



ON THE APPROXIMATE PARTITION FUNCTION IN THE STATISTICAL THEORY OF ADSORPTION*

By C. F. Ying (應崇福)

Department of Physics, Huachung University

(Received 5 December, 1944)

ABSTRACT

Wang's theory for determining the approximate configurational partition function of the adsorbed layer is modified in two different ways. One is to assume that the configurational energy should be corrected; the other to advocate that the deficiency due to a wrong expression for the a priori probability of the central site is more significant. The configurational partition function is evaluated in both methods and the adsorption isotherm and the heat of adsorption computed for the case of quadratic lattice with dipole interaction. Values for the last two quantities when a uniform continuous distribution of the distant adsorbed particles is assumed are further given for comparison. The second method, which surpasses the first, is compared with Kirkwood's method in the case of hexagonal lattice with neighbour interaction. Numerical work is also carried out in this case.

1. Introduction

In Beth's theory, as applied to the adsorption of gas particles^{** 1,2,3}, the partition function for the whole assembly of adsorbed particles is not evaluated. What actually is evaluated is only the partition function of a small group of particles chosen out of the whole. Thus although the consequences deduced from the "local" partition function are assumed to hold for the entire adsorbed layer, the local partition function itself can evidently not be regarded as equivalent to the true partition function of the whole assembly. In certain problems, such as the critical condensation phenomenon, the latter, however, is indispensable. Wang⁴ accordingly advanced a device for its approximate evaluation without

* An abridged version of an M. Sc. dissertation, National Tsinghua University, 1945.

** The term "particle" represents either a molecule or an atom as the case may be. In this paper the problem of dissociation is not considered.

1. R. Peierls, *Proc. Camb. Phil. Soc.* 32 (1936), 471.

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

3. J. S. Wang, *Proc. Camb. Phil. Soc.* 34 (1938), 238.

4. J. S. Wang, "Free Energy in the Statistical Theory of Order-Disorder Transformation", *Science Report of National Tsinghua University*, series A, (1941), (printed but failed to appear).

breaking from Bethe's scheme. Nevertheless the theory suffers from two defects. One is theoretical and the other practical. In the special case of neighbour interaction it leads to the conclusion that the condition of mathematical consistency is automatically satisfied so that a partition function always exists. This is not true in general. A second defect of the theory is that the numerical work involved is definitely laborious. It seems the theory should first be modified. Two different ways to effect this are suggested and formulated here. One way is to modify the energy expression (§ 2) and the other to modify the formulas of equilibrium distribution (§ 3).

2. The method of modifying the configurational energy expression

We shall still take the condition of mathematical consistency as our starting point, just as in Wang's paper⁴. The original expression for the configurational energy of the adsorbed layer was (Wang⁴, eq. (11))

$$E_c = \frac{1}{2} N \theta (U_0 + f_{1\tau} V_1), \quad (1)$$

where N is the total number of sites available for adsorption, θ is the fraction of sites occupied by adsorbed particles, V_1 is the interaction between two neighbouring adsorbed particles, U_0 is the interaction of an adsorbed particle with all the adsorbed particles other than its nearest neighbours and is given by (Wang⁴, eq. (12), obtained upon the assumption of uniform distribution)

$$U_0 = \theta (U^* - z V_1), \quad (2)$$

U^* being the interaction of an adsorbed particle with all other adsorbed particles when all sites are occupied and z being the number of sites neighbouring to any given site. The symbol $f_{1\tau}$ is an abbreviation for the function $f_1(e\tau/\epsilon)$, where

$$\tau = -V_1/kT \quad (3)$$

and

$$f_1(x) = x \frac{d}{dx} \ln f(x), \quad (4)$$

$f(x)$ being the basic function in Wang's theory⁴ (see eq. (23), § 4 below). In Wang's paper⁴ cited above the expression (2) was modified while (1) was assumed to be correct. Now a different procedure will be adopted. We shall modify the expression (1) for the configurational energy by adding a term $NV_1 w$ to it, but (2) will be retained:

$$E_c/NV_1 = \frac{1}{2} \theta (\theta v^* + f_{1\tau}) + w, \quad (5)$$

where

$$v^* = (U^*/V_1) - z. \quad (6)$$

The quantity w will be determined by the condition of mathematical consistency, namely, that the partial differential equations

$$\frac{1}{N} \frac{\partial}{\partial \tau} \ln Q = \frac{E_c}{NV_1}, \quad (7)$$

$$\frac{1}{N} \frac{\partial}{\partial \theta} \ln Q = -\ln \xi, \quad (8)$$

which determine the required configurational partition function $Q(\theta, \tau)$, should be integrable. This requires the relation

$$\frac{\partial}{\partial \theta} \frac{E_c}{NV_1} = -\frac{\partial}{\partial \tau} \ln \xi \quad (9)$$

