = J/T$). The equation

$$\exp(\theta\sigma_{kl}\sigma_{k'l'}) = \cosh \theta + \sigma_{kl}\sigma_{k'l'} \sinh \theta = \cosh \theta (1 + \sigma_{kl}\sigma_{k'l'} \tanh \theta)$$

is easily verified by expanding both sides in powers of θ and using the fact that all the $\sigma_{kl}^2 = 1$. The expression (151.2) can therefore be written

$$Z = (1-x^2)^{-N} S, \quad (151.3)$$

where

$$S = \sum_{(\sigma)} \prod_{k,l=1}^L (1 + x\sigma_{kl}\sigma_{k,l+1}) (1 + x\sigma_{kl}\sigma_{k+1,l}) \quad (151.4)$$

and $x = \tanh \theta$.

The summand in (151.4) is a polynomial in the variables x and σ_{kl} . Since each point (k, l) has four neighbours, each σ_{kl} can appear in the polynomial in powers from zero to four. After summation over all the $\sigma_{kl} = \pm 1$ the terms containing odd powers of σ_{kl} vanish, and so a non-zero contribution comes only from terms containing σ_{kl} in powers 0, 2 or 4. Since $\sigma_{kl}^0 = \sigma_{kl}^2 = \sigma_{kl}^4 = 1$, each term of the polynomial which contains all the variables σ_{kl} in even powers gives a contribution to the sum which is proportional to the total number of configurations, 2^N .

Each term of the polynomial can be uniquely correlated with a set of lines or “bonds” joining various pairs of adjoining lattice points. For example, the diagrams shown in Fig. 70 correspond to the terms

- (a) $x^2\sigma_{kl}\sigma_{k+1,l}^2\sigma_{k+1,l-1}$,
- (b) $x^8\sigma_{kl}^2\sigma_{k+1,l}^2\sigma_{k+1,l-1}^2\sigma_{k,l-1}^4\sigma_{k,l-2}^2\sigma_{k-1,l-1}^2\sigma_{k-1,l-2}^2$,
- (c) $x^{10}\sigma_{kl}^2\sigma_{k+1,l}^2\sigma_{k+1,l-1}^2\sigma_{k,l-1}^2\sigma_{k-2,l-1}^2\sigma_{k-1,l-1}^2$
 $\times \sigma_{k-1,l-2}^2\sigma_{k-1,l-3}^2\sigma_{k-2,l-3}^2\sigma_{k-2,l-2}^2$.

† The number L is, of course, assumed macroscopically large, and edge effects (due to the special properties of points near the edges of the lattice) will be neglected throughout the following discussion.

Each line in the diagram is assigned a factor x and each end of each line a factor σ_{kl} .

The fact that a non-zero contribution to the partition function comes only from terms in the polynomial which contain all the σ_{kl} in even powers signifies geometrically that either 2 or 4 bonds must end at each point in the diagram. Hence the summation is taken only over closed diagrams, which may be self-intersecting (as at the point $k, l-1$ in Fig. 70b).

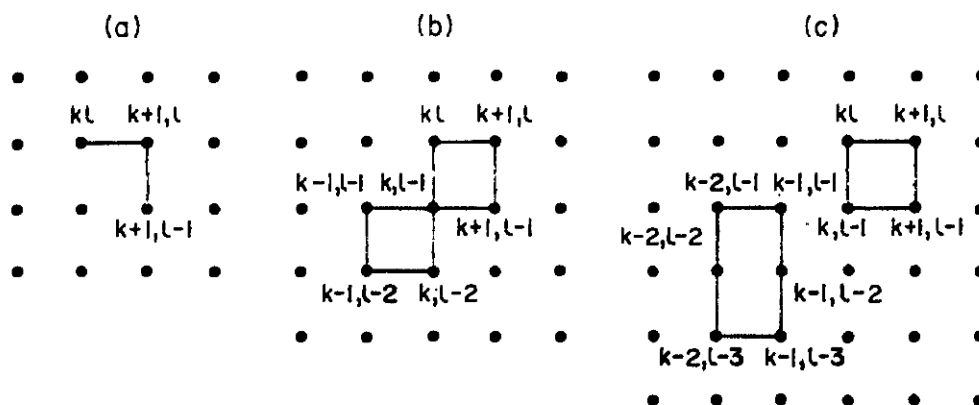


FIG. 70

Thus the sum S may be expressed in the form

$$S = 2^N \sum_r x^r g_r, \quad (151.5)$$

where g_r is the number of closed diagrams formed from an (even) number r of bonds, each multiple diagram (e.g. Fig. 70c) being counted as one.

