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A Theory of Cooperative Phenomena

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A new method of approximation for order-disorder phenomena is developed. In Sec. A, the method is explained for the one-dimensional Ising lattice. Sections B and C cover the approximations already known, such as those of Bethe (Sec. B) and of Kramers-Wannier (Sec. C), which are shown to be derived as special cases of the method with suitable choices of variables. In Sec. D, an improved treatment is explained for the three-dimensional simple cubic Ising lattice. This approximation is found to agree with the rigorous expansion of the partition function up to the fourth moment by Kirkwood's moment method, so far as the disordered state is concerned. In Sec. E the general formula for the entropy is given. In Sec. H an improved treatment of the face-centered lattice (Ising model) is given.

I. INTRODUCTION

WE shall develop a new method of approximation to the entropy of an order-disorder system. It gives, by suitable choices of the variables, the approximations already known, such as that of Bethe,[1] and the "variation method" derived by Kramers and Wannier.[2] Our improved treatment for a simple cubic lattice has been tested by comparison with the rigorous expansion of the partition function by Kirkwood's method of moments,[3] and is found to agree with his expansion up to the fourth moment, so far as the disordered state is concerned.

Though most of the two-dimensional problems have been solved,[4] the new approach for the three-dimensional problems seems to be worthwhile, especially at the present stage of the theory when the theory is confronted with formidable mathematical difficulties and various new approximations[5–8] are still being reported.

II. SIMPLE LATTICES

A. Linear Ising Lattice

We call a linear lattice composed of M lattice points a *system*, and consider an *ensemble* which contains L systems as illustrated in Fig. 1. The totality of the kth lattice points (one from each of the L systems, marked with black circles) will be called the *set* of kth lattice point, and the *set* of the kth bond will mean the whole of the bonds marked with heavy lines in the figure.

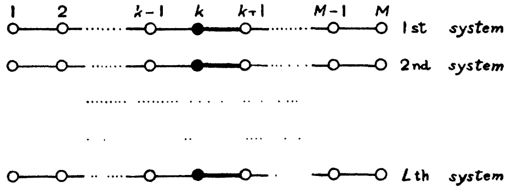

FIG. 1. An *ensemble* of linear lattices.

The probability of appearance of a bond having one of the configurations shown in the left column of Table I is denoted by y_i as shown in the second column.[9] Without loss of generality, configurations $(+\ -)$ and $(-\ +)$ can be assumed to have the same probability of appearance due to their symmetry. β_i indicates the number of different configurations having the same probability. y_i's are normalized by the equation

$$\sum_{i=1}^{3}\beta_i y_i=1. \tag{A.1}$$

We say that "the set of the kth bond has *right distribution of spin*" or, briefly, "the kth bond has *r.d.*", when, among the L bonds belonging to the set of heavy lines in Fig. 1, y_1L bonds have the configuration $(+\ +)$, y_2L have $(+\ -)$, y_2L have $(-\ +)$, and y_3L have $(-\ -)$. We show in Table II, which can be derived from

TABLE I. Probabilities of appearance of configurations of a bond.

Bond	Prob.	β_i*	ε_i**
⊕—⊕	y_1	1	$-\varepsilon$
⊕—⊖ ⊖—⊕	y_2	2	$+\varepsilon$
⊖—⊖	y_3	1	$-\varepsilon$

* β_i indicates the number of different configurations having the same probability.
** ε_i denotes the energy per bond.

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[6] D. ter Haar and B. Martin, Phys. Rev. **77**, 721 (1950).

[7] T. L. Hill, J. Chem. Phys. **18**, 988 (1950).

[8] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[9] We shall call a bond a *basic figure* for Sec. A, as the configurations of a bond are chosen as variables upon which the whole theory of Sec. A is constructed.

TABLE II. Probabilities of appearance of spins.

Spin	Probability
$+$	$x_1=y_1+y_2$
$-$	$x_2=y_2+y_3$

Table I, the probability x_i of a lattice point having the respective spin.

Similarly to the bonds, we say that "(the set of) the kth lattice points has right distribution of spins," when, among the L lattice points belonging to the set of black circles in Fig. 1, x_1L have $(+)$ spins, and x_2L, $(-)$ spins. When the set of a bond has r.d., each of the end points of the bond naturally has r.d.

Analogously to the treatment by means of the eigenvalue problems,[4] we fill up the lattice points one by one from an end. In Fig. 2, we assume that each bond on the left side of B has been put with r.d., and we are going to fill up the point A. What will be the number of ways of putting a spin on A so that the bond $B-A$ has r.d.?

As the set of the lattice point B is assumed to have r.d., x_1L lattice points among the set have $(+)$ spins and x_2L, $(-)$ spins. Among the first x_1L points, we can select y_1L at random, so that for these y_1L, we put $(+)$ spins on A and for the remaining y_2L, $(-)$ spins on A, making y_1L bonds having the configuration $(+\,+)$ and y_2L bonds having the configuration $(+\,-)$ among the set of the bond $B-A$. In this process, the number of ways of putting x_1L spins on A is

$$g_1=(x_1L)!/[(y_1L)!(y_2L)!]. \qquad \text{(A.2)}$$

For the remaining x_2L of the set of the point B having $(-)$ spins, we can pick up y_2L at random in order to make $y_2L(-\,+)$'s and $y_3L(-\,-)$'s. The number of ways of making this selection is

$$g_2=(x_2L)!/[(y_2L)!(y_3L)!]. \qquad \text{(A.3)}$$

Thus, the number G_L of ways of putting a spin on A so that $B-A$ has r.d. becomes finally

$$G_L=g_1g_2=\prod_{i=1}^{2}(x_iL)!\Big/\prod_{i=1}^{3}(y_iL)!^{\beta_i}. \qquad \text{(A.4)}$$

We introduce the abbreviated expression "to put (a spin on) A *with reference to* B," meaning "to put a spin on A so that the bond $B-A$ has r.d., provided B has had r.d." The words in the parenthesis might sometimes be omitted. And at the same time, for simplicity's sake, we put

$$\begin{aligned}&\prod_{i=1}^{2}(x_iL)!\equiv X_L\equiv\{\text{Point}\}_L,\\ &\prod_{i=1}^{3}(y_iL)!^{\beta_i}\equiv Y_L\equiv\{\text{Bond}\}_L.\end{aligned} \qquad \text{(A.5)}$$

The notations on the right-hand sides are conveniently used when we briefly compose G_L. That is, the number of ways G_L of putting a spin on a lattice point A with reference to the adjacent point B, completing a bond $B-A$, so that the bond has r.d., is calculated schematically as follows:

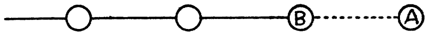

FIG. 2. An intermediate stage of constructing a linear Ising lattice.

$$G_L=\frac{\{\text{the part already filled}\}_L}{\{\text{the whole to be completed}\}_L}=\frac{\{\text{Point } B\}_L}{\{\text{Bond } BA\}_L}=\frac{X_L}{Y_L}. \qquad \text{(A.6)}$$

As the number of ways of filling any lattice point is equally G_L, the number required to complete a system filling M lattice points is $(G_L)^M$ for an ensemble. The number of ways for one system G is given by the Lth root of $(G_L)^M$, and when we apply Stirling's formula and the condition (A.1), the entropy S for a system becomes

$$\begin{aligned}S&=k\ln G=k(M/L)\ln G_L\\ &=k(M/L)[\textstyle\sum x_iL\ln(x_iL)-\sum\beta_iy_iL\ln(y_iL)]\\ &=kM\left[\sum_{i=1}^{2}x_i\ln x_i-\sum_{i=1}^{3}\beta_iy_i\ln y_i\right].\end{aligned} \qquad \text{(A.7)}$$

The total energy for a system is easily calculated, and combining it with (A.7), we can formulate the free energy, whose minimum gives the equilibrium state. Thus proceeding, we can verify that the well-known solution for linear Ising lattice[4] can be attained, of which the details are omitted here.

B. Bethe's Approximation (Two-Dimensional Square Lattice)

In this case also, we choose a bond as a basic figure, and the y_i's in Table I and the x_i's in Table II are sufficient to represent the variables. The entropy of the system is formulated when we calculate the number of ways of putting a spin on the point A in Fig. 3, so that the bonds $B-A$ and $C-A$ have r.d., respectively, assuming that every bond in the part of solid lines has had r.d. This number can be calculated in three steps:

(i) The number of ways of putting a spin on A with reference to B so that $B-A$ has r.d., independent of the bond $C-A$, is as follows (see (A.2)-(A.6)):

$$g=\{\text{Point } B\}_L/\{\text{Bond } BA\}_L=X_L/Y_L. \qquad \text{(B.1)}$$

(ii) Thus, the bond $B-A$ has had r.d., but the distribution of the bond $C-A$ is not known. We will correct the latter. This correction cannot be done perfectly, but as a best approximation, following the idea of Takagi,[10] we can multiply (B.1) by the proba-

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[10] Y. Takagi, Proc. Phys. Math. Soc. Japan 23, 44 (1941).

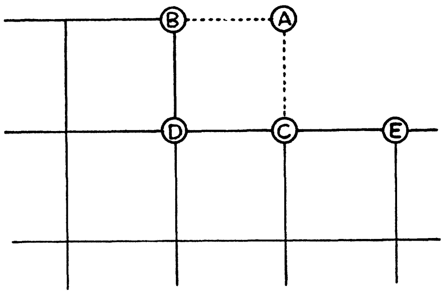

FIG. 3. An intermediate stage of constructing a two-dimensional square lattice.

bility that the bond $C-A$ has r.d. after the step (i). This probability Γ is

$$\Gamma=\frac{\{\text{Point } C\}_L}{\{\text{Bond } AC\}_L}\div\frac{L!}{\{\text{Point } A\}_L}=\frac{X_L{}^2}{Y_L L!},\qquad\text{(B.2)}$$

because, in the step (i), we have put a spin on A independently of C, which is identical with having calculated the number of ways of putting a spin on A as

$$L!/[(x_1L)!(x_2L)!]=L!/X_L,\qquad\text{(B.3)}$$

so far as the bond $C-A$ is concerned; whereas the correct number of ways of putting a spin on A so that the bond $C-A$ has r.d. is, analogously to (B.1) or (A.6), expressed by

$$\{\text{Point } C\}_L/\{\text{Bond } CA\}_L.$$

TABLE III. Probabilities of appearance of configurations of a square.

