

The Combinatorial Factor Method for Investigation of Surface Adsorption

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In this work, we have used the combinatorial factor method to find the thermodynamic properties of the monolayer surface adsorption with a limited number of rows and nearest neighbor interactions so that the maximum coordination number of each adsorbed particle could be varied from zero to four. The results show that the thermodynamic properties of models with different number of rows are close to each other. In addition, for adsorbed particles with the nearest neighbor interactions, when the fractional coverage becomes 1/2, a phase transition takes place.

Keywords: Ising model, Combinatorial factor, Phase transition, Surface adsorption

INTRODUCTION

The adsorbate-adsorbate interactions in adsorbed layers on surfaces have been attracting a great deal of interest for a long time [1-3]. These interactions have provided insights into the study of chemical reactions on catalyst surfaces, microelectronics fabrication, chemical sensors, electrodes, and surfaces undergoing corrosion [4,5]. Among the earliest models are the Langmuir adsorption theory [6,7] and the Ising model applied to ferromagnetism [8-15]. The order-disorder transition and ferromagnetism have their origins in quite different manifestations of atomic interactions and are exhibited in quite different kinds of materials. However, the Ising model, with considerable success, can describe both. In fact, there are other phenomena that are different from both magnetism and order-disorder that can also be described by similar models. These include adsorption of atoms or molecules on surfaces, adsorption of gases in solids and formation of nano-self-assembled monolayer [16].

Various theories have been proposed to describe

monolayer adsorption of interacting particles [1,2]. A simple description of such phenomena is provided by the lattice-gas model [1,2,17-19], which is easily shown to be equivalent to the Ising model. Lattice-gas model is one of the most widely used and practically applied. In this framework, a lattice of adsorption sites usually represents the adsorption field. This reduction to simplicity has not only been of academic interest but essential for interpretation of adsorption experiments, determination of gas-solid interaction potentials, and characterization of solid adsorbents.

Phase transitions and ordering phenomena in adsorbed films formed on well-defined crystal surfaces have been attracting a great deal of interest for many years [20-24] and research in this field is ever-growing. The progress in this field has gained a particular impetus due to the introduction of several powerful experimental techniques (*e.g.*, neutron scattering [25-29], various forms of electron spectroscopy [30-39], light particle, *e.g.* helium, scattering [3,40,41]), the extensive use of computer simulation methods (Monte Carlo and molecular dynamics [5,42-48]) and, last but surely not least, owing to very intensive theoretical studies [20-22,49-53], whereby the discovery of rich two-dimensional world of

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phase transitions and substrate induced forms of order in adsorbed layers has become a challenge. At the same time, this has created a unique opportunity to verify various ideas and predictions stemming out of theoretical work.

In this research, to investigate surface adsorption, a simple lattice-gas model is introduced. Surface is a rectangular lattice which consists of M rows and L columns ($L \rightarrow \infty$) and is in equilibrium with an ideal gas. For simplicity, only the nearest neighbors' adsorbate-adsorbate and surface-adsorbate interactions are considered. To find the thermodynamic properties of the model based on combinatorial factor method [13], an exact equation for the grand canonical partition function [Eq. (17)] is derived. Using this equation, the exact grand canonical partition function for one-dimensional ($M = 1$) surface adsorption is determined [Eq. (34)]. Neglecting the adsorbate-adsorbate interactions (ideal model), the equation is solved analytically for any row, by whose use the Langmuir isotherm equation is derived [Eq. (28)], whereas by paying heed to these interactions, Eq. (17) is solved only for small M .

The Model

Consider an adsorbent surface made up of σ ($\sigma \rightarrow \infty$) sites each of which can adsorb one gas molecule. Suppose that the surface is in contact with an ideal gas with the chemical potential μ (determined by the pressure P and temperature T). Some of the molecules of the gas will be adsorbed onto the surface, and the number of adsorbed particles, N ($N \rightarrow \infty$), will be a function of pressure of the gas, surface size, temperature, adsorbed-adsorbed, and adsorbed-surface interactions. A simple statistical mechanical model for this system at equilibrium is to picture the solid surface to be a two-dimensional lattice which is made up of L columns and M rows so that, $\sigma = LM$. Each of these σ sites can be occupied only by one particle (monolayer adsorption). Let the partition function of an occupied site be $q_a(T)$ and an unoccupied site be unity (actually, $q_a = q_{\text{vib}} q_{\text{ele}} q_{\text{nu}}$ where q_{vib} , q_{ele} and q_{nu} are the vibrational, electronic, and nuclear partition function of the adsorbed particle, respectively). We assume q_{ele} and q_{nu} are equal to unity in the temperatures range, which we deal with. In this model, we also assume that the energy of each adsorbed particle is $-U$ ($U > 0$) and it interacts only with its nearest neighbour particles (the coordination number of each adsorbed particle can be varied from 0 to 4). The interaction energy

between one pair can be considered as $-J$ ($J > 0$). To avoid the end effects, we include the periodic boundary conditions assuming that the first and end sites of each column are the nearest neighbors.

