# New Isotherm for Multisite Occupancy Adsorption of Long, Straight Rigid Rods

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ABSTRACT: The adsorption of long, straight rigid rods of length k (k-mers) on 2D lattices is described by using a new theoretical approach based on a generalization of the classical Guggenheim—DiMarzio approximation. In this scheme, the Helmholtz free energy and its derivatives are written in terms of the order parameter δ, which characterizes the nematic phase occurring in the system at intermediate densities. Then, using the principle of minimum free energy with δ as a parameter, the main adsorption properties are calculated. Comparisons with Monte Carlo simulations are performed in order to test the validity of the theoretical model. The obtained results indicate that the new thermodynamic description is significantly better than the existing theoretical models developed to treat the polymer adsorption problem.
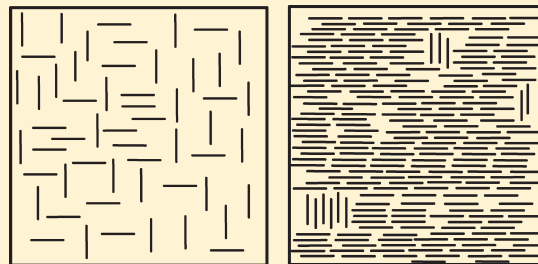
1. INTRODUCTION

The adsorption of gases on solid surfaces is an interesting theoretical problem with important applications related to thin surface films. Many studies have been carried out on the adsorption behavior of small molecules in such systems.[1−5] However, the theoretical description of equilibrium and dynamic properties of polyatomic species adsorbed on 2D substrates still represents a major challenge in surface science.[6] The inherent difficulty common to processes involving the adsorption of k-mers (particles occupying several k contiguous lattice sites) is to calculate the configurational (entropic) contribution to the thermodynamic potentials properly, which means the degeneracy of the energy spectrum compatible with a given number of particles and adsorption sites.

However, several attempts were made in the past to solve the k-mers problem. Among them, Onsager,[7] Zimm,[8] and Isihara[9] made important contributions to the understanding of the statistics of rigid rods in dilute solution. These treatments are limited in their application because they are valid for dilute solution only and because they are not applicable to systems of nonsimple shapes. The FH theory, due independently to Flory[10] and to Huggins,[11] has overcome the restriction to dilute solution by means of a lattice calculation. The approach is a direct generalization of the theory of binary liquids in two dimensions or 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 with the binary solutions of polymer—monomeric solvent.

The FH statistics, given for the packing of molecules of arbitrary shape but isotropic distribution, provide a natural foundation onto which the effect of the orientation of the admolecules can be added. Following this line of thought, DiMarzio[12] developed an approximate method of counting the number of ways, Ω, to pack together linear polymer molecules of arbitrary shape and of arbitrary orientations. In the case of allowing only those orientations for which the molecules fit exactly onto the lattice and for an isotropic distribution, the value of Ω reduces to the value obtained previously by Guggenheim.[13] We call this limit the Guggenheim—DiMarzio (GD) approximation.

More recently, two new theories to describe adsorption with multisite occupancy have been introduced. In the first, Ramirez-Pastor et al.[14−16] 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 fractional statistical theory of adsorption of polyatomics (FSTA), the configuration of the molecule in the adsorbed state is incorporated as a parameter of the model.[17,18] The theory in refs 17 and 18 is based on a generalization of the formalism of quantum fractional statistics, proposed by Haldane[19] and Wu[20] 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.

Detailed comparisons between theoretical and simulation results of adsorption[21] showed that the GD approach fits the numerical data at low coverage very well and the EA model behaves excellently at high coverage. On the basis of these findings, the semiempirical model for the adsorption of polyatomics (SE) was developed.[18,21] The SE model is a combination of exact calculations in 1D and the GD approximation with adequate weights.

On the basis of the latter models, generalizations have been made to take into account the effects of geometric confinement,[22]
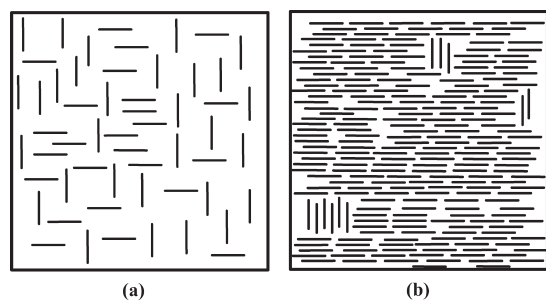
Figure 1. (a) [(b)] Typical configuration in the isotropic [nematic] phase.