Square	Prob.	γ_i*
$\begin{matrix}+&+\\+&+\end{matrix}$	z_1	1
$\begin{matrix}+&+\\+&-\end{matrix}$ etc.	z_2	4
$\begin{matrix}+&-\\+&-\end{matrix}$ etc.	z_3	4
$\begin{matrix}-&+\\+&-\end{matrix}$ etc.	z_4	2
$\begin{matrix}+&-\\-&-\end{matrix}$ etc.	z_5	4
$\begin{matrix}-&-\\-&-\end{matrix}$	z_6	1

* γ_i is the number of different configurations having the same probability.

(iii) Multiplying g and Γ, we get the approximate number of ways G_L of putting a spin on A so that both bonds $B-A$ and $C-A$ have r.d.:

$$G_L=g\Gamma=X_L{}^3/(Y_L{}^2L!),\qquad\text{(B.4)}$$

which can easily be proved to coincide with the formula derived by Takagi,[10] which is identical with Bethe's first approximation.[1]

Moreover, for other types of lattices also, the y_i's and x_i's are sufficient to give Bethe's approximation. Generally, for the lattice with coordination number 2ω, the number of ways of constructing a system $(G_L)^{M/L}$ is easily shown to be approximated[11] by

$$(G_L)^{M/L}=[X_L{}^{2\omega-1}/(Y_L{}^{\omega}L!^{\omega-1})]^{M/L},$$

giving Bethe's approximation.

C. The Kramers-Wannier Approximation (Two-Dimensional Square Lattice)

(C1) *Free Energy*

To improve the approximation, we choose a square as a basic figure, and use as variables the probabilities of appearance z_i's of configurations of a "square" shown in the left column of Table III. From this table, we derive Table IV, which gives the probabilities of appearance w_i's of configurations of an "angle." Just as was mentioned above concerning Table I, the configurations interchangeable by symmetry operations, say,

$$\begin{pmatrix}+&+\\+&-\end{pmatrix},\ \begin{pmatrix}+&-\\+&+\end{pmatrix},\ \begin{pmatrix}-&+\\+&+\end{pmatrix}\ \text{and}\ \begin{pmatrix}+&+\\-&+\end{pmatrix}$$

are naturally assumed to appear with the same probability. The γ_i's and δ_i's denote the numbers of different configurations with the same probability. The concepts of *set*, *r.d.*, and *with reference to* are extended for the new variables, but no explanation seems to be necessary.

Extending Eq. (A.5), we define

$$\prod_{i=1}^{6}(z_iL)!^{\gamma_i}\equiv Z_L\equiv\{\text{Square}\}_L,\qquad\text{(C1.1)}$$

$$\prod_{i=1}^{6}(w_iL)!^{\delta_i}\equiv W_L\equiv\{\text{Angle}\}_L.\qquad\text{(C1.2)}$$

We also use the y_i's of Table I and the x_i's of Table II.

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[11] Except for the case $2\omega=3$.

The entropy of a system is obtained when we calculate the number of ways of putting a spin on A in Fig. 3, so that both the square $ABDC$ and the angle ACE have r.d., provided that every square and every angle in the part drawn with solid lines have had r.d.

To calculate this number, we proceed in three steps, just as in Sec. B:

(i) The number of ways of putting a spin on A with reference to the angle BDC, so that the square $ABDC$ has r.d. independent of the angle ACE, is given, using the rule (A.6),

$$g=\{\text{Angle } BDC\}_L/\{\text{Square } ABDC\}_L=W_L/Z_L. \tag{C1.3}$$

(ii) The correction factor for the angle ACE to have r.d. is, (see Eq. (B.2)),

$$\Gamma=\frac{\{\text{Bond } CE\}_L}{\{\text{Angle } ACE\}_L}\div\frac{\{\text{Point } C\}_L}{\{\text{Bond } AC\}_L}=\frac{Y_L{}^2}{W_LX_L}. \tag{C1.4}$$

(iii) Multiplying g and Γ, we obtain the approximate number desired:

$$G_L=g\Gamma=Y_L{}^2/(X_LZ_L). \tag{C1.5}$$

It should be noted that W_L does not appear in the final result. This fact was to be anticipated at the outset; the details will be stated in Sec. E2.

From Eq. (C1.5), we obtain the entropy S of a system composed of M lattice points:

$$\begin{aligned}S&=k(M/L)\ln G_L\\&=kM[2\sum\beta_iy_i\ln y_i-\sum x_i\ln x_i-\sum\gamma_iz_i\ln z_i].\end{aligned} \tag{C1.6}$$

Next, the energy of a system is composed rigorously as follows: when we denote the energy between the same spins by $-\epsilon$, and that between the different spins by $+\epsilon$, each bond has the energy represented by ϵ_i in Table I. As the total number of bonds in a system composed of M lattice points is $2M$, the energy E of a system is given by

$$E=2M\sum_{i=1}^{3}\epsilon_i\beta_iy_i=2M\epsilon(2y_2-y_1-y_3). \tag{C1.7}$$

Therefore, combining Eqs. (C1.7) and (C1.6), we obtain the free energy μ per lattice point:

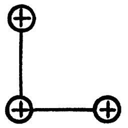
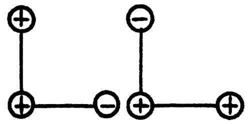
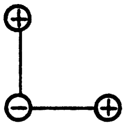
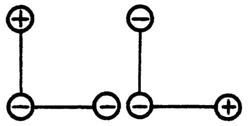
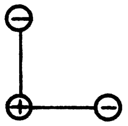
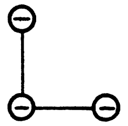
$$\begin{aligned}\mu&=(E-ST)/M\\&=2\epsilon(4y_2-1)\\&\quad-kT[2\sum\beta_iy_i\ln y_i-\sum x_i\ln x_i-\sum\gamma_iz_i\ln z_i].\end{aligned} \tag{C1.8}$$

(C2) *Fundamental Equations*

Before minimizing μ, we determine the independent variables. Because of Eq. (A.1), the x_i's in Table II satisfy the normalization equation:

$$x_1+x_2=1. \tag{C2.1}$$

TABLE IV. Probabilities of appearance of configurations of an angle.

Angle	Prob.	δ_i^*
	w_1	1
	w_2	2
	w_3	1
	w_4	2
	w_5	1
	w_6	1

* δ_i is the number of different configurations having the same probability.

The y_i's in Table I and z_i's in Table III are geometrically connected by the relations:

$$\begin{cases}y_1=z_1+2z_2+z_3,\\y_2=z_2+z_3+z_4+z_5,\\y_3=z_3+2z_5+z_6.\end{cases} \tag{C2.2}$$

Taking Eqs. (C2.1) and (C2.2) into account, we use for the independent variables, y_2, z_3, z_4, ξ_1 and ξ_2, among which the last two are defined by

$$\begin{cases}\xi_1\equiv x_1-x_2, & \text{(C2.3)}\\\xi_2\equiv z_2-z_5. & \text{(C2.4)}\end{cases}$$

Dependent variables are expressed by linear combinations of independent ones; e.g.,

$$2z_1=1+\xi_1-4y_2+2z_4-2\xi_2. \tag{C2.5}$$

These relations are summarized in Table V, in which the quantities except 1 in the upper row, are the independent variables. ξ_1 and ξ_2 are conveniently

TABLE V. Relations between the dependent variables (on the left column) and the independent ones (on the upper row except 1). The meaning of this table is, for example, $2y_3=1-\xi_1-2y_2$.

	1	ξ_1	y_2	z_3	z_4	ξ_2
$2x_1$	1	1				
$2x_2$	1	−1				
$2y_1$	1	1	−2			
$2y_3$	1	−1	−2			
$2z_1$	1	1	−4		2	−2
$2z_2$			1	−1	−1	1
$2z_5$			1	−1	−1	−1
$2z_6$	1	−1	−4		2	2

chosen as independent because they become zero for the disordered state, and consequently they can be interpreted as parameters representing the long range order of the usual terminology.

Differentiating Eq. (C1.8) with respect to the independent variables, and putting the derivatives to zero, we get the fundamental equations:

$$\partial\mu/\partial\xi_1=0:\quad (x_1/x_2)(y_3/y_1)^2(z_1/z_6)=1, \qquad \text{(C2.6)}$$

$$\partial\mu/\partial y_2=0:\quad H^4=[y_2^2/(y_1y_3)][(z_1z_6)/(z_2z_5)]$$

where

$$H\equiv\exp(\epsilon/kT), \qquad \text{(C2.7)}$$

$$\partial\mu/\partial z_3=0:\quad z_3^2=z_2z_5, \qquad \text{(C2.8)}$$

$$\partial\mu/\partial z_4=0:\quad (z_2z_5)^2=z_4^2z_1z_6, \qquad \text{(C2.9)}$$

$$\partial\mu/\partial\xi_2=0:\quad (z_2/z_5)^2=z_1/z_6. \qquad \text{(C2.10)}$$

When μ is minimum, we can simplify Eq. (C1.8) as follows:

$$\begin{aligned}\mu&=\mu-\xi_1(\partial\mu/\partial\xi_1)-y_2(\partial\mu/\partial y_2)-z_3(\partial\mu/\partial z_3)\\&\quad-z_4(\partial\mu/\partial z_4)-\xi_2(\partial\mu/\partial\xi_2)\\&=-2\epsilon+kT(\tfrac{1}{2}\ln x_1+\tfrac{1}{2}\ln x_2-\ln y_1-\ln y_3\\&\qquad+\tfrac{1}{2}\ln z_1+\tfrac{1}{2}\ln z_6),\end{aligned} \qquad \text{(C2.11)}$$

or defining λ by the relation

$$\lambda\equiv\exp(-\mu/kT) \qquad \text{(C2.12)}$$

and combining Eq. (C2.11) with Eq. (C2.6), we have

$$\lambda=H^2y_1^2/(x_1z_1). \qquad \text{(C2.13)}$$

(C3) *Disordered State*

The disordered state is defined by

$$\xi_1=\xi_2=0, \qquad \text{(C3.1)}$$

which gives, from Table V,

$$\begin{cases}x_1=x_2=\tfrac{1}{2} & \text{(C3.2)}\\ y_1=y_2=\tfrac{1}{2}-y_2 & \text{(C3.3)}\\ z_1=z_6=\tfrac{1}{2}-2y_2+z_4 & \text{(C3.4)}\\ z_2=z_5=\tfrac{1}{2}(y_2-z_3-z_4). & \text{(C3.5)}\end{cases}$$

Equations (C2.6) and (C2.10) becoming identities, the fundamental equations reduce to the following, for the determination of the three independent variables, y_2, z_3, and z_4:

$$\begin{cases}H^2=(y_2z_3)/(y_1z_4), & \text{(C3.6)}\\ z_3=z_2, & \text{(C3.7)}\\ z_2^2=z_1z_4. & \text{(C3.8)}\end{cases}$$

On substitution of Eq. (C3.7) into Eq. (C3.5), we have

$$y_2=3z_3+z_4. \qquad \text{(C3.9)}$$

We can now derive Table VI, which gives the relation between the independent variables z_3 and z_4 and the dependent ones y_1, y_2, and z_1, which appear in Eqs. (C3.6) and (C3.8).

