

# Statistical distribution of adsorption of quantum particles

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**Abstract.** There is a need to compute and work out the theoretical relationship between the single fermion cell and single fermion particle and the single boson cell and more than one boson particle in the assumed processes for developing the theory of adsorption, simply by maximising the entropy of the system for both types of particles. In this work, the reduction of the general expression of adsorption to the special case of the Langmuir adsorption isotherm and closely related family of curves or types of adsorption isotherms in dimensionless form have been derived using statistical mechanics for an adsorbate. The classification of the laboratory data, for adsorption distribution concept, power of generalised method in terms of nonlinear parameter least square fits by selecting different sets of derived functional form one by one is demonstrated.

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## 1. Introduction

All experimentally observed particles are either bosons or fermions in nature. The general principles of quantum mechanics do not challenge the existence of some objects and basic particles obeying intermediate statistics, especially when referring to the finite number of adsorbents absorbed on a surface [1–4]. In this paper, we employed three types of basic isotherms, namely adsorption due to fermion character in terms of a single cell or site occupied by a single adsorbent particle, boson character in terms of more than one particle in a single cell and a mixture of fermions and bosons in different ratios to correlate with the experimental adsorption isotherm data, which were obtained in the laboratory. The graphical representation of laboratory results in terms of Langmuir expression and other sets of expression of adsorption isotherm shows that nonlinear parameter model fitting the data is better than other least square fitting techniques involving sets of linear parameters.

Section 2 lists the basic definitions followed by suitable algebraic identities to develop the formulation of Langmuir adsorption isotherm using the generalised distribution model for the equilibrium adsorption coverage in terms of equilibrium concentration and their

brief description is given in §3. Section 4 presents the conversion of experimental data to the present model expression. Results and discussion are given in §5. Finally, §6 describes our conclusions.

## 2. Definition and identities

We have the following definition [1] for the thermodynamic probability  $W$  using two dimensionless physical parameters:

$$W(\alpha_1, \alpha_2) = \frac{\Gamma(\alpha_1 + \alpha_2)}{\Gamma(\alpha_1) \cdot \Gamma(\alpha_2)}. \quad (1)$$

The thermodynamic probability  $W$  is related to entropy  $S$  through a basic postulate of statistical mechanics. The required expression in terms of dimensionless entropy  $S^*$  is given as follows:

$$S^* = \frac{S}{k_B} = \ln[W(\alpha_1, \alpha_2)]. \quad (2)$$

Based on this definition, it is easy to build or check the following useful identity for thermodynamic probability  $W$  in higher dimension using three independent parameters  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  as

$$W(\alpha_1, \alpha_2, \alpha_3) = \frac{\Gamma(\alpha_1 + \alpha_2 + \alpha_3)}{\Gamma(\alpha_1) \cdot \Gamma(\alpha_2) \cdot \Gamma(\alpha_3)}. \quad (3)$$

Hence, we have from eq. (3)

$$W(\alpha_3, \alpha_2, \alpha_1) = W(\alpha_3, \alpha_2 + \alpha_1) \cdot W(\alpha_2, \alpha_1). \quad (4)$$

The related dimensionless entropy  $S^*$  from eqs (3) and (4) becomes, in terms of three independent parameters,

$$S^* = \frac{S}{k_B} = \ln[W(\alpha_1, \alpha_2, \alpha_3)], \quad (5)$$

$$S^* = \ln[W(\alpha_3, \alpha_2 + \alpha_1)] + \ln[W(\alpha_2, \alpha_1)]. \quad (6)$$

Similarly, the identity for thermodynamic probability  $W$  using four independent parameters  $\alpha_1, \alpha_2, \alpha_3$  and  $\alpha_4$  is

$$W(\alpha_1, \alpha_2, \alpha_3, \alpha_4) = \frac{\Gamma(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)}{\Gamma(\alpha_1) \cdot \Gamma(\alpha_2) \cdot \Gamma(\alpha_3) \cdot \Gamma(\alpha_4)}, \quad (7)$$

$$W(\alpha_1, \alpha_2, \alpha_3, \alpha_4) = W(\alpha_1, \alpha_2 + \alpha_3 + \alpha_4) \cdot W(\alpha_2, \alpha_3 + \alpha_4) \cdot W(\alpha_3, \alpha_4). \quad (8)$$

Using eqs (7) and (8), the expression for dimensionless entropy  $S^*$  becomes

$$S^* = \frac{S}{k_B} = \ln[W(\alpha_1, \alpha_2, \alpha_3, \alpha_4)], \quad (9)$$

$$S^* = \frac{S}{k_B} = \ln[W(\alpha_1, \alpha_2 + \alpha_3 + \alpha_4)] + \ln[W(\alpha_2, \alpha_3, \alpha_4) + \ln[W(\alpha_3, \alpha_4)]]. \quad (10)$$

