A Generalization of the QuasiChemical Method in the Statistical Theory of Superlattices

C. N. Yang

Additional information on J. Chem. Phys.

A Generalization of the Quasi-Chemical Method in the Statistical Theory of Superlattices

C. N. YANG*

National Tsing Hua University, Kunming, China

(Received November 17, 1944)

The quasi-chemical method in the investigation of the equilibrium distribution of atoms in the pairs of neighboring sites in a superlattice is generalized by considering groups containing large numbers of sites. The generalized method may be used to obtain successive approximations of the free energy of the crystal. The labor of integration is avoided by the introduction of a Legendre transformation. In order to analyze the fundamental assumption underlying the method more closely, the number of arrangements of the atoms for given long-distance order is calculated and the hypothesis of the non-interference of local configurations discussed. The method is applied to the calculation of the free energy in the different approximations discussed in this paper, including Bethe's second approximation and a simple approximation for the face-centered cubic crystal Cu_3Au.

1. INTRODUCTION

IT was shown by Fowler and Guggenheim[1] that the quasi-chemical method, originally devised for the theory of regular solutions, applies equally well to the theory of superlattices with long-distance order. The method is, as they have emphasized, definitely one stage further towards an exact theory than Bragg-Williams' method.[2] Compared with Bethe's[3] or Kirkwood's[4] method it also distinguishes itself in mathematical simplicity. But in its original form the method does not lead to a consistent scheme of successive approximations and cannot be regarded as a method of approach towards the rigorous evaluation of the configurational free energy of an alloy. In the present paper a new formulation of the quasi-chemical method is developed which is capable of yielding successively higher approximations.

The free energy expression in both Bethe's method and the quasi-chemical method involves an integral. Its evaluation is very complicated and has been carried out[1,5] so far only in Bethe's approximation for simple and body-centered cubic crystals. In the new formulation of the quasi-chemical method, however, it will be shown that a Legendre transformation helps to effect the integration. (It might be noticed that a similar Legendre transformation is used to essentially the same effect in Fowler's formulation of general statistical mechanics. Compare Fowler.[6]) The free energy is obtained directly as a closed expression. Its values are given for Bethe's first and second (modified) approximations and for the face-centered alloy Cu_3Au in Sections 7 and 8.

To make sure that the quasi-chemical method may actually be used to obtain a series of successively better approximations, we must investigate the free energy in high order approximations and compare it with the partition function of the crystal. This is done in Section 5 together with a comparison of the quasi-chemical and Bethe's methods.

Except in the last section we shall be concerned only with binary alloys with atomic ratio 1:1 forming a (quadratic), simple cubic, or body-centered cubic lattice. The generalization of the method to the investigation of alloys with other atomic ratios and forming other types of lattices is easy. In fact, the superior power of the quasi-chemical method appears to be even more fully revealed when a face-centered lattice is studied. This problem is taken up at the end of the paper where an approximate free energy

[1] R. H. Fowler and E. A. Guggenheim, Proc. Roy. Soc. A174, 189 (1940).
[2] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. A145, 699 (1934); 151, 540 (1935); 152, 231 (1935).
[3] H. A. Bethe, Proc. Roy. Soc. A150, 552 (1935).
[4] J. G. Kirkwood, J. Chem. Phys. 6, 70 (1938).
[5] T. S. Chang, Proc. Camb. Phil. Soc. 35, 265 (1939); J. G. Kirkwood, J. Chem. Phys. 8, 623 (1940); J. S. Wang, "Free energy in the statistical theory of order-disorder transformation," Science Report of National Tsing Hua University, Series A, 30th Anniversary Memorial Number (1941), printed but failed to appear.
[6] R. H. Fowler, *Statistical Mechanics*, second edition, p. 188.

66

expression for Cu_3Au is obtained and its critical phenomena discussed.

2. REFORMULATION OF THE QUASI-CHEMICAL METHOD

Consider an alloy of type AB with altogether $N = 2N_1$ atoms. Let z be the number of nearest neighbors of each atom. Those sites in the superlattice occupied by the A atoms at the absolute zero of temperature will be called the α-sites, and the rest, the β-sites. The partition function of the crystal may be written in the form

$$\sum_w P(w, T), \quad (1)$$

where $P(w, T)$ is equal to $e^{-E/kT}$ summed over all possible configurations of the crystal having $N_1 w$ α-sites occupied by B (wrong) atoms. The average energy over all these configurations is

$$\bar{E}(w, T) = kT^2 \frac{\partial}{\partial T} \log P(w, T). \quad (2)$$

But evidently

$$P(w, \infty) = g(w) = \left[\frac{N_1!}{(N_1 w)!(N_1 - N_1 w)!} \right]^2. \quad (3)$$

Hence

$$\log P(w, T) = \log g(w) + \int_\infty^T \frac{1}{kT^2} \bar{E}(w, T) dT. \quad (4)$$

The problem of finding the partition function of the crystal therefore reduces to one of finding $\bar{E}(w, T)$. An approximate solution has been obtained by Fowler and Guggenheim. Their method will now be presented in a new form better suited to generalization.

There are in the crystal zN_1 pairs of nearest neighboring sites $\alpha - \beta$. Let $[q_\alpha, q_\beta]$ of these be occupied by $q_\alpha (=0, 1)$ wrong (B) atoms on the α-site and $q_\beta (=0, 1)$ wrong (A) atoms on the β-site. For given w the following relations hold:

$$[0, 0] + [0, 1] + [1, 0] + [1, 1] = zN_1,$$

$$[1, 0] + [1, 1] = zN_1 w,$$

and $\qquad\qquad\qquad\qquad\qquad\qquad (5)$

$$[0, 1] \qquad + [1, 1] = zN_1 w.$$

Upon the approximation of the nearest neighbor interaction the energy of the crystal may be written as

$$E(r, T) = [0, 0] V_{AB} + [0, 1] V_{AA}$$
$$+ [1, 0] V_{BB} + [1, 1] V_{AB}, \quad (6)$$

where the V's are the interaction energies between the different kinds of pairs of nearest neighbors.

