Phase behavior of attractive *k*-mers on two-dimensional lattices: a study from quasi-chemical approximation

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Abstract The phase behavior of attractive linear rigid *k*-mers on two-dimensional lattices was studied by theoretical and simulation calculations in the framework of the lattice-gas model. Combining (*i*) the analytical expression for the partition function of non-interacting *k*-mers, and (*ii*) a generalization of the classical quasi-chemical approximation (QCA) in which the adsorbate can occupy more than one adsorption site, the main thermodynamic functions of the system were explicitly obtained. It was found that, for temperatures below a certain condensation temperature, the system undergoes a first-order phase transition which is observed as a clear discontinuity in the adsorption isotherms. The transition was studied in detail by calculating the temperature–density phase diagrams. Comparisons with analytical data from Bragg–Williams approximation and Monte Carlo simulations were performed in order to test the validity of the theoretical model. The results obtained allowed us not only to analyze the effect of introducing the lateral interactions by following the configuration-counting procedure of the QCA, but also to discuss the consequences of choosing the configurational factor associated to adsorption of non-interacting *k*-mers from different models developed to treat the multisite occupancy adsorption problem.

Keywords Multisite occupancy adsorption ·
Phase transitions · Quasi-chemical approximation

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1 Introduction

The study of systems in the presence of multisite-occupancy adsorption has been an attractive and important topic in statistical physics for a long time (Onsager 1949; Zimm 1946; Isihara 1950, 1951; Flory 1942, 1953; Huggins 1942a, b, c; Guggenheim 1944; DiMarzio 1961; Firpo et al. 1978; Nitta et al. 1984; Des Cloiseaux and Janninck 1990; Rudzinski and Everett 1992; Riccardo et al. 2006). While there is little exact or analytical information available for this problem, a large amount of numerical work has been done using Monte Carlo (MC) methods (Ramirez-Pastor et al. 1998, 2000; Nazzaro et al. 1997; Romá et al. 2000, 2001, 2003a, 2005; Pasinetti et al. 2006, 2012; Romá et al. 2006; Borówko and Rżysko 2001, 2002a, b, 2003, 2006). Thus, the phase diagram for nearest-neighbor (NN) repulsive dimers on square lattices was studied in (Ramirez-Pastor et al. 1998). The analysis revealed the presence of the two well-defined structures: a (4 × 2) ordered phase at $\theta = 1/2$ and a "zigzag" order at $\theta = 2/3$, being θ the surface coverage. The thermodynamic implication of such a structural ordering was demonstrated through the analysis of adsorption isotherms (Ramirez-Pastor et al. 2000), collective-diffusion coefficient (Nazzaro et al. 1997), and configurational entropy of the adlayer (Romá et al. 2000, 2001).

Later, MC simulations and finite-size scaling techniques have been used to study the critical behavior of repulsive linear *k*-mers in the low-coverage ordered structure (at $\theta = 1/2$) (Romá et al. 2003a, 2005; Pasinetti et al. 2006, 2012). A (2*k* × 2) ordered phase, which is characterized by alternating lines, each one being a sequence of adsorbed *k*-mers separated by *k* adjacent empty sites, was found. The results revealed that the nature of the phase transition occurring at half coverage in a system of repulsive rigid *k*-mers on a square lattice changes from second order (Ising universality class) for

$k = 1$ to first order for $k \geq 2$. A similar scenario was found for k-mers adsorbed on the triangular lattice at coverage $k/(2k + 1)$. Recently, the critical properties of repulsive dimers on two-dimensional square lattices at 2/3 coverage were studied (Romá et al. 2006). Although it was not possible to exclude the existence of a more complex critical behavior, the results indicated that the phase transition is continuous and does not belong to the 2D Ising universality class.

On the other hand, Rżysko and Borówko have studied a wide variety of systems in the presence of multisite occupancy (Borówko and Rżysko 2001, 2002a, b, 2003, 2006). Among them, attracting dimers in the presence of energetic heterogeneity (Borówko and Rżysko 2001), heteronuclear dimers consisting of different segments (A and B) adsorbed on square lattices (Borówko and Rżysko 2002a, b, 2003), and trimers with different structures adsorbed on square lattices (Borówko and Rżysko 2006). In these leading papers, a rich variety of phase transitions was reported along with a detailed discussion about critical exponents and universality class.

From the theoretical point of view, three objectives motivated the development of the main approximations existing in the literature, they are (1) to calculate the different ways to array N k-mers on a regular lattice of M equivalent sites, $\Omega(M, N)$; (2) to study the influence of surface heterogeneity on the main adsorption properties of polyatomics and (3) the possibility of phase transitions in the adsorbate when NN interacting k-mers are adsorbed on homogeneous surfaces. With respect to the first point, Onsager (1949), Zimm (1946) and Isihara (1950, 1951) made important contributions to the understanding of the statistics of k-mers 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 non-simple shapes. The Flory–Huggins (FH) theory, due independently to Flory (1942, 1953) and to Huggins (1942a, b, c), 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 to the binary solutions of polymer-monomeric solvent. A great deal of work has been done on checking the predictions of the FH theory against experimental results, the theory being completely satisfactory in a qualitative, or semi-quantitative way. There is no doubt that this simple theory contains the essential features which distinguish high polymer solutions from ordinary solutions of small molecules.

In 1944, Guggenheim proposed an interesting method to calculate the combinatory term in the canonical partition function (Guggenheim 1944). Later, in a valuable contribution,

DiMarzio (1961) obtained the Guggenheim's factor for a model of rigid rod molecules with arbitrary orientations. More recently, two new theories to describe adsorption with multisite occupancy have been introduced (Ramirez-Pastor et al. 1999a, b; Romá et al. 2003b; Riccardo et al. 2004, 2006). In the first, Ramirez-Pastor et al. (1999a, b; Romá et al. 2003b; Riccardo et al. 2006) 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 (Riccardo et al. 2004, 2006). The theory in (Riccardo et al. 2004) is based on a generalization of the formalism of quantum fractional statistics, proposed by Haldane (1991; Wu 1994) 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.

Regarding the point (2), the patchwise heterogeneous surface can be solved relatively simple. 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 three decades ago, when the first solution of that problem was proposed by Nitta et al. (1984), Rudzinski and Everett 1992). Nitta's original approach could be applied only to surfaces characterized by discrete distributions of adsorption energy. Later, Rudzinski et al. (Rudzinski and Everett 1992 and references therein) have developed further Nitta's approach to apply also continuous adsorption energy distributions.