### 2.1 Fermi–Dirac and Bose–Einstein distributions

For Fermi–Dirac distribution, the thermodynamic probability  $W_f$  is parametrised by the permutable fermion ( $N_f$ ) =  $\alpha_1$  and the number of permutable free cells ( $g_f - N_f$ ) =  $\alpha_2$  is

$$W_f(N_f, g_f - N_f) = \frac{\Gamma(g_f)}{\Gamma(N_f) \cdot \Gamma(g_f - N_f)}. \quad (11)$$

The corresponding expression of a dimensionless entropy  $S_f^*$  for fermion system becomes

$$S_f^* = \frac{S_f}{k_B} = \ln[W_f(N_f, g_f - N_f)], \quad (12)$$

$$S_f^* = \ln[\Gamma(g_f)] - \{\ln[\Gamma(N_f)] + \ln[\Gamma(g_f - N_f)]\}. \quad (13)$$

For Bose–Einstein distribution, the thermodynamic probability  $W_b$  is parametrised by the permutable boson ( $N_b$ ) =  $\alpha_1$  and the number of permutable partitions ( $g_b - 1$ ) =  $\alpha_2$  is

$$W_b(N_b, g_b - 1) = \frac{\Gamma(g_b - 1 + N_b)}{\Gamma(N_b) \cdot \Gamma(g_b - 1)}. \quad (14)$$

The corresponding expression of dimensionless entropy  $S_b^*$  for the boson system becomes

$$S_b^* = \frac{S_b}{k_B} = \ln[W_b(N_b, g_b - 1)], \quad (15)$$

$$S_b^* = \ln[\Gamma(g_b - 1 + N_b)] - \{\ln[\Gamma(N_b)] + \ln[\Gamma(g_b - 1)]\}. \quad (16)$$

As  $N_b$  and  $g_b$  are considerably large, we can neglect the term  $(-1)$  in eq. (14). For Bose–Einstein statistics, the thermodynamic probability in terms of partition  $g_b$  becomes

$$W_b(N_b, g_b) = \frac{\Gamma(g_b + N_b)}{\Gamma(N_b) \cdot \Gamma(g_b)}. \quad (17)$$

The corresponding expression of dimensionless entropy  $S_b^*$  becomes

$$S_b^* = \frac{S_b}{k_B} = \ln[W_b(N_b, g_b)], \quad (18)$$

$$S_b^* = \ln[\Gamma(g_b + N_b)] - \{\ln[\Gamma(N_b)] + \ln[\Gamma(g_b)]\}. \quad (19)$$

### 2.2 Haldane distribution

For intermediate distribution [5], to get expression of the thermodynamic probability in terms of two parameters, we simply construct the first parameter  $\alpha_1$  as the sum of  $\mu_b$  times boson +  $\mu_f$  times fermions and with weight condition, which is given by

$$N = [\mu_b N_b + \mu_f N_f] = \alpha_1, \quad (20)$$

$$[\mu_b + \mu_f] = 1, \quad g = [\mu_b g_b + \mu_f g_f].$$

Here  $\mu_b$  and  $\mu_f$  denote the probabilities of bosons and fermions, respectively, such that  $\mu_b + \mu_f = 1$ . For the second parameter  $\alpha_2$ , we take the sum of the effective number of partitions  $\mu_b(g_b - 1)$  + effective number of free cells  $\mu_f(g_f - N_f)$  and with the condition, which is given by the following expression:

$$[\mu_b(g_b - 1) + \mu_f(g_f - N_f)] = g - \mu_b - \mu_f N_f = \alpha_2. \quad (21)$$

In this way, we have a simple and short derivation for the thermodynamic probability of the Haldane system:

$$W_h(\alpha_1, \alpha_2) = W_h(N, g - \mu_b - \mu_f N_f). \quad (22)$$

We obtain Haldane’s starting, using eq. (20). The expression of thermodynamic probability becomes

$$W_h(N, g - \mu_b - \mu_f N_f) = \frac{\Gamma(g + \mu_b N_b - \mu_b)}{\Gamma(N) \cdot \Gamma(g - \mu_b - \mu_f N_f)}, \tag{23}$$

$$W_h(N, g - \mu_b - \mu_f N_f) = W_h(N, g + \mu_b(N_b - 1) - N). \tag{24}$$

The related expression of dimensionless entropy  $S_h^*$  would be

$$S_h^* = \ln[\Gamma(g + \mu_b(N_b - 1))] - \{\ln[\Gamma(N)] + \ln[\Gamma(g + \mu_b N_b - \mu_b - N)]\}. \tag{25}$$

We could also get the simple form of Haldane’s starting expression by assuming

$$W_f(N, g - N) = \frac{\Gamma(g)}{\Gamma(N) \cdot \Gamma(g - N)}, \tag{26}$$

$$W_b(N, g - 1) = \frac{\Gamma(g - 1 + N)}{\Gamma(N) \cdot \Gamma(g - 1)}. \tag{27}$$

