PHYSICAL REVIEW VOLUME 67, NUMBERS 3 AND 4 FEBRUARY 1 AND 15, 1945

Approximate Partition Function in Generalized Bethe's Theory of Superlattices

J. S. WANG
Department of Physics, National Tsing Hua University, China*
(Received September 20, 1944)

An approximate expression for the partition function in a generalization of Bethe's theory of superlattices including long range interaction is obtained as an integral of the approximate energy expression in the generalized Bethe's theory. An alternative form of the energy expression is also considered, and higher approximations are treated. The paper ends with an application to the problem of adsorption.

1. INTRODUCTION

SINCE the appearance of Bragg and Williams' first paper many methods for the approximate solution of the problem of superlattices have been devised,[1] of which the method of Bethe is quite a good one. In Bethe's method the equilibrium values of the superlattice order and other quantities are obtained by an indirect method without evaluating the partition function. In some problems, such as the critical condensation phenomenon in adsorption, the true critical temperature in a face-centered cubic lattice, and the separation into phases studied by Easthope,[2] the value of the partition function itself is indispensable for their investigation, and Bethe's theory becomes powerless here.

Some time ago the author put forward a theory[3] of obtaining an approximate expression for the partition function in Bethe's theory, in its generalized form including long range interactions. Upon closer investigation it is found that the theory has two defects. First, the theory assumes that Bethe's method is consistent when applied to the case of neighbor interaction so that the condition of integrability is satisfied and a partition function always exists. Although this is true in the cases considered then, it is found that in the case of Bethe's second approximation and in the case of face-centered cubic lattice this is not true. Secondly, the numerical work involved in the calculation of the partition function is too laborious to be of any value in practical application.

In this paper a modification of the theory is given. The present theory is perfectly general and applicable in all cases. Moreover, the numerical work has been lessened considerably so that practical applications are possible. The general theory is given in Section 3 and Section 4 below.

In the application of Bethe's theory one works with what may be called the local grand partition function, instead of the ordinary partition function. The use of the grand partition function in the theory of superlattices has been justified in a general way in the paper of the author cited above. It is found, however, that a slight modification of the theory there given helps to clarify some points concerned with the procedure of obtaining the approximate partition function from Bethe's theory. This is done in Section 2.

In the problem of adsorption the number of adsorbed atoms depends on the presence of the gas from which the adsorbed atoms come, and it is evident that the grand partition function should be used. But since the grand partition function is also used in the theory of superlattices, the theory of adsorption is mathematically the same as the theory of superlattices. The corresponding quantities in the two theories have, however, different meanings, and some of them have to be treated differently. Thus the problem of adsorption receives a special treatment in Section 5.

The notation used in the present paper is nearly the same as that employed in the previous one. To facilitate the reading of the paper it is perhaps better to explain some of the basic quantities first. We consider a binary alloy composed of two kinds of atoms A and B with a total

* At present a member of National Southwest Associated University, Kunming, China.

[1] See a general review by F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).

[2] C. E. Easthope, Proc. Camb. Phil. Soc. **34**, 68 (1938).

[3] J. S. Wang, "Free energy in the statistical theory of order-disorder transformation," Science Report of National Tsing Hua University [A], **IV**, Nos. 4–6 (April, 1941), (printed but failed to appear).

number N. The number of A atoms will be denoted by $N\theta$, and that of B atoms by $N(1-\theta)$. The N sites occupied by the N atoms are divided into two classes α and β, the number of α-sites is Nr and that of β-sites $N(1-r)$. The value of r is $\frac{1}{2}$ for a simple cubic and a body-centered cubic lattice, and is $\frac{1}{4}$ for a face-centered cubic lattice ($r=\frac{1}{2}$ is also possible, e.g., AuCu). To simplify the writing we sometimes use the abbreviation N_α for Nr, and N_β for $N(1-r)$. In any given state of order let there be $Nr\theta_\alpha$ A atoms in α-sites and $N(1-r)\theta_\beta$ A atoms in β-sites. Since the total number of A atoms is $N\theta$, we have

$$r\theta_\alpha+(1-r)\theta_\beta=\theta. \tag{1}$$

The degree of order s is defined by

$$s=\theta_\alpha-\theta_\beta. \tag{2}$$

This definition of s reduces to that of Bragg and Williams in the special case of $\theta=r$.

Other symbols will be explained when they are first introduced.

Recently a very interesting generalization of the quasi-chemical method of Fowler and Guggenheim has been made by Mr. C. N. Yang.[4] This method is very powerful, and perhaps Bethe's method will be superseded by it. The chief merit of the method is that the approximate partition function can be easily obtained as a closed expression. Mr. Yang is now making further investigation of the method.

2. THE GRAND PARTITION FUNCTION

The (configuration) energy of the alloy in the general case of long range interaction has been found to be[5]

$$\begin{aligned} &E=\tfrac{1}{2}\sum Z_\nu V_\nu^{BB}+\theta\sum Z_\nu(V_\nu^{AB}-V_\nu^{BB})+E_1,\\ &E_1=\sum M_\nu^{AA}V_\nu, \quad V_\nu=V_\nu^{AA}+V_\nu^{BB}-2V_\nu^{AB}, \end{aligned} \tag{3}$$

where M_ν^{AA} is the number of AA pairs of atoms situated at a distance a_ν apart, $\nu=1, 2, 3, \cdots$; V_ν^{AA}, V_ν^{BB}, V_ν^{AB} are the interaction energies of AA, BB, AB pairs at the distance a_ν; Z_ν is the sum of z_ν for all sites of the crystal, z_ν being the number of sites situated at a distance a_ν from a given site. The sign $\sum$ in (3) denotes a summation over the values of ν.

