Multisite Occupancy Adsorption: Comparative Study of New Different Analytical Approaches

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The adsorption of dimers on honeycomb, square, and triangular lattices is studied by combining theoretical modeling and Monte Carlo simulations in canonical and grand canonical ensembles. The adsorption thermodynamics is analyzed through the adsorption isotherm and the configurational entropy of the adsorbate. Three theoretical models to study dimers' adsorption on two-dimensional lattices have been proposed: (i) the first, which we called occupation balance, is based on the expansion of the reciprocal of the fugacity; (ii) the second is an extension to 2-D of the exact partition function obtained in 1-D; and (iii) the third is a virial expansion. Results are compared with corresponding ones from the Flory's approximation and from the Monte Carlo simulations. Significant quantitative differences are shown and discussed. In all cases, the occupation balance appears as the more accurate model.

1. Introduction

Adsorption of gases on solid surfaces is an important problem in physical chemistry and chemical engineering.[1,2] Works belonging to this topic are based on Langmuir's model of adsorption. One fundamental feature of the Langmuir's model is presented in all these theories. This is the assumption that an adsorbed molecule occupies one site in the lattice of adsorption sites (single-particle statistics).[2] In contrast, experiments show that most adsorbates, except noble gases, are polyatomic. Typical examples are O_2, N_2, CO, and CO_2 adsorbed in carbon and zeolite molecular sieves[3] and oligomers in activated carbons.[4] In these systems, the size of the molecules can significantly affect the entropic contribution to the adsorbate's free energy, and multisite-occupancy theory must be considered.

The difficulty in the analysis of the multisite statistics is mainly associated with three factors which differentiate the *k*-mers' (particles occupying several *k* contiguous lattice sites) statistics from the usual single-particle statistics. They are (i) no statistical equivalence exists between particles and vacancies; (ii) the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied; and (iii) an isolated vacancy cannot serve to determine whether that site can ever become occupied.

For these reasons, it has been difficult to formulate, in an analytical way, the statistics of occupation for correlated particles such as dimers. In this sense, exact solutions have been obtained for the one-dimensional case.[5,6] For higher dimensionality, exact solutions can be found for special cases, by using Pfaffians[7,8] and the matrix transference method.[9,10] In other words, from an analytical point of view, the problem in which a two-dimensional lattice contains isolated lattice points (vacancies) as well as dimers has not been solved in closed form and approximated methods have been utilized to study this problem.

Two objectives motivated the development of the main approximations existing in the literature; they are (i) the possibility of phase transitions in the adsorbate when nearest-neighbor interacting *k*-mers are adsorbed on homogeneous surfaces and (ii) the inclusion of heterogeneous substrates and its influence on the main adsorption properties. The theories of the first group have been derived from the well-known Flory's approximation (FA)[11,12] for binary solutions of polymer molecules diluted in a monomeric solvent (it is worth mentioning that, in the framework of the lattice−gas approach, the adsorption of *k*-mers on homogeneous surfaces is an isomorphous problem to the binary solutions of polymer−monomeric solvent).

In the FA, the canonical partition function for *N* interacting *k*-mers adsorbed on *M* sites can be written as

$$Q(M,N,T) = \Omega(M,N) \exp\left[-\frac{E(N)}{k_B T}\right] \qquad (1)$$

where $E(N)$ is the total energy, which is obtained in the Bragg−Williams approximation,[13] k_B is the Boltzmann constant, and $\Omega(M,N)$ is the combinatory factor representing the number of ways to array N *k*-mers on M sites distributed on a homogeneous lattice of *c* connectivity

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$$\Omega(M,N) = \frac{M!}{N!(M-kN)!}\left(\frac{c-1}{M}\right)^{(k-1)N} \qquad (2)$$

The mean-field term, $\exp[-E(N)/kT]$ is responsible for the phase transitions occurring in the adsorbate. A comprehensive discussion on this subject is included in the book of Des Cloiseaux and Janninck[14] and in ref 15.

In the second direction, the patchwise heterogeneous surface can be solved relatively simply. One can apply the solution to multisite-occupancy adsorption on homogeneous surfaces, which are now the patches. In the case of random heterogeneous surfaces, the problem becomes much more complicated, and it was only two decades ago when the first solution of that problem was proposed by Nitta et al.[2,16]

However, Nitta's original approach could be applied only to surfaces characterized by discrete distributions of adsorption energy. Later, Rudziński and Everett (ref 2 and references therein) developed further Nitta's approach to apply also to continuous adsorption energy distributions.

As emphasized by Nitta, it is very difficult to find a rigorous expression for $\Omega(M,N)$ (see eq 2), when the M sites are distributed on a random heterogeneous surface. To solve this problem, Nitta proposed two contributions for $\Omega(M,N)$, the first being the different ways to array N k-mers on M homogeneous sites (obtained as in eq 2) and the second being a term that takes into account the effect of the heterogeneity.

As can be observed from the previous paragraph, all the theories treating the multisite-occupancy (including lateral interactions between k-mers, heterogeneity in the adsorbent, or both properties) depend on the Flory's configurational factor given in eq 2. Recent studies[6,17] have demonstrated the crucial importance of this factor on the thermodynamic properties of k-mers adsorbed on homogeneous and heterogeneous surfaces. In this sense, strong discrepancies appear when the exact thermodynamic functions obtained for linear species adsorbed on a one-dimensional lattice are compared with the Flory's predictions under similar conditions.[6] These differences are associated with approximations in the calculation of the Flory configurational factor. On the other hand, it is clearly shown in ref 17 that the Nitta's model can be notably improved by introducing a better way to take into account $\Omega(M,N)$.