From the intermediate distribution [5] and using eqs (26) and (27), we get a simple proof for Haldane’s starting expression with  $\mu$  as an arbitrary parameter:

$$W_h(N, \mu(g - 1) + (1 - \mu)(g - N)) = \frac{\Gamma(g + \mu(N - 1))}{\Gamma(N) \cdot \Gamma((g - N) + \mu(N - 1))}. \tag{28}$$

The related expression of the dimensionless entropy  $S_h^*$  of the Haldane system is

$$S_h^* = \ln[\Gamma(g + \mu(N - 1))] - [\ln[\Gamma(N)] + \ln[\Gamma(g - N + \mu(N - 1))]]. \tag{29}$$

### 2.3 Intermediate distribution

For intermediate distribution [1], we take the thermodynamic probability in terms of three parameters: the number of bosons  $N_b = \alpha_3$ , the number of fermions  $N_f = \alpha_1$  and the number of free cells  $(g_f - N_f) = \alpha_2$ , with inter-relation number of fermions equal to the number of partitions. Hence, we have

$$W(\alpha_3, \alpha_2, \alpha_1) = W(\alpha_3, \alpha_2 + \alpha_1) \cdot W(\alpha_2, \alpha_1), \tag{30}$$

$$W_{fb}(N_b, g_f - N_f, N_f) = W_b(N_b, g_b - 1) \cdot W_f(g_f - N_f, N_f). \tag{31}$$

We have, from eqs (30) and (31), the following simple relation between the distribution under consideration:

$$\begin{aligned} \alpha_3 &= N_b, & \alpha_2 &= g_f - N_f, \\ \alpha_1 &= N_f, & \alpha_2 + \alpha_1 &= g_f = g_b - 1. \end{aligned} \tag{32}$$

The related dimensionless entropy  $S_{fb}^*$  becomes, in terms of three independent parameters,

$$S_{fb}^* = \frac{S_{fb}}{k_B} = \ln[W_{fb}(N_b, g_f - N_f, N_f)]. \tag{33}$$

The expression of entropy for extensively used composite system in the theoretical developing set of adsorption isotherms for analysing the laboratory sample data will be

$$S_{fb}^* = \ln[W_b(N_b, g_b - 1)] + \ln[W_f(N_f, g_f - N_f)]. \tag{34}$$

The present expressions of  $S_h^*$  and  $S_{fb}^*$  give the same reductions for fermions and bosons but different results for the mixed system of fermions–bosons.

### 3. Formulation of Langmuir adsorption isotherm using the generalised distribution $W_{fb}$

The present formulation is based on the following normal assumptions:

- (1) The surface of the adsorbent is uniform, i.e. all the adsorption sites are equivalent to similar set of particles.
- (2) Involved molecules do not interact.
- (3) All the adsorption occurs through the same mechanism.
- (4) Types II and III adsorption isotherms show large deviation from the Langmuir model. Hence, we deviate from the assumption that from the maximum adsorption, only a monolayer is formed. In short, we need to use the concept of single cell with single particle and single cell with more than one particle distribution.

The partition function of the finite number of adsorbed particles on a surface in a canonical ensemble is given by

$$Z_f(N) = W_f(N_f^i, g^i - N_f^i) \zeta^{N_f^i}. \tag{35}$$

Similarly, the partition function of the finite number of adsorbed particles on a surface for fermion–boson mixture is given by

$$\begin{aligned} Z_{fb}(N) &= W_{fb}(N_f^i, g^i - N_f^i, N_b^i) \zeta^{N^i}, \\ N_b^i &= \mu_b \cdot N^i, & N_f^i &= \mu_f \cdot N^i. \end{aligned} \tag{36}$$

Here  $\mu_b$  and  $\mu_f$  denote the probabilities of bosons and fermions, respectively, such that  $\mu_b + \mu_f = 1$ . Taking the logarithm of both sides of eqs (35) and (36) and using the relation between entropy and

thermodynamic probability, we have the following expressions of fermions and fermion–boson mixture:

$$\ln[Z_f(N)] = \ln[W_f(N_f^i, g^i - N_f^i)] + N_f^i \cdot \ln(\zeta), \tag{37}$$

$$\ln[Z_{fb}(N)] = \ln[W_{fb}(N_b^i, g^i - N_b^i, N_f^i)] + N^i \cdot \ln(\zeta). \tag{38}$$

Here,  $\zeta$  represents the partition function of a single absorbed molecule,  $g_i = g^i$  is the number of sites available for adsorption and  $N_i = N_f^i$  is the number of molecules absorbed which should be less than or equal to  $g_i = g^i$ . The terms within the bracket =  $[\zeta^{N_f^i} \Gamma(g^i) / \Gamma(g^i - N_f^i)]$  give the total partition function of the  $N_i = N_f^i$  absorbed molecules by taking the product of the individual partition function (partition function of the subsystem). The bracket  $[1 / \Gamma(N_f^i)]$  accounts for the overcounting arising due to the indistinguishable nature of the adsorption sites. The terms within the bracket  $[\Gamma(g^i) / (\Gamma(N_f^i) \Gamma(g^i - N_f^i))] = C(N_f^i, g^i)$  are the binomial coefficients used for counts. The canonical partition functions for fermions and fermion–boson system are given below:

$$W_f = \prod_{i=1}^k W^i(N_f^i, g^i - N_f^i) = \prod_{i=1}^k \frac{\Gamma(g^i)}{\Gamma(N_f^i) \cdot \Gamma(g^i - N_f^i)}, \tag{39}$$

$$W_{fb} = \prod_{i=1}^k W^i(N_b^i, N_f^i, g^i - N_f^i) = \prod_{i=1}^k \frac{\Gamma(N_b^i + g^i)}{\Gamma(N_b^i) \cdot \Gamma(N_f^i) \cdot \Gamma(g^i - N_f^i)}. \tag{40}$$

If  $\mu$  is the chemical potential for the absorbed molecule, then the grand canonical partition function  $Z_f$  for the fermion particles is as follows:

$$[Z_f(\mu, N)] = \prod_{i=1}^k W^i(N_f^i, g^i - N_f^i) \exp(N_f^i \beta \mu^i) = \prod_{i=1}^k C(N_f^i, g^i)(X)^{N_f^i}. \tag{41}$$

The expression for activity  $X$  is given by

$$X = \zeta \cdot \exp(\beta \mu). \tag{42}$$

Activity depends on temperature, pressure and the composition of the mixture. The activity is related to the effective partial pressure in the case of gases or concentrations in the case of liquid mixtures. Sometimes it

is referred to as fugacity. Taking the natural log of both sides of eq. (41), we get an expression for the dimensionless entropy  $S_f^*$  for fermions. Taking the log of grand canonical partition function  $[Z_f(\mu, N)]$  simplifies to

$$\ln[Z_f] = \sum_{i=0}^k [N_f^i \ln(X) + \ln \Gamma(g^i) - \ln \Gamma(N_f^i) - \ln \Gamma(g^i - N_f^i)]. \tag{43}$$

Simplifying eq. (43) we have the expression of log of grand partition function in terms of entropy of fermions:

$$\ln[Z_f] = N_f \ln(X) + S_f^*, \quad \sum_{i=0}^k (N_f^i) = N_f. \tag{44}$$

The expression for the dimensionless entropy for fermions,  $S_f^*$ , is given as follows:

$$S_f^* = \sum_{i=0}^k [\ln \Gamma(g^i) - \ln \Gamma(N_f^i) - \ln \Gamma(g^i - N_f^i)]. \tag{45}$$

Similarly, we have dimensionless expression for the fermion–boson system,  $S_{fb}^*$ :

$$S_{fb}^* = \sum_{i=0}^k [\ln \Gamma(N_b^i + g^i) - \ln \Gamma(N_b^i) - \ln \Gamma(N_f^i) - \ln \Gamma(g^i - N_f^i)]. \tag{46}$$

For the mixture of fermion–boson system, the log of the grand canonical partition function simplifies to

$$\ln[Z_{fb}] = \sum_{i=0}^k (N^i \ln(X)) + S_{fb}^* = N \cdot \ln(X) + S_{fb}^*. \tag{47}$$

Now, to get the expression of Langmuir adsorption isotherm, we maximise eq. (44) with respect to  $N$ . We have the dimensionless entropy term for maximisation of grand canonical partition function, which is a condition for maximisation of eq. (47) with respect to  $N$ . Equation (47) easily reduces to eq. (44), because  $N_b^i = \mu_b \cdot N^i$ ,  $N_f^i = \mu_f \cdot N^i$  and  $\mu_b + \mu_f = 1$ . Taking the natural log of both sides of eq. (40), we get an expression of dimensionless entropy  $S_{fb}^* = \ln(W_{fb})$ :

$$\ln W_{fb} = \sum_{i=0}^k [\ln \Gamma(N_b^i + g^i) - \ln \Gamma(N_b^i) - \ln \Gamma(N_f^i) - \ln \Gamma(g^i - N_f^i)]. \tag{48}$$

Using Stirling’s approximation for  $\Gamma(N)$ , i.e.  $\ln \Gamma(N) \cong N \cdot (\ln N - 1)$ , we get

$$\begin{aligned} \ln W_{fb} = & \sum_{i=1}^k [(N_b^i + g^i) \cdot (\ln(N_b^i + g^i) - 1) \\ & - N_b^i \cdot (\ln N_b^i - 1) - N_f^i \cdot (\ln N_f^i - 1) \\ & - (g^i - N_f^i) \cdot (\ln(g^i - N_f^i) - 1)]. \end{aligned} \quad (49)$$