From the above expression for the energy the ordinary partition function is obtained as

$$\begin{aligned} P_\theta=&\exp\left(-\tfrac{1}{2}\sum Z_\nu V_\nu^{BB}/kT\right)\\ &\times\{\exp\left[-\sum Z_\nu(V_\nu^{AB}-V_\nu^{BB})/kT\right]\}^\theta\\ &\times\sum Q(\theta_\alpha,\theta_\beta,T), \end{aligned} \tag{4}$$

$$Q(\theta_\alpha,\theta_\beta,T)=\sum\gamma_M\exp\left(-\sum M_\nu^{AA}V_\nu/kT\right),$$

where γ_M is the number of arrangements for given values of θ_α, θ_β, M_ν^{AA}. The summation of $Q(\theta_\alpha,\theta_\beta,T)$ in the expression for P_θ is taken over all θ_α and θ_β satisfying the relation (1) with a fixed θ, and the summation in the expression for $Q(\theta_\alpha,\theta_\beta,T)$ is taken over all possible values of M_ν^{AA} for given θ_α and θ_β.

The purpose of the present paper is to obtain an approximate expression for $Q(\theta_\alpha,\theta_\beta,T)$ in Bethe's method.

The equilibrium values of θ_α, θ_β, and E_1 are given in terms of Q by the usual formulae

$$\frac{\partial}{\partial s}\log Q=0,$$

or

$$\frac{1}{r}\frac{\partial}{\partial\theta_\alpha}\log Q=\frac{1}{1-r}\frac{\partial}{\partial\theta_\beta}\log Q, \tag{5}$$

$$E_1=kT^2\frac{\partial}{\partial T}\log Q. \tag{6}$$

These equations can be deduced from the standard formula in terms of P_θ on replacing P_θ by its maximum term Q.

Let us now form the grand partition function K by considering the number of A atoms as variable. We have

$$\begin{aligned} &K=\sum\lambda^{N\theta}P_\theta=\exp\left(-\tfrac{1}{2}\sum Z_\nu V_\nu^{BB}/kT\right)K_1,\\ &K_1=\sum\xi^{N_\alpha\theta_\alpha+N_\beta\theta_\beta}Q(\theta_\alpha,\theta_\beta,T),\\ &\xi=\lambda\exp\left[-\sum Z_\nu(V_\nu^{AB}-V_\nu^{BB})/NkT\right], \end{aligned} \tag{7}$$

where the summation in K_1 is taken over all possible values of θ_α and θ_β. In order to obtain the equilibrium values of θ_α, θ_β, E_1 from the grand partition function, it is more convenient to introduce two ξ's, ξ_α and ξ_β, say, such that K_1 becomes

$$K_1=\sum\xi_\alpha^{N_\alpha\theta_\alpha}\xi_\beta^{N_\beta\theta_\beta}Q(\theta_\alpha,\theta_\beta,T). \tag{8}$$

[4] C. N. Yang, Chinese J. Phys. (in press).

[5] Equation (3) is given in J. S. Wang, reference 3, Eq. (36). It can be easily obtained by the procedure given in J. S. Wang, Proc. Roy. Soc. **A168**, 56 (1938), especially p. 58.

Then the usual formulae for the equilibrium values of θ_α, θ_β, E_1 are

$$\begin{aligned} Nr\theta_\alpha &= \xi_\alpha \frac{\partial}{\partial \xi_\alpha} \log K_1, \\ N(1-r)\theta_\beta &= \xi_\beta \frac{\partial}{\partial \xi_\beta} \log K_1, \end{aligned} \tag{9}$$

$$E_1 = kT^2 \frac{\partial}{\partial T} \log K_1, \tag{10}$$

and in the final result we must put

$$\xi_\alpha = \xi_\beta = \xi. \tag{11}$$

To prove that the equilibrium values determined from the grand partition function K_1 by means of (9)–(11) are the same as those calculated from the ordinary partition function Q by means of (5) and (6), we may adopt the procedure of replacing K_1 by its maximum term. The maximum term in the summand of K_1 given by (8) occurs at the values of θ_α and θ_β satisfying

$$\begin{aligned} \log \xi_\alpha + \frac{1}{N_\alpha} \frac{\partial}{\partial \theta_\alpha} \log Q = 0, \\ \log \xi_\beta + \frac{1}{N_\beta} \frac{\partial}{\partial \theta_\beta} \log Q = 0. \end{aligned} \tag{12}$$

When K_1 is replaced by its maximum term, Eqs. (9) become identities, Eq. (10) reduces to (6), and Eq. (11) reduces to (5) with the help of (12).

Thus the use of grand partition function is justified.