heterogeneity in adsorbent sites,[23−25] mixtures of gases,[26−32] lateral interactions,[15,33] multilayer adsorption,[34−36] and other factors neglected in the classical theories. In all of these systems of hard nonspherical colloidal particles, the orientation of the molecules can significantly affect the entropic contribution to the adsorbate's free energy. An early seminal contribution to this subject was made by Onsager[7] with his paper on the isotropic−nematic (I−N) phase transition in liquid crystals. Onsager's theory predicted that very long and thin rods interacting with only the excluded volume interaction can lead to long-range orientational (nematic) order. Thus, at low densities, the molecules are typically far from each other and the resulting state is an isotropic gas. However, at large densities, it is more favorable for the molecules to align spontaneously (there are many more ways of placing nearly aligned rods than randomly oriented ones), and a nematic phase is present at equilibrium.

Interestingly, a number of papers have appeared recently in which the I−N transition was studied in 2D lattices.[37−41] In ref 37, the authors presented strong numerical evidence that a system of square geometry, with two allowed orientations, shows nematic order for $k \geq 7$. The nematic phase, characterized by a big domain of parallel k-mers, is separated from the isotropic state by a continuous transition occurring at a finite density. Figure 1 shows a typical configuration in the isotropic (nematic) phase. Reference 37 also provided a qualitative description of a second phase transition (from a nematic order to a non-nematic state) occurring at a density of close to 1. However, the authors were not able to determine the critical quantities (critical point and critical exponents) characterizing the I−N phase transition occurring in the system. This problem was solved in refs 38−41, where an accurate determination of the critical exponents, along with the behavior of Binder cumulants, showed that the transition from the low-density disordered phase to the intermediate-density ordered phase belongs to the 2D Ising universality class for square lattices and to the three-state Potts universality class for honeycomb and triangular lattices.

Given that the existence of an I−N phase transition in 2D lattices has been very recently reported, no theoretical results have been published on multisite occupancy adsorption in the presence of nematic order in the adlayer. In this context, the main idea of the present paper is to build a new theoretical approach to the problem of k-mers adsorption, which allows us to include the effects of the I−N phase transition occurring at intermediate densities on the thermodynamic functions of the system. For this purpose, we use the formalism of the GD approximation and write the Helmholtz free energy and its derivatives in terms of the order parameter δ. Then, using the principle of minimum free energy with δ as a parameter, we derive the main thermodynamic functions of the system. In addition, an exhaustive MC simulation study has been 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 paper is organized as follows. In section 2, the new theoretical approximation for polyatomics is developed. In section 3, the results of the present approach are compared with corresponding ones from MC simulations and from the main theoretical models developed to treat the polymer adsorption problem. Finally, the conclusions are drawn in section 4.

2. THEORY

In 1944, Guggenheim proposed an interesting method to calculate the combinatory term in the canonical partition function for the packing of molecules of arbitrary shape.[13] Later, in a valuable contribution, DiMarzio obtained the Guggenheim factor[12] for a model of rigid rod molecules. In this section, we reproduce the calculations developed by DiMarzio, who obtained the number of ways to pack rigid rods onto a cubic lattice and its generalization to lattices of connectivity γ.

Let us place N straight rigid rods onto a cubic lattice. We will assume that only the three mutually perpendicular base vector directions are directions in which the rigid rods lie. The number of molecules that lie in the direction i will be denoted by $N_i (i = 1, 2, 3)$. We wish to determine the number of ways, $\Omega(\{\cdots N_i \cdots\}, N_0)$ to pack the N molecules such that N_i of them lie in the direction i and there are N_0 holes. The advantage of allowing only those orientations for which the molecules fit exactly onto the lattice is that for the case of an isotropic distribution the value of Ω reduces to the value obtained previously by Guggenheim.[13]

Let us place the N_1 molecules, one at a time, onto the lattice in orientation 1, the N_2 molecules, one at a time, in orientation 2, and then the remaining N_3 molecules, one at a time, in orientation 3. To estimate the number of ways to place the $(j_1 + 1)$th molecule onto the lattice, given that j_1 molecules have already been placed, we must know the probability that k contiguous sites lying in this orientation are empty. Here the subscript reminds us that we are discussing type 1 molecules. Consider a contiguous pair of sites arbitrarily chosen except for the fact that the line determined by the centers of these sites lies along orientation 1. Label the sites A and B. Site A has a probability of being empty equal to the fraction of sites unoccupied by molecular segments because site A can be thought of as chosen arbitrarily. If site A is empty, then the ratio of the number of times it adjoins a polymer to the number of times it adjoins a vacant site is $2j_1/2(M - kj_1)$, where M is the total number of sites in the lattice. Notice that in writing this expression for the ratio we counted only those pairs of contiguous sites that lie along orientation 1. The pairs that lie along orientations 2 and 3 are of no consequence as far as the nearest-neighbor statistics along orientation 1 are concerned.