The most likely distribution can be obtained by maximising the log-likelihood of the grand partition function  $Z_{fb}$ . The solution to this maximisation problem leads to the family of adsorption isotherms. The Langmuir adsorption isotherm is a special case of this general family of isotherms. Consider the following optimisation problem:

$$\text{maximise } \ln Z_{fb}. \\ (N^0, N^1, \dots, N^k)$$

For solving this, we start by defining the derivative of the generalised Lagrangian  $\mathcal{L}_i$  if we have only one energy level  $i$ , so that we can neglect the sum. We have

$$\begin{aligned} \delta \mathcal{L}_i = & \left[ \ln\left(\frac{g^i}{N_b^i} + 1\right) \cdot \delta N_b^i + \ln\left(\frac{g^i}{N_f^i} - 1\right) \cdot \delta N_f^i \right] \\ & + \ln(X) \cdot \delta N^i. \end{aligned} \quad (50)$$

Let  $N_b^i = \mu_b \cdot N^i$  and  $N_f^i = \mu_f \cdot N^i$ , where  $\mu_b$  and  $\mu_f$  denote the probabilities of bosons and fermions, respectively, such that  $\mu_b + \mu_f = 1$ . Equation (50) becomes

$$\begin{aligned} & \left( \mu_b \cdot \ln\left(\frac{g^i}{\mu_b \cdot N^i} + 1\right) + \mu_f \right. \\ & \left. \cdot \ln\left(\frac{g^i}{\mu_f \cdot N^i} - 1\right) + \ln(X) \right) \cdot \delta N^i = 0. \end{aligned} \quad (51)$$

The occupation index is defined as  $N^i/g^i = y^i$ . As  $\delta N^i \neq 0$ , we get

$$\begin{aligned} & \mu_b \cdot \ln\left(\frac{1}{\mu_b \cdot y^i} + 1\right) \\ & + \mu_f \cdot \ln\left(\frac{1}{\mu_f \cdot y^i} - 1\right) + \ln(X) = 0. \end{aligned} \quad (52)$$

Simplification of expression (52) yields

$$X \left( \frac{1}{\mu_b \cdot y^i} + 1 \right)^{\mu_b} \cdot \left( \frac{1}{\mu_f \cdot y^i} - 1 \right)^{\mu_f} = 1. \quad (53)$$

### 3.1 Change of variables in the adsorption isotherm

It should be noted that  $X$ ,  $y$ ,  $\mu_b$  and  $\mu_f$  are dimensionless physical quantities. Now, for application (computation) purposes, we change the variables by replacing  $X = x/a$ ,  $y = Y/c$ ,  $\mu_b = b$  and  $\mu_f = 1 - b$  that yields the following equation which is used for testing the sample laboratory data:

$$\begin{aligned} x = & \frac{a}{\left(\frac{c}{b \cdot Y} + 1\right)^b \cdot \left(\frac{c}{(1-b) \cdot Y} - 1\right)^{(1-b)}} \\ = & G_b(Y, c, a). \end{aligned} \quad (54)$$

3.1.1 *Special cases of adsorption isotherm.* The special cases of eq. (52) are as follows:

1. Fermi particles are present, requiring  $\mu_b$  to be zero. We get  $y^i = X/(1 + X)$ , correspondingly a first basic Langmuir adsorption isotherm.
2. Boson particles are present, requiring  $\mu_f$  to be zero. We get  $y^i = X/(1 - X)$ , correspondingly a second modified adsorption isotherm.
3. The number of boson particles is equal to the number of Fermi particles present, requiring  $\mu_b = \mu_f = 1/2$ . We get  $y^i = 2X/(\sqrt{X^2 + 1})$ , correspondingly a third modified adsorption isotherm. For understanding the adsorption process, an expression can be plotted in the figure, demonstrating that the surface coverage increases quite rapidly such that the saturation limits double,  $y^i = y_{\max} = 2$ .
4. If we select variable  $X = P/P^0 = (K^A \cdot P_A)$ , then we have a Langmuir adsorption isotherm  $y = (K^A \cdot P_A)/(1 + (K^A \cdot P_A))$  with single system parameters.
5. We slightly modify the Langmuir isotherm  $y = (K^A \cdot P_A)/(1 + \alpha \cdot (K^A \cdot P_A))$  with two system parameters.

The plot for the solution of the occupation index  $y^i$  in eq. (52) for various values of  $\mu_b$  is shown in figure 1. In the plot, the occupation index or adsorption is along the  $y$ -axis and concentration  $X$  is along the  $x$ -axis. Here  $K^A$  is the ratio of forward adsorption reaction to the backward desorption reaction.  $P_A$  is the partial pressure of molecule  $A$  over the surface. It can be plotted in the figure, for demonstrating that surface coverage increases quite rapidly with the partial pressure on the adsorbents but levels off after