to hold, in which E_c is given by (5) and ξ is determined by

$$\frac{\theta}{1-\theta} = \xi e^{-U_0/kT} \frac{f_\tau}{f}, \quad (10)$$

where f and f_τ stand for $f(\epsilon)$ and $f(\theta\tau\epsilon)$ respectively. The argument ϵ in the function f is determined as a function of θ and τ by the equation

$$\frac{\theta}{1-\theta} = \frac{f_\tau}{z - f_{1\tau}}. \quad (11)$$

Substituting (5) and (10) into (9), we obtain

$$\frac{\partial w}{\partial \theta} = \frac{\partial}{\partial \tau} \ln \frac{f_\tau}{f} - \frac{\partial}{\partial \theta} \left(\frac{1}{2} \theta f_{1\tau} \right). \quad (12)$$

To solve this equation we remember that (1) holds at $\theta=1$. We can therefore take it as the boundary condition for w at $\theta=1$. The solution is

$$w = \frac{1}{2} (z - \theta f_{1\tau}) - \int_\theta^1 \frac{\partial}{\partial \tau} \left(\ln \frac{f_\tau}{f} \right) d\theta. \quad (13)$$

The configurational partition function Q is then, from (7) and (8),

$$\begin{aligned} \frac{1}{N} \ln Q = & \int_0^\tau \left\{ \frac{1}{2} (z + \theta^2 v^*) - \int_\theta^1 \frac{\partial}{\partial \tau} \left(\ln \frac{f_\tau}{f} \right) d\theta \right\}_{\theta=0} d\tau \\ & + \int_0^\theta \left\{ -\ln \frac{\theta}{1-\theta} + \ln \frac{f_\tau}{f} + \theta v^* \tau \right\} d\theta. \end{aligned}$$

the path of integration being so chosen that θ is first held constant at 0 while τ varied from 0 to τ and then τ held constant at τ while θ varied from 0 to θ , or

$$\frac{1}{N} \ln Q = -\theta \ln \theta - (1-\theta) \ln (1-\theta) + \frac{1}{2} (z + 6^2 v^*) \tau - \int_0^1 \ln \frac{f_\tau}{f} d\theta. \quad (14)$$

Equation (10) represents the adsorption isotherm in the present method. The heat of adsorption q can be calculated either from the formula

$$q_0 - q = \frac{1}{N} \frac{\partial E_c}{\partial \theta} \quad (15)$$

or from

$$q_0 - q = -V_1 \frac{\partial}{\partial \tau} \ln \xi, \quad (16)$$

for here the configurational partition function exists. The result is

$$\frac{q_0 - q}{V_1} = \frac{\partial}{\partial \tau} \ln \frac{f_\tau}{f} + \theta v^*. \quad (17)$$

q_0 in these equations is the value of q at $\theta = 0$.

While yielding simpler formulas than the method of modifying U_0 , the present method can only be applied to the case of adsorption without superlattice formation. In the case of superlattice, on the other hand, there are three equations expressing the condition of integrability⁴, of which one does not involve E_c . It is evident that the present method will not work if this particular equation is not satisfied.

3. The method of modifying the a priori probability expression

We shall in this section attempt to formulate a more suitable method. It is the method of modifying the quantity ξ . The physical background is as follows: ξ is the statistical weight or the a priori probability of the central site. Since the condition of integrability (9) is not satisfied we argue that the procedure of assigning a parameter ϵ to each of the first shell particles is too rough and should be supplemented by assigning also a factor to the central site. We shall therefore add a factor e^σ to ξ and thus alter the equation (10) to

$$\theta = \frac{\xi e^\sigma e^{\theta v^* \tau} f_\tau}{1 + \xi e^\sigma e^{\theta v^* \tau} f_\tau}. \quad (18)$$

The quantity σ will be determined by (9), in which the value of ξ determined

by (18) should be used, while E_c is still given by (1). Thus we have the following differential equation for determining σ :

$$\frac{\partial \sigma}{\partial T} = \frac{\partial}{\partial \theta} \left(\frac{1}{2} \theta f_{1T} \right) - \frac{\partial}{\partial T} \ln \frac{f_T}{f}. \quad (19)$$

In order to solve this equation we investigate the value of σ at $T = 0$. When T approaches zero, T approaches ∞ , the Boltzmann factor in the configurational partition function approaches 1, and Q reduces to the expression for the case of no interaction between the adsorbed particles, when ξ is related to θ by the equation $\xi = \theta/(1-\theta)$, and consequently σ becomes 0 as $T \rightarrow 0$. With this boundary condition we obtain from (19)

$$\sigma = \ln \frac{f}{f_T} + \frac{1}{2} \int_0^T \frac{\partial}{\partial \theta} (\theta f_{1T}) dT. \quad (20)$$