We may give (5) and (6) a different interpretation by imagining $[0, 0]$, $[0, 1]$, $[1, 0]$, $[1, 1]$ and V_{AB}, V_{AA}, V_{BB}, V_{AB} to be, respectively, the numbers and the molecular internal energies of four different kinds of molecules, say, X, XZ, XY, XYZ of a gaseous assembly. The interpretation of (6) is that the assembly has the same internal (non-kinetic) energy as the crystal at the given value of w. Equation (5) would mean that the total numbers of X, Y, Z atoms are, respectively, zN_1, $zN_1 w$, $zN_1 w$.

The quasi-chemical method consists in taking the averages $\langle 0, 0 \rangle_{Av}$, $\langle 0, 1 \rangle_{Av}$, $\langle 1, 0 \rangle_{Av}$, $\langle 1, 1 \rangle_{Av}$ of the chemical assembly at any temperature as approximately representing the corresponding averages of the crystal at the same temperature.

A detailed treatment of the problem of a gaseous assembly has been given by Fowler.[7] We are only interested in our assembly of four different kinds of molecules, for which the results may be summarized as:

$$\langle 0, 0 \rangle_{Av} = \xi \exp [- V_{AB}/kT],$$

$$\langle 0, 1 \rangle_{Av} = \xi \nu \exp [- V_{AA}/kT],$$

$$\langle 1, 0 \rangle_{Av} = \xi \mu \exp [- V_{BB}/kT], \qquad (7)$$

$$\langle 1, 1 \rangle_{Av} = \xi \mu \nu \exp [- V_{AB}/kT],$$

where ξ, μ, and ν are to be determined from (6).

In Fowler and Guggenheim's work the starting point is the equation

$$\langle 0, 0 \rangle_{Av} \langle 1, 1 \rangle_{Av} / \langle 0, 1 \rangle_{Av} \langle 1, 0 \rangle_{Av}$$

$$= \exp [(V_{AA} + V_{BB} - 2 V_{AB})/kT], \quad (8)$$

which can be obtained by eliminating ξ, μ, and ν from our equation (7). We shall, however, make use of (7) instead of (8) to obtain the free energy by means of a Legendre transformation which enables us to avoid the labor of integration. It will appear that this procedure is applicable to the general case studied in this paper.

In order to calculate the free energy from (4) we first write the energy of the crystal in the

---

[7] R. H. Fowler, *Statistical Mechanics*, second edition, pp. 162-163.

form

$$\bar{E}(w, T) = kT^2 \frac{\partial}{\partial T} \phi(\xi, \mu, \nu, T),$$

where

$$\phi(\xi, \mu, \nu, T) = \xi \exp[-V_{AB}/kT]$$
$$+ \xi\nu \exp[-V_{AA}/kT] + \xi\mu \exp[-V_{BB}/kT]$$
$$+ \xi\mu\nu \exp[-V_{AB}/kT].$$

From (5) it is evident that

$$\xi\frac{\partial\phi}{\partial\xi} = zN_1, \quad \mu\frac{\partial\phi}{\partial\mu} = zN_1w, \quad \nu\frac{\partial\phi}{\partial\nu} = zN_1w.$$

If these last three equations are regarded as defining ξ, μ, and ν in terms of w and T, i.e., if the Legendre transformation:

$$\log \xi, \log \mu, \log \nu, T \rightarrow zN_1, zN_1w, zN_1w, T$$

is made, the derivative of the function

$$\Psi(w, T) = \phi - zN_1 \log \xi - zN_1w \log \mu - zN_1w \log \nu,$$

with respect to T is found to be

$$\frac{\partial\Psi}{\partial T} = \frac{\partial\phi}{\partial T} = \frac{1}{kT^2}\bar{E}(w, T).$$

This shows that the integral in (4) may be expressed directly as a function of ξ, μ, ν and T:

$$\int_\infty^T \frac{1}{kT^2}\bar{E}(w, T)dT = \Psi(w, T) - \Psi(w, \infty).$$

The values of the parameters at $T = \infty$ are easily determined from (5) and (7):

$$\xi = zN_1(1-w)^2, \quad \mu = \nu = \frac{w}{1-w}.$$

Thus (4) becomes

$$\log P(w, T) = 2 \log \frac{N_1!}{(N_1w)!\{N_1(1-w)\}!}$$
$$+ zN_1 \log \frac{zN_1(1-w)^2}{\xi} + zN_1w \log \frac{w^2}{(1-w)^2\mu\nu},$$

so that the free energy of the crystal is

$$F_0(w, T) = -kT \log P(w, T) = -kT\{zN_1 \log zN_1$$
$$+ 2(z-1)N_1[w \log w + (1-w) \log(1-w)]$$
$$- zN_1 \log \xi - zN_1w \log \mu\nu\}. \quad (9)$$

We shall have occasion to return to this expression for the free energy later in Section 4.

3. GENERALIZATION TO GROUPS OF FOUR SITES

So far our attention has been fixed on the pairs of nearest neighbors in the crystal. They are classified into four different kinds and the average number of pairs in each class is obtained from chemical analogy. Now we shall generalize the whole procedure by taking into consideration all the groups of sites of a certain arbitrarily chosen form in the crystal. These groups will be classified according to the way they are occupied by atoms and the average number of groups in each class is to be obtained by chemical analogy.