TABLE VI. Relations between the dependent variables (y_1, y_2, and z_1) and the independent ones (z_3 and z_4) for the disordered state. The meaning of this table is the same as Table V.

	1	z_3	z_4
y_1	½	−3	−1
y_2		3	1
z_1	½	−6	−1

Using Table VI, we can solve Eqs. (C3.6) and (C3.8) easily for z_3 and z_4, finding the results:

$$\begin{cases}z_3=(3H^2-1)(3-H^2)/[16H^2(6-H^2-H^{-2})]. & \text{(C3.10)}\\ z_4=(3-H^2)^2/[16H^2(6-H^2-H^{-2})]. & \text{(C3.11)}\end{cases}$$

Combining Eqs. (C3.10) and (C3.11) with Eqs. (C3.9), (C3.6), and (C2.13), we get, finally,

$$\lambda=8[6-H^2-H^{-2}]^{-1}=2[1-\sinh^2(\epsilon/kT)]^{-1}, \qquad \text{(C3.12)}$$

which is identical with Eq. (90) of Kramers-Wannier's paper,[2] in which ϵ/kT is denoted by K, and λ has the same meaning as our λ.

(C4) *The Transition Temperature*, T_t

As the general properties of the second-order phase change, each of ξ_1 and ξ_2 indicating the long-range order has two non-zero values with equal absolute magnitude and different signs below the transition temperature. Therefore, at T_t, $d\xi_1/dT$ and $d\xi_2/dT$ become infinite, but a certain combination of them remains finite. At the same time, it should be noted that at T_t the variables satisfy the equations for the disordered state treated in Sec. C3. Hence, we can determine the value of the second-order transition temperature using the solution for the disordered state.

By differentiation of Eqs. (C2.6) and (C2.10) at T_t, we have:

$$\begin{cases}\dfrac{d\xi_1}{d\xi_2}=\dfrac{2}{z_6}\Big/\left\{2-\dfrac{2}{y_1}+\dfrac{1}{z_6}\right\}, & \text{(C4.1)}\\[2ex] \dfrac{d\xi_1}{d\xi_2}=\left\{\dfrac{2}{z_1}+\dfrac{2}{z_2}\right\}\Big/\dfrac{1}{z_1}. & \text{(C4.2)}\end{cases}$$

Equating the right-hand sides of Eqs. (C4.1) and (C4.2), we get

$$(1/z_1+z_3)-(2/y_1)+2=0. \qquad \text{(C4.3)}$$

This is the equation to be added to determine T_t.

Using the formulas (C3.10) and (C3.11), we transform Eq. (C4.3) into an equation for H, the solution of which gives the value for the transition temperature:

$$H_t^2=[5+(17)^{\frac{1}{2}}]/4, \qquad \text{(C4.4)}$$

which coincides with Eq. (92) of Kramers and Wannier.[2]

(C5) *The Ordered State*

For the ordered state, we must solve Eqs. (C2.6)–(C2.10) without any special conditions such as Eq. (C3.1). Generally speaking, these simultaneous algebraic equations for many variables can be reduced to a single algebraic equation for one variable. Therefore, in every case we can solve the problem if we resort to the numerical calculation of a higher order algebraic equation. This might be counted among the merits of our method. In the present case we can solve the problem analytically as we fortunately get a quadratic equation.

For the sake of convenience, we add Eq. (C2.13) to the fundamental equations and solve the six simultaneous equations for the six variables, ξ_1, y_2, z_3, z_4, ξ_2, and λ. Omitting the detailed accounts of the process of transformations, we list the results at once. The reduced single algebraic equation is

$$(\lambda H^6)^2-(H^8+8H^4-11)(\lambda H^6)+8H^{12}-12H^8+6H^4-1=0. \qquad \text{(C5.1)}$$

The six independent variables are connected with λ by the following relations:

$$\begin{aligned}
\xi_1&=\xi_2\theta,\\
z_3&=y_2+z_4(1-\theta),\\
\xi_2{}^2&=z_4[2-8y_2-\theta(\theta-4)z_4],\\
z_4&=r(\theta r-\Lambda+1)^{-1},\\
2y_2&=1-(\theta r-\Lambda+1)^{-1},
\end{aligned}$$

$$\theta^2(\theta-2)(\Lambda+1)r+[(H^4-2)\theta\Lambda+H^4-(\theta+1)]=0,$$

$$\Lambda=-(a\theta+c)/\{\theta(a\theta+b)\}. \qquad \text{(C5.2)}$$

$$1-\frac{H^2}{\lambda}=\frac{2H^4a\theta+(a+b)(2H^4-1)-d}{(2H^4-1)[(b+d)\theta+c(2H^4-1)]},$$

$$a=H^8-6H^4+1,$$

$$b=3H^8+2H^4-1,$$

$$c=(H^4-1)^2(2H^4-1),$$

$$d=H^{16}-8H^{12}+10H^8-4H^4+1.$$

The solution of Eq. (C5.1) is

$$\lambda=[H^8+8H^4-11+(H^4-5)^{\frac{1}{2}}(H^4-1)^{\frac{1}{2}}]/(2H^6). \qquad \text{(C5.3)}$$

The plus sign has been adopted before the root, so that at the transition temperature, when we insert Eq. (C4.4) into H_t^2, Eq. (C5.3) gives the same value for λ as that calculated from the disordered formula (C3.12):

$$\lambda_t=[9-(17)^{\frac{1}{2}}]/2. \qquad \text{(C5.4)}$$

Thus, the problem has been solved completely.

Next we show that our results are identical with those of Kramers and Wannier. They found the following results:[11a]

$$\lambda=H^2+(1+H^2z)(1-z^2)/[H^4(H^2-H^{-2})], \qquad \text{(C5.5)}$$

where z is a root of[11b]

$$[1+2zH^{-2}+z^2]^2=(H^2-H^{-2})^3z. \qquad \text{(C5.6)}$$

We found that Eq. (C5.6) can be factorized as

$$[H^2z^2+(H^4+1)z+H^6]\times[H^4z^2-H^2(H^4-3)z+1]=0. \qquad \text{(C5.7)}$$

Adopting the second factor we can simplify Eq. (C5.5), obtaining

$$z=(H^8+2-\lambda H^6)/[H^2(H^4-5)]. \qquad \text{(C5.8)}$$

On inserting Eq. (C5.8) into the last factor of Eq. (C5.7), we obtain an equation for λ which proves nothing but Eq. (C5.1).

Therefore, our approximation described in Sec. C is identical throughout all temperatures with that explained by Kramers and Wannier under the name of the "variation method."

D. An Improved Treatment for the Simple Cubic Lattice (Ising Model)

(D1) *Free Energy and Fundamental Equations*

The shortest way to improve Bethe's approximation for the simple cubic lattice is to take a square as a basic figure, adopting the z_i's in Table III as variables. The w_i's in Table IV, the y_i's in Table I, and the x_i's in Table II are also used. The concepts of *set*, *r.d.*, and *with reference to* are extended to the three-dimensional lattice.

The entropy of a system is obtained when we calculate the number of ways of putting a spin on the point A in Fig. 4, so that all of the squares and angles containing A have r.d., provided every square and every angle in the part drawn with solid lines have had r.d. This number of ways is calculated in the following seven steps:

(i) The number of ways G_1 of putting a spin on A with reference to the angle FGB, so that the square $AFGB$ has r.d., is (see Eq. (C1.3)):

$$G_1=\{\text{Angle } FGB\}_L/\{\text{Square } AFGB\}_L=W_L/X_L.$$

(ii) The correction between A and $D-C$: so far as the face $ABDC$ is concerned, by the process (i), we

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[11a] Reference 2, Eq. (91b).
[11b] Reference 2, Eq. (91a).

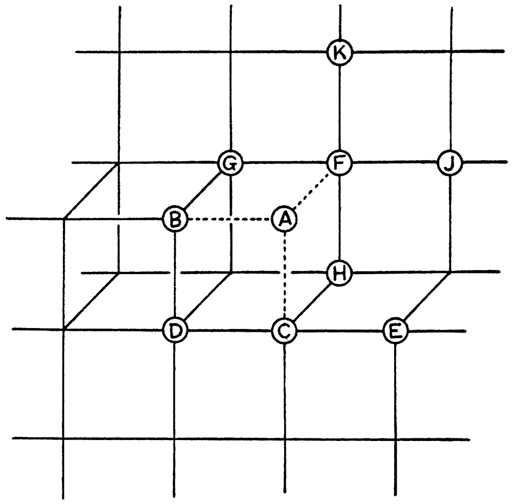

FIG. 4. An intermediate stage of constructing a simple cubic lattice.

have put A with reference to only B, while ideally we have to put A with reference to the angle BDC. Therefore, the correction factor Γ_1 becomes

$$\Gamma_1=\frac{\{\text{Angle } BDC\}_L}{\{\text{Square } ABDC\}_L}\div\frac{\{\text{Point } B\}_L}{\{\text{Bond } BA\}_L}=\frac{W_LY_L}{Z_LX_L}.$$