Consider one of the L columns which contain r particles. For this column the number of configurations which must be considered are $M!/(M-r)!r!$, each of which can be labelled as A_{rm} , where $r = 0, 1, \dots, M$ and $m = 1, 2, \dots, M!/(M-r)!r!$. If N_{rm} is equal to the number of configurations of A_{rm} , then we must impose the following condition

$$\sum_{r=0}^M \sum_{m=1}^{Z(r)} N_{rm} = L, \quad r = 0, 1, 2, \dots, M \quad (1)$$

where

$$Z(r) \equiv \frac{M!}{(M-r)!r!} \quad (2)$$

With the definition of $N_{rm} \equiv LP_{rm}$, Eq. (1) can be re-written as

$$\sum_{r=0}^M \sum_{m=1}^{Z(r)} P_{rm} = 1, \quad (3)$$

If we define $N_{rm}^{sn} \equiv LP_{rm}^{sn}$ as the number of the nearest neighbor columns with A_{rm} and A_{sn} configurations, then, the following constraints must be considered:

$$\sum_{s=0}^M \sum_{n=1}^{Z(s)} P_{rm}^{sn} = P_{rm}, \quad \begin{cases} r = 0, 1, \dots, M \\ m = 1, 2, \dots, Z(r) \end{cases} \quad (4)$$

Moreover, the number of adsorbed particles must be satisfied by the following condition

$$\sum_{r=0}^M \sum_{m=1}^{Z(r)} r N_{rm} = N$$

or

$$\sum_{r=0}^M \sum_{m=1}^{Z(r)} r P_{rm} = M\theta, \quad (5)$$

where θ or fractional coverage is,

$$\theta \equiv \frac{N}{\sigma} \quad (6)$$

Applying the nearest neighbor interactions only, the exact total energy of adsorbed particles (with nearest neighbour interaction energy) can be written as

$$E = -LJ \left(\sum_{r=0}^M \sum_{m=1}^{Z(r)} P_{rm} \varepsilon_{rm} + \sum_{r=0}^M \sum_{s=0}^M \sum_{m=1}^{Z(r)} \sum_{n=1}^{Z(s)} P_{rm}^{sn} \varepsilon_{rm}^{sn} \right) - LU \sum_{r=0}^M \sum_{m=1}^{Z(r)} r P_{rm}. \quad (7)$$

where $-J\varepsilon_{rm}$ and $-J\varepsilon_{rm}^{sn}$ are interaction energies within the columns and between the nearest neighbor columns, respectively. The coefficients ε_{rm} and ε_{rm}^{sn} have discrete values each of which changes from 0 to M . The grand canonical partition function for the adsorbed particles is

$$\Xi = \sum_{N=0}^{\infty} Q(N, \sigma, T) \lambda^N, \quad (8)$$

where

$$\lambda = e^{\mu/kT}, \quad (9)$$

and Q , the canonical partition function, is

$$Q(N, \sigma, T) = q_a^N(T) \sum_{\{P_{rm}, P_{rm}^{sn}\}} \Omega \{E, P_{rm}, P_{rm}^{sn}\} e^{-E\{P_{rm}, P_{rm}^{sn}\}/kT}. \quad (10)$$

where Ω is the exact combinatorial factor for distribution of N adsorbed particles upon σ sites and can be written as [13]

$$\Omega = \prod_{r=0}^M \prod_{m=1}^{Z(r)} \frac{(LP_{rm})!}{\prod_{s=0}^M \prod_{n=1}^{Z(s)} (LP_{rm}^{sn})!}. \quad (11)$$

Using the fluctuation theory, Stirling's approximation, and Eqs. (7), (10) and (11), Eq. (8) becomes

$$\begin{aligned} \frac{\ln \Xi}{L} &= \sum_{r=0}^M \sum_{m=1}^{Z(r)} P_{rm} (j\varepsilon_{rm} + \ln P_{rm}) + \sum_{r=0}^M \sum_{s=0}^M \sum_{m=1}^{Z(r)} \sum_{n=1}^{Z(s)} P_{rm}^{sn} (j\varepsilon_{rm}^{sn} - \ln P_{rm}^{sn}) \\ &+ \sum_{r=0}^M \sum_{m=1}^{Z(r)} r P_{rm} (u + \ln q_a \lambda), \end{aligned} \quad (12)$$

where $j = J/kT$, $u = U/kT$.