Among the theories of the third group, an early seminal contribution is the mentioned FH approximation (Flory 1942, 1953; Huggins 1942a, b, c), in which not only a configurational factor Ω is proposed, but also intermolecular forces between the adsorbed molecules are introduced, bringing about the possibility of phase transitions in the adlayer. Later, an important contribution to the theoretical study of phase transitions in monolayers of polyatomics has been made by Firpo et al. (1978). Although this model was proposed to describe monolayers of long hydrocarbon chains spread at the gas–liquid interface, its theoretical foundation would remain unchanged if one wanted to apply it to gas–solid systems. In this approach, the configurational factor in the canonical partition function was obtained from the Guggenheim–DiMarzio (GD) statistics for rigid rod molecules (Guggenheim 1944; DiMarzio 1961). More recently, Aranovich and Donohue (1999) have studied the adsorption of chain molecules by using the Ono and Kondo theory (1960). In all cases, the lateral interactions, which are the

responsible of the phase transitions occurring in the adsorbate, were taken into account in the framework of the Bragg–Williams approximation (BWA). A comprehensive discussion on this subject is included in the book of Des Cloiseaux and Janninck (1990).

The critical behavior of interacting dimers has also been analyzed by using transfer matrix techniques (Phares et al. 1986, 1993, 2011). In (Phares et al. 1986, 1993), the structural ordering of first-neighbor interacting dimers has been analyzed. The authors calculated the entropy of dimers on semi-infinite $M \times N$ square lattices ($N \to \infty$). They concluded that there are a finite number of ordered structures for dimers with repulsive NN interactions. In (Phares et al. 2011), a more realistic model was considered by including both first- (V) and second-neighbor (W) interaction energies. A complete phase diagram was obtained for different values of the control parameters: V and W.

In recent work, an analytical approach to the adsorption of interacting polyatomic adsorbates has been proposed (Dávila et al. 2006, 2009). The new formalism was obtained by combining (i) any of the configurational factors associated to adsorption of non-interacting k-mers (FH factor, GD factor, EA factor, FSTA factor, etc.), and (ii) a generalization of the classical quasi-chemical approach (QCA) in which the adsorbate can occupy more than one adsorption site. The new theory was compared with MC simulation and analytical data from the classical BWA. The results obtained showed that: (1) the theory is greatly improved by introducing the lateral interactions by following the configuration-counting procedure of the QCA; and (2) appreciable differences can be seen between BWA and QCA, with the last being the most accurate for all cases.

In (Dávila et al. 2006, 2009), the main adsorption properties (adsorption isotherm, isosteric heat of adsorption, configurational entropy of the adsorbed layer) were studied. In this paper, the analysis was extended to examine the behavior of attractive k-mers on two-dimensional lattices at low-temperature regime. A first-order phase transition was found, which can be observed as a clear discontinuity in the adsorption isotherms. The results obtained allowed us not only to analyze this phase transition by following the configuration-counting procedure of the QCA, but also to discuss the consequences of choosing the configurational factor associated to adsorption of non-interacting k-mers from different models developed to treat the multisite occupancy adsorption problem.

The present work is organized as follows. In Sect. 2, we provide the theoretical formalism. The results of the theoretical approach are presented in Sect. 3 (adsorption isotherms and "temperature-coverage" phase diagram) and Sect. 4 (critical coverage and critical temperature). Finally, the conclusions are drawn in Sect. 5.

2 Description of the theoretical model

Let us assume a system of N interacting linear rigid k-mers adsorbed on a lattice of M sites and connectivity c. The adsorbate molecules contain k identical units and each of one occupies a lattice site. Small adsorbates with spherical symmetry would correspond to the monomers limit ($k = 1$). The distance between k-mer units is assumed in registry with the lattice constant a; hence exactly k sites are occupied by a k-mer when adsorbed. Two different energies are considered in the adsorption process: (1) U_0, constant interaction energy between a k-mer unit and an adsorption site and (2) w, lateral interaction energy between two NN units belonging to different k-mers. Under these conditions, the Hamiltonian can be written as:

$$H = w \sum_{\langle i,j \rangle} c_i c_j - N(k-1)w + (U_o - \mu) \sum_i c_i, \qquad (1)$$

where $\langle i, j \rangle$ represents pairs of NN sites, μ is the chemical potential and c_i is the occupation variable, which can take the following values: $c_i = 0$ if the corresponding site is empty and $c_i = 1$ if the site is occupied. The term $N(k-1)w$ is subtracted in Eq. (1) since the summation over all the pairs of NN sites overestimates the total energy by including $N(k-1)$ bonds belonging to the N adsorbed k-mers.

For this system, the dependence on temperature T and coverage $\theta = kN/M$ of the free energy per site, $f(\theta, T)$, was obtained explicitly in (Dávila et al. 2009), by following the configuration-counting procedure of the QCA,

$$\beta f(\theta, T) = -\frac{\theta}{k}\ln q + \beta\frac{\theta}{k}\left(\frac{\lambda w}{2} + k U_0\right) - \lambda\frac{\theta}{k}\ln\frac{\lambda\theta}{ck}$$
$$+ \left[c - 2\left(\frac{k-1}{k}\right)\theta\right]\ln\left[1 - \frac{2}{c}\left(\frac{k-1}{k}\right)\theta\right]$$
$$- \left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta\right]\ln\left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta\right]$$
$$+ \frac{\lambda\theta}{2k}\ln\left(\frac{\lambda\theta}{2k} - \alpha\right) - c\left[1 - \frac{2}{c}\left(\frac{k-1}{k}\right)\theta - \frac{\lambda\theta}{ck}\right]$$
$$\ln\left[1 - \frac{2}{c}\left(\frac{k-1}{k}\right)\theta - \frac{\lambda\theta}{ck}\right] + \left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta - \frac{\lambda\theta}{2k}\right]$$
$$\ln\left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta - \frac{\lambda\theta}{2k} - \alpha\right] - \ln\gamma \qquad (2)$$

where $\lambda = (c-2)k + 2$, $\beta = 1/k_B T$ (being k_B the Boltzmann constant), α is

$$\alpha = \frac{\lambda c}{2k} \frac{\theta(1-\theta)}{\left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta + b\right]}, \qquad (3)$$

$$b = \left\{\left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta\right]^2 - \frac{\lambda c}{k}A\theta(1-\theta)\right\}^{1/2}, \qquad (4)$$

and

$$\gamma = \Omega(N,M)^{1/M}. \tag{5}$$

$\Omega(N,M)$ is number of ways to arrange N k-mers on M sites. In general, $\Omega(N,M)$ depends on the spatial configuration of the k-mer and the surface geometry. Even in the simplest case of linear k-mers, there not exist the exact form of $\Omega(N,M)$ in two (or more) dimensions. However, as discussed in Sect. 1, different approximations have been developed for $\Omega(N,M)$ (Riccardo et al. 2006). In this paper, four theories have been considered: the first is the well-known FH approximation (Flory 1942, 1953; Huggins 1942a, b, c); the second is the GD approach for rigid rod molecules (Guggenheim 1944; DiMarzio 1961); the third (EA) is based on exact forms of the thermodynamic functions of linear adsorbates in one dimension and its generalization to higher dimensions (Ramirez-Pastor et al. 1999a, b; Romá et al. 2003b; Riccardo et al. 2006); and the fourth is the recently developed FSTA (Riccardo et al. 2004, 2006).

