The Statistical Problem in Cooperative Phenomena

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IT is in the very nature of cooperational phenomena that their statistical treatment is a difficult problem. For statistics is easily applied to an assembly of independent units. If such an approach is invalid even as a first approximation, then we are faced with a cooperational process. The general rule is that if an event (crystallization, magnetization) takes place for one unit of a cooperational assembly, then this same event will be favored in other units, because of a strong internal coupling. The result will be that the transition from one state to the other will tend to become more abrupt than would be the case if the elementary units were independent. This abruptness manifests itself in nature by the appearance of sharp transition temperatures.

From a mathematical point of view, a transition temperature means that the properties of an assembly must be described by a function of temperature possessing a singular point. Yet we have no reason to doubt that one of the distribution laws of statistical mechanics is applicable to such an assembly. These laws involve the temperature in a continuous, analytic manner. The question when and how they can give rise to singular temperatures is, therefore, of considerable theoretical interest. This problem has become an object of serious research in the last decade.

The first case to receive attention was the problem of condensation of gases. Even an ideal gas does possess a transition temperature, when obeying Einstein-Bose statistics.[1] This "Einstein condensation," however, is of interest for liquid helium only and has no connection with conventional condensation. Gases condense because of the attractive forces between the molecules; hence, we must be able to predict this behavior for an assembly of such molecules if we use Boltzmann statistics rigorously. This success has finally been achieved.[2] The calculations are, fortunately, somewhat reassuring for the traditional two-phase method. The two-phase approach, in neglecting intermediate states, cannot, of course, prove the existence of a phase change. But if the phase change occurs, a correct description of it will be obtained, provided the statistical treatment of each phase is adequate.

There are other types of transitions having no latent heat, sometimes classified as transitions of the second or third kind. Instances of such transitions are the Curie point of ferromagnets, the λ-point in liquid helium, and the order-disorder change in alloys. For these cases, the two-phase approach is of little value because the assembly actually passes through a continuity of intermediate states as the temperature varies. Most statistical approximations to this type of phenomenon can be lumped together as "inner field" approximations. In other words, they try to describe the system by a small number of parameters one of which is assumed to be zero in the high temperature "phase." On the low temperature side, this parameter varies and becomes zero at the transition point. These methods have become so commonly accepted that it is often not realized that they are approximations only. An exact statistical treatment of some special model is thus of twofold interest. It gives us full information for the model in question and also helps us judge the value of approximate methods for similar problems.

I. THE EIGENVALUE METHOD IN STATISTICS

The statistical treatment of cooperation in crystals is somewhat less forbidding than the corresponding problem in gases. The task of enumerating all complexions of an assembly is simplified if the cooperating units have a definite location. In addition, the periodicity of the system permits a simplifying transformation which was discovered independently by Kramers

[1] F. London, Phys. Rev. **54**, 947 (1938).

[2] J. E. Mayer, J. Chem. Phys. **5**, 74 (1937); J. E. Mayer and Ph. G. Ackermann, J. Chem. Phys. **5**, 74 (1937); M. Born, Physica **4**, 1034 (1937); B. Kahn, Dissertation, Utrecht (1938). The last paper has the best treatment of the matter.

and Wannier,[3] Lassettre and Howe,[4] and Montroll and Mayer.[5]

The transformation can be derived under very generalized assumptions. Let there be a number of units identical in structure which are lined up as beads on a string, and let them be numbered 1, 2, 3, 4, 5, $\cdots m$ (Fig. 1). Let the state of each unit be described by a (discrete or continuous) variable $x_1, x_2, x_3 \cdots x_m$. We must further assume that the kinetic energy is either of no importance, or else separable from the potential energy, and finally, that there is interaction between pairs of direct neighbors only; this interaction is symbolized by connecting lines in Fig. 1. The restriction of the interaction to nearest neighbors is actually not serious, because the interacting unit is left undetermined. We denote this interaction potential by $V(x, y)$. Then the probability for a given state of the assembly is proportional to the Boltzmann exponential

$$\exp\left[-\frac{1}{kT}(V(x_1, x_2)+V(x_2, x_3)+\cdots + V(x_m, x_1))\right], \quad (1)$$

from which the partition function is formed by summation (or integration)

$$f(T)=\sum_{x_1}\sum_{x_2}\cdots\sum_{x_m} \exp\left[-\frac{1}{kT}(V(x_1, x_2)+\cdots V(x_m, x_1))\right]. \quad (2)$$

Many physical questions can be considered solved if $f(T)$ is known. We note here the formulas for the total energy U and the total magnetization M (for an assembly assumed to have magnetic properties)

$$U=kT^2\frac{\partial \ln f}{\partial T}, \quad (3)$$

and

$$M=kT\frac{\partial \ln f}{\partial H}. \quad (4)$$

k denotes here Boltzmann's constant and H, the imposed magnetic field.

A reasoning from probability calculus[3,4] leads one to associate the following eigenvalue problem with the problem formulated in Eq. (2):

$$\sum_y \exp\left[-\frac{V(y, z)}{kT}\right]a(y)=\lambda a(z). \quad (5)$$

λ may have a series of different eigenvalues λ_ν. To each, there belongs one eigenvector a_ν if multiple values are counted as often as they arise. The orthogonality relation for the a's is well known

$$\sum_y a_\mu(y)a_\nu(y)=\delta_{\mu\nu}. \quad (6)$$

The formula developing the kernel in terms of the eigenvectors is also generally known for integral equations:

$$\exp\left[-\frac{V(y, z)}{kT}\right]=\sum_\nu \lambda_\nu a_\nu(y)a_\nu(z). \quad (7)$$

It obviously must apply to matrices too, because the two sides of Eq. (7) have identical eigenvectors and eigenvalues.