To obtain the equilibrium state, Eq. (12) must be maximized using the Lagrange multipliers method and constraints which were given in Eqs. (3) and (4). The result will be

$$\Psi = \frac{\ln \Xi}{L} - \eta \sum_{r=0}^M \sum_{m=1}^{Z(r)} P_{rm} + \sum_{r=0}^M \sum_{m=1}^{Z(r)} \alpha_{rm} \left(P_{rm} - \sum_{s=0}^M \sum_{n=1}^{Z(s)} P_{rm}^{sn} \right). \quad (13)$$

where η and α_{rm} s are the Lagrange multipliers. Because $\varepsilon_{rm}^{sn} = \varepsilon_{sn}^{rm}$, we can use the equal *a priori* probabilities principle and put

$$P_{rm}^{sn} = P_{sn}^{rm}. \quad (14)$$

From maximization of Ψ , we conclude the following expressions

$$P_{rm}^{sn} = \sqrt{P_{rm}^{rm} P_{sn}^{sn}} \exp \left[\frac{j}{2} (2\varepsilon_{rm}^{sn} - r - s) \right], \quad (15)$$

$$P_{rm} = P_{rm}^{rm} \frac{P_{M1}}{P_{M1}^{M1}} \varphi^{M-r} \exp[(2M - \varepsilon_{rm} - r)j], \quad (16)$$

$$\ln \Xi = \sigma \ln \xi, \quad (17)$$

$$\begin{aligned} \sum_{s=0}^M \sum_{n=1}^{Z(s)} \sqrt{P_{sn}^{sn}} \{ \exp[(\varepsilon_{rm}^{sn} + \varepsilon_{rm} + (r-s)/2)j] \varphi^r - \xi^M \delta_{rm,sn} \} &= 0, \\ \left\{ \begin{array}{l} r = 0, 1, \dots, M \\ m = 1, 2, \dots, Z(r) \end{array} \right. & \end{aligned} \quad (18)$$

$$\xi^M \sum_{r=0}^M \sum_{m=1}^{Z(r)} P_{sn}^{sn} [\varphi^{-r} \exp(-j\varepsilon_{rm} - jr)] = 1, \quad (19)$$

where $\delta_{rm,sn}$ is Kronecker delta and also

$$\varphi \equiv \lambda q_a e^u, \quad \xi \equiv e^{2j} \varphi \left(\frac{P_{M1}}{P_{M1}^{M1}} \right)^{1/M}. \quad (20)$$

In Eqs. (17-20) ξ can be defined as: the partition function for each adsorbed particle in the M rows model.

Equation (18) is a set of 2^M simultaneous, linear homogeneous equations in the 2^M unknowns $X_{01}, X_{11}, \dots, X_{M1}$. For this set, to have a nontrivial solution, the determinant of the coefficients must vanish, namely

$$\det \{ \exp[j(\varepsilon_{rm}^{sn} + \varepsilon_{rm} + (r-s)/2)] \varphi^r - \xi^M \delta_{rm,sn} \} = 0, \quad (21)$$

$$\left\{ \begin{array}{l} r = 0, 1, \dots, M \\ m = 1, 2, \dots, Z(r) \\ s = 0, 1, \dots, M \\ n = 1, 2, \dots, Z(s) \end{array} \right.$$

Expansion of Eq. (21) gives an algebraic equation of degree

2^M in the unknown ξ . This algebraic equation has 2^M roots, which in at equilibrium. We must choose its maximum root, ξ_{\max}^M [because, at equilibrium Ξ is maximum, and based on Eq. (17), we can conclude ξ must be maximum, too]. Using this root, all of the variables and the thermodynamic properties of lattice such as the fractional coverage, internal energy, and entropy [Eqs. (5), (7) and (11)] can be calculated. In the next sections, these calculations will be accomplished for simple models.

The Ideal Model

For the ideal lattice where $j = 0$, Eqs. (17) and (18) can be simplified as

$$\ln \Xi = \sigma \left(\ln \varphi + \frac{1}{M} \ln x \right) \quad (22)$$

and

$$x_{r,m} x = \varphi^{r-M} \sum_{s=0}^M \sum_{n=1}^{Z(r)} x_{s,n}, \quad \begin{cases} r = 0, 1, \dots, M \\ m = 1, 2, \dots, Z(r) \end{cases} \quad (23)$$

where $x \equiv P_{M1} / P_{M1}^{M1}$ and $x_{r,m} = \sqrt{P_{rm}^m}$. From Eq. (23) we can derive

$$x_{s,n} = x_{r,m} \varphi^{s-r}, \quad (24)$$

and

$$x = \varphi^{r-M} \sum_{s=0}^M \sum_{n=1}^{Z(r)} \varphi^{s-r} = \varphi^{-M} \sum_{s=0}^M Z(r) \equiv \frac{M!}{(M-s)!rs!} \varphi^s = \varphi^{-M} (1 + \varphi). \quad (25)$$

Now, using Eq. (20) and (25), the grand canonical partition function, Eq. (20), becomes

$$\ln \Xi = \sigma \ln(1 + \lambda q_a e^u). \quad (26)$$

For an ideal gas,

$$\lambda = e^{\frac{\mu_0}{kT}} \frac{P}{P^0}. \quad (27)$$

Considering Eq. (27) and differentiation Eq. (26) with respect to λ , the Langmuir isotherm equation can be derived

$$\theta = \frac{\bar{N}}{\sigma} = \left(\frac{\partial \ln \xi}{\partial \ln \lambda} \right)_{\sigma, T} = \frac{P}{P^* + P}, \quad P^* \equiv \frac{P^0}{e^{\frac{\mu_0}{kT}} q_a e^u}. \quad (28)$$

