

# ON THE COMBINATORY FACTOR IN REGULAR ASSEMBLIES

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The thermodynamic functions of the Ising model for square and triangular plane lattices were determined exactly by Onsager and Houtappel. These results are used to derive the exact value of the combinatory factor which gives the number of configurations with a pre-assigned number of neighbouring anti-parallel dipoles. The values obtained are compared with the approximate combinatory factor deduced from the quasi-chemical method of Bethe and Guggenheim. For certain simple lattices (square plane lattices, cubic lattices) the quasi-chemical approximation is improved by adding a new parameter chosen to fit the perfectly ordered cases. The approximation thus obtained is remarkably good for the square plane lattice at all temperatures.

1. INTRODUCTION.—The mathematical problem involved in the statistical evaluation of the thermodynamic properties of what Fowler and Guggenheim<sup>1</sup> call regular assemblies is the evaluation of the combinatory factor. The regular assemblies include the Ising model for ferromagnetism, the usual model for order-disorder problems and regular solutions. There are also many other applications of regular assemblies.<sup>2</sup>

Using the Kramers-Wannier method,<sup>3</sup> Onsager succeeded in calculating the free energy corresponding to the Ising model without external magnetic field for a square plane lattice.<sup>4</sup> Recently Houtappel<sup>5</sup> and Wannier<sup>6</sup> performed analogous calculations for other plane lattices.

For the three-dimensional case, it is necessary to use approximate methods.<sup>7, 8</sup> One of the most useful is the quasi-chemical method due to Guggenheim,<sup>8</sup> which is based on an assumption about the combinatory factor and is equivalent to Bethe's well-known approximate method of construction of the grand partition function. In order to clarify the approximation introduced by the quasi-chemical method, we deduced from Onsager's result the exact value of the combinatory factor. It will be shown that the quasi-chemical method is a good approximation only in the immediate neighbourhood of complete random mixing. This comparison suggests a new approximation for the combinatory factor of some simple lattices, which is in much better agreement with Onsager's results.

2. We shall first deduce from Onsager's results the combinatory factor corresponding to Ising model for ferromagnetism with a vanishing external magnetic field. We shall limit ourselves to the square plane lattice,<sup>4</sup> the  $N$  sites of which are occupied by dipoles capable of two orientations only.

Let us call  $J$  the interaction energy of two antiparallel neighbouring dipoles. The energy of two parallel neighbouring dipoles is equal to  $-J$ . We number the rows and columns of the lattice by the suffixes  $i$  and  $j$  respectively. The partition function  $Z$  of the system is

$$Z = \sum_{\mu(i,j)} \exp \left\{ \sum_{i,j} K[\mu(i,j)\mu(i+1,j) + \mu(i,j)\mu(i,j+1)] \right\}, \quad (2.1)$$

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where  $K = J/kT$  and where the sum  $\sum_{\mu(i,j)}$  is extended over all configurations with  $\mu(i,j) = \pm 1$  according to the orientation of the dipole  $(i,j)$ .

Let us assume that in a definite configuration, there are  $n$  pairs of antiparallel neighbouring dipoles. We put  $n/N = \nu$ ; clearly  $0 \leq \nu \leq 2$ .

We denote by  $g(N, \nu)$ , the number of configurations having  $n = N\nu$  pairs of antiparallel neighbouring dipoles. Then eqn. (2.1) becomes

$$Z = \sum_{\nu} g(N, \nu) \exp 2NK(1 - \nu). \quad (2.2)$$

The partition function per dipole, which we shall call  $\lambda_R$  ( $\lambda_R = \lim_{N \rightarrow \infty} Z^{1/N}$ ), has been computed rigorously by Onsager.<sup>4</sup> It is given by

$$\log \left( \frac{\lambda_R}{2 \cosh 2K} \right) = \frac{1}{2\pi} \int_0^\pi \log \left\{ \frac{1}{2} [1 + (1 - k_1^2 \sin^2 \phi)^{\frac{1}{2}}] \right\} d\phi, \quad (2.3)$$

$$k_1 = \frac{2 \sinh 2K}{\cosh^2 2K}. \quad (2.4)$$

In order to obtain the partition function per dipole  $\lambda_R$  one can replace the sum in (2.2) by its maximum term; this gives with