On first fixing θ at zero, but varying T from 0 to T and then fixing T at T while varying θ from 0 to θ , Q is found to be

$$\begin{aligned} \frac{1}{N} \ln Q = & \int_0^T \left\{ \frac{1}{2} \theta^2 v^* + \frac{1}{2} \theta f_{1T} \right\} dT \\ & + \int_0^\theta \left\{ -\ln \frac{\theta}{1-\theta} + \sigma + \theta v^* T + \ln \frac{f_T}{f} \right\} d\theta, \end{aligned}$$

$$\text{or } \frac{1}{N} \ln Q = -\theta \ln \theta - (1-\theta) \ln (1-\theta) + \frac{1}{2} \theta^2 v^* T + \frac{1}{2} \int_0^T \theta f_{1T} dT. \quad (21)$$

For the heat of adsorption we have

$$\frac{q_0 - q}{V_1} = \frac{1}{2} \frac{\partial}{\partial \theta} (\theta f_{1T}) + \theta v^*. \quad (22)$$

It is to be noted that the present method has not the flaw the previous methods of modifying U_0 and modifying E_c possess. The present method is numerically much simpler than Wang's original method and is also applicable to the case of superlattice. In the case of superlattice there are two ξ 's (see a recent paper of Wang⁵) and hence there will be two σ 's if the present method is applied. The three partial differential equations of the two σ 's expressing the condition of integrability can be verified to form a complete Jacobian system so

5. J. S. Wang, "Approximate Partition Function in Generalized Bethe's Theory of Superlattices", (to be published).

that the mathematical consistency of the method is assured and the equations can be integrated.

It may be mentioned that the present method is mathematically equivalent to one recently proposed by Wang⁵, although they start from different physical principles.

4. Numerical calculations for a quadratic lattice with dipole interaction

For a quadratic lattice with dipole interaction the function $f(x)$ takes the form⁵

$$f(x) = 1 + 4x + (4e^{\frac{1}{2}\sqrt{2}\tau} + 2e^{\frac{1}{2}\tau})x^2 + 4e^{(\frac{1}{2}\sqrt{2} + \frac{1}{2})\tau}x^3 + e^{(\sqrt{2} + \frac{1}{2})\tau}x^4, \quad (23)$$

and $z = 4$, $v^* = 5.0336$ (this value of v^* has been calculated by Topping⁶). Theoretically the configurational partition function is fundamental, but experimentally only the adsorption isotherm and the heat of adsorption can be measured. We shall, therefore, calculate only the last two quantities.

It can be verified from the above form of $f(x)$ that the following relation holds:

$$f(x) = (e^{\mu\tau/2}x)^z f(e^{-\mu\tau}x^{-1}), \quad (24)$$

where $z = 4$ and $\mu = \frac{1}{2}\sqrt{2} + \frac{1}{2}$.

With the help of this relation it can be proved that

$$\frac{q_0 - q}{V_1} \sim \frac{1}{z} (z + v^*)$$

is an odd function of $\theta - \frac{1}{2}$, both in the method of modifying E_c and in the method of modifying $\frac{1}{2}$. Consequently it is only necessary to calculate q for $\theta < \frac{1}{2}$.

As has been pointed out by Wang himself⁴, the heat of adsorption as originally given for the case when the distant adsorbed particles are uniformly and continuously distributed³ is in error. We shall calculate its correct numerical values. The correct formula is (Wang⁴, footnote 10)

5. J. S. Wang, "Approximate Partition Function in Generalized Lattice Theory," *J. Topping, Proc. Roy. Soc., A*, 114 (1927), 67.

$$\begin{aligned} \frac{q_0 - q}{V_1} = & \left(1 - \frac{2\pi}{u^2 G'}\right) \left\{ \varphi_T - \varphi + \frac{f_{1T} [(z - f_{1T})f_2 + f_{1T}f_{2T}]}{(z - f_{1T})f_2 + f_{1T}f_{2T}} \right. \\ & + \left. \frac{(f_1 - f_{1T})[(z - f_{1T})\varphi_1 + f_{1T}\varphi_{1T}]}{(z - f_{1T})f_2 + f_{1T}f_{2T}} \right\} \\ & + \frac{2\pi}{u^2 G'} \frac{f_{1T}f_{2T} + (z - f_{1T})\varphi_1 + f_{1T}\varphi_{1T}}{(z - f_{1T})f_2 + f_{1T}f_{2T}} + K a_1^2 \theta \frac{2\pi}{u} \left(1 + \frac{G}{u G'}\right), \end{aligned} \quad (25)$$

where

$$f_2 = f_2(\epsilon) = \epsilon \frac{d}{d\epsilon} \ln f_1,$$

$$\varphi = \left(\frac{\partial}{\partial \tau} \ln f\right)_\epsilon, \quad \varphi_1 = \left(\frac{\partial}{\partial \tau} \ln f_1\right)_\epsilon,$$

the differentiation with respect to τ in φ and φ_1 being taken at constant ϵ . Equation (25) was obtained by utilizing (16) and evidently would be the same as (17) were the two U_0 's not different.