Finally, the exact grand canonical partition function, internal energy and entropy can be determined as

$$\Xi = \left(1 + \frac{P}{P^*} \right)^\sigma \quad (29)$$

$$E = -\sigma U \theta = kT^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{\varepsilon, \lambda} = -\sigma U \frac{P}{P^* + P}, \quad (30)$$

$$S = k \ln \Omega = k \ln \Xi + kT \left(\frac{\partial \ln \Xi}{\partial T} \right)_{T, \mu} = \sigma k [-\theta \ln \theta - (1-\theta) \ln(1-\theta)] \quad (31)$$

The Nonideal Models

(1). In the simplest nonideal model with $j > 0, M = 1$ (one-dimensional surface adsorption). When $M = 1, r = 0, 1$, thus, $\varepsilon_{01} = \varepsilon_{11} = 0$. The coefficients of the interaction energies between the columns are $\varepsilon_{01}^{01} = \varepsilon_{11}^{01} = \varepsilon_{01}^{11} = 0$ and $\varepsilon_{11}^{11} = 1$. From Eqs. (18) and (21), we have

$$x_{01}(1 - \xi) + x_{11}e^{-j/2} = 0, \quad (31)$$

$$x_{01}e^{j/2}\varphi + x_{11}(e^j\varphi - \xi) = 0, \quad (32)$$

$$\begin{vmatrix} 1 - \xi & e^{-j/2} \\ e^{j/2}\varphi & e^j\varphi - \xi \end{vmatrix} = 0. \quad (33)$$

The maximum root is then

$$\xi_{\max} = \frac{1 + e^j\varphi}{2} + \frac{1}{2} \sqrt{(1 - e^j\varphi)^2 + 4\varphi},$$

thus, the exact grand canonical partition function for one-dimensional surface adsorption with the nearest neighbor interactions can be determined as

$$\ln \Xi = \sigma \ln \left(\frac{1 + e^j\varphi}{2} + \frac{1}{2} \sqrt{(1 - e^j\varphi)^2 + 4\varphi} \right). \quad (34)$$

When we use it, we can calculate thermodynamic properties of the model with $M = 1$.

(2). In the next simplest nonideal model with $j > 0$ we set $M = 3$ ($r = 0, 1, 2, 3$). Now, each column can possess one of

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the eight possible states (because $\sum_{r=0}^3 3!/(3-r)!r! = 8$). Using the boundary conditions and referring to Tables 1, 2 and Eq. (21), after simplifications, we have

$$\begin{vmatrix} y^6 - \xi^3 \varphi^{-3} & 3y^{5.5} & 3y^5 & y^{4.5} \\ y^{2.5} & 2y^2 + y^3 - \xi^3 \varphi^{-2} & 2y^{2.5} + y^{1.5} & y^2 \\ 1 & 2y^5 + y^{-5} & 2 + y - \xi^3 \varphi^{-1} & y^5 \\ y^{-1.5} & 3y^{-1} & 3y^{-5} & 1 - \xi^3 \end{vmatrix} = 0. \quad (35)$$

where $y = e^j$. Maximum root of Eq. (35) is the partition function of the model with three rows.

(3). The same approach as above can be used to calculate the partition function for the model with $M > 3$.

When M increases, the solution of the secular determinant becomes more complicated. Thus, we were able to solve it only for $M \leq 14$. It means that the model cannot be solved for

the square lattice when $M \rightarrow \infty$. However, for $M = 4$ to 14, the modified secular determinants [such as Eq. (35)] give a polynomial with the order of 6, 8, 13, 18, 29, 46, 75, 126, 201, 374 and 615, respectively. Such polynomials cannot be solved analytically. For this reason, we have not been able to obtain an analytic expression for the partition function. However, the maximum root of such polynomials and also the variables P_{rm} and P_{rm}^{sn} can be obtained numerically. The results of such calculations are given in Figs. 1 to 8, for the fractional coverage, the reduced internal energy, and the reduced entropy. In these figures we have assumed that the particles are monatomic ($q_a = 1$), also in the gas-phase, the particles are assumed to have ideal behavior. The last assumption implies that the chemical potential of monatomic ideal gas with mass m , can be written as

$$\mu = kT \ln \frac{P}{P^*}, \quad P^* = J q_{ele} q_{nu} \left(\frac{2\pi m J}{h^2} \right)^{3/2} \quad (36)$$

Table 1. The Total Energies and Coefficients \mathcal{E}_{rm} within each Row for $M = 3$. The Solid and Nonsolid Circles Represent Occupied and Unoccupied Sites, Respectively

r	3	2			1			0
m	1	1	2	3	1	2	3	1
Configuration								
A_{rm}	A_{31}	A_{21}	A_{22}	A_{23}	A_{11}	A_{12}	A_{13}	A_{01}
Total energy	$-3J-3U$	$-J-2U$			$-U$			0
\mathcal{E}_{rm}	3	1			0			0

Table 2. The Coefficients of Interaction Energies between the Nearest Neighbor Columns (\mathcal{E}_{rm}^{sn}) For $M = 3$

