

# Semiempirical Model for Adsorption of Polyatomics

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Multisite-occupancy adsorption is described by using a new formalism based on the occupation balance approximation (Romá, F.; Ramirez-Pastor, A. J.; Riccardo, J. L. *J. Chem. Phys.* **2001**, *114*, 10932). In this framework, the adsorption isotherm is characterized by a correction function  $\tilde{C}$ , which relates to the conditional probability of finding the  $i$ th empty site to a lattice with  $i - 1$  already vacant sites. A simple semiempirical adsorption isotherm is proposed by approximating  $\tilde{C}$  as a combination of the correction functions corresponding to exact 1-D calculations and the Guggenheim–DiMarzio approximation, with adequate weights. Results are compared with corresponding ones from Monte Carlo simulations.

## 1. Introduction

The adsorption of gases on solid surfaces has been actively investigated since the beginning of the past century. However, the theoretical description of equilibrium and dynamical properties of polyatomic species adsorbed on 2-D substrates still represents a major challenge in surface science.<sup>1–4</sup> The inherent difficulty common to processes involving the adsorption of  $k$ -mers (particles that occupy more than one lattice site) is to calculate the configurational entropic contributions to the thermodynamic potentials properly, which means the degeneracy of the energy spectrum compatible with given number of particles and adsorption sites.

A good starting point for further investigation is an analysis of the results obtained for  $k$ -mers adsorbed on homogeneous surfaces. An early seminal contribution to this subject was the well-known Flory–Huggins approximation (FH), due independently to Flory<sup>5</sup> and to Huggins,<sup>6</sup> which is a direct generalization of the Bragg–Williams approximation in the lattice model of binary liquids in two dimensions.<sup>1</sup> Modified forms of the Flory–Huggins approximation have been also proposed. A comprehensive discussion on this subject is included in the book by Des Cloizeaux and Jannink<sup>7</sup> and ref 8. It is worth mentioning that, in the framework of the lattice gas approach, the adsorption of pure linear molecules is isomorphous to polymer mixture adsorption (linear polymer–monatomic solvent). Guggenheim soon proposed another method to calculate the combinatorial term in the canonical partition function.<sup>9</sup> Later, in a valuable contribution, DiMarzio obtained the Guggenheim factor for a model of rigid rod molecules.<sup>10</sup> We call this theory the Guggenheim–DiMarzio’s approximation (GD).

More recently, two new theories to describe adsorption with multisite occupancy have been introduced. In the first, Ramirez-Pastor et al.<sup>11–13</sup> presented a model to study the adsorption of linear adsorbates on homogeneous surfaces. The model, hereafter denoted EA, is based on exact forms of the thermodynamic functions of linear adsorbates in one dimension and its generalization to higher dimensions. In the second, which is called the fractional statistical theory of the adsorption of polyatomics (FSTA), the configuration of the molecule in the adsorbed state is incorporated as a model parameter.<sup>14</sup> The theory in ref 14 is based on a generalization of the formalism of quantum fractional statistics, proposed by Haldane<sup>15,16</sup> as an extended form of the Pauli exclusion principle. FSTA has been proposed to extend quantum fractional statistics so as to describe a broad set of classical systems, such as the adsorption of polyatomics at the gas–solid interface.

In ref 13, FH and EA, along with two analytical approaches to study dimer adsorption on 2-D lattices (occupation balance approximation and virial expansion), were tested in comparison with Monte Carlo simulations in the particular case of  $k = 2$ . In general, the agreement between theoretical and simulation data is good, with the occupation balance approximation being the most accurate in all geometries (honeycomb, square, and triangular lattices). However, the classical theories fail to reproduce adsorption results for higher values of  $k$ , and it becomes exceedingly difficult to generalize the occupation balance approximation for  $k \geq 2$ . From an experimental point of view, in many systems the molecules consist of a number of single  $k$  components or elementary units.<sup>17–22</sup> Thus, linear molecules such as  $C_nH_{2(n+1)}$  ( $n$ -alkanes) adsorbed onto solid surfaces should be regarded in light of a multisite adsorption model that is capable of consistently interpreting thermodynamic adsorption experiments ranging from simple species to elaborate polyatomics with

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$k \geq 2$ . This work represents an effort in this direction. For this purpose, a simple semiempirical adsorption model for polyatomics (SE) is presented. SE is obtained by combining exact 1-D calculations and the Guggenheim–DiMarzio approximation. In addition, Monte Carlo (MC) simulations in the grand canonical ensemble are performed to test the validity of the theoretical model. The new theoretical scheme allows us to obtain an approximation that is significantly better than the other existing approaches and provides a simple model from which experiments may be reinterpreted.

