

## Accepted Manuscript

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PII: S0378-4371(17)31308-0  
DOI: <https://doi.org/10.1016/j.physa.2017.12.065>  
Reference: PHYSA 18995

To appear in: *Physica A*

Received date: 27 October 2017  
Revised date: 1 December 2017

Please cite this article as: G.J. dos Santos, D.H. Linares, A.J. Ramirez-Pastor, Statistical thermodynamics of aligned rigid rods with attractive lateral interactions: Theory and Monte Carlo simulations, *Physica A* (2017), <https://doi.org/10.1016/j.physa.2017.12.065>

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**Statistical thermodynamics of aligned rigid rods with attractive lateral interactions: Theory and Monte Carlo simulations**

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**Highlights**

- > The phase behavior of aligned rigid rods on a square lattice is studied. > Monte Carlo simulations and histogram reweighting technique were applied.
- > A new theoretical approach (Nematic Mean Field approximation) was presented. > The transition temperature and coverage were obtained as a function of the rod size.

# Statistical thermodynamics of aligned rigid rods with attractive lateral interactions: Theory and Monte Carlo simulations

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## Abstract

The phase behavior of aligned rigid rods of length  $k$  ( $k$ -mers) adsorbed on two-dimensional square lattices has been studied by Monte Carlo (MC) simulations and histogram reweighting technique. The  $k$ -mers, containing  $k$  identical units (each one occupying a lattice site) were deposited along one of the directions of the lattice. In addition, attractive lateral interactions were considered. The methodology was applied, particularly, to the study of the critical point of the condensation transition occurring in the system. The process was monitored by following the fourth order Binder cumulant as a function of temperature for different lattice sizes. The results, obtained for  $k$  ranging from 2 to 7, show that: (i) the transition coverage exhibits a decreasing behaviour when it is plotted as a function of the  $k$ -mer size and (ii) the transition temperature,  $T_c$ , exhibits a power law dependence on  $k$ ,  $T_c \sim k^{0.4}$ , shifting to higher values as  $k$  increases. Comparisons with an analytical model based on a generalization of the Bragg-Williams approximation (BWA) were performed in order to support the simulation technique. A significant qualitative agreement was obtained between BWA and MC results.

*Key words:* Statistical mechanics of model systems, Adsorption, Multisite-Occupancy, Phase transitions, Monte Carlo methods

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## 1 Introduction

The study of systems of hard nonspherical particles is one of the central problems in statistical mechanics, and it has attracted the attention of researchers for several decades [1–26]. In this framework, many authors have focused their investigations on monolayer films of large particles formed on uniform surfaces, and especially on the adsorption properties of these systems [1–16].

Despite the large number of contributions in the field of lattice-gas models and extended adsorbates or  $k$ -mers (particles occupying  $k$  contiguous lattice sites), there are many aspects of the problem which have not yet been completely solved. In fact, most studies have been devoted to adsorption of non-interacting particles; however, if some type of adsorbate-adsorbate interaction exists, the statistical problem becomes extremely difficult. Thus, an exact statistical mechanical treatment, including lateral interactions and adsorption with multisite occupancy, is unfortunately not yet available.

One way of overcoming these drawbacks complications is to use the Monte Carlo (MC) simulation method [27–46] and approximations such as Bragg-Williams approximation (BWA) [47]. MC technique is a valuable tool for studying surface molecular processes, which has been extensively used to simulate many surface phenomena including phase transitions [27–42], adsorption [43–45], diffusion [46], among others. Here we will try to demonstrate that numerical simulations, combined with a correct theoretical interpretation of the results, can be very useful to obtain a very reasonable description of the adsorption of interacting  $k$ -mers on two-dimensional (2D) lattices.

In this line of work, a new methodology based on a combination of the histogram reweighting technique [48–50] and on the fourth order Binder cumulant [51] was developed in a recent article from our research group [52]. The technique, which will be called “Maximum Cumulant Method” (MCM), was applied to the study of the phase transition occurring in a system of attractive dimers<sup>2</sup> adsorbed on 2D square lattices.