To make this clear let us consider in detail groups of four sites forming the corners of squares (as shown in Fig. 1) in a quadratic lattice. We
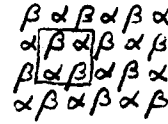

FIG. 1.

classify these groups into $2^4 = 16$ classes and denote them by $(0, 0, 0, 0)$, $(0, 0, 0, 1)$, $\cdots$, $(1, 1, 1, 1)$, respectively, so that all groups in the class (q_1, q_2, q_3, q_4) have q_1 wrong atoms in their upper α-sites, q_2 wrong atoms in their lower α-sites, q_3 wrong atoms in their upper β-sites, and q_4 wrong atoms in their lower β-sites. The total number of these groups is N, hence if we denote the number of groups in the class (q_1, q_2, q_3, q_4) by $[q_1, q_2, q_3, q_4]$,

$$\sum_{q_i=0}^{1} [q_1, q_2, q_3, q_4] = N_1. \quad (10)$$

Now the number of all those groups in the crystal with a wrong atom on the upper α-site is just the number of wrong atoms on the α-sites. Similar reasoning may be applied to the other three sites, so we obtain

$$\sum_q q_i[q_1, q_2, q_3, q_4] = N_1w, \quad i = 1, 2, 3, 4. \quad (11)$$

Let $\chi(q_1, q_2, q_3, q_4)$ be the energy of each group in the class (q_1, q_2, q_3, q_4). It is easy to show that

$$\chi = (2 - q_1 - q_2)(q_3 + q_4) V_{AA}$$
$$+ \{(2 - q_1 - q_2)(2 - q_3 - q_4)$$
$$+ (q_1 + q_2)(q_3 + q_4)\} V_{AB}(2 - q_3 - q_4)(q_1 + q_2) V_{BB}.$$

The total energy of the crystal is given in terms of $\chi(q_1, q_2, q_3, q_4)$ by

$$E(w, T) = \sum_q [q_1, q_2, q_3, q_4] \chi(q_1, q_2, q_3, q_4). \quad (12)$$

We may give (10), (11), and (12) interpretations similar to those given in Section 2 for Eqs. (5) and (6). The same quasi-chemical method used there to obtain (7) leads now to the following averages for given w:

$$\langle q_1, q_2, q_3, q_4 \rangle_{Av} = \xi \mu_1{}^{q_1} \mu_2{}^{q_2} \mu_3{}^{q_3} \mu_4{}^{q_4}$$
$$\times \exp[-\chi(q_1, q_2, q_3, q_4)/kT]. \quad (13)$$

In this expression the parameters ξ, μ_1, μ_2, μ_3, and μ_4 are to be determined from (10) and (11), which may be written in the form

$$\xi \frac{\partial \phi}{\partial \xi} = N_1, \quad \mu_i \frac{\partial \phi}{\partial \mu_i} = N_1 w, \quad (i = 1, 2, 3, 4) \quad (14)$$

if we put

$$\phi(\xi, \mu_1, \mu_2, \mu_3, \mu_4) = \sum_q \xi \mu_1{}^{q_1} \mu_2{}^{q_2} \mu_3{}^{q_3} \mu_4{}^{q_4}$$
$$\times \exp[-\chi(q_1, q_2, q_3, q_4)/kT]. \quad (15)$$

It can be shown[8] that ξ and μ_i are uniquely determined by (14) at given w and T. Their values at $T = \infty$ are

$$(\xi)_{T=\infty} = N_1 (1-w)^4,$$

$$(\mu_i)_{T=\infty} = \frac{w}{1-w}, \quad i = 1, 2, 3, 4; \quad (16)$$

as can be shown by substitution into (14).

To calculate the free energy it is necessary first to evaluate the integral in (4). By (12) and (13) the integrand may be written as

$$\frac{1}{kT^2} \bar{E}(w, T) = \frac{1}{kT^2} \sum_q \langle q_1, q_2, q_3, q_4 \rangle_{Av}$$
$$\times \chi(q_1, q_2, q_3, q_4) = \frac{\partial \phi}{\partial T}, \quad (17)$$

where the partial differentiation is to be taken with ξ, μ_1, μ_2, μ_3, μ_4, and T as the independent variables. If, however, we regard them as functions of w and T defined by (14) and introduce

----

[8] The proof follows easily from Lemma 2.42 in Fowler's *Statistical Mechanics*, second edition.

the Legendre transformation

$$\log \xi, \log \mu_1, \log \mu_2, \log \mu_3, \log \mu_4$$
$$\rightarrow N_1, N_1 w, N_1 w, N_1 w, N_1 w, \quad (18)$$

(17) reduces to

$$\frac{1}{kT^2} \bar{E}(w, T) = \frac{\partial \phi}{\partial T} = \frac{\partial}{\partial T} \Psi(w, T), \quad (19)$$

where the function Ψ is defined by

$$\Psi = \phi - N_1 \log \xi - \sum_i N_1 w \log \mu_i. \quad (20)$$

Substituting (19) into (4) we get

$$\log P(w, T) = \log g(w) + \Psi(w, T) - \Psi(w, \infty), \quad (21)$$

so that the free energy may be written down directly as

$$F(w, T) = -kT \log P(w, T)$$
$$= -kT[\log g(w) + \Psi(w, T) - \Psi(w, \infty)]. \quad (22)$$

The equilibrium value $\bar{w}$ of w is obtained by minimizing F, so we have

$$0 = \frac{\partial}{\partial \bar{w}} F(\bar{w}, T) = -kT \left[\frac{d}{d\bar{w}} \log g(\bar{w}) \right.$$
$$\left. + \frac{\partial}{\partial \bar{w}} \Psi(\bar{w}, T) - \frac{\partial}{\partial \bar{w}} \Psi(\bar{w}, \infty) \right]. \quad (23)$$

But by (14) and (20)

$$\frac{\partial}{\partial w} \Psi(w, T) = -\sum_i N_1 \log \mu_i,$$

and by (3)

$$\frac{d}{dw} \log g(w) = -2N_1 \log \frac{w}{1-w},$$

so by (16)

$$\sum_i \log \mu_i = -2 \log \frac{\bar{w}}{1-\bar{w}}$$
$$+ \left[\sum_i \log \mu_i \right]_{T=\infty} = 2 \log \frac{\bar{w}}{1-\bar{w}};$$

i.e.,

$$\prod_i \mu_i = \left(\frac{\bar{w}}{1-\bar{w}} \right)^2. \quad (24)$$

It will be shown in the next section that we may put $V_{AA} = V_{BB}$, and $V_{AB} = 0$ without altering the specific heat of the crystal if

$$V = \tfrac{1}{2}(V_{AA} + V_{BB}) - V_{AB}$$

is left unchanged. When this is done, ϕ will be symmetrical with respect to μ_1, μ_2, μ_3, and μ_4, and we conclude that all the μ's are equal, because: (i) Eq. (14) has only one set of solutions; and (ii) if the conclusion is true, (14) becomes, with all μ_i put equal to μ,