In this context, this paper has two main objectives: (1) To develop alternative approaches to calculate the different ways to array N dimers on M equivalent sites distributed on a two-dimensional lattice. In this sense, three methods have been proposed. (i) The first, which we called occupation balance (OB), is based on the expansion of the reciprocal of the fugacity; (ii) The second (EA) is an extension to 2-D of the exact partition function obtained in 1-D. (iii) The third is a virial expansion (VE). (2) To compare with the Flory's approximation, analyzing the accuracy of the results presented here. For this purpose, the adsorption isotherm and configurational entropy of the adsorbate are obtained for the four theoretical models (OB, EA, VE, and FA) and compared between each other and with Monte Carlo simulations in canonical and grand canonical ensembles. The comparisons are realized for honeycomb, square, and triangular lattices.

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The present work is organized as follows. The dimers' adsorption model and the theoretical approaches are presented in Section 2. The results and discussion are given in Section 3. Finally, the conclusions are drawn in Section 4.

2. Basic Definitions: Model and Theoretical Approaches

2.1. Lattice−Gas Model. In this section we describe the lattice−gas model for the adsorption of particles with multisite-occupancy in the monolayer regime. We consider the adsorption of homonuclear linear k-mers on two-dimensional lattices. The adsorbate molecules are assumed to be composed by k identical units in a linear array with constant bond length equal to the lattice constant a. The k-mers can only adsorb flat on the surface occupying k lattice sites (each lattice site can only be single-occupied). The surface is represented as an array of $M = L \times L$ adsorptive sites in a square, honeycomb, or triangular lattice arrangement, where L denotes the linear size of the array. To describe a system of N k-mers adsorbed on M sites at a given temperature T, let us introduce the occupation variable c_i which can take the values $c_i = 0$ or 1, if the site i is empty or occupied by a k-mer unit, respectively. The k-mers retain their structure upon adsorption, desorption, and diffusion. The Hamiltonian of the system is given by

$$H = (\epsilon_0 - \mu)\sum_i c_i \qquad (3)$$

where ϵ_0 is the adsorption energy of a k-mer unit ($k\epsilon_0$ being the total adsorption energy of a k-mer) and μ is the chemical potential. Finally, ϵ_0 is set equal to zero, without any loss of generality.

2.2. Exact Thermodynamic Functions in One Dimension and Extension to Higher Dimensions (EA). Let us assume a one-dimensional lattice of M sites with lattice constant a ($M \rightarrow \infty$) where periodic boundary conditions apply. Under this condition all lattice sites are equivalent; hence, border effects will not enter our derivation.

N linear k-mers are adsorbed on the lattice in such a way that each mer occupies one lattice site and double site occupancy is not allowed as to represent properties in the monolayer regime. Since different k-mers do not interact with each other through their ends, all configurations of N k-mers on M sites are equally probable; henceforth, the canonical partition function $Q(M,N,T)$ equals the total number of configurations, $\Omega(M,N)$, times a Boltzmann factor including the total interaction energy between k-mers and lattice sites, $E(N)$

$$Q(M,N,T) = \Omega(M,N)\exp\left[-\frac{E(N)}{k_B T}\right] \qquad (4)$$

Since the lattice is assumed to be homogeneous, $E(N)$ can be arbitrarily chosen equal to zero for all N without losing generality (i.e, the interaction energy between every unit forming a k-mer and the substrate is set to be zero).

$\Omega(M,N)$ can be readily calculated as the total number of permutations of the N indistinguishable k-mers out of n_e entities, being[6]

$$n_e = \text{number of } k\text{-mers} + \text{number of empty sites}$$

$$= N + M - kN = M - (k-1)N \qquad (5)$$

Accordingly,

$$\Omega(M,N) = \binom{n_e}{N} = \frac{[M - (k-1)N]!}{N![M - kN]!} \quad (6)$$

(a particular solution for dimers was presented in ref 13).

In the canonical ensemble the Helmholtz free energy $F(M,N,T)$ relates to $\Omega(M,N)$ through

$$\beta F(M,N,T) = -\ln Q(M,N,T) = -\ln \Omega(M,N) \quad (7)$$

where $\beta = 1/k_B T$.

The remaining thermodynamic functions can be obtained from the general differential form[13]

$$dF = -S\,dT - \Pi\,dM + \mu\,dN \quad (8)$$

where S, Π, and μ designate the entropy, spreading pressure, and chemical potential, respectively, which, by definition, are

$$S = -\left(\frac{\partial F}{\partial T}\right)_{M,N}; \quad \Pi = -\left(\frac{\partial F}{\partial M}\right)_{T,N}; \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,M} \quad (9)$$

Thus, from eqs 6 and 7

$$\beta F(M,N,T) = \\ -\{\ln[M - (k-1)N]! - \ln N! - \ln[M - kN]!\} \quad (10)$$

which can be accurately written in terms of the Stirling approximation

$$\beta F(M,N,T) = -[M - (k-1)N]\ln[M - (k-1)N] + \\ [M - (k-1)N] + [N\ln N - N] + \\ [(M - kN)\ln(M - kN) - (M - kN)] \\ = -[M - (k-1)N]\ln[M - (k-1)N] + \\ N\ln N + (M - kN)\ln(M - kN) \quad (11)$$

