

ON THE APPLICATION OF KIRKWOOD'S THEORY OF ORDER-DISORDER TRANSFORMATION TO ADSORPTION

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ABSTRACT

The phenomenon of superlattice formation on an adsorbed layer is investigated by using both Kirkwood's theory and Bethe's theory of order-disorder transformation. It is shown that when the interaction energy between the adsorbed atoms is positive and when the temperature is below a certain critical temperature the slope of the adsorption isothermals and the heat of adsorption have a discontinuity at a certain transition θ , where θ is the fraction of the surface covered by adsorbed atoms. This transition θ is situated symmetrically about the value $\theta=1/2$, such that if θ_t is the transition θ , then $1-\theta_t$ is also one. When $\theta < \theta_t$ and $\theta > 1-\theta_t$ no superlattice is formed.

1. Introduction.

The phenomenon of superlattice formation on an adsorbed layer was first investigated by Chang¹, using both the crude theory of Bragg and Williams and the more elaborate one of Bethe². In this Note the application of Kirkwood's theory³ is investigated and com-

1. T. S. Chang, *Proc. Camb. Phil. Soc.* 55, 70 (1939).
2. W. L. Bragg and E. J. Williams, *Proc. Roy. Soc. A* 145, 699 (1934); A151, 540 (1935); E. J. Williams, *ibid.* A152, 231 (1935); H. A. Bethe, *ibid.* A150, 552 (1935). See a general review by F. G. Nix and W. Shockley, *Rev. Mod. Phys.* 10, 1 (1938).
3. J. G. Kirkwood, *J. Chem. Phys.* 6, 70 (1938); H. A. Bethe and J. G. Kirkwood, *ibid.* 7, 578 (1939).

pared with the results of Bethe's theory. Incidentally, a more detailed analysis of Bethe's theory than the current ones is undertaken.

In the theoretical treatment an adsorbed layer is regarded as a two-dimensional lattice in which each site is capable of accommodating one and only one adsorbed atom. To study the phenomenon of superlattice formation we divide the lattice into two classes of sites called α -sites and β -sites respectively. For simplicity the number of α -sites is taken to be equal to the number of β -sites. In the customary terminology a perfectly ordered distribution of adsorbed atoms is assigned to the distribution in which the number of adsorbed atoms is exactly half of the number of sites and all of them are situated entirely in one of the two classes of sites only, while the sites of the other class are all empty. Such a state of perfect order can never be realized on account of the thermal agitation of the adsorbed atoms. At any temperature the distribution of the adsorbed atoms is only partially ordered.

When an ordered distributions (partially) of adsorbed atoms exists we say that a superlattice is formed. It may happen that no distinction can be made between the two classes of sites in that the average number of adsorbed atoms in one class is equal to that in the other so that the distribution may be termed disordered and no superlattice is formed. It is known that the superlattice formation is possible only when the interaction energy between the adsorbed atoms is positive. This is easily understood physically, for when the adsorbed atoms repel one another, they must be distributed in such a way that it is more probable to find a vacant place in the neighbourhood of an adsorbed atom than to find another adsorbed atom.

2. The partition function.

The central problem in the statistical treatment of the phenomenon of adsorption is the construction of the partition function of the adsorbed layer.

Let N be the total number of sites on the adsorbed layer, and N_0 the total number of adsorbed atoms. Let N_α be the number of α -

sites and $N_\alpha \theta_\alpha$ the number of adsorbed atoms on α -sites. Let N_β and $N_\beta \theta_\beta$ be the corresponding numbers for β -sites. These numbers satisfy the following relations

$$N_\alpha + N_\beta = N, \quad N_\alpha \theta_\alpha + N_\beta \theta_\beta = N\theta. \quad (1)$$

For simplicity we assume that the number of α -sites is equal to the number of β -sites. Then

$$N_\alpha = N_\beta = \frac{1}{2}N, \quad \theta_\alpha + \theta_\beta = 2\theta. \quad (2)$$

The degree of order in the distribution of adsorbed atoms is measured by the difference between θ_α and θ_β . We define the degree of order s by

$$s = \theta_\alpha - \theta_\beta. \quad (3)$$

This definition reduces to that of Bragg and Williams and of Bethe when θ is $1/2$.

To construct the partition function we assume that the adsorbed atoms interact with an energy V when they are situated on neighbouring sites and that they have no interaction when they are farther apart. Let X be the number of pairs of adsorbed atoms which are neighbouring to one another, and let χ be the energy of the lowest state of adsorption referred to the energy of the lowest state in the gas phase as zero. Then the configurational energy of the adsorbed layer is

$$U = -N\theta\chi + XV \quad (4)$$

and the partition function is

$$P = (v_s e^{\chi/kT})^{N\theta} Q, \quad (5)$$

$$Q = Q(\theta_\alpha, \theta_\beta, T) = \sum_X \gamma(\theta_\alpha, \theta_\beta, X) e^{-XV/kT}$$

where v_s is the vibrational partition function of an adsorbed atom and Q is the configurational partition function.

† See J. S. Wang, *Proc. Roy. Soc. A* 161, 127 (1937).

The adsorption isotherm may be obtained from the partition function by the condition of equal partial potential for the adsorbed layer and for the gas phase in equilibrium with the adsorbed layer. Thus

$$-\frac{\partial \ln P}{\partial N\theta} = \ln p - \ln \frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}} b}{h^3} = \ln \lambda,$$

where p is the gas pressure and b is the partition function for the internal motion of the gas molecule. Denoting $\lambda v_{se}^{X/kT}$ by ξ , we have

$$-\frac{\partial \ln Q}{\partial N\theta} = \ln p + \ln \frac{h^3 v_{se} e^{X/kT}}{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}} b} = \ln \xi. \quad (6)$$

If the partition function has been determined, the adsorption isotherm will be given by (6) and the equilibrium value of the degree of order given by

$$\frac{\partial}{\partial s} \ln Q = 0 \quad \text{or} \quad \frac{\partial}{\partial \theta_\alpha} \ln Q = \frac{\partial}{\partial \theta_\beta} \ln Q. \quad (7)$$

Kirkwood's theory consists in expanding the partition function in powers of $1/kT$. Let us denote V/kT by σ and normalize the weight factor γ to γ_0 such that $\sum \gamma_0 = 1$. Now since

$$\sum_X \gamma(\theta_\alpha, \theta_\beta, X) = \binom{N_\alpha}{N_\alpha \theta_\alpha} \binom{N_\beta}{N_\beta \theta_\beta} \quad (8)$$

we have

$$Q = \binom{N_\alpha}{N_\alpha \theta_\alpha} \binom{N_\beta}{N_\beta \theta_\beta} \sum_{n=0}^{\infty} \frac{M_n (-\sigma)^n}{n!}. \quad (9)$$

where

$$M_n = \sum_X \gamma_0 X^n. \quad (10)$$

The quantity M_n is called the n -th moment in the theory of probability.