The above ratio is also the ratio of the number of times a polymer adjoins site A (presumed empty) to the number of times a vacant site adjoins site A. Thus, the probability that site B is empty given that site A is empty is

$$\frac{2(M - kj_1)}{2(M + kj_1) + 2j_1} \qquad (1)$$

We see that ν_{j_1+1}, the number of ways to place the $(j_1 + 1)$th molecule onto the lattice, is

$$\nu_{j_1+1} = (M - kj_1)\left[\frac{2(M - kj_1)}{2(M + kj_1) + 2j_1}\right]^{k-1} \qquad (2)$$

The total number of ways to place N_1 indistinguishable molecules onto the lattice in this orientation is

$$\frac{\prod_{j_1=0}^{N_1-1} \nu_{j_1+1}}{(N_1)!} = \frac{M!(M - kN_1 + N_1)!}{(M - kN_1)!M!(N_1)!}$$

$$= \frac{(M - kN_1 + N_1)!}{(M - kN_1)!(N_1)!} \qquad (3)$$

Note that this result so far is equal to the exact number. That is to say, the number of ways to pack the molecules is the number of ways to arrange N_1 linear molecules and N_0 holes on a linear lattice.

To count the number of ways to pack the N_2 molecules in the second orientation, given that we have already placed the N_1 molecules, we need to know the statistics for those pairs of neighboring sites whose centers are connected by a line in this direction. The number of this kind of nearest neighbors to polymer molecules is $2kN_1 + 2j_2$, where j_2 is the number of polymer molecules in the second orientation and the number of this kind of nearest neighbors to holes is $2M - (2kN_1 + 2kj_2)$.

The first segment of the $(j_2 + 1)$th molecule can go into the lattice in $(M - kN_1 - kN_2)$ places. The expectancy that a site is unoccupied when it is known that the adjacent site in the direction in which the molecules lies is unoccupied is

$$\frac{2(M - kN_1 - kj_2)}{2(M - kN_1 - kj_2) + 2(kN_1 + j_2)} \qquad (4)$$

We therefore have for ν_{j_2+1}

$$\nu_{j_2+1} = (M - kN_1 - kj_2)\left[\frac{(M - kN_1 - kj_2)}{(M - kN_1 - kj_2) + (kN_1 + j_2)}\right]^{k-1} \qquad (5)$$

The total number of ways to pack these indistinguishable molecules is

$$\frac{\prod_{j_2=0}^{N_2-1} \nu_{j_2+1}}{(N_2)!} = \frac{(M - kN_1)!(M - kN_2 + N_2)!}{(M - kN_1 - kN_2)!M!(N_2)!} \qquad (6)$$

By an exactly analogous reasoning process, we obtain for ν_{j_3+1}

$$\nu_{j_3+1} =$$

$$(M - kN_1 - kN_2 - kj_3)\left[\frac{(M - kN_1 - kN_2 - kj_3)}{(M - kN_1 - kN_2 - kj_3) + (kN_1 + kN_2 + j_3)}\right]^{k-1} \qquad (7)$$

$$\frac{\prod_{j_3=0}^{N_3-1} \nu_{j_3+1}}{(N_3)!} = \frac{(M - kN_1 - kN_2)!(M - kN_3 + N_3)!}{(M - kN_1 - kN_2 - kN_3)!M!(N_3)!} \qquad (8)$$

The product obtained from eqs 3, 6, and 8 gives the total number of ways to pack the molecules:

$$\Omega(N_0, N_1, N_2, N_3) = \frac{(M - kN_1 + N_1)!}{(M - kN_1)!(N_1)!}$$

$$\times \frac{(M - kN_1)!(M - kN_2 + N_2)!}{(M - kN_1 - kN_2)!M!(N_2)!}$$

$$\times \frac{(M - kN_1 - kN_2)!(M - kN_3 + N_3)!}{(M - kN_1 - kN_2 - kN_3)!M!(N_3)!}$$

$$= \frac{\prod_{j=1}^{3}[M - (k - 1)N_j]!}{(N_0)! \prod_{i=1}^{3}(N_i)!(M!)^2} \qquad (9)$$

As remarked before, this expression is exact when all of the molecules are in one direction. Equation 9 has the proper symmetry requirements. It is invariant under the permutation of N_i.