The classical FH theory (Flory 1942, 1953; Huggins 1942a, b, c) defines the volume of a polymer system as a lattice which is divided into microscopic subspaces (called sites) of the same volume. In the case of polymer solutions, the solvent molecules are assumed to occupy single sites, while a polymer chain occupies k adjacent sites. In the lattice-gas language, the FH theory allows to study the general problem of molecules of arbitrary shape (but isotropic distribution) adsorbed on homogeneous surfaces. In the case straight rigid rods with c allowed orientations (Riccardo et al. 2006), the factor γ results

$$\ln \gamma(\theta) = -\frac{\theta}{k} \ln \frac{\theta}{k} - (1-\theta) \ln (1-\theta)$$
$$- \frac{\theta}{k}\left[k - 1 - \ln \left(\frac{c}{2}\right)\right] \qquad \text{(FH).} \tag{6}$$

The FH statistics provides a natural foundation onto which the effect of the orientation of the admolecules can be added. Following this line of thought, DiMarzio (1961) developed an approximate method of counting the number of ways, Ω, to pack together linear polymer molecules of arbitrary shape and of arbitrary orientations. Accordingly, Ω was evaluated as a function of the number of molecules in each permitted direction. These permitted directions can be continuous, so that Ω is derived as a function of the continuous function $f(r)$ which gives the density of rods lying in the solid angle Δr, or the permitted directions can be discrete, so that Ω is the number of ways to pack molecules onto a lattice. Based on the detailed knowledge of the orientations of the molecules, the various types (nematic, smectic, and cholestic) of liquid crystals were argued for and the reasons for their existence were ascertained. 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 (1944). In this limit, which we call the Guggenheim DiMarzio approximation, the corresponding expression for γ is

$$\ln \gamma(\theta) = -\frac{\theta}{k} \ln \frac{\theta}{k} - (1-\theta) \ln (1-\theta) + \left(\theta - \frac{c}{2}\right) \ln \left(\frac{c}{2}\right)$$
$$+ \left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta\right] \ln \left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta\right] \quad \text{(GD).} \tag{7}$$

As mentioned in Sect. 1, EA is based on exact forms of the thermodynamic functions of linear adsorbates in one dimension and its generalization to higher dimensions. In this framework, the configurational factor in Eq. (5) is calculated considering that the molecules are distributed completely at random on the lattice, and assuming the arguments given by different authors (Flory 1942, 1953; Nitta et al. 1984; Ramirez-Pastor et al. 1999a) to relate the configurational factor $\Omega(M,N,c)$ for any connectivity c, with the same quantity in one dimension $\Omega(M,N,c=2)$,

$$\Omega(M,N,c) = K(c,k)^N \Omega(M,N,c=2), \tag{8}$$

where $K(c,k)$ represents the number of available configurations (per lattice site) for a k-mer at zero coverage. $K(c,k)$ is, in general, a function of the connectivity and the size/shape of the adsorbate. It's easy demonstrate that,

$$K(c,k) = \begin{cases} c/2 & \text{for linear } k-\text{mers} \\ \left[c(c-1)^{(k-2)}\right]/2 - m' & \text{for flexible } k-\text{mers} \end{cases} \tag{9}$$

the term m' is subtracted in Eq. (9) since the first term overestimates $K(c,k)$ by including m' configurations providing overlaps in the k-mer. The resulting expression for γ is:

$$\ln \gamma(\theta) = -\frac{\theta}{k} \ln \frac{\theta}{k} - (1-\theta) \ln(1-\theta) + \frac{\theta}{k} \ln K(c,k)$$
$$+ \left[1 - \left(\frac{k-1}{k}\right)\theta\right] \ln \left[1 - \left(\frac{k-1}{k}\right)\theta\right] \quad \text{(EA).} \tag{10}$$

Finally, we summarize the basis of the FSTA description (Riccardo et al. 2004, 2006), which allows us to describe the configurational factor through a single function (parameter), namely, the statistical exclusion, g, accounting for the configuration of the molecules in the adsorbed state. In this approximation, the interaction of one isolated molecule with a solid surface confined in a fixed volume is represented by an adsorption field having a total number G of local minima in the space of coordinates necessary to define the adsorption configuration. Thus, G is the number of equilibrium states of a single molecule at infinitely low density. In general, more

than one state out of G are prevented from occupation upon adsorption of a molecule. Furthermore, because of possible concurrent exclusion of states by two or more molecules, the number of states excluded per molecule, $g(N)$, being a measure of the statistical interactions, depends in general on the number of molecules N within the volume. From the definition of the number of states available for a Nth molecule after $(N - 1)$ ones are already in the volume, $d_N = G - \sum_{N'=1}^{N-1} g(N')$, which is a generalization of the one recently established by Haldane (1991; Wu 1994), the generalized configurational factor, $\Omega = (d_N + N - 1)!/[N!(d_N - 1)!]$, can be calculated.

The simplest approximation for $g(N)$ can be obtained, assuming independence of the adsorption sites. Under this consideration, if one molecule has m different ways of adsorbing on one site, $g = mk$ states are excluded when one k-mer is adsorbed occupying k sites on the lattice. In the case of straight rigid k-mers adsorbed on a lattice of connectivity c, $g = ck/2$ and the factor γ takes the form:

$$\ln \gamma(\theta) = -\frac{\theta}{k} \ln \frac{2\theta}{ck} - \frac{c}{2}(1 - \theta) \ln (1 - \theta) \\ + \frac{c}{2} \left[1 - \left(\frac{kc - 2}{kc} \right) \theta \right] \ln \left[1 - \left(\frac{kc - 2}{kc} \right) \theta \right] \text{(FSTA)}.$$

(11)

3 Adsorption isotherms and "temperature-coverage" phase diagram

The equilibrium properties of the adlayer can be deduced from Eq. (2) along with the differential form of the Helmholtz free energy F in the canonical ensemble

$$dF = -SdT - \Pi dM + \mu dN$$ (12)

where S, Π and μ represent the entropy, the spreading pressure and the chemical potential, respectively.