In order to apply (6) and (7) it is more convenient to expand the logarithm of the partition function in powers of σ . Applying Stirling's asymptotic formula to the right-hand side of (8), we obtain

$$\ln Q = -\frac{1}{2} N \{ \theta_\alpha \ln \theta_\alpha + (1 - \theta_\alpha) \ln (1 - \theta_\alpha) + \theta_\beta \ln \theta_\beta + (1 - \theta_\beta) \ln (1 - \theta_\beta) \} + \sum_{n=1}^{\infty} \frac{\lambda_n (\frac{1}{2} \sigma)^n}{n!}, \quad (11)$$

where the summation begins from $n=1$ and the coefficients λ_n are calculated from the moments by the equations

$$\sum_{m=1}^n \binom{n-1}{m-1} \lambda_m M_{n-m} = M_n. \quad (12)$$

It now remains to calculate M_n . For this purpose we shall simplify our calculation by assuming that all the sites neighbouring to an α -site are β -sites and *vice versa*. Then if we label the α -sites in any manner from 1 to N_α and specify the state of

occupation of the i th α -site by the number ν_i^α , being 1 or 0 according as the i th site is occupied by an adsorbed atom or not, and if we label the β -sites in a similar manner, we obtain

$$X = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \mu_{ij} \nu_i^\alpha \nu_j^\beta, \quad (13a)$$

or

$$X = \sum_{i=1}^{N_\alpha} n_i \nu_i^\alpha, \quad (13b)$$

where μ_{ij} is 1 or 0 according as the two sites i and j are neighbours or not, and

$$n_i = \sum_{j=1}^{N_\beta} \mu_{ij} \nu_j^\beta$$

is the number of adsorbed atoms in β -sites which are neighbours to the i th α -site. The maximum value of n_i is

$$\sum_{j=1}^{N_\beta} \mu_{ij} = \sum_{i=1}^{N_\alpha} \mu_{ij} = z. \quad (14)$$

We can adopt either (13a) or (13b) as basis for the calculation of the moments; the results must be the same in both cases. To fix the ideas we shall use (13b), and shall write ν_i instead of ν_i^α for the sake of simplicity. If we denote the average value by a bar, then

$$M_n = (\sum n_i \nu_i)^n \quad (15)$$

It will be observed that when F is a product of F_1 and F_2 , where F_1 does not involve ν_i and F_2 does not involve n_i , then

$$\bar{F} = \bar{F}_1 \cdot \bar{F}_2.$$

This follows from the fact that n_i and ν_i are mutually independent. Again the average value of $\nu_i^k \nu_j^{k'} \nu_l^{k''}$, where the k 's are integers, does not depend on i, j, l and so we may write

$$\overline{\nu_i^k \nu_j^{k'} \nu_l^{k'}} = \overline{\nu^k \nu^{k'} \nu^{k'}}.$$

on account of the fact $\nu_i^k = \nu_i^k$. This holds for any number of factors. A similar result also holds for the average value of n_i^k , which may be written as \bar{n}^k . But the average value of $n_i^k n_j^{k'}$ depends on i, j , because n_i may contain contributions from n_j when the sites i and j lie sufficiently near each other.

The above considerations lead to the following results

$$\begin{aligned} M_1 &= \left(\sum n_i \right) \nu, & M_2 &= \left(\sum n_i^2 \right) \nu + \left(\sum_{i \neq j} n_i n_j \right) \nu \nu', \\ M_3 &= \left(\sum n_i^3 \right) \nu + 3 \left(\sum_{i \neq j} n_i^2 n_j \right) \nu \nu' + \left(\sum_{i \neq j \neq l} n_i n_j n_l \right) \nu \nu \nu' \text{ etc.} \end{aligned} \quad (16)$$

Let us first calculate the average values of quantities involving ν_i . We have

$$\overline{\nu^m} = \overline{\nu} = (\sum \nu_i) / N_\alpha = \theta_\alpha. \quad (17)$$

To calculate $\overline{\nu\nu'}$ we use the relation

$$(\sum \nu_i)^2 = \sum \nu_i^2 + \sum_{i \neq j} \nu_i \nu_j.$$

Since

$$\sum \nu_i = N_\alpha \theta_\alpha, \quad \sum \nu_i^2 = N_\alpha \overline{\nu^2}, \quad \sum_{i \neq j} \nu_i \nu_j = N_\alpha (N_\alpha - 1) \overline{\nu\nu'},$$

we obtain

$$\overline{\nu^2} = \frac{\theta_\alpha (N_\alpha \theta_\alpha - 1)}{N_\alpha - 1}. \quad (18)$$

Similarly from the relation

$$(\sum \nu_i)^3 = \sum \nu_i^3 + 3 \sum_{i \neq j} \nu_i^2 \nu_j + \sum_{i \neq j \neq l} \nu_i \nu_j \nu_l$$

and

$$\sum_{i \neq j} \nu_i^2 \nu_j = N_\alpha (N_\alpha - 1) \overline{\nu^2 \nu'},$$

$$\sum_{i \neq j \neq l} \nu_i \nu_j \nu_l = N_\alpha (N_\alpha - 1) (N_\alpha - 2) \overline{\nu\nu\nu'},$$

we obtain

$$\overline{\nu\nu\nu'} = \frac{\theta_\alpha (N_\alpha \theta_\alpha - 1) (N_\alpha \theta_\alpha - 2)}{(N_\alpha - 1) (N_\alpha - 2)}. \quad (19)$$

In general it can be proved by induction that

$$\overline{\nu\nu' \dots \nu^{(m)}} = \frac{\theta_\alpha (N_\alpha \theta_\alpha - 1) \dots (N_\alpha \theta_\alpha - m)}{(N_\alpha - 1) \dots (N_\alpha - m)}. \quad (20)$$