Isotropic Distribution of the Adsorbed k-mers. For the case of an isotropic distribution of the k-mers ($N_1 = N_2 = N_3 = N/3$), we obtain

$$\Omega = \frac{\{[N_0 + (2kN/3) + (N/3)]!\}^3}{N_0![(N/3)!]^3(M!)^2} \qquad (10)$$

Equation 9 can be generalized for a lattice of connectivity γ. If one uses a mole fraction for molecules that are parallel to one another and a volume fraction for molecules that are perpendicular (it is assumed that the base vectors of the new space are orthogonal), then the appropriate generalization of eq 9 is

$$\Omega(N_0, \{N_i\}) = \frac{\prod_{i=1}^{\gamma/2}[M - (k - 1)N_i]!}{(N_0)! \prod_{i=1}^{\gamma/2}(N_i)!(M!)^{\gamma/2 - 1}} \qquad (11)$$

where $\gamma/2$ is the dimensionality of the space. Again, if we allow $N_i = (2/\gamma)N$ (and $N_0 = M - kN$) then eq 9 reduces to the well-known Guggenheim factor:

$$\Omega(M, N, \gamma) =$$

$$\left(\frac{\gamma}{2}\right)^N \frac{M!}{N!(M - kN)!}\left[\frac{\{M - kN + [(\gamma - 2)k + 2]N\}!}{M!}\right]^{\gamma/2} \qquad (12)$$

From eq 12, the canonical partition function $Q(M, N, T)$ can be easily calculated. Thus,

$$Q(M, N, T) = \Omega(M, N, \gamma) \exp(-\beta k\varepsilon_o N) \qquad (13)$$

where $\beta = 1/k_B T$ (with k_B being the Boltzmann constant) and ε_o is the interaction energy between every unit forming a k-mer and the substrate. In addition, the Helmholtz free energy $F(M, N, T)$ relates to $\Omega(M, N, \gamma)$ through

$$\beta F(M, N, T) = -\ln Q(M, N, T) = -\ln \Omega(M, N, \gamma) + \beta k\varepsilon_o N \qquad (14)$$

Then, the remaining thermodynamic functions can be obtained from the general differential form[1]

$$dF = -S\,dT - \Pi\,dM + \mu\,dN \qquad (15)$$

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

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,M} \tag{16}$$

Finally, from eqs 12−16 and by using the lattice coverage $\theta = kN/M$, the adsorption isotherm $[\mu(\theta)]$ can be written in terms of the intensive variables θ and T:

$$\beta(\mu - k\varepsilon_\text{o}) = \ln\left(\frac{\theta}{k}\right) - k\ln(1-\theta) - \ln\left(\frac{\gamma}{2}\right)$$
$$+ (k-1)\ln\left[1 - \frac{(k-1)}{k}\frac{2\theta}{\gamma}\right] \tag{17}$$

Effects of the Orientational Order on the Adsorption Thermodynamic Functions. As discussed in the Introduction, recent results showed that long, straight rigid rods on a lattice, interacting with only an excluded volume interaction, can lead to nematic order at intermediate density.[37−41] To introduce the effect of this orientational order in the GD statistics, we will rewrite the equations above in terms of the well-known nematic order parameter δ,[37] which is given by

$$\delta = \frac{\left|\sum\limits_{i=1}^{m} \vec{N}_i\right|}{\sum\limits_{i=1}^{m} |\vec{N}_i|} \tag{18}$$

δ represents a general order parameter measuring the orientation of the k-mers on a lattice with m directions. For simplicity, we restrict the calculations to the case of square lattices, where $m = 2$ and the angle between $\vec{N}_1$ and $\vec{N}_2$ is π. Accordingly, the order parameter reduces to $\delta = |N_1 - N_2|/(N_1 + N_2)$, with N_1 (N_2) being the number of k-mers aligned along the horizontal (vertical) direction. Without a loss of generality, we can assume that the nematic order occurs in the direction of N_1 and

$$\delta = \frac{N_1 - N_2}{N_1 + N_2} \tag{19}$$

From eq 19 and using $\theta = k(N_1 + N_2)/M$, the number of k-mers aligned along the horizontal and vertical directions can be obtained as

$$\frac{N_1}{M} = \frac{\theta}{2k}(1+\delta) \text{ and } \frac{N_2}{M} = \frac{\theta}{2k}(1-\delta) \tag{20}$$