$$\gamma(\nu) = \lim_{N \rightarrow \infty} g(N, \nu)^{1/N}, \quad (2.5)$$

$$\lambda_R(K) = \lim_{N \rightarrow \infty} Z^{1/N} = \gamma(\nu) \exp 2(1 - \nu)K, \quad (2.6)$$

where  $\nu$  is determined as a function of  $K$  by the condition

$$\frac{\partial}{\partial \nu} [\gamma(\nu) \exp 2K(1 - \nu)] = 0, \quad (2.7)$$

or

$$\partial \gamma / \partial \nu = 2K\gamma. \quad (2.8)$$

Combining (2.6) and (2.8) we get

$$\nu = 1 - \frac{1}{2} \frac{\partial \log \lambda}{\partial K}. \quad (2.9)$$

$\partial \log \lambda / \partial K$  is deduced from (2.3):

$$\frac{\partial \log \lambda}{\partial K} = \coth 2K \left[ 1 + \frac{2}{\pi} (2 \tanh^2 2K - 1) \int_0^{\pi/2} (1 - k_1^2 \sin^2 \phi)^{-\frac{1}{2}} d\phi \right], \quad (2.10)$$

or, expressing  $\tanh 2K$  and  $\coth 2K$  as functions of  $k_1$ ,

$$\frac{\partial \log \lambda}{\partial K} = \frac{\pm \sqrt{2}}{[1 \pm (1 - k_1^2)^{\frac{1}{2}}]^{\frac{1}{2}}} \left( 1 \pm \frac{2}{\pi} (1 - k_1^2)^{\frac{1}{2}} \int_0^{\pi/2} (1 - k_1^2 \sin^2 \phi)^{-\frac{1}{2}} d\phi \right). \quad (2.11)$$

The sign of  $\sqrt{2}$ , being the same as the sign of  $\coth 2K$ , is positive if  $K > 0$ , negative if  $K < 0$ . To determine what sign has to be taken in front of  $(1 - k_1^2)^{\frac{1}{2}}$  we notice that for  $T = 0$ , the order is complete and thus  $\nu = 0$  or  $\nu = 2$  according to the sign of the energy. Simple calculations with the aid of eqn. (2.4), (2.9) and (2.11), show that the positive sign is then required. In the opposite case, when  $T = \infty$ , complete disorder occurs, hence  $\nu = 1$  and the negative sign has to be taken.

As shown by (2.6), (2.9) and (2.11),  $\gamma$  and  $\nu$  are given by two different analytical expressions below and above a certain critical temperature  $T_c$ . Putting (2.11) in (2.9) one finds

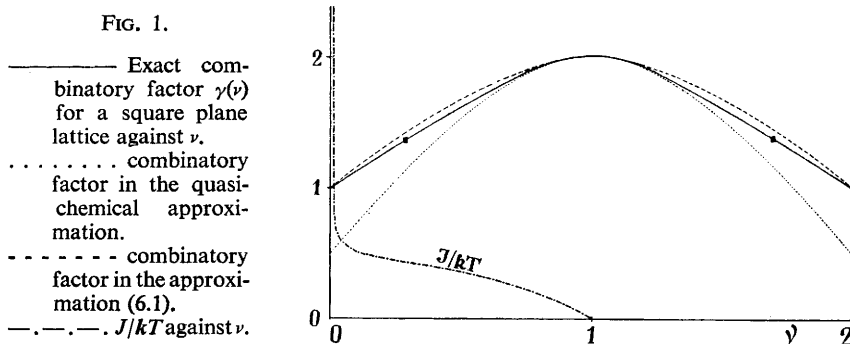
$$\nu = 1 - \frac{1}{2} \left\{ \frac{\pm \sqrt{2}}{[1 \pm (1 - k_1^2)^{\frac{1}{2}}]^{\frac{1}{2}}} \left[ 1 \pm \frac{2}{\pi} (1 - k_1^2)^{\frac{1}{2}} \int_0^{\pi/2} (1 - k_1^2 \sin^2 \phi)^{-\frac{1}{2}} d\phi \right] \right\} \quad (2.12)$$

Combining (2.6) and (2.12), one gets

$$\gamma(\nu) = \lambda(K) \exp \frac{\pm K\sqrt{2}}{[1 \pm (1-k_1^2)^{\frac{1}{2}}]^{\frac{1}{2}}} \left( 1 \pm \frac{2}{\pi} (1-k_1^2)^{\frac{1}{2}} \int_0^{\pi/2} (1-k_1^2 \sin^2 \phi)^{\frac{1}{2}} d\phi \right). \quad (2.13)$$

To compute  $\lambda(K)$ , we used a formula given by Onsager;<sup>9</sup>  $\gamma$ , obtained with the aid of equation (2.13), has been plotted as a function of  $\nu$  (fig. 1).