The article is organized as follows: the theoretical scheme is presented in section 2. In section 3, analytical results are compared with Monte Carlo simulations. Finally, general conclusions are given in section 4.

## 2. Theory

Here, we address the general case of adsorbates assumed to be linear molecules containing  $k$  identical units ( $k$ -mers), with each one occupying a lattice site. Small adsorbates with spherical symmetry would correspond to the monomer limit ( $k = 1$ ). The distance between  $k$ -mer units is assumed to be equal to the lattice constant  $a$ ; hence exactly  $k$  sites are occupied by a  $k$ -mer when adsorbed. 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 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

$$H = (U_0 - \mu) \sum_i c_i \quad (1)$$

where  $U_0$  is the adsorption energy of a  $k$ -mer unit ( $kU_0$  being the total adsorption energy of a  $k$ -mer) and  $\mu$  is the chemical potential.

Hereafter, we propose an approximation of the adsorption isotherm for noninteracting linear  $k$ -mers on a regular lattice based on semiempirical arguments, which leads to very accurate results.

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

$$\bar{N} = \lambda \left[ \frac{\partial \ln \Xi(M, \lambda)}{\partial \lambda} \right]_M \quad (2)$$

where  $\lambda = \exp[\beta(\mu - kU_0)]$  (being  $\beta = 1/k_B T$  and  $U_0$  the Boltzmann constant) and  $\Xi$  is the grand partition function. By solving for  $\lambda^{-1}$  in eq 2, we find that

$$\lambda^{-1} = \frac{1}{\bar{N}} \left[ \frac{\partial \ln \Xi(M, \lambda)}{\partial \lambda} \right]_M = \frac{R(M, \lambda)}{\bar{N}} \quad (3)$$

In the last equation, which is called occupation balance,<sup>13,23</sup> the mean number of states available to a particle on  $M$  sites at  $\lambda$  (i.e.,  $R(M, \lambda)$ ) can be written as

$$R = \left( \frac{\gamma}{2} M \right) \prod_{i=1}^k P_i \quad (4)$$

with  $\gamma$  being the connectivity of the lattice. Equation 4 can be

interpreted as follows. The term between parentheses corresponds to the total number of  $k$ -uples on the surface. These  $k$ -uples can be separated into three groups: full  $k$ -uples (occupied by  $k$ -mers), empty  $k$ -uples (available for adsorption), and frustrated  $k$ -uples (partially occupied or occupied by segments belonging to different adsorbed  $k$ -mers). Then, an additional factor must be incorporated that takes into account the probability of having an empty  $k$ -uple. We suppose that this factor can be written as a product of  $k$  functions ( $P_i$ 's), with  $P_i$  being the conditional probability of finding the  $i$ -th empty site in the lattice with  $i - 1$  already vacant sites. (The  $i$  sites are assumed to be arranged in a linear  $k$ -uple.) In the particular case of  $i = 1$ ,

$$P_1 = 1 - \theta \quad (5)$$

where  $\theta = kN/M$  is the surface coverage. Equation 5 represents an exact result.

Now, let us consider the simplest approximation within this scheme, namely,  $P_i = P_1$  for all  $i$ . Then, from eqs 3–5, we may write

$$\lambda^{-1} = \frac{R}{\bar{N}} = \frac{\gamma k}{2} \frac{M}{k\bar{N}} P_1^k = \frac{\gamma k(1 - \theta)^k}{2\theta} \quad (6)$$

Equation 6 reduces to the FH isotherm of noninteracting linear  $k$ -mers adsorbed flat on homogeneous surfaces (Appendix 1). This is a simple example out of a wide variety of multisite adsorption models that the proposed formalism allows us to deal with.