Then, starting from eq 9, operating as in the previous section and using eq 20, the Helmholtz free energy per site and adsorption isotherm can be written in terms of θ and δ:

$$\beta f(\theta, \delta) = -\left[1 - \frac{(k-1)(1+\delta)\theta}{2k}\right]\ln\left[1 - \frac{(k-1)(1+\delta)\theta}{2k}\right]$$
$$-\left[1 - \frac{(k-1)(1-\delta)\theta}{2k}\right]\ln\left[1 - \frac{(k-1)(1-\delta)\theta}{2k}\right]$$
$$+\frac{(1+\delta)\theta}{2k}\ln\left[\frac{(1+\delta)\theta}{2k}\right] + \frac{(1-\delta)\theta}{2k}\ln\left[\frac{(1-\delta)\theta}{2k}\right]$$
$$+ (1-\theta)\ln(1-\theta) + \beta\varepsilon_\text{o}\theta \tag{21}$$

and

$$\beta(\mu - k\varepsilon_\text{o}) = (k-1)\left[\frac{(1+\delta)}{2} + \frac{\theta}{2}\frac{\partial\delta}{\partial\theta}\right]\ln\left[1 - \frac{(k-1)(1+\delta)\theta}{2k}\right]$$
$$+ (k-1)\left[\frac{(1-\delta)}{2} - \frac{\theta}{2}\frac{\partial\delta}{\partial\theta}\right]\ln\left[1 - \frac{(k-1)(1-\delta)\theta}{2k}\right]$$
$$+ \left[\frac{(1+\delta)}{2} + \frac{\theta}{2}\frac{\partial\delta}{\partial\theta}\right]\ln\left[\frac{(1+\delta)\theta}{2k}\right]$$
$$+ \left[\frac{(1-\delta)}{2} - \frac{\theta}{2}\frac{\partial\delta}{\partial\theta}\right]\ln\left[\frac{(1-\delta)\theta}{2k}\right] + k\ln(1-\theta) \tag{22}$$

As it can be observed from eq 22, the calculation of the adsorption isotherm requires a knowledge of an analytical expression for the dependence of the nematic order parameter on the coverage. As expected, eq 22 simplifies to eq 17 when $\delta(\theta) = $ constant and $\delta \to 0$ (isotropic case). In addition, it can be easily demonstrated that eqs 21 and 22 reduce to the corresponding exact thermodynamic functions of noninteracting k-mers adsorbed flat on a 1D lattice[14] when $\delta(\theta) = $ constant and $\delta \to 1$ (fully anisotropic case).

In the general case, a free-energy-minimization approach is applied to establish $\delta(\theta)$ and then to obtain a general expression for the adsorption isotherm (without orientational restrictions). The theoretical procedure can be described as follows:

(1) By differentiating eq 21 with respect to δ and setting the result equal to zero, we found the condition

$$(1+\delta)^{-1/(k-1)}\left\{(k-1)\left[1 - \frac{\theta}{2}(1-\delta)\right] + 1\right\}$$
$$- (1-\delta)^{-1/(k-1)}\left\{(k-1)\left[1 - \frac{\theta}{2}(1+\delta)\right] + 1\right\} = 0. \tag{23}$$

(2) $\delta(\theta)$ is calculated from solving[42] eq 23.
(3) $\delta(\theta)$ is introduced into eq 22, and the adsorption isotherm is obtained.

Items 1−3 are summarized in the following scheme:

differentiating eq 21 with respect to $\delta \to$ eq 23

solving eq 23 $\to \delta(\theta)$

$\delta(\theta) + $ eq 22 $\to \mu(\theta)$

3. RESULTS AND DISCUSSION

In this section, we analyze the main characteristics of the new adsorption isotherm given in eq 22, in comparison with MC simulation results and the main theoretical models developed to treat the polymer adsorption problem.[10−13,18,21] Three theories have been considered: the first is the well-known FH approximation for straight rigid rods;[10,11,18] the second is the GD approach for an isotropic distribution of admolecules;[12,13,18] and the third is the recently developed SE model for the adsorption of polyatomics.[18,21]

The equation of the GD adsorption isotherm for an isotropic distribution of adsorbed rods was given in eq 17. The corresponding

expressions in the FH[10,11,18] and SE[18,21] theories can be written as

$$\beta(\mu - k\varepsilon_o) = \ln\left(\frac{\theta}{k}\right) - k\ln(1 - \theta) - \ln\left(\frac{\gamma}{2}\right), \text{ FH}(k \geq 2)$$
(24)

and

$$\beta(\mu - k\varepsilon_o) = \ln\left(\frac{\theta}{k}\right) - k\ln(1 - \theta) - \ln\left(\frac{\gamma}{2}\right)$$
$$+ (1 - \theta)(k - 1)\ln\left[1 - \frac{(k-1)}{k}\frac{2\theta}{\gamma}\right]$$
$$+ \theta(k - 1)\ln\left[1 - \frac{(k-1)\theta}{k}\right], \text{ SE}$$
(25)

As previously indicated, we restrict the study to square lattices ($\gamma = 4$).