$$\xi\frac{\partial\phi}{\partial\xi} = N_1, \quad \mu\frac{\partial\phi}{\partial\mu} = 4N_1 w, \qquad (25)$$

which *does* have a set of solutions in ξ and μ. Now ϕ is given by

$$\phi = \xi[1 + 4\mu x^2 + (4\mu^2 x^2 + 2\mu^2 x^4) + 4\mu^3 x^2 + \mu^4], \quad (26)$$

where

$$x = \exp[-\tfrac{1}{2}(V_{AA} + V_{BB} - 2V_{AB})/kT]. \quad (27)$$

Introducing the degree of order s by $s = 1 - 2w$ and eliminating ξ from (25), we obtain

$$(1+s)\mu^4 + (2+4s)\mu^3 x^2 + 2sx^2(x^2+2)\mu^2$$
$$+ (4s-2)x^2\mu + (s-1) = 0. \quad (28)$$

The free energy is given by (16) and (22):

$$\frac{-F(w, T)}{2N_1 kT} = (1-w)\log(1-w)$$

$$+ w\log w - 2w\log\mu + \tfrac{1}{2}\log(1 + 4\mu x^2$$
$$+ 4\mu^2 x^2 + 2\mu^2 x^4 + 4\mu^3 x^2 + \mu^4), \quad (29)$$

and the condition of equilibrium by (24):

$$\mu = \left(\frac{1-s}{1+s}\right)^{\frac{1}{2}}. \quad (30)$$

To obtain the critical temperature, we expand (28) in powers of s and find, after identifying coefficients,

$$\log\mu = -\frac{1 + 6x^2 + x^4}{2 + 2x^2}s + Ks^3 + \cdots$$

which is the only real solution for $\log\mu$. Next we expand (30);

$$\log\mu = -s - \tfrac{1}{3}s^3 - \cdots.$$

At the critical value x_c of x, these last two equations have a multiple solution at $s = 0$. Hence

$$-\frac{1 + 6x_c^2 + x_c^4}{2 + 2x_c^2} = -1,$$

i.e.,

$$x_c = (\sqrt{5} - 2)^{\frac{1}{2}} = 0.4858.$$

4. GENERAL FORM OF THE QUASI-CHEMICAL METHOD

Let us now take a group of any size and form. Let it have a α-sites, b β-sites, and γ pairs of nearest neighbors. The procedures to obtain an approximate expression for the free energy of the crystal follow exactly the same line as in the special case considered in the last section. Equations (13), (14), and (16) are essentially unchanged:

$$\langle q_1, q_2, \cdots\rangle_{Av} = \xi\mu_1^{q_1}\mu_2^{q_2}\cdots\exp[-\chi/kT], \quad (31)$$

$$\phi = \sum_q \xi\mu_1^{q_1}\mu_2^{q_2}\cdots\exp[-\chi/kT],$$

$$\xi\frac{\partial\phi}{\partial\xi} = N_1, \quad \mu_i\frac{\partial\phi}{\partial\mu_i} = N_1 w, \quad (32)$$

and

$$(\mu_i)_{T=\infty} = \frac{w}{1-w}. \quad (33)$$

But now the total number of pairs in the whole set of groups is $N_1\gamma$ while the total number of pairs of nearest neighbors in the actual crystal is $N_1 z$. Hence the energy expression (12) should be modified by multiplying the right-hand side with a factor z/γ. Thus we have, in place of (17),

$$\bar{E} = \frac{z}{\gamma}\sum_q \langle q_1, q_2, \cdots\rangle_{Av}\chi(q_1, q_2, \cdots)$$

$$= \frac{z}{\gamma}kT^2\frac{\partial\phi}{\partial T}. \quad (34)$$

And (22) becomes, with the help of (3), (20), and (33),

$$F(w, T) = -\frac{z}{\gamma}N_1 kT\left[\log N_1 + \left(a + b - \frac{2\gamma}{z}\right)\right.$$

$$\times\{(1-w)\log(1-w) + w\log w\}$$

$$\left. -\log\xi - w\sum_i\log\mu_i\right]. \quad (35)$$

Differentiate (35) and we obtain

$$\frac{\partial}{\partial w} F(w, T)$$

$$= -N_1 kT \frac{z}{\gamma} \log \left[\left(\prod_i \mu_i \right) \left(\frac{1-w}{w} \right)^{a+b-(2\gamma/z)} \right], \quad (36)$$

where use has been made of (32). So the condition of equilibrium is given by

$$\prod_i \mu_i = \left(\frac{w}{1-w} \right)^{a+b-(2\gamma/z)} \quad (37)$$

In actual calculations the following points may prove helpful:

(i) *The free energy is changed by a constant if V_{AA} and V_{BB} are both replaced by $\frac{1}{2}(V_{AA}+V_{BB})$ − V_{AB}, and V_{AB} by 0.* To prove this let z_i be the number of sites in the group neighboring to the site i. Let χ be changed into χ' by the replacement. It is evident that $\chi'-\chi = -\gamma V_{AB} +$ (No. of BB pairs)$(V_{AA}-V_{BB}/2)+$ (No. of AA pairs) $\times (V_{BB} - V_{AA}/2)$, and that

$$\sum_{\alpha\text{-sites}} q_i z_i - \sum_{\beta\text{-sites}} q_i z_i$$

$$= (\text{No. of } BB \text{ pairs}) - (\text{No. of } AA \text{ pairs}). \quad (38)$$

Hence

$$\langle q_1, q_2, \cdots \rangle_{Av} = \xi \mu_1{}^{q_1} \mu_2{}^{q_2} \cdots \exp\left[-\chi/kT\right]$$

$$= \xi' \mu_1'{}^{q_1} \mu_2'{}^{q_2} \cdots \exp\left[-\chi'/kT\right],$$

if we put

$$\xi' = \xi \exp\left[-\gamma V_{AB}/kT\right],$$

$$\mu_i' = \mu_i \exp\left[\pm z_i(V_{AA}-V_{BB})/2kT\right]$$

where the + sign or the − sign is to be taken according as the site i is an α-site or a β-site. We can now calculate the new free energy and verify the above statement.