If we substitute Eq. (7) into Eq. (2), the summations over $x_1, x_2, x_3, \cdots x_m$ can be carried out explicitly with the help of Eq. (6). The result is:

$$f(T)=\sum_\nu \lambda_\nu{}^m. \quad (8)$$

Relation (8) becomes particularly useful in the case where the number m of cooperating units is very large. We may then neglect all but the largest eigenvalue λ_1:

$$f(T)=\lambda_1{}^m. \quad (9)$$

This is usually the case in applications.

The eigenvector a_1 going with this largest eigenvalue has also a particular significance. If it is normalized, then its square equals the proba-

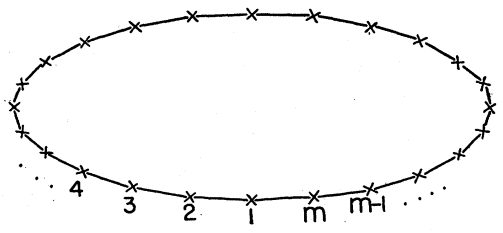


FIG. 1. A chain of m cooperating units.

[3] H. A. Kramers and G. H. Wannier, Phys. Rev. **60**, 252 and 263 (1941).
[4] Edwin N. Lassettre and John P. Howe, J. Chem. Phys. **9**, 747 and 801 (1941).
[5] E. W. Montroll and J. E. Mayer, J. Chem. Phys. **9**, 626 (1941).

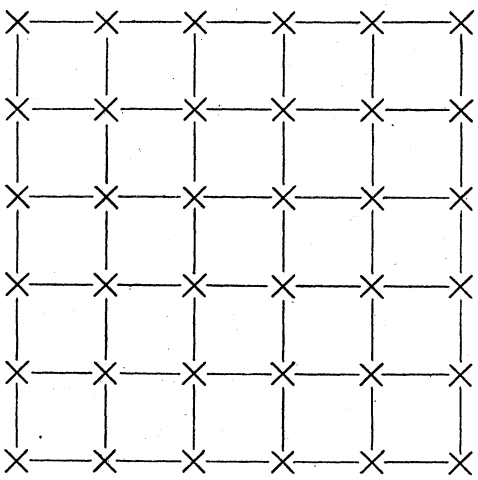


FIG. 2. The Ising square net. The crosses represent spins, the connecting lines coupling forces.

bility that the internal coordinate has a particular value z. Also, in the case of a chain with free ends, a_1 itself measures the probability for a state z in the end member. Both propositions may be proved directly from Eqs. (1), (6), and (7), if we follow the reasoning that led to Eq. (8) and thence to Eq. (9).

II. THE ISING MODEL

Among the systems to which the previous calculation applies, the model proposed by Ising[6] is probably the simplest one. It has been considered a schematic representation, sometimes of ferromagnetism, sometimes of order-disorder phenomena in alloys. Taking the former view, we can explain it as follows:

Assume a set of spins $\mu_1, \mu_2, \cdots \mu_N$ arranged in some regular order. Let each of the spins be capable of two orientations which we characterize by $\mu_i = +1$ and $\mu_i = -1$. Then the Ising model assumes that there is an energy difference between the two orientations of a given spin which depends on the orientations of its direct neighbors and, in addition, perhaps on an applied magnetic field. In particular, if all direct neighbors of one spin are equivalent, the model contains only two parameters, namely, the magnetic moment ν of each spin, and a quantity J which is the energy gained if two neighbors change from an antiparallel to a parallel position. With these two definitions, the interaction energy E takes the form

$$E = -\tfrac{1}{2}J \sum_{\langle i,k\rangle} \mu_i\mu_k - \nu H \textstyle\sum_i \mu_i, \qquad (10)$$

where $\sum_{\langle i,k\rangle}$ means that the sum is carried out over all pairs $\langle i, k\rangle$ which are direct neighbors. A more generalized form of this model assumes several different interactions $J_1, J_2, \cdots$ corresponding to different mutual positions. Such models are of interest to study the effects of anisotropy. But no basically new idea has evolved from the use of such models, and only results will be quoted for them in the following.

The partition function connected with Eq. (10) reads

$$f(T) = \boldsymbol{\sum}_{\mu_i=\pm 1} \exp\left[L \sum_{\langle i,k\rangle} \mu_i\mu_k + C \textstyle\sum_i \mu_i\right], \qquad (11)$$

with

$$L = J/2kT \qquad (12)$$

and

$$C = \nu H/kT. \qquad (13)$$

The bold face summation sign $\boldsymbol{\sum}_{\mu_i=\pm 1}$ is to be understood to extend over all possible states of the system; i.e., it would have to be written explicitly as

$$\boldsymbol{\sum}_{\mu_i=\pm 1} \sim \sum_{\mu_1=\pm 1} \sum_{\mu_2=\pm 1} \sum_{\mu_3=\pm 1} \cdots \sum_{\mu_N=\pm 1}.$$

Once f is known, the energy and magnetization follow from Eqs. (3) and (4):

$$U = -MH - \tfrac{1}{2}J(\partial \ln f/\partial L), \qquad (14)$$

$$M = \nu(\partial \ln f/\partial C). \qquad (15)$$

If the Ising model is interpreted in terms of superstructure, the quantity M retains its meaning as "long range order" even though H and C have no significance.