The coverage dependence of the chemical potential, $\mu \left[= (\partial F / \partial N)_{M,T} \right]$ arises straightforwardly from Eqs. (2) and (12). Then,

$$\beta \mu = - \ln q + \beta \left(\frac{\lambda w}{2} + k U_0 \right) - \lambda \ln \frac{\lambda \theta}{ck} \\ - 2(k - 1) \ln \left(1 - \frac{2\theta}{c} + \frac{2\theta}{ck} \right) \\ + (k - 1) \ln \left(\frac{c}{2} - \theta + \frac{\theta}{k} \right) + c\, k \ln(1 - \theta) \\ - \frac{c\, k}{2} \ln \left[\frac{c}{2}(1 - \theta) - \alpha \right] + \frac{\lambda}{2} \ln \left(\frac{\lambda \theta}{2k} - \alpha \right) - k \frac{\partial \ln \gamma}{\partial \theta}.$$

(13)

Typical adsorption isotherms, obtained from Eq. (13) with the function γ from Eq. (10), are shown in Fig. 1 for various k-mer's sizes and interaction energies. Because the surface was assumed to be homogeneous, the interaction energy between the adsorbed dimer and the atoms of the substrate U_o was neglected for the sake of simplicity. In addition, w was assumed to be attractive [negative in Eq. (1)].

In part (a) of Fig. 1, the adsorption isotherms have been calculated for $k = 2$ and different values of the reduced temperature $T^* = |\beta w|^{-1}$. As expected, isotherms shift to lower values of $\beta \mu$ and their slope increases as the temperature decreases. For a characteristic value of temperature T_c^* (in the case of the figure $T_c^* \approx 1$), an inflection point (with infinite slope) occurs in the corresponding adsorption isotherm at coordinates (θ_c, μ_c). T_c^* (μ_c) $[\theta_c]$ is the called transition or condensation temperature (chemical potential) [coverage]. At low-temperature regime $(T^* < T_c^*)$, the system undergoes a first-order phase transition that shows as the typical loops in the theoretical isotherms. In this situation, which has been observed experimentally in numerous systems (Clark 1970; Patrykiejew et al. 2000), the only phase which one expects is a lattice-gas phase at low coverage, separated by a two-phase coexistence region from a "lattice-fluid" phase at higher coverage. This transition of a two-dimensional gas to a two-dimensional liquid is similar to that of a lattice-gas of attractive monomers. However, the symmetry particle-vacancy (valid for monoatomic particles) is broken for k-mers and the isotherms are asymmetric with respect to $\theta = 0.5$. The condensation shown in Fig. 1a has been also observed in recent calculations based on transfer-matrix technique (Phares 2011).

In Fig. 1b, the adsorption isotherms have been obtained for a fixed value of $T^*(< T_c^*)$ and different k-mer's sizes $(k = 1, 2, 3, 4)$. Curves shift to the left for increasing k, because larger molecules with attractive units facilitate the adsorption. In addition, the loop is more pronounced for larger values of k, as a first indication that the transition reduced temperature increases as k is increased.

The phase diagram of the adsorbed monolayer in "temperature-coverage" coordinates can be constructed from the curves of the adsorption isotherms. To understand this procedure, it is instructive to consider the theoretical curve shown schematically in Fig. 2a. As it is can be observed, the chemical potential is a non-monotonic function of coverage at temperatures below the condensation temperature T_c^*. The real value of the chemical potential in the two-phase region $[\mu^*$ in Fig. 2a] is defined by the phenomenological Maxwell rule: the shaded regions in Fig. 2a should be equal to each other. Once μ^* is obtained, the corresponding critical densities $[\theta_1$ and θ_2 in Fig. 2a] can be easily calculated[1]. The procedure is thereby extended to different temperatures ranging between $T^* = 0$ and $T^* = T_c^*$ and the corresponding phase diagram is obtained. A typical phase diagram for

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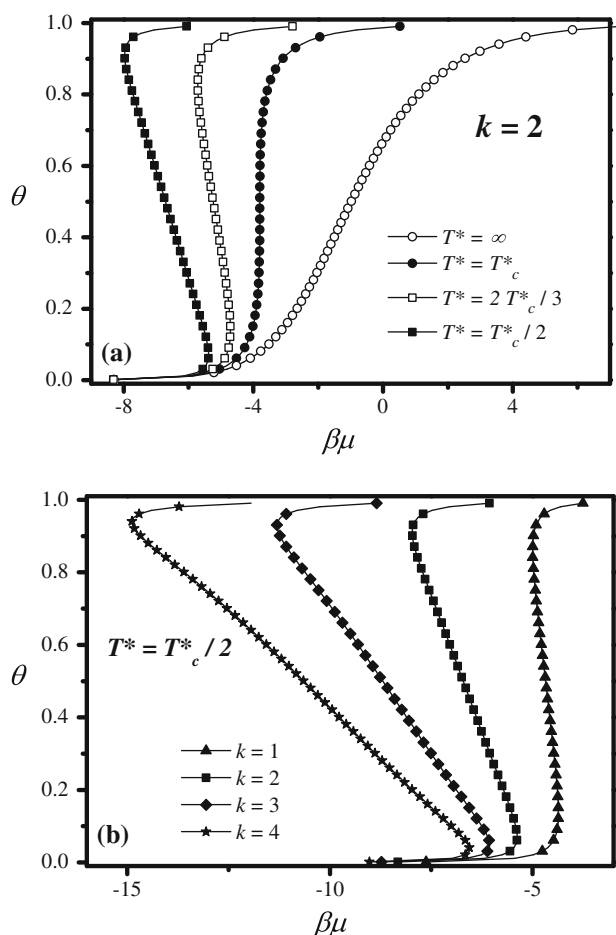[1] The calculations were performed by using Maple software.