FIG. 1.



3. We have performed analogous calculations for an isotropic plane triangular lattice.<sup>5, 6</sup> We obtain here instead of (2.6) and (2.9),

$$\lambda(K) = \gamma(\nu) \exp K(3 - 2\nu), \quad (3.1)$$

and

$$\nu = \frac{1}{2} \left( 3 - \frac{\partial \log \lambda}{\partial K} \right). \quad (3.2)$$

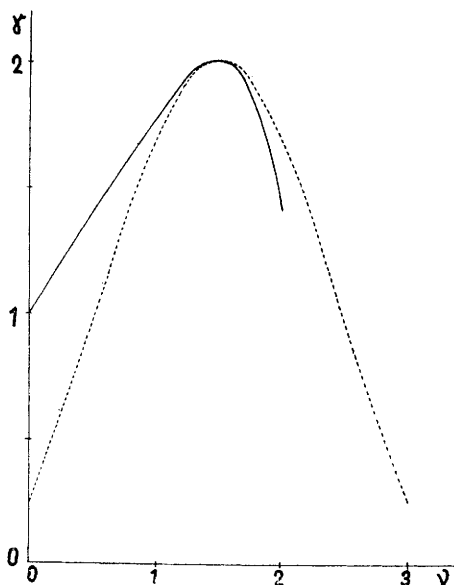


FIG. 2.

— exact combinatorial factor  $\gamma(\nu)$  for the plane triangular lattice against  $\nu$ .  
 - - - - - combinatorial factor in the quasi-chemical theory.

The value of  $\lambda$  has been computed by using a formula given by Wannier,<sup>10</sup> by reducing the double integral into a simple one,\* and by computing graphically the simple integral. Fig. 2 gives the results we have obtained. We must notice

\* This reduction has been performed by using the well-known formula

$$\int_0^{2\pi} \log(a \pm b \cos x) dx = 2\pi \log \left[ \frac{a + \sqrt{a^2 - b^2}}{2} \right].$$

the asymmetrical shape of  $\gamma(\nu)$  and the fact that  $\gamma(\nu)$  presents a discontinuity for  $\nu = 2$ , and remains zero for  $\nu > 2$ . As explained in Wannier's paper this is related to the impossibility of dividing such a lattice into sublattices in such a way that a site of a sublattice has nearest neighbours which all belong to the other sublattice.

4. We now go over to the more general order-disorder problem, equivalent to Ising model for ferromagnetism with non-vanishing external magnetic field.

We first consider an arbitrary lattice, of  $N$  sites,  $N_A = N\nu_A$  of which are occupied by particles of type A, and  $N_B = (N - N_A)$  by particles of type B. We call  $g(N_A, N_B, N_{AB})$  the number of configurations of the particles such that  $N_{AB} = N\nu$  pairs of neighbouring sites are occupied by particles of different type. We put

$$\gamma(\nu_A, \nu) = \lim_{N \rightarrow \infty} [g(N_A, N_B, N_{AB})]^{1/N},$$

$$\gamma(\nu) = \lim_{N \rightarrow \infty} [g(N, \nu)]^{1/N} = \lim_{N \rightarrow \infty} \left[ \sum_{N_A} g(N_A, N_B, N_{AB}) \right]^{1/N}, \quad (4.1)$$

$$\gamma(\nu) = \gamma(\nu, \nu_A^{\max}), \quad (4.2)$$

where  $\nu_A^{\max}$  is any value of  $\nu_A$  making  $\gamma(\nu_A, \nu)$  a maximum for the given value of  $\nu$ . We want to show that this maximum is always attained for  $\nu_A = \frac{1}{2}$ . For that purpose, we divide the lattice into two identical parts  $L_1, L_2$  and, among the configurations for which  $N_A = N/2$  and  $N_{AB} = N\nu$  we select those for which  $L_1$  contains  $N\nu_A^{\max}/2$  particles A and  $N\nu/2$  neighbouring pairs AB.