To any Ising system of spins showing periodicity, the general theory of Part I can be applied. The simplest among them is the linear chain, preferably closed so as to form a ring (Fig. 1). In this case, formula (11) becomes

$$f(T) = \boldsymbol{\sum}_{\mu_i=\pm 1} \exp\left[L(\mu_1\mu_2 + \mu_2\mu_3 + \mu_3\mu_4 + \cdots + \mu_m\mu_1) + C(\mu_1 + \mu_2 + \mu_3 + \cdots \mu_m)\right]. \qquad (16)$$

[6] E. Ising, Zeits. f. Physik **31**, 253 (1925).

This fits easily into the pattern explained in Part I, if the repeating unit is taken to be the individual spin. The variable denoted there by x_i is our spin μ_i. It is only capable of two discrete values $+1$ and -1. It follows that the eigenvalue problem (5) becomes a two-dimensional matrix problem. Comparing Eq. (16) with Eq. (2), we see that the interaction potential $V(\mu, \mu')$ must be taken as

$$-\frac{V(\mu, \mu')}{kT}=L\mu\mu'+\tfrac{1}{2}C\mu+\tfrac{1}{2}C\mu',^{7}$$

where the abbreviations (12) and (13) have been used on the right-hand side. We thus get for Eq. (5)

$$\sum_{\mu'=\pm 1} \exp\left[L\mu\mu'+\tfrac{1}{2}C\mu+\tfrac{1}{2}C\mu'\right]a(\mu') = \lambda a(\mu); \quad (17a)$$

or, in explicit matrix notation

$$\begin{pmatrix} e^{L+C} & e^{-L} \\ e^{-L} & e^{L-C} \end{pmatrix}\begin{pmatrix} a(+) \\ a(-) \end{pmatrix}=\lambda\begin{pmatrix} a(+) \\ a(-) \end{pmatrix}. \quad (17b)$$

Equation (8) reduces in the present case to

$$f(T)=\lambda_1{}^m+\lambda_2{}^m. \quad (18)$$

If Eq. (9) can be used, then the larger root λ_1 is the partition function per spin. It equals

$$\lambda_1=e^L \cosh C+(e^{2L}\sinh^2 C+e^{-2L})^{\frac{1}{2}}. \quad (19)$$

It has been pointed out by Ising himself that a linear Ising chain is not ferromagnetic. This can easily be verified by calculating the magnetization with the help of Eq. (15)

$$M=m\nu \sinh C/(\sinh^2 C+e^{-4L})^{\frac{1}{2}},$$

an expression which, because of Eq. (13), vanishes with H. In the absence of a magnetic field we have

$$\lambda_1=2\cosh L,$$

which, through Eq. (14), gives for the energy as function of temperature

$$U=-\tfrac{1}{2}mJ\tanh L.$$

This is a smooth increase from $-\frac{1}{2}mJ$ to 0 as the temperature rises.

[7] The splitting of the C-term in two halves is not necessary; the advantage is purely aesthetic, the symmetry of $V(\mu, \mu')$ is maintained.

III. THE ISING SQUARE NET

The case of the linear Ising chain is an exceptional one, for we cannot usually assert that a statistical problem is solved by bringing it in the form of Eq. (5). This equation will only have a standard form known in analysis if the system is infinite in one dimension only. Unfortunately, no such system can exhibit temperature singularities. The reason is that singularities are connected with the appearance or disappearance of long range order. Long range order, however, cannot exist in one dimension only, because the disarrangement of just two nearest neighbors is sufficient to destroy it. This reasoning is confirmed by another one-dimensional calculation[8] in addition to the one carried out in Part II.

The Ising square net has been the sample case which has led to a good understanding of two-dimensional Ising models. It is shown in Fig. 2. The crosses are to indicate the location of the spins, and the lines are drawn to connect interacting neighbors. Peierls[9] has shown that this model possesses a non-zero spontaneous magnetization at absolute zero and, hence, that it must possess a critical temperature separating regions with and without spontaneous magnetization (or long range order, when considered as a model for superstructure).

The statistical calculation for the Ising square net is indicated formally in Eq. (11). It can be transformed into an eigenvalue problem of the

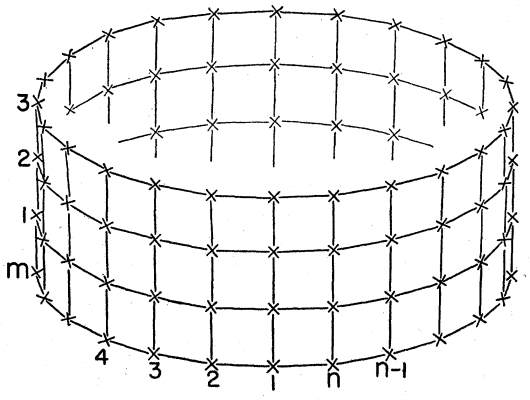


FIG. 3. Adaptation of Ising square net to eigenvalue method.

[8] K. F. Herzfeld and Maria Goeppert-Mayer, J. Chem. Phys. **2**, 38 (1934).

