

## Statistical Mechanics of Multimolecular Adsorption. I

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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It compares the energy released by a 100-megaton explosion to a 100-megaton earthquake. This is not right. If the authors would have used the correct relationship between seismic moment and energy, they would find that the energy released by a 100-megaton earthquake is about 100 times as much energy as a 100-megaton explosion. The article does not have any references.

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Written by Edgar McCarroll, 14 July 2012 19:59

## Statistical Mechanics of Multimolecular Adsorption. I

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Cassie's statistical treatment of multimolecular adsorption on a free surface, leading to the BET equation, is criticized and corrected. The method is generalized to include adsorption when the maximum number of layers of adsorbate is restricted. The isotherm equation obtained is the same as that found by Brunauer, Emmett, and Teller for this case, rather than the equation proposed by Pickett. The BET equation, though not completely satisfactory, is apparently the correct equation for the particular model used. Real improvements in the theory should follow from refinements in the model rather than from modifications in the treatment of the BET model. A more refined

model is proposed and the general method of using it is discussed. The BET model is shown to be a crude special case of the model suggested here, but it has the advantage of presenting no mathematical difficulties. Preliminary results, based on improved models, indicate that a somewhat refined multimolecular adsorption theory is capable of predicting capillary condensation for suitable values of parameters, thus suggesting that the ideas of multimolecular adsorption and capillary condensation are not really in conflict, as is generally assumed. Further discussion is deferred to a subsequent paper.

SEVERAL papers have appeared recently which direct attention to the foundations of the Brunauer-Emmett-Teller<sup>1</sup> theory of multimolecular adsorption. Cassie<sup>2</sup> has derived the BET equation for adsorption on a free surface (Eq. (15)) using a statistical argument. Pickett<sup>3</sup> has proposed a modification of the BET equation for adsorption when the number of layers of adsorbate is restricted (Eq. (27)). Actually, it appears to the present writer that Cassie has obtained the correct result by an incorrect argument and that Pickett's modification lacks theoretical justification,<sup>4</sup> though it seems to extend the range of agreement with experiment in some cases. The work of Cassie and of Pickett will be discussed further below in the light of results obtained here. We consider only localized adsorption in this paper.

## MULTIMOLECULAR ADSORPTION ON A FREE SURFACE

We adopt the notation of Cassie as far as convenient and the BET model. That is, we suppose that there are  $B$  localized sites per unit surface area of adsorbent, that  $X$  of these sites are occupied by adsorbed molecules (first layer of adsorbate), and that  $A-X$  molecules have been adsorbed on top of the  $X$  molecules in the

first layer (thus forming second and higher layers). Also, molecules in the first adsorbed layer are characterized by a potential energy  $-\epsilon_1$  and those in the second and higher layers by  $-\epsilon_L$  (assumed the same as in the liquid state), both referred to infinite separation as energy zero. The partition function for a molecule in the first layer is then  $j_S \exp(\epsilon_1/kT)$  and that for a molecule in higher layers is  $j_L \exp(\epsilon_L/kT)$ . One can approximate  $j_S$  and  $j_L$  by harmonic oscillator models:<sup>5</sup>

$$j_S = (kT/h\nu_S)^3 j, \quad (1)$$

$$j_L = (kT/h\nu_L)^3 j, \quad (2)$$

where  $j$  is the partition function for all internal degrees of freedom. This approximation is not essential to the argument.

The separate partition functions for the  $X$  molecules in the first layer and the  $A-X$  in higher layers are then

$$Q_S = \frac{B!}{(B-X)!X!} [j_S \exp(\epsilon_1/kT)]^X, \quad (3)$$

$$Q_L = \frac{(A-1)!}{(A-X)!(X-1)!} [j_L \exp(\epsilon_L/kT)]^{A-X}. \quad (4)$$

The factor  $B!/(B-X)!X!$  is the number of distinguishable ways  $X$  identical molecules may be distributed among  $B$  sites. The factor

<sup>1</sup> S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).

<sup>2</sup> A. B. D. Cassie, *Trans. Faraday Soc.* **41**, 450 (1945).

<sup>3</sup> G. Pickett, *J. Am. Chem. Soc.* **67**, 1958 (1945).

<sup>4</sup> T. L. Hill, *J. Am. Chem. Soc.* (March, 1946).

<sup>5</sup> See Eqs. (802,7) and (803,4) of Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939).

$(A-1)!/(A-X)!(X-1)!$  is the number of distinguishable ways  $A-X$  identical molecules may be distributed on top of the  $X$  molecules of the first layer (that is, the number of ways  $A-X$  objects may be placed in  $X$  boxes, there being no restriction on the number per box).