On starting from (15) we can get for q in the same case of uniform continuous distribution another expression which will be different from (25) since (15) and (16) are now no more equivalent. We have $U_0 = 2\pi\theta K a_1^2 V_1 / u$, and consequently

$$\begin{aligned} \frac{q_0 - q}{V_1} = & \frac{f_{1T}}{2} \left\{ 1 + \frac{(z + f_1 - f_{1T})f_{2T}}{(z - f_{1T})f_2 + f_{1T}f_{2T}} \right\} \\ & + \frac{\pi}{u^2 G' \tau} \frac{1}{1 - \theta} \left\{ 1 - \frac{(z - f_{1T})(1 - f_1 + f_{1T})}{(z - f_{1T})f_2 + f_{1T}f_{2T}} \right\} \\ & + K a_1^2 \theta \frac{2\pi}{u} \left(1 + \frac{G}{2u G'}\right). \end{aligned} \quad (26)$$

Numerical values of this expression are also calculated.

In calculation we assign definite values to τ . When $\tau = -0.25$ the adsorption isotherms and variations of the heat of adsorption with θ are shown in figures 1 and 2. It will be seen that for this value of τ the two methods yield indistinguishable results. When $\tau = -7.5$, however, the corresponding values are different. These are shown, together with the values for uniform continuous distribution, in figures 3 and 4. For both values of τ the two methods do not agree with the method assuming uniform continuous distribution.

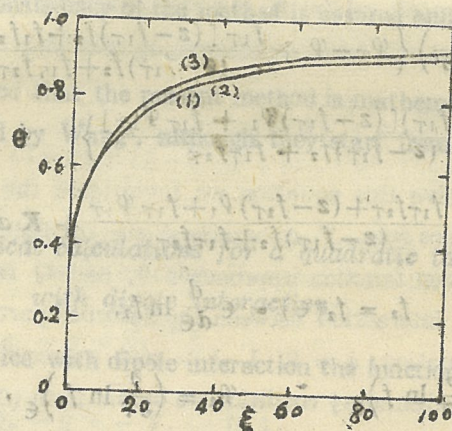


Fig. 1—The adsorption isotherm for a quadratic lattice when $\tau = -0.25$.

Curve (1), the method of modifying E_c .

Curve (2), the method of modifying ξ .

Curve (3), the old theory of uniform continuous distribution.

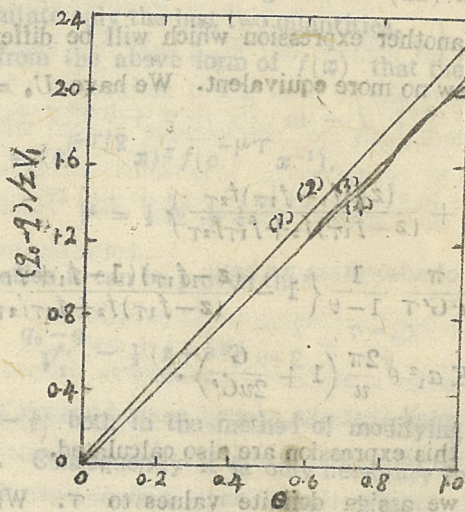


Fig. 2—Variation of the heat of adsorption with θ for a quadratic lattice when $\tau = -0.25$.

Curve (1), the method of modifying E_c .

Curve (2), the method of modifying ξ .

Curve (3), the old theory of uniform continuous distribution, from

eq. (16).

Curve (4), the old theory of uniform continuous distribution, from

eq. (15)

We also compute for one value of τ the quantity σ of the method of modifying ϵ . This measures the deviation from the ordinary expression of ϵ . With the help of (24) it can be shown that σ is an even function of $\epsilon - \frac{1}{2}$. The numerical values of σ for $\tau = -7.5$ are plotted in figure 3. The numerical values of σ for $\tau = -7.5$ are plotted in figure 3.