A more rigorous proof of the above result by means of contour integrals has been given in the paper of the author cited above. This proof will be briefly indicated here with a slight change. Consider the series

$$S(x, y) = \sum x^{N_\alpha \theta_\alpha} y^{N_\beta \theta_\beta} Q(\theta_\alpha, \theta_\beta, T).$$

Thus K_1 given by (8) is $S(\xi_\alpha, \xi_\beta)$ and that given by (7) is $S(\xi, \xi)$. By Cauchy's theorem we have

$$Q(\theta_\alpha, \theta_\beta, T) = \frac{1}{(2\pi i)^2} \oint\oint \frac{S(x, y)}{x^{N_\alpha \theta_\alpha + 1} y^{N_\beta \theta_\beta + 1}} dx\, dy.$$

By the general theory of statistical mechanics given in Fowler's book, the integrand has a unique maximum modulus at the saddle point $x = \xi_\alpha$, $y = \xi_\beta$ determined by

$$\begin{aligned} N_\alpha \theta_\alpha &= \xi_\alpha \frac{\partial}{\partial \xi_\alpha} \log S(\xi_\alpha, \xi_\beta), \\ N_\beta \theta_\beta &= \xi_\beta \frac{\partial}{\partial \xi_\beta} \log S(\xi_\alpha, \xi_\beta). \end{aligned}$$

This proves (9). Differentiating Q with respect to θ_α we have

$$\frac{1}{N_\alpha} \frac{\partial Q}{\partial \theta_\alpha} = \frac{1}{(2\pi i)^2} \oint\oint (-\log x) \frac{S(x, y)}{x^{N_\alpha \theta_\alpha + 1} y^{N_\beta \theta_\beta + 1}} dx\, dy.$$

There is a similar equation for $\partial Q / \partial \theta_\beta$. Using the method of steepest descent we obtain (12).

To determine the equilibrium value of θ_α for a given value of θ, we put $y = x$ in $S(x, y)$ and obtain

$$\sum{}' Q(\theta_\alpha, \theta_\beta, T) = \frac{1}{2\pi i} \oint \frac{S(x, x)}{x^{N\theta + 1}} dx$$

and

$$\sum{}' N_\alpha \theta_\alpha Q(\theta_\alpha, \theta_\beta, T) = \frac{1}{2\pi i} \oint \left[x \frac{\partial}{\partial x} \log S(x, y) \right]_{y=x} \frac{S(x, x)}{x^{N\theta + 1}} dx,$$

where the symbol $\sum'$ denotes summation over θ_α with θ_β given as a function of θ_α by (1). Hence the equilibrium value of $N_\alpha \theta_\alpha$ is given by

$$N_\alpha \theta_\alpha = \left[\xi_\alpha \frac{\partial}{\partial \xi_\alpha} \log S(\xi_\alpha, \xi_\beta) \right]_{\xi_\alpha = \xi_\beta = \xi},$$

where ξ is the saddle point determined by

$$N\theta = \xi \frac{\partial}{\partial \xi} \log S(\xi, \xi).$$

This proves (11).

3. APPROXIMATE PARTITION FUNCTION

In Bethe's method one fixes one's attention on a group of quite a small number of sites and constructs the grand partition function for these sites; the effect of omitting other sites of the crystal is taken account of by introducing suitable parameters for the outermost sites of the group. The group of sites are usually divided into the central site, the first shell sites which are nearest neighbors to the central site, the second shell sites which are nearest neighbors to the first shell sites, and so on. In the first approximation the group of sites considered include only the central site and the first shell.

The extension of Bethe's first approximation to include long range interaction has been given in an earlier paper,[6] and the results will be quoted here. The equilibrium values of θ_α and θ_β are given by

$$\begin{aligned}\frac{\theta_\alpha}{1-\theta_\alpha}&=\xi_\alpha \exp(-U_\alpha/kT)\frac{F_\eta}{F},\\ \frac{\theta_\beta}{1-\theta_\beta}&=\xi_\beta \exp(-U_\beta/kT)\frac{G_\eta}{G},\end{aligned}\tag{13}$$

where F and G are functions of the parameters ϵ_α, ϵ_β, and ζ_α, ζ_β, respectively, and the subscript η attached to a function means that the variables ϵ_α, etc. in that function are changed to $\eta_1\epsilon_\alpha$, etc., where

$$\eta_\nu=\exp(-V_\nu/kT), \qquad \nu=1, 2, \cdots.$$

The parameters ϵ_α, ϵ_β, ζ_α, ζ_β are determined by the following equations:

$$\begin{aligned}z_{\alpha\alpha}\theta_\alpha&=(1-\theta_\alpha)\varphi+\theta_\alpha\varphi_\eta,\\ z_{\alpha\beta}\theta_\beta&=(1-\theta_\alpha)\psi+\theta_\alpha\psi_\eta,\end{aligned}\tag{14}$$

$$\begin{aligned}z_{\beta\alpha}\theta_\alpha&=(1-\theta_\beta)\omega+\theta_\beta\omega_\eta,\\ z_{\beta\beta}\theta_\beta&=(1-\theta_\beta)\chi+\theta_\beta\chi_\eta,\end{aligned}\tag{15}$$

where

$$\varphi=\epsilon_\alpha\frac{\partial}{\partial\epsilon_\alpha}\log F, \quad \psi=\epsilon_\beta\frac{\partial}{\partial\epsilon_\beta}\log F;$$

$$\omega=\zeta_\alpha\frac{\partial}{\partial\zeta_\alpha}\log G, \quad \chi=\zeta_\beta\frac{\partial}{\partial\zeta_\beta}\log G.$$

The quantities U_α and U_β are given by

$$\begin{aligned}U_\alpha&=(U_{\alpha\alpha}-z_{\alpha\alpha}V_1)\theta_\alpha+(U_{\alpha\beta}-z_{\alpha\beta}V_1)\theta_\beta,\\ U_\beta&=(U_{\beta\alpha}-z_{\beta\alpha}V_1)\theta_\alpha+(U_{\beta\beta}-z_{\beta\beta}V_1)\theta_\beta.\end{aligned}\tag{16}$$