(ii) *Sites that are symmetrically situated in the group have μ's equal irrespective of their nature if $V_{AA}=V_{BB}$ and $V_{AB}=0$.* This has already been shown in the last section for the special case considered there. With allowances for change of notation, the proof holds in general. Since the most troublesome part of the calculations is the elimination of the parameters, much might be gained by choosing a group with a large number of sites symmetrically situated.

(iii) *The free energy is a function of s^2, so that (37) is always satisfied at $\bar{w}=\frac{1}{2}$ (i.e., long-distance order = 0).* The proof is simple when we have already made $V_{AA}=V_{BB}$ and $V_{AB}=0$, so that an interchange of A and B atoms does not alter the energy:

$$\chi(q_1, q_2, \cdots) = \chi(1-q_1, 1-q_2, \cdots).$$

For, putting

$$\xi' = \xi \mu_1 \mu_2 \cdots$$

and

$$\mu_i' = 1/\mu_i, \quad (39)$$

we get

$$\xi \mu_1{}^{q_1} \mu_2{}^{q_2} \cdots \exp\left[-\chi/kT\right]$$

$$= \xi' \mu_1'{}^{1-q_1} \mu_2'{}^{1-q_2} \cdots \exp\left[-\chi/kT\right].$$

Thus if (32) is satisfied

$$\sum_q (1-q_i) \xi' \mu_1'{}^{1-q_1} \mu_2'{}^{1-q_2} \cdots \exp\left[-\chi/kT\right]$$

$$= \sum_q \xi \mu_1{}^{q_1} \mu_2{}^{q_2} \cdots \exp\left[-\chi/kT\right]$$

$$- \sum_q q_i \xi \mu_1{}^{q_1} \mu_2{}^{q_2} \cdots \exp\left[-\chi/kT\right] = N(1-w);$$

i.e., ξ', μ_1', μ_2', $\cdots$ would be the solution of (32) with $(1-w)$ substituted for w. Hence by (32) and (20)

$$\Psi(1-w, T) = N_1 - N_1 \log \xi'$$

$$- \sum_i N_1(1-w) \log \mu_i' = \Psi(w, T)$$

showing that

$$F(w, T) = F(1-w, T). \quad (40)$$

(iv) *The parameter for a corner site is always given by:*

$$\epsilon = \frac{1}{1+s} \{ [x^2 s^2 + (1-s^2)]^{\frac{1}{2}} - sx \} \quad (41)$$

where x is given by (27) and $s = 1-2w$, irrespective of the size of the group, if $V_{AA}=V_{BB}$, $V_{AB}=0$. By a corner site is meant a site that has only one nearest neighbor in the group. Let ϵ be the selective variable (parameter) of a corner site, and μ_1 that of its only neighbor in the group. If the corner site is dropped, a new group is obtained. We distinguish all quantities referring to this new group by a prime, and obtain at

once

$$\xi'\frac{\partial\phi'}{\partial\xi'}=N_1, \quad \mu_i'\frac{\partial\phi'}{\partial\mu_i'}=N_1w, \quad i=1,2,\cdots. \quad (42)$$

The sites of the primed group are numbered in the same way as in the unprimed group. Introducing the variable x defined in (27) we may write

$$\phi=\sum_q \xi\mu_1{}^{q_1}\mu_2{}^{q_2}\cdots\exp[-\chi/kT]$$

$$=\sum_{q_2\cdots} \xi(1+\epsilon x)\mu_2{}^{q_2}\mu_3{}^{q_3}\cdots\exp[-\chi'/kT]$$

$$+\mu_1\sum_{q_2\cdots}\xi(\epsilon+x)\mu_2{}^{q_2}\cdots\exp[-\chi'/kT]. \quad (43)$$

Let these two terms be denoted by ϕ_0 and ϕ_1, respectively. Since

$$\phi=N_1, \quad \mu_1\frac{\partial\phi}{\partial\mu_1}=N_1w,$$

we have

$$\phi_0=N_1(1-w), \quad \phi_1=N_1w. \quad (44)$$

Now

$$\epsilon\frac{\partial\phi_0}{\partial\epsilon}=\frac{\epsilon x}{1+\epsilon x}\phi_0, \quad \epsilon\frac{\partial\phi_1}{\partial\epsilon}=\frac{\epsilon}{\epsilon+x}\phi_1.$$

Hence $\epsilon\frac{\partial\phi}{\partial\epsilon}=N_1w$ leads to

$$\frac{\epsilon x}{1+\epsilon x}N_1(1-w)+\frac{\epsilon}{\epsilon+x}N_1w=N_1w, \quad (45)$$

or

$$\frac{w}{1-w}=\frac{\epsilon(\epsilon+x)}{1+\epsilon x}, \quad (46)$$

the solution of which is (41). Thus the two parameters μ and ν in the approximation discussed in Section 2 are all equal to ϵ.

(v) *The contribution to the free energy from a corner atom is such that, in the notation of* (iv)

$$F(w,T)=\frac{\gamma-1}{\gamma}F^\gamma(w,T)+\frac{1}{\gamma}F_0(w,T), \quad (47)$$

where $F_0(w,T)$ *is the free energy obtained when* $\gamma=1$, *i.e., the free energy (9) for the approximation discussed in Section 2.* This is proved as follows. If we put

$$\xi=\xi''\frac{1}{1+\epsilon x}, \quad \mu_1=\mu_1''\frac{1+\epsilon x}{\epsilon+x}, \quad \mu_i=\mu_i'', \quad i\geqq2, \quad (48)$$

it is evident from (43) that ϕ would become a function of ξ'', μ_1'', μ_2'', $\cdots$ satisfying the relations

$$\xi''\frac{\partial\phi}{\partial\xi''}\left(=\xi\frac{\partial\phi}{\partial\xi}\right)=N_1, \quad \mu_i''\frac{\partial\phi}{\partial\mu_i''}\left(=\mu_i\frac{\partial\phi}{\partial\mu_i}\right)=N_1w,$$

$$i=1,2,\cdots. \quad (49)$$

It is also evident that ϕ is the same function of ξ'', μ_1'', μ_2'', $\cdots$ as ϕ' is of ξ', μ_1', μ_2', $\cdots$. Now (42) has only one[8] set of solutions in ξ' and μ_i'. Hence from (49) we infer that $\xi'=\xi''$, and $\mu_i'=\mu_i''$. Thus

$$\xi=\frac{\xi'}{1+\epsilon x}, \quad \mu_1=\mu_1'\frac{1+\epsilon x}{\epsilon+x}, \quad \mu_i=\mu_i', \quad i\geqq2. \quad (50)$$

