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Monolayer Adsorption with Nearest Neighbor Interactions

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A sequence of approximate combinatorial treatments of the localized monolayer adsorption of a gas on a lattice of uniform sites with only nearest neighbor interactions allowed generates a one parameter family of isotherm equations. For each of those cases where the general lattice problem has been solved exactly, it is possible to find a value of the adjustable parameter such that critical behavior on the lattice in question is reproduced exactly.

In 1939 Fowler and Guggenheim⁽¹⁾ analyzed the treatment of localized monolayer adsorption of a gas on a lattice of uniform sites with only nearest neighbor (n. n.) interactions allowed in an elegant manner and discussed in detail two isotherm relations (*crude* and *refined*) showing first order phase change behavior under suitable conditions. Since the 1939 formulation of Fowler and Guggenheim, the parallel problem of the Ising model for ferromagnetism has received a great deal of attention.

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1) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Ch. X, Cambridge University Press (1939).

The many advances made toward a complete solution of the general problem of nearest neighbor (n. n.) lattice statistics and the powerful and sophisticated mathematical methods employed by recent workers in the field have been reviewed by (e. g.) Temperley,2) Hill,3) and Domb.4) The known exact solutions for two-dimensional lattices4) show that it is not enough to consider only the coordination number of a lattice (as in the work of Fowler and Guggenheim1))—more specific properties of the lattice must also be taken into account. In this paper, however, we shall consider a sequence of approximate combinatorial treatments of the adsorption problem based on coordination number arguments alone. Our results will generate a one parameter family of isotherm equations with the rather unexpected property of *exactly* reproducing critical behavior on the lattice in question for a suitable choice of the adjustable parameter. The effect of the more detailed features of the lattice that are neglected in the approximate treatments is merely to shift the value of the parameter in the basic family of equations. The combinatorial arguments, then, establish a set of "calibration points," with an easily comprehended physical basis, across the spectrum of possible values of the adjustable parameter.

In what follows we shall deal in a simple combinatorial manner with the problem of N identical gas molecules adsorbed on N_s identical sites, trying to take into account the n. n. (nearest neighbor) interactions among the adsorbed molecules.

The Combinatorial Problem

In many respects we shall follow the notation of Fowler and Guggenheim1) closely; however, we shall feel free to vary that notation wherever it proves convenient to do so. We express the Helmholtz free energy for the macro state of a localized monolayer with N identical gas molecules adsorbed on N_s identical sites by

$$F^{\text{ads}}/\boldsymbol{k}T = -\ln \Omega\,(n_i) - N(n_i)\ln a^\circ(T) + \varepsilon(n_i)/\boldsymbol{k}T \quad (1)$$

where the n_i are parameters of a geometric nature (bonds, triangles, etc.) by means of which we shall take into account n. n. interactions among the adsorbed molecules, A is the *extra* potential energy (relative to the gas state at infinite separation) due to n. n. interactions, $a^\circ(T)$ is the partition function of an isolated adsorbed molecule,* and Ω is a combinatorial expression for the number of micro states corresponding to the set of parameters n_i.5)

We shall minimize $F^{\text{ads}}/\boldsymbol{k}T$ with respect to the parameters n_i, subject to the restriction $N=N(n_i)$ $=$constant:

$$\delta\left(\frac{F^{\text{ads}}}{\boldsymbol{k}T}\right) = -\textstyle\sum_i\left[\dfrac{\partial \ln\Omega}{\partial n_i} + \dfrac{\partial N}{\partial n_i}\ln a^\circ(T) - \dfrac{1}{\boldsymbol{k}T}\dfrac{\partial A}{\partial n_i}\right]\delta n_i = 0$$

$$\delta N = \textstyle\sum_i(\partial N/\partial n_i)\delta n_i = 0 \quad (2)$$

Introducing the Lagrange multiplier α, we obtain i equations of the form

$$\frac{\partial \ln\Omega}{\partial n_i} + \frac{\partial N}{\partial n_i}(\ln a^\circ(T)-\alpha) - \frac{1}{\boldsymbol{k}T}\frac{\partial A}{\partial n_i} = 0 \qquad i=1,2,\cdots \quad (3)$$

Solution of the set of simultaneous equations given by Eq. 3 leads to the isotherm relation.