A_{rm}	A_{31}	A_{21}	A_{22}	A_{23}	A_{11}	A_{12}	A_{13}	A_{01}
A_{31}	3	2	2	2	1	1	1	0
A_{21}	2	2	1	1	1	1	0	0
A_{22}	2	1	2	1	1	0	1	0
A_{23}	2	1	1	2	0	1	1	0
A_{11}	1	1	1	0	1	0	0	0
A_{12}	1	1	0	1	0	1	0	0
A_{13}	1	0	1	1	0	0	1	0
A_{01}	0	0	0	0	0	0	0	0

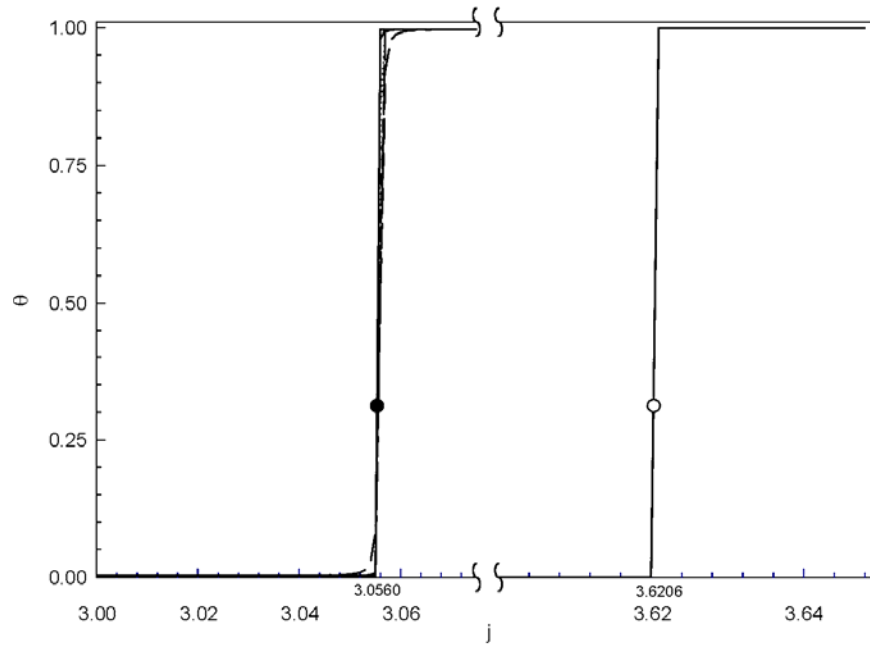


Fig. 1. The fractional coverage, θ vs. the reduced reciprocal temperature, j , for various isobars [$P/P^* = 2 \times 10^{-5}$ (\circ) and 1×10^{-4} (\bullet)] when $U = J/10$. The left-hand side curves include models with $M = 3$ to 14, and the right-hand side curves are for the cases when $M = 7$ to 14.

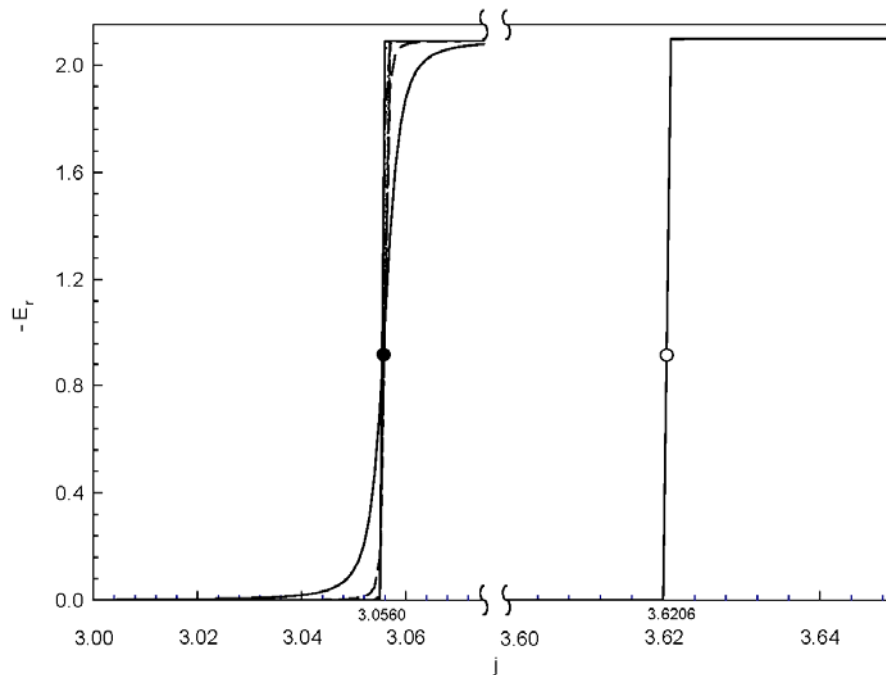


Fig. 2. The same as Fig. 1 for the reduced internal energy, $-E/\sigma J$ or $-E_r$.