(41) and (50) give the parameters μ_i in terms of μ_i'. Inserting them into (35) we obtain

$$F(w,T)=-N_1kT\frac{z}{\gamma}\Bigg[\log N_1+\left(a+b-\frac{2\gamma}{z}\right)$$

$$\times\{(1-w)\log(1-w)+w\log w\}$$

$$-\log\xi'+(1-w)\log(1+\epsilon x)$$

$$+w\log(\epsilon+x)-w\log\epsilon-w\sum_i\log\mu_i'\Bigg]$$

$$=\frac{\gamma-1}{\gamma}F'(w,T)-N_1kT\frac{z}{\gamma}\Bigg[\left(1-\frac{2}{z}\right)$$

$$\times\{(1-w)\log(1-w)+w\log w\}$$

$$+(1-w)\log(1+\epsilon x)+w\log\frac{\epsilon+x}{\epsilon}\Bigg]. \quad (51)$$

If the original group (unprimed) is a pair of neighboring sites, we have $\gamma=1$, and (51) reduces to Eq. (9), i.e., to the free energy in the approximation discussed in Section 2:

$$F_0(w,T)=-zN_1kT\Bigg[\left(1-\frac{2}{z}\right)$$

$$\times\{(1-w)\log(1-w)+w\log w\}$$

$$+(1-w)\log(1+\epsilon x)w\log\frac{\epsilon+x}{\epsilon}\Bigg]. \quad (52)$$

Inserting (52) back into (51) we get (47).

5. COMPARISON WITH BETHE'S METHOD

Both the quasi-chemical method and Bethe's method start from some assumption regarding the relative probabilities of finding a definite group of sites occupied in different ways by atoms. Although in the two methods the arguments leading to the assumptions are in no way similar the assumptions themselves are closely related. In fact, a comparison of Bethe's local partition function and our function ϕ shows that the quasi-chemical method would give the same probabilities of occurrence of the local configurations as Bethe's method if the free energy (35) has a minimum when

$$(\mu)_{\text{interior sites}} = 1, \qquad (53)$$

i.e., if (37) and (53) are mathematically equivalent. This is not true in general. But it holds approximately when the group of sites under consideration becomes very large. For then,

$$a + b - \frac{2\gamma}{z} \ll \gamma,$$

hence if (53) is true, we should have

$$\left[(\prod_i \mu_i) \left(\frac{1-w}{w} \right)^{a+b-(2\gamma/z)} \right]^{1/\gamma}$$

$$\cong [\prod (\mu)_{\text{interior sites}}]^{1/\gamma} \cong 1,$$

so that by (37)

$$\frac{\partial}{\partial w} F(w, T) \cong 0.$$

To see how the equilibrium free energy $\bar{F}(\bar{w}, T)$ varies with T in high order approximations, we substitute (37) into (35) and obtain by making use of (32)

$$-\frac{F}{zN_1kT} = \frac{1}{\gamma} \log \left(\sum_q \mu_1{}^{q_1} \mu_2{}^{q_2} \cdots \exp \left[-\chi/kT \right] \right)$$

$$+ \frac{1}{\gamma} \left(a + b - \frac{2\gamma}{z} \right) \log (1 - \bar{w}).$$

The last term is very small for large groups, so that by (53)

$$-\frac{F}{zN_1kT} = \frac{1}{\gamma} \log \left(\sum \exp \left[-\chi/kT \right] \right).$$

This shows that in high order approximations the free energy in the quasi-chemical method reduces to the exact form demanded by statistical mechanics.

Recently a modification of Bethe's method has been developed by Wang.[9] This modified Bethe's method bears a very close relation to the quasi-chemical method. The difference between the two lies in the calculation of energy which is discussed in length in Wang's paper.

6. THE NON-INTERFERENCE OF LOCAL CONFIGURATIONS

Let us return to the fundamental assumption of the quasi-chemical method, i.e., to (31) which gives the average numbers of the different local configurations (so far called groups) in the crystal. This equation expresses the exact distribution law of an assembly of molecules (cf. the example in Section 2) which has an energy γ/z times as large as the crystal. Distinguishing all quantities referring to the assembly of molecules by a subscript m, we get from (4),

$$\frac{1}{kT} F(w, T) + \log g(w)$$

$$= \frac{z}{\gamma} \left[\frac{1}{kT} F_m(w, T) + \log g_m(w) \right].$$

But if H is the number of arrangements in the crystal lattice having the given values of $[q_1, q_2, \cdots]$,

$$F(w, T) = -kT \log (\bar{H}) + \bar{E}. \qquad (54)$$

Thus

$$\log \frac{\bar{H}}{g(w)} = \frac{z}{\gamma} \log \frac{\bar{H}_m}{g_m(w)}. \qquad (55)$$

But[*]

$$H_m = \frac{N_1!}{\prod_q [q_1, q_2, \cdots]!}.$$

On substituting this into (55) and dropping the bars we get

$$H = h(w) \left\{ \frac{N_1!}{\prod_q [q_1, q_2, \cdots]!} \right\}^{z/\gamma}, \qquad (56)$$

[9] J. S. Wang, "Approximate partition function in generalized Bethe's theory of superlattices" (to be published).
[*] R. H. Fowler, *Statistical Mechanics*, second edition, 2.6 and 5.11.

where

$$h(w) = g(w)/\{g_m(w)\}^{z/\gamma}. \qquad (57)$$

Equation (56) has been referred to in Fowler and Guggenheim's paper[1] as the mathematical expression of the "hypothesis of the non-interference of local configurations (pairs);" because when $z/\gamma=1$, the number of arrangements in the crystal consistent with the distribution law $[q_1, q_2, \cdots]$ for the groups of sites is, except for the factor $h(r)$, equal to

$$H_m = \frac{N_1!}{\prod_q [q_1, q_2, \cdots]!},$$

which would be the number of arrangements in the crystal having the given values of $[q_1, q_2, \cdots]$ if the N_1 groups in the crystal were *separated* and were filled *independently* with atoms. The term "non-interference" comes from the fact that the N_1 groups are *not separated* but are *interlocked* and *cannot be filled independently* with atoms, i.e., they "interfere" with each other.