The complete partition function of the system is then

$$Q = \sum_{X=1}^k Q_S Q_L = \sum_{X=1}^k \left\{ \frac{A!B!}{(A-X)!(B-X)!(X!)^2} \times [j_S \exp(\epsilon_1/kT)]^X [j_L \exp(\epsilon_L/kT)]^{A-X} \right\} \quad (5)$$

$$k = A \quad (A < B) \\ k = B \quad (A > B)$$

in which we have neglected unity as compared to  $A$  and  $X$ . The difference between the present treatment and that of Cassie should now be evident. Essentially, he omitted<sup>6</sup> the factorial expression in Eq. (4) and then incorrectly<sup>7</sup> introduced a factor  $A!/X!(A-X)!$  on combining  $Q_S$  and  $Q_L$ . The two errors happened to cancel each other because unity may be neglected compared to  $A$  and  $X$  in Eq. (4).

We make the usual excellent approximation of setting  $\log Q$  equal to the logarithm of the largest term in the sum. The value of  $X$  which gives this term is found from

$$\frac{\partial \log Q_S Q_L}{\partial X} = 0. \quad (6)$$

On taking the logarithm and differentiating as

indicated, there results

$$(A-X)(B-X) = \beta X^2, \quad (7)$$

with

$$\beta = \frac{j_L}{j_S} \exp[(\epsilon_L - \epsilon_1)/kT]. \quad (8)$$

The chemical potential of the adsorbed molecules is

$$\frac{\mu_A}{kT} = -\frac{\partial \log Q_S Q_L}{\partial A} \quad (9)$$

$$= \log \frac{A-X}{A} - \frac{\epsilon_L}{kT} - \log j_L, \quad (10)$$

where  $X$  is to be obtained from Eq. (7). For the gas phase, we write

$$\frac{\mu_G}{kT} = \frac{\alpha}{kT} + \log p, \quad (11)$$

where  $\alpha$  is a constant which need not be further specified for our purposes. Equating  $\mu_A$  and  $\mu_G$ :

$$\log \frac{A-X}{A} - \frac{\epsilon_L}{kT} - \log j_L = \frac{\alpha}{kT} + \log p. \quad (12)$$

For the pure liquid:

$$-\frac{\epsilon_L}{kT} - \log j_L = \frac{\alpha}{kT} + \log p_0. \quad (13)$$

Hence, we have

$$x = p/p_0 = (A-X)/A. \quad (14)$$

Combining Eqs. (7) and (14) gives the BET equation

$$A/B = cx/(1-x)(1-x+cx) \quad (15)$$

with

$$c = 1/\beta. \quad (16)$$

### MULTIMOLECULAR ADSORPTION WITH A LIMITED NUMBER OF LAYERS

In this section we shall extend the above treatment to the case of  $n$  (the maximum number of layers) finite.

If  $A$  molecules are adsorbed, suppose  $X_1$  are in the first layer,  $X_2$  in the second,  $\dots$ , and  $X_n$  in the  $n$ th layer. Then

$$X_1 + X_2 + \dots + X_n = A. \quad (17)$$

For given values of  $X_1, X_2, \dots, X_n$ , the number of distinguishable arrangements for the second and higher layers is found by taking the product of (1) the number of ways  $X_2$  objects may be distributed among  $X_1$  sites, (2) the number of ways  $X_3$  objects may be distributed among  $X_2$  sites,

<sup>6</sup> This resulted from his treatment of second and higher layers as being structureless—the BET model was not introduced.

<sup>7</sup> There is no entropy of mixing when identical molecules are exchanged between two energy levels. The argument in the introduction of Cassie's paper should refer to the corresponding factor in Eq. (4).

etc. That is,

$$\frac{X_1!}{X_2!(X_1-X_2)!} \frac{X_2!}{X_3!(X_2-X_3)!} \cdots \frac{X_{n-1}!}{X_n!(X_{n-1}-X_n)!} = \frac{X_1!}{(X_1-X_2)!(X_2-X_3)! \cdots (X_{n-1}-X_n)!X_n!}. \quad (18)$$

Then

$$Q_S = \frac{B!}{(B-X_1)!X_1!} [j_S \exp(\epsilon_1/kT)]^{X_1}, \quad (19)$$

$$Q_L = \frac{X_1! [j_L \exp(\epsilon_L/kT)]^{A-X_1}}{(X_1-X_2)!(X_2-X_3)! \cdots (X_{n-1}-X_n)!X_n!}; \quad (20)$$

and

$$Q = \sum_{X_1} \cdots \sum_{X_{n-1}} Q_S Q_L, \quad (21)$$

where the limits of summation in Eq. (21) are complicated, but are not needed here.