Next we proceed to calculate the average values of quantities involving n_i . Let $p(n_i)$ be the probability of finding n_i adsorbed

atoms in the $z\beta$ -sites surrounding the i th α -site, i.e. the number of distributions for given n_i divided by the total number of distributions. The number of distributions for given n_i is evidently

$$\binom{z}{n_i} \frac{N_{\beta}^{z-n_i}}{(N_{\beta}\theta_{\beta}-n_i)!}$$

The total number of distributions is the sum of the above expression for all values of n_i from 0 to z and can be shown to be

$$\frac{(N_{\beta}\theta_{\beta})!(N - N_{\beta}\theta_{\beta})!}{(N_{\beta}\theta_{\beta})!(N - N_{\beta}\theta_{\beta})!} \quad (20)$$

by means of the formula⁵

$$\sum_{n=0}^m \binom{m}{n} \binom{a-m}{b-n} = \binom{a}{b} \quad (21)$$

Hence

$$p(n_i) = \frac{\binom{z}{n_i} \frac{N_{\beta}^{z-n_i}}{(N_{\beta}\theta_{\beta}-n_i)!}}{(N_{\beta}\theta_{\beta})!(N - N_{\beta}\theta_{\beta})!} \quad (22)$$

The average value of n_i^m can now be calculated by the formula

$$\overline{n_i^m} = \frac{1}{N} \sum_{n=0}^z n^m p(n) \quad (23)$$

5. The formula (21) may be proved thus:

$$\begin{aligned} \sum_{n=0}^m \binom{m}{n} \binom{a-m}{b-n} &= F(-m, -b, a-b-m+1; 1) \\ &= \frac{\Gamma(a-b-m+1)\Gamma(a+1)}{\Gamma(a-b+1)\Gamma(a-m+1)} \\ &= \binom{a}{b} \binom{a-m}{b-m} \end{aligned}$$

⁵ See Whittaker and Watson, *Modern Analysis*, p. 282.

Using (22) we find

$$\begin{aligned}\bar{n} &= z\theta_\beta, \quad \bar{n^2} = z\theta_\beta \left\{ 1 + \frac{(z-1)(N_\beta\theta_\beta-1)}{N_\beta-1} \right\}, \\ \bar{n^3} &= z\theta_\beta \left\{ 1 + \frac{3(z-1)(N_\beta\theta_\beta-1)}{N_\beta-1} \right. \\ &\quad \left. + \frac{(z-1)(z-2)(N_\beta\theta_\beta-1)(N_\beta\theta_\beta-2)}{(N_\beta-1)(N_\beta-2)} \right\}. \quad (24)\end{aligned}$$

It should be noted that \bar{n} may also be calculated from the relation

$$\sum_{i=1}^{N_\alpha} n_i = \frac{1}{2} N z \theta_\beta. \quad (25)$$

This relation also enables us to calculate the average values of $\sum n_i n_j$, etc. From

$$(\sum n_i)^2 = \sum n_i^2 + \sum_{i \neq j} n_i n_j$$

we obtain

$$\sum_{i \neq j} n_i n_j = \frac{1}{2} N z \theta_\beta \left\{ \frac{1}{2} N z \theta_\beta - 1 + \frac{(z-1)(N_\beta\theta_\beta-1)}{N_\beta-1} \right\}, \quad (26a)$$

and from

$$(\sum n_i)^3 = \sum n_i^3 + 3 \sum_{i \neq j} n_i^2 n_j + \sum_{i \neq j \neq l} n_i n_j n_l$$

and

$$(\sum n_i^2)(\sum n_i) = \sum n_i^3 + \sum_{i \neq j} n_i^2 n_j$$

we obtain

$$\sum_{i \neq j} n_i n_j = \frac{1}{2} N z \theta_\beta \left\{ \frac{1}{2} N z \theta_\beta - 1 + \frac{(z-1)(\frac{1}{2} N z \theta_\beta - 3)(N_\beta \theta_\beta - 1)}{(N_\beta - 1)(N_\beta - 2)} \right\} \quad (26b)$$

and

$$\sum_{i \neq j \neq l} n_i n_j n_l = \frac{1}{6} N z \theta_\beta \left\{ \frac{1}{2} N z \theta_\beta - 1 \right\} \frac{1}{N_\beta - 1} + \frac{3(z-1)(\frac{1}{2} N z \theta_\beta - 2)(N_\beta \theta_\beta - 1)}{(N_\beta - 1)(N_\beta - 2)} \quad (26c)$$

Substituting the average values calculated above into (16) and using (12) we obtain

$$\lambda_1 = \frac{1}{2} N z \theta_\alpha \theta_\beta (1 - \theta_\alpha)(1 - \theta_\beta) \quad (27a)$$

$$\lambda_2 = \frac{1}{2} N z \theta_\alpha \theta_\beta (1 - \theta_\alpha)(1 - \theta_\beta)(1 - 2\theta_\alpha)(1 - 2\theta_\beta) \quad (27b)$$

neglecting terms of order less than N . Then (11) becomes

$$\ln Q = -\frac{1}{2} N \left\{ \theta_\alpha \ln \theta_\alpha + (1 - \theta_\alpha) \ln (1 - \theta_\alpha) + \theta_\beta \ln \theta_\beta + (1 - \theta_\beta) \ln (1 - \theta_\beta) \right\} - \frac{1}{2} N z \left\{ \sigma \theta_\alpha \theta_\beta \right.$$

$$- \frac{\sigma^2}{2!} \theta_\alpha \theta_\beta (1 - \theta_\alpha)(1 - \theta_\beta) + \frac{\sigma^3}{3!} \theta_\alpha \theta_\beta (1 - \theta_\alpha) \times (1 - \theta_\beta)(1 - 2\theta_\alpha)(1 - 2\theta_\beta) + \dots \left. \right\} \quad (28)$$

3. *The adsorption isotherm.* With the form (28) of the partition function eqs. (6) and (7) become

$$\ln \xi = \frac{1}{2} \sigma + \frac{1}{2} \ln \frac{\theta_\alpha \theta_\beta}{(1-\theta_\alpha)(1-\theta_\beta)} + \frac{1}{2} (\theta - \frac{1}{2}) \{ \sigma + \sigma^2 (2 + \frac{1}{2} \sigma^2) + \frac{1}{6} \sigma^3 (1-6\sigma^2) + \frac{1}{2} \sigma^4 (1-12\sigma^2) - \frac{1}{6} \sigma^5 + \dots \} \quad (29)$$

and

$$f_1(s) = f_2(s), \quad f_1(s) = \ln \frac{\theta_\alpha(1-\theta_\beta)}{\theta_\beta(1-\theta_\alpha)}, \quad (30)$$

$$f_2(s) = \frac{1}{2} \sigma \{ \sigma - \sigma^2 (\frac{1}{2} - \frac{1}{2} \sigma^2) + \frac{\sigma^3}{6} (1-6\sigma^2) + \frac{\sigma^4}{2} (5-12\sigma^2) + \frac{\sigma^5}{6} + \dots \},$$

with the abbreviation $\theta = \theta_\alpha(1-\theta_\beta)$.