To find the value of $g(w)$ we notice that by definition $g_m = \Sigma H_m$. But ΣH_m is the number of arrangements in the *separated* groups considered above if they are to be so filled with atoms that $N_1 w$ of them have wrong atoms on the sites i, where $i = 1, 2, \cdots$. For the N_1 sites i of the N_1 groups,

$$\frac{N_1!}{\{N_1(1-w)\}!(N_1 w)!}$$

different arrangements are possible. Hence

$$g_m = \sum H_m = \sum \frac{N_1!}{\prod_q [q_1, q_2, \cdots]!}$$

$$= \left[\frac{N_1!}{\{(1-w)N_1\}!(N_1 w)!}\right]^{a+b}. \qquad (58)$$

Thus

$$h(w) = \left[\frac{N_1!}{\{N_1(1-w)\}!(N_1 w)!}\right]^{2-(z/\gamma)(a+b)}. \qquad (59)$$

The free energy of the crystal may be obtained from (40), (42), and (45) as:

$$F(w, T) = \bar{E} - \frac{zN_1 kT}{\gamma}\left\{\left(a+b-\frac{2\gamma}{z}\right)\right.$$

$$\times [(1-w) \log (1-w) + w \log w] + \log N_1$$

$$\left. - \sum_q \frac{1}{N_1}\langle q_1, q_2, \cdots \rangle_{Av} \log \langle q_1, q_2, \cdots \rangle_{Av}\right\},$$

which is reducible to Eq. (35) obtained above.

7. SPECIAL CONSIDERATIONS CONCERNING BETHE'S FIRST AND SECOND APPROXIMATIONS

The First Approximation

If an α-site together with its z nearest neighbors are taken as our group of interest, all the sites except the central one are corner sites. Hence their selective variables are all equal to the value of ϵ given in (41). By successive applications of (47) we see that the free energy is exactly $F_0(w, T)$, a fact which has already been pointed by Fowler and Guggenheim.[1] The selective variable of the central site is given by successive applications of (50):

$$\lambda = \frac{w}{1-w}\left(\frac{1+\epsilon x}{\epsilon + x}\right)^z. \qquad (60)$$

The factor $w/(1-w)$ is the selective variable of the central site when it alone forms the group. The equilibrium condition (38) becomes

$$\lambda \epsilon^z = [\bar{w}/(1-\bar{w})]^{z-1}. \qquad (61)$$

But by (60) and (45)

$$\lambda = [w/(1-w)]^{1-z}\epsilon^z.$$

Hence at equilibrium

$$\lambda = 1. \qquad (62)$$

Thus the approximation is completely equivalent to Bethe's first approximation, as already mentioned in Section 5.

The Second Approximation

Now consider the group of sites occurring in Bethe's second approximation. According to Section 4 (iv), the selective variables for the corner sites in the second shell are all equal to the parameter ϵ given by (41). In Bethe's original calcula-

tions, however, the selective variables for the corner sites and the medium sites are made equal, and are found to be different from ϵ. Thus if we use his original method, Eq. (32) would not be satisfied. In other words, the probabilities of occurrence of wrong atoms in the corner and medium sites would be unequal.

For simplicity we shall drop the corner sites and take as our group of interest the central site, the first shell sites and the medium sites with selective variables μ, ν, and λ, respectively. The contribution by the corner sites can be included in the free energy by simple addition, as shown in Section 4. With the notations n and g_{nm} of Bethe[3] we find

$$\phi = \xi \sum_n (x^n + \mu x^{z-n}) P_n(x, \nu, \lambda), \qquad (63)$$

where

$$P_n(x, \nu, \lambda) = \nu^n \sum_m g_{nm}[(1+\lambda)x]^m$$
$$\times (x^2+\lambda)^{([z/2]-1)n-(m/2)}(1+\lambda x^2)^{([z/2]-1)(z-n)-(m/2)}.$$

After the elimination of ξ and μ, (32) becomes

$$zw = \frac{\sum_{l,n}\left\{2x^{l+z-n}\left[(1-w)P_n\lambda\dfrac{\partial}{\partial\lambda}P_l+wP_l\lambda\dfrac{\partial}{\partial\lambda}P_n\right]\right\}}{(z-2)(\sum_n x^n P_n)(\sum_n x^{z-n}P_n)}$$
$$= \frac{\sum_{l,n}\left\{x^{l+z-n}\left[(1-w)P_n\nu\dfrac{\partial}{\partial\nu}P_l+wP_l\nu\dfrac{\partial}{\partial\nu}P_n\right]\right\}}{(\sum_n x^n P_n)(\sum_n x^{z-n}P_n)}. \qquad (64)$$

The free energy is obtained from (35):

$$F(w, T) = -\frac{N_1 kT}{z-1}\left[\tfrac{1}{2}(z^2-4z+4)\right.$$
$$\times \{(1-w)\log(1-w)+w\log w\}$$
$$+(1-w)\log\left(\sum_n x^n P_n\right)$$
$$+w\log\left(\sum_n x^{z-n}P_n\right)-zw\log\nu$$
$$\left.-w\frac{z(z-2)}{2}\log\lambda\right]. \qquad (65)$$

8. APPLICATION TO THE CRYSTAL Cu₃Au

For the face-centered crystal Cu_3Au, we may of course follow Peierls[10] and take as our group

[10] R. Peierls, Proc. Roy. Soc. A154, 207 (1936).

of interest a central site together with its twelve first shell neighbors. The free energy expression would then contain seven selective variables, four of which may be easily eliminated. The resulting expression is very cumbersome and numerical calculations would be laborious. We therefore make a simpler approximation: The group is taken to be four nearest neighbors forming a tetrahedron. (See Fig. 2.) A little
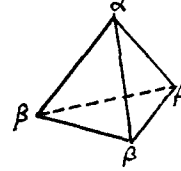

FIG. 2.

geometrical consideration assures us that all such tetrahedrons contain an α-site (for gold atoms) and three β-sites (for copper atoms), an interesting conclusion showing that the tetrahedron might be regarded as a sort of "molecular" structure in a faced-centered lattice with atomic ratio 1:3. Our approximation may thus be reasonably expected to reveal the more important features of the order-disorder transformation in such alloys.