(iii) The correction between A and H: considering the fact that, so far as the face $ACHF$ is concerned, we must put A with reference to the angle CHF, the correction factor Γ_2 must be

$$\Gamma_2=\frac{\{\text{Angle } CHF\}_L}{\{\text{Square } ACHF\}_L}\div\left[\frac{\{\text{Point } F\}_L}{\{\text{Bond } AF\}_L}\times\frac{\{\text{Point } C\}_L}{\{\text{Bond } AC\}_L}\div\frac{L!}{\{\text{Point } A\}_L}\right]$$
$$=(W_LY_L^2L!)/(Z_LX_L^3),$$

where the factor in the square brackets is derived by the following considerations. So far as this face is concerned, we have put $A-F$ with reference to F in the process (i), and in the process (ii) we have corrected between A and C, i.e., have multiplied the factor,

$$[\{\text{Point } C\}_L/\{\text{Bond } AC\}_L]\div[L!/\{\text{Point } A\}_L].$$

(iv) The correction between A and E: just as in Sec. C1 (ii), the correction factor Γ_3 becomes

$$\Gamma_3=\frac{\{\text{Bond } CE\}_L}{\{\text{Angle } ACE\}_L}\div\frac{\{\text{Point } C\}_L}{\{\text{Bond } AC\}_L}=\frac{Y_L^2}{W_LX_L}.$$

(v) The correction between A and J: following (iv) gives

$$\Gamma_4=\frac{\{\text{Bond } FJ\}_L}{\{\text{Angle } AFJ\}_L}\div\frac{\{\text{Point } F\}_L}{\{\text{Bond } FA\}_L}=\frac{Y_L^2}{W_LX_L}.$$

(vi) The correction between A and K: following (iv) gives

$$\Gamma_5=\frac{\{\text{Bond } FK\}_L}{\{\text{Angle } AFK\}_L}\div\frac{\{\text{Point } F\}_L}{\{\text{Bond } FA\}_L}=\frac{Y_L^2}{W_LX_L}.$$

(vii) Therefore, the number of ways G_L of putting a spin on A is

$$G_L=G_1\prod_{i=1}^{5}\Gamma_i=Y_L^9L!/(Z_L^3X_L^7). \tag{D1.1}$$

Hence, the entropy for a system with M lattice points is

$$S=k(M/L)\ln G_L$$
$$=kM[9\sum\beta_iy_i\ln y_i-7\sum x_i\ln x_i-3\sum\gamma_iz_i\ln z_i]. \tag{D1.2}$$

Next, considering that the total number of bonds for a system is $3M$, and following Eq. (C1.7), we have the energy for a system as

$$E=3M\sum_{i=1}^{3}\epsilon_i\beta_iy_i=3M\epsilon(4y_2-1), \tag{D1.3}$$

where ϵ_i is given in Table I.

Differentiating the free energy μ per lattice point

$$\mu=(E-TS)/M, \tag{D1.4}$$

with respect to the independent variables shown in Table V, and setting the derivatives equal to zero, we get the following fundamental equations:

$$\partial\mu/\partial\xi_1=0:\quad (x_1/x_2)^7(y_3/y_1)^9(z_1/z_6)^3=1 \tag{D1.5}$$

$$\partial\mu/\partial y_2=0:\quad H^4=[y_2^2/(y_1y_3)]^3[z_1z_6/(z_2z_5)]^2, \tag{D1.6}$$

where

$$H\equiv\exp(\epsilon/kT)$$

$$\partial\mu/\partial z_3=0:\quad z_3^2=z_2z_5 \tag{D1.7}$$

$$\partial\mu/\partial z_4=0:\quad z_2^2z_5^2=z_4^2z_1z_6 \tag{D1.8}$$

$$\partial\mu/\partial\xi_2=0:\quad (z_2/z_5)^2=z_1/z_6. \tag{D1.9}$$

(D2) *The Disordered State*

Just as in Sec. C3 of the two-dimensional case, the relations (C3.1)–(C3.5) hold, Eqs. (D1.5) and (D1.9) becoming identities. The fundamental equations reduce to the following for the determination of the three independent variables y_2, z_3, and z_4:

$$\begin{cases} H^2=(y_2/y_1)^3(z_1/z_2)^2, & \text{(D2.1)}\\ z_3=z_2, & \text{(D2.2)}\\ z_2^2=z_1z_4. & \text{(D2.3)}\end{cases}$$

Inserting Eq. (D2.2) into Eq. (C3.5), we get Eq. (C3.9). Hence, Table VI holds, where z_3 and z_4 are the independent variables, and are determined by the following relations derived from Eqs. (D2.1) and (D2.3):

$$H^2[\tfrac{1}{2}-3z_3-z_4]^3z_4^2=(3z_3+z_4)^3z_3^2, \tag{D2.4}$$

$$2z_3^2+12z_4z_3+z_4(2z_4-1)=0. \tag{D2.5}$$

Putting

$$\varphi \equiv z_3/z_4, \tag{D2.6}$$

we have, from Eq. (D2.5),

$$z_4 = [2(\varphi^2+6\varphi+1)]^{-1}. \tag{D2.7}$$

Inserting Eqs. (D2.6) and (D2.7) into Eq. (D2.4), we get

$$H^2 = [(3\varphi+1)/(\varphi+3)]^3/\varphi. \tag{D2.8}$$

Thus, the disordered state has been solved with a parameter φ. The other variables are expressed through φ as follows:

$$\begin{cases} y_1 = (\varphi^2+3\varphi)z_4, \\ y_2 = (3\varphi+1)z_4, \\ z_1 = \varphi^2 z_4, \\ z_3 = \varphi z_4. \end{cases} \tag{D2.9}$$

Here we add a few remarks on the region of existence of the solution for the disordered state. Equation (D2.8) gives the H^2 *vs* φ curve shown schematically in Fig. 5. By the physical considerations, $\varphi \equiv z_3/z_4$ must be equal to unity when $H^2=1$, because we have the perfectly disordered state as T tends to infinity. Hence, the point P is realized. Moreover, taking into account the fact that the hatched portion cannot be realized, we can conclude that the part PQ drawn with the heavy curve corresponds to the real state, where the maximum point Q is easily shown to have the abscissa

$$\varphi_Q = \tfrac{1}{3}[7+(40)^{\frac{1}{2}}] \doteqdot 4.4415. \tag{D2.10}$$

The part QR corresponds to the unstable state, the specific heat becoming negative as explained in the following section.

The situation that the solution for the disordered state cannot be extended as far as $T=0$ occurs in the Kramers-Wannier case also. Equation (C3.12) is the solution for the disordered state, but does not hold for H large enough, as λ must be positive.

(D3) *Specific Heat for the Disordered State*

The specific heat c per spin is defined by the following:

$$c/k = (1/kM)dE/dT = 12dy_2/d\tau, \tag{D3.1}$$

where we put

$$\tau \equiv kT/\epsilon. \tag{D3.2}$$

Using the relations derived in the previous section, we get the desired result:

$$\frac{c}{k} = \frac{12}{\tau^2}\frac{\varphi(\varphi+3)(3\varphi+1)(3\varphi^2+2\varphi+3)}{(\varphi^2+6\varphi+1)^2(3\varphi^2-14\varphi+3)}. \tag{D3.3}$$

As mentioned in the previous section, c becomes negative for $\varphi > \varphi_Q$, because φ_Q is a root of[12]

$$3\varphi^2-14\varphi+3=0. \tag{D3.4}$$

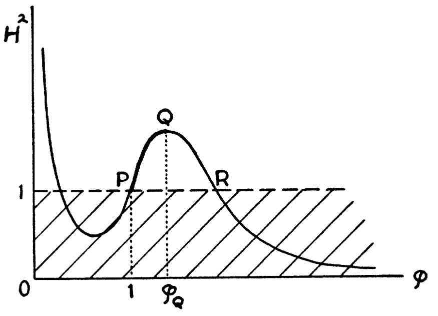

FIG. 5. H^2 *vs* φ of the equation (D2.8). In the curve, the part outside the portion PQ is not realized.

Combining Eqs. (D2.8) and (D3.3), we obtain the specific heat *vs* temperature curve, which is shown in Fig. 6 by the solid curve for $\tau > 4.610$.

(D4) *The Transition Temperature, T_t*

We can determine T_t following the method explained in Sec. C4. Differentiating Eqs. (D1.5) and (D1.9) and using the relation $\xi_1=\xi_2=0$, we get

$$\frac{d\xi_1}{d\xi_2} = \frac{6}{z_1}\Big/\left\{14-\frac{9}{y_1}+\frac{3}{z_1}\right\} = \left\{\frac{2}{z_1}+\frac{2}{z_2}\right\}\Big/\frac{1}{z_1}. \tag{D4.1}$$

Transforming the right-hand equation, and inserting Eqs. (D2.7) and (D2.9), we get

$$\varphi(\varphi-3)(\varphi-5)=0, \tag{D4.2}$$

of which the solution corresponding to a stable state is

$$\varphi_t = 3, \tag{D4.3}$$

since all of the part other than $1<\varphi<\varphi_Q$ is not realized, as is explained by Fig. 5. Equation (D4.3) is the value corresponding to T_t. Inserting Eq. (D4.3) into Eq. (D2.8), we get

$$\begin{aligned} H_t^2 &= 125/81 \doteqdot 1.5432, \\ 1/\tau_t &\doteqdot 0.21693, \\ \tau_t &= kT_t/\epsilon \doteqdot 4.6097. \end{aligned} \tag{D4.4}$$

The last value is to be compared with that of Bethe's second approximation[1]

$$kT_t/\epsilon \doteqdot 4.744.$$

Inserting Eq. (D4.3) into Eq. (D3.3), we obtain the value for the specific heat c_+ at T_t on the higher temperature side:

$$c_+/k \doteqdot 0.389. \tag{D4.5}$$

(D5) *The Specific Heat c_- at T_t on the Low Temperature Side*

To solve the ordered state is not easy, but the specific heat c_- at T_t on the low temperature side can be obtained without difficulty. Simply speaking, c_- is derived when we insert into Eq. (D3.1) the value of $dy_2/d\tau$ at T_t determined from the five simultaneous

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[12] As we shall see in the following section, the state corresponding to φ_Q is not realized. Hence, the specific heat always remain finite.

equations derived from Eqs. (D1.5)–(D1.9) by differentiation with respect to τ. But it should be noted that the equations derived from Eqs. (D1.5) and (D1.9) are nothing but the two relations in Eq. (D4.1), being dependent on each other; and therefore we need another equation in order to determine $dy_2/d\tau$. This extra equation is derived as follows.