Eq. (30) determines the equilibrium value of the degree of order. It is seen that $s=0$ is always a solution. When the temperature is not too high there exists another solution $s \neq 0$. It can be shown that when the second solution exists we have

$$(\sigma > \sigma_t) : f_1'(0) < f_2'(0), \quad f_1'(s) > f_2'(s), \quad (31)$$

and when $s=0$ is the only solution we have

$$(\sigma > \sigma_t) : f_1'(0) > f_2'(0), \quad (32)$$

where $f_1'(s)$ and $f_2'(s)$ are the derivatives of f_1 and f_2 with respect to s . The transition from (31) to (32) occurs at a transition temperature T_t given by $T_t = V/k\sigma_t$, where σ_t is the solution of the equation

$$(\sigma = \sigma_t) : f_1'(0) = f_2'(0), \quad (33)$$

or, on using (30),

$$\frac{1}{2} = \left\{ \sigma_t - \sigma_t^2 \left(\frac{1}{2} - \frac{1}{2} \sigma_t^2 \right) + \frac{\sigma_t^3}{6} (1-6\sigma_t^2) + \frac{\sigma_t^4}{2} (5-12\sigma_t^2) + \dots \right\}, \quad (34)$$

By the condition of minimum free energy or maximum partition function the solution $s=0$ at $\sigma > \sigma_t$ should be discarded as not physically possible. We have

$$\frac{1}{N} \frac{\partial}{\partial s} \ln Q = -\frac{1}{2} \left\{ f_1(s) - f_2(s) \right\}, \quad (35)$$

$$\frac{1}{N} \frac{\partial^2}{\partial s^2} \ln Q = -\frac{1}{2} \left\{ f_1'(s) - f_2'(s) \right\},$$

and so the condition for Q to be a maximum is

$$f_1'(s) > f_2'(s). \quad (36)$$

It is seen that the solution $s=0$ in (32) and the solution $s \neq 0$ in (31) satisfy this condition, but the solution $s=0$ in (31) gives a minimum of Q .

In order that the solution $s \neq 0$ may be consistent with the expansion in powers of σ , we must not solve eq. (30) as if it is an exact equation, but must expand s in powers of σ , retaining the same number of terms as contained in $f_2(s)$. Unfortunately such an expansion of s is impossible, as shown by the fact that the coefficient of every power of σ vanishes. The reason for this failure of expansion in powers of σ is that when σ becomes vanishingly small we obtain Bragg and Williams approximation and we must at the same time take z to be infinitely great in such a way that $z\sigma$ is finite. We must therefore expect that the correct expansion is one in powers of $1/z$ with coefficients as functions of θ and s .

When expansions in powers of $1/z$ are carried out, (34), (30) and (29) become

$$\sigma = \frac{1}{z} + \frac{1-2s}{2z^2} + \frac{1-3s}{3z^3} + \dots, \quad (37)$$

$$(\sigma > \sigma_c): \sigma = \alpha + \left(\frac{1}{2} - s - \frac{1}{2}s^2\right)\alpha^2 + \frac{1}{3}(1-3s-\frac{1}{2}s^2)\alpha^3 + \dots \quad (38)$$

with

$$\alpha = \frac{f_1(s)}{z^2}$$

and

$$\ln(\xi \eta^{\frac{1}{2}z}) = \frac{1}{2} \ln \frac{\theta_\alpha \theta_\beta}{(1-\theta_\alpha)(1-\theta_\beta)} + z \chi(\theta) \left\{ 1 + \frac{1}{2} + \frac{1}{3}(1 - \frac{1}{2}s^2)\alpha^2 + \dots \right\}, \quad (39)$$

with $\eta = e^{-\sigma}$. In particular when $\theta = \frac{1}{2}$, (37) reduces to $\sigma_t = \sigma_c$,

where

$$\sigma_c = \frac{4}{z} \left(1 + \frac{1}{z} + \frac{4}{3z^2} + \dots \right), \quad (40)$$

a formula which is first given by Bethe and Kirkwood*.

Formula (39) gives the adsorption isotherm with s determined implicitly by (38), the independent variables being taken to be θ and T . The calculations are much simpler if θ and s are taken as independent variables, but such a procedure does not correspond to experimental conditions and so is not adopted. The choice of $\xi \eta^{\frac{1}{2}z}$ instead of p or ξ has the advantage that $\ln(\xi \eta^{\frac{1}{2}z})$ is an odd function of $\theta - \frac{1}{2}$, thus reducing the calculations by one half.

For $T > T_c$ we have $s=0$ and all the quantities may be consistently expressed as power series in σ . Thus (23) becomes, for $s=0$,

$$\ln(\xi \eta^{\frac{1}{2}z}) = \ln \frac{\theta}{1-\theta} + z(\theta - \frac{1}{2}) \{ \sigma + \sigma^2 \beta - \frac{1}{2} \sigma^3 \gamma (1-6\beta) + \dots \}. \quad (41)$$

But at a given temperature the expansion in powers of σ for $s=0$ is not convenient for comparison with the expansion in powers of $1/z$ for $s \neq 0$, especially at the transition point. In order that numerical calculations should be consistent throughout the whole range of θ we must also employ an expansion in powers of $1/z$ for $s=0$. We write formally, in connexion with (38),

$$\sigma = \alpha + (\frac{1}{2} - \beta) \alpha^2 + (\frac{1}{2} - \beta^2) \alpha^3 + \dots \quad (42)$$

Here α is a quantity to be determined by this equation for given values of σ and θ . The value of α lies between 0 and $1/z$. With this form of σ , (41) reduces to,

$$\ln(\xi \eta^{\frac{1}{2}z}) = \ln \frac{\theta}{1-\theta} + z \alpha (\beta - \frac{1}{2}) \{ 1 + \frac{1}{2} \alpha + \frac{1}{2} (1 - \beta) \alpha^2 + \dots \}. \quad (43)$$

In Fig. 1 the quantity $\xi \eta^{\frac{1}{2}z}$ for a square lattice ($z=4$) is plotted against θ for various temperatures as indicated by the values of σ . The value of θ runs from 0 to $1/2$ only, for the value of $\xi \eta^{\frac{1}{2}z}$ for positive value of $\theta - \frac{1}{2}$, being the reciprocal of that for negative value of $\theta - \frac{1}{2}$, may be omitted in the plot. For $\sigma=0$, 0.5 and 1, no superlattice is formed and the isotherms are regular, the same as usual*. For $\sigma=2$ and 4, superlattice begins to form at $\theta=0.274$ and 0.169 respectively, which may be denoted by θ_t and called the transition θ . The values of θ_t are determined by eq. (37), which may be regarded as an equation determining the transition temperature for given values of θ .