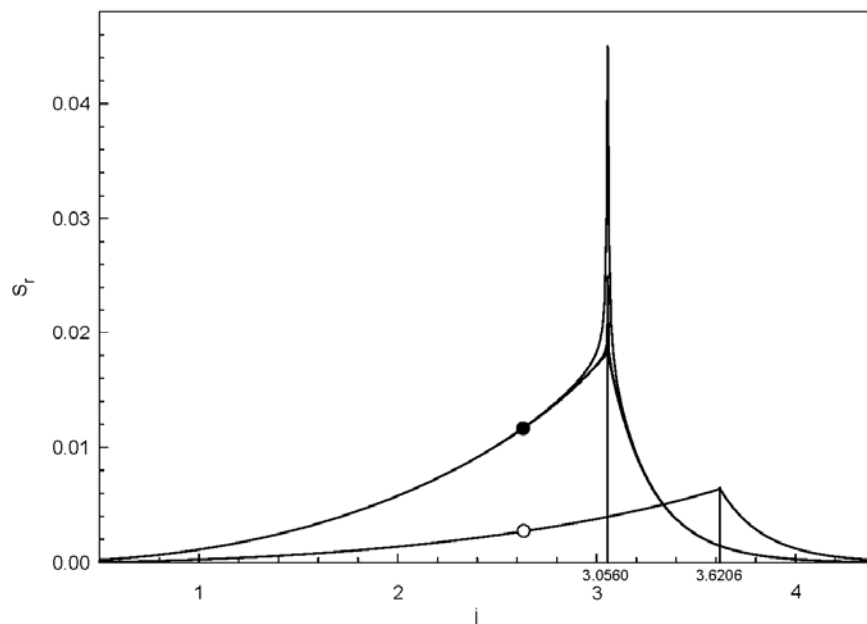


Fig. 3. The same as Fig. 1 for the reduced entropy, $S/\sigma K$ or S_r .

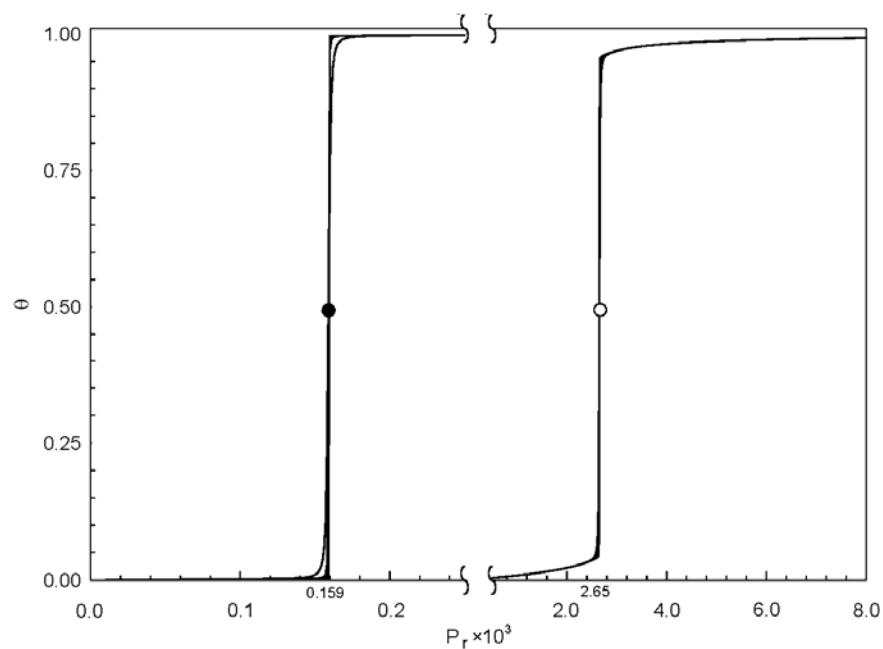


Fig. 4. The fractional coverage, θ , vs. the reduced pressure, P/P^* or P_r , in the various isotherms [$j = 2$ (\circ) and 3 (\bullet)] when $U \rightarrow 0$. The left-hand side curves include models with $M = 3$ to 14 , and the right-hand side curves are for the cases when $M = 7$ to 14 .