Expanding Eqs. (D1.5) and (D1.9), we get

$$\begin{cases} \xi_2/\xi_1=[\zeta_2/2(\zeta_1+\zeta_2)][1+(1-2\xi_2/\xi_1)(\xi_2/\zeta_2)^2], & \text{(D5.1)} \\ \xi_2/\xi_1=(\zeta_1/6)[7-(9/\eta)+3/\zeta_1]+B\xi_1^2+O(\xi^4), & \text{(D5.2)} \end{cases}$$

with

$$\begin{aligned} B=(7/6)\zeta_1[5-(27/\eta)+(36/\eta^2)-12/\eta^3] \\ +\tfrac{3}{2}(1-2\xi_2/\xi_1)[7-(21/\eta)+12/\eta^2] \\ +(1/2\zeta_1)(1-2\xi_2/\xi_1)^2[7-9/\eta] \\ +(1/6\zeta_1^2)(1-2\xi_2/\xi_1)^3, \end{aligned} \tag{D5.3}$$

where we put

$$\begin{cases} \eta\equiv 1-2y_2, \\ \zeta_1\equiv 1-4y_2+2z_4, \\ \zeta_2\equiv y_2-z_3-z_4. \end{cases} \tag{D5.4}$$

Equating the right-hand sides of Eqs. (D5.1) and (D5.2), we get

$$\Psi+A\xi_2^2+O(\xi^4)=0, \tag{D5.5}$$

where

$$\begin{aligned} \Psi&=(\zeta_1/6)[7-(9/\eta)+3/(\zeta_1+\zeta_2)] \\ A&=-[1/2\zeta_2(\zeta_1+\zeta_2)](1-2\xi_2/\xi_1)+B\cdot(\xi_1/\xi_2)^2. \end{aligned} \tag{D5.6}$$

Differentiating Eq. (D5.5) with respect to τ and assuming[13] that $d\xi_2^2/d\tau$ is finite and $dO(\xi^4)/d\tau$ can be set equal to zero at T_t, we get

$$\frac{dy_2}{d\tau}+3\frac{dz_3}{d\tau}-3\frac{dz_4}{d\tau}+\frac{1514}{1323}\cdot 28\xi_2\frac{d\xi_2}{d\tau}=0, \tag{D5.7}$$

where we have utilized the following relation derived from Eq. (D4.1) at T_t:

$$d\xi_1/d\xi_2=8. \tag{D5.8}$$

Equation (D5.7) is used as the additional equation to determine $dy_2/d\tau$ other than the three derived from Eqs. (D1.6)–(D1.8) by differentiation and insertion of the value at T_t:

$$\begin{cases} 42\dfrac{dy_2}{d\tau}-45\dfrac{dz_3}{d\tau}-75\dfrac{dz_4}{d\tau}+5\left(28\xi_2\dfrac{d\xi_2}{d\tau}\right)=\dfrac{135}{112}\left(\dfrac{2}{\tau_t}\right)^2, \\ 3\dfrac{dy_2}{d\tau}-9\dfrac{dz_3}{d\tau}-3\dfrac{dz_4}{d\tau}-28\xi_2\dfrac{d\xi_2}{d\tau}=0, \\ 5\dfrac{dy_2}{d\tau}-3\dfrac{dz_3}{d\tau}-13\dfrac{dz_4}{d\tau}+28\xi_2\dfrac{d\xi_2}{d\tau}=0: \end{cases} \tag{D5.9}$$

We can solve for $dy_2/d\tau$ from Eqs. (D5.7) and (D5.9) and, inserting it into Eq. (D3.1), we get

$$\frac{c_-}{k}=\frac{39285}{2548}\left(\frac{2}{\tau_t}\right)^2\doteqdot 2.902. \tag{D5.10}$$

(D6) *The Ordered State*

The equations for the ordered state (D1.5)–(D1.9) can be solved numerically. Putting

$$\theta\equiv\xi_1/\xi_2, \tag{D6.1}$$

we can derive, from Eqs. (D1.7), (D1.8), and (D1.9),

$$\begin{aligned} z_3&=y_2+z_4(1-\theta), \\ \xi_2^2&=z_4[2-8y_2-\theta(\theta-4)z_4], \\ 2y_2&=z_4[2\theta+\{2(\theta^2-z_4^{-1})\}^{\frac{1}{2}}]. \end{aligned} \tag{D6.2}$$

Assigning a value for θ, we can determine z_4 from Eq. (D1.5) by trial and error. The equations are solved by this process, Eq. (D1.6) being used to determine H.

We derive the specific heat from Eq. (D3.1), inserting the value $dy_2/d\tau$ obtained from Eqs. (D1.5)–(D1.9) by differentiation with respect to τ. The relation between the specific heat and the temperature for the ordered state is shown in Fig. 6 by the solid curve for $\tau<4.610$. In the same figure we illustrated the first and the second approximations by Bethe[1] for comparison.

(D7) *Discussion and Comparison with the Rigorous Expansion*

On the basis of the above analysis, we wish to infer the range of existence of the correct transition temperature. We put two hypotheses induced from the known results:

> "So far as this scheme of the variational method is used,
>
> (i) the approximate transition temperature is higher than the correct one, and
>
> (ii) the value of the specific heat for the disordered state is smaller than the correct one corresponding to the same temperature."

Of these two, (i) was noticed by Kramers and Wannier without proof.[2] No verification exists for (ii) either; but if we accept these hypotheses, we can conclude the range for the true transition temperature τ_c:

$$\tau_Q=4.2221<\tau_c<4.6097, \tag{D7.1}$$

because, at $\varphi=\varphi_Q$ which corresponds to τ_Q, the specific heat for the disordered state becomes infinite. Equation (D7.1) does not contradict the prediction by Oguchi,[14]

$$0.21<1/\tau_c<0.24. \tag{D7.2}$$

Next, we compare our result of this section with the rigorous expansion of the partition function. We expand physical quantities of the disordered state in powers of the reciprocal temperature. Expanding for $K\equiv 1/\tau$ from

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[13] This assumption is verified from Eqs. (D5.7) and (D5.9).

[14] T. Oguchi, Busseiron-Kenkyu (Japanese) 22, 26 (1950).

Eq. (D2.8) and inserting the expansion into Eq. (D1.3), we get

$$-E/(M\epsilon)=3K+11K^3+(422/5)K^5+O(K^7). \quad \text{(D7.3)}$$

Kirkwood's moment method, which gives the correct expansion,[3] when retained up to the fourth moment, gives

$$-E/(M\epsilon)=-3+3K+11K^3, \quad \text{(D7.4)}$$

where the term (-3) comes in because of the different choice of the zero point of energy. Comparing Eq. (D7.3) with Eq. (D7.4), we know that our approximation in this section is valid up to the fourth moment of Kirkwood's method so far as the disordered state is concerned. For the ordered state, however, we could not transform our results into forms to be compared with Kirkwood's, owing to the complexity of the equations.

It is interesting to compare Eq. (D7.3) with the rigorous expansion derived by Oguchi[14, 15]

$$-E/(M\epsilon)=3K+11K^3+(542/5)K^5 +(123547/105)K^7+\cdots. \quad \text{(D7.5)}$$

Our Eq. (D7.3) deviates at the coefficient of K^5.

It may be of interest to mention here our further attempt at an approximation. When we take a cubic cell as a basic figure, we get the following expansion:

$$-E/(M\epsilon)=3K+11K^3+(542/5)K^5 +(121027/105)K^7+O(K^9), \quad \text{(D7.6)}$$

which is correct up to the coefficient of K^5 and is to be compared with ter Haar and Martin's result,[6] which is the extension of Kramers-Wannier's "variation method" to the three-dimensional case:

$$-E/(M\epsilon)=3K+11K^3+(542/5)K^5 +(107587/105)K^7+\cdots. \quad \text{(D7.7)}$$

Equation (D7.6) seems to be a better approximation than is Eq. (D7.7). Our cubic-cell approximation gives the transition temperature

$$\tau_t \doteqdot 4.5810. \quad \text{(D7.8)}$$

As the method explained in Sec. D is one of approximations, the value for the transition temperature Eq. (D4.4) and those for the specific heat Eqs. (D4.5), (D5.10) do not have rigorous meaning beyond the fourth moment of Kirkwood's method.

E. General Discussion Concerning the Method

(E1) *The Relation between our Free Energy and the Rigorous Partition Function*

The rigorous partition function for a system can be expressed as follows:

$$\exp(-F/kT)=\textstyle\sum_i G(E_i)\exp(-E_i/kT), \quad \text{(E1.1)}$$

where F is the free energy, E_i is a total energy of the system, and $G(E_i)$ is the number of configurations having the energy E_i. Our mathematical problem is to find the functional form of $G(E_i)$.

In the methods explained in the previous sections, we got only the approximate function $G(E_i)$. The origin of the approximation lies in the method of counting the number of ways of putting a lattice point. We will examine each case.

In Sec. B, after the process (i), the bond $B-A$ has r.d.; but even after the correction (ii), $C-A$ does not have r.d. perfectly, because the correction cannot be made completely with the knowledge of the y_i's only.

In Sec. C1, after the process (i), the square $ABDC$ has r.d. (provided the angle BDC has had r.d.); but even after the correction (ii), the angle ACE does not have r.d. perfectly. So we can say that in Sec. C, every bond has r.d. rigorously, but any angle or any square has r.d. only approximately. In other words, in Sec. C the correlation between two neighboring lattice points (e.g., A and B in Fig. 3) is fully considered, but the correlation between points situated diagonally in a square (e.g., A and D in Fig. 3) is only partially considered, and the correlation between two points farther apart is completely neglected.

Generally,[16] the larger the basic figure becomes, the farther the correlation reaches and the better the approximation becomes.