Henceforth, from eqs 9 and 11

$$\frac{S(M,N)}{k_B} = [M - (k-1)N]\ln[M - (k-1)N] - \\ N\ln N - (M - kN)\ln(M - kN) \quad (12)$$

$$\beta\Pi = \ln[M - (k-1)N] - \ln[M - kN] \quad (13)$$

$$\beta\mu = \ln\frac{N}{M} + (k-1)\ln\left[1 - (k-1)\frac{N}{M}\right] - k\ln\left[1 - \frac{kN}{M}\right] \quad (14)$$

Then, by defining the lattice coverage $\theta = kN/M$, molar free energy $f = F/M$, and molar entropy $s = S/M$, eqs 11–14 can be rewritten in terms of the intensive variables θ and T.

$$\beta f(\theta,T) = -\left\{\left[1 - \frac{(k-1)}{k}\theta\right]\ln\left[1 - \frac{(k-1)}{k}\theta\right] - \\ \frac{\theta}{k}\ln\frac{\theta}{k} - (1 - \theta)\ln(1 - \theta)\right\} \quad (15)$$

$$\frac{s(\theta)}{k_B} = \left[1 - \frac{(k-1)}{k}\theta\right]\ln\left[1 - \frac{(k-1)}{k}\theta\right] - \frac{\theta}{k}\ln\frac{\theta}{k} - \\ (1 - \theta)\ln(1 - \theta) \quad (16)$$

$$\exp(\beta\Pi) = \frac{\left[1 - \frac{(k-1)}{k}\theta\right]}{(1 - \theta)} \quad (17)$$

$$C_k\exp(\beta\mu) = \frac{\theta\left[1 - \frac{(k-1)}{k}\theta\right]^{k-1}}{(1 - \theta)^k} \quad (18)$$

where $C_k = k$.

Hereafter, we address the calculation of approximated thermodynamical functions of linear chains adsorbed on lattices with connectivity c higher than 2 (i.e., dimensions higher than 1).

In general, the number of configurations of N k-mers on M sites, $\Omega(M,N,c)$, depends on the lattice connectivity c. $\Omega(M,N,c)$ can be approximated considering that the molecules are distributed completely at random on the lattice, and assuming the arguments given by different authors[12–16] to relate the configurational factor $\Omega(M,N,c)$ for any c with respect to the same quantity in one dimension ($c = 2$). Thus,

$$\Omega(M,N,c) = K(k,c)^N\,\Omega(M,N,2) \quad (19)$$

where $\Omega(M,N,2)$ can be readily calculated from eq 6. In the particular case of rigid straight k-mers, it follows that $K(c,k) = c/2$. In this way, the entropy s and the adsorption isotherm corresponding to a lattice of connectivity c result,

$$\frac{s(\theta)}{k_B} = \left[1 - \frac{(k-1)}{k}\theta\right]\ln\left[1 - \frac{(k-1)}{k}\theta\right] - \frac{\theta}{k}\ln\frac{\theta}{k} - \\ (1 - \theta)\ln(1 - \theta) + \frac{\theta}{k}\ln\frac{c}{2} \quad (20)$$

$$k\frac{c}{2}\exp(\beta\mu_c) = \frac{\theta\left[1 - \frac{(k-1)}{k}\theta\right]^{k-1}}{(1-\theta)^k} \quad (21)$$

Equations 19–21 provide the basic thermodynamic functions for non-interacting linear adsorbates in lattices with general connectivity c.

2.3. Occupation Balance Approximation (OB). Here we propose an approximation of $s(\theta)$ for non-interacting dimers on a regular lattice, based on general arguments, which leads to very accurate results.

The mean number of particles in the adlayer $\bar{N}$ and the chemical potential μ are related through the following general relationship in the grand canonical ensemble

$$\bar{N} = \lambda\left[\frac{\partial\ln\Xi(M,\lambda)}{\partial\lambda}\right]_M \quad (22)$$

where $\lambda = \exp(\mu/k_B T)$ and Ξ is the grand partition function. By solving λ^{-1} from eq 22

$$\lambda^{-1} = \frac{1}{\bar{N}}\left[\frac{\partial\ln\Xi(M,\lambda)}{\partial\lambda}\right]_M = \frac{\bar{R}(M,\lambda)}{\bar{N}} \quad (23)$$

where the quantity $\bar{R}(M,\lambda)$ can be proven to be the mean number of states available to a particle on M sites at λ. If $Y_t(M,N)$ and $R_i(M,N)$ denote the total number of configurations of N distinguishable particles on M sites and the number of states available to the $(N+1)$th particle in the ith configuration [out of $Y_t(M,N)$], respectively, then

$$Y_t(M,N+1) = \sum_{i=1}^{Y_t(M,N)} R_i(M,N) \quad (24)$$

The total number of configurations of $(N + 1)$ indistinguishable particles on M sites, $G_t(M,N+1)$, can be obtained from eq 24.

$$G_t(M,N+1) = \frac{Y_t(M,N+1)}{(N+1)!} = \frac{\sum_{i=1}^{Y_t(M,N)} R_i(M,N)}{(N+1)!}$$

$$= \frac{N!}{(N+1)!} \sum_{i=1}^{G_t(M,N)} R_i(M,N) =$$

$$\frac{1}{N+1} \sum_{i=1}^{G_t(M,N)} R_i(M,N) \quad (25)$$

In the last arguments, we consider that for each configuration of N indistinguishable particles there exist $N!$ configurations of N distinguishable particles.