The equilibrium value of the energy E_1 is given by

$$\begin{aligned}E_1=&\tfrac{1}{2}N_\alpha\theta_\alpha\{(\varphi_\eta+\psi_\eta)V_1+U_\alpha\}\\ &+\tfrac{1}{2}N_\beta\theta_\beta\{(\omega_\eta+\chi_\eta)V_1+U_\beta\}.\end{aligned}\tag{17}$$

In order to obtain an approximate expression for the partition function Q consistent with Bethe's approximation, it seems that a natural way would be to assume that the equilibrium values of θ_α, θ_β, and E_1 given by (13) and (17) are correct, and to substitute the values of ξ_α and ξ_β given by (13) into (12) and the value of E_1 given by (17) into (6) to obtain Q by integration. Unfortunately this procedure does not work, because the system of differential equations for Q so obtained does not, in general, satisfy the condition of integrability.

In my previous paper this difficulty was avoided by regarding U_α and U_β as unknown functions to be determined by the condition of integrability. A system of partial differential equations for these two quantities was thus obtained, whose solutions were made unique by the condition that U_α and U_β reduce to the expressions given by (16) in the special case $\theta_\alpha=\theta_\beta$ and in the special case $\theta=1$. These conditions are evidently obtained from physical requirement.

The physical basis for the above procedure is that the assumption of a uniform distribution of A atoms with a fraction θ_α on α-sites and a fraction θ_β on β-sites (outside the small group of sites) used in deriving (16) is not true and should be replaced by the condition of integrability. But the assumption is certainly true in the special cases $\theta_\alpha=\theta_\beta$ and $\theta=1$, and so (16) serves as a boundary condition.

It has been mentioned in the Introduction that the above theory suffers from two defects. The most serious defect is that in the special case of neighbor interaction the two quantities U_α and U_β should be zero, but then the condition of integrability is not satisfied in general. If we again introduce U_α and U_β into the formula to restore the condition of integrability, it is hard to interpret their physical significance. A second defect is that the numerical work involved in calculating U_α and U_β is too laborious.

We shall now modify the theory by preserving formulae (16) and (17) for U_α, U_β, and E_1, but regarding ξ_α and ξ_β given by (13) as incorrect. *We shall obtain Q by integrating (6), and take (12) as the equations determining ξ_α and ξ_β.* To integrate (6) we remember that as $T\to\infty$, Q approaches the value

$$g=g(\theta_\alpha, \theta_\beta)=\binom{N_\alpha}{N_\alpha\theta_\alpha}\binom{N_\beta}{N_\beta\theta_\beta}.\tag{18}$$

Hence

$$\log Q=\log g-\int_0^{1/T}\frac{E_1}{k}d\left(\frac{1}{T}\right),\tag{19}$$

in which the value of E_1 given by (17) should be used.

[6] J. S. Wang, Proc. Roy. Soc. **A168**, 56 (1938).

When Q has been obtained in this way, the equilibrium values of θ_α and θ_β will be given by (5), instead of by (13) and (11).

We shall now transform the integral in (19) to a simpler form. Let us denote the local grand partition function for central α-site by K_α, and write λ_α in place of $\xi_\alpha \exp(-U_\alpha/kT)$, remembering that λ_α has no real connection with ξ_α in (12) owing to the breakdown of the integrability condition. Similarly, we have K_β and λ_β for central β-site. Thus

$$K_\alpha = F + \lambda_\alpha F_\eta, \quad K_\beta = G + \lambda_\beta G_\eta. \tag{20}$$

The quantities λ_α, ϵ_α, etc., are determined as functions of θ_α, θ_β, T by (13)–(15). As $T \to \infty$, these quantities reduce to

$$\lambda_\alpha = \epsilon_\alpha = \zeta_\alpha = \frac{\theta_\alpha}{1-\theta_\alpha}, \quad \lambda_\beta = \epsilon_\beta = \zeta_\beta = \frac{\theta_\beta}{1-\theta_\beta}. \tag{21}$$

Then the result of integrating (19) is

$$\begin{aligned}\log Q = \log g &- \tfrac{1}{2}(N_\alpha\theta_\alpha U_\alpha + N_\beta\theta_\beta U_\beta)/kT + \tfrac{1}{2}N_\alpha\{\log K_\alpha - \theta_\alpha \log \lambda_\alpha - z_{\alpha\alpha}\theta_\alpha \log \epsilon_\alpha - z_{\alpha\beta}\theta_\beta \log \epsilon_\beta\} \\ &+ \tfrac{1}{2}N_\beta\{\log K_\beta - \theta_\beta \log \lambda_\beta - z_{\beta\alpha}\theta_\alpha \log \zeta_\alpha - z_{\beta\beta}\theta_\beta \log \zeta_\beta\} \\ &+ \tfrac{1}{2}(z+1)[N_\alpha\theta_\alpha \log \theta_\alpha + N_\alpha(1-\theta_\alpha)\log(1-\theta_\alpha) + N_\beta\theta_\beta \log \theta_\beta + N_\beta(1-\theta_\beta)\log(1-\theta_\beta)] \\ &+ \tfrac{1}{2}\int_0^{1/T} \{N_\alpha(1-\theta_\alpha)F^* + N_\alpha\theta_\alpha F_\eta^* + N_\beta(1-\theta_\beta)G^* + N_\beta\theta_\beta G_\eta^*\}\frac{V_1}{k} d\left(\frac{1}{T}\right),\end{aligned} \tag{22}$$

where F^* is defined by

$$F^* = \frac{kT^2}{V_1}\frac{\partial}{\partial T}\log F(\epsilon_\alpha, \epsilon_\beta). \tag{23}$$