(E2) *The Rigorous Formula for the Entropy*

In order to make the approximation clearer and at the same time to suggest the procedure for reaching the rigorous solution, we derive the general formula for

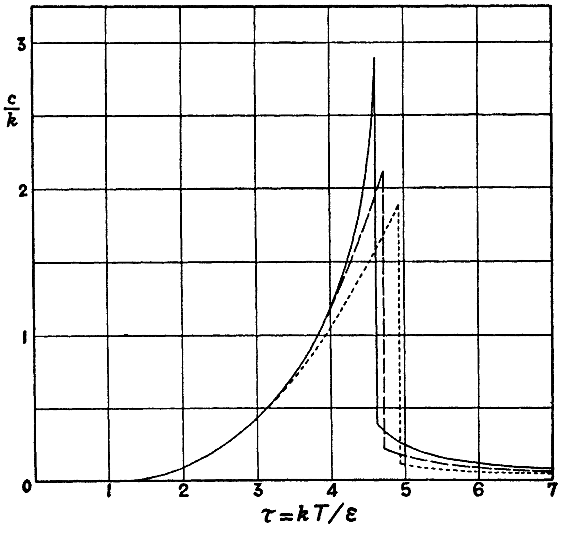

FIG. 6. The specific heat c per lattice point for the simple cubic Ising lattice plotted against $\tau=kT/\epsilon$. ·········· Bethe's first approximation. — — — — Bethe's second approximation. ———— This paper.

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[15] T. Oguchi, private communication.

[16] The increase in the number of lattice sites does not necessarily result in a better approximation. Yin-Yuan Li reports the same situation in reference 5. The intrinsic meaning is not yet clear.

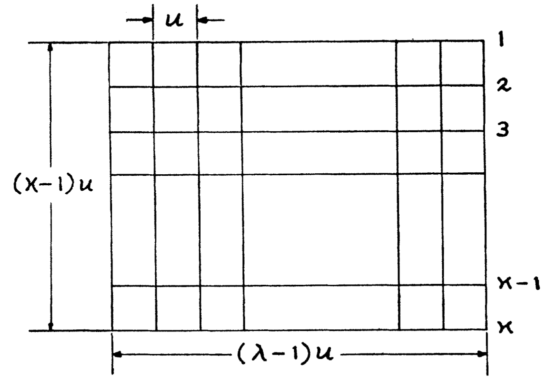


FIG. 7. A rectangle having the width $(\kappa-1)u$ and the length $(\lambda-1)u$.

the entropy. We explain it for the two-dimensional square lattice as an example.

Let us consider a rectangle having the width $(\kappa-1)u$ and the length $(\lambda-1)u$ as shown in Fig. 7, where u is the lattice constant. On each of the $\kappa\lambda$ lattice points, we put $(+)$ or $(-)$ spin, obtaining various configurations of the rectangle. We denote the probability of appearance of a configuration by $x_{\kappa\lambda,i}$ $(i=1,2,\cdots,2^{\kappa\lambda})$ and for brevity's sake we put

$$\prod_{\substack{i\\ \text{all configurations}}} (x_{\kappa\lambda,i}L)!\equiv\Phi_L(\kappa,\lambda). \tag{E2.1}$$

We take as a basic figure a square with $\kappa=\lambda=m$. Following the method in Sec. A, the number of ways Ω_m of constructing a strip with the width $(m-1)u$[16a] and the length M_1u becomes[17]

$$\Omega_m=[\Phi_L(m,m-1)/\Phi_L(m,m)]^{M_1}. \tag{E2.2}$$

The number of ways Ω_{m-1} of constructing an $(m-1)$-strip of the length M_1u is[17]

$$\Omega_{m-1}=[\Phi_L(m-1,m-1)/\Phi_L(m-1,m)]^{M_1}. \tag{E2.3}$$

Ω_m/Ω_{m-1} gives the number of ways of adding a one-strip to the $(m-1)$-strip getting an m-strip. Adding a one-strip over and over again, we complete a whole lattice. The number G of adding M_2 one-strips and completing the whole lattice is[17]

$$\begin{aligned}G&=[\Omega_m/\Omega_{m-1}]^{M_2}\\&=[\Phi_L(m,m-1)\Phi_L(m-1,m)/\\&\qquad\Phi_L(m,m)\Phi_L(m-1,m-1)]^M,\end{aligned} \tag{E2.4}$$

where $M=M_1M_2$ is the total number of lattice points.

When we put $m=2$, we get

$$G=[Y_L^2/X_LZ_L]^M, \tag{E2.5}$$

which is identical with the Mth power of G_L defined in Eq. (C1.5).

The approximation in this method of counting the number of ways originates in the fact that we substituted Ω_m, which is calculated for a separate m-strip, for the number of ways of constructing an m-strip which lies in the whole lattice plane and closely connected with other strips.

Equation (E2.4) gives the approximate formula for the entropy $S_2(m)$ for a system[18]

$$\begin{aligned}S_2(m)&=(k/L)\ln G\\&=-k(M/L)[\{\ln\Phi_L(m,m)-\ln\Phi_L(m,m-1)\}\\&\qquad-\{\ln\Phi_L(m-1,m)-\ln\Phi_L(m-1,m-1)\}],\end{aligned} \tag{E2.6}$$

which can be simplified as[18]

$$S_2(m)=-k(M/L)[\Delta_\kappa\Delta_\lambda\ln\Phi_L(\kappa,\lambda)]_{\kappa=\lambda=m}, \tag{E2.7}$$

where Δ_κ is the notation for the difference:

$$\Delta_\kappa f(\kappa)\equiv f(\kappa)-f(\kappa-1). \tag{E2.8}$$

The rigorous entropy S_2 for a system of the two-dimensional square lattice is the limiting case of $S_2(m)$:

$$S_2=\lim_{m\to\infty}S_2(m). \tag{E2.9}$$

For the case of the three-dimensional cubic lattice, we choose a cube of edge mu as a basic figure. For a rectangular parallelepiped having edges $(\kappa-1)u$, $(\lambda-1)u$, and $(\mu-1)u$, we denote the probability of appearance of a configuration by $x_{\kappa\lambda\mu,i}$ $(i=1,2,\cdots,2^{\kappa\lambda\mu})$, and we introduce Φ_L as follows:

$$\prod_{\substack{i\\ \text{all configurations}}} (x_{\kappa\lambda\mu,i}L)!\equiv\Phi_L(\kappa,\lambda,\mu). \tag{E2.10}$$

Then proceeding just as for the two-dimensional case, we find the approximate formula for the entropy of a system[18]

$$S_3(m)=-k(M/L)[\Delta_\kappa\Delta_\lambda\Delta_\mu\ln\Phi_L(\kappa,\lambda,\mu)]_{\kappa=\lambda=\mu=m}, \tag{E2.11}$$

and the rigorous formula of the entropy S_3 for a system is expressed by

$$S_3=\lim_{m\to\infty}S_3(m). \tag{E2.12}$$

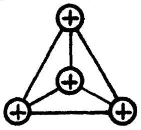
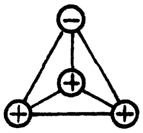
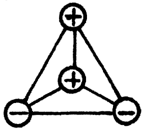
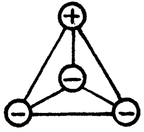
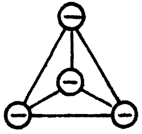
When we put $m=2$, we get a case in which a cube is the basic figure to which we referred at the end of Sec. D7. In every case, no matter what the lattice form and the basic figure, we can obtain the formula of entropy following the method explained in this section, but the details are omitted here.

[16a] We shall call such a strip an m-strip following Kramers and Wannier (reference 2), as there lie m lattice points transversely.

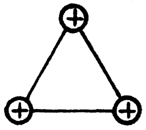
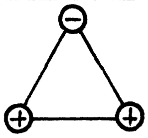
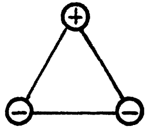
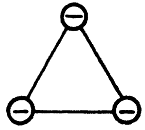
[17] We neglect the end effect, assuming that M_1 and M_2 are very large numbers.

[18] L is canceled out of this formula when we apply the Stirling formula.

TABLE VII. Probabilities of appearance of configurations of (a) a tetrahedron, (b) a triangle, (c) a bond, and (d) a lattice point.

Tetrahedron	Prob.	α_i^*
	x_1	1
 etc.	x_2	4
 etc.	x_3	6
 etc.	x_4	4
	x_5	1

(a)

Triangle	Prob.	β_i^*
	y_1	1
 etc.	y_2	3
 etc.	y_3	3
	y_4	1

(b)

Bond	Prob.	γ_i^*	ε_i^{**}
⊕—⊕	z_1	1	$-\varepsilon$
⊕—⊖	z_2	2	ε
⊖—⊖	z_3	1	$-\varepsilon$

(c)

Spin	Prob.
⊕	w_1
⊖	w_2

(d)

* α_i, β_i, and γ_i indicate the number of different configurations having the same probability.
** ϵ_i is the energy per bond.

III. FACE-CENTERED LATTICES (ISING MODEL)

F. Variables

The probabilities of appearance of a group of lattice points having some configurations are taken as variables, as shown in Table VII (a)–(d).

These variables are subject to the normalizations:

$$\sum_{i=1}^{5}\alpha_i x_i=\sum_{i=1}^{4}\beta_i y_i=\sum_{i=1}^{3}\gamma_i z_i=\sum_{i=1}^{2}w_i=1, \qquad \text{(F.1)}$$

and they are connected by the relations shown in Table VIII, the meaning of which is, for example,

$$2x_1=1+\xi_1-4z_2-2\xi_2+2x_3, \qquad \text{(F.2)}$$

where ξ_1 and ξ_2 are defined by

$$\begin{cases}\xi_1\equiv w_1-w_2,\\ \xi_2\equiv y_2-y_3,\end{cases} \qquad \text{(F.3)}$$

which represent the long-range orders.

TABLE VIII. The relations between the dependent variables (on the left column) and the independent ones (on the upper row except 1). The meaning of this table is, for example,

$$2z_1=1+\xi_1-2z_2.$$

	1	ξ_1	z_2	ξ_2	x_3
$2w_1$	1	1			
$2w_2$	1	−1			
$2z_1$	1	1	−2		
$2z_3$	1	−1	−2		
$2y_1$	1	1	−3	−1	
$2y_2$			1	1	
$2y_3$			1	−1	
$2y_4$	1	−1	−3	1	
$2x_1$	1	1	−4	−2	2
$2x_2$			1	1	−2
$2x_4$			1	−1	−2
$2x_5$	1	−1	−4	2	2

We adopt the simplified expressions (see Sec. II):

$$\left.\begin{aligned}
X_L&\equiv\prod_{i=1}^{5}(x_iL)!^{\alpha_i}=\{\text{Tetrahedron}\}_L,\\
Y_L&=\prod_{i=1}^{4}(y_iL)!^{\beta_i}=\{\text{Triangle}\}_L,\\
Z_L&=\prod_{i=1}^{3}(z_iL)!^{\gamma_i}=\{\text{Bond}\}_L,\\
W_L&\equiv\prod_{i=1}^{2}(w_iL)!=\{\text{Point}\}_L.
\end{aligned}\right\}\tag{F.4}$$

As stated at the end of Sec. IIB, we can obtain Bethe's approximation when we adopt the z_i's and w_i's as variables,[19] for both the two-dimensional triangular lattice and the three-dimensional face-centered lattice. We consider better approximations in the following sections. As the method and the terminologies are the same in the following as in Sec. II, no explanation will be repeated except when necessary.