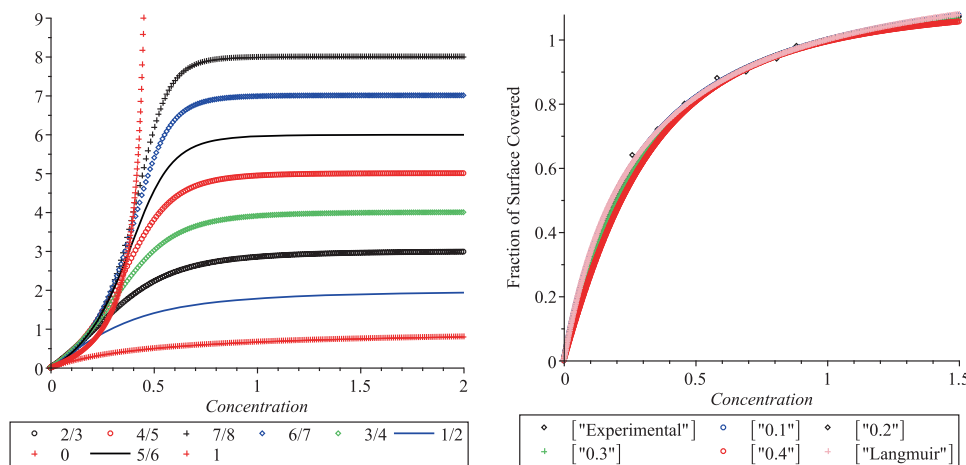
$$P = \frac{Nk_B T}{V} \quad (55)$$

reaches

$$P^0 = \left[ \frac{Nk_B T}{\zeta} \right] \cdot \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2}. \quad (56)$$

3.1.2 *Adsorption isotherms with different saturation limits.* The higher order solutions along with an earlier simple solution can be plotted in the figure, demonstrating that the surface coverage increases quite rapidly to  $y_{\max} = 1-8$ . It can be plotted in the figure, demonstrating that the surface coverage increases quite rapidly even at low concentrations with  $y_{\max} =$





**Figure 1.** Theoretical and computed adsorption isotherms for various values of  $\mu_b$  when  $0 < \mu_b < 1$ .

**Table 1.** Experimental data: Concentration ( $X$ ) and fraction of the surface covered ( $Y$ ).

Sl. No.	$X$	$Y$
1	$10^{-5}$	$10^{-5}$
2	0.8824	0.7647
3	1.1176	0.9412
4	1.5294	1.0588
5	1.9706	1.1765
6	2.5000	1.2941
7	2.9706	1.3230
8	3.4706	1.3824
9	3.7941	1.4412
10	4.2941	1.4706

**Table 2.** Computed adsorption isotherms in terms of eq. (54) for various values of parameters  $a, b$  and  $c$ .

$G_n$	$a$	$b$	$c$
$G_1$	0.28118	0.00	1.28154
$G_2$	0.36389	0.10	1.12081
$G_3$	0.40917	0.20	0.96638
$G_4$	0.43785	0.30	0.81911
$G_5$	0.45711	0.40	0.67970

$1/(1 - b)$ . In figure 1, we plotted different curves for  $b = (0, 1/2, 2/3, 3/4, 4/5, 5/6, 6/7, 7/8)$ , so that  $y_{\max} = 1-8$ . This flexibility in terms of  $b$  is very much useful for studying adsorption isotherms for different ratios. In figure 1, for parameter  $b = (0.1, \dots, 0.8)$ , different adsorption isotherms along with the experimental data is shown.  $b = 0$  corresponds to the Langmuir adsorption curve, and the gradual variation in terms of parameter  $b$  is seen. In order to visualise the complex adsorption process and data representation, there is a need to select two curves forming a closed loop.

#### 4. Conversion of experimental data to the present model expression

Experimental data used for computation are given in table 1 and different set of equation  $x = G_b(Y, c, a)$  is given in table 2.

In figure 1, for parameter  $b = [0.1, 0.2, 0.3, 0.4]$ , different adsorption isotherms along with the experimental data is shown.  $b = 0$  corresponds to the Langmuir adsorption curve. This set of graphs shows the dominance of the fermion character in terms of single cell or site occupied by a single adsorbent particle. All graphs are so close to the experimental data point that it justifies the Langmuir assumption of an experimental data.

#### 4.1 Analytic expressions of adsorption isotherms

Here we list out the algebraic representation of absorption data in terms of  $x = (G_1, G_2, G_3, G_4, G_5)$ . The Langmuir adsorption isotherms have the representation as  $x = G_1$ ,

$$x = G_1(Y, c, a) = \frac{0.28118}{\left(\frac{1.28154}{Y} - 1\right)^{1.0}}. \tag{57}$$

For intermediate distribution, neither fully Fermi-Dirac distribution nor fully Bose-Einstein distribution adsorption isotherms are suitably generated by selecting the third parameter  $b$ . We have followed the equation for adsorption isotherm constructed by nonlinear least square fit for the assumed experimental data as  $[x = G_2, \dots, x = G_5]$ . When

comparing its graphical representation with the experimental data, one can easily select the closest functional representation. Looking towards the closest functional form in terms of parameter  $b$ , the experimental data are easily interpreted and the domain can be decided:

$$x = G_2(Y, c, a) = \frac{0.36389}{\left(\frac{11.20813}{Y} + 1\right)^{0.10} \cdot \left(\frac{1.24534}{Y} - 1\right)^{0.90}}, \tag{58}$$

$$x = G_3(Y, c, a) = \frac{0.40917}{\left(\frac{4.83190}{Y} + 1\right)^{0.20} \cdot \left(\frac{1.20797}{Y} - 1\right)^{0.80}}, \tag{59}$$

$$x = G_4(Y, c, a) = \frac{0.43785}{\left(\frac{2.73038}{Y} + 1\right)^{0.30} \cdot \left(\frac{1.17016}{Y} - 1\right)^{0.70}}, \tag{60}$$

$$x = G_5(Y, c, a) = \frac{0.45711}{\left(\frac{1.69927}{Y} + 1\right)^{0.40} \cdot \left(\frac{1.13284}{Y} - 1\right)^{0.60}}. \tag{61}$$