Fig. 1 **a** Surface coverage versus chemical potential (in units of $1/\beta$) for attractive interacting dimers on square lattices. *Curves from right to left* correspond to: $T^* = \infty$; $T^* = T_c^*$, $T^* = 2T_c/3^*$ and $T^* = T_c/2^*$ ($T_c^* \approx 1$). **b** Same as **a** for attractive interacting k-mers with $T^* = T_c/2^*$ and different sizes of the adsorbate. *Curves from right to left* correspond to: $k = 1, 2, 3$ and 4

Fig. 2 Chemical potential as a function of coverage at $T^* \approx 0.6\ T_c^*$ ($T_c^* \approx 1$) **a** and phase diagram of the adsorbed layer **b** obtained for $k = 2$, $c = 4$ and γ from Eq. (7). A and B denote the one- and two-phase regions. The *dashed line* shows the value of the chemical potential in the two-phase region

$k = 2$, $c = 4$ and γ from Eq. (7) is shown in Fig. 2b. The coexistence line (open circles joined by line) defines the boundary between the one-phase region (A), characterized by a random distribution of particles on the surface, and the two-phase region (B), where the adsorbate segregates in compact islands.

Next, we will study the effect of the lattice geometry on the characteristics of the temperature-coverage phase diagram. As an example, Fig. 3 shows the coexistence curves obtained for dimers adsorbed on square, honeycomb and triangular lattices. As in Fig. 1, γ was taken from Eq. (10). The shape of the diagrams is fairly independent of the lattice connectivity. However, and as expected, T_c^* increases as the connectivity is increased. A rather simple explanation for this behavior is the following: in order to take a k-mer out of a condensed island one needs an energy equivalent to $[2(c-1) + (k-2)(c-2)]w$. Accordingly, the low-temperature structure is energetically more stable as the
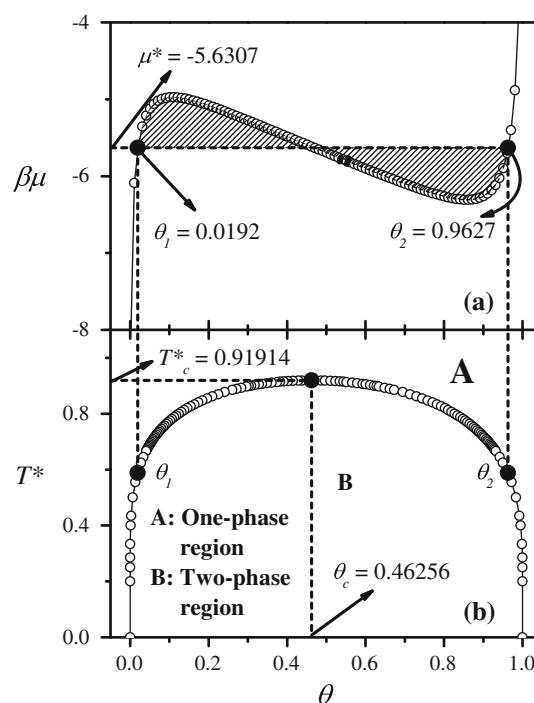
number of NNs increases and the transition temperature is shifted to a higher value. A similar behavior was observed by using the function γ from Eqs. (6, 7, 11).

Figure 4 shows the phase diagrams obtained for k-mers of different sizes adsorbed on square lattices. As in Fig. 3, γ was taken from Eq. (10). Following the same argument used in the preceding figure, the condensed phase is reinforced with the increasing of the k-mer size and consequently, the maximum of the coexistence curves increases with k. An identical behavior is observed for triangular and honeycomb lattices.

The properties of the phase diagram are also affected by theoretical approach used for γ. As an example, Fig. 5 shows the case of $k = 10$ and different expressions of the configurational factor γ as indicated. The figure also includes (dashed line) the value of T_c^* obtained from MC simulations. Details of the MC procedure and the differences between theoretical and simulation results will be given in the next section. As it is possible to observe from Figs. 2, 3, 4, and 5, the main features of the phase diagram can be rationalized by analyzing the maximum of the curve of coexistence (θ_c, T_c^*). The dependence of this characteristic point on k, c and γ will be discussed in details in the next section.
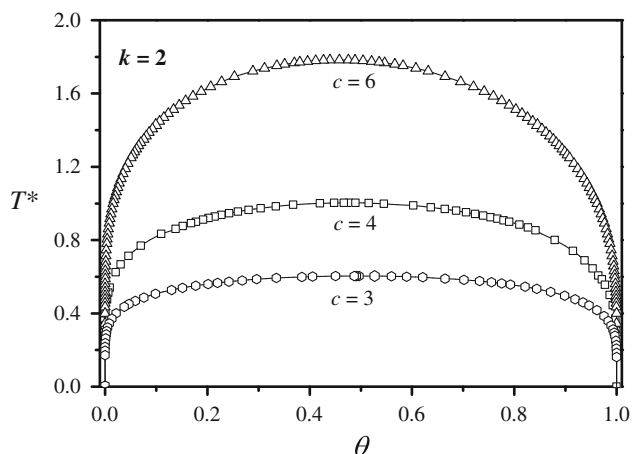
Fig. 3 Phase diagrams for dimers adsorbed on square (*squares*), honeycomb (*hexagons*) and triangular (*triangles*) lattices. In all cases, γ was taken from Eq. (10)

Fig. 4 Phase diagrams for *k*-mers of different sizes (as indicated) adsorbed on square lattices. As in Fig. 3, γ was taken from Eq. (10)

4 Critical coverage, θ_c^k, and critical temperature, T_c^k

For a given value of k, the transition temperature and coverage, T_c^* and θ_c, are obtained from the conditions:

$$\left(\frac{\partial\mu}{\partial\theta}\right)_{T=T_c^*;\,\theta=\theta_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2\mu}{\partial\theta^2}\right)_{T=T_c^*;\,\theta=\theta_c} = 0. \quad (14)$$

The dependence of the transition point, (θ_c, T_c^*), on k, c and γ is shown in Figs. 6, 7, 8, and 9. The results obtained from QCA are also compared with data from BWA[2]. In this framework, μ adopts the following expression (Ramirez-Pastor et al. 2000):

$$\beta\mu = -\ln q + \beta(k U_0 + \lambda w \theta) - k\frac{\partial \ln \gamma}{\partial\theta}. \quad (15)$$

Two well-differentiated behavior can be observed according to the choice of the factor γ. Thus, the results from EA [Eq. (10)] and FSTA [Eq. (11)] look very different to those obtained from GD [Eq. (7)] and FH [Eq. (6)] and consequently, will be shown in separate figures.