The subsequent calculation is in two stages: (1) the sum over diagrams of this type is converted into one over all possible closed loops, (2) the resulting sum is calculated by reducing it to the problem of the "random walk" of a point in the lattice.

We shall regard each diagram as consisting of one or more closed loops. For non-self-intersecting diagrams this is obvious; for example, the diagram in Fig. 70c consists of two loops. For self-intersecting diagrams, however, the resolution into loops is not unique: a given diagram may consist of different numbers of loops for different ways of construction. This is illustrated by Fig. 71, which shows three ways of representing the diagram in Fig. 70b as one or two non-self-intersecting loops or as one self-intersecting loop. Any intersection may similarly be traversed in three ways on more complicated diagrams.

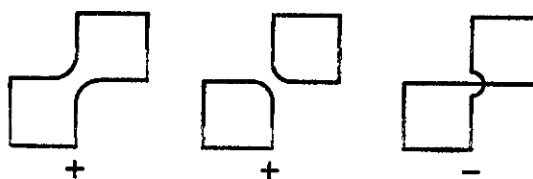


FIG. 71

It is easy to see that the sum (151.5) can be extended to all possible sets of loops if, in computing the number of diagrams g_r , each diagram is taken with the sign $(-1)^n$, where n is the total number of self-intersections in the loops of a given set, since when this is done all the extra terms in the sum necessarily cancel. For example, the three diagrams in Fig. 71 have signs $+$, $+$, $-$ respectively, so that two of them cancel, leaving a single contribution to the sum, as they should. The new sum will also include diagrams with "repeated bonds", of which the simplest example is shown in Fig. 72a. These diagrams are not permissible, since some points have an odd number of bonds meeting at them, namely three, but in fact they cancel from the sum, as

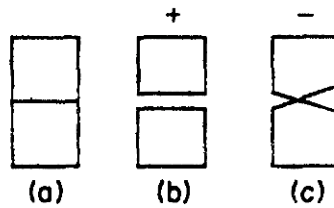


FIG. 72

they should: when the loops corresponding to such a diagram are constructed each bond in common can be traversed in two ways, without intersection (as in Fig. 72b) and with self-intersection (Fig. 72c); the resulting sets of loops appear in the sum with opposite signs, and so cancel. We can also avoid the need to take into account explicitly the number of intersections by using the geometrical result that the total angle of rotation of the tangent in going round a closed plane loop is $2\pi(l+1)$, where l is a (positive or negative) integer whose parity is the same as that of the number ν of self-intersections of the loop. Hence, if we assign a factor $e^{il\phi}$ to each point of the loop (with the angle of rotation there $\phi = 0, \pm \frac{1}{2}\pi$), the product of these factors after going round the whole loop will be $(-1)^{\nu+1}$, and for a set of s loops the resultant factor is $(-1)^{n+s}$, where $n = \sum \nu$.

Thus the number of intersections need not be considered if each point on the loop is taken with a factor $e^{il\phi}$ and a further factor $(-1)^s$ is taken for the whole diagram (set of loops) in order to cancel the same factor in $(-1)^{n+s}$.