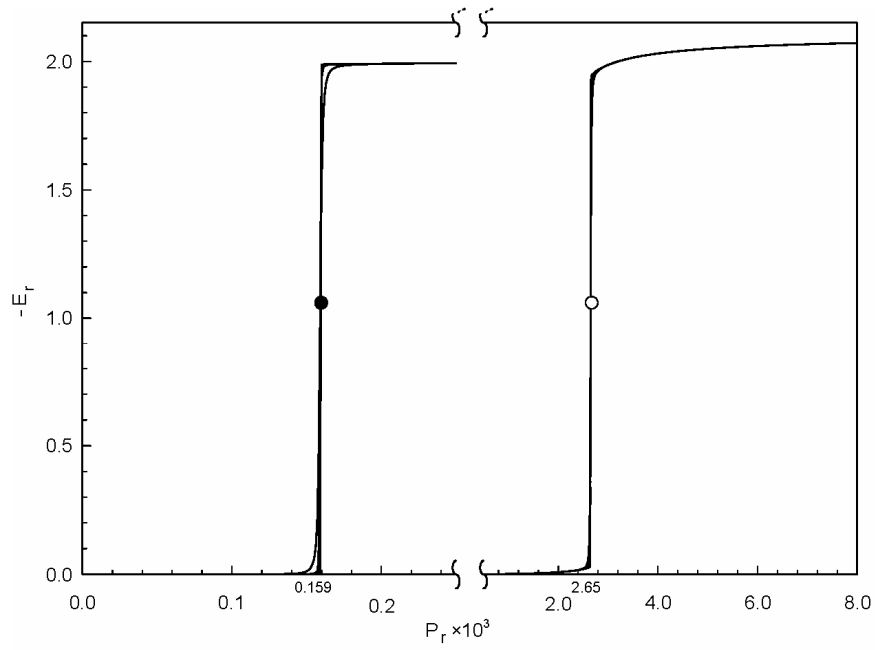


Fig. 5. The same as Fig. 4 for the reduced internal energy, $-E/\sigma J$ or $-E_r$.

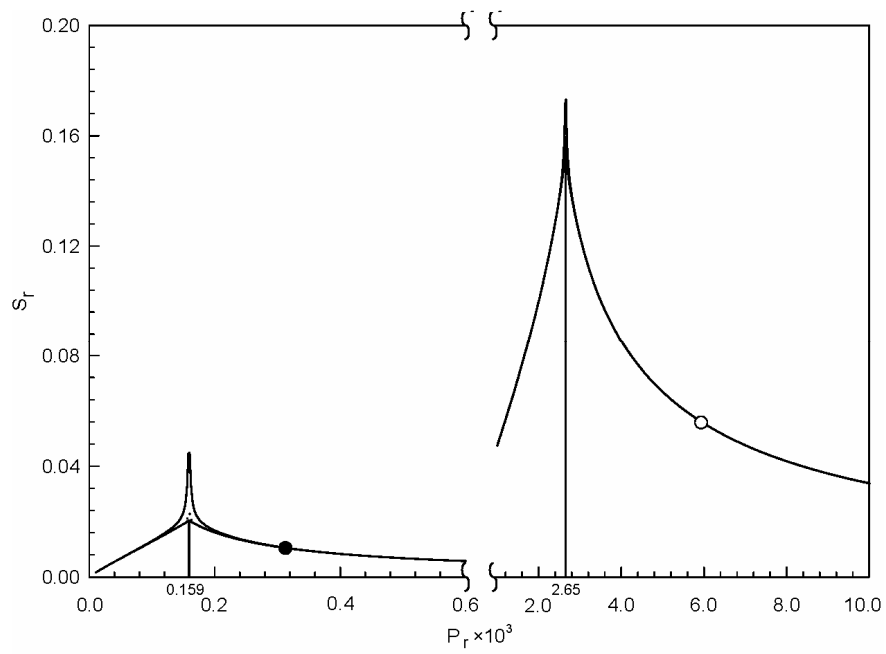


Fig. 6. The same as Fig. 4 for the reduced entropy, $S/\sigma K$ or S_r .

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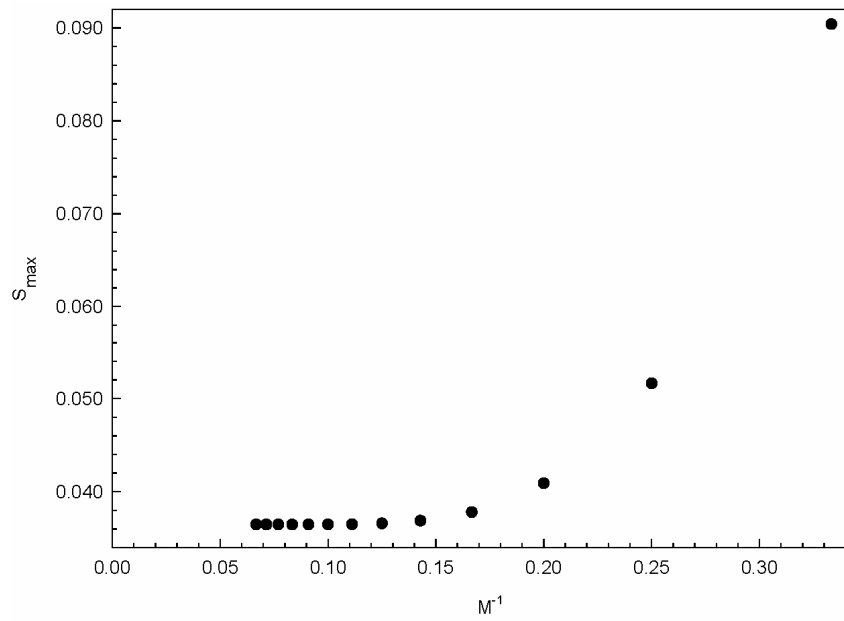


Fig. 7. The exact value of the reduced entropy at the transition point (S_{\max}) vs. $1/M$ when $U = J/10$ and $P/P^* = 1 \times 10^{-4}$.