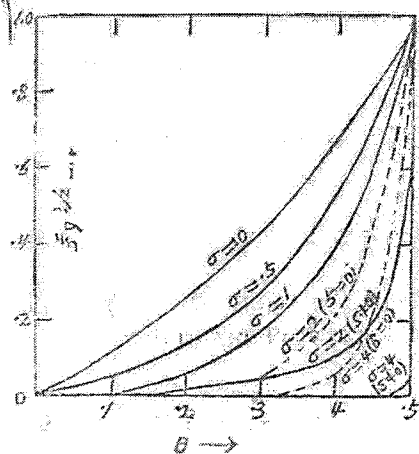


Fig. 1 Adsorption isotherm in Kirkwood's approximation

The right-hand side of (37) is a minimum for $\theta = \frac{1}{2}$ with the minimum value σ_c given by (40). When $\sigma < \sigma_c$ no solution θ_t of (37) exists, and no superlattice can be formed. We may conveniently refer to $T_c = V/k\sigma_c$ as the critical temperature in the sense that no superlattice occurs at temperatures higher than T_c .

It is seen from the figures that the modification of the adsorption isotherm due to superlattice formation is that the covering by

adsorbed atoms becomes more difficult. In the limit when $V \rightarrow \infty$, the value of θ can never exceed $1/2$ and we have the case of the exclusion pattern in adsorption studied by Roberts and Tonks⁶.

4. The heat of adsorption

The heat of adsorption per atom is defined as the decrease of energy when one more atom is adsorbed at constant temperature⁴. If q denotes the heat of adsorption and q_0 its value at $\theta = 0$, we have

$$q_0 - q = \chi + \frac{1}{N} \frac{\partial U}{\partial \theta}, \quad q_0 = \chi + \frac{5}{2} kT + kT^2 \frac{d}{dT} \ln \frac{b}{v_s}, \quad (44)$$

where U is the configurational energy given by (4). The statistical formula for the equilibrium value of the configurational energy is

$$U = -N\theta\chi + kT^2 \frac{\partial}{\partial T} \ln Q,$$

or

$$U = -N\theta\chi + V\eta \frac{\partial}{\partial \eta} \ln Q. \quad (45)$$

Substituting into (44) and making use of (6) we obtain the following alternative form for the heat of adsorption

$$\frac{q_0 - q}{V} = -\eta \frac{\partial}{\partial \eta} \ln \xi = \frac{\partial}{\partial \sigma} \ln \xi. \quad (46)$$

This is the so-called Clausius-Clapeyron equation in adsorption and can be deduced from purely thermodynamic theorems in a way exactly similar to what we have done here except that the free energy of Helmholtz is used instead of the partition function (see reference⁴, section 5).

With the form (28) for the partition function (45) becomes

6. J. K. Roberts, *Proc. Camb. Phil. Soc.* 36, 53 (1940); L. Tonks, *J. Chem. Phys.* 8, 477 (1940).

$$U = -N\theta\chi + \frac{1}{2}NVz \{ \theta_{\alpha}\theta_{\beta} - \theta_{\alpha}\theta_{\beta}(1-\theta_{\alpha})(1-\theta_{\beta}) + \frac{1}{2}s^2\theta_{\alpha}\theta_{\beta}(1-\theta_{\alpha})(1-\theta_{\beta})(1-2\theta_{\alpha})(1-2\theta_{\beta}) + \dots \}, \quad (47)$$

or expanded in powers of $1/z$,

$$U = -N\theta\chi + \frac{1}{2}NVz \{ \theta_{\alpha}\theta_{\beta} - \theta_{\alpha}\theta_{\beta}(1-\theta_{\alpha})(1-\theta_{\beta})\alpha - \theta_{\alpha}\theta_{\beta}(1-\theta_{\alpha})(1-\theta_{\beta})(-\frac{1}{2}s^2)\alpha^2 + \dots \}. \quad (48)$$

For $T > T_c$ this becomes

$$U = -N\theta\chi + \frac{1}{2}NVz \{ \theta^2 - \frac{1}{2}s^2\alpha - \frac{1}{2}s^2\alpha^2 + \dots \}. \quad (49)$$

Now applying (44) or (46), we obtain

$$\frac{q_0 - q}{zV} - \frac{1}{2} = (\theta - \frac{1}{2})(\alpha_0 + \alpha_1\alpha + \alpha_2\alpha^2 + \dots), \quad (50)$$

where

$$\begin{aligned} \alpha_0 &= 1 + \rho, & \alpha_1 &= 2 - (1 - 3 - \frac{1}{2}s^2)\rho + (\frac{1}{2} - \frac{1}{2}s^2)\rho^2, \\ \alpha_2 &= [2 - (\frac{1}{2} - \frac{1}{2}s^2)\rho] \alpha_1 - \frac{2}{3}z\alpha\theta_{\alpha}\theta_{\beta}(1-\theta_{\alpha})(1-\theta_{\beta})\rho^2, \\ \rho &= \frac{\frac{1}{2}s^2}{-\frac{1}{2}s^2 - z\alpha\theta_{\alpha}\theta_{\beta}(1-\theta_{\alpha})(1-\theta_{\beta})}. \end{aligned}$$

This formula shows that the quantity $(q_0 - q - \frac{1}{2}zV)/zV$ is an odd function of $\theta - \frac{1}{2}$, and the calculations can be confined to $\theta \leq \frac{1}{2}$.

When $T > T_c$ or $T < T_c$, the formula (50) is still true, provided α is now determined from (42) and ρ is put equal to zero. Thus

$$\frac{q_0 - q}{zV} - \frac{1}{2} = (\theta - \frac{1}{2})(1 + 2\alpha + 4\alpha^2 + \dots). \quad (51)$$

Now when $s \rightarrow 0$, ρ does not approach zero, it follows that (50) and (51) do not approach to the same limit at θ_c and there occurs a discontinuity. The different limits are

$$(\beta \rightarrow \beta_t + 0): \frac{q_0 - q}{zV} \rightarrow \frac{1}{z} \rightarrow (\theta_t - \frac{1}{2}) \left\{ \frac{1}{1-3\beta} + \frac{6\beta-1}{(1-3\beta)^2 z} + \frac{9\beta-2}{(1-3\beta)^3 z^2} + \dots \right\}, \quad (52)$$

$$(\beta \rightarrow \beta_t - 0): \frac{q_0 - q}{zV} \rightarrow \frac{1}{z} \rightarrow (\theta_t - \frac{1}{2}) \left\{ 1 + \frac{2}{z} + \frac{4}{z^2} + \dots \right\}.$$