## 5. Result and discussion

For  $\mu_b = 0, 1/2, 2/3, \dots, 1$ , the occupation index  $y^i$  in figure 1 along the  $y$ -axis is  $1, 2, 3, \dots, \infty$ , respectively, i.e. as  $\mu_b \rightarrow 1, y^i \rightarrow \infty$ . From figure 1, we can infer that the intercept term on the  $y$ -axis is  $1/(1 - \mu_b)$ .

Equation (54) is tested for laboratory data, where the set parameters are  $a = [a_1, a_2, \dots, a_5], b = [b_1, b_2, \dots, b_5]$  and  $c = [c_1, c_2, \dots, c_5]$ . It is observed that  $[a_1 < a_2 < \dots < a_5], [c_1 > c_2 > \dots > c_5], [b_1 < b_2 < \dots < b_5]$  and the adsorption isotherms are identified by  $(G_1 = [a_1, b_1, c_1], \dots, G_5 = [a_5, b_5, c_5])$ .

It is observed from the first graph that  $x = G_1$ , which is Langmuir, while  $x = G_2, G_3, G_4$  and  $G_5$ , are good adsorption isotherm curves representing the laboratory data. All are related to the selection of a function. Its in-built flexibility has important role in model development and understanding the adsorption process. The modelling of experimental adsorption isotherm data is an essential way for predicting the mechanics of adsorption.

### 5.1 Adsorption isotherm models

We list the expressions of seven known adsorption isotherm models for the equilibrium adsorption coverage in terms of equilibrium concentrations and describe them briefly. Seven adsorption isotherm models are normally used to analyse the absorption data. They are the Langmuir [6], Freundlich [7], Temkin [8], Kiselev [9],

Elovich [10], Fowler–Guggenheim [11] and Hill [12] models.

### 5.2 Langmuir model

The Langmuir model can be written as

$$\theta_{eq} = \frac{k \cdot C_{eq}}{1 + k \cdot C_{eq}}, \tag{62}$$

where  $\theta_{eq}$  is the equilibrium adsorption coverage,  $C_{eq}$  is the equilibrium concentration of the adsorbate in the bulk phase and  $k$  is the Langmuir equilibrium constant. In this work, we slightly modify this expression as

$$\theta_{eq} = \frac{k \cdot C_{eq}}{1 + \alpha \cdot k \cdot C_{eq}}, \tag{63}$$

where  $\alpha$  is an adjustable parameter. A linearised version of the expression for the revised Langmuir term is shown as follows:

$$\frac{1}{\theta_{eq}} = \frac{1}{k \cdot C_{eq}} + \frac{1}{\alpha}. \tag{64}$$

### 5.3 Freundlich model

$$\theta_{eq} = K_F C_{eq}^\alpha, \tag{65}$$

where  $K_F$  is a constant that indicates the adsorption capacity of the substrate and  $\alpha$  is a constant that indicates the adsorption intensity. The linearised expression for the Freundlich model is shown as follows:

$$\ln(\theta_{eq}) = \ln(K_F) + \alpha \cdot \ln(C_{eq}). \tag{66}$$

### 5.4 Temkin model

$$\theta_{eq} = \frac{RT}{\Delta Q} \cdot \ln(K_0 \cdot C_e), \tag{67}$$

where  $R$  is the universal gas constant,  $T$  is the temperature,  $\Delta Q$  is the desorption energy and  $K_0$  is the Temkin equilibrium constant. The linearised expression for the Temkin model is itself.

### 5.5 Kiselev model

$$k_1 \cdot C_{eq} = \frac{\theta_{eq}}{(1 - \theta_{eq}) \cdot (1 + k_n \cdot \theta_{eq})} \tag{68}$$

where  $k_1$  is the Kiselev equilibrium constant and  $k_n$  is a constant representing the complex formation between the adsorbed molecules. The linearised expression for the Kiselev model is as follows:

$$\frac{1}{C_{eq} \cdot (1 - \theta_{eq})} = \frac{k_1}{\theta_{eq}} + k_1 \cdot k_n. \tag{69}$$