The average of $R_i(M,N)$ over a grand canonical ensemble is

$$\bar{R}(M,\lambda) = \langle R_i(M,N) \rangle = \frac{1}{\Xi} \sum_{N=0}^{N_m} \left\{ \lambda^N \sum_{i=1}^{G_t} R_i(M,N) \right\}$$

$$= \frac{1}{\Xi} \sum_{N=0}^{N_m-1} (N+1)\lambda^N G_t(M,N+1)$$

$$= \frac{\lambda^{-1}}{\Xi} \sum_{N=1}^{N_m} \lambda^N N\, G_t(M,N) = \frac{\bar{N}}{\lambda} \quad (26)$$

as already advanced in eq 23 with $N = N+1$, N_m being the maximum number of particles that fit in the lattice, and $R_i(M,N_m) = 0$.

The advantage of using eq 23 to calculate the coverage dependence of the fugacity λ can be seen by dealing with adsorption of dimers in the monolayer regime. $\bar{R}[M,\lambda(\bar{N})] = \bar{R}(M,\bar{N})$ for dimers (occupying two nearest-neighbor lattice sites) is, at first order, $\bar{R}(M,\bar{N}) \approx cM/2 - (2c-1)\bar{N}$, where the second terms account for the mean number of states excluded by the adsorbed dimers on a lattice with connectivity c. (If it is assumed that each dimer is independent from the neighboring ones, each dimer excludes $(2c-1)$ states out of total $cM/2$.) Thus,

$$\lim_{M\to\infty} \lambda^{-1} \approx \lim_{M\to\infty} \frac{cM/2 - (2c-1)\bar{N}}{\bar{N}} = \frac{c}{\theta} - (2c-1) \quad (27)$$

where $\lim_{M\to\infty} 2\bar{N}/M = \theta$.

The term $(2c-1)$ overestimates the number of excluded states because of simultaneous exclusion of neighboring particles. Then, the approximation can be further refined by considering the mean number of states that are simultaneously excluded by $\bar{N}$ dimers, $\bar{L}(M,\bar{N})$. It is possible to demonstrate that, in general, $\bar{R}(M,\bar{N}) = cM/2 - (2c-1)\bar{N} + \bar{L}(M,\bar{N})$ for straight k-mers.

For dimers, $\bar{L}(M,\bar{N})$ is the average number of occupied nearest-neighbors. Due to the fact that it is not possible to obtain exact solutions for $\bar{L}(M,\bar{N})$, we approximate

$$\bar{L}(M,\bar{N}) \approx \frac{\bar{N}(\bar{N}-1)}{2} \bar{L}(M,2) \quad (28)$$

where $\bar{N}(\bar{N}-1)/2$ is the number of possible pairs for $\bar{N}$ indistinguishable particles.

Considering a system of two adsorbed dimers on a square lattice ($c = 4$), we can write

$$\bar{L}(M,2) = \frac{g_1(M,2) + 2g_2(M,2)}{G_t(M,2)} = \frac{18}{(2M-7)} \quad (29)$$

where $G_t(M,2) = M(2M-7)$. In addition, $g_1(M,2) = 14M$ and $g_2(M,2) = 2M$ are the number of states with one and two occupied nearest-neighbors. Finally, we can write

$$\lim_{M\to\infty} \lambda^{-1} = \lim_{M\to\infty} \frac{2M - 7\bar{N} + \bar{L}(M,\bar{N})}{\bar{N}}$$

$$\approx \lim_{M\to\infty} \frac{1}{\bar{N}} \left[2M - 7\bar{N} + \frac{9\bar{N}(\bar{N}-1)}{(2M+7)} \right]$$

$$\approx \frac{4}{\theta} - 7 + \frac{9}{4}\theta + O(\theta^2) \quad (30)$$

Finally, by considering that the terms neglected in eq 28 are $O(\theta^2)$, it becomes

$$\lambda^{-1} = \frac{4}{\theta} - 7 + \frac{9}{4}\theta + a\theta^2 \quad \text{(square lattice)} \quad (31)$$

and the constant $a = {}^3/_4$ can be determined from the limiting condition $\lambda \to \infty$ for $\theta \to 1$. Similarly,

$$\lambda^{-1} = \frac{3}{\theta} - 5 + \frac{4}{3}\theta + \frac{2}{3}\theta^2 \quad \text{(honeycomb lattice)} \quad (32)$$

$$\lambda^{-1} = \frac{6}{\theta} - 11 + \frac{23}{6}\theta + \frac{7}{6}\theta^2 \quad \text{(triangular lattice)} \quad (33)$$

From the thermodynamic relationship $\mu = (\partial F/\partial N)_{M,T}$ (F denotes the Helmholtz free energy), the entropy per lattice site $s(\theta)$ can be evaluated in the limit $T \to \infty$ as follows

$$\frac{\mu}{k_B T} = \ln \lambda =$$

$$-\frac{1}{k_B} \lim_{M,T\to\infty} \left[\frac{\partial S(M,N,T)}{\partial N} \right]_{M,T} = -\frac{2}{k_B} \left[\frac{ds(\theta)}{d\theta} \right] \quad (34)$$

then

$$\frac{s(\theta)}{k_B} = -\frac{1}{2}\int_0^\theta \ln \lambda(\theta')\, d\theta' \quad (35)$$

From eqs 31–33 and 35 we obtain

$$\frac{s(\theta)}{k_B} = \frac{\theta}{2}[\ln C - \ln \theta - 2] - \frac{(1-\theta)}{2}\ln(1-\theta) -$$

$$\frac{(A-\theta)}{2}\ln(A-\theta) + \frac{(B+\theta)}{2}\ln(B+\theta) +$$

$$\frac{A}{2}\ln A - \frac{B}{2}\ln B \quad (36)$$

where

$$A = 2(\sqrt{7/3} - 1),\ {}^3/_2(\sqrt{3} - 1),\ \text{and}\ {}^{15}/_7(\sqrt{53/5} - 1)$$

$$C = {}^3/_4,\ {}^2/_3,\ \text{and}\ {}^7/_6$$

$$B = 2(\sqrt{7/3} + 1),\ {}^3/_2(\sqrt{3} + 1),\ \text{and}\ {}^{15}/_7(\sqrt{53/5} + 1)$$

for square, honeycomb, and triangular lattices, respectively.