In general, the  $P_i$ 's can be written as

$$P_i = (1 - \theta)C_i \quad (7)$$

where a correction factor,  $C_i$ , has been included (where  $C_1 = 1$  and  $C_i \rightarrow 1$  as  $\theta \rightarrow 0$ ). From eqs 4–7, we obtain

$$R = \frac{\gamma}{2} M (1 - \theta)^k \prod_{i=2}^k C_i = \frac{\gamma}{2} M (1 - \theta)^k \tilde{C}^{k-1} \quad (8)$$

and

$$\tilde{C} = \left( \prod_{i=2}^k C_i \right)^{1/(k-1)} \quad (9)$$

with  $\tilde{C}$  being the average correction function, which is calculated as the geometrical mean of the  $C_i$ 's. Then, from eqs 3 and 8, the general form of the adsorption isotherm can be obtained:

$$\lambda^{-1} = \frac{\gamma k (1 - \theta)^k \tilde{C}^{k-1}}{2\theta} \quad (10)$$

or

$$\beta(\mu - kU_0) = \ln\left(\frac{\theta}{k}\right) - k \ln(1 - \theta) - \ln\left(\frac{\gamma}{2}\right) - (k - 1) \ln \tilde{C} \quad (11)$$

It is interesting to compare eq 11 with corresponding ones obtained from the main theories of the adsorption of polyatomics. For this purpose, four theoretical isotherms to study  $k$ -mer adsorption on homogeneous lattices have been compiled in Appendix 2: (i) the well-known Flory–Huggins approximation,<sup>5,6</sup> as discussed in Appendix 1; (ii) an extension to 2-D of the exact adsorption isotherm obtained in 1-D;<sup>11,13</sup> (iii) the Guggenheim–DiMarzio's approximation;<sup>9,10</sup> and (iv) a fractional statistical thermodynamic theory of the adsorption of polyatomics, which is based on the formalism of Haldane statistics.<sup>14–16</sup>

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As can be observed, FH, EA, and GD already have the structure of eq 11. In the case of FSTA, an identical structure can be obtained after simple algebraic operations. From this new perspective, the differences between the theoretical models arise from the distinct strategies of approximating  $\tilde{C}$ . These arguments can be better understood with an example: EA and GD provide the exact solution for the 1-D case. Then, the comparison between eq 11 and the adsorption isotherm from EA (or GD with  $\gamma = 2$ ) allows us to obtain

$$\tilde{C}^{-1} = 1 - \frac{k-1}{k}\theta \quad (\gamma = 2) \quad (12)$$

The result in eq 12 is exact. Moreover, it can be demonstrated that  $C_i = \tilde{C}$  for all  $i$ .<sup>10</sup>

Once the equations are written as in Appendix 2, it is clear that the differences between EA and GD can be associated only with the average correction function  $\tilde{C}$ . In addition, as will be shown in Figures 3–5, GD fits the numerical data at low coverage very well whereas EA behaves excellently at high coverage. These findings, along with the structure proposed for the adsorption isotherm (eq 11), allow us to build a new semiempirical adsorption isotherm for polyatomics (SE):

$$\begin{aligned} \beta(\mu - kU_0) &= \ln\left(\frac{\theta}{k}\right) - k \ln(1 - \theta) - \ln\left(\frac{\gamma}{2}\right) \\ &+ (1 - \theta)(k - 1)\ln\left[1 - \frac{(k - 1)2\theta}{k\gamma}\right] \\ &+ \theta(k - 1)\ln\left[1 - \frac{(k - 1)\theta}{k}\right] \end{aligned} \quad (13)$$

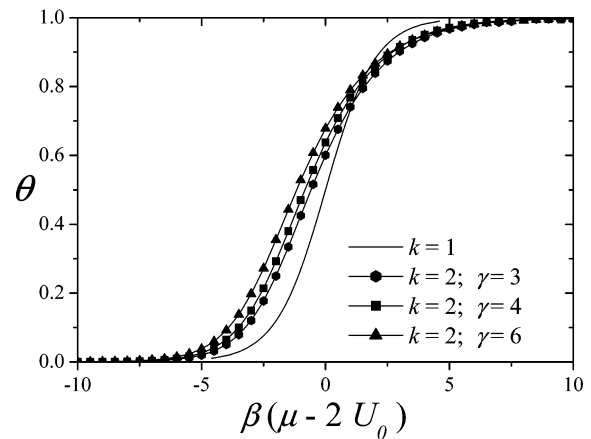
The last equation can be interpreted as follows. The first line includes three terms that are identical in both EA and GD. The second and third lines represent a combination of the average correction functions corresponding to GD and EA, with  $(1 - \theta)$  and  $\theta$  as weights, respectively. The behavior of SE will be discussed in the next section, in comparison with MC simulation results.