The method introduced in Ref. [52] proved to be a very useful tool for the research of phase transitions in lattice-gas models. In the present paper, this scheme is applied to the study of the phase behavior of attractive  $k$ -mers adsorbed on square lattices in the presence of anisotropy. To simulate the effect of the anisotropy, the  $k$ -mers were deposited along one of the directions of the lattice, forming a nematic phase as depicted in Fig. 1. Under these conditions, the dependence of the critical point (temperature-coverage) on the size  $k$  ( $2 \leq k \leq 7$ ) was determined for the first time.

<sup>2</sup> The dimer is the simplest case of a polyatomic adsorbate and contains all the properties of the multisite occupancy adsorption.

In order to back up the simulation results, an analytical approximation was developed on a generalization in line with the lattice-gas model and the classical Bragg-Williams approximation (BWA). The new theoretical framework is obtained by combining (i) the exact analytical expression for the Helmholtz free energy function of interacting linear  $k$ -mers adsorbed in one dimension and its extension to higher dimensions, with (ii) a generalization of BWA to introduce the effect of the nearest-neighbour (NN) interactions in the two-dimensional (2D) system. Theoretical and simulation results were compared, showing a good qualitative agreement.

The study developed here is a natural continuation of our previous paper [52], and also contributes to the comprehension of some essential characteristics of the phase transitions occurring in adsorbed monolayer films by means of a very simple model. It is well-known, that the model of a two-dimensional gas of rigid  $k$ -mers is the simplest representation of a strongly adsorbed film of linear molecules in submonolayer or monolayer regime. Examples of this kind of systems are monolayer films of  $n$ -alkanes adsorbed on monocrystalline surfaces of metals, such as Pt(111) [53] and Au(111) [54,55].

This paper is organized as follows: the lattice-gas model, the MC simulation scheme and the results obtained from the simulations are presented in Sec. 2. In Sec. 3 we present the analytical approximation (Nematic Mean Field approximation) and we compare the MC results with the theoretical calculations. Finally, the general conclusions are given in Sec 4.

## 2 Lattice-gas model and simulation scheme

### 2.1 The model

In this section, the lattice-gas model for the adsorption of straight rigid rods of length  $k$  ( $k$ -mers) is described. The surface is represented as a 2D square lattice of  $M = L \times L$  adsorptive sites with periodic boundary conditions. The  $k$ -mers are adsorbed on the lattice with the following restrictions: (1) the depositing objects contain  $k$  identical units and each unit occupies a lattice site. Small adsorbates with spherical symmetry correspond to the monomer limit ( $k = 1$ ); (2) the distance between  $k$ -mer units is assumed to be equal to the lattice constant, hence exactly  $k$  sites are occupied by a  $k$ -mer when adsorbed; (3) the  $k$ -mers are deposited along one preferential direction in the lattice, forming a nematic phase (as depicted in Fig. 1); and (4) the energy involved in the adsorption of each  $k$ -mer unit is smaller than the bond energy between the  $k$  units. Thus, molecules are adsorbed or desorbed as one unit neglecting any possible dissociation.

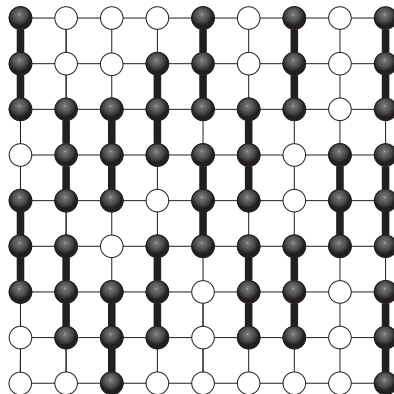


Fig. 1. Lattice-gas model for aligned trimers  $k = 3$ . The surface is modelled by a square array of  $M = L \times L$  adsorptive sites and each adsorbed  $k$ -mer will occupy  $k$  consecutive lattice sites. Full and empty circles represent the  $k$ -mer units and empty sites, respectively.