Since it follows from Stirling's formula that

$$\log g = -N_\alpha[\theta_\alpha \log \theta_\alpha + (1-\theta_\alpha)\log(1-\theta_\alpha)] - N_\beta[\theta_\beta \log \theta_\beta + (1-\theta_\beta)\log(1-\theta_\beta)], \tag{24}$$

we have

$$\begin{aligned}\log Q = \left(1-\frac{z}{2}\right)\log g &- \tfrac{1}{2}(N_\alpha\theta_\alpha U_\alpha + N_\beta\theta_\beta U_\beta)/kT + \tfrac{1}{2}N_\alpha[\theta_\alpha \log F_\eta + (1-\theta_\alpha)\log F \\ &- z_{\alpha\alpha}\theta_\alpha \log \epsilon_\alpha - z_{\alpha\beta}\theta_\beta \log \epsilon_\beta] + \tfrac{1}{2}N_\beta[\theta_\beta \log G_\eta + (1-\theta_\beta)\log G - z_{\beta\alpha}\theta_\alpha \log \zeta_\alpha - z_{\beta\beta}\theta_\beta \log \zeta_\beta] \\ &+ \tfrac{1}{2}\int_{\eta_1}^1 \{N_\alpha(1-\theta_\alpha)F^* + N_\alpha\theta_\alpha F_\eta^* + N_\beta(1-\theta_\beta)G^* + N_\beta\theta_\beta G_\eta^*\}\frac{d\eta_1}{\eta_1}.\end{aligned} \tag{25}$$

The last integral should be evaluated by numerical integration.

4. HIGHER APPROXIMATIONS

The method of obtaining the partition function in the first approximation given in the preceding section is evidently applicable to higher approximations. The group of sites considered in the general case is divided into the central site, the first shell sites which are at a distance a_1 from the central site, the sites which are at a distance a_2 from the central site, and so on. Let the numbers of α- and β-sites among those which are at a distance a_ν from the central site be $z_{\nu\alpha\alpha}$, $z_{\nu\alpha\beta}$ if the central site is an α, and $z_{\nu\beta\alpha}$, $z_{\nu\beta\beta}$ if the central site is a β. These numbers satisfy the relations

$$z_{\nu\alpha\alpha} + z_{\nu\alpha\beta} = z_{\nu\beta\alpha} + z_{\nu\beta\beta} = z_\nu. \tag{26}$$

Let us consider the group with a central α-site. We shall introduce a parameter λ_α for an A atom on the central site, and parameters $\epsilon_{\nu\alpha}$ and $\epsilon_{\nu\beta}$, respectively, for an A atom on the α- and β-sites which are at a distance a_ν from the central site. In any distribution of A atoms in the group of sites considered, let there be n_0 A atoms in the central site ($n_0 = 1$ or 0 according as the central site is occupied or not), $n_\nu = n_\nu' + n_\nu''$ A atoms in the sites at a distance a_ν from the central site, n_ν' being the number in the α-sites and n_ν'' the number in the β-sites of them. Let m_ν be the number of pairs of A atoms in the

group at a distance a_ν apart, and let γ_α be the number of arrangements for a given set of values n_ν', n_ν'', and m_ν. Then the local grand partition function is

$$K_\alpha = F + \lambda_\alpha F_\eta,$$

with

$$F = F(\epsilon_{1\alpha}, \epsilon_{1\beta}, \epsilon_{2\alpha}, \epsilon_{2\beta}, \cdots) = \sum \gamma_\alpha \prod_{\nu=1}^{\kappa} (\epsilon_{\nu\alpha}^{n_\nu'} \epsilon_{\nu\beta}^{n_\nu''} \eta_\nu^{m_\nu'}) \prod_{\nu>\kappa} \eta_\nu^{m_\nu}, \tag{27}$$

$$F_\eta = F(\eta_1\epsilon_{1\alpha}, \eta_1\epsilon_{1\beta}, \eta_2\epsilon_{2\alpha}, \eta_2\epsilon_{2\beta}, \cdots),$$

in which the suffix κ denotes the outermost sites of the group and the relations

$$m_\nu = n_0 n_\nu + m_\nu', \quad (\nu \leqq \kappa)$$

have been used.

The parameters will be determined by the conditions

$$\theta_\alpha = \lambda_\alpha \frac{\partial}{\partial \lambda_\alpha} \log K_\alpha, \tag{28}$$

$$z_{\nu\alpha\alpha}\theta_\alpha = \epsilon_{\nu\alpha}\frac{\partial}{\partial \epsilon_{\nu\alpha}} \log K_\alpha, \quad z_{\nu\alpha\beta}\theta_\beta = \epsilon_{\nu\beta}\frac{\partial}{\partial \epsilon_{\nu\beta}} \log K_\alpha. \tag{28$_\nu$}$$

These equations will also be expressed in a new notation, analogous to (14),

$$z_{\nu\alpha\alpha}\theta_\alpha = (1-\theta_\alpha)\varphi_\nu + \theta_\alpha \varphi_{\nu\eta}, \quad z_{\nu\alpha\beta}\theta_\beta = (1-\theta_\alpha)\psi_\nu + \theta_\alpha \psi_{\nu\eta}, \tag{29}$$

where

$$\varphi_\nu = \epsilon_{\nu\alpha}\frac{\partial}{\partial \epsilon_{\nu\alpha}} \log F, \quad \psi_\nu = \epsilon_{\nu\beta}\frac{\partial}{\partial \epsilon_{\nu\beta}} \log F.$$

There are a similar set of equations for the group with central β-site.