In Fig. 6, θ_c is plotted as a function of k (in logarithmic units) for the EA and FSTA cases. The behavior of the curves strongly depends on the procedure used to incorporate the lateral couplings. When the interactions are introduced by QCA, all the curves can be divided into two regions: (i) for small values of k ($k < 50$), notorious differences are observed between EA and FSTA data. In the EA case, the curves are highly dependent on connectivity. This behavior is not observed in the FSTA case, where all
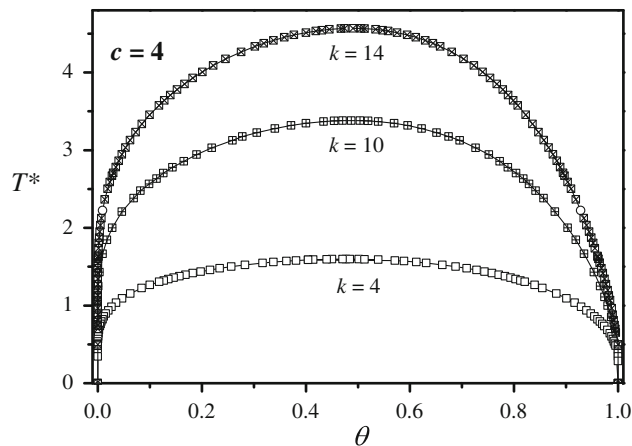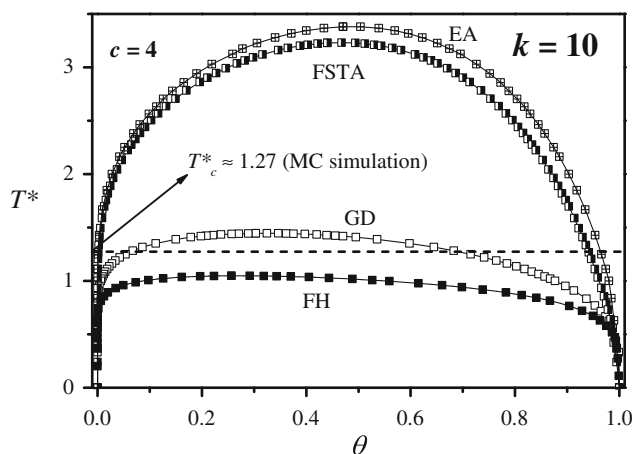

Fig. 5 Phase diagrams obtained for $k = 10$, $c = 4$ and different expressions of the configurational factor γ as indicated

curves show pronounced minima at $k = 2$; and (ii) for larger k-mer sizes, EA and FSTA results coincide and θ_c remains practically constant as k increases. The value of $\theta_c(k \to \infty)$ is very sensitive to the lattice connectivity, being $\theta_c(k \to \infty) = c/(3c - 4)$ (= 3/5, 1/2 and 3/7 for honeycomb, square and triangular lattices, respectively).

On the other hand, when the NN couplings are introduced by BWA, while FSTA curves vary slightly with connectivity for small values of k, EA data do not show dependence of θ_c on c. In all cases, the curves exhibit a monotonic decrease up to $k \approx 50$, followed by a constant value for larger values of k, being $\theta_c(k \to \infty) = 1/3$. This limit value does not depend on neither the lattice geometry nor the approximation used to calculate the factor γ.

In the case of GD (Fig. 7) and FH (inset of Fig. 7), the curves decrease with k and tend to zero for larger k-mer sizes. This is the main difference with the results reported in Fig. 6: while $\theta_c(k \to \infty)$ is a constant non-zero value for EA and FSTA, $\theta_c(k \to \infty) = 0$ for GD and FH.

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[2] A great deal of work has been done on checking the predictions of the BWA theory against experimental results, the theory being completely satisfactory in a qualitative, or semi-quantitative way. A comprehensive discussion on this subject is included in the book of Des Cloiseaux and Janninck (1990). There is no doubt that this simple theory contains the essential features which distinguish interacting adsorbates from non-interacting ad-molecules.
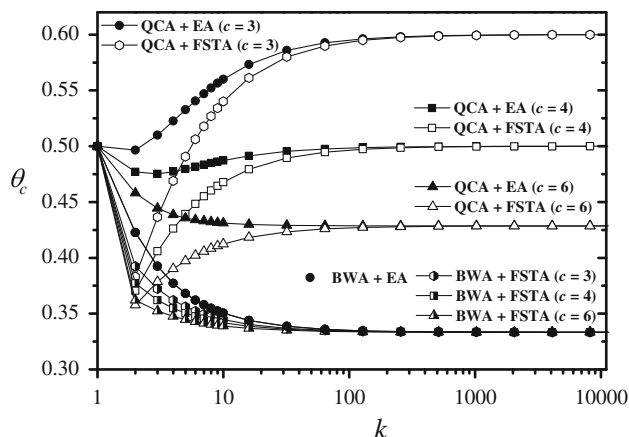
Fig. 6 Dependence of θ_c on k for γ obtained from EA [Eq. (10)] and FSTA [Eq. (11)]. The lateral interactions have been incorporated via QCA and BWA. The symbology is indicated in the figure
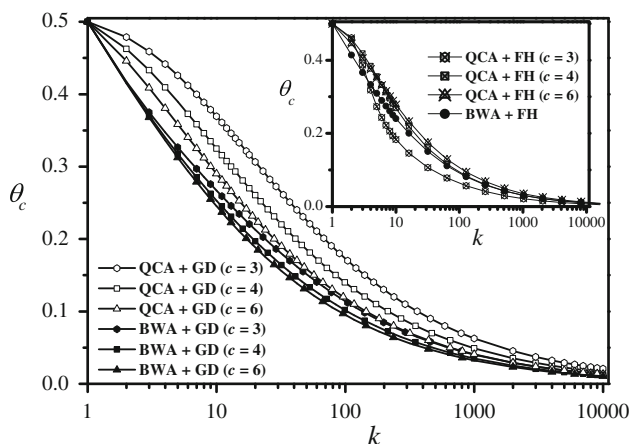

Fig. 8 Dependence of T_c^* on k for the same cases shown in Fig. 6. The symbology is indicated in the figure

Fig. 7 Same as Fig. 7 for γ from GD [Eq. (7)] and FH [Eq. (6)]

To conclude with the analysis of Fig. 7, it is interesting to note that FH data do not depend on connectivity when the lateral interactions are introduced by BWA.

We now analyze the behavior of T_c^* as a function of k. Figure 8 shows the results corresponding to EA and FSTA. As it can be observed, all curves behave in a similar way showing a linear dependence on k in almost all range of values of the k-mer size ($k > 10$). In addition, the theoretical data only depend on connectivity, being not sensitive to the factor γ and the manner to incorporate lateral interactions. The situation is different when GD and FH equations are used (Fig. 9). In this case, T_c^* increases with k up to a certain point and thereafter it tends to a saturation value for larger sizes k. In addition, the results not only depend on connectivity (as occurred with the data in Fig. 8), but also depends on γ and the methodology to introduce lateral interactions.