[9] R. Peierls, Proc. Camb. Phil. Soc. **32**, 477 (1936).

type (5) in several different ways. The most fruitful approach is shown in Fig. 3. We think of the net as being composed of circular tiers of n spins each, forming a circular cylinder. This cylinder becomes a torus when the first and last of the m tiers are joined in the manner outlined in Part I. The tier is the elementary "unit" mentioned there, and, consequently, its coordinate x is a variable capable of 2^n different discrete values, corresponding to the 2^n different configurations of spins $\mu_1, \mu_2, \mu_3, \cdots \mu_n$. The potential $V(y, z)$ entering Eqs. (1) and (5) becomes thus the interaction between two tiers. It must contain the coupling within the tiers also, as the sum $V(x_1, x_2)+V(x_2, x_3)+\cdots$ is to equal the total interaction. It is preferable to allot to $V(y, z)$ one-half of the interaction within y, and one-half of the interaction[7] within z. This gives

$$V(y, z) = -\tfrac{1}{2}J \sum_{i=1}^{n} (\mu_i\mu_i' + \tfrac{1}{2}\mu_i\mu_{i+1} + \tfrac{1}{2}\mu_i'\mu_{i+1}') - \tfrac{1}{2}\nu H \sum_{i=1}^{n} (\mu_i + \mu_i').$$

As in (17a), the μ's of the two tiers are distinguished here by calling the ones $\mu_1, \mu_2, \cdots \mu_n$, the others $\mu_1', \mu_2', \cdots \mu_n'$. The conventions $\mu_{n+1}=\mu_1$, $\mu_{n+1}'=\mu_1'$ are to be assumed in agreement with Fig. 3. Thus, our eigenvalue problem (5) reads

$$\sum_{\mu_i'} \mathcal{K}(\mu_i, \mu_i')a(\mu_i') = \lambda a(\mu_i), \tag{20a}$$

with

$$\mathcal{K}(\mu_i, \mu_i') = \exp\left[L \sum_i \mu_i\mu_i' + \tfrac{1}{2}L \sum_i \mu_i\mu_{i+1} + \tfrac{1}{2}L \sum_i \mu_i'\mu_{i+1}' + \tfrac{1}{2}C \sum_i \mu_i + \tfrac{1}{2}C \sum_i \mu_i'\right] \tag{20b}$$

where the quantities L and C are defined by Eqs. (12) and (13).

IV. TEMPERATURE SYMMETRY AND CURIE POINT

The Curie point of the Ising square net was first located by Kramers and Wannier.[3] Reasoning on a matrix problem similar to Eq. (20), they discovered that it possesses a symmetry between high and low temperatures. The argument as presented in the following is due to Onsager.[10] In this new form, it transcends by far the original limitation and applies, in fact, to any net which can be spread on a simply connected surface (like a sphere) without crossing of lines of interaction. Figures 4–7 show four examples of such nets, two of which are finite, two infinite. They are to be interpreted the same way as the earlier figures, the dots representing spins, the lines representing interactions between the spins. Each figure contains, in addition to this net, another one which is obtained from it by placing spins (shown as circles) into every elementary polygon and drawing lines of interaction between them so that each old line is crossed by a new one (dotted lines). We shall refer to the new net as the "dual" of the original one; it is immediately observed that this duality relation is a reciprocal one: the number of polygons in one net equals the number of corners (spins) in the other while the number of sides is the same. In Figs. 5 and 6, the dual net happens to be topologically identical with the original. Such nets we shall refer to as "self-dual." This duality enters now in the following way:

The general expression to be evaluated is given by formula (11). If we assume zero magnetic field, i.e., $C=0$, then it is a sum of terms each of which is a product of factors of the type $e^{L\mu\mu'}$ where μ and μ' are neighboring spins. This exponential is only capable of two values because the product $\mu\mu'$ can only be $+1$ or -1. It follows that the exponential can be replaced at will by some other expression, provided it yields the same two values e^L and e^{-L}. We do just this if we set

$$e^L = (\tfrac{1}{2}\sinh 2L)^{\frac{1}{2}}(e^{L^*} + \mu\mu' e^{-L^*}), \tag{21}$$

where the parameter L^* is given by

$$e^{2L} = \coth L^*, \tag{22a}$$

or more symmetrically

$$\sinh 2L \sinh 2L^* = 1 \tag{22b}$$

or also

$$\cosh 2L \tanh 2L^* = \cosh 2L^* \tanh 2L = 1. \tag{22c}$$

This gives for the sum (11)

$$f(T) = (\tfrac{1}{2}\sinh 2L)^{s/2} \sum_{\mu_i=\pm 1} \prod_{r=1}^{s} (e^{L^*} + \mu_r\mu_r' e^{-L^*}).$$

Here the product over r extends over all con-

[10] L. Onsager, private communication.

FIG. 4.

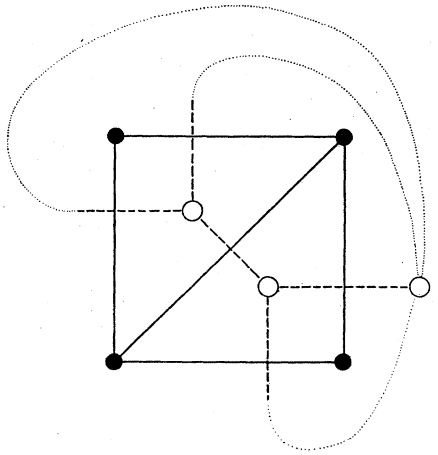


FIG. 6.