In the case of the MC simulations, the calculations have been developed for straight rigid rods of length k, with k ranging between 2 and 14. The surface was represented as a square array of $M = L \times L$ adsorptive sites with $L/k = 20$ and periodic boundary conditions. As was shown in ref 40, finite-size effects are negligible for the coverage dependence of the chemical potential with this lattice size.

To obtain the curve of μ versus θ, we have used the hyperparallel tempering Monte Carlo simulation method.[43,44] This method consists of generating a compound system of R noninteracting replicas of the system under study. The ith replica is associated with a chemical potential μ_i. To determine the set of chemical potentials, $\{\mu_i\}$, we set the lowest chemical potential, μ_1, in the isotropic phase where relaxation (correlation) time is expected to be very short and there exists only one minimum in the free-energy space. However, the highest chemical potential, μ_R, is set in the nematic phase whose properties we are interested in. Finally, the difference between two consecutive chemical potentials, μ_i and μ_{i+1} with $\mu_i > \mu_{i+1}$, is set as $\Delta\mu = (\mu_1 - \mu_R)/(R - 1)$ (equally spaced temperatures).

Under these conditions, the algorithm to carry out the simulation process is built on the basis of two major subroutines: replica update and replica exchange.

Replica Update. The adsorption–desorption and diffusional relaxation procedure is as follows: (1) One out of R replicas is randomly selected. (2) A linear k-uple of nearest-neighbor sites, belonging to the replica selected in (1), is chosen at random. Then, if the k sites are empty, an attempt is made to deposit a rod with probability $W = \min\{1, \exp(\beta\mu)\}$. If the k sites are occupied by units belonging to the same k-mer, then an attempt is made to desorb this k-mer with probability $W = \min\{1, \exp(-\beta\mu)\}$; otherwise, the attempt is rejected. In addition, the displacement (diffusional relaxation) of adparticles to nearest-neighbor positions, by either jumps along the k-mer axis or reptation by rotation around the k-mer end, must be allowed in order to reach equilibrium in a reasonable time.

Replica Exchange. The exchange of two configurations X_i and X_j, corresponding to the ith and jth replicas, respectively, is tried and accepted with probability $W = \min\{1, \exp(-\Delta)\}$, where Δ in a nonthermal grand canonical ensemble given by $\exp[\beta(\mu_j - \mu_i)(N_j - N_i)]$.

An MC step (MCs) is completed after we repeat (1) and (2) RM times. The equilibrium state can be well reproduced after discarding the first r_0 MCs. Then, the next r MCs are used to compute averages.

For each value of the chemical potential μ_i, the corresponding surface coverage θ_i is obtained through simple averages:

$$\theta_i = \frac{1}{r}\sum_{t=1}^{r}\theta[X_i(t)]$$
(26)

In eq 26, X_i stands for the state of the ith replica (at chemical potential μ_i).

As mentioned before in ref 37, the relaxation time increases very quickly as the k-mer size increases. Consequently, MC simulations for large adsorbates are very time-consuming and may produce artifacts related to nonaccurate equilibrium states. To discard this possibility, equilibration times of order O(10^8 MCs) were used in this study, with an effort reaching almost the limits of our computational capabilities.[45]

An extensive comparison among the new adsorption isotherm (eq 22, solid line), the simulation data (symbols), and the isotherm equations obtained from the analytical approaches depicted as GD (eq 17, dashed line), FH (eq 24, dashed and dotted line), and SE (eq 25, dotted line) is shown in Figure 2: (a) $k = 3$, (b) $k = 6$, (c) $k = 11$, and (d) $k = 14$.

In part a, the behavior of the different approaches can be explained as follows. The new theory and GD agree very well with the simulation results for coverage values of up to $\theta \approx 0.6$; however, the disagreement between theoretical and simulation data increases for larger θ values. The coincidence between the new theory and GD results is due to the fact that, for small values of k ($k < 4$), the function $\delta(\theta)$ minimizing the free energy is $\delta(\theta) = 0$ and, under this condition, eqs 22 and 17 become identical. However, SE provides a good approximation with very small differences between simulation and theoretical results in all ranges of coverage.

We now analyze the case corresponding to $k = 6$ (Figure 2b). The agreement between simulation and analytical data is very good for small values of coverage. However, as the surface coverage is increased, two different behaviors are observed. Although SE and the new theory provide good results, the classical FH and GD approximations fail to reproduce the simulation data. The differences between GD and the theory presented here are associated with the behavior of the order parameter $\delta(\theta)$ (obtained from eq 23 with $k = 6$), which is shown in the inset of the Figure. The functionality of δ with coverage is indicative of the existence of nematic order for $\theta > 0.4$. Even though this result is not exact,[37] the inclusion of $\delta(\theta)$ in eq 22 leads to an extremely good approximation of the adsorption isotherm.