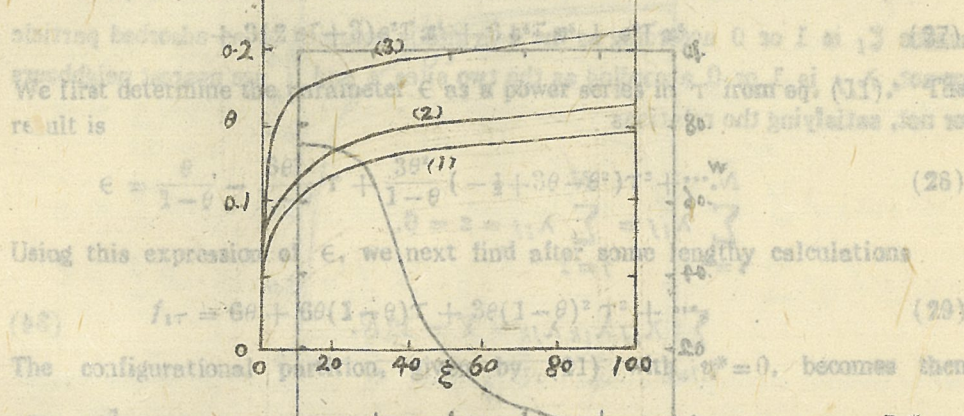


Fig. 3--The adsorption isotherm for a quadratic lattice when $\tau = -7.5$.

Curves numbered as in fig. 1.

The variation of the correction term of ϵ with ϵ for $\tau = -7.5$ is plotted in figure 4. We shall then compare the configuration partition function in accordance with Kirkwood's theory. The configuration partition function in the case of a quadratic lattice when $\tau = -7.5$ is plotted in figure 4.

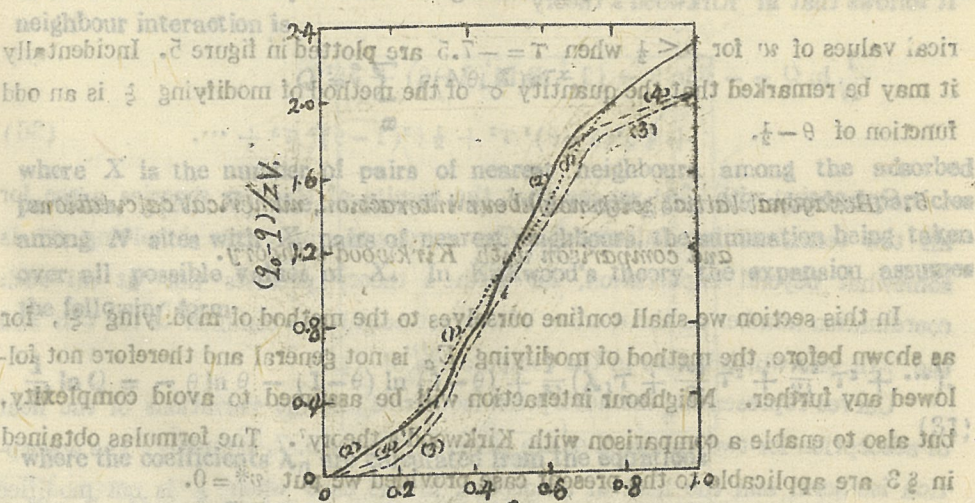


Fig. 4--Variation of the heat of adsorption with θ for a quadratic lattice when $\tau = -7.5$. Curves numbered as in fig. 2.

We also compute for one value of τ the quantity w of the method of modifying E_c . This measures the deviation from the ordinary expression of E_c . With the help of (24) it can be shown that w is an even function of $\theta - \frac{1}{2}$. The nume-

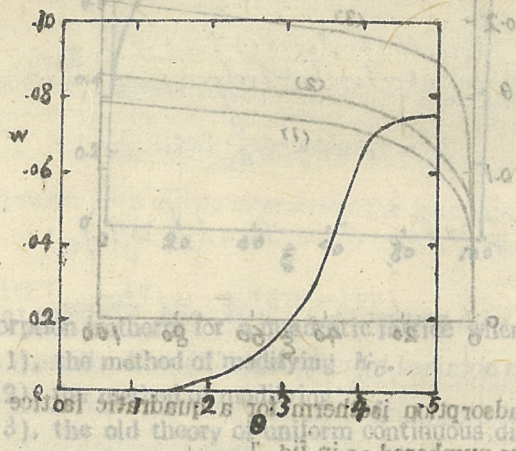


Fig. 5—Variation of the correction term of E_c with θ for a quadratic lattice when $\tau = -7.5$.

rical values of w for $\theta < \frac{1}{2}$ when $\tau = -7.5$ are plotted in figure 5. Incidentally it may be remarked that the quantity σ of the method of modifying ξ is an odd function of $\theta - \frac{1}{2}$.

5. Hexagonal lattice with neighbour interaction, numerical calculations and comparison with Kirkwood's theory.

In this section we shall confine ourselves to the method of modifying ξ , for as shown before, the method of modifying E_c is not general and therefore not followed any further. Neighbour interaction will be assumed to avoid complexity, but also to enable a comparison with Kirkwood's theory⁷. The formulas obtained in § 3 are applicable to the present case provided we put $\psi^* = 0$.