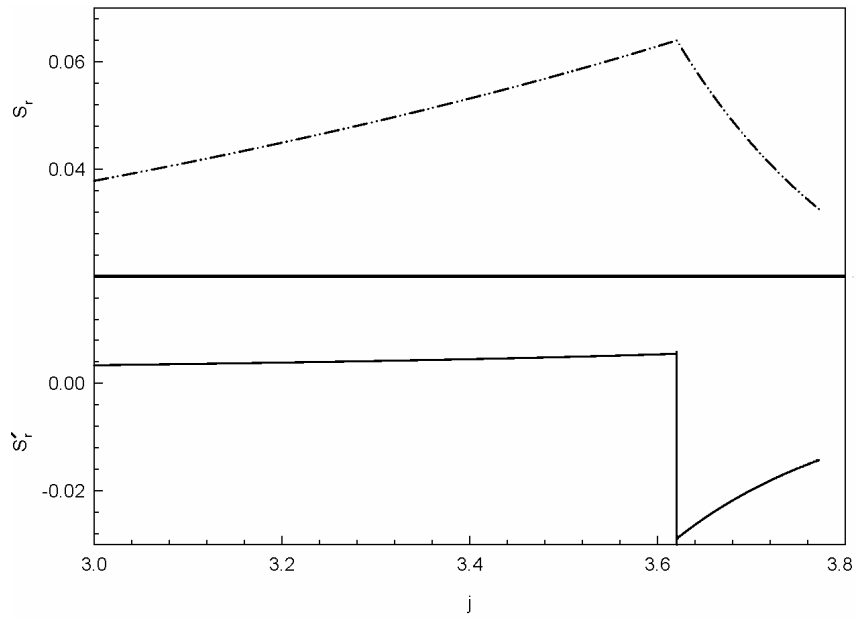


Fig. 8. The reduced entropy, $S/\sigma k$ or S_t , and the first derivatives of the reduced entropy, $(\partial S/\partial j)/\sigma k$ or S'_t vs. the reduced reciprocal temperature, j , in the constant reduced pressure ($P/P^* = 2 \times 10^{-5}$) when $M = 13$ and $U = J/10$.

CONCLUSIONS

In this work, we have considered the two-dimensional surface adsorption model with a limited number of rows (M) and unlimited number of columns (L). In the process, we used combinatorial factor method for distribution of N adsorbed particles upon σ sites with nearest neighbor interactions. Then, using the grand canonical ensemble, we investigated the thermodynamic properties of the models with limited number of rows. The results are given in Figs. 1 to 8. In these figures, there are some important points to be considered:

1. We see that the thermodynamic properties of models with different number of rows ($M > 6$) are similar (note that, θ , E and S are the first derivatives of the grand canonical partition function). In fact, they reveal the important point that θ , E and S are independent of the number of rows. To elaborate, we have plotted its maximum value of entropy (S_{\max}) vs. $1/M$ (Fig. 7). Thus, we conclude that the calculated thermodynamics properties for the model with $M = 7-14$ (where the size effect becomes insignificant) are almost the same as those for the actual model ($M \rightarrow \infty$).

2. In the isobar plots (Figs. 1-3) or isotherm plots (Figs. 4-6), we notice that for each M , there are specific inverse reduced reciprocal temperatures or reduced pressures wherein the fractional coverage is exactly $1/2$, the internal energy rapidly increases and the entropy is at its maximum value. These points must be considered as the critical points because at these points the energy as well as entropy slope become discontinuous. Thus, we can deduce that in surface adsorption there is a phase transition which can be predicted by this method. This finding is in agreement with the experimental and theoretical results [51-53]. However, we must note that this phase transition can be classified neither as the first-nor as the second-order. This is because in a first-order phase transition, E and S are discontinuous, while in a second-order phase transition, only the first derivatives of E and S are discontinuous. For further clarification, we have plotted S and the first derivatives of S against j in Fig. 8 for $M = 13$ when $U = J/10$ and $P/P^* = 2 \times 10^{-5}$. In conclusion, for adsorbed monatomic particles with nearest neighbor interactions, when the fractional coverage becomes $1/2$, some kind of a phase transition takes place which can be classified as neither the first-nor the second-order transition (in fact, this transition is

related to the *monolayer* adsorbed particles and takes place in the two-dimensional space).

3. In Fig. 3, we see that the entropy goes to zero as temperature increases or decreases. This behavior is logical, because the entropy (in fact the configurational entropy) adsorbed particles depends on θ , thus when $\theta \rightarrow 0$ or $\theta \rightarrow 1$, the entropy must go to zero. The same explanation can be applied to Fig. 6.

Finally, it must be pointed out that the approach presented in this report can be extended to surface adsorption models with consideration of the other nearest neighbors as well as double layer adsorption.

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