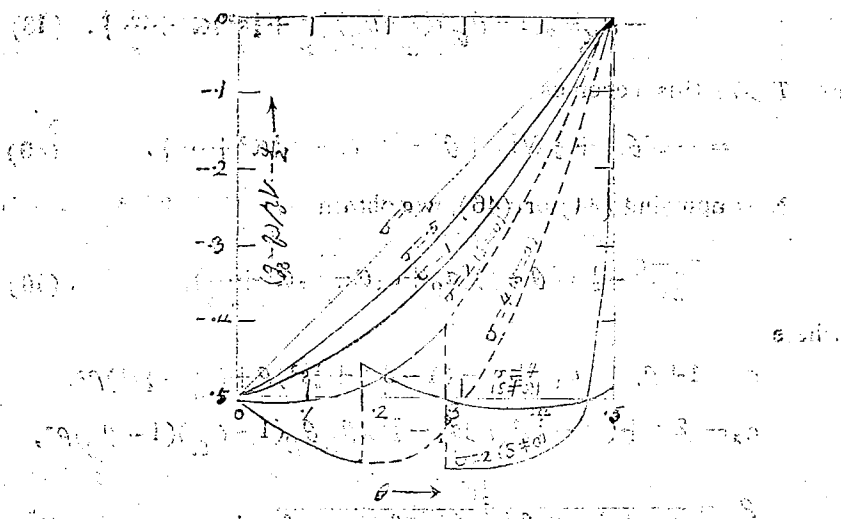


Fig. 2 Heat of adsorption in Kirkwood's approximation

In Fig. 2 the heat of adsorption is plotted against θ from $\theta=0$ to $1/2$ for various values of σ . The discontinuity which occurs at temperatures below T_c is quite large and should be observable. When accurate experimental data are available it will be possible to test the correctness of the theory.

Before leaving Kirkwood's theory it is perhaps worth while to give the expression for the configurational heat capacity in the form of an expansion in powers of $1/z$. It is found that

$$C_r/Nk = \frac{1}{2} z \alpha \theta_\alpha \theta_\beta (1 - \theta_\alpha) (1 - \theta_\beta) (c_0 + c_1 \alpha + c_2 \alpha^2 + \dots) \quad (53)$$

where

$$c_0 = \alpha\beta, \quad c_1 = 1 - (1 - 2\alpha)\alpha\beta + (2 - \frac{1}{2}\alpha^2)\alpha\beta^2,$$

$$c_2 = \left[2\alpha + \left(2 - \frac{1}{2}\alpha^2 \right) \beta \right] c_1 - \left(\frac{1}{12} - \alpha - \frac{1}{6}\alpha^2 \right) \alpha\beta^2 - \frac{2}{3} \left(2 - \frac{1}{2}\alpha^2 \right) \alpha\beta^3.$$

5. Comparison with Bethe's first approximation.

It has been shown by Fowler and Guggenheim* that Bethe's first approximation can be obtained by the quasi-chemical method introduced by them. This method consists in making a guess on a reasonable approximate form for the weight γ in (5). Their guess is that γ is proportional to the number of ways of arranging the various types of pairs of occupied and unoccupied sites. There are four types of pairs: (i) the pair of adsorbed atoms, in number X ; (ii) the pair of vacant sites, in number $\frac{1}{2}Nz(1 + 2\theta_\alpha + \theta_\beta)$; (iii) the pair consisting of an occupied α -site and an unoccupied β -site, in number $\frac{1}{2}Nz\theta_\alpha - X$; (iv) the pair consisting of an occupied β -site and an unoccupied α -site, in number $\frac{1}{2}Nz\theta_\beta - X$. The assumption of the quasi-chemical method is

$$\gamma(\theta_\alpha, \theta_\beta, X) = g(\theta_\alpha, \theta_\beta) \frac{(X!)^2}{(\frac{1}{2}Nz\theta_\alpha - X)! (\frac{1}{2}Nz\theta_\beta - X)! (\frac{1}{2}Nz(1 + 2\theta_\alpha + \theta_\beta) + X)!} \quad (54)$$

where the factor g is determined by the condition (8). Using (21) we find

$$g(\theta_\alpha, \theta_\beta) = \frac{\left(\frac{1}{2}Nz\theta_\alpha \right)! \left(\frac{1}{2}Nz\theta_\beta \right)!}{\left(\frac{1}{2}Nz\theta_\alpha \right)! \left(\frac{1}{2}Nz\theta_\beta \right)!} \quad (55)$$

By means of Stirling's asymptotic formula for the factorials, the logarithm of the summand in (5) becomes

$$\ln \gamma(\theta_\alpha, \theta_\beta, X) = \ln g(\theta_\alpha, \theta_\beta) + 2X \ln X - (\frac{1}{2}Nz\theta_\alpha - X) \ln (\frac{1}{2}Nz\theta_\alpha - X) - (\frac{1}{2}Nz\theta_\beta - X) \ln (\frac{1}{2}Nz\theta_\beta - X) - (\frac{1}{2}Nz(1 + 2\theta_\alpha + \theta_\beta) + X) \ln (\frac{1}{2}Nz(1 + 2\theta_\alpha + \theta_\beta) + X) \quad (56)$$

* B. H. Fowler and E. A. Guggenheim, *Philosophical Magazine*, **1**, 159 (1926).

$$\begin{aligned} \Phi = & \frac{1}{2}N(z-1) \{ \theta_\alpha \ln \theta_\alpha + (1-\theta_\alpha) \ln (1-\theta_\alpha) + \theta_\beta \ln \theta_\beta \\ & + (1-\theta_\beta) \ln (1-\theta_\beta) \} \\ & - \frac{1}{2}Nz \{ \varphi \ln \varphi + (\theta_\alpha - \varphi) \ln (\theta_\alpha - \varphi) + (\theta_\beta - \varphi) \ln (\theta_\beta - \varphi) \\ & + (1-2\theta + \varphi) \ln (1-2\theta + \varphi) - \varphi \ln \eta \}. \end{aligned} \quad (56)$$

where

$$\varphi = X / \frac{1}{2}Nz, \quad \text{and} \quad \eta = e^{-\sigma}.$$

Φ becomes a maximum for the value of φ satisfying the equation

$$\varphi(1-2\theta+\varphi) = \eta(\theta_\alpha - \varphi)(\theta_\beta - \varphi), \quad (57)$$

of which the solution is

$$\varphi = \frac{u - (1-2\theta+2\theta\eta)}{2(1-\eta)}, \quad u = \sqrt{1-4s(1-\eta)-s^2\eta(1-\eta)}. \quad (58)$$