2.4. Virial Expansion (VE). In this section we will obtain the entropy and the adsorption isotherm for a system of dimers adsorbed on a regular lattice by using the formalism of virial expansion.[19]

As usual, the activity z is written in terms of the density, ρ $(=N/M)$,

$$z(\rho) = \sum_{j=1}^{\infty} a_j \rho^j \tag{37}$$

and z is related to the fugacity, λ, by

$$z = \lambda \frac{Q_1}{M} \tag{38}$$

where Q_1 is the partition function of one particle. The first, second, and third coefficients a_j are given by[19]

$$a_1 = \frac{1}{b_1}, \quad a_2 = -2b_2, \quad a_3 = -3b_3 + 8b_2^2 \tag{39}$$

The coefficients b_1, b_2, and b_3 can be obtained from the partition function for one, Q_1, two, Q_2, and three, Q_3, particles. Defining Z (configurational canonical function) by

$$Z_N = N!\left(\frac{M}{Q_1}\right)^N Q_N \tag{40}$$

the b_j coefficients adopt the following form

$$b_1 = \frac{Z_1}{1!M}, \quad b_2 = \frac{1}{2!M}(Z_2 - Z_1^2),$$

$$b_3 = \frac{1}{3!M}(Z_3 - 3Z_2 Z_1 + 2Z_1^3) \tag{41}$$

The first and second a_i coefficients can be calculated as follows. By using $Q_1 = G_t(M,1) = 2M(T\rightarrow\infty)$, the partition functions for one and two particles can be written as

$$Z_1 = M \tag{42}$$

and

$$Z_2 = \frac{M}{2}(2M - 7) \tag{43}$$

then,

$$b_1 = 1 \Rightarrow a_1 = 1 \tag{44}$$

and

$$b_2 = -\frac{7}{4} \Rightarrow a_2 = \frac{7}{2} \tag{45}$$

To obtain a_3, we need to know Q_3. In this sense, from eq 25

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$$Q_{N+1} = G_t(M,N+1) =$$

$$\frac{1}{N+1}G_t(M,N)\left[\frac{1}{G_t(M,N)}\sum_{i=1}^{G_t(M,N)} R_i(M,N)\right]$$

$$= \frac{1}{N+1}G_t(M,N)\,\bar{R}(M,N) = \frac{1}{N+1}Q_N\bar{R}(M,N) \tag{46}$$

Equation 46 relates the partition function of $N + 1$ particles with the same quantity for N particles (due to the equivalence between the different ensembles, we calculate $\bar{R}(M,N)$ in the canonical ensemble). From this argument,

$$Q_3 = \frac{1}{3}Q_2\bar{R}(M,2) = \frac{4}{3}M^3 - 14M^2 + \frac{116}{3}M \tag{47}$$

and

$$b_3 = \frac{29}{6} \Rightarrow a_3 = 10 \tag{48}$$

Then, the adsorption isotherm of dimers on a square lattice is

$$\frac{\mu}{k_B T} = \ln\left(\frac{1}{4}\theta + \frac{7}{16}\theta^2 + \frac{5}{8}\theta^3\right) \quad \text{(square lattice)} \tag{49}$$

with $\theta = 2\rho$.

For other connectivities,

$$\frac{\mu}{k_B T} = \ln\left(\frac{1}{3}\theta + \frac{5}{9}\theta^2 + \frac{7}{9}\theta^3\right) \quad \text{(honeycomb lattice)} \tag{50}$$

and

$$\frac{\mu}{k_B T} = \ln\left(\frac{1}{6}\theta + \frac{11}{36}\theta^2 + \frac{49}{108}\theta^3\right) \quad \text{(triangular lattice)} \tag{51}$$

In addition, the entropy can be obtained from eqs 49–51 and 35

$$\frac{s(\theta)}{k_B} = \frac{\theta}{2}\{3 - \ln(A\theta) -$$

$$\ln[B^2 + (\theta + C)^2]\} - \frac{C}{2}\ln\left[\frac{B^2 + (\theta + C)^2}{B^2 + C^2}\right] +$$

$$B\left\{\arctan\left(\frac{C}{B}\right) - \arctan\left(\frac{\theta + C}{B}\right)\right\} \tag{52}$$

where

$$A = \frac{5}{8}, \frac{7}{9}, \text{ and } \frac{49}{108}$$

$$B = \sqrt{111/400}, \sqrt{59/196}, \text{ and } \sqrt{2439/9604}$$

$$C = \frac{7}{20}, \frac{5}{14}, \text{ and } \frac{33}{98}$$

for square, honeycomb, and triangular lattices, respectively.