To complete our study, parts c and d of Figure 2 are devoted to the analysis of large adsorbates, $k = 11$ and 14, respectively. The results are very clear: FH, GD, and SE predict a smaller θ than the simulation data over the entire range of coverage. In the case of the new isotherm, the results are excellent and represent a significant advance with respect to the existing development of k-mer thermodynamics.

For each value of k, the differences between theoretical and simulation data can be very easily rationalized with the help of the average percent error in the chemical potential ε_μ^k, which is defined as

$$\varepsilon_\mu^k = \frac{1}{N}\left(\sum_\theta\left|\frac{\mu_{\text{sim}} - \mu_{\text{appr}}}{\mu_{\text{sim}}}\right|_\theta\right) \times 100\%$$
(27)

where μ_{sim} (μ_{appr}) represents the value of the chemical potential obtained by using the MC simulation (analytical approach). Each pair of values ($\mu_{\text{sim}}, \mu_{\text{appr}}$) is obtained at fixed θ. The sum runs
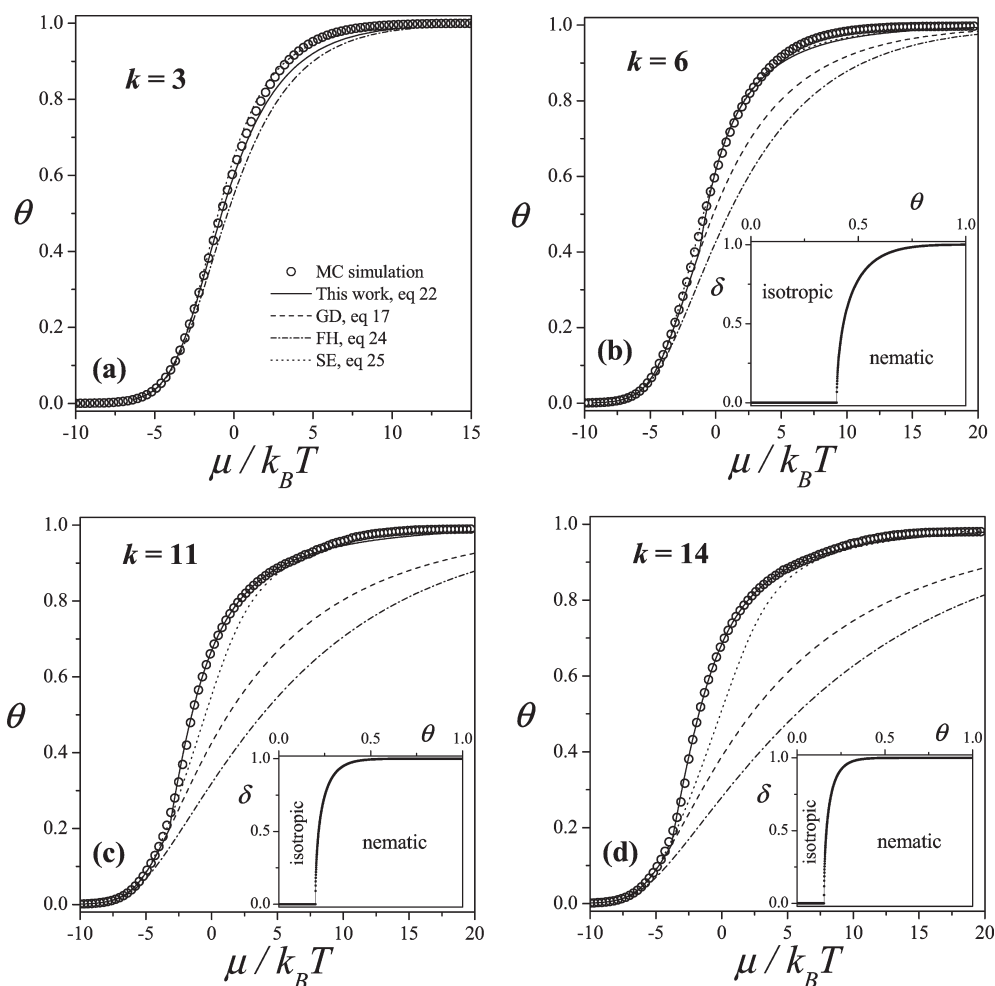
Figure 2. Adsorption isotherms for rigid k-mers on a square lattice: (a) $k = 3$, (b) $k = 6$, (c) $k = 11$, and (d) $k = 14$. Symbols represent the MC results, and lines correspond to different theoretical approaches as indicated in part a.
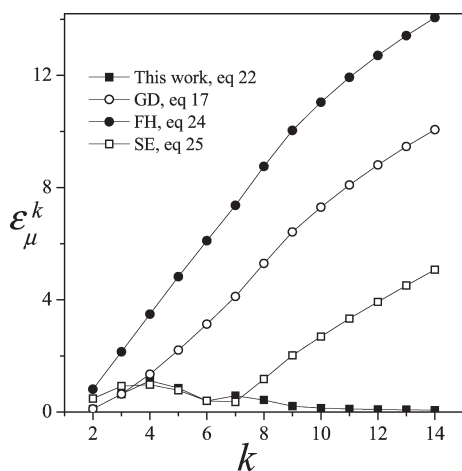