Let f_r denote the sum over single loops of length r (i.e. consisting of r bonds), each loop having a factor $e^{il\phi}$ at each point on it. Then the sum over all pairs of loops with total number of bonds r is

$$\frac{1}{2!} \sum_{r_1+r_2=r} f_{r_1} f_{r_2};$$

the factor $1/2!$ takes into account the fact that the same pair of loops is obtained when the suffixes r_1 and r_2 are interchanged, and similarly for groups

of three or more loops. Thus the sum S becomes

$$S = \sum_{s=0}^{\infty} (-1)^s \frac{1}{s!} \sum_{r_1, r_2, \dots = 1}^{\infty} x^{r_1 + \dots + r_s} f_{r_1} \dots f_{r_s}.$$

Since S includes sets of loops with every total length $r_1 + r_2 + \dots$, the numbers r_1, r_2, \dots in the inner sum take independently all values from 1 to ∞ .[†] Hence

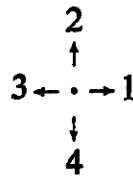
$$\sum_{r_1, \dots, r_s} x^{r_1 + \dots + r_s} f_{r_1} \dots f_{r_s} = \left(\sum_{r=1}^{\infty} x^r f_r \right)^s$$

and S becomes

$$S = \exp \left(- \sum_{r=1}^{\infty} x^r f_r \right). \tag{151.6}$$

This completes the first stage of the calculation.

It is now convenient to assign to each lattice point the four possible directions from it and to number them by a quantity $\nu = 1, 2, 3, 4$, say, as follows:



We define as an auxiliary quantity $W_r(k, l, \nu)$ the sum over all possible paths of length r from some given point k_0, l_0, ν_0 to a point k, l, ν (each bond having as usual the factor $e^{i\phi}$, where ϕ is the change of direction to the next bond); the final step to the point k, l, ν must not be from the point to which the arrow ν is directed.[‡] With this definition, $W_r(k_0, l_0, \nu_0)$ is the sum over all loops leaving the point k_0, l_0 in the direction ν_0 and returning to that point. It is evident that

$$f_r = \frac{1}{2r} \sum_{k_0, l_0, \nu_0} W_r(k_0, l_0, \nu_0): \tag{151.7}$$

both sides contain the sum over all single loops, but $\sum W_r$ contains each loop $2r$ times, since it can be traversed in two opposite directions and can be assigned to each of r starting points on it.

[†] Loops with more than N points make no contribution to the sum, since they must necessarily contain repeated bonds.

[‡] In fact $W_r(k, l, \nu)$ depends, of course, only on the differences $k - k_0, l - l_0$.

From the definition of $W_r(k, l, v)$ we have the recurrence relations

$$\begin{aligned}
 W_{r+1}(k, l, 1) &= W_r(k-1, l, 1) + e^{-i\pi}W_r(k, l-1, 2) \\
 &\quad + 0 + e^{i\pi}W_r(k, l+1, 4), \\
 W_{r+1}(k, l, 2) &= e^{i\pi}W_r(k-1, l, 1) + W_r(k, l-1, 2) \\
 &\quad + e^{-i\pi}W_r(k+1, l, 3) + 0, \\
 W_{r+1}(k, l, 3) &= 0 + e^{i\pi}W_r(k, l-1, 2) \\
 &\quad + W_r(k+1, l, 3) + e^{-i\pi}W_r(k, l+1, 4), \\
 W_{r+1}(k, l, 4) &= e^{-i\pi}W_r(k-1, l, 1) + 0 \\
 &\quad + e^{i\pi}W_r(k+1, l, 3) + W_r(k, l+1, 4).
 \end{aligned} \tag{151.8}$$

The method of constructing these relations is evident: for example, the point $k, l, 1$ can be reached by taking the last $(r+1)$ th step from the left, from below or from above, but not from the right; the coefficients of W_r arise from the factors $e^{i\pi}$.

Let A denote the matrix of the coefficients in equations (151.8) (with all k, l), written in the form

$$W_{r+1}(k, l, v) = \sum_{k', l', v'} A(klv | k'l'v') W_r(k', l', v').$$

The method of constructing these equations enables us to associate with this matrix an intuitive picture of a point moving step by step through the lattice with a "transition probability" per step from one point to another which is equal to the corresponding element of the matrix A ; its elements are in fact zero except when either k or l changes by ± 1 and the other remains constant, i.e. the point traverses only one bond per step. It is evident that the "probability" of traversing a length r will be given by the matrix A^r . In particular the diagonal elements of this matrix give the "probability" that the point will return to its original position after traversing a loop of length r , i.e. they are equal to $W_r(k_0, l_0, v_0)$. Hence