3. Results and Discussion

The adsorption process is simulated through a grand canonical ensemble Monte Carlo (GCEMC) method.[20] For a given value of the temperature T and chemical potential μ, an initial configuration with N dimers adsorbed at

random positions (on $2N$ sites) is generated. Then an adsorption−desorption process is started, where a pair of nearest-neighbor sites is chosen at random and an attempt is made to change its occupancy state with the probability given by the Metropolis[21] rule:

$$P = \min\{1, \exp(-\Delta H/k_B T)\} \qquad (53)$$

where $\Delta H = H_f - H_i$ is the difference between the Hamiltonians of the final and initial states. A Monte Carlo step (MCS) is achieved when M pairs of sites have been tested to change its occupancy state. The equilibrium state can be well reproduced after discarding the first $m' = 10^5$ to 10^6 MCSs. Then, averages are taken over $m = 10^5$ to 10^6 successive configurations.

The adsorption isotherm, or mean coverage as a function of the chemical potential $[\theta(\mu)]$, is obtained as a simple average:

$$\theta(\mu) = \frac{1}{M}\sum_i^M \langle c_i \rangle = \frac{2\langle N \rangle}{M} \qquad (54)$$

where $\langle N \rangle$ is the mean number of adsorbed particles and $\langle ... \rangle$ means the time average over the Monte Carlo simulation runs.

The configurational entropy S of the adsorbate cannot be directly computed. To calculate entropy, various methods have been developed.[22] Among them, the thermodynamic integration method (TIM) is one of the most widely used and practically applicable.[23−26] To understand the TIM, we begin from the basic relationship

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{M,N} \qquad (55)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{M,T} \qquad (56)$$

The TIM method relies upon integration along a reversible path between an arbitrary reference state and the desired state of the system,

$$S(M,N,T) = S(M,N,T_0) + \int_{U(T_0)}^{U(T)} \frac{dU}{T} \qquad (57)$$

$$S(M,N,T) = S(M,N_0,T) +$$
$$\frac{U(M,N,T) - U(M,N_0,T)}{T} - \frac{1}{T}\int_{N_0}^{N}\mu\, dN \qquad (58)$$

In the first (second) case [eq 57 (58)], the integration must be developed in a canonical ensemble (grand canonical ensemble). In both situations, the TIM requires the knowledge of a reference state [represented in eqs 57 and 58 with the subindex 0]. To obtain the entropy independently of the adsorption isotherm (calculated in the GCE), we used eq 57 in the calculation of S. Finally, the desired value of the entropy, $[S(M,N,\infty)]$, was calculated from a reference state at $T = 0$, which was obtained

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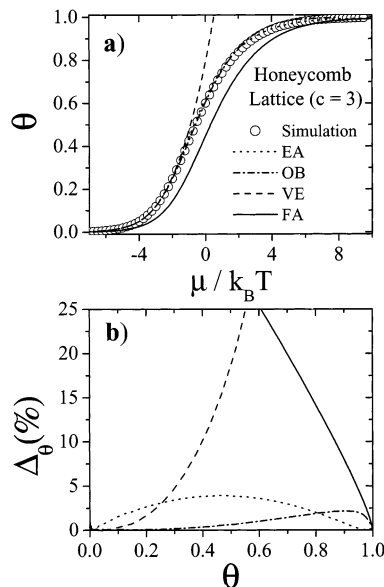
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Figure 1. (a) Adsorption isotherms of dimers on a honeycomb lattice ($c = 3$). Symbols represent MC results, and lines correspond to different approaches (see inset). (b) Percentage reduced coverage, $\Delta_\theta(\%)$, versus surface coverage. The symbols are as in part a.
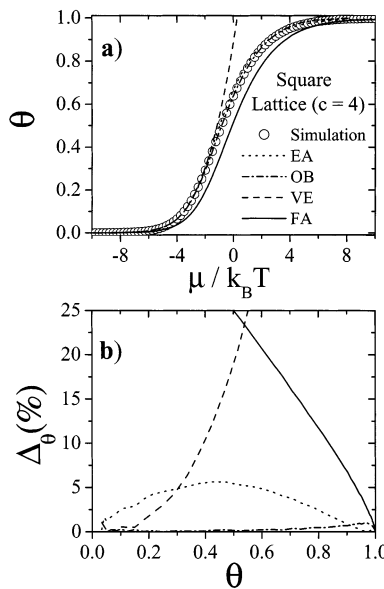
**Figure 2.** As in Figure 1 for a square lattice ($c = 4$).

for each coverage by using the method of the "artificial Hamiltonian" recently presented by Romá et al.[27,28]

The computational simulations have been developed for square, honeycomb, and triangular $L \times L$ lattices, with $L = 150$ and periodic boundary conditions. With this lattice size we verified that finite size effects are negligible.