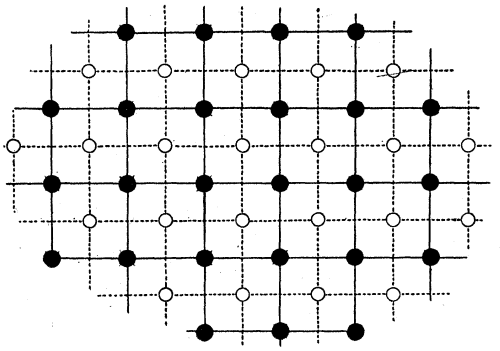


FIG. 5.

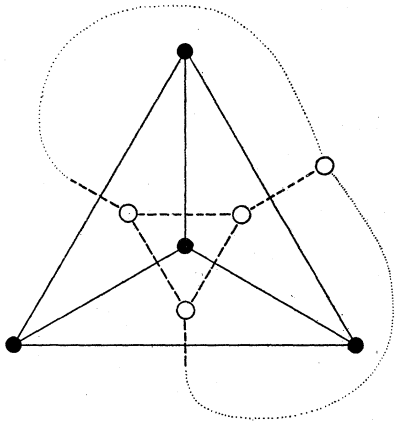
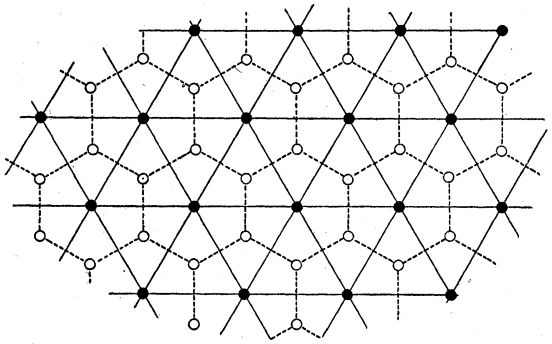


FIG. 7.



FIGS. 4–7. Two-dimensional Ising nets and their duals.

necting rods in our net, and s is the total number of such connections. In developing the product, we get a sum of μ products each of which can be represented in our net by a polygon running along the connecting rods. Only closed polygons give a non-zero contribution because an open polygon means that some spin is present in an odd power; this is sufficient to make the term equal to zero when it is summed over all values of the μ's. The magnitude of the term is such that every connecting rod not included in the polygon contributes a factor e^{L^*} to it, and every connection included a factor e^{-L^*}. Since it is a topological property of every closed polygon to divide a simply connected surface into two regions, we can characterize every term in our product develop ment by one- or more exactly two-spin arrangements $\nu_i = \pm 1$ in the dual net, namely, an arrangement having positive spins on one and negative spins on the other side of the closed polygon. The value of the term can, by this device, be written in the form

$$\exp\left[\sum_{r=1}^{s} L^* \nu_r \nu_r'\right].$$

To obtain all terms in the above product expansion, we must sum over all possible configurations of the dual spins ν_i and divide by two. The sum over μ_i is then trivial and gives a factor 2^N where N is the total number of spins in the original net. In this manner, the partition function over the original net has been transformed into a partition function for the dual. If we denote by $f^*(T)$ this dual partition function, and by T^* the temperature which, through Eq. (12),

is associated with L^* then we may write

$$f(T)=2^{N-1-\frac{1}{2}s}(\sinh 2L)^{s/2}f^*(T^*).$$

With the help of Eq. (22) and the topological relation

$$N+N^*=s+2,$$

we can bring this equation in the symmetric form

$$\frac{f(T)}{2^{N/2}(\cosh 2L)^{s/2}}=\frac{f^*(T^*)}{2^{N^*/2}(\cosh 2L^*)^{s/2}}. \tag{23}$$

In the general case, Eq. (23) represents a reciprocity relation connecting the partition functions of the two-dual lattices. In the special case, however, where the net is self-dual, f and f^* refer to the same assembly, and therefore,

$$f(T)=f^*(T).$$

The equation represents then a symmetry property of f connecting the value of $f(T)$ with the value of the same f at the "dual" temperature T^*. One sees from (22b) that these two temperatures form a pair, one of which lies high if the other lies low. All singularities of $f(T)$, if existing, would thus have to exist in pairs unless we have a singularity at the temperature T_c for which

$$\sinh 2L_c=1, \tag{24a}$$

$$L_c=0.4407. \tag{24b}$$

This argument applies for instance to the infinite square net (Fig. 6), and thus locates its Curie point.