The number of these special configurations is

$$g\left[\frac{N\nu_A^{\max}}{2}, \frac{N}{2}(1 - \nu_A^{\max}), \frac{N\nu}{2}\right] \cdot g\left[\frac{N}{2}(1 - \nu_A^{\max}), \frac{N\nu_A^{\max}}{2}, \frac{N\nu}{2}\right], \quad (4.3)$$

and cannot exceed the total number  $g(N/2, N/2, N\nu)$  of configurations for which  $N_A = N/2$  and  $N_{AB} = N\nu$ . Applying the symmetry relation,

$$g(N_A, N_B, N_{AB}) = g(N_B, N_A, N_{AB}),$$

we get

$$\left[ g\left(\frac{N}{2}, \frac{N\nu_A^{\max}}{2}, \frac{N\nu}{2}\right) \right]^2 \leq g\left(\frac{N}{2}, \frac{N}{2}, N\nu\right), \quad (4.4)$$

and in the limit  $N \rightarrow \infty$

$$\gamma(\nu_A^{\max}, \nu) \leq \gamma\left(\frac{1}{2}, \nu\right).$$

This shows that, for given  $\nu$ , the maximum of  $\gamma(\nu_A, \nu)$  is always obtained for  $\nu_A = \frac{1}{2}$ . In particular, (4.2) gives the important relation

$$\gamma\left(\frac{1}{2}, \nu\right) = \gamma(\nu). \quad (4.5)$$

It expresses in a most direct way the fact that for any lattice the treatment of the Ising model is equivalent to the solution of the order-disorder problem for  $N_A = N_B = N/2$ .

5. The rigorous values of  $\gamma(\nu)$  will now be compared to the quasi-chemical approximation. Let us call  $z$  the number of nearest neighbours of each particle. If one makes first the very crude approximation that the pairs of particles are independent, the combinatory factor is then simply equal to the number  $g^*$  of ways of subdividing  $zN/2$  pairs of neighbouring particles into a group of  $N_{AB}\nu$  pairs AB,  $(zN_A - N_{AB}/2)$  pairs AA and  $(zN - N_{AB}/2)$  pairs BB.

$$g^*(N_A, N_B, N_{AB}) = \frac{(\frac{1}{2}zN)!}{\left(\frac{N_{AB}}{2}\right)! \left(\frac{zN_A - N_{AB}}{2}\right)! \left(\frac{zN - N_{AB}}{2}\right)!}. \quad (5.1)$$

This formula gives a number of configurations which is in large excess of the exact one that we had calculated with the aid of (2.13) (for instance, in the square plane lattice, when  $N_A = N_B, N_{AB}/N = 1$ , we find  $g^{*1/N} = 16$  instead of 2).

The quasi-chemical treatment reduces this error by multiplying  $g^{*1/N}$  by a factor independent of  $\nu = N_{AB}/N$  such that the maximum value becomes exact

$$g_{9c.}^{1/N} = h \left( \frac{N_A}{N}, \frac{N_B}{N} \right) g^{*1/N}, \quad (5.2)$$

where  $h$  is such that

$$g_{9c.}^{\max} = \frac{N!}{N_A! N_B!} \quad (5.3)$$

$g_{9c.}^{1/N}$  (for  $N_A = N_B = N/2$ ) has been plotted in fig. 1 and 2. In order to show in what energy region the quasi-chemical method is a good approximation, we also plotted on fig. 1,  $J/kT$  as a function of  $\nu$ . [ $J/kT = f(\nu)$  has been computed with the aid of eqn. (2.4) and (2.12)]. This graph shows that the quasi-chemical approximation gives good results in the neighbourhood of complete disorder, which corresponds to the adjusted maximum, but it becomes worse as the temperature decreases; it is already far from the exact curve at the critical temperature ( $T_c = 0.293$ ) and leads even to  $g_{9c.}^{1/N} < 1$ , for instance when  $\nu = 0$ .

A second source of error in formula (5.2) is the asymmetry of  $\gamma(\nu)$  in lattices like the triangular lattice (fig. 2).