### 5.6 Elovich model

$$\theta_{\text{eq}} = K_E \cdot C_{\text{eq}} \cdot \exp(-\theta_{\text{eq}}), \quad (70)$$

where  $K_E$  is the Elovich equilibrium constant. The linearised expression for the Elovich model is as follows:

$$\ln\left(\frac{\theta_{\text{eq}}}{C_{\text{eq}}}\right) = \ln(K_E) - \theta_{\text{eq}}. \quad (71)$$

### 5.7 Fowler–Guggenheim model

$$K_{\text{FG}} \cdot C_{\text{eq}} = \frac{\theta_{\text{eq}}}{(1 - \theta_{\text{eq}})} \cdot \exp\left(\frac{2\theta_{\text{eq}} \cdot W}{RT}\right), \quad (72)$$

where  $K_{\text{FG}}$  is the Fowler–Guggenheim equilibrium constant and  $W$  is the interaction energy between the adsorbed molecules. The linearised expression for the Fowler–Guggenheim model is as follows:

$$\ln\left(\frac{C_{\text{eq}}(1 - \theta_{\text{eq}})}{\theta_{\text{eq}}}\right) = -\ln(K_{\text{FG}}) + \left(\frac{2\theta_{\text{eq}} \cdot W}{RT}\right). \quad (73)$$

### 5.8 Hill–de Boer model

$$K_1 \cdot C_{\text{eq}} = \frac{\theta_{\text{eq}}}{(1 - \theta_{\text{eq}})} \cdot \exp\left(\frac{\theta_{\text{eq}}}{(1 - \theta_{\text{eq}})} - \frac{K_2\theta_{\text{eq}}}{RT}\right), \quad (74)$$

where  $K_1$  is the Hill–de Boer constant and  $K_2$  is a constant representing the interaction energy between the adsorbed molecules. The linearised expression for the Hill–de Boer model is as follows:

$$\ln(K_1) + \ln(C_{\text{eq}}) = \ln\left(\frac{\theta_{\text{eq}}}{(1 - \theta_{\text{eq}})}\right) + \left(\frac{\theta_{\text{eq}}}{(1 - \theta_{\text{eq}})} - \frac{K_2\theta_{\text{eq}}}{RT}\right). \quad (75)$$

To determine the best nonlinear fit isotherm model, there is no need to work out the statistical correlation coefficients and standard errors of each parameter. Only the graphical display using the least square method of arbitrary function is sufficient to conclude the data and probability of the process.

When the function predicts a high probability that the difference could occur by chance, one should then accept the hypothesis that the distributions are the same as far as the given experimental data are concerned. The distribution fits the data and it means the data decide the nature of the distribution. Visually, some significant differences can be seen in the two distributions. However, one can sometimes be misled by just a visual look.

## 6. Conclusion

There is a fundamental difference between the Langmuir model and the Freundlich model. Here, the Langmuir model and the present formulation are the part of the same theoretical construct (maximisation of grand canonical partition function approach). On the other hand, the Freundlich model and other model are mixed and empirically observed in nature.

Adsorption process in terms of thermodynamic language is also represented as  $F$  (concentration, pressure, temperature, parameters) = 0. However, this approach for the mixture of two basic statistical distributions yields a general equation for the adsorption process:

$$x = \frac{a}{\left(\frac{c}{b \cdot Y} + 1\right)^b \cdot \left(\frac{c}{(1-b) \cdot Y} - 1\right)^{(1-b)}} = G_b(Y, c, a). \quad (76)$$

We conclude from the nonlinear model that using the variation principles of the in-built model parameters lead to a better graphical fit for arbitrary range and a better understanding of the statistical process, in terms of maximisations of grand partition function with respect to a suitable physical parameter. The set of curves, which are outputs of maximisations of grand partition function, appears to be useful in fitting the experimental data.

If  $[X = x/a]$ , then we have figure 1, a good graphical representation of the adsorption isotherm, and if we substitute  $[X = \exp[-b(x - 1)]]$ ,  $b = 8$ , then we have the earlier graphical representation [1] of Fermi–Dirac (FD), Bose–Einstein (BE) and their mixtures.

### 6.1 Algorithm

- (1) The theory of adsorption poses the argument that it is not sufficient to consider just single particles occupying single cells, but many particles occupying single cells should also be considered, as assumed in the case of the Langmuir adsorption. Hence, consideration of mixtures of fermions and bosons is needed.
- (2) In the present formulation, the statistical probability distribution is to count the number of accessible states in distributing a mixture of non-interacting fermions and bosons into a finite number of sites.
- (3) The probability distribution is then related to the entropy of the process according to the statistical postulate  $[S = k_B \log W]$  which is in turn maximised to obtain the most probable distribution.



- (4) The ratio of the number of sites occupied to the number of free sites is interpreted as the quantification of adsorption and the fugacity or activity as the concentration of the mixture.
- (5) The maximisation of the entropy then produces an adsorption isotherm according to the theoretical model.
- (6) The experimental data are then fitted with the theoretical isotherms using the nonlinear least square fit as being the closest functional forms to obtain the model parameters.
- (7) The results reduce to the Langmuir isotherms in the case of just fermionic adsorption.

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