G. Two-Dimensional Triangular Lattice (Ising Model)

As the exact solution of this case has been already obtained,[4,20] we report only the results of our calculation for comparison.

We choose a triangle as the basic figure, and adopt the y_i's, z_i's, and w_i's as variables. The number of ways of putting A in Fig. 8, so that the triangles ABC and ACD have r.d., provided every triangle in the part drawn with solid lines has had r.d., is expressed by

$$\begin{aligned}
G_L&=\frac{\{\text{Bond }BC\}_L}{\{\text{Triangle }ABC\}_L}\\
&\qquad\times\left[\frac{\{\text{Bond }CD\}_L}{\{\text{Triangle }ACD\}_L}\div\frac{\{\text{Point }C\}_L}{\{\text{Bond }AC\}_L}\right]\\
&=Z_L{}^3/(Y_L{}^2W_L).
\end{aligned}\tag{G.1}$$

Constructing the entropy from (G.1) and minimizing the free energy, we get for the transition temperature

$$\tau_t\equiv kT_t/\epsilon=\tfrac{1}{2}\ln(5/3)\doteqdot 3.9153,\tag{G.2}$$

and for the specific heat c_+ and c_- at the transition temperature on the higher and lower temperature sides

$$c_+/k\doteqdot 0.734\quad\text{and}\quad c_-/k\doteqdot 3.486.\tag{G.3}$$

The c *vs* τ curve is shown in Fig. 9 by the solid line. Bethe's approximation and the correct transition temperature obtained by Wannier[21] are shown in the same figure for comparison.

H. An Improved Treatment for the Face-Centered Cubic Lattice (Ising Model)

(H1) *Fundamental Equation*

Figure 10 illustrates the structure of the face-centered cubic lattice viewed from the direction of a body-diagonal. The lattice points shown with greater circles are on a lattice plane higher than those with small ones. Capital letters indicate the higher lattice points and small letters, the lower. $Afge$ and $ACDf$ are tetrahedrons.

We adopt a tetrahedron as the basic figure. The entropy is obtained when we calculate the number of ways, G_L, of putting a spin on A so that all the tetrahedrons and the triangles containing A have r.d., provided every tetrahedron and every triangle in the part drawn with solid lines have had r.d.

G_L is shown to be

$$\begin{aligned}
G_L=&\frac{\{\text{Triangle }feg\}_L}{\{\text{Tetrahedron }Afeg\}_L}\\
&\times\left[\frac{\{\text{Triangle }CDf\}_L}{\{\text{Tetrahedron }ACDf\}_L}\div\frac{\{\text{Point }f\}_L}{\{\text{Bond }Af\}_L}\right]\\
&\times\left[\frac{\{\text{Bond }BC\}_L}{\{\text{Triangle }ABC\}_L}\div\frac{\{\text{Point }C\}_L}{\{\text{Bond }AC\}_L}\right]\\
&\times\left[\frac{\{\text{Bone }Be\}_L}{\{\text{Triangle }ABe\}_L}\div\left(\frac{\{\text{Point }e\}_L}{\{\text{Bond }Ae\}_L}\right.\right.\\
&\qquad\left.\left.\times\frac{\{\text{Point }B\}_L}{\{\text{Bond }AB\}_L}\div\frac{L!}{\{\text{Point }A\}_L}\right)\right]\\
=&(Z_L{}^6L!)/(X_L{}^2W_L{}^5).
\end{aligned}\tag{H1.1}$$

Hence, the entropy S of a system with M lattice points is

$$\begin{aligned}
S&=k(M/L)\ln G_L\\
&=kM[6\textstyle\sum\gamma_iz_i\ln z_i-2\sum\alpha_ix_i\ln x_i-5\sum w_i\ln w_i].
\end{aligned}\tag{H1.2}$$

For the system, the total number of bonds being $6M$,

---

[19] The notation is different in this Section from that of Sec. II.

[20] G. F. Newell, Phys. Rev. **79**, 876 (1950); K. Husimi and I. Syozi, Prog. Theor. Phys. **5**, 177 (1950); I. Syozi, Prog. Theor. Phys. **5**, 341 (1950).

[21] G. H. Wannier, Revs. Modern Phys. **17**, 50 (1945).

the energy E becomes

$$E=6M\sum_{i=1}^{3}\gamma_i\epsilon_i z_i=6M\epsilon(4z_2-1). \tag{H1.3}$$

When we minimize the free energy μ per lattice point,

$$\mu=(E-TS)/M \tag{H1.4}$$

referring to Table VIII, we get the fundamental equations:

$$\partial\mu/\partial\xi_1=0:\quad (w_2/w_1)^5(z_1/z_3)^6(x_5/x_1)^2=1, \tag{H1.5}$$
$$\partial\mu/\partial z_2=0:\quad H^{12}=[z_2^2/(z_1z_3)]^3[(x_1x_5)/(x_2x_4)]^2,$$

where

$$H\equiv\exp(\epsilon/kT), \tag{H1.6}$$

$$\partial\mu/\partial\xi_2=0:\quad (x_1/x_5)(x_4/x_2)^2=1, \tag{H1.7}$$

$$\partial\mu/\partial x_3=0:\quad (x_2x_4)^4=x_1x_3^6x_5. \tag{H1.8}$$

(H2) *Disordered State*

In this case

$$\xi_1=\xi_2=0, \tag{H2.1}$$

resulting in

$$\begin{cases} w_1=w_2=\frac{1}{2}, \\ z_1=z_3=\frac{1}{2}-z_2, \\ x_1=x_5=\frac{1}{2}-2z_2+x_3, \\ x_2=x_4=\frac{1}{2}z_2-x_3. \end{cases} \tag{H2.2}$$

Equations (H1.5) and (H1.7) become identities and Eqs. (H1.6) and (H1.8) are simplified to

$$\begin{cases} H^6=(z_2/z_1)^3(x_1/x_2)^2, & \text{(H2.3)} \\ x_2^4=x_1x_3^3. & \text{(H2.4)} \end{cases}$$

Introducing a parameter φ defined by

$$\varphi\equiv x_2/x_3, \tag{H2.5}$$

we can solve the equations, finding the results:

$$\begin{cases} x_2=z_2\varphi/[2(\varphi+1)], \\ z_1=z_2(\varphi^3-\varphi^2+\varphi+1)/2, \\ z_2=1/(\varphi^3-\varphi^2+\varphi+3), \end{cases} \tag{H2.6}$$

and

$$H^2=2\varphi^2/(\varphi^3-\varphi^2+\varphi+1). \tag{H2.7}$$

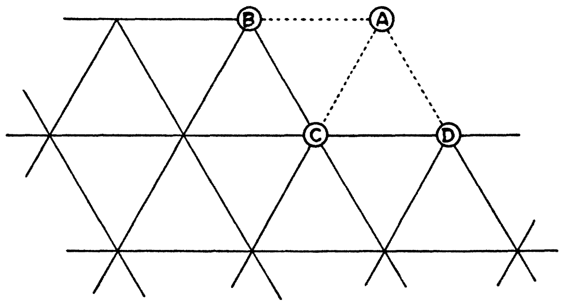


FIG. 8. An intermediate stage of constructing a two-dimensional triangular lattice.

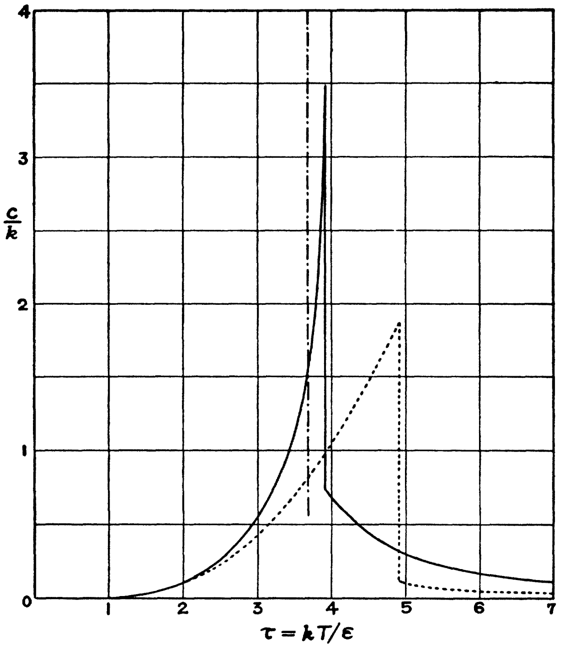


FIG. 9. The specific heat c per lattice point for the two-dimensional triangular lattice (Ising model) plotted against $\tau=kT/\epsilon$. ---------- Bethe's approximation. ———— This paper. — — — — — — The correct transition temperature by Wannier.