The equilibrium value of s is determined by the equation

$$(z-1) \ln \frac{\theta_\alpha}{1-\theta_\alpha} - z \ln (\theta_\alpha - \varphi) = (z-1) \ln \frac{\theta_\beta}{1-\theta_\beta} - z \ln (\theta_\beta - \varphi), \quad (59)$$

or

$$\frac{\partial \Phi}{\partial s} = -\frac{1}{2}N \{ f_1(s) - f_2(s) \} = 0$$

with

$$f_1(s) = \ln \frac{\theta_\alpha(1-\theta_\beta)}{\theta_\beta(1-\theta_\alpha)}, \quad f_2(s) = z \ln \frac{u+1+s(1-\eta)}{u+1-s(1-\eta)}. \quad (60)$$

With the present form for the function f_2 , eq. (33) determining the transition temperature gives

$$\eta_2 = 1 - \frac{z-1}{z^2} \quad \text{or} \quad \eta_2 = \frac{z-1}{z^2(1-\eta)} \quad (61)$$

Replacing $\ln Q$ by the maximum value of Φ and substituting into (6) and (45) we find

$$\ln(\xi \eta^{\frac{1}{2}z}) = \frac{1}{2} \ln \frac{\theta \alpha \theta_\beta}{(1-\theta_\alpha)(1-\theta_\beta)} - \frac{1}{2} z \ln \frac{\theta \alpha (u+1-2\theta+s\eta)}{(1-\theta_\beta)(u-1+2\theta+s\eta)} \quad (62)$$

and

$$U = -N\theta X + \frac{1}{2} NV z \frac{u - (1-2\theta+2\theta\eta)}{2(1-\eta)} \quad (63)$$

The corresponding expressions for $\beta < \beta_t$ are obtained from (62) and (63) by putting $s=0$. It is seen that the expression (62), like (39), is an odd function of $\theta - \frac{1}{2}$.

The heat of adsorption is again calculated by means of (44) or (46) and the result is

$$\frac{q_0 - q}{zV} - \frac{1}{2} = \frac{\theta - \frac{1}{2}}{u} + \frac{\eta s}{4u} \frac{\partial s}{\partial \theta} \quad (64)$$

where

$$\frac{\partial s}{\partial \theta} = \frac{\partial}{\partial \theta} \left[\frac{2s(\theta - \frac{1}{2}) \{ u + \frac{1}{2} z (1 - 2(\theta - \frac{1}{2} + \frac{1}{2}s^2)(1-\eta) + u) \}}{[(\beta - \frac{1}{2}s^2)u - \frac{1}{2}z \{ (\beta - \frac{1}{2}s^2)u - 1 + 4\beta(1-\eta) \} - \frac{1}{2}s^2(1-4\beta)(1-\eta)]} \right],$$

which is calculated from (60). It is seen that the right-hand side of (64), like (50), is an odd function of $\theta - \frac{1}{2}$. The heat of adsorption for $\beta < \beta_t$ is obtained from (34) by putting the second term on the right to zero. The discontinuity at $\beta = \beta_t$ is

$$\left(-\frac{\eta s}{4u} \frac{\partial s}{\partial \theta} \right)_{s \rightarrow 0} = \frac{3z}{z-2} \frac{\beta z^2 - z - 1}{(1-3\beta)z^2 - z + 1} \left(\theta - \frac{1}{2} \right). \quad (65)$$

In Fig. 3 the adsorption isotherm given by (62) is plotted for the same values of σ as in the case of Kirkwood's approximation. It is seen that the shapes of the curves are in general the same in both theories. The transition θ are now 0.313 for $\sigma=2$ and 0.257 for $\sigma=4$ respectively.

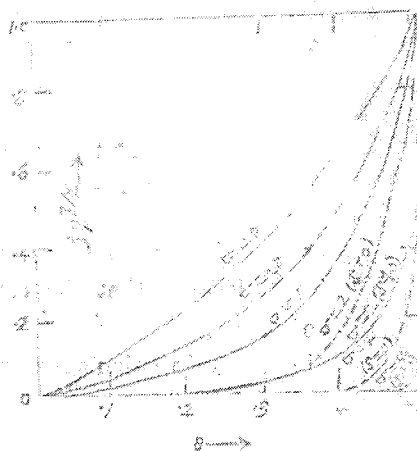


Fig. 3. Adsorption isotherm in Bethe's approximation

In Fig. 4 the heat of adsorption is plotted against θ . The curves show the same kind of behaviour as in Kirkwood's approximation, but the values at the transition point are somewhat different in the two cases. The difference would naturally be smaller when c is

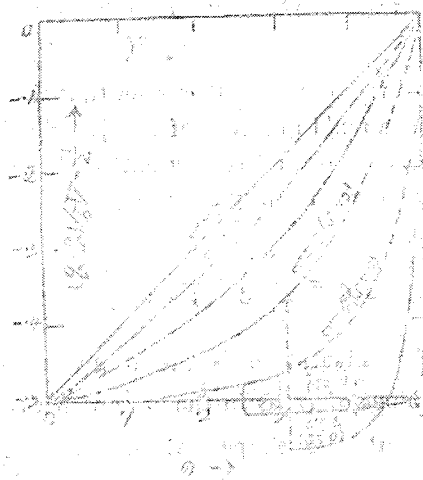


Fig. 4. Heat of adsorption in Bethe's approximation

comes larger, and when z is not large we should expect Bethe's approximation to be the better of the two.

It is interesting to observe that when $f_2(s)$ in Bethe's first approximation given by (60) is expanded in powers of σ the first three terms are identical with Kirkwood's approximation given in (30), but the 4th term is different. Such a comparison shows clearly how close is Bethe's first approximation to the true solution.

6. Alternative forms of Bethe's first approximation.

Bethe's approximation may be expressed in two other alternative forms: the usual form in terms of parameters and the form in terms of θ and s as independent variables in analogy with eqs. (38), (39) and (50) of Kirkwood's approximation.

To obtain the usual form we make the substitution

$$1 - 2\theta + \varphi = \eta\epsilon\zeta, \quad \begin{matrix} \theta_\alpha - \varphi \\ \theta_\beta - \varphi \end{matrix} = \begin{matrix} \zeta \\ \epsilon \end{matrix}. \quad (66)$$

With the help of (57) we find

$$\varphi = \frac{\eta\epsilon}{1+\eta\epsilon} \theta_\alpha = \frac{\eta\zeta}{1+\eta\zeta} \theta_\beta = \frac{\eta\epsilon\zeta}{1+\epsilon+\zeta+\eta\epsilon\zeta} \quad (67)$$

and

$$\theta_\alpha = \frac{\eta\zeta}{1+\eta\zeta} \theta_\beta + \frac{\zeta}{1+\zeta} (1 - \theta_\beta), \quad \theta_\beta = \frac{\eta\epsilon}{1+\eta\epsilon} \theta_\alpha + \frac{\epsilon}{1+\epsilon} (1 - \theta_\alpha). \quad (68)$$

The equations (68) were first derived by Easthope⁸ using Bethe's method.