In order to compare the result with that of Kirkwood's theory we expand $\ln Q$ obtained in § 3 into power series of τ . For hexagonal lattice in the case

7. J. G. Kirkwood, *J. Chem. Phys.* 6 (1938), 70; H. Bethe and J. G. Kirkwood, *ibid.* 7 (1939), 578.

of neighbour interaction the function $f(x)$ reads (putting $\eta_\nu = 1$ for $\nu > 1$ and $\eta_1 = e^\tau$ in eq. (28) of Wang's paper, loc. cit.²)

$$f(x) = 1 + 6x + 3(2e^\tau + 3)x^2 + 2(3e^{2\tau} + 6e^\tau + 1)x^3 + 3(2e^\tau + 3)e^{2\tau}x^4 + 6e^{2\tau}x^5 + e^{2\tau}x^6 \quad (27)$$

We first determine the parameter ϵ as a power series in τ from eq. (11). The result is

$$\epsilon = \frac{\theta}{1-\theta} - \frac{3\theta^2}{1-\theta} \tau + \frac{3\theta^2}{1-\theta} \left(-\frac{1}{2} + 3\theta - \theta^2\right) \tau^2 + \dots \quad (28)$$

Using this expression of ϵ , we next find after some lengthy calculations

$$f_1\tau = 6\theta + 6\theta(1-\theta)\tau + 3\theta(1-\theta)^2\tau^2 + \dots \quad (29)$$

The configurational partition, given by (21) with $\varphi^* = 0$, becomes then

$$\frac{1}{N} \ln Q = -\theta \ln \theta - (1-\theta) \ln (1-\theta) + 3\theta^2 \tau + \frac{1}{2} \theta^2 (1-\theta)^2 \tau^2 + \frac{1}{2} \theta^2 (1-\theta)^2 \tau^2 + \dots \quad (30)$$

We shall then expand the configurational partition function in accordance with Kirkwood's theory. The configurational partition function in the case of neighbour interaction is

$$Q = \sum_X g(N\theta, X) e^{X\tau} \quad (31)$$

where X is the number of pairs of nearest neighbours among the adsorbed particles, $g(N\theta, X)$ the number of ways of arranging the $N\theta$ adsorbed particles among N sites with X pairs of nearest neighbours, the summation being taken over all possible values of X . In Kirkwood's theory the expansion assumes the following form

$$\frac{1}{N} \ln Q = -\theta \ln \theta - (1-\theta) \ln (1-\theta) + \frac{1}{N} \left(\lambda_1 \tau + \frac{\lambda_2}{2} \tau^2 + \frac{\lambda_3}{3!} \tau^3 + \dots \right) \quad (32)$$

where the coefficients λ_n are calculated from the equations

$$\sum_{m=1}^n \binom{n-1}{m-1} \lambda_m M_{n-m} = M_n, \quad M_n = X^n \quad (32)$$

the bar over X^n meaning the average of X^n for all possible distributions. The M 's are calculated by using the formula

$$X = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \lambda_{ij} \zeta_i \zeta_j \quad (33)$$

where ζ_i is 1 or 0 according as the i -th site is occupied by an adsorbed particle or not, λ_{ij} is 1 or 0 according as the two sites i and j are nearest neighbours or not, satisfying the relations

$$\sum_{j=1}^N \lambda_{ij} = \sum_{i=1}^N \lambda_{ij} = z = 6, \quad (34)$$

$$\sum_{i,j,k} \lambda_{ij} \lambda_{ik} \lambda_{jk} = Y = 12N. \quad (35)$$

The actual calculations are rather lengthy and are given in the Appendix. The result is

$$\lambda_1 = 3N\theta^2, \quad \lambda_2 = \lambda_3 = 3N\theta^2(1-\theta); \quad (36)$$

It follows that in Kirkwood's theory

$$\frac{1}{N} \ln Q = -\theta \ln \theta - (1-\theta) \ln (1-\theta) + 3\theta^2 \tau + \frac{1}{2} \theta^2 (1-\theta)^2 \tau^2 + \frac{1}{4} \theta^2 (1-\theta)^2 \tau^3 + \dots \quad (37)$$

Comparing with (30) we see that the results of the two theories agree for all the terms so far calculated. The agreement of terms involving τ^2 is somewhat beyond expectation, for Bethe's theory predicts not at all such coordination number as the number of nearest neighbours common to the i -th and the j -th site which occurs in the computation of λ_2 .

Curves representing the adsorption isotherms and the variations of the heat of adsorption for two values of τ are given in figures 6, 7, 8 and 9. The adsorption isotherm and the heat of adsorption in the case when ξ is not modified (i.e., $\sigma \equiv 0$) and when (16) is employed are also plotted in the same figures for comparison. The value of q when ξ is not modified but when (15) is applied is the same as in the case when ξ is modified. In both cases $q_0 - q - 3V_1$ is an odd function of $\theta - \frac{1}{2}$, for eq. (24) is still true with $z=6$ and $\mu=2$. Hence only its values for $\theta < \frac{1}{2}$ are shown.