Our chief problem is the finding of adequate expressions for $\Omega=\Omega(n_i)$. We shall examine special cases, starting with simple ones and gradually proceeding to those more complex. Our ultimate goal is to find the appropriate form of the isotherm relation for the general case where adsorption takes place on a plane lattice for which each site is surrounded by z nearest neighbor (n. n.) sites.

Isolated Clusters

Turning now to the basic combinatorial problem, let us consider a set of N_s adsorption sites. If we were actually to draw in bonds between n. n. sites, we could divide those bonds into classes on the basis of the state—occupied (O) or unoccupied (U) by an adsorbed molecule—of the sites connected by a n. n. bond. Allowing the n. n. bonds to have a directional character (for proper multiplicity) we could distinguish four classes of bonds OO, OU, UO, and UU. We shall often find it convenient to discuss the combinatorial problem on a given lattice in terms of these classes of n. n. bonds.

Let us first turn to the case where the sites of a given set are treated as isolated clusters of sites. We consider the N_s sites as divided up into N_s/i clusters such that the clusters are relatively far apart but within any cluster each site has i-1 *equivalent* n. n. sites. If we denote a cluster containing i sites, everyone of which can be connected to each of the other i-1 sites by a n. n. bond, as an (i)-cluster, then in a (2)-cluster we have a pair of sites connected (connectable) by a n. n. bond,

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2) H. V. N. Temperley, "Changes of State," Ch. VI, Cleaver-Hume Press Ltd., London (1956).

3) T. L. Hill, "Statistical Mechanics," Ch. 7, McGraw-Hill Book Company, Inc., New York (1956).

4) C. Domb, *Advances in Physics*, **9**, 149 (1960).

* See Ref. 1, p. 429.

5) J. Hijmans and J. de Boer, *Physica*, **21**, 471 (1955).

and in a (3)-cluster the triplet of sites may be regarded as forming an equilateral triangle with n. n. bonds for sides. For clusters of higher order it is not possible to arrange the sites in a plane configuration so that all the sites of a cluster are equivalent, i. e. each site of the cluster connected to the other i-1 sites of the cluster by n. n. bonds.

In distributing N molecules over the N_s sites grouped into isolated clusters we need a scheme for counting the number of n. n. bonds of the type OO and for keeping track of configurational permutations. We could set up a scheme in terms of the n. n. bond classes mentioned at the beginning of this section, but in this particular case we choose to proceed differently.

Let us first turn to the case of isolated (2)-clusters. Suppose we place our N molecules on the N_s sites in such a way that the number of clusters containing *at least* one molecule is n_1 and the number of clusters containing *at least* two molecules is n_2. The number of clusters containing *at least* zero molecules is equal to the total number of clusters, i. e. $n_0=N_s/2$, and (included for convenience in notation) the number of clusters containing *at least* three molecules (n_3) is zero. Similarly the number of clusters containing *exactly* i molecules ($i=0$, 1, 2) is just n_i-n_{i+1}; here, and in the remainder of the paper, the symbol n_i denotes the number of clusters (of a given type) containing *at least* i molecules.

With due allowance for the possible permutations within a cluster, the number of micro states corresponding to the above specification (in terms of the n_i) is

$$\Omega=\frac{2^{n_1-n_2}\,n_0!}{(n_0-n_1)!\,(n_1-n_2)!\,n_2!} \tag{4}$$

If $-\varepsilon$ is the interaction potential energy (relative to the gas state at infinite separation) of a pair of adsorbed molecules a n. n. distance apart, then the total extra potential energy due to n. n. interactions among the adsorbed molecules is just $-\varepsilon$ times the number of n. n. bonds of type OO. Thus, for isolated (2)-clusters

$$A=-\varepsilon n_2 \tag{5}$$

and

$$N=n_1+n_2 \tag{6}$$

Setting $n_i/n_0=f_i$, where f_i is the fraction of the total number of clusters containing *at least* i molecules, and making use of Stirling's approximation for the logarithm of a factorial, we obtain from Eqs. 3, 4—6 the relations