$$\text{tr } A^r = \sum_{k_0, l_0, v_0} W_r(k_0, l_0, v_0).$$

Comparison with (151.7) shows that

$$f_r = \frac{1}{2^r} \text{tr } A^r = \frac{1}{2^r} \sum_i \lambda_i^r,$$

where the λ_i are the eigenvalues of the matrix A . Substituting this expression in (151.6) and interchanging the order of summation over i and r , we obtain

$$\begin{aligned}
 S &= \exp \left\{ -\frac{1}{2} \sum_r \sum_{i=1}^{\infty} \frac{1}{r} x^r \lambda_i^r \right\} \\
 &= \exp \left\{ \frac{1}{2} \sum_i \log (1 - x\lambda_i) \right\} \\
 &= \prod_i \sqrt{1 - x\lambda_i}.
 \end{aligned} \tag{151.9}$$

The matrix Λ is easily diagonalised with respect to the suffixes k and l by using a Fourier transformation:

$$W_r(p, q, \nu) = \sum_{k, l=0}^L e^{-2\pi i(pk+q)l/L} W_r(k, l, \nu). \quad (151.10)$$

Taking Fourier components on both sides of equations (151.8), we find that each equation contains only $W_r(p, q, \nu)$ with the same p, q , so that the matrix Λ is diagonal with respect to p and q . For given p, q its elements are

$$\Lambda(pq\nu | pq\nu) = \begin{bmatrix} \varepsilon^{-p} & \alpha^{-1}\varepsilon^{-q} & 0 & \alpha\varepsilon^q \\ \alpha\varepsilon^{-p} & \varepsilon^{-q} & \alpha^{-1}\varepsilon^p & 0 \\ 0 & \alpha\varepsilon^{-q} & \varepsilon^p & \alpha^{-1}\varepsilon^q \\ \alpha^{-1}\varepsilon^{-p} & 0 & \alpha\varepsilon^p & \varepsilon^q \end{bmatrix},$$

where $\alpha = e^{i\pi}$, $\varepsilon = e^{2\pi i/L}$.

For given p, q a simple calculation shows that

$$\begin{aligned} \prod_{i=1}^4 (1 - x\lambda_i) &= \det(\delta_{\nu\nu} - x\Lambda_{\nu\nu}) \\ &= (1 + x^2)^2 - 2x(1 - x^2) \left(\cos \frac{2\pi p}{L} + \cos \frac{2\pi q}{L} \right). \end{aligned}$$

Hence, from (151.3) and (151.9), we finally obtain the partition function

$$\begin{aligned} Z &= 2^N (1 - x^2)^{-N} \prod_{p, q=0}^L \left[(1 + x^2)^2 \right. \\ &\quad \left. - 2x(1 - x^2) \left(\cos \frac{2\pi p}{L} + \cos \frac{2\pi q}{L} \right) \right]^{1/2}. \end{aligned} \quad (151.11)$$

The thermodynamic potential is†

$$\begin{aligned} \Phi &= -T \log Z \\ &= -NT \log 2 + NT \log (1 - x^2) \\ &\quad - \frac{1}{2} T \sum_{p, q=0}^L \log \left[(1 + x^2)^2 - 2x(1 - x^2) \left(\cos \frac{2\pi p}{L} + \cos \frac{2\pi q}{L} \right) \right] \end{aligned}$$

† In the model under discussion the temperature affects only the ordering of dipole orientations, not the distances between dipoles (the “thermal expansion coefficient” of the lattice is zero). It is then immaterial whether we consider the free energy or the thermodynamic potential.

or, changing from summation to integration,

$$\begin{aligned} \Phi = & -NT \log 2 + NT \log (1 - x^2) \\ & - \frac{NT}{2(2\pi)^2} \int_0^{2\pi} \int_0^{2\pi} \log [(1 + x^2)^2 - 2x(1 - x^2)(\cos \omega_1 + \cos \omega_2)] d\omega_1 d\omega_2 \end{aligned} \tag{151.12}$$

(remembering that $x = \tanh (J/T)$).