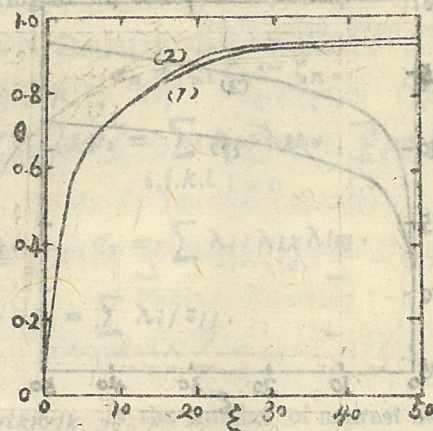


Fig. 6—The adsorption isotherm for a hexagonal lattice when $T = -0.25$.
Curve (1), ξ modified; curve (2), ξ not modified.

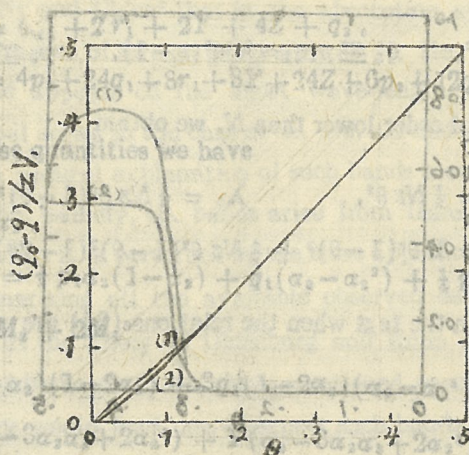


Fig. 7—Variation of the heat of adsorption with θ for a hexagonal lattice when $T = -0.25$. Curve (1), ξ modified; curve (2), ξ not modified, from eq. (16).

The writer wishes in conclusion to express his gratitude to Professor J. S. Wang of Tsinghua University for his very kind help.

J. S. Wang, Science Record 1 (1942), 100.

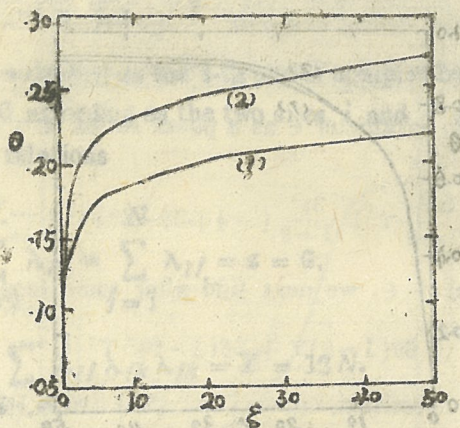


Fig. 8—The adsorption isotherm for a hexagonal lattice when $T = -7.5$. Curve (1), ξ modified; curve (2), ξ not modified.

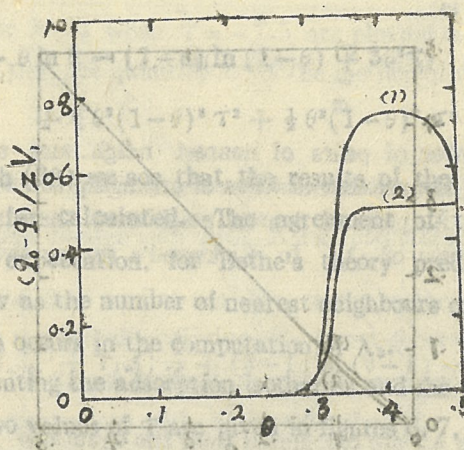


Fig. 9—Variation of the heat of adsorption with θ for a hexagonal lattice when $T = -7.5$. Curve (1), ξ modified; curve (2), ξ not modified, from eq. (16).

The writer wishes in conclusion to express his gratitude to Professor J. S. Wang of Tsinghua University for his very kind help.

$$\frac{(1+n-3N) \text{Appendix } (1-3N)0}{(1+n-3N)(2-3N)(1-3N)} = n^3$$

To simplify writing we introduce the notation:

$$\alpha_n = \zeta_1 \zeta_2 \cdots \zeta_n.$$

$$p_1 = \sum_{i,j} \lambda_{ij}, \quad p_2 = \sum_{i,j,k,l} \lambda_{ij} \lambda_{kl}, \quad p_3 = \sum_{i,j,\dots} \lambda_{ij} \lambda_{kl} \lambda_{mn}.$$

$$q_1 = \sum \lambda_{ij} \lambda_{ik}, \quad q_2 = \sum \lambda_{ij} \lambda_{ik} \lambda_{lm}, \quad r_1 = \sum \lambda_{ij} \lambda_{ik} \lambda_{il}.$$