In order to describe a system of  $N$   $k$ -mers adsorbed on  $M$  lattice sites at a given temperature  $T$  and chemical potential  $\mu$ , the occupation variable  $c_j$  was introduced ( $c_j = 0$  or  $1$ , if the site  $j$  is empty or occupied by a  $k$ -mer unit, respectively). Then the adsorbed phase can be described by the following Hamiltonian:

$$H = w \sum_{\langle i,j \rangle} c_i c_j - N(k-1)w + \epsilon_0 \sum_i c_i, \quad (1)$$

where  $w$  is the nearest-neighbour (NN) interaction energy which is assumed to be attractive (negative);  $\langle i, j \rangle$  represents pairs of NN sites and  $\epsilon_0$  is the adsorption energy of one lattice site. The energies  $w$  and  $\epsilon_0$  will be measured in  $(k_B T)$  units where  $k_B$  is the Boltzmann's constant. 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. In the simulations, given the surface homogeneity,  $\epsilon_0$  is set equal to zero without any loss of generality.

## 2.2 Monte Carlo simulation scheme

The thermodynamic equilibrium is reached in the grand canonical ensemble by using the parallel tempering MC simulation method [56–58].

This simulation scheme is based on the parallelization of the computational calculation through several replicas of the system under study, allowing it to reach equilibrium faster than standard Metropolis Monte Carlo. The methodology is specially effective to unblock “freezing” states of the system by swapping the configurations of two adjacent replicas every certain number of simulation steps. This particular algorithm generates a set of  $N_{rep}$  different replicas of the same system where each one has a different value of the

chemical potential  $\mu$ . First, one of the  $N_{rep}$  replicas is selected randomly along with a linear  $k$ -uple (a set of  $k$  consecutive lattice sites) belonging to that particular replica of the system. If the selected  $k$ -uple is empty, a  $k$ -mer is adsorbed with probability  $P_{ads} = \min\{1, \exp(-\Delta H/k_B T + \mu\Delta N/k_B T)\}$  where  $\Delta H$  is the difference between the Hamiltonians of the initial and final states and  $\Delta N$  is the difference in the number of adsorbed molecules. On the other hand, if the  $k$ -uple is full, the  $k$ -mer is desorbed with probability  $P_{des} = \min\{1, \exp(-\Delta H/k_B T - \mu\Delta N/k_B T)\}$ . This adsorption-desorption sequence is repeated  $M = L \times L$  times and then a replica exchange step is followed: the configurations of two adjacent replicas is swapped with probability  $P = \min\{1, \exp(-\Delta N\Delta\mu)\}$ , where  $\Delta N$  is the difference in the number of molecules and  $\Delta\mu$  is the difference in chemical potential between the two interchanging replicas.

A MC step (MCS) is defined as  $L \times L$  adsorption-desorption steps per each replica, then  $MCS = L \times L \times N_{rep}$ . Each replica starts from a randomly generated initial configuration and the simulations were run with  $r = 4 \times 10^6$  MCS. It was tested that the first  $2 \times 10^6$  MCS were sufficient to reach equilibrium and the next  $2 \times 10^6$  MCS were used to compute averages. The linear dimensions of the systems  $L$  employed in the simulations depend on the size of the  $k$ -mer ( $k$ ). Typically the sizes of the lattices simulated were  $L = 10 \times k, 15 \times k, 20 \times k, \dots, 50 \times k$  and the number of replicas was set to  $N_{rep} = 100$ .

Typical quantities monitored in the simulations are the surface coverage  $\theta$  ( $\theta = kN/M$ ) and energy per site,  $u$ , which are calculated as simple averages,

$$\theta = \frac{1}{M} \sum_i^M \langle c_i \rangle, \quad (2)$$

$$u = \frac{1}{M} \langle H \rangle, \quad (3)$$

where  $\langle \dots \rangle$  means time average over the MC simulation.