6. The assumed form of the combinatory factors in the quasi-chemical method (5.2) is proportional to  $g^{*1/N}$ . Instead of such a proportionality, we may consider the more general, linear relation

$$\tilde{g}^{1/N} = \gamma g^{*1/N} + \delta \quad (6.1)$$

between the combinatory factor  $\tilde{g}^{1/N}$  and  $g^{*1/N}$ . In this relation,  $\gamma$  and  $\delta$  are parameters which may depend on the composition but are independent of  $\nu$ . We may choose these parameters in order to impose on  $\tilde{g}^{1/N}$  some restrictions. As in the quasi-chemical method we may fix one of the parameters by the condition  $\tilde{g}_{\max}^{1/N} = 2$ . The remaining parameter may be chosen in several ways. It is possible to use it in order to fix the second derivative of  $\tilde{g}^{1/N}$  corresponding to the maximum. In the neighbourhood of  $\tilde{g}_{\max}^{1/N}$ , the free energy  $\lambda$  may be expanded as a power series corresponding to successive powers of  $1/T$  (high temperature expansion). To this expansion we may apply the method developed in our first paragraph. It is then readily shown that the correct curvature (for  $N_A = N_B$ ) is obtained by putting  $\delta = 0$ . The quasi-chemical method gives not only the correct value for  $\tilde{g}_{\max}^{1/N}$  but also the correct value of the curvature at  $\nu = 1$ .

Another condition which may serve to fix one of the parameters in (6.1) is the value of  $\tilde{g}^{1/N}$  for  $\nu = 0$  or  $\nu = 2$ . This corresponds to perfect order and so  $\tilde{g}^{1/N} = 1$  for  $\nu = 0$  or  $\nu = 2$ . For such a choice of  $\gamma$  and  $\delta$ , the curvature of  $\tilde{g}^{1/N}$  at the maximum is no more correct, but on the other hand, it may be useful for an intermediate range of temperature which is covered by none of the usual high and low temperature expansions.

We shall write (6.1) in the equivalent form

$$\tilde{g}^{1/N} - 1 = \alpha \left( \frac{g^{*1/N}}{\beta} - 1 \right), \quad (6.2)$$

where the parameters  $\alpha$  and  $\beta$  are independent of  $\nu$ ;  $\beta$  is chosen such that in the state of perfect order,  $\tilde{g} = 1$ . Hence

$$\beta = \left[ \frac{(\frac{1}{2}zN)!}{\left(\frac{zN_A}{2}\right)! \left(\frac{zN_B}{2}\right)!} \right]^{1/N};$$

$\alpha$  is such that

$$\tilde{g}_{\max} = \frac{N!}{N_A! N_B!}$$

Hence

$$\alpha = \left[ \left( \frac{N!}{N_A! N_B!} \right)^{1/N} - 1 \right] \times \left[ \left( \frac{\left( \frac{zN_A}{2} \right)! \left( \frac{zN_B}{2} \right)!}{\left( \frac{zN_A N_B}{2N} \right)! \left( \frac{zN_A - \frac{zN_A N_B}{N}}{2} \right)! \left( \frac{zN_B - \frac{zN_A N_B}{N}}{2} \right)!} \right)^{1/N} - 1 \right]^{-1}$$

Fig. 1 shows that this new approximation is close to Onsager's exact curve over the complete range of temperatures, but, of course, is not so good as the quasi-chemical approximation in the neighbourhood of complete disorder. So, according to the physical problem considered, one may choose one approximation or the other. In problems related to ferromagnetism and antiferromagnetism, the whole range of temperature is of physical interest. In solutions with endothermic mixing, the region below the critical point is irrelevant, for there is separation into 2 phases, and the quasi-chemical method is more useful in the neighbourhood of complete random mixing.\* The approximation (6.2) is, of course, really justified only for  $z = 2$  (one dimension) and for the two dimensional square lattice,  $z = 4$ . For one dimension ( $z = 2$ ) one has

$$\beta = \left( \frac{N!}{N_A! N_B!} \right)^{1/N}; \quad \alpha = 1.$$

Hence

$$\tilde{g}^{1/N} = g^{*1/N} \beta^{-1}.$$

As  $\beta$  is independent of  $\nu$ , one sees that, for one dimension, our approximation reduces to the quasi-chemical method which is exact in that case.

For the two-dimensional square lattice, the approximation (6.2) is justified by the agreement with Onsager's calculations. For other values of  $z$ , it is purely empirical but gives the correct limiting values of  $\tilde{g}^{1/N}$  both for perfect order and perfect disorder. We have to limit ourselves to symmetrical lattices like the square plane lattice or lattices like the body centred lattice because fig. 2 shows that the concept of independence of pairs, which is symmetrical with respect to ferromagnetism and antiferromagnetism, is meaningless in asymmetrical lattices.