$$\frac{f_1-f_2}{1-f_1}=2x \qquad \frac{f_2}{f_1-f_2}=\frac{\zeta x}{2} \tag{7}$$

where $\zeta=\exp(\varepsilon/\boldsymbol{k}T)$ and $x=a^\circ(T)e^{-\alpha}=\lambda_g a^\circ(T)=p/p^\circ$ (λ_g being the absolute activity of the gas molecules*). Our ζ corresponds to the quantity $\exp(-2\omega/z\boldsymbol{k}T)$ in the notation of Fowler and Guggenheim.1) Equation 7 yields the relation

$$4f_2(1-f_1)/(f_1-f_2)^2=\zeta \tag{8}$$

Equation 8 is a slightly disguised version of the equation of quasichemical equilibrium discussed by Fowler and Guggenheim1); it is an exact equation for the case of isolated (2)-clusters and is often invoked as an approximation in the case of more complex lattice situations.

From Eq. 7 and the relation $f_1+f_2=2\theta$ we obtain

$$\frac{\theta}{1-\theta}=\frac{x(1+\zeta x)}{1+x} \tag{9}$$

Solving Eq. 9 for x we get

$$x=\frac{\theta}{1-\theta}\cdot\frac{1}{\zeta}\cdot\left[\frac{\beta-1+2\theta}{2\theta}\right] \tag{10}$$

where

$$\beta=[1-4\theta(1-\theta)(1-\zeta)]^{1/2}$$

If there are no interactions among the adsorbed molecules, then $\varepsilon=0$, $\zeta=1$, and Eqs. 9 and 10 reduce to the simple Langmuir equation $x=\theta/(1-\theta)$. If there are attractive interactions among the adsorbed molecules, then $\varepsilon>0$, $\zeta>0$, and the coverage θ is greater for a given temperature and pressure than that predicted by the Langmuir equation.

The treatment of isolated clusters is useful because it allows us to examine the effect of n. n. interactions on the adsorption isotherm for a simple case for which the combinatorial expression $\Omega(n_i)$ can be evaluated exactly. The formalism that we have set up for treating isolated clusters then serves as a starting point for the treatment of connected lattices where the exact evaluation of the combinatorial expression $\Omega(n_i)$ is an extremely difficult problem.

Rule of Thumb Approximation

We now wish to consider a plane connected lattice* for which each site has z n. n. sites and wish to treat the adsorption problem on such a lattice according to an approximate method which is modeled after the treatment of isolated clusters. The connectivity of the lattice is a great source of trouble in setting up an appropriate combinatorial expression. While in the isolated cluster treatment it was possible to change the parametric specification n_i in unitary steps by the addition of

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* See Ref. 1, p. 431, for details.

* A lattice is called *connected* if the sites are all equivalent and it is possible to pass from an arbitrary site to any other site of the set by traveling along n. n. bonds only.

single molecules, on a connected lattice the parameters more often change by z units upon the addition of single molecules to the lattice; thus, if we place one molecule on an otherwise empty connected lattice we immediately form z n. n. bonds of type OU (or UO).

Now it is reasonably evident that to the first molecule placed on a uniform lattice (connected or otherwise) all the N_s sites are equivalent, and the connectivity of the lattice is a dormant feature which becomes important when more molecules are added. Thus there are just N_s ways of placing one molecule on N_s uniform sites, regardless of the connectivity of the lattice. We now adopt the following rule of thumb condition:

In any approximate treatment of adsorption on a connected lattice the combinatorial expression when evaluated for the case of one molecule on N_s sites must be at least approximately equal to N_s for all values of z.

If we let $\Omega(1)$ represent the value of the combinatorial expression Ω for the case of one molecule on the N_s sites of a plane connected lattice, then the mathematical form of the rule of thumb requirement is that

$$\lim_{N_s\to\infty} \{\ln \Omega(1)/\ln N_s\} = 1$$

for all values of z.