In addition, bi-dimensional histograms  $W(H, N)$  are constructed for each value of  $\mu$  in every single temperature simulation. The histograms are needed to apply the MCM [52] in order to obtain the temperature of the condensation transition. Under this framework, the fourth order Binder cumulant  $U_L$  is obtained with the aid of the Histogram Reweighting (HR) technique,

$$\langle U \rangle_L = 1 - \frac{\langle m \rangle^4}{3\langle m^2 \rangle^2}, \quad (4)$$

where  $m = \theta - \langle \theta \rangle$  is the standard order parameter for liquid-vapor transitions.

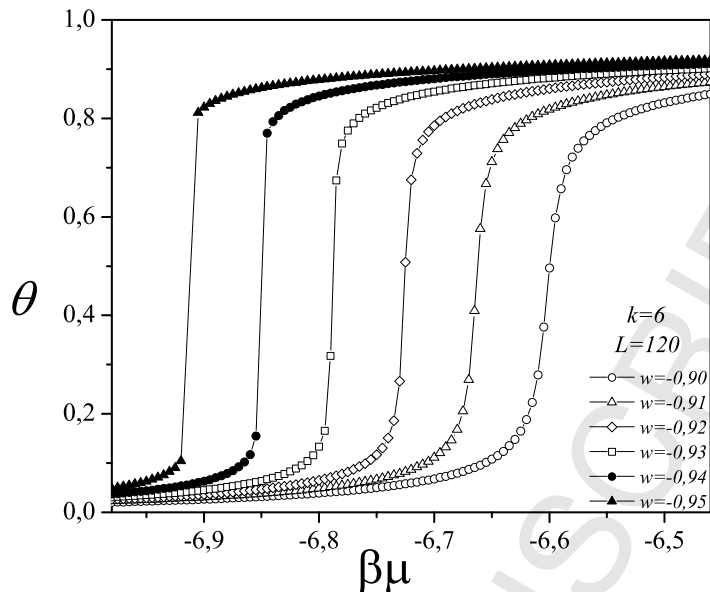


Fig. 2. MC adsorption isotherms for  $k = 6$  on a square lattice of size  $M = 120 \times 120$  for different values of  $w$ . It can be seen the typical behaviour of the isotherm when the system experiences a first order phase transition for  $w < -0.93$ .

In order to obtain the phase diagram, the two-state approximation was used [59] along with the HR technique. From a bi-dimensional histogram  $W(H, N)$  obtained from the simulations for a given temperature and with the aid of the HR technique, the chemical potential is tuned until the resultant histogram is one such that the areas under the two peaks are equal. The coverage values for which the maximums of the two peaks occur are the two coexistence points of the phase diagram for that precise temperature. This procedure is described in further detail in [52].

### 2.3 Simulation results

MC calculations have been developed for straight, rigid and aligned  $k$ -mers with  $k$  ranging from 2 to 7. First, we will analyse the results regarding the properties of the equilibrium adsorption isotherms obtained directly from the simulations for fixed  $k$  and different lateral interaction energies, as shown in Fig. 2.

As  $w$  increases, the isotherms become steeper and the typical discontinuity that characterize the first order condensation transition becomes more noticeable. As expected, higher attractive interactions (lower temperatures) favour the condensation transition.

As is known, this condensation-evaporation transition is characterized by a low-density phase or “lattice-gas” phase at low surface coverage, separated