### 3. Results and Discussion

MC simulations are used to test the applicability of the new theoretical proposition. The adsorption isotherms are simulated through a grand canonical ensemble Monte Carlo (GCEMC) method.<sup>24,25</sup> The procedure is as follows. For a given value of the temperature  $T$  and chemical potential  $\mu$ , an initial configuration with  $N$   $k$ -mers adsorbed at random positions (on  $kN$  sites) is generated. Then an adsorption–desorption process is started where a  $k$ -uple 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<sup>26</sup> rule

$$P = \min\left\{1, \exp\left(-\frac{\Delta H}{k_B T}\right)\right\} \quad (14)$$

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  $M$   $k$ -uples of sites have been tested to change its occupancy state. The equilibrium state can be well reproduced



**Figure 1.** Comparison between the exact adsorption isotherm of monomers and the simulation adsorption isotherms of dimers on honeycomb, square, and triangular lattices.

after discarding the first  $m' = 10^6$  MCS. Then, averages are taken over  $m = 10^6$  successive configurations.

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

$$\theta(\mu) = \frac{1}{M} \sum_i^M \langle c_i \rangle = \frac{k\langle N \rangle}{M} \quad (15)$$

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

Computational simulations have been developed for honeycomb, square, and triangular  $L \times L$  lattices, with  $L/k = 120$ , and periodic boundary conditions. With this lattice size, we verified that finite size effects are negligible.

We shall first discuss some basic characteristics of the adsorption isotherms. For this purpose, Figure 1 shows a comparison between the exact adsorption isotherm of monomers and the simulation adsorption isotherms of dimers on honeycomb, square, and triangular lattices. As can be observed, the symmetry particle vacancy, which is valid for monatomic species, is broken for  $k \geq 2$ . In addition, even though adsorption isotherms of dimers look very similar for all connectivities, curves shift to lower values of  $\beta(\mu - 2U_0)$  as  $\gamma$  is increased. In other words, for a given value of  $\beta(\mu - 2U_0)$ , the equilibrium surface coverage increases as  $\gamma$  is increased. This behavior can be easily understood from the following equation

$$\ln \theta = \ln\left(\frac{\gamma k}{2}\right) + \beta(\mu - kU_0) \quad (16)$$

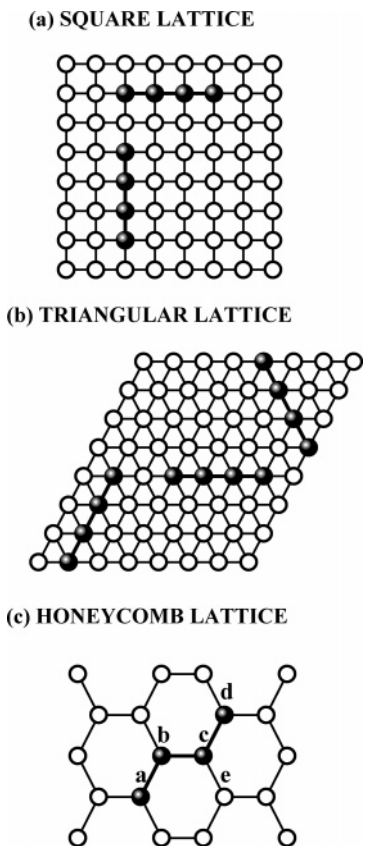
which is valid for linear  $k$ -mers at low concentrations (eq 11). The effect diminishes as the chemical potential is increased and, consequently, the slope of the isotherms diminishes as  $\gamma$  is increased.

We now analyze the case corresponding to linear adsorbates larger than dimers. The concept of linear  $k$ -mer is trivial for square and triangular lattices (Figure 2a and b, respectively). However, in a honeycomb lattice, the geometry does not allow the existence of a linear array of monomers with  $k \geq 2$ . In this case, we call a linear  $k$ -mer a chain of adjacent monomers with the following sequence: once the first monomer is in place, the second monomer occupies one of the three nearest-neighbor positions with respect to the first monomer. The third monomer occupies one of the two nearest-neighbor positions with respect to the second monomer. The  $i$ -esime monomer (for  $i \geq 4$ ) occupies one of the two nearest-neighbor positions with respect to the preceding monomer, which maximizes the distance between the

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**Figure 2.** Linear tetramers adsorbed on (a) square, (b) triangular, and (c) honeycomb lattices. Full and empty circles represent tetramer units and empty sites, respectively.