An extensive comparison between the simulated adsorption isotherm and the isotherm equations obtained from the analytical approaches depicted as EA, OB, VE, and FA is shown in Figures 1a, 2a, and 3a, for honeycomb, square, and triangular lattices, respectively. The symbols represent the simulation data points, and the lines correspond to theoretical isotherms. The behavior of the different approaches can be explained as follows: (i) VE

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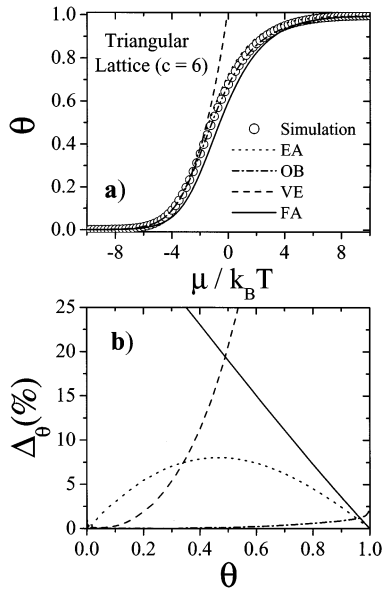
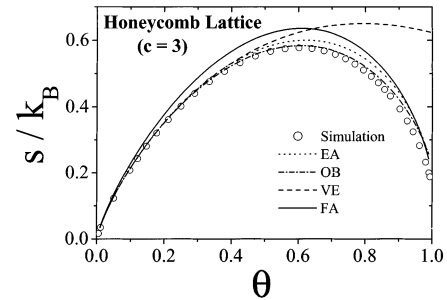**Figure 3.** As in Figure 1 for a triangular lattice ($c = 6$).

(dashed line) agrees very well with the simulation result for small values of the coverage; however, the disagreement turns out to be significantly large for larger θ's. (ii) FA (solid line) predicts a smaller θ than the simulation data over the range.[0,1] This separation diminishes when the connectivity is increased. Finally, (iii) EA (dotted line) and OB (dashed and dotted line) provide good approximations with very small differences between simulated and theoretical results. These differences can be very easily rationalized with the help of the percentage reduced coverage, which is defined as

$$\Delta_\theta \ (\%) = 100 \left| \frac{\theta_{\text{sim}} - \theta_{\text{appr}}}{\theta_{\text{sim}}} \right|_\mu \qquad (59)$$

where θ_{sim} (θ_{appr}) represents the coverage obtained by using the MC simulation (analytical approach). Each pair of values (θ_{sim}, θ_{appr}) is obtained at fixed μ.

The dependence of Δ_θ (%) on the coverage is shown in Figures 1b, 2b, and 3b for the different connectivities. As it is possible to observe, the discrepancies between EA and MC simulations vary for different values of θ, with a maximum appearing around $\theta = 0.5$. The maximum values of Δ_θ (%) are $\approx$ 4%, 5.5%, and 8%, for $c = 3$, 4, and 6, respectively. This analysis reinforces the discussion of Figures 1a, 2a, and 3a and implies that EA is a good approximation for representing the dimer adsorption on homogeneous surfaces. On the other hand, the agreement between OB and MC results is excellent. Δ_θ (%) is practically constant for all θ, taking a maximum value of $\approx$2%, 1%, and 1%, for $c = 3$, 4, and 6, respectively. Definitively, OB performs better than the other approximations over the whole coverage range.

The differences between the approaches presented in this work are better appreciated by comparing the coverage dependence of the configurational entropy per site, $s(\theta)$, which is presented in Figures 4−6, for honeycomb, square, and triangular lattices, respectively. The overall behavior can be summarized as follows: for $\theta \rightarrow 0$ the entropy tends to zero. For low coverage, $s(\theta)$ is an increasing function of θ, reaches a maximum at θ_m, then decreases monotonically to zero for $\theta > \theta_m$. The position of θ_m, which is $\theta_m \approx$ 0.6 for a honeycomb lattice ($c = 3$), shifts to higher coverage as the connectivity c gets larger. In addition, the value of the entropy in θ_m, $s(\theta_m)$, increases as the connectivity

Figure 4. Configurational entropy per site (in units of k_B) versus surface coverage for dimers adsorbed on a honeycomb lattice ($c = 3$). The symbols are as in Figure 1.
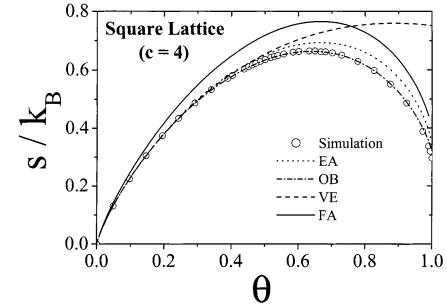
Figure 5. As in Figure 4 for a square lattice ($c = 4$).
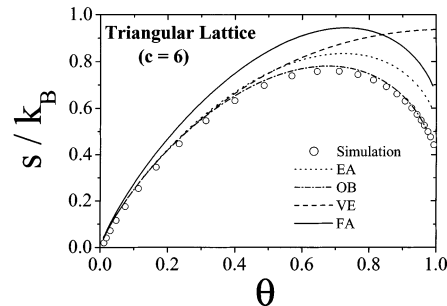
Figure 6. As in Figure 4 for a triangular lattice ($c = 6$).

increases. In the limit $\theta \rightarrow 1$ the entropy tends to a finite value, which is associated with the different ways to arrange the dimers at full coverage. This value depends on the geometry, being $s(\theta=1) \approx 0.19$, 0.29, and 0.44 for $c = 3$, 4, and 6, respectively.

As in Figure 1, VE appears as a good approximation in the low surface coverage region ($\theta < 0.4$). For $\theta > 0.4$, VE predicts a larger entropy than the simulation data. On the other hand, the disagreement turns out to be significantly large for $s(\theta_m)$ and $s(1)$.

EA and FA shown a qualitative agreement with MC simulations. In the two cases, the position of the maximum θ_m is well reproduced, but both approaches overestimate the value of the entropy in the whole range of θ, in particular, at full coverage. This discrepancy is more remarkable for FA.

Finally, in the case of OB, the agreement is notable for all θ, reproducing the MC results for $s(\theta_m)$ and $s(1)$.