The present formulation of the higher approximations is different from Bethe's original formulation and from the modified one given by the author[7] for the case of adsorption with long range interaction. Bethe considered only the special case of equal A and B atoms and treated them symmetrically, so that in the first approximation he put $\lambda_\alpha = 1$ and in the second approximation he put $\lambda_\alpha = 1$, $\epsilon_{1\beta} = 1$ (in Bethe's case there are no α-sites in the first shell surrounding a central α-site). When the numbers of A and B atoms are not equal, it is more convenient to concentrate attention solely on A atoms and to introduce a λ_α different from unity, as first done by Peierls.[8] Such a procedure also works in the case of equal A and B atoms.[9] Peierls put $\lambda_\alpha = \xi_\alpha = \xi$ as the condition of equilibrium. This was also followed by the author[6,9] in the case of long range interaction by putting $\lambda_\alpha = \xi \exp(-U_\alpha/kT)$, the second factor being introduced to take account of the influence of exterior sites. Since this does not lead to consistent results when the partition function is sought, we have replaced it by Eq. (5) in the preceding section. In accordance with a procedure adopted in the theory of adsorption with long range interaction,[7] a natural generalization to higher approximations would be to put

$$\epsilon_{\nu\alpha} = \xi_\alpha \exp(-U_{\nu\alpha}'/kT), \quad \epsilon_{\nu\beta} = \xi_\beta \exp(-U_{\nu\alpha}''/kT), \tag{30}$$

where $U_{\nu\alpha}'$ is the energy owing to exterior sites on an α-site at a distance a_ν from a central α-site, and $U_{\nu\alpha}''$ is the energy owing to exterior sites on a β-site at a distance a_ν from a central α-site. Such a generalization evidently fails for the same reason as Peierls' assumption on λ_α does. Therefore we replace it by the condition (28$_\nu$).

---

[7] J. S. Wang, Proc. Camb. Phil. Soc. **34**, 238 (1938).
[8] R. Peierls, Proc. Roy. Soc. **A154**, 207 (1936).
[9] See J. S. Wang, Proc. Roy. Soc. **A168**, 68 (1938).

The approximate partition function will still be given by (19), in which the energy now has the form

$$E_1=\tfrac{1}{2}N_\alpha\theta_\alpha\left\{\sum_{\nu=1}^{\kappa}(\varphi_{\nu\eta}+\psi_{\nu\eta})\,V_\nu+U_\alpha\right\}+\tfrac{1}{2}N_\beta\theta_\beta\left\{\sum_{\nu=1}^{\kappa}(\omega_{\nu\eta}+\chi_{\nu\eta})\,V_\nu+U_\beta\right\}, \tag{31}$$

where U_α and U_β are given by

$$\begin{aligned}U_\alpha&=\left(U_{\alpha\alpha}-\sum_{\nu=1}^{\kappa}z_{\nu\alpha\alpha}V_\nu\right)\theta_\alpha+\left(U_{\alpha\beta}-\sum_{\nu=1}^{\kappa}z_{\nu\alpha\beta}V_\nu\right)\theta_\beta,\\ U_\beta&=\left(U_{\beta\alpha}-\sum_{\nu=1}^{\kappa}z_{\nu\beta\alpha}V_\nu\right)\theta_\alpha+\left(U_{\beta\beta}-\sum_{\nu=1}^{\kappa}z_{\nu\beta\beta}V_\nu\right)\theta_\beta.\end{aligned} \tag{32}$$

If we introduce the notation

$$F^*=\frac{kT^2}{V_1}\frac{\partial}{\partial T}\log F(\epsilon_{1\alpha},\,\epsilon_{1\beta},\,\epsilon_{2\alpha},\,\epsilon_{2\beta},\,\cdots)=\frac{1}{FV_1}\sum\gamma_\alpha\left(\sum_{\nu=1}^{\kappa}m_\nu'V_\nu+\sum_{\nu>\kappa}m_\nu V_\nu\right)\prod_{\nu=1}^{\kappa}(\epsilon_{\nu\alpha}^{n_\nu'}\epsilon_{\nu\beta}^{n_\nu''}\eta_\nu^{m_\nu'})\prod_{\nu>\kappa}\eta_\nu^{m_\nu} \tag{33}$$

similar to (23), then

$$\begin{aligned}\log Q=&\log g-\tfrac{1}{2}\left(1+\sum_{\nu=1}^{\kappa}z_\nu\right)\log g-\tfrac{1}{2}(N_\alpha\theta_\alpha U_\alpha+N_\beta\theta_\beta U_\beta)/kT\\ &+\tfrac{1}{2}N_\alpha\left\{\log K_\alpha-\theta_\alpha\log\lambda_\alpha-\sum_{\nu=1}^{\kappa}z_{\nu\alpha\alpha}\theta_\alpha\log\epsilon_{\nu\alpha}-\sum z_{\nu\alpha\beta}\theta_\beta\log\epsilon_{\nu\beta}\right\}\\ &+\tfrac{1}{2}N_\beta\{\log K_\beta-\theta_\beta\log\lambda_\beta-\sum z_{\nu\beta\alpha}\theta_\alpha\log\zeta_{\nu\alpha}-\sum z_{\nu\beta\beta}\theta_\beta\log\zeta_{\nu\beta}\}\\ &+\tfrac{1}{2}\int_0^{1/T}\{N_\alpha(1-\theta_\alpha)F^*+N_\alpha\theta_\alpha F_\eta^*+N_\beta(1-\theta_\beta)G^*+N_\beta\theta_\beta G_\eta^*\}\frac{V_1}{k}\alpha\left(\frac{1}{T}\right).\end{aligned} \tag{34}$$