Let us now examine this expression. The function $\Phi(T)$ has a singularity at the value of x for which the argument of the logarithm in the integrand can vanish. As a function of ω_1 and ω_2 , this argument is a minimum for $\cos \omega_1 = \cos \omega_2 = 1$, when it equals $(1 + x^2)^2 - 4x(1 - x^2) = (x^2 + 2x - 1)^2$. This expression has a minimum value of zero for only one (positive) value of x , $x_c = \sqrt{2} - 1$; the corresponding temperature T_c ($\tanh (J/T_c) = x_c$) is the phase transition point.

The expansion of $\Phi(t)$ in powers of $t = T - T_c$ near the transition point includes a singular term as well as the regular part. Here we are interested only in the singular term, the regular part being simply replaced by its value at $t = 0$. To find the form of the singular term, we expand the argument of the logarithm in (151.12) in powers of ω_1, ω_2 and t about the minimum; the integral then becomes

$$\int_0^{2\pi} \int_0^{2\pi} \log [c_1 t^2 + c_2(\omega_1^2 + \omega_2^2)] d\omega_1 d\omega_2,$$

where c_1 and c_2 are constants. Carrying out the integration, we find that the thermodynamic potential near the transition point has the form

$$\Phi \cong a - \frac{1}{2} b (T - T_c)^2 \log |T - T_c|, \tag{151.13}$$

where a and b are further constants (with $b > 0$). The potential itself is continuous at the transition point, but the specific heat becomes infinite in accordance with the formula

$$C \cong b \log |T - T_c|, \tag{151.14}$$

which is symmetrical about the transition point.

In this model, the order parameter is represented by the mean dipole moment at the lattice point (the spontaneous polarisation of the lattice), which is non-zero below the transition point and zero above it. The temperature dependence of this quantity can also be ascertained; near the transition point, the order parameter tends to zero according to

$$\eta = \text{constant} \times (T_c - T)^{1/8} \tag{151.15}$$

(L. Onsager, 1947).[†]

[†] A comparatively simple method of solving this problem is given by N. V. Vdovichenko, *Soviet Physics JETP* **21**, 350, 1965.

The correlation function is defined as the mean value of the product of the fluctuations of the dipole moment at two lattice points. The correlation radius is found to tend to infinity as $1/|T-T_c|$ when $T \rightarrow T_c$, and at the point $T = T_c$ itself the correlation function decreases with increasing distance according to

$$\langle \Delta\sigma_{kl} \Delta\sigma_{mn} \rangle \propto [(k-m)^2 + (l-n)^2]^{-1/8}.$$

These results, and those of solving the problem of the properties of the same model in an external field, show that the behaviour of the model near the phase transition point satisfies the requirements of the scale invariance hypothesis. The critical indices have the following values:

$$\begin{aligned} \alpha = 0, \quad \beta = \frac{1}{8}, \quad \gamma = \frac{7}{4}, \quad \delta = 15, \quad \varepsilon = 0, \quad \mu = \frac{8}{15}, \\ \nu = 1, \quad \zeta = \frac{1}{4}; \end{aligned} \quad (151.16)$$

ζ is found from (148.7) with $d = 2$.†

§ 152. Van der Waals theory of the critical point

It has been noted in § 83 that the critical point of liquid/gas phase transitions is a singularity of the thermodynamic functions of the substance. The physical nature of this singularity is similar to that which occurs at phase transition points of the second kind: in the latter case it is due to the increased fluctuations of the order parameter, and in the approach to the critical point there are increased fluctuations of the density of the substance. This analogy in the physical nature results in a certain analogy in the possible mathematical description of the two phenomena, to be discussed in § 153.

First, however, let us consider as a necessary preliminary the description of critical phenomena based on neglecting the fluctuations. In such a theory (analogous to the Landau approximation in the theory of phase transitions of the second kind) the thermodynamic quantities for the substance as functions of the variables V and T are assumed to have no singularities, so that they can be expanded in powers of the small changes in these variables. The results given in the rest of this section therefore depend only on the vanishing of the derivative $(\partial P/\partial V)_T$.

Let us first ascertain the conditions for the substance to be stable when

$$(\partial P/\partial V)_T = 0. \quad (152.1)$$

† As regards the critical indices, a logarithmic increase corresponds to a zero exponent (see after (148.7)).