Figure 3. Average percent error in the chemical potential, ε_μ^k, as a function of k for the different approximations studied in this contribution.

over the N points of the simulation adsorption isotherm (in this case, $N = 100$ for all k).

The dependence of ε_μ^k on the k-mer size is shown in Figure 3 for the different theoretical approximations. Several conclusions can be drawn from the Figure:

(1) In the FH and GD cases, ε_μ^k increases monotonically with increasing k and the disagreement between MC and analytical data turns out to be very large for $k \geq 3$ and $k \geq 5$, respectively.

(2) The behavior of SE is more complex. In fact, there exists a range of k ($2 \leq k \leq 7$) where ε_μ^k remains almost constant around 1% and SE provides a very good fitting of the simulation data. However, for $k \geq 8$, the differences between simulation and theoretical data increase with k. This deviation is associated with the appearance of an I—N phase transition in the adlayer for $k > 7$, which is not covered by the SE theory.

(3) The agreement between the new theoretical approach and the simulation data is excellent in all ranges of k. This result provides valuable insight into how the adsorption process takes place. Namely, for $k \geq 7$ and intermediate densities, it is more favorable for the rods to align spontaneously because the resulting loss of orientational entropy is compensated for by the gain of translational entropy.

The study in Figures 2 and 3 demonstrates that explicitly considering the isotropic and nematic states occurring in the adlayer at different densities is crucial to understanding the adsorption process of rigid rods. In this sense and to the best of our knowledge,

this is the first report of a generalized lattice-gas model that includes such an I−N phase-transition effect.

We will finish this section by showing how the SE model, which was recently introduced in a semiempirical form,[18,21] can now be easily understood from the arguments given in the previous paragraphs.

As discussed in refs 18 and 21, GD and EA were found to be good expressions for representing the k-mers' adsorption at low and high concentrations, respectively. On the basis of this finding, eq 25 was built as a combination of the GD approximation and the exact isotherm in 1D, with $(1 - \theta)$ and θ as weights, respectively. The explanation of this procedure in terms of the I−N phase transition occurring in the adsorbate is simple: at low coverage, an isotropic state is formed on the surface and the system is well represented by the GD adsorption isotherm equation. However, at high coverage, a nematic order appears in the adlayer, which is excellently represented by the 1D isotherm.

The last example reinforces the discussion above. Namely, the possibility of understanding the adsorption process from a detailed knowledge of the spatial configuration of the molecules in the adsorbed state represents a qualitative difference with the previous generation of models for k-mer adsorption, which assumes isotropy in the adlayer.[10−13,16,22−36,46] Consequently, the theory presented here (1) represents a significant qualitative advance in our understanding of the adsorption of rigid k-mers and (2) is the most accurate and complete approximation to this complex problem.

4. CONCLUSIONS

A new theoretical approach to the adsorption of long, straight rigid rods has been presented on the basis of a generalization of the classical Guggenheim−DiMarzio approximation. The proposed formalism is capable of including the effects of the I−N phase transition occurring at intermediate densities on the thermodynamic functions of the system.

The reaches and limitations of the theory have been analyzed in comparison with MC simulation and the main analytical models developed to treat the polymer adsorption problem. The results obtained represent a significant qualitative advance with respect to the existing development of k-mer thermodynamics and show that the treatment of this complex problem can be significantly simplified if viewed from the new theoretical perspective.

Finally, the new formalism seems to be a promising way to develop a more accurate description of the adsorption thermodynamics of polyatomic molecules, allowing us to include heterogeneous surfaces, lateral interactions between the adparticles, and multilayer adsorption.

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(45) As an example, it took about 400 days to obtain the adsorption isotherm corresponding to $k = 14$ on one node of the BACO parallel cluster. This facility, located at Instituto de Física Aplicada, Universidad Nacional de San Luis-CONICET, San Luis, Argentina, consists of 120 CPUs, each with a 2.4 GHz Core 2 Quad processor.

(46) Interested readers are referred to ref 12, where this point is explicitly considered.