The improved approximate expression  $\tilde{g}$  of the combinatory factor can be used to calculate the thermodynamic properties of the system. The partition function is

$$Z = \sum_{N_{AB}} \left[ 1 + \alpha \left( \frac{g^{*1/N}}{\beta} - 1 \right) \right]^N \exp \frac{1}{kT} \left( -\chi_{AA} N_A - \chi_{BB} N_B - \frac{\omega N_{AB}}{z} \right), \quad (6.3)$$

where

$$\omega = 2\chi_{AB} - \chi_{AA} - \chi_{BB}, \quad (6.4)$$

and  $2\chi_{AB}/z$  is the interaction energy of a molecule A with a molecule B.

As usual, we may replace the sum by its maximum term. One obtains

$$Z = \left[ 1 + \alpha \left( \frac{g^{*1/N}}{\beta} - 1 \right) \right]^N \exp \frac{1}{kT} \left( -\chi_{AA} N_A - \chi_{BB} N_B - \frac{\omega N_{AB}}{z} \right), \quad (6.5)$$

where  $N_{AB}$  has to satisfy the condition of maximum

$$\frac{\partial}{\partial N_{AB}} \left( \frac{\omega N_{AB}}{zkT} \right) = \frac{\partial}{\partial N_{AB}} \left\{ N \log \left[ 1 + \alpha \left( \frac{g^{*1/N}}{\beta} - 1 \right) \right] \right\}. \quad (6.6)$$

\* If the system is formed by two phases as for solutions with endothermic mixing below the critical point, a formula like (6.2) has to be applied to each phase. Also, for order-disorder problems below the critical point, it is useful to introduce into the combinatory factor the long range order  $s$  (cf. Fowler and Guggenheim<sup>1</sup>), eqn. (1317). A similar correction may be introduced into (6.2). But it does not seem worth while to give more details here.

Working out equation (6.6) and denoting by  $x_A$ ,  $x_B$ , the molar fractions of A and B, and by  $\nu$  the ratio  $N_{AB}/N$ , one finds

$$\frac{\omega}{zkT} = \frac{\log [(zx_B - \nu)^{\frac{1}{2}} (zx_A - \nu)^{\frac{1}{2}} \nu^{-1}]}{1 + \left(\frac{1}{\alpha} - 1\right) \frac{\beta \nu^{\frac{1}{2}} (zx_A - \nu)^{\frac{1}{2}} (zx_B - \nu)^{\frac{1}{2}}}{z^{\frac{1}{2}} x_A^{\frac{1}{2}} x_B^{\frac{1}{2}}}} \quad (6.7)$$

or, denoting by (AB) the number of neighbouring pairs A, B

$$\frac{\omega}{zkT} = \frac{\log \frac{(AA)^{\frac{1}{2}} (BB)^{\frac{1}{2}}}{(AB)}}{1 + \frac{\beta \left(\frac{1}{\alpha} - 1\right)}{g^* 1/N}} \quad (6.8)$$

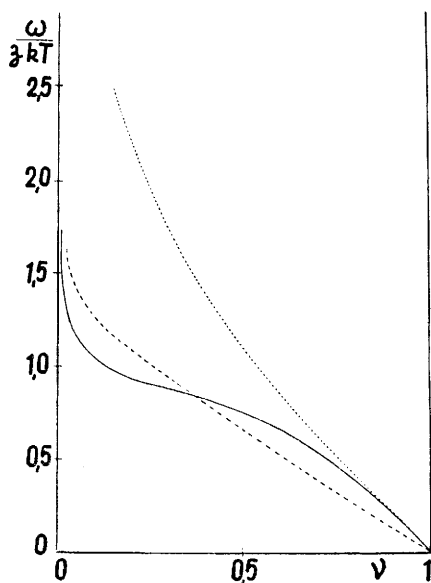


FIG. 3.— $\omega/zkT$  against  $\nu = N_{AB}/N$  for a square plane lattice.

----- approximation (6.8).  
 ————— exact curve.  
 ..... quasi-chemical formula.