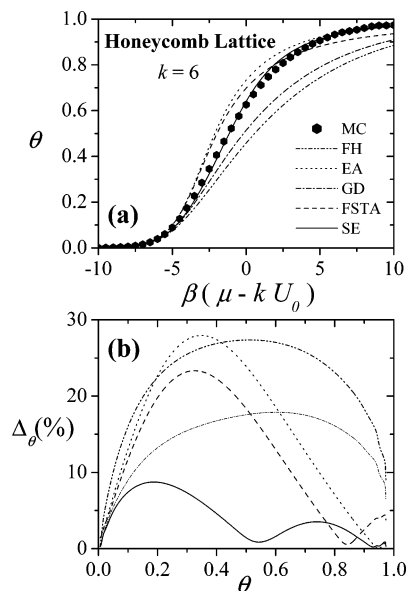
first monomer and the  $i$ -esime monomer. This procedure allows us to place  $k$  monomers on a honeycomb lattice without creating an overlap. As an example, Figure 2c shows an available configuration for a linear tetramer adsorbed on a honeycomb lattice. Once the first, second, and third monomers were adsorbed in positions denoted as a, b, and c, respectively, there exist two possible positions for adsorbing the fourth monomer, d and e. To maximize the distance between the position of first and fourth monomers, site d is selected, and site e is discarded. Then, once a site is chosen, there exist six equilibrium states available to a single  $k$ -mer ( $k \geq 2$ ) on a honeycomb lattice at infinitely low density. Consequently, the term between parentheses in eq 4, which corresponds to the total number of  $k$ -uplets on the surface, results in  $3M$  ( $\gamma = 6$ ), as in the case of triangular lattices.

Under these considerations, an extensive work of simulation has been carried out for linear adsorbates with  $k$  ranging between 2 and 10. As an example, Figures 3a, 4a, and 5a show the comparison between simulation adsorption isotherms and the corresponding ones obtained from theoretical approaches for 6-mers adsorbed on honeycomb, square, and triangular lattices, respectively. In all cases, the agreement between simulation and analytical data is very good for small values of coverage. However, as the surface coverage is increased, the classical theories fail to reproduce adsorption results.

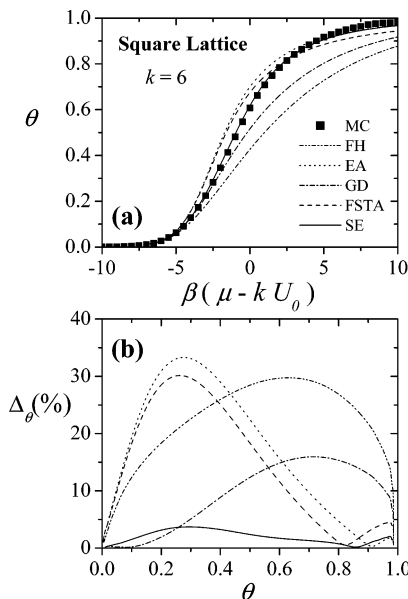
The differences between simulation and theoretical results can be expressed by the mean of the percentage reduced coverage, which is defined as<sup>13</sup>

$$\Delta_{\theta}(\%) = 100 \left| \frac{\theta_{\text{sim}} - \theta_{\text{appr}}}{\theta_{\text{sim}}} \right|_{\mu} \quad (17)$$

where  $\theta_{\text{sim}}$  ( $\theta_{\text{appr}}$ ) represents the coverage obtained by using MC



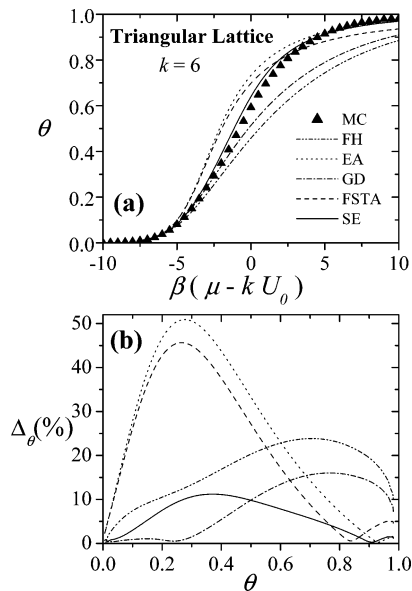
**Figure 3.** (a) Adsorption isotherms of 6-mers on a honeycomb lattice. Symbols represent MC results, and lines correspond to different approaches (inset). (b) Percentage reduced coverage,  $\Delta_{\theta}(\%)$ , vs surface coverage. The symbols are the same as in part a.