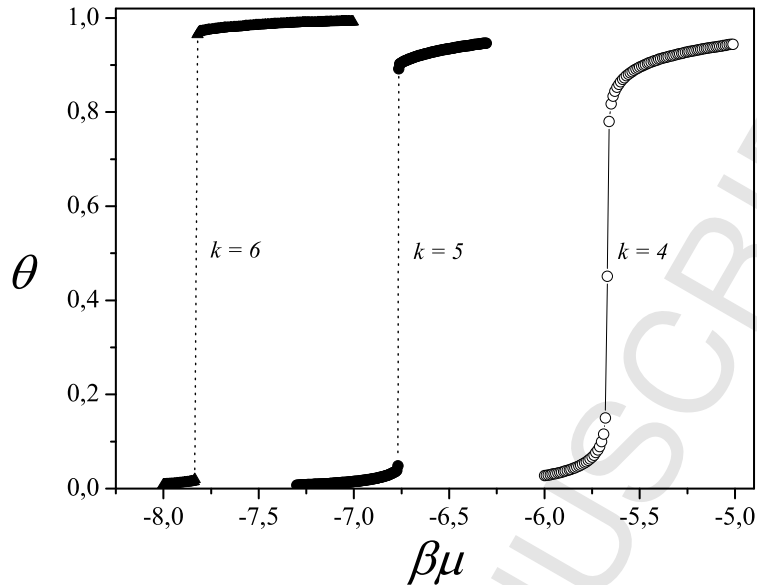


Fig. 3. Simulation isotherms for fixed interaction energy  $w = -1.1$  and different  $k$ -mer sizes ( $k = 4, 5, 6$ ), as indicated in the figure.

from a high-density or “lattice-liquid” phase at higher coverage values. This transition has been observed in several experimental systems [60,45] and also in theoretical calculations based on Transfer-Matrix calculations [61].

The behaviour of the adsorption isotherms when  $k$  is varied is shown in Fig. 3. For fixed  $w$ , the isotherms become steeper and the discontinuity is enlarged when  $k$  increases. From this behaviour, it is clear that the critical interaction energy  $w_c$  shifts to less negative values (less attractive interactions) as the size of the  $k$ -mers increases. It is worth remembering that the critical interaction energy and the transition temperature are related according to:  $w_c = 1/T_c$  ( $k_B = 1$ ). Furthermore, the isotherms shift to lower values of the chemical potential (to the left) when  $k$  increases since larger molecules with attractive interactions will favour the adsorption.

Next, we will discuss the behaviour of the interaction energy  $w_c$  as a function of the  $k$ -mer size. The resulting fourth order Binder cumulant ( $U_L$ ) curves, obtained from MCM, are exhibited in Fig. 4. As an example, the figure shows the intersection plots for  $k = 3$  (Fig. 4 (a)) and  $k = 4$  (Fig. 4 (b)) where a precise and well located intersection point can be observed. This procedure is repeated for  $k$ -mers ranging between 2-7 and the results are presented in Table 1 and in Fig. 5.

As expected, the critical interaction energy shifts to less attractive values as  $k$  increases (Fig. 5 (a)). This plot confirms the observation related to the beha-