We again set  $\log Q$  equal to the logarithm of the largest term in the sum. The values of  $X_1, X_2, \dots, X_{n-1}$  which give this term are found from

$$\partial \log Q_S Q_L / \partial X_i = 0, \quad i=1, 2, \dots, n-1, \quad (22)$$

using Eq. (17) for  $X_n$ . One finds, in the same way as Eq. (7) is obtained,

$$\begin{cases} (B-X_1)X_n = \beta(X_1-X_2)(X_{n-1}-X_n), \\ (X_1-X_2)X_n = (X_2-X_3)(X_{n-1}-X_n), \\ \vdots \\ (X_{n-3}-X_{n-2})X_n = (X_{n-2}-X_{n-1})(X_{n-1}-X_n), \\ (X_{n-2}-X_{n-1})X_n = (X_{n-1}-X_n)^2. \end{cases} \quad (23)$$

Also, from Eqs. (9), (11), (13), and (17) (the steps are the same as for Eq. (14)),

$$X_n = x(X_{n-1}-X_n). \quad (24)$$

Combining Eqs. (23) and (24),

$$\begin{aligned} X_1 - X_2 &= \frac{(B-X_1)x}{\beta}, \\ X_i - X_{i+1} &= (X_{i-1} - X_i)x = (X_1 - X_2)x^{i-1} \\ &= \frac{(B-X_1)x^i}{\beta} \quad (i=2, 3, \dots, n-1), \\ X_n &= \frac{(B-X_1)x^n}{\beta}. \end{aligned} \quad (25)$$

Finally, by Eqs. (17) and (25),

$$\frac{A}{B} = \frac{(X_1-X_2) + 2(X_2-X_3) + \cdots + (n-1)(X_{n-1}-X_n) + nX_n}{(B-X_1) + (X_1-X_2) + \cdots + (X_{n-1}-X_n) + X_n} \quad (26)$$

$$\begin{aligned} &= \frac{\frac{B-X_1}{\beta}(x + 2x^2 + \cdots + nx^n)}{(B-X_1) + \frac{(B-X_1)}{\beta}(x + x^2 + \cdots + x^n)} \\ &= \frac{cx[1 - (n+1)x^n + nx^{n+1}]}{(1-x)(1-x+cx-cx^{n+1})}, \end{aligned} \quad (27)$$

which is the BET result.

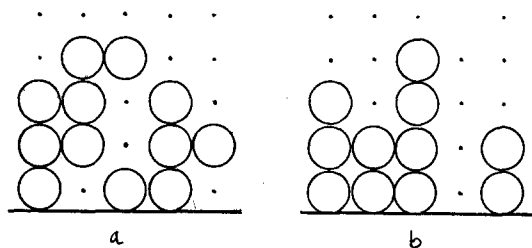


FIG. 1.

Pickett gives an alternative equation. However, the fact that Eq. (27) can be obtained from statistical mechanics (considering only possible states of the system, without recourse to a mechanism), as well as from the kinetic argument of the BET theory, indicates that it is certainly the correct equation for this model. The obvious implication is that real improvements in the theory must come from refining the model itself rather than from modifications of the type introduced by Pickett. We begin the discussion of other models in the next section.

#### INTRODUCTION TO A REFINED TREATMENT

In this section we shall indicate how the BET model may be considerably refined, at least in principle.<sup>8</sup> A more detailed treatment of the subject will be presented in a later paper of this series. We shall also treat, in future papers, multimolecular adsorption on a mobile first layer, the transition from a localized to a mobile first layer, and the relations between the adsorption isotherm and the two-dimensional equation of state (in mobile monomolecular adsorption).

The most general model to be considered here is the following. Molecules are adsorbed onto vacant sites of a lattice, with the restriction that a particular vacant lattice site cannot be occupied by a molecule unless at least one nearest neighbor site is already occupied or unless the site is in the first layer of the lattice (i.e., in the layer next to the surface of the adsorbent). The lattice is built up on the surface of the solid and sites correspond to possible equilibrium positions of molecules in the liquid state. Ordinarily the packing is assumed to be face-centered cubic, with 12 nearest neighbors ( $z=12$ ). As before, the potential energy of interaction between the

adsorbent and adsorbed molecules in the first layer is  $-\epsilon_1$  and the average potential energy of a molecule in the liquid state is  $-\epsilon_L$ . Hence, the potential energy associated with each pair of nearest neighbors is  $-2\epsilon_L/z$ . The total potential energy of the system is

$$U = -\epsilon_1 X - 2\epsilon_L N/z, \quad (28)$$

where  $X$  is the number of adsorbed molecules in the first layer and  $N$  is the number of pairs of nearest neighbors in the particular configuration being considered, *including* pairs involving molecules in the first layer.