Even if the net is not self-dual, the argument can often be completed with little additional labor. Assuming, as an example, that $f(T)$ refers to the triangle net shown in Fig. 7, we see that $f^*(T^*)$ refers to the honeycomb. Now it is possible to remove from the latter state sum all the spins represented by circles in Fig. 8. This is done by carrying out for them the summation (11) ahead of the others (star-triangle transformation). Taking as an example the spin μ_0 in Fig. 8, we can apply the same reasoning that led to Eq. (21) to justify the following transformation:

$$\sum_{\mu_0=\pm 1}\exp\left[L^*\mu_0(\mu_1+\mu_2+\mu_3)\right]=2(\cosh 3L^*\cosh^3 L^*)^{\frac{1}{2}}\times\exp\left[L^+(\mu_1\mu_2+\mu_2\mu_3+\mu_3\mu_1)\right],$$

where

$$(e^{4L}-1)(e^{4L+}-1)=4. \tag{25}$$

The remaining spins μ_1, μ_2, μ_3, etc., shown by dots in Fig. 8 will again form a triangle net equivalent to the original one. The new interactions, shown

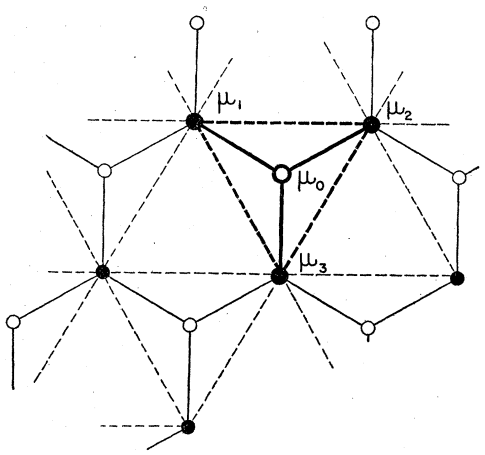


FIG. 8. Illustrating the star-triangle transformation connecting honeycomb and triangle nets.

by dashed lines, also conform to that pattern, with the parameter L^* replaced by L^+. Thus, the temperature symmetry now evolves around Eq. (25) instead of Eq. (22). Hence, the Curie point is given by

$$e^{4L_c}=3. \tag{26}$$

The same calculation furnishes also the Curie point for the honey comb lattice. We find

$$\cosh 2L_c=2. \tag{27}$$

The formulas (24), (26), and (27) can be united into a single statement by the use of the Gudermannian function gdx:

$$gd2L_c=\pi/Z. \tag{28}$$

Here Z stands for the number of nearest neighbors of one spin in the lattice. In our three cases, Z equals 3, 4, and 6, respectively.

Onsager[10] has succeeded in extending the symmetry reasoning to systems containing several different interactions J, J', J''. The reasoning ceases then to be one of temperature symmetry because $f^*(T^*)$ refers to a net with different interactions. The generalized argument is based on the proof that if the dual transformation (23)

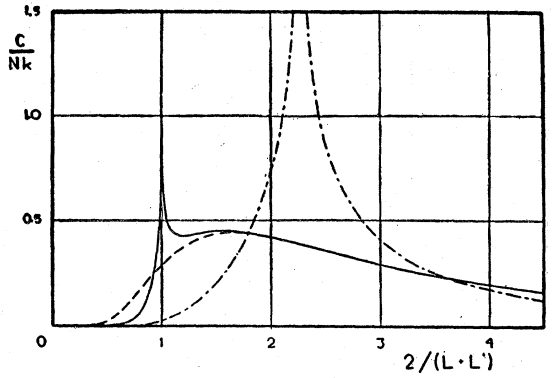


FIG. 9. Specific heat curves for rectangular Ising net, with various degrees of anisotropy. $-\cdot-\cdot-\cdot-$ $J'/J=1$. ——— $J'/J=1/100$. - - - - - - $J'=0$.

is applicable to a matrix problem of the type (20) then it always does convert order and disorder into each other. Hence, if there exists a temperature for which the partition function of a two-dimensional net can be transformed into itself using the dual transformation only once, then such a temperature must be the Curie temperature.

V. COMPLETE SOLUTION FOR RECTANGULAR NET

Even in its most powerful form, the symmetry reasoning does not tell us much about the thermal behavior of an Ising net in the neighborhood of the singular temperature. Fortunately, the missing information has been supplied to us by Onsager[11] who derived the complete solution for the Ising rectangular net. The reasoning, which uses the methods of operator algebra familiar from quantum mechanics, is too intricate to be contained in a survey of this type. We shall restrict ourselves to a short description and quotation of results.

The basic matrix equation which is to be solved is Eq. (20) minus the C-terms referring to an applied magnetic field. The vector space in which it is formulated possesses 2^n dimensions. Two types of operators form a complete generating basis of the corresponding matrix algebra. They are defined as follows:

$$s_i a(\mu_1, \mu_2, \cdots \mu_n) = \mu_i a(\mu_1, \cdots \mu_n), \quad (29)$$

and

$$C_i a(\mu_1, \mu_2 \cdots, \mu_i, \cdots \mu_n) = a(\mu_1, \mu_2, \cdots, -\mu_i, \cdots \mu_n). \quad (30)$$

[11] Lars Onsager, Phys. Rev. 65, 117 (1944).

These $2n$ operators satisfy the algebraic relations

$$\begin{aligned} &s_i^2 = C_i^2 = 1, \quad && s_i C_i + C_i s_i = 0, \\ &s_i s_k - s_k s_i = 0, \quad && C_i C_k - C_k C_i = 0, \\ &s_i C_k - C_k s_i = 0, \quad \text{if} && i \neq k. \end{aligned}$$

It is a relatively straightforward matter to express the operator $\mathfrak{H}$ in terms of our s's and C's. Within our matrix algebra, Onsager was able to construct a subalgebra containing $\mathfrak{H}$ which is invariant with respect to rotation of the cylinder shown in Fig. 3. This subalgebra can be generated as a direct product of mutually commuting quaternion algebras. This quaternion basis has the property that $\mathfrak{H}$ can be written as a direct product of operators belonging to each basis:

$$\mathfrak{H} = \mathfrak{H}_1 \times \mathfrak{H}_2 \times \mathfrak{H}_3 \times \cdots \times \mathfrak{H}_n.$$