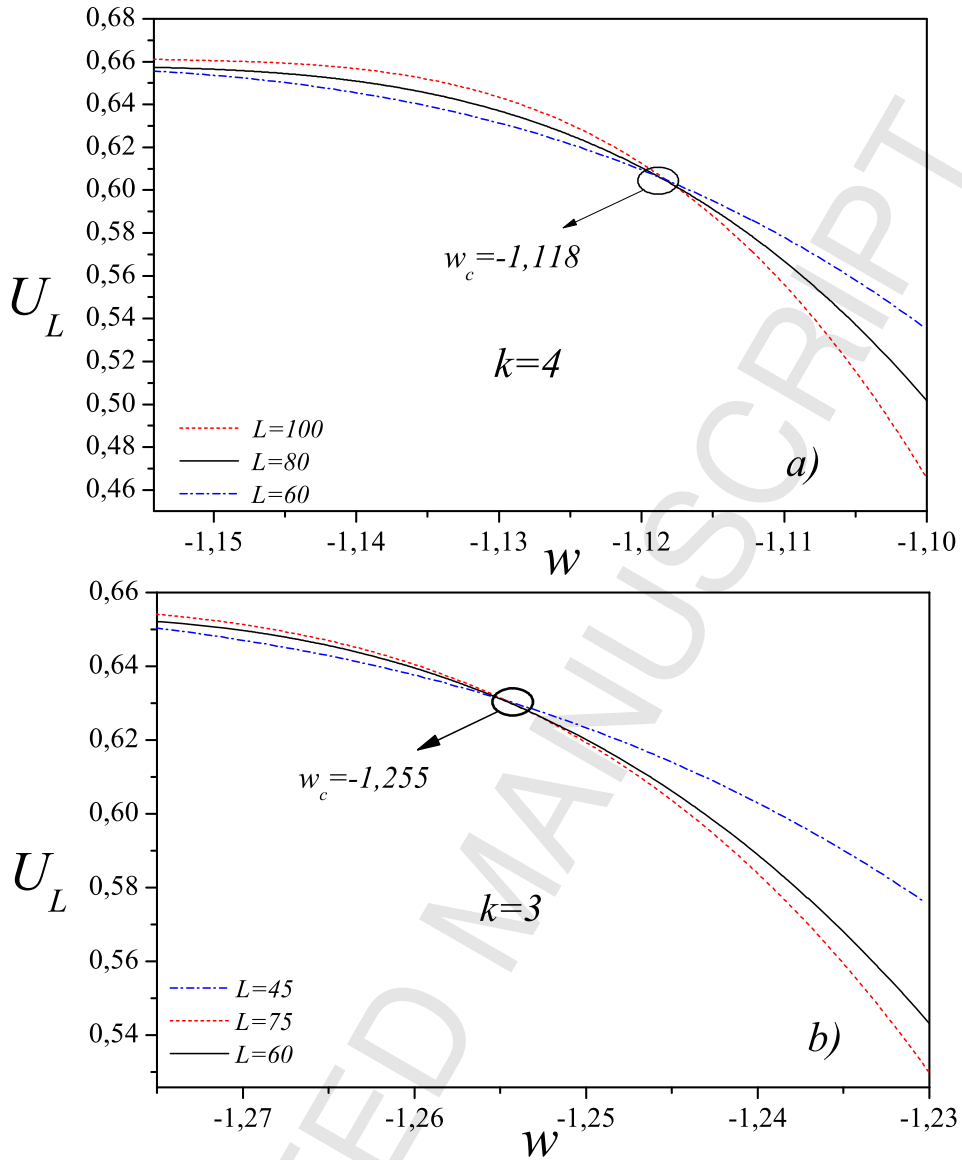


Fig. 4. Intersection plot of the fourth order Binder cumulants for tetramers ( $k = 4$ ) (a) and trimers ( $k = 3$ ) in (b). The interaction energies found  $w_c = -1,118$  for  $k = 4$  and  $w_c = -1,255$  for  $k = 3$ , are related to the transition temperatures by  $T_c = 1/w_c = 0.894$  ( $k = 4$ ) and  $T_c = 1/w_c = 0,796$  ( $k = 3$ ).

viour of the isotherms in Fig. 3. A rather simple explanation of this behaviour is the following: in the “condensed” phase the molecules are adsorbed forming compact islands. As the size of the molecules increases (as  $k$  increases), this phase becomes more and more stable, thus less energy is needed to form this “condensed” phase and as a consequence, the critical interaction energy shifts to less attractive values. Therefore, the transition temperature  $T_c$  increases with  $k$ . In addition, a power law behaviour was found for the transition temperature as a function of the  $k$ -mer size ( $T_c \sim k^{0,4}$ ) and it is shown in the logarithmic plot of Fig. 5 (b). This functionality is the same as the one found

$k$	$w_c$	$T_c$	$\theta_c$
2	-1,44	0,694	0,485
3	-1,255	0,796	0,465
4	-1,118	0,894	0,457
5	-1,01	0,99	0,452
6	-0,94	1,064	0,448
7	-0,88	1,136	0,445

Table 1

Transition temperature  $T_c$ , interaction energy  $w_c$  and transition coverage  $\theta_c$  for different values of  $k$  ranging from 2 to 7. The data for the temperature and the interaction were obtained from the intersection plot of  $U_L$  according to the MCM. The transition coverage is obtained from the location of the inflection point in the critical isotherm.

for the isotropic (non-restricted) case [62].

The transition coverage  $\theta_c$  is obtained from the location of the inflexion point of the critical isotherm as detailed in [52]. In Fig. 6, the transition coverage is plotted as a function of the  $k$ -mer size. It is known that in a system of attractive monomers,  $k = 1$  (exactly solvable), the transition coverage is  $\theta_c = 0,5$  due to symmetry arguments. For  $k = 2$  and larger  $k$ -mers this particle-vacancy symmetry is broken and it is expected that the transition coverage shifts to lower values. Figure 6 confirms this statement showing that the transition coverage is a decreasing function of the  $k$ -mer size, since the condensed phase is energetically more stable for larger molecules.