In order to test the theoretical results, T_c^* was obtained by MC simulation. For this purpose, a typical adsorption-desorption algorithm was used. The procedure is as
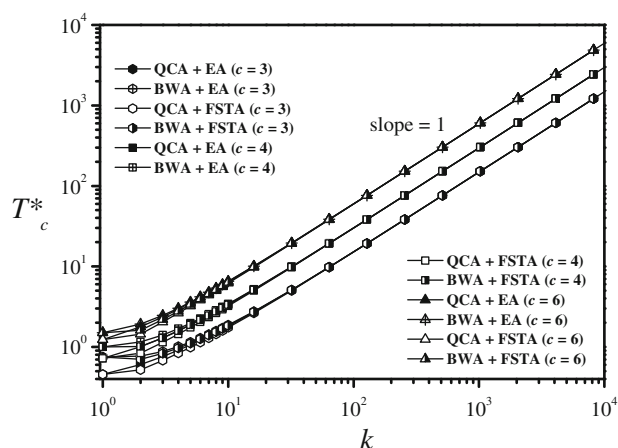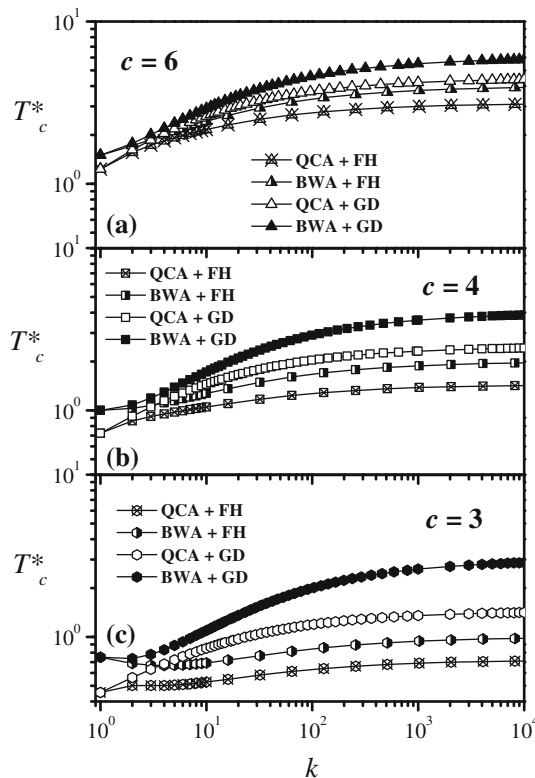

Fig. 9 Dependence of T_c^* on k for the same cases shown in Fig. 7. **a** Triangular lattices. **b** Square lattices. **c** Honeycomb lattices. The symbology is indicated in the figure

follows. Once the value of the chemical potential μ is set, a linear k-uple of NN sites is chosen at random and an attempt is made to change its occupancy state with probability $W = \min\{1, \exp(-\beta\Delta H)\}$ is the transition probability given by the Metropolis rule (Metropolis et al. 1953), where $\Delta H = H_f - H_i$ is the difference between the Hamiltonians of the final and initial states. In addition,

displacement (diffusional relaxation) of adparticles to NN 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. A MC step is achieved when M k-uples of sites have been tested to change its occupancy state. Typically, the equilibrium state can be well reproduced after discarding the first $r_0 = 10^7$ MCs. Then, the next $r = 2 \times 10^7$ MCs are used to compute averages. In our MC simulations, we varied the chemical potential μ and monitored the density θ, which can be calculated as simple averages.

As shown in Fig. 1, the phase transition occurring in the system can be clearly visualized in the behavior of the adsorption isotherms. Thus, a good estimate of T_c^* can be obtained by looking at the temperature where the adsorption isotherm is vertical at intermediate concentrations[3]. This procedure was performed for k-mer sizes ranging between $k = 3$ and $k = 10$ and square lattices of $L \times L$ adsorptive sites, with $L/k = 40$ and periodic boundary conditions[4]. With this size of the lattice, it has been verified that finite size effects are negligible (Linares et al. 2008; Longone et al. 2010, 2012). The simulation results are shown in Fig. 10a. The points corresponding to $k = 1$ (full circle) and $k = 2$ (full square) were previously reported in the literature (Onsager 1944; Ramirez-Pastor et al. 1998).

As mentioned above, the adsorbed k-mers are distributed in compact islands at low temperatures and, as the k-mer's size increases, the low-temperature phase is energetically more stable, so the critical temperature is shifted to higher value. This hypothesis is corroborated by the simulation data, which behave as a increasing function of k ($T_c^* \propto k^{0.4}$).

The differences between simulated and theoretical results (see Fig. 10b) can be very easily rationalized with the help of the total relative error ε, which is defined as

$$\varepsilon = \frac{1}{N_k} \sum_{k=1}^{N_k} \left| \frac{T_{c,sim}^* - T_{c,appr}^*}{T_{c,sim}^*} \right|_k, \tag{16}$$

where $T_{c,sim}^*$ ($T_{c,appr}^*$) represents the critical temperature obtained by using the MC simulation (analytical approach). Each pair of values ($T_{c,sim}^*$, $T_{c,appr}^*$) is obtained at fixed k. N_k is the number of values of k used in the comparison (in the present case, $N_k = 10$).