The specific heat c per spin becomes

$$c/k=24dz_2/d\tau$$
$$=\frac{48\varphi(\varphi^3-\varphi^2+\varphi+1)(3\varphi^2-2\varphi+1)}{\tau^2(-\varphi^3+\varphi+2)(\varphi^3-\varphi^2+\varphi+3)^2}, \tag{H2.8}$$

where

$$\tau\equiv kT/\epsilon. \tag{H2.9}$$

The equation

$$\varphi^3-\varphi-2=0 \tag{H2.10}$$

has one real root

$$\varphi_1\doteqdot 1.5214. \tag{H2.11}$$

Therefore, c becomes negative for

$$\varphi>1.5214. \tag{H2.12}$$

(H3) *The Transition Temperature, T_t*

Differentiating Eqs. (H1.5) and (H1.7) and inserting Eqs. (H2.1) and (H2.2), we get

$$\frac{d\xi_1}{d\xi_2}=\frac{2}{x_1}\bigg/\left\{5-\frac{3}{z_1}+\frac{1}{x_1}\right\}=\left\{\frac{2}{x_1}+\frac{2}{x_2}\right\}\bigg/\frac{1}{x_1}. \tag{H3.1}$$

Using Eq. (H2.6), we get from the right-hand side equation,

$$[\Phi(\varphi)-2][\Phi(\varphi)-3]=0, \tag{H3.2}$$

where

$$\Phi(\varphi)\equiv\varphi^3-\varphi^2+\varphi. \tag{H3.3}$$

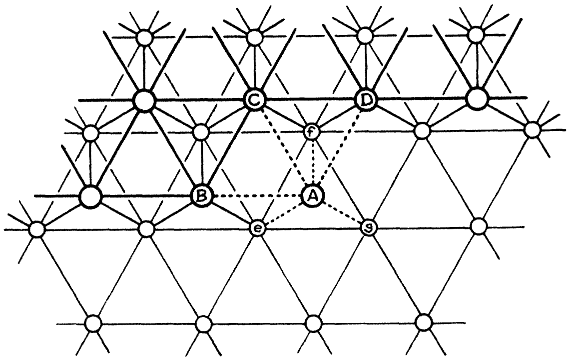


FIG. 10. An intermediate stage of constructing a face-centered lattice.

Considering the restriction (H2.12), we get the correct root from the first factor:

$$\varphi_t \doteqdot 1.3532. \tag{H3.7}$$

This is the value corresponding to the transition temperature. Hence,[22]

$$\begin{cases} H_t^2 \doteqdot 1.221, \\ \tau_t \doteqdot 10.025. \end{cases} \tag{H3.8}$$

The specific heat c_+ at T_t on the higher temperature side is obtained from Eq. (H2.8):

$$c_+/k \doteqdot 0.335\ 5. \tag{H3.9}$$

Equations (H3.8) are to be compared with the results of Bethe's approximation:

$$\begin{cases} H_t^2 = 1.2. \\ \tau_t \doteqdot 10.970. \end{cases} \tag{H3.10}$$

Following the discussion of Sec. IID7, we infer that the correct transition temperature τ_c would be in the range

$$\tau_1 \doteqdot 9.239 < \tau_c < 10.025,$$

where τ_1 corresponds to the value of φ_1 (H2.11), and at τ_1 the specific heat for the disordered state becomes infinite.

(H4) *The Specific Heat c_- at T_t on the Low Temperature Side*

Following the idea explained in Sec. IID5, and equating the formulas for ξ_2/ξ_1 obtained from Eqs. (H1.5) and (H1.7), we get

$$\Psi + A\xi_1^2 + O(\xi^4) = 0, \tag{H4.1}$$

where

$$\begin{aligned} \Psi &= \{5-(6/\zeta)+[2/(\eta_1+\eta_2)]\}\eta_1/4, \\ A &= (5\eta_1/4)[2-(12/\zeta)+(15/\zeta^2)-4/\zeta^3] \\ &\quad +(5/2)(1-2\theta)[2-(6/\zeta)+3/\zeta^2] \\ &\quad +(1/4\eta_1)(1-2\theta)^2(5-6/\zeta) \\ &\quad -[(1-2\theta)\theta^2/2\eta_2(\eta_1+\eta_2)], \end{aligned} \tag{H4.2}$$

and

$$\begin{cases} \zeta = 1-2z_2 \\ \eta_1 = 1-4z_2+2x_3 \\ \eta_2 = z_2-2x_3 \\ \theta = \xi_2/\xi_1. \end{cases} \tag{H4.3}$$

Differentiating Eqs. (H4.1), (H1.6), and (H1.8) with respect to τ, and inserting the value at T_t, we get

$$5(dz_2/d\tau)+[(675-187\alpha)/144\alpha]d\xi_1^2/d\tau = 0, \tag{H4.4}$$

$$10(5\alpha^2-6\alpha+5)\frac{dz_2}{d\tau}-80\alpha^2\frac{dx_3}{d\tau} + \frac{25}{24}(\alpha^2-1)\frac{d\xi_1^2}{d\tau} = \frac{12}{\tau_t^2}(\alpha^2-1), \tag{H4.5}$$

$$-4(dz_2/d\tau)+(3\alpha+5)dx_3/d\tau = 0, \tag{H4.6}$$

with

$$\alpha \equiv \varphi_t + 1 \doteqdot 2.3532. \tag{H4.7}$$

Solving for $dz_2/d\tau$ from Eqs. (H4.4)–(H4.6), we get the specific heat c_- at T_t on the low temperature side:

$$\frac{c_-}{k} = \frac{(3\alpha+5)(675-187\alpha)}{(3\alpha-5)(675-187\alpha)-15\alpha(3\alpha+5)}\frac{144}{25\tau_t^2} \doteqdot 2.7888. \tag{H4.8}$$

(H5) *The Ordered State*

Equations (H1.5)–(H1.8) can be solved numerically. Putting

$$\begin{cases} \psi \equiv x_2/x_4, \\ q \equiv x_4/x_3, \end{cases} \tag{H5.1}$$

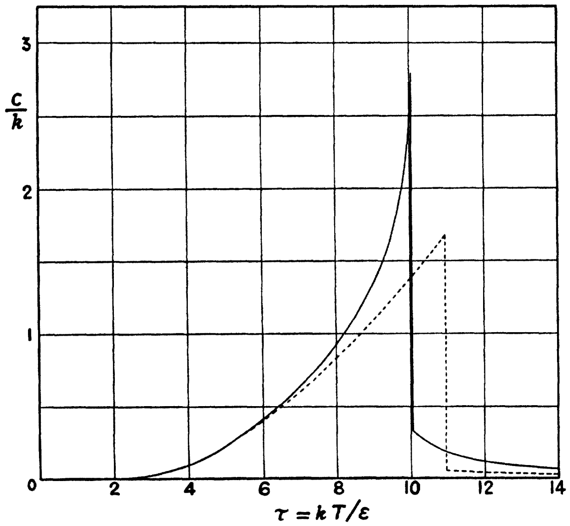


FIG. 11. The specific heat c per lattice point for the face-centered cubic lattice (Ising model) plotted against $\tau = kT/\epsilon$. -------- Bethe's approximation. ———— This paper.

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[22] The value 10.026 0 for τ_t reported earlier [Ryoichi Kikuchi, Phys. Rev. **79**, 718 (1950)] has been revised by later calculations.

we get the equation

$$\left\{\frac{3+(3+\psi)q+\psi q^4}{3+(1+3\psi)q+\psi^3q^4}\right\}^5\left\{\frac{1+2\psi q+\psi^3q^4}{1+2q+\psi q^4}\right\}^6=\psi^4, \qquad \text{(H5.2)}$$

which determines q for an assigned value of ψ.

Other variables are expressed with ψ and q:

$$H^4=[2+(\psi+1)q]^2q^4\psi^2 \\ (1+2\psi q+\psi^3q^4)^{-1}(1+2q+\psi q^4)^{-1}, \qquad \text{(H5.3)}$$

and

$$z_2=[2+(\psi+1)q]/[6+4(\psi+1)q+(\psi^3+\psi)q^4]. \qquad \text{(H5.4)}$$

Differentiating Eqs. (H5.3) and (H5.4), we obtain the specific heat, which is shown together with Eq. (H2.8) in Fig. 11 by solid curves. Bethe's result is drawn in the figure for comparison.

The author wishes to express his hearty thanks to Prof. T. Sakai of University of Tokyo and members of his laboratory especially to Mr. N. Hashitsume for their deep interest in this work.

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Photo-Mesons from Carbon*

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Photons from the Berkeley 322-Mev electron synchrotron have been used to produce mesons from a carbon target. These mesons have been observed with nuclear emulsions at angles of 45°, 90°, and 135° to the photon beam. The ratio of the number of π^- to π^+ mesons produced is 1.29±0.22, 1.30±0.12, and 1.34±0.20, respectively, at each of the above angles. The energy spectra and the differential cross sections of π-mesons at each of these angles have been obtained. The total cross section for the production of π-mesons is $4.0\pm1.6\times10^{-28}$ cm^2 per nucleus per "equivalent quantum." The number of "equivalent quanta," Q, is defined as the total energy in the beam divided by the maximum photon energy. The cross section for production of μ-meson pairs at the target is estimated to be less than 2 percent of the cross section for π-meson production.

I. INTRODUCTION

THE production of mesons by photons was definitely established for the first time when they were observed in the x-ray beam of the 322-Mev electron synchrotron at the University of California Radiation Laboratory by McMillan and Peterson[1] in January, 1949. Carbon was the first pure target material to be bombarded by the x-ray beam for the production of mesons.[2] Carbon was chosen because of its relatively low atomic number and its ready availability and ease of fabrication. The background is due largely to electrons, positrons, and photons which are produced and scattered in the target material and which tend to fog the nuclear emulsions used as detectors in this experiment. Since the electron pair production cross section varies as the second power of the atomic number, while meson production varies by about the two-thirds power,[3] the background is reduced by use of as low an atomic number as possible.

For pure photon-nucleon interactions the ideal targets to bombard with photons are either protons or neutrons. Ordinary hydrogen is perfect for the former, and deuterium is the nearest experimental approach to the latter. Experiments using hydrogen have been performed by Cook[4] and by Steinberger and Bishop.[5] An experiment with deuterium is now in progress.

Although it was realized that with a carbon target one might not get a true picture of a pure photon-nucleon interaction because of possible distortion by the other nucleons in a carbon nucleus, it was felt that one might get a first approximation. Also, if distortion by the neighboring nucleons were important, it could be measured by comparison of the negative and positive meson spectra from carbon with those from hydrogen and deuterium. Furthermore, the energy spectra and the ratio of negative to positive mesons from carbon are each of interest in themselves.

An exploratory experiment[2] using a line target of carbon had given a rough energy spectrum of mesons emitted near 90° to the beam direction in the laboratory system. It had indicated that the angular distribution of mesons was approximately spherically symmetric, at least in the region near 90°, and also that more π^- mesons are produced than π^+ mesons by a ratio of 1.7±0.2. The present experiment was designed to display more fully the angular and energy spectra of mesons produced in carbon by x-rays generated by 322-Mev electrons.

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