A plane connected lattice, each site having z n. n. sites, has $zN_s/2$ n. n. bonds between the sites. We should now like to treat these $zN_s/2$ n. n. bonds in a manner similar to the treatment of n. n. bonds in isolated (2)-clusters. In the case of isolated (2)-clusters we had a 1 - 1 correspondence between the number of clusters and the number of n. n. bonds, and we were at liberty to set up the combinatorial expression in terms of cluster parameters or bond parameters; in fact we chose cluster parameters. In this section we wish to deal with the n. n. bonds themselves, carrying the development through in terms of n. n. bond parameters.

In a familiar fashion we set m_i $(i=0,\ 1,\ 2)$ equal to the number of n. n. bonds whose terminal sites are occupied by *at least* i adsorbed molecules. We shall assume that our directional convention for n. n. bonds is such that for any distribution of N molecules on the N_s sites the number of n. n. bonds of type OU is approximately equal to the number of type UO. Letting the symbol itself (OO e.g.) stand for the number of n. n. bonds of that type, we have, in terms of our more familiar parameters,

$$\left.\begin{aligned} zN_s/2 &= m_0 \\ \mathrm{UU} &= m_0 - m_1 \\ \mathrm{UO} = \mathrm{OU} &= (m_1 - m_2)/2 \\ \mathrm{OO} &= m_2 \end{aligned}\right\} \qquad (11)$$

If we were to treat the $zN_s/2$ n. n. bonds as *permutable things,* the number of distinguishable bond configurations corresponding to a definite set m_i would be

$$\Omega = \frac{m_0!}{(m_0-m_1)!\,[(1/2)(m_1-m_2)]!^2\, m_2!} \qquad (12)$$

Within the limits of Stirling's approximation for factorials Eq. 12 is the same as

$$\Omega = \frac{m_0!\, 2^{m_1-m_2}}{(m_0-m_1)!\,(m_1-m_2)!\, m_2!} \qquad (13)$$

which bears out what we were saying previously about the treatment of isolated (2)-clusters.

In dealing with n. n. bond configurations (with $m_0=zN_s/2$) we are (for $z>1$) counting many more configurations than can be physically realized by distributing N molecules on N_s sites; we find, in fact, that

$$\lim_{N_s\to\infty} \{\ln \Omega(1)/\ln N_s\} = z$$

for Eq. 13. We note, however, that if we set

$$\Omega = \left\{\frac{m_0!}{(m_0-m_1)!\,[(1/2)(m_1-m_2)]!^2\, m_2!}\right\}^{1/z} \qquad (14)$$

the rule of thumb condition is satisfied.

Equations 3 and 14 together with the conditions

$$\left.\begin{aligned} A &= -\varepsilon m_2 \\ N &= (m_1 + m_2)/z \\ m_0 &= zN_s/2 \\ g_i &= m_i/m_0 \\ 2\theta &= g_1 + g_2 \end{aligned}\right\} \qquad (15)$$

lead to the isotherm equation

$$x = \frac{\theta}{1-\theta} \cdot \frac{1}{\zeta^z} \cdot \left[\frac{\beta^{(1)}-1+2\theta}{2\theta}\right] \qquad (16)$$

where $\beta^{(\nu)}=[1-4\theta(1-\theta)(1-\zeta^{z/\nu})]^{1/2}$. According to this convention our previous β (Eq. 10) is to be written as $\beta=\beta^{(z)}$.

In establishing Eq. 12 we assumed that all the n. n. bonds were freely permutable; for a connected lattice such is not the case, e. g. it is not physically meaningful to *singly* permute a bond of type OO with one of type UU. In the following we shall try to obtain a better treatment of the combinatorial problem.

For convenience we shall consider only connected lattices for which z is even. Let us adopt some convention whereby the z n. n. bonds connecting a given site with its z n. n. sites can be specified as pointing to the *left* or to the *right,* $z/2$ bonds belonging to each category. We now demand that all the n. n. bonds be considered as pointing to the *right,* say; this uniquely fixes the site of origin of each n. n. bond. We identify a given n. n. bond by giving the name of the site of origin and the name of the site of termination. There are

N_s sites which can serve as origin; and, for any of those sites, there are $z/2$ additional sites which can serve as terminus (lie to the *right*) for a n. n. bond—$zN_s/2$ possibilities in all, which is as it should be.