Since each quaternion basis is two-dimensional, the problem demands only the solution of a series of quadratic equations. The eigenvalue λ is thus obtained as a product of the form

$$\lambda = \lambda_1 \lambda_2 \lambda_3 \cdots \lambda_n.$$

It follows that the logarithm of the partition function will appear as a sum, or, in the limit when the number n of spins fitting one tier becomes very large, an integral. This integral looks as follows

$$\frac{1}{N} \ln f(T) = \ln (2 \cosh 2L) + \frac{1}{\pi} \int_0^{\pi/2} \ln \left\{ \frac{1+(1-\kappa^2 \sin^2 \phi)^{\frac{1}{2}}}{2} \right\} d\phi \quad (31)$$

where $N=mn$ is the total number of spins in the net and κ is an auxiliary parameter defined through

$$\kappa = \frac{2 \sinh 2L}{\cosh^2 2L} = \frac{2 \sinh 2L^*}{\cosh^2 2L^*}. \quad (32)$$

One sees from Eq. (22c) that κ has the same value for the two dual temperatures T and T^*. Thus the symmetry property (23) is explicit in (31).

The nature of the temperature singularity is readily deduced from Eq. (31) and Eq. (32). The parameter κ is contained between 0 and 1. It reaches its minimum value 0 either for very large or very small temperatures. It takes up its

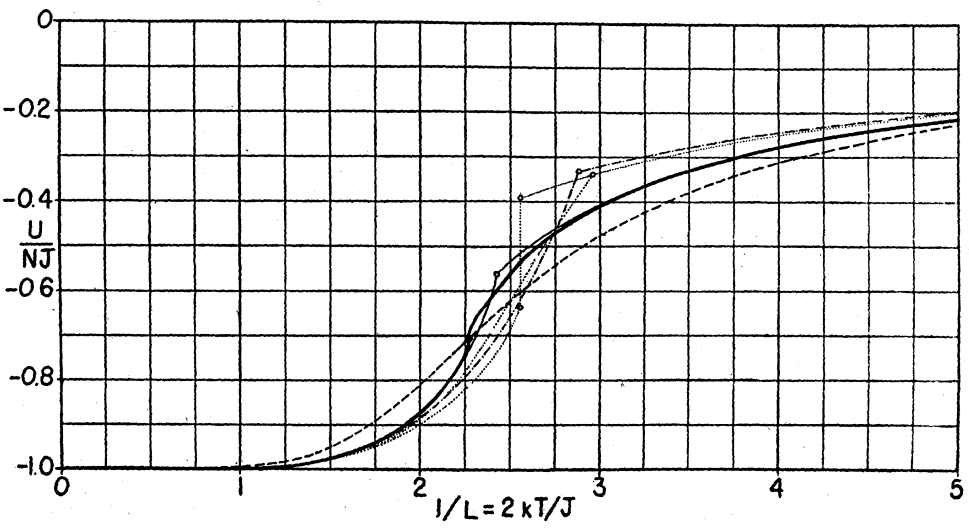


FIG. 10. Energy *versus* temperature for Ising square net. ——— Correct curve. ——— Approximation of Kramers and Wannier. -·-·-·- Method of Bethe. ..... Methods of Heisenberg and Kirkwood. – – – – – – Approximation by a finite matrix equation.

maximum value when

$$\sinh 2L_c = 1$$

i.e., at the critical point as defined by Eq. (24). Now from Eq. (14) and Eq. (31) we get for the energy U of the system

$$U(T) = -\tfrac{1}{2}NJ \coth 2L\left[1 \pm \frac{2}{\pi}(1-\kappa^2)^{\frac{1}{2}}K(\kappa)\right], \quad (33)$$

the + sign holding below the Curie point, the − sign above. Here $K(k)$ is the complete elliptic integral of the first kind according to standard definitions. The singularity is contained in the second term in the square bracket. The term equals zero at the Curie point and behaves as

$$-(T-T_c)\ln(T-T_c)$$

in its immediate neighborhood, because of the logarithmic singularity contained in $K(\kappa)$. From this, we find by differentiation that the specific heat is logarithmically infinite at the critical point.

These conclusions are not basically altered if we have to deal with a rectangular rather than a quadratic Ising net. If we denote the two interactions by J and J' and associate with them L and L' through Eq. (12), then we find the Curie point from the formula

$$\sinh 2L_c \sinh 2L_c' = 1. \quad (34)$$

The type of singularity stays the same. Figure 9 shows a plot of the specific heat *versus* temperature for three different ratios J'/J, including the value 1 of the quadratic case.

VI. CONCLUSIONS

The main importance of the numerical results of the last section consists in the fact that they were obtained rigorously, assuming only a plausible mechanical model and Boltzmann's distribution law. Thus, they form a proof that Boltzmann's law may result in a temperature singularity without latent heat if the mechanical interactions are favorable. The detailed structure of our singularity, on the other hand, is not of as much significance. The logarithmic infinity of the specific heat, for instance, is probably due to the fact that the model is two-dimensional. It is not likely to show up in three-dimensional cases.