A little reflection shows that the statement made in Section 4 (i) still holds, so that we may put $V_{AA} = V_{BB}$ and $V_{AB} = 0$. Let μ and ν be the parameters (for the wrong atoms) of the β-sites and the α-sites, respectively. Let there be altogether $N = 4N_1$ atoms. It is easy to see that there are $8N_1$ groups in the crystal. When $N_1 w$ atoms on the α-sites are wrong, the equations determining the parameters are

$$8N_1 = \phi = \xi[x^3+3x^2\mu+3x^3\mu^2+x^6\mu^3$$
$$+\nu(x^6+3x^3\mu+3x^2\mu^2+x^3\mu^3)], \quad (66a)$$

$$8N_1 w = \nu\frac{\partial\phi}{\partial\nu} = \xi\nu(x^6+3x^3\mu+3x^2\mu^2+x^3\mu^3), \quad (66b)$$

and

$$8N_1\left(\frac{w}{3}\right)+8N_1\left(\frac{w}{3}\right)+8N_1\left(\frac{w}{3}\right) = \mu\frac{\partial\phi}{\partial\mu}$$
$$= 3x^2\xi\mu[1+2x\mu+x^4\mu^2+\nu(x+2\mu+x\mu^2)], \quad (66c)$$

where x is defined by (27). The energy of the

crystal is [cf. (34)],

$$\bar{E} = \frac{1}{2}kT^2\frac{\partial \phi}{\partial T} + \text{constant};$$ (67)

so that the free energy becomes [cf. (35)]:

$$F(w, T) = -kT[\log g(w) + \frac{1}{2}(\phi - 8N_1 \log \xi$$

$$- 8N_1 w \log \nu - 8N_1 w \log \mu)_{T=\infty}].$$

But

$$\log g(w) = -N_1\left[(1-w)\log(1-w) + w\log w\right.$$

$$\left. + w\log\frac{w}{3} + (3-w)\log\{(3-w)/3\}\right],$$

and at $T = \infty$,

$$\nu = \frac{w}{1-w}, \quad \mu = \frac{w}{3-w}, \quad \xi = 8N_1(1-w)\left(1-\frac{w}{3}\right)^3.$$

Hence

$$-\frac{F(w, T)}{N_1 kT} = -9\log 3 + 4\log(8N_1)$$

$$+ 6w\log w + 3(1-w)\log(1-w)$$

$$+ 3(3-w)\cdot\log(3-w) - 4\log\xi$$

$$- 4w\log\mu - 4w\log\nu. \quad (68)$$

Since ξ and ν can be very easily solved from (66), numerical calculations are quite simple. The value of the free energy is plotted in the accompanying figure (Fig. 3).

The equilibrium value of w is given by [cf. (36) and (37)]:

$$0 = -3\log\frac{(1-\bar{w})(3-\bar{w})}{\bar{w}^2} + 4\log\mu\nu. \quad (69)$$

This is always satisfied at $w = \frac{3}{4}$.* Actual calculation shows that the absolute minimum of the free energy is or is not at $w = \frac{3}{4}$ according as $x > 0.2965$ or $x < 0.2965$. From the form of the

---

* This is not evident from (69) directly. But if we divide the whole crystal into four simple cubic sublattices and introduce a w for each sublattice so that Nw is the number of A atoms on the jth sublattice, $j=1, 2, 3, 4$, it is obvious that the free energy is symmetrical in the w's. From this we infer that (69) is satisfied at $w = \frac{3}{4}$.

curve in Fig. 3 it is seen that the crystal has a critical temperature at which the long-distance order, and hence also the energy, is discontinuous. The critical temperature T_c and the latent heat Q are found to be given by

$$T_c = 0.8228\frac{1}{k}[\frac{1}{2}(V_{AA} + V_{BB}) - V_{AB}],$$

and

$$Q = 0.8824N_1[\frac{1}{2}(V_{AA} + V_{BB}) - V_{AB}].$$

In terms of the total energy change from $T=0$ to $T=\infty$:

$$E_0 = 3N_1[\frac{1}{2}(V_{AA} + V_{BB}) - V_{AB}],$$
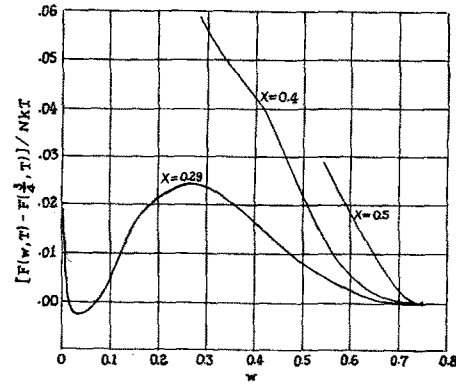
these quantities become, with the usual notation

FIG. 3.

$$R = 4N_1 k,$$

$$T_c = 1.097E_0/R, \quad \text{and} \quad Q = 0.2941E_0.$$

In Bragg and Williams' approximation, they are given by

$$T_c = 2.19E_0/R, \quad \text{and} \quad Q = 0.218E_0;$$

and in Peierls' approximation,[10] they are given by

$$T_c \cong 1.3E_0/R, \quad \text{and} \quad Q \cong 0.36E_0.$$

It will be noticed that because of the lack of a free energy expression Peierls did not give the exact values of these quantities.

In conclusion the author wishes to express his thanks to Professor J. S. Wang for valuable criticism and advice.