We now freely permute only n. n. bonds of similar origin; i. e. we permute bonds of type OV among themselves and those of type UV among themselves (V=O, U). The number of distinguishable n. n. bond configuarations corresponding to the above restriction is

$$\Omega=\frac{[(1/2)zN]!\,[(1/2)z(N_s-N)]!}{(m_0-m_1)!\,[(1/2)(m_1-m_2)]!\,[(1/2)(m_1-m_2)]!\,m_2!} \tag{17}$$

Within the limits of Stirling's approximation, Eq. 17 is the same as

$$\Omega=\frac{m_0!\,2^{m_1-m_2}}{(m_0-m_1)!\,(m_1-m_2)!\,m_2!}\times\frac{[(1/2)zN]!\,[(1/2)z(N_s-N)]!}{[(1/2)\,zN_s]!} \tag{18}$$

Once again we find that if we set

$$\Omega=\left\{\frac{[(1/2)zN]!\,[(1/2)z(N_s-N)]!}{(m_0-m_1)!\,[(1/2)(m_1-m_2)]!^2\,m_2!}\right\}^{2/z} \tag{19}$$

the rule of thumb condition is satisfied.

Equations 3, 15, and 19 lead to the isotherm equation

$$x=\frac{\theta}{1-\theta}\cdot\frac{1}{\zeta^z}\cdot\left[\frac{\beta^{(2)}-1+2\theta}{2\theta}\right]^2 \tag{20}$$

Finally, after a little casting about, we find that the expression

$$\Omega=\frac{m_0!\,2^{m_1-m_2}}{(m_0-m_1)!\,(m_1-m_2)!\,m_2!}\times\frac{[(z-1)N]!\,[(z-1)(N_s-N)]!}{[(z-1)N_s]!} \tag{21}$$

satisfies the rule of thumb condition and together with Eqs. 3 and 15 leads to the isotherm equation

$$x=\frac{\theta}{1-\theta}\cdot\frac{1}{\zeta^z}\cdot\left[\frac{\beta^{(z)}-1+2\theta}{2\theta}\right]^z \tag{22}$$

which (remembering that $\beta^{(z)}=\beta$) is just the *refined* isotherm relation of Fowler and Guggenheim.[1)]

In order to solve the problem of adsorption with n. n. interactions by the methods of this section what is needed is a way of counting the number of *coherent* bond configurations corresponding to the set of parameters m_i. A bond configuration is called *coherent* if for each lattice site the bonds originating and terminating at that site are physically compatible; i. e., for a site occupied by an adsorbed molecule the bonds originating and terminating at that site must be of type O- and -O, respectively. In Eqs. 12 and 17 we counted the number of *incoherent* and *semi-coherent* bond configurations, respectively, corresponding to the set of parameters m_i; these numbers being considerably larger than the number sought, we reduced them to approximately the right order by raising them to fractional powers (Eqs. 14 and 19). In Eq. 21 we took the number of incoherent bond configurations and multiplied it by a (variable) reduction factor.

The sequence *incoherent, semicoherent, coherent* brings to mind a geometric progression, and we ask ourselves if perhaps it may not be the case (approximately) that

$$\Omega_{\mathrm{coh}}/\Omega_{\mathrm{semicoh}}=\Omega_{\mathrm{semicoh}}/\Omega_{\mathrm{incoh}}$$

Carrying out the implications of this assumption (Eqs. 14 and 19) we produce the isotherm equation

$$x=\frac{\theta}{1-\theta}\cdot\frac{1}{\zeta^z}\cdot\left[\frac{\beta^{(3)}-1+2\theta}{2\theta}\right]^3 \tag{23}$$