Solving for θ_α and θ_β from (67) and using their combinations θ and s , we obtain

$$1 - 2\theta = \frac{1 - \eta\epsilon\zeta}{1 + \epsilon + \zeta + \eta\epsilon\zeta}, \quad s = \frac{\zeta - \epsilon}{1 + \epsilon + \zeta + \eta\epsilon\zeta}, \quad (69)$$

of which the first equation may be regarded as an equation determining ζ in terms of ϵ , θ , and η .

8. C. E. Easthope, *Proc. Camb. Phil. Soc.* 33,

If we regard η , ϵ and ζ as independent variables, then the equilibrium values of ϵ and ζ are determined by (59) and (62), which now read

$$\left(\frac{1+\eta\epsilon}{1+\epsilon} \right)^{z-1} = \left(\frac{1+\eta\zeta}{1+\zeta} \right)^{z-1} \quad (70)$$

and

$$\xi = \frac{\theta_\alpha}{1-\theta_\alpha} \left(\frac{1+\epsilon}{1+\eta\epsilon} \right)^{z-1} = \frac{\theta_\beta}{1-\theta_\beta} \left(\frac{1+\zeta}{1+\eta\zeta} \right)^{z-1} \quad (71)$$

Eqn. (71) gives the adsorption isotherm.

The heat of adsorption in terms of ϵ and ζ is

$$\begin{aligned} \frac{q_a - q}{zV} = & \left\{ \eta(1+\epsilon) \left[1 - \frac{(z-1)(1-\eta)\epsilon}{(1+\epsilon)(1+\eta\epsilon)} \right] \right. \\ & \left. + \eta(1+\zeta) \left[1 - \frac{(z-1)(1-\eta)\zeta}{(1+\zeta)(1+\eta\zeta)} \right] \right\} \\ & + \left\{ \frac{(1+2\eta\epsilon+\eta\epsilon^2)}{\epsilon} \left[1 - \frac{(z-1)(1-\eta)\epsilon}{(1+\epsilon)(1+\eta\epsilon)} \right] \right. \\ & \left. + \frac{(1+2\eta\zeta+\eta\zeta^2)}{\zeta} \left[1 - \frac{(z-1)(1-\eta)\zeta}{(1+\zeta)(1+\eta\zeta)} \right] \right\} \quad (72) \end{aligned}$$

The quantity $\bar{\Phi}$ defined by (56) can be put in the form

$$\begin{aligned} \bar{\Phi} = & -\frac{1}{2}N \left\{ \theta_\alpha \ln \theta_\alpha + (1-\theta_\alpha) \ln(1-\theta_\alpha) + \theta_\beta \ln \theta_\beta \right. \\ & \left. + (1-\theta_\beta) \ln(1-\theta_\beta) \right\} - \frac{1}{2}Nz \left\{ (1-2\theta) \ln \frac{(1+\eta\epsilon)(1+\eta\zeta)}{(1+\epsilon)(1+\zeta)} \right. \\ & \left. + \ln \frac{(1+\epsilon+\zeta+\eta\epsilon\zeta)^2}{(1+\epsilon)(1+\eta\epsilon)(1+\zeta)(1+\eta\zeta)} + s \ln \frac{(1+\epsilon)(1+\eta\zeta)}{(1+\zeta)(1+\eta\epsilon)} \right\} \quad (73) \end{aligned}$$

The second alternative form of Bethe's first approximation may be obtained from the usual form by solving for ϵ , ζ and η in terms of θ and s . The results of

sublattice in which the numbers of the two classes of sites are equal. It might happen that other types of superlattice also occur, and the form of the adsorption isotherm and of the heat of adsorption may be substantially influenced. This problem may be an interesting subject for further investigation. The method to be used is of course statistical mechanics, and the type of superlattice that actually occurs for a given θ should be determined by the condition of maximum summand in the partition function.

The comparison between Bethe's theory and Kirkwood's theory shows that they give qualitatively the same result. Bethe's theory has the advantage that it holds for all values of z , while Kirkwood's

$$\ln \left(\xi \eta^{\frac{1}{2}z} \right) = \frac{1}{2} \ln \frac{\theta_{\alpha} \theta_{\beta}}{(1-\theta_{\alpha})(1-\theta_{\beta})} + \frac{1}{2} z \ln \frac{1-\theta_{\alpha}}{1-\theta_{\beta}} + \frac{1}{2} z \ln \left[\left(\frac{\theta_{\beta}}{\theta_{\alpha}} \right)^{1/z} \left(\frac{1-\theta_{\beta}}{1-\theta_{\alpha}} \right)^{1-1/z} - 1 \right] - \frac{1}{2} z \ln \left[\left(\frac{\theta_{\alpha}}{\theta_{\beta}} \right)^{1-1/z} \left(\frac{1-\theta_{\alpha}}{1-\theta_{\beta}} \right)^{1/z} - 1 \right]. \quad (75)$$

The expression for ξ is obtained from that for ϵ by interchanging θ_{α} and θ_{β} and replacing s by $-s$. The expression for the heat of adsorption is very complicated and is therefore not written down; it may be obtained from (72) with the help of (74) if desired.

7. Discussion.

The theory so far developed is confined to the type of superlattice in which the numbers of the two classes of sites are equal. It might happen that other types of superlattice also occur, and the form of the adsorption isotherm and of the heat of adsorption may be substantially influenced. This problem may be an interesting subject for further investigation. The method to be used is of course statistical mechanics, and the type of superlattice that actually occurs for a given θ should be determined by the condition of maximum summand in the partition function.

The comparison between Bethe's theory and Kirkwood's theory shows that they give qualitatively the same result. Bethe's theory has the advantage that it holds for all values of z , while Kirkwood's

theory is only valid when z is large. On the other hand Kirkwood's theory gives the exact result as an expansion in powers of $1/z$ and so the error of the theory can be estimated by the value of z , whereas in Bethe's theory there is no way of estimating the error. From the result of expressing Bethe's theory in the form of expansions in powers of z it follows that Bethe's first approximation is at least as good as Kirkwood's theory including the first three moments and may probably be better than it. Since Bethe's first approximation involves much less labour in mathematical manipulation and numerical work than Kirkwood's approximation, it appears that Bethe's theory is better for practical purposes.