Beyond this fundamental importance, the calculations have a certain indirect value. By applying various approximate methods to the same Ising square net, we can form an opinion as to the accuracy and usefulness of such treatments. We may dispense here with a detailed discussion of these methods as this is done amply elsewhere.[12,13] The necessary numerical work has also been carried out.[13] We may bring these older surveys up to date, however, by mentioning the

[12] F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).
[13] Reference 3, Sections 7 and 8.

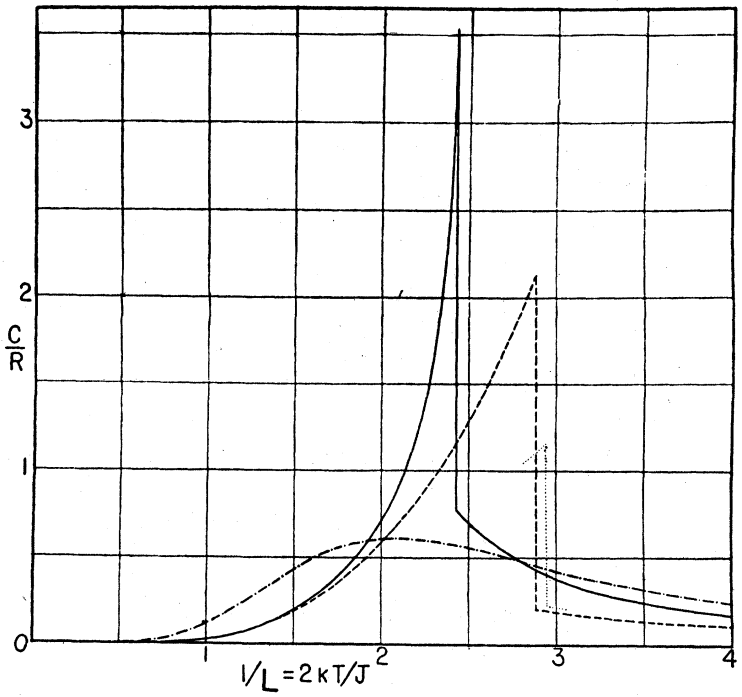


FIG. 11. Approximate specific heat curves for Ising square net. ———— Approximation of Kramers-Wannier. – – – – – – Bethe method. ..... Method of Kirkwood. -·-·-·- Finite matrix approximation.

approximations devised by Montroll[14] and by Fuchs.[15] The former proposes several perturbation methods based on the matrix approach, the latter is an application of the Mayer cluster method to the present problem, a method which had originally been devised to discuss the condensation of gases.[2]

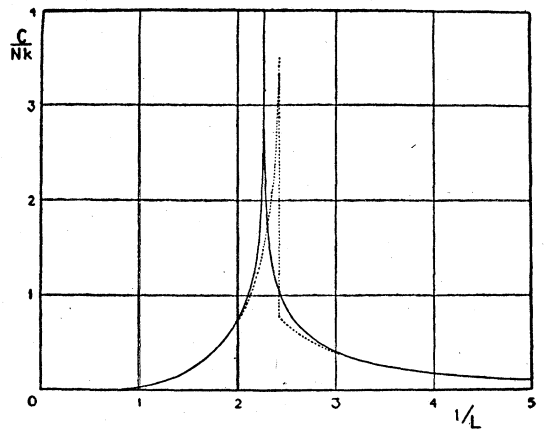


FIG. 12. Specific heat curves for Ising square net. Exact curve and typical approximation in comparison.

We shall restrict ourselves here to actual comparison and interpretation of results. Figure 10 shows an energy *versus* temperature plot for the Ising square net. The result of formula (33) is shown in heavy outline, and the other curves refer to various approximate procedures. It is interesting to observe that all these procedures are qualitatively in error in their result concerning the nature of the temperature singularity. This error shows up best in the specific heat curves shown in Figs. 11 and 12. Figure 11 shows the result of three well-established approximation methods. They agree with each other in predicting a jump in the specific heat. Yet this result is incorrect as can be seen from Fig. 12 which shows the best of them in comparison with the exact curve. The source of this error is not difficult to trace. All three approximations are of the "inner field" type, as explained in the introduction. This means that they have an extra parameter on the low temperature side. Actually, the state of disorder is just as complicated to describe as the state of order (see

[14] Elliott W. Montroll, J. Chem. Phys. **9**, 706 (1941), and **10**, 61 (1942).
[15] K. Fuchs, Proc. Roy. Soc. **A179**, 340 (1942); Gregory H. Wannier, Proc. Roy. Soc. **A181**, 409 (1943).

Part IV) and the use of an extra parameter for one of them means a more accurate description. Consequently, the specific heat of the ordered phase comes out higher simply because it is calculated more accurately. Thus the specific heat jump is a spurious effect which is due to the approximation method only. Another incidental effect which may be mentioned here is the tendency of the ordered phase to extend too far.

This result is somewhat disturbing because a specific heat jump is also the customary result of these same approximations when applied to more realistic three-dimensional models. The result is generally considered in good agreement with experiment. Yet we have just seen that the theoretical evidence for such a jump is not conclusive. On the contrary, it would be surprising if the specific heat remained finite at the Curie point for a three-dimensional Ising model. It is conceivable, on the other hand, that we may find a curve which is more asymmetric about the singularity than our test case. The reason is that the symmetric behavior, as discussed in Part IV, is specific to two dimensions. It is to be hoped that a three-dimensional calculation will, before long, furnish the answer to these questions.