The actual calculation may sometimes be simplified by assuming reasonable values for some of the $\epsilon_{\nu\alpha}$, etc., and dropping the corresponding equations in (28_ν). Thus in the case of the second approximation, for example, one may assume $\epsilon_{1\alpha}$ and $\epsilon_{1\beta}$ to be given by (30), with ξ_α, ξ_β determined by the first approximation, and drop the corresponding equation (28_1). In a certain sense, it is better to drop the equation (28_2) and retain (28_1) to determine $\epsilon_{2\alpha}$ and $\epsilon_{2\beta}$. This alternative procedure has the advantage in making the approximation better for the central site and the first shell, and actually corresponds to Bethe's original procedure. Bethe also assumed one and the same parameter for A atoms in the corner and medium sites of the second shell. This procedure has the disadvantage of losing the symmetry, and it is perhaps still better to retain all the equations (28_ν), in which the corner and medium sites are distinguished by the difference in ν, i.e., in their distances from the central site.

A different way of calculating the energy has been adopted by Mr. Yang in his generalization of the quasi-chemical method. His method can also be slightly modified to apply to the present problem. In obtaining the expression (31) for the energy we have assumed that the equilibrium values of M_ν^{AA} for $\nu\leqq\kappa$ are given by

$$\tfrac{1}{2}N_\alpha\langle(n_0n_\nu)_\alpha\rangle_{Av}+\tfrac{1}{2}N_\beta\langle(n_0n_\nu)_\beta\rangle_{Av}.$$

We shall now modify this assumption for $\nu=1$ but shall retain the assumption for $\nu>1$. In the case of $\nu=1$, let us assume that $\tilde{m}_1$ is the same fraction of μ as $\langle M_1^{AA}\rangle_{Av}$ is of $\frac{1}{2}Z_1=\frac{1}{2}Nz$, where μ and $\frac{1}{2}Nz$ are the total numbers of pairs of neighboring sites for the group and for the whole crystal, respectively.[10]

[10] The value of μ is the same for central α- and for central β-site on account of equal z for them.

Under this assumption, we have

$$kT^2\frac{\partial}{\partial T}\log K_\alpha=\frac{1}{K_\alpha}\sum\gamma_\alpha(\sum m_\nu V_\nu)\lambda_\alpha{}^{n_0}\prod_{\nu=1}^{\kappa}\epsilon_{\nu\alpha}{}^{n_\nu'}\epsilon_{\nu\beta}{}^{n_\nu''}\prod_\nu\eta_\nu{}^{m_\nu}$$

$$=\sum\bar{m}_\nu V_\nu=\frac{2\mu}{Nz}\langle M_1{}^{AA}\rangle_{Av}V_1+\sum_{\nu>1}\bar{m}_\nu V_\nu.$$

Summing over all central α-groups and all central β-groups we obtain

$$N_\alpha kT^2\frac{\partial}{\partial T}\log K_\alpha+N_\beta kT^2\frac{\partial}{\partial T}\log K_\beta=\frac{2\mu}{z}\langle M_1{}^{AA}\rangle_{Av}V_1+N_\alpha(\sum_{\nu>1}\bar{m}_\nu V_\nu)_\alpha+N_\beta(\sum_{\nu>1}\bar{m}_\nu V_\nu)_\beta.$$

Hence the modified energy expression is

$$E_1=\frac{z}{2\mu}kT^2\frac{\partial}{\partial T}(N_\alpha\log K_\alpha+N_\beta\log K_\beta)-\frac{z}{2\mu}\{N_\alpha(\sum_{\nu>1}\bar{m}_\nu V_\nu)_\alpha+N_\beta(\sum_{\nu>1}\bar{m}_\nu V_\nu)_\beta\}$$
$$+\tfrac{1}{2}N_\alpha\theta_\alpha\Big\{\sum_{\nu=2}^{\kappa}(\varphi_{\nu\eta}+\psi_{\nu\eta})V_\nu+U_\alpha\Big\}+\tfrac{1}{2}N_\beta\theta_\beta\Big\{\sum_{\nu=2}^{\kappa}(\omega_{\nu\eta}+\chi_{\nu\eta})V_\nu+U_\beta\Big\}. \quad (35)$$