$$Y = \sum \lambda_{ij} \lambda_{ik} \lambda_{jk} = \sum \lambda_{ij} z_{ij}, \quad Z = \sum \lambda_{ij} \lambda_{ik} \lambda_{jl}.$$

where $z_{ij} = \sum \lambda_{ik} \lambda_{jk}$ is the number of nearest neighbours common to the i -th and the j -th site, and in the summation the different subscripts do not take equal values. These quantities satisfy the relations

$$p_1^2 = 2p_2 + 4q_1 + p_3.$$

$$p_1 q_1 = 4q_1 + 2r_1 + 2Y + 4Z + q_2.$$

$$p_1^3 = 4p_1 + 24q_1 + 8r_1 + 8Y + 24Z + 6p_2 + 12q_2 + p_3.$$

In terms of these quantities we have

$$\lambda_1 = M_1 = \frac{1}{2} p_1 \alpha_1.$$

$$\lambda_2 = M_2 - M_1^2 = \frac{1}{2} p_1 \alpha_2 (1 - \alpha_2) + q_1 (\alpha_2 - \alpha_2^2) + \frac{1}{2} p_2 (\alpha_4 - \alpha_2^2).$$

$$\lambda_3 = M_3 - 3M_1 M_2 + 2M_1^3 = \frac{1}{2} p_1 \alpha_3 (1 - 2\alpha_2) + 3q_1 (1 - 2\alpha_2) (\alpha_3 - \alpha_2^2)$$

$$+ r_1 (\alpha_4 - 3\alpha_2 \alpha_3 + 2\alpha_2^2) + Y (\alpha_4 - 3\alpha_2 \alpha_3 + 2\alpha_2^2)$$

$$+ 3Z (\alpha_4 - \alpha_2 \alpha_3 - 2\alpha_2 \alpha_3 + 2\alpha_2^2) + \frac{1}{2} p_2 (1 - 2\alpha_2) (\alpha_4 - \alpha_2^2)$$

$$+ \frac{1}{2} p_3 \{ (\alpha_5 - \alpha_2 \alpha_3) - 2\alpha_2 (\alpha_4 - \alpha_2^2) \} + \frac{1}{2} p_3 (\alpha_6 - 3\alpha_2 \alpha_3 + 2\alpha_2^2).$$

$$2. \text{ Ny and Ch'en, Nature } 138, 1065, (1936).$$

$$\text{The } \alpha's \text{ are given by }^3 \text{ Physik } 41, 184 (1923), 55, 1 (1923) \text{ and}$$

$$\text{Phys. Rev. } 47, 72 (1932).$$

$$\alpha_n = \frac{\theta(N\theta-1)(N\theta-2)\cdots(N\theta-n+1)}{(N-1)(N-2)\cdots(N-n+1)}$$

For the other quantities we have, using (34),

$$\begin{aligned} p_1 &= \sum_{i,j} \lambda_{ij} \sum_{a=1}^N \lambda_{ia} = \sum_{i,j} \lambda_{ij}^2 = Nz(z-1) \\ \tau_1 &= \sum_{i,j,k} \lambda_{ij} \lambda_{ik} \sum_a \lambda_{ia} = \sum_{i,j,k} \lambda_{ij}^2 \lambda_{ik} = Nz(z-1)(z-2) \\ Z &= \sum_{i,j,k} \lambda_{ij} \lambda_{ik} \sum_a \lambda_{ja} = \sum_{i,j,k} \lambda_{ij}^2 \lambda_{ik} = Nz(z-1)^2 - Y \end{aligned}$$

It is clear then that the α 's are of order 1 and p_1, q_1, τ_1, Y, Z are of order N , p_2 and q_2 are of order N^2 , and p_3 is of order N^3 . It may be remarked that owing to the neglect of surface effects the expressions for p_1, q_1, τ_1 and Y are actually approximate. Consequently, if the surface effects are taken into account, it is legitimate only to conclude from the relations between these quantities that

$$p_2 \cong p_1^2 = N^2 z^2, \quad q_2 \cong p_1 q_1 = N^2 z^2 (z-1), \quad p_3 \cong p_1^3 = N^3 z^3.$$

Neglecting terms of order lower than N , we obtain

$$\lambda_1 = \frac{1}{2} Nz \theta^2, \quad \lambda_2 = \frac{1}{2} Nz \theta^2 (1-\theta)^2,$$

$$\lambda_3 = Y \theta^2 (1-\theta)^2 + \frac{1}{2} Nz \theta^2 (1-\theta)^2 (1-2\theta)^2,$$

which reduce to (35) in the text when the relations (34) are used.

The writer wishes in conclusion to express his gratitude to Professor J. S. Wang of Tsinghua University for his very kind help.

J. S. Wang, Science Record 1 (1952), 110.