It is of interest to note that the various approximate isotherm relations of this section all have the common form

$$x=\frac{\theta}{1-\theta}\cdot\frac{1}{\zeta^z}\cdot\left[\frac{\beta^{(\nu)}-1+2\theta}{2\theta}\right]^\nu \qquad \nu=1,\,2,\,3,\,z \tag{24}$$

The family of isotherms represented by Eq. 24 contains members that show first order phase change behavior. The critical condition is found by setting $\partial x/\partial\theta=0$ for $\theta=1/2$;* this operation leads to the relation

$$\zeta_c^{1/2}=[\nu/(\nu-2)]^{\nu/z} \tag{25}$$

We see that the class of isotherm equations with $\nu\leqq 2$ does not show first order phase change behavior, whereas the class of equations with $\nu>2$ does show such behavior. Now it is our conjecture that in deriving those equations with $\nu\leqq 2$ (in the context of the present series of approximations) we consistently *overcount* the number of distinguishable configurations Ω corresponding to a *given* amount of energy A and that in deriving the equation with $\nu=z$ we consistently *undercount* the requisite number of configurations. If our conjecture is valid, then $\Omega_{\mathrm{correct}}$ should lie somewhere between the Ω values of Eqs. 19 and 21.

The foregoing considerations suggest that by suitable averaging of pairs of combinatorial expressions, one of which overcounts while the other undercounts, new approximations can be made to $\Omega_{\mathrm{correct}}$. By way of example, using the notation $\Omega_{(y)}$ to stand for the combinatorial expression stated in Eq. y, let us investigate the combinations

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* See Ref. 1. All the members of the family of Eq. 24 have the same symmetry properties as the *refined* isotherm relation discussed by Fowler and Guggenheim.

$$\Omega_{\varphi}=\Omega_{(14)}{}^{1-\varphi}\Omega_{(21)}{}^{\varphi} \tag{26φ}$$

$$\Omega_{\chi}=\Omega_{(19)}{}^{1-\chi}\Omega_{(21)}{}^{\chi} \tag{26χ}$$

$$\Omega_{\phi}=\left[\frac{N_s!}{N!\,(N_s-N)!}\right]^{1-\phi}\Omega_{(21)}{}^{\phi} \tag{26ϕ}$$

These combinatorial expressions together with Eqs. 3 and 15 lead to isotherm relations of the form 24 with $\nu=2+\varphi(z-2)$, $1+\chi(z-1)$, ϕz respectively.

Conclusion

It is now clear that combinatorial arguments of the present type will preserve the form of Eq. 24 and will merely change the numerical value of the parameter ν. We have, then, as the end result of our combinatorial considerations the family of Eq. 24 containing the adjustable parameter ν. The individual values of ν thus far produced cannot be entirely satisfactory since the derivations took no explicit notice of lattice properties other than coordination number. The surprising thing about Eq. 24 is that it can reproduce *exactly* critical behavior on any given lattice by suitable adjustment of the parameter ν; this result should be of some importance in the general problem of lattice statistics.

In order to display the properties of Eq. 24 we have tabulated some exact results for two-dimensional lattices, as well as some "best" results for three-dimensional ones, as given in the article by Domb.4) In Table I we display the quantity $(\ln\zeta_c{}^{z/4})^{-1}$, which corresponds to the quantity $\boldsymbol{k}T_c/qJ$ in Domb's notation,4) together with the corresponding z and ν values for a number of lattice situations:

$$(\ln\zeta_c{}^{z/4})^{-1}=2[\nu\ln(\nu/(\nu-2))]^{-1} \tag{27}$$

TABLE I. EXACT OR "BEST" VALUES OF $(\ln\zeta_c{}^{z/4})^{-1}$ AND ν FOR VARIOUS LATTICE SITUATIONS

Lattice	z	$(\ln\zeta_c{}^{z/4})^{-1}$	ν
Linear chain	2	0	2
Honeycomb	3	0.506	2.54
Kagomé	4	0.536	2.65
Simple quadratic	4	0.567	2.79
Triangular	6	0.607	3.00
Simple cubic	6	0.752	4.42
Body centered cubic	8	0.794	5.25
Face centered cubic	12	0.816	5.78