4. Conclusions

The problem of equilibrium adsorption of dimers has been dealt with from various perspectives. Here we have presented new analytical contributions to this problem and contrasted with former development (FA) on k-mers' themodynamics. The artificial effects that the FA induces on the main thermodynamic functions can now be rationalized and compared with other analytical ap-

proaches. From the comparison of the adsorption isotherm and the configurational entropy arising from the discussed approximations for dimers on honeycomb, square, and triangular lattices, appreciable differences can be seen for the different approximations, with OB being the most accurate for all lattices, predicting the behavior of $s(\theta)$ in the whole range of θ.

The larger the lattice connectivity, the better OB reproduces the Monte Carlo results with respect to the other approaches. The finite values of $s(\theta)$ at full coverage are also very well reproduced by OB. $s(\theta=1) > 0$ arises because local reordering of dimers is possible at full coverage. The knowledge of thermodynamic properties of polyatomic gases is limited, owing, basically, to the difficulties that accurate calculations of entropy and free energies pose. It is worth noticing that even for the simple problem of non-interacting dimers on regular lattices, which we are addressing here, there exists no rigorous solution for the configurational entropy, and the OB presented here is, to the best of our knowledge, the most accurate approximation to this problem.

The OB approach seems to be a promising way toward a more accurate description of the adsorption thermodynamics of polyatomic molecules, allowing us to include heterogeneous surfaces, lateral interactions between the ad-particles, and multilayer adsorption. Work in this sense is in progress.

5. Appendix: Flory's Approximation

The theory to be presented here, due to Flory,[11,12] investigates the thermodynamics of solvent−polymer solutions. The model is a generalization of the lattice−gas theory of binary solutions,[13] but in this case, whereas a solvent molecule occupies only one site in the lattice, the polymer molecule occupies k sites.

By using the same arguments as in section 3.1, we calculate first the number $\Omega(N_1,N_2)$ of possible configurations of N_2 polymers and N_1 molecules of a monatomic solvent on a lattice with M sites and connectivity c.

The number $\Omega(N_1,N_2)$ is just equal to the number of ways of arranging N_2 polymer molecules on M sites, for after we place the polymer molecules in the originally empty lattice, there is only one way to place the solvent molecules (i.e., we simply fill up all the remaining unoccupied sites). Imagine that we label the polymer molecules from 1 to N_2 and introduce them one at a time, in order, into the lattice. Let w_i be the number of ways of putting the i-th polymer molecule into the lattice with $i-1$ molecules already there (assumed to be arranged in an average, random distribution). Then the approximation to $\Omega(N_1,N_2)$ which we use is

$$\Omega(N_1,N_2) = \frac{1}{N_2!}\prod_{i=1}^{N_2} w_i \qquad (60)$$

The factor $(N_2!)^{-1}$ is inserted because we have treated the molecules as distinguishable in the product, whereas they are actually indistinguishable.

Next, we derive an expression for w_{i-1}. With i polymer molecules already in the lattice, the fraction of sites filled is $f_i = ki/M$. The first unit of the $(i+1)$-th molecule can be placed in any one of the $M-ki$ vacant sites. The first unit has c nearest-neighbor sites, of which $c(1-f_i)$ are empty (random distribution assumed). Therefore, the number of possible locations for the second unit is $c(1-f_i)$. Similarly, the third unit can go in $(c-1)(1-f_i)$ different places. At this point we make the approximation that units 4, 5, ..., k also each have $(c-1)(1-f_i)$ possibilities, though this is not quite correct. Multiplying all of these factors together, we have for w_{i+1}

$$w_{i+1} = (M-ki)c(c-1)^{k-2}(1-f_i)^{k-1}$$
$$= (M-ki)^k\left(\frac{c-1}{M}\right)^{k-1} \qquad (61)$$

where we replaced c by $c-1$ as a further approximation.

Now we will need

$$\ln\prod_{i=1}^{N_2} w_i = N_2(k-1)\ln\left(\frac{c-1}{M}\right) + k\sum_{i=0}^{N_2-1}\ln(M-ki) \qquad (62)$$

We approximate the sum by an integral:

$$\sum \approx \int_0^{N_2}\ln(M-ki)\,di = \frac{1}{k}\int_{N_1}^M \ln u\,du$$
$$= \frac{1}{k}(M\ln M - M - N_1\ln N_1 + N_1) \qquad (63)$$

We put eqs 61 and 62 in eq 59 and find

$$\ln\Omega(N_1,N_2) = -N_2\ln N_2 + N_2 - N_1\ln N_1 + N_1 +$$
$$M\ln M - M + N_2(k-1)\ln\left[\frac{(c-1)}{M}\right] \quad (64)$$

All results presented here can be straightforwardly applied to the corresponding k-mers' adsorption problem, with $N_2 \equiv N$ (number of k-mers) and $N_1 \equiv M-kN$ (number of empty sites). Then, by rewriting $\Omega(N_1,N_2)$ in terms of $\theta \equiv kN/M$, and by using eqs 7 and 9, we get the adsorption isotherm and the molar configurational entropy,

$$k\left(\frac{c-1}{e}\right)^{k-1}\exp(\beta\mu) = \frac{\theta}{(1-\theta)^k} \qquad (65)$$

$$\frac{s(\theta)}{k_B} = -\frac{\theta}{k}\ln\frac{\theta}{k} - (1-\theta)\ln(1-\theta) +$$
$$\left(\frac{k-1}{k}\right)\theta\ln\left(\frac{c-1}{e}\right) \quad (66)$$