When this expression is substituted into (19), the partition function becomes, after integration,

$$\log Q=\log g-\frac{z}{2\mu}(1+\sum z_\nu)\log g-\tfrac{1}{2}(N_\alpha\theta_\alpha U_\alpha+N_\beta\theta_\beta U_\beta)/kT$$
$$+\frac{z}{2\mu}N_\alpha\{\log K_\alpha-\theta_\alpha\log\lambda_\alpha-\sum z_{\nu\alpha\alpha}\theta_\alpha\log\epsilon_{\nu\alpha}-\sum z_{\nu\alpha\beta}\theta_\beta\log\epsilon_{\nu\beta}\}$$
$$+\frac{z}{2\mu}N_\beta\{\log K_\beta-\theta_\beta\log\lambda_\beta-\sum z_{\nu\beta\alpha}\theta_\alpha\log\zeta_{\nu\alpha}-\sum z_{\nu\beta\beta}\theta_\beta\log\zeta_{\nu\beta}\}$$
$$+\frac{z}{2\mu k}\sum_{\nu>1}V_\nu\int_0^{1/T}\{N_\alpha(\bar{m}_\nu)_\alpha+N_\beta(\bar{m}_\nu)_\beta\}\,d\left(\frac{1}{T}\right)$$
$$-\frac{1}{2}\sum_{\nu=2}^{\kappa}\frac{V_\nu}{k}\int_0^{1/T}\{N_\alpha\theta_\alpha(\varphi_{\nu\eta}+\psi_{\nu\eta})+N_\beta\theta_\beta(\omega_{\nu\eta}+\chi_{\nu\eta})\}d\left(\frac{1}{T}\right). \quad (36)$$

The advantage of this alternative formulation in the case of neighbor interaction is evident. For then the integral in (36) is identically zero and the partition function is obtained as a closed expression. In the particular case of first approximation for the simple cubic and body-centered cubic lattices these two formulations are the same.

It may be argued that since Bethe's method would give a better equilibrium value for the central site than for the outer sites, the expression (31) for the energy is perhaps better than (35).

5. THE PROBLEM OF ADSORPTION

In the problem of adsorption with a single kind of adsorbed atoms, the theory of superlattices can be applied provided the A atoms are interpreted as the adsorbed atoms. It is now more convenient to choose θ, s, T as independent variables, the relations between θ, s and θ_α, θ_β are given by (1) and (2). The equilibrium value of s as a function of θ and T is still given by (5). But θ depends on the pressure p of the gas, and so instead of regarding (12) as equations determining ξ_α and ξ_β in terms of θ and s, we regard them as determining θ in terms of ξ and T, with ξ connected with the pressure by the relation:[11]

$$\xi=\frac{h^3e^{\chi/kT}}{(2\pi m)^{3/2}(kT)^{5/2}}\frac{v_s(T)}{b_g(T)}p. \quad (37)$$

[11] See J. S. Wang, Proc. Roy. Soc. **A161**, 127 (1937).

In terms of θ and s, each one of Eq. (12) becomes

$$\log \xi = -\frac{1}{N}\frac{\partial}{\partial \theta}\log Q. \tag{38}$$

This equation gives the relation between θ, p, and T, and is commonly known as the adsorption isotherm.

The heat of adsorption q is defined as the decrease of energy when one atom is transferred from the gas phase to the adsorbed phase and is given by[11]

$$\begin{aligned} q &= q_0 - \frac{1}{N}\frac{\partial E_1}{\partial \theta}, \\ q_0 &= \chi + \tfrac{3}{2}kT + kT^2\frac{d}{dT}\log\frac{b_g}{v_s}, \end{aligned} \tag{39}$$

where E_1 is considered as a function of θ and T and the equilibrium value of s determined by (5) should be substituted in it.

The special case of equal numbers of α- and β-sites is interesting for its simplicity. It is easy to see that in this case E_1 is symmetrical in α and β, and so it is an even function of s. To study the nature of the dependence of E_1 on θ, we shall consider the first approximation for simplicity. It will be evident that the higher approximations can be treated in the same way. In the case of first approximation, there is a single ϵ and a single ζ. The functions ψ and ω satisfy the relation[9]

$$f(x) = z - f(\eta_1^{2\mu+1}x^{-1}), \quad (f = \psi \text{ or } \omega). \tag{40}$$

It then follows from (14) and (15) that the transformation

$$\epsilon \rightarrow \eta_1^{2\mu}\zeta^{-1}, \quad \zeta \rightarrow \eta_1^{2\mu}\epsilon^{-1} \tag{41}$$

changes θ_α to $1-\theta_\beta$ and θ_β to $1-\theta_\alpha$, so that s is unaltered while θ is changed to $1-\theta$. Then (17) shows that

$$E_1 = \tfrac{1}{2}NU(\theta - \tfrac{1}{2}), \quad (U = U_{\alpha\alpha} + U_{\alpha\beta}),$$

is an even function of $\theta - \frac{1}{2}$. Consequently

$$\log \xi - \frac{U}{2kT} \quad \text{and} \quad q - q_0 + \tfrac{1}{2}U$$

are both odd functions of $\theta - \frac{1}{2}$ and even functions of s.

The same conclusion holds in the case of vanishing order ($s=0$) in a general lattice (i.e., r need not be $\frac{1}{2}$). For then $\theta_\alpha = \theta_\beta = \theta$, $\epsilon_\alpha = \epsilon_\beta = \zeta_\alpha = \zeta_\beta = \epsilon$, $F(\epsilon, \epsilon) = G(\epsilon, \epsilon) = f(\epsilon)$, and E_1 in the first approximation becomes

$$E_1 = \tfrac{1}{2}N\theta\{\psi_\eta V_1 + (U - zV_1)\theta\}. \tag{42}$$

It is easily seen that $E_1 - \frac{1}{2}NU(\theta - \frac{1}{2})$ is an even function of $\theta - \frac{1}{2}$, and so the same conclusion on ξ and q follows.