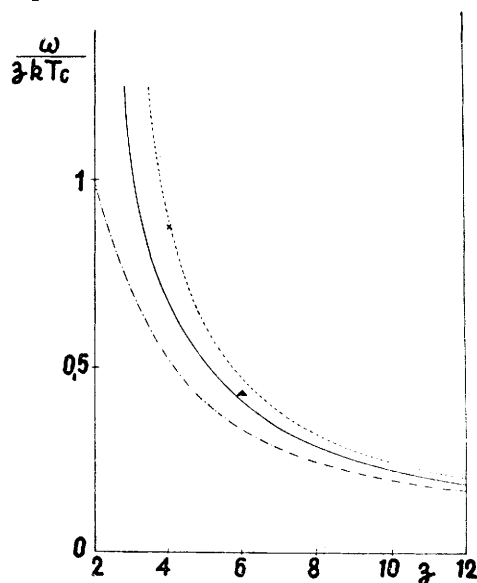


FIG. 4.

— · — · — · Bragg and Williams.  
 ————— quasi-chemical method.  
 ----- our approximation.  
 × exact value for  $z = 4$  (Onsager).<sup>11</sup>  
 ▲ Rushbrooke's value for the simple cubic lattice.<sup>13</sup>

This equation replaces the equation deduced from the quasi-chemical approximation which is

$$\frac{\omega}{zkT} = \log \frac{(AA)^{\frac{1}{2}} (BB)^{\frac{1}{2}}}{(AB)} \quad (6.9)$$

Fig. 3 gives, for a square plane lattice, a comparison between the curves obtained for  $\omega/zkT$  as a function of  $\nu$  in the quasi-chemical approximation, in our approximation and in the exact treatment.

It has been observed that the better the approximation, the lower the critical temperature for a given value of  $\omega$ . As a test of the improvement introduced by

formula (6.1), we thus compute the critical temperature. We may start from eqn. (6.5) and apply the definition of the critical point

$$\partial F / \partial x_A = 0 \quad (6.10)$$

$$\partial^2 F / \partial x_A^2 = 0 \quad (6.11)$$

where  $x_A$  is the mole fraction.

Eqn. (6.10) gives

$$\frac{\partial F}{\partial x_A} = g^{*1/N} \frac{z\alpha}{2\beta} \log \frac{[z(1-x_A) - \nu]x_A}{(zx_A - \nu)(1-x_A)} + \left( \frac{g^{*1/N}}{\beta} - 1 \right) \alpha^2 x_A^{-x} (1-x_A) x_A^{A-1} \log \frac{x_A}{1-x_A} = 0. \quad (6.12)$$

This relation is verified at all temperatures when  $x_A = x_B = 0.5$ . Eqn. (6.11) gives the condition

$$-\frac{\nu_{\text{crit}}}{z/2 - \nu_{\text{crit}}} + \alpha \left( 1 - \frac{\beta}{g^{*1/N}} \right) \frac{4}{z} = 0. \quad (6.13)$$

This equation gives the value of  $\nu_{\text{crit}}$ . When substituting in (6.7), we obtain  $\omega/zkT_c = 0.89$ , which is quite near Onsager's exact value (0.88). Fig. 4 gives  $\omega/zkT_c$  as a function of  $z$ .

It is interesting to note that Rushbrooke's value for the simple cubic lattice, based on the direct enumeration of the configurations, gives also an  $\omega/zkT_c$  which seems much too low.

The location of the critical conditions seems to be satisfactory but, of course, such a crude approximation cannot give any reliable indications concerning the analytical nature of the singularity.

<sup>1</sup> Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939), p. 244.

<sup>2</sup> Miller, *Theory of Solutions of High Polymers* (Oxford University Press, 1949).

<sup>3</sup> Kramers and Wannier, *Physic. Rev.*, 1941, **60**, 252.

<sup>4</sup> Onsager, *Physic. Rev.*, 1944, **65**, 117.

<sup>5</sup> Houttappel, *Physica*, 1950, **16**, 425.

<sup>6</sup> Wannier, *Physic. Rev.*, 1950, **79**, 357.

<sup>7</sup> Nix and Shockley, *Rev. Modern Physics*, 1938, **10**, 1.

<sup>8</sup> Fowler and Guggenheim, ref. 1, p. 576.

<sup>9</sup> Onsager, *Physic. Rev.*, 1944, **65**, 140, formula 119a.

<sup>10</sup> Wannier, *Physic. Rev.*, 1950, **79**, 363, formula 33.

<sup>11</sup> Onsager, *Physic. Rev.*, 1944, **65**, 141.

<sup>12</sup> Fowler and Guggenheim, ref. 1, p. 581.

<sup>13</sup> Rushbrooke, *Nuovo cimento, supplemento al vol. 6, serie 9, no. 2* (1949), p. 251.