The behavior of ε for the different approximations discussed here is shown in the bar graph of Fig. 10c. From left to right, the meaning of each bar is as follows: first bar, QCA and FH; second bar, BWA and FH; third bar, QCA and GD; fourth bar, BWA and GD; fifth bar, QCA and
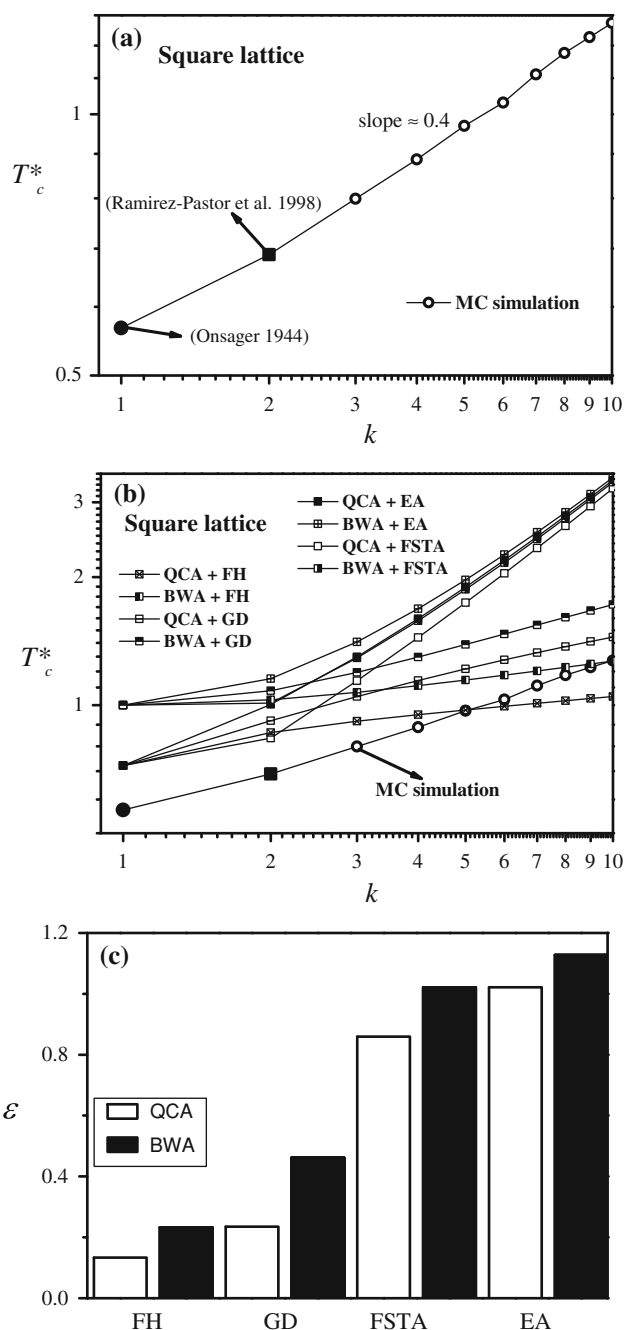
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[3] A more exact determination of T_c^* based on finite-size scaling theory will be the object of future studies.

[4] As is well-known, the relaxation time increases very quickly as the k-mer size increases and, consequently, MC simulations for large adsorbates are very time-consuming.

Fig. 10 **a** Simulation results for T_c^* vs k and $c = 4$. **b** Comparison between theoretical and simulation results. **c** Total relative error [Eq. (16)] for the different theoretical approximations discussed in the present work. The symbology is indicated in the figure

FSTA; sixth bar, BWA and FSTA; seventh bar, QCA and EA; and eighth bar, BWA and EA. The analysis of the results can be separated into two aspects. The first aspect refers to the way of introducing the lateral interactions between the ad-particles. As it can be observed in the figure, the counting procedure of the QCA (open bars) allows to obtain an approximation that is significantly better than the BWA (solid bars). The second aspect refers

to the calculation of the factor γ. In this sense, FH and GD provide more accurate results than those obtained from FSTA and EA. The assumption of independence of sites used to calculate the parameters K (EA) and g (FSTA) is the main cause of error in the FSTA and EA data.

The limited range of values of k explored in Fig. 10 does not allow to draw definitive conclusions about the behavior of T_c for $k \to \infty$. In order to solve this problem, future efforts will be directed to extend the computational analysis to large adsorbates.

5 Conclusions

In this paper, the phase behavior of attractive k-mers on two-dimensional lattices has been addressed. The results were obtained by theoretical analysis, based on a generalization of the quasi-chemical approximation for interacting polyatomic adsorbates and comparisons with analytical data from Bragg-Williams approach.

Besides considering the lateral couplings between the adparticles, the main thermodynamic functions were explicitly written in terms of the configurational $\Omega(N, M)$, which represents the number of ways to arrange N k-mers on M sites for the non-interacting problem. Accordingly, the study presented here allowed us not only to analyze the effect of introducing the lateral interactions by following the configuration-counting procedure of the QCA, but also to discuss the consequences of choosing the configurational factor associated to adsorption of non-interacting k-mers from the main models developed to treat the multisite occupancy adsorption problem (EA, FSTA, GD and FH).

The results obtained revealed that, for temperatures below a certain condensation temperature, the system undergoes a first-order phase transition which is observed in the clear discontinuity in the adsorption isotherms. Based on these findings, the main properties characterizing the phase behavior of the system were calculated. The conclusions of this study are briefly summarized here as follows.

- As the γ factor is chosen from EA and FSTA, the behavior of θ_c as a function of k strongly depends on the procedure used to incorporate the lateral couplings. In the case of QCA, notorious differences are observed between EA and FSTA data for small values of k ($k < 50$). As k is increased, EA and FSTA results coincide and θ_c tends to a saturation value $\theta_c(k \to \infty) = c/(3c - 4)$. On the other hand, when the NN couplings are introduced by BWA, while FSTA curves vary slightly with connectivity for small values of k, EA data do not show dependence of θ_c on c. In all cases, the curves exhibit a monotonic decrease up to

$k \approx 50$, followed by a constant value for larger values of k, being $\theta_c(k \to \infty) = 1/3$. This limit value does not depend on neither the lattice geometry nor the approximation used to calculate the factor γ.

- As the γ factor is chosen from GD and FH, θ_c decreases with k and tends to zero for larger k-mer sizes. This is the main difference with the results obtained from EA and FSTA: while $\theta_c(k \to \infty)$ is a constant non-zero value for EA and FSTA, $\theta_c(k \to \infty) = 0$ for GD and FH.

- As the γ factor is chosen from EA and FSTA, T_c shows a linear dependence on k in almost all range of values of the k-mer size ($k > 10$). In addition, the theoretical data only depend on connectivity, being not sensitive to the factor γ and the manner to incorporate lateral interactions.

- As the γ factor is chosen from GD and FH, T_c^* increases with k up to a certain point and thereafter it tends to a saturation value for larger sizes k. In addition, the results not only depend on connectivity (as occurred with the data obtained from EA and FSTA), but also depends on γ and the methodology to introduce lateral interactions.

- Preliminary MC simulation analysis, in a limited range of k-mer sizes ($k \leq 10$), would seem to show that T_c^* increases in all the range of k. A simple explanation for this behavior is the following: below the transition temperature, the adsorbed k-mers are distributed in compact islands. Then, to take a k-mer out of a condensed island one needs an energy equivalent to $[2(c - 1) + (k - 2)(c - 2)]w$. Accordingly, the low-temperature structure is energetically more stable as the k-mer size and the number of NNs increases and the transition temperature is shifted to a higher value.

On the other hand, the comparison between simulated and theoretical data indicates that (i) the QCA behaves significantly better than the BWA and (ii) FH and GD provide more accurate values of T_c than those obtained from FSTA and EA.

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