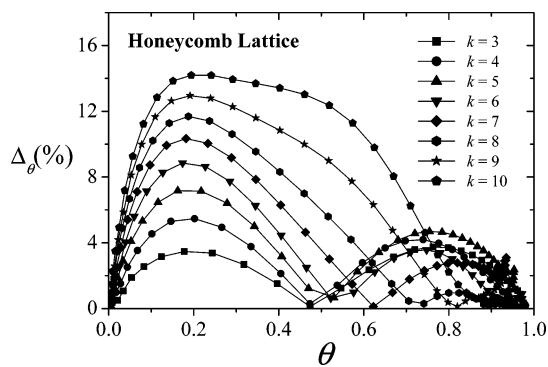
**Figure 4.** (a) Adsorption isotherms of 6-mers on a square lattice. Symbols represent MC results, and lines correspond to different approaches (inset). (b) Percentage reduced coverage,  $\Delta_{\theta}(\%)$ , vs surface coverage. The symbols are the same as in part a.

simulation (analytical approach). Each pair of values ( $\theta_{\text{sim}}$ ,  $\theta_{\text{appr}}$ ) is obtained at fixed  $\mu$ .

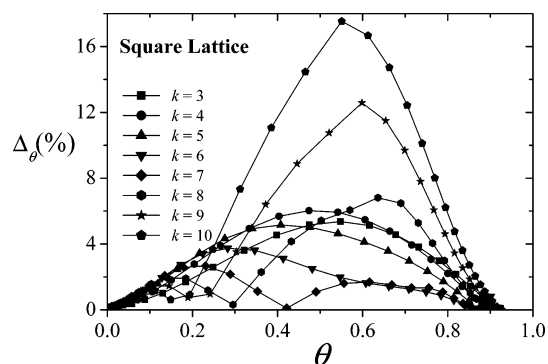
The dependence of  $\Delta_{\theta}(\%)$  on the surface coverage is shown in Figures 3b, 4b, and 5b for the different connectivities. The behavior of the analytical approaches can be explained as follows. FSTA (dashed line) provides a good approximation with a very small differences between simulated and theoretical results. FH (dash dot dot line) and GD (dash dot line) predict a smaller  $\theta$  than the simulation data over the entire range of coverage. In the case of EA (dotted line), the disagreement turns out to be large for intermediate  $\theta$  values, and a good approximation is recovered for high coverage. With respect to the connectivity, EA and FSTA (FH and GD) become more accurate as  $\gamma$  decreases (increases). The behavior of GD and EA justifies the methodology used to build the SE isotherm (solid line) in eq 13. This situation is also reflected in Figures 6–8, where the percentage reduced



**Figure 5.** (a) Adsorption isotherms of 6-mers on a triangular lattice. Symbols represent MC results, and lines correspond to different approaches (inset). (b) Percentage reduced coverage,  $\Delta_\theta(\%)$ , vs surface coverage. The symbols are the same as in part a.



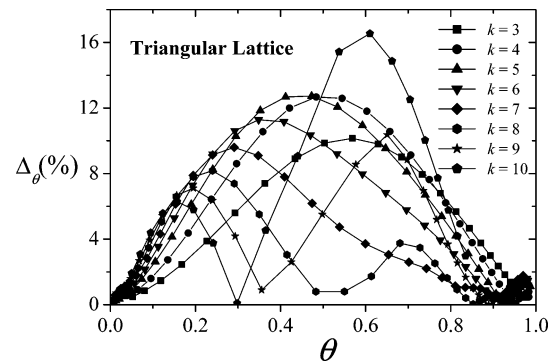
**Figure 6.** Percentage reduced coverage vs concentration for  $k$ -mers adsorbed on a honeycomb lattice and the SE approximation. Symbols are indicated in the inset.



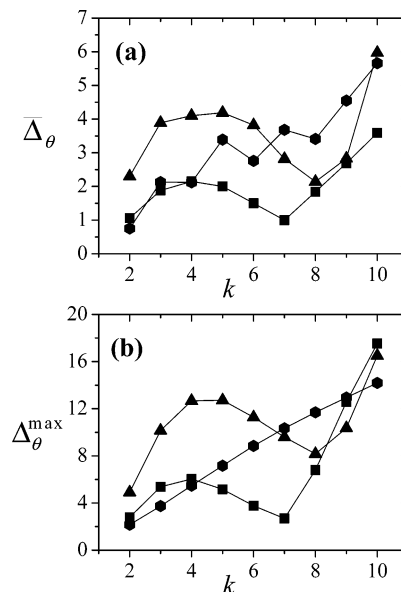
**Figure 7.** Percentage reduced coverage vs concentration for  $k$ -mers adsorbed on a square lattice and the SE approximation. Symbols are indicated in the inset.

coverage is plotted as a function of concentration for the SE approximation and different values of  $\gamma$  and  $k$ .