As an example, in the two-dimensional simple cubic configuration of Fig. 1a,  $z=4$ ,  $X=3$ , and  $N=11$ . This may be contrasted with a two-dimensional BET configuration, illustrated in Fig. 1b. The BET model allows (the same is true in three dimensions) only vertical additions to the lattice and also only takes into account vertical nearest neighbors. Thus,  $z=2$ ,  $N=A-X$ , and, from Eq. (28),

$$U = -\epsilon_1 X - \epsilon_L (A - X). \quad (29)$$

In Fig. 1b,  $X=4$  and  $N=A-X=7$ .

We return now to the general problem. For given values of  $X$ ,  $A$ , and  $B$ , there are  $p(X, A, B)$  distinguishable configurations such that each molecule has either at least one nearest neighbor or is in the first layer, or both. We group these configurations according to the value of  $N$ : there are  $g(N, X, A, B)$  configurations with exactly  $N$  pairs of nearest neighbors. Hence,

$$\sum_N g(N, X, A, B) = p(X, A, B). \quad (30)$$

We have implicitly been considering the case of adsorption on a free surface ( $n=\infty$ ). If  $n$  is finite, there is a new obvious restriction on acceptable configurations. In this case we may write

$$\begin{aligned} \sum_N G(N, X, A, B, n) &= P(X, A, B, n), \\ G(N, X, A, B, \infty) &= g(N, X, A, B), \\ P(X, A, B, \infty) &= p(X, A, B). \end{aligned} \quad (31)$$

The partition function for the system ( $n=\infty$ ) is

$$\begin{aligned} Q &= \sum_{X=1}^k \{ [j_s \exp(\epsilon_1/kT)]^X j_L^{A-X} \\ &\quad \times \sum_N g(N, X, A, B) \exp(2\epsilon_L N/zkT) \}. \end{aligned} \quad (32)$$

$$k = A \quad (A < B), \quad k = B \quad (A > B).$$

<sup>8</sup> See Chapter X of Fowler and Guggenheim (reference 5) for an analogous discussion of monolayers.

For  $n$  finite replace  $g$  by  $G$ . The general procedure is the same as in the previous sections, with Eq. (13) still applying.

The above formal treatment can easily be modified so as to apply to capillaries with two parallel walls, and with the same lattice sites available to molecules building up on either wall. This is a more satisfactory but more difficult approach than the above ( $n$  finite), where,

$$p(X, A, B) = g(A - X, X, A, B) = \frac{A!B!}{(A - X)!(B - X)!(X!)^2}, \quad (33)$$

$$P(X, A, B, n) = G(A - X, X, A, B, n)$$

$$= \sum_{x_2} \cdots \sum_{x_{n-1}} \frac{B!}{(B - X)!(X - X_2)!(X_2 - X_3)! \cdots (X_{n-1} - X_n)!X_n!}. \quad (34)$$

Obvious successive improvements in the BET model would follow from (1) taking into account non-vertical configurations, (2) taking into account non-vertical nearest neighbors, and (3) using a lattice more suitable than simple cubic. To what extent the mathematics can actually be carried out in these cases is, of course, another question.

Although the subject will be discussed in more detail in a later paper, certain preliminary results for capillaries ( $n$  small), obtained by the use of improved models, may be mentioned briefly.

If one takes into account, even though crudely, interactions between horizontal as well as vertical nearest neighbors, the resulting somewhat

essentially, an artificial ceiling is introduced half way between the walls.

The BET model is a very crude special case of the present one. Eqs. (5) and (21) follow from Eq. (32) if only vertical configurations are allowed and only vertical nearest neighbors counted ( $z=2$ ). Then all configurations (for given values of  $A$  and  $X$ ) have the same value of  $N$ :  $N=A-X$ . Also,

refined theory of multimolecular adsorption predicts capillary condensation quite naturally for suitable values of the parameters. One obtains regions of instability, corresponding to a sudden jump in  $A/B$  from a small value to a large value. The phenomenon is analogous to the instabilities in monolayers discussed by Fowler and Guggenheim.<sup>8</sup> The multimolecular adsorption and the capillary condensation points of view are therefore really not in conflict, as is generally assumed, except that Kelvin's equation should not be considered valid on this microscopic scale.

The author is indebted to Professor W. A. Noyes, Jr. for helpful discussions.