The results in Figures 6–8 can be much more easily rationalized with the help of (1) the average of the absolute values of the difference between simulation and analytical results,  $\bar{\Delta}_\theta$ , and (2) the maximum value of the percentage reduced coverage,  $\Delta_\theta^{\max}$ . These quantities are shown in Figure 9. Several conclusions can be drawn from the Figure: (i) in general, the theoretical isotherm



**Figure 8.** Percentage reduced coverage vs concentration for  $k$ -mers adsorbed on a triangular lattice and the SE approximation. Symbols are indicated in the inset.



**Figure 9.** (a) Average maximum percentage reduced coverage  $\Delta_\theta^{\max}$  as a function of  $k$  for different connectivities. (b) Average percentage reduced coverage  $\bar{\Delta}_\theta$  as a function of  $k$  for different connectivities. The symbols are the same as in Figure 1.

performs better for square lattices; (ii)  $\bar{\Delta}_\theta$  and  $\Delta_\theta^{\max}$  remain practically constant for  $k$  ranging between 2 and 8; and (iii)  $\bar{\Delta}_\theta$  and  $\Delta_\theta^{\max}$  increase for  $k > 8$ . Finally, the values obtained for  $\bar{\Delta}_\theta$ , which are lower than 6%, imply that SE is a very good approximation for representing multisite occupancy adsorption, at least for the sizes considered here.

#### 4. Concluding Remarks

A new theoretical description of adsorption phenomena of polyatomics based on the occupation balance approximation was presented. The proposed formalism represents a general framework that is capable of including the main theories treating multisite occupancy adsorption as particular cases. Taking advantage of its definition, a simple semiempirical adsorption isotherm was obtained with contributions from two well-known approaches: the Guggenheim–DiMarzio approximation and the exact isotherm in 1-D and its extension to higher dimensions. GD and EA are found to be good expressions for representing the adsorption isotherms at low and high coverages, respectively. From the comparison with Monte Carlo simulations in 2-D lattices, appreciable differences can be seen for the different approximations studied in this contribution, with SE being the most accurate for all cases. Finally, it can be concluded that this

simple semiempirical model could be very useful in interpreting experimental data of the adsorption of polyatomics. Work in this sense is in progress.

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### 5. Appendix 1: Flory–Huggins’s Approximation for Linear Adsorbates

The theory to be presented here, due to Flory<sup>5</sup> and Huggins,<sup>6</sup> is a generalization of the lattice-gas theory of binary solutions,<sup>1</sup> but in this case, whereas a solvent molecule occupies only one site in the lattice, the polymer molecule occupies  $k$  sites.

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  $\gamma$ .  $\Omega(N_1, N_2)$  is just equal to the number of ways of arranging  $N_2$  polymer molecules on  $M$  sites, and 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 of 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  $\Omega(N_1, N_2)$  that we use is

$$\Omega(N_1, N_2) = \frac{1}{N_2!} \prod_{i=1}^{N_2} w_i \quad (18)$$

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 filled sites 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  $\gamma$  nearest neighbor sites, of which  $\gamma(1 - f_i)$  are empty (random distribution assumed). Therefore, the number of possible locations for the second unit is  $\gamma(1 - f_i)$ . Similarly, the third unit can go in  $(\gamma - 1)(1 - f_i)$  different places. At this point, we make the approximation that units 4, 5, ...,  $k$  also each have  $(\gamma - 1)(1 - f_i)$  possibilities, though this is not quite correct. Multiplying all of these factors together, we have for  $w_{i+1}$

$$\begin{aligned} w_{i+1} &= (M - ki)\gamma(\gamma - 1)^{k-2}(1 - f_i)^{k-1} \\ &= (M - ki)^k \left(\frac{\gamma - 1}{M}\right)^{k-1} \end{aligned} \quad (19)$$

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

Now we will need

$$\ln \prod_{i=1}^{N_2} w_i = N_2(k - 1) \ln \left(\frac{\gamma - 1}{M}\right) + k \sum_{i=0}^{N_2-1} \ln(M - ki) \quad (20)$$

We approximate the sum by an integral

$$\begin{aligned} \sum &\approx \int_0^{N_2} \ln(M - ki) \, di = \frac{1}{k} \int_{N_1}^M \ln u \, du \\ &= \frac{1}{k} (M \ln M - M - N_1 \ln N_1 + N_1) \end{aligned} \quad (21)$$

From eqs 18–21, we find

$$\begin{aligned} \ln \Omega(N_1, N_2) &= -N_2 \ln N_2 + N_2 - N_1 \ln N_1 + N_1 + \\ &M \ln M - M + N_2(k - 1) \ln \left[\frac{(\gamma - 1)}{M}\right] \end{aligned} \quad (22)$$

All of the results presented here can be straightforwardly applied to the corresponding  $k$ -mer 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  $\beta\mu = -(\partial \ln \Omega / \partial N)_{T,M}$ , we get

$$\exp[\beta(\mu - kU_0)] = \frac{\theta}{k(\gamma - 1)^{k-1}(1 - \theta)^k} \quad (23)$$

The last equation is the classical adsorption isotherm in the framework of the Flory–Huggins approximation, which was developed for flexible polymers. In the following, we will introduce appropriate modifications into the formalism to obtain the adsorption isotherm corresponding to linear  $k$ -mers. In this case,

$$w_{i+1} = \frac{\gamma}{2} (M - ki)^k \left(\frac{1}{M}\right)^{k-1} \quad (\text{linear } k\text{-mers}) \quad (24)$$

where two modifications have been included with respect to eq 19: (i) the number of possible locations for the third and successive units is  $(1 - f_i)$  instead of  $\gamma(1 - f_i)$ , as was considered for flexible  $k$ -mers, and (ii) a factor  $1/2$  is inserted because we have treated the extremes of the  $k$ -mers as distinguishable, whereas they are actually indistinguishable. Under these considerations, the desired Flory–Huggins adsorption isotherm of linear  $k$ -mers results:

$$\exp[\beta(\mu - kU_0)] = \frac{2\theta}{k\gamma(1 - \theta)^k} \quad (25)$$

The validity of the last equation is restricted to the range  $k \geq 2$ . Note that eq 25 does not reproduce the Langmuir isotherm for monomers.<sup>1</sup>

### 6. Appendix 2: Main Theoretical Adsorption Isotherms of Linear $k$ -mers Adsorbed on Regular Lattices at Monolayer

$$\beta(\mu - kU_0) = \ln\left(\frac{\theta}{k}\right) - k \ln(1 - \theta) - \ln\left(\frac{\gamma}{2}\right) \quad (k \geq 2) \quad \text{FH}^a$$

$$\begin{aligned} \beta(\mu - kU_0) &= \ln\left(\frac{\theta}{k}\right) - k \ln(1 - \theta) - \\ &\ln\left(\frac{\gamma}{2}\right) + (k - 1) \ln\left[1 - \frac{(k - 1)\theta}{k}\right] \end{aligned} \quad \text{EA}^b$$

$$\begin{aligned} \beta(\mu - kU_0) &= \ln\left(\frac{\theta}{k}\right) - k \ln(1 - \theta) - \\ &\ln\left(\frac{\gamma}{2}\right) + (k - 1) \ln\left[1 - \frac{(k - 1)2\theta}{k\gamma}\right] \end{aligned} \quad \text{GD}^c$$

$$\begin{aligned} \beta(\mu - kU_0) &= \ln\left(\frac{\theta}{k}\right) - \frac{k\gamma}{2} \ln(1 - \theta) - \\ &\ln\left(\frac{\gamma}{2}\right) + \left(\frac{k\gamma}{2} - 1\right) \ln\left[1 - \theta \frac{(k\gamma - 2)}{k\gamma}\right] \end{aligned} \quad \text{FSTA}^d$$

<sup>a</sup> FH: Flory–Huggins’s approximation. (See refs 5 and 6 and Appendix 1.) <sup>b</sup> EA: Exact isotherm in 1-D and extension to higher dimensions. (See refs 11 and 13.) <sup>c</sup> GD: Guggenheim–DiMarzio’s approximation. (See refs 9 and 10.) <sup>d</sup> FSTA: fractional statistics thermodynamic theory of adsorption of polyatomics. (See refs 14–16.) The expression in the Table correspond to the simplest approximation within FSTA, namely,  $g = 1/a = k/2$ . (See eq 2 in ref 14.)