Finally, the temperature-coverage phase diagrams obtained from the MC simulations and the two-state approximation can be observed in Fig. 7. The figure shows the phase diagrams for  $k = 5, 6, 7$  where the coexisting line defines the boundary among the lattice-gas (diluted phase) at low coverage, the two-phase region at intermediate coverage, and the condensed phase (lattice-fluid) at higher concentrations where the adsorbate segregates in compact islands. As can be seen, the condensed phase is reinforced with the size of the  $k$ -mer, which results in an increase of the maximum of the coexistence curve for larger values of  $k$ .

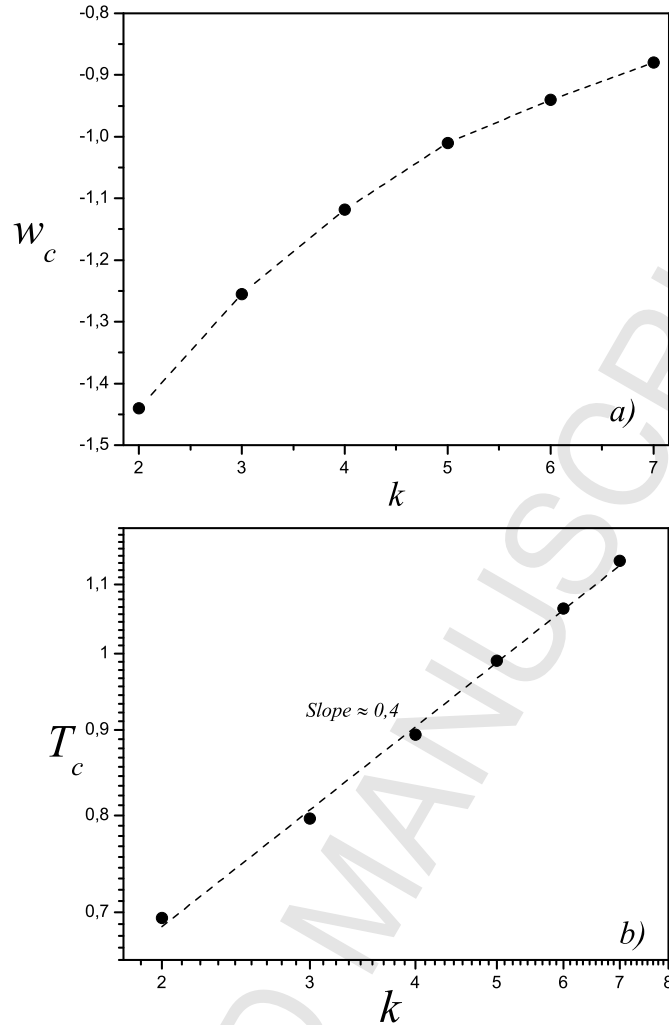


Fig. 5. Simulation results for the critical interaction energy  $w_c$  as a function of the  $k$ -mer size ( $k$ ) are shown in part (a). In (b) the transition temperature  $T_c$  is plotted (in logarithmic units) as a function of  $k$ .

### 3 ANALYTICAL APPROXIMATION AND COMPARISON BETWEEN THEORETICAL AND SIMULATED RESULTS

#### 3.1 Nematic Mean Field (NMF) approximation

In this section, we will introduce an analytical approximation developed for the nematic phase of an interacting  $k$ -mers system adsorbed on 2D lattices. We will consider the special case of  $N$   $k$ -mers adsorbing on a square lattice of  $M = L \times L$  sites, parallel to each other in only one preferential orientation and with nearest-neighbour interaction energy  $w$ . This approximation will allow us to obtain an expression for the nematic free energy per site  $f_{nem}$  for this system. Firstly we will focus on a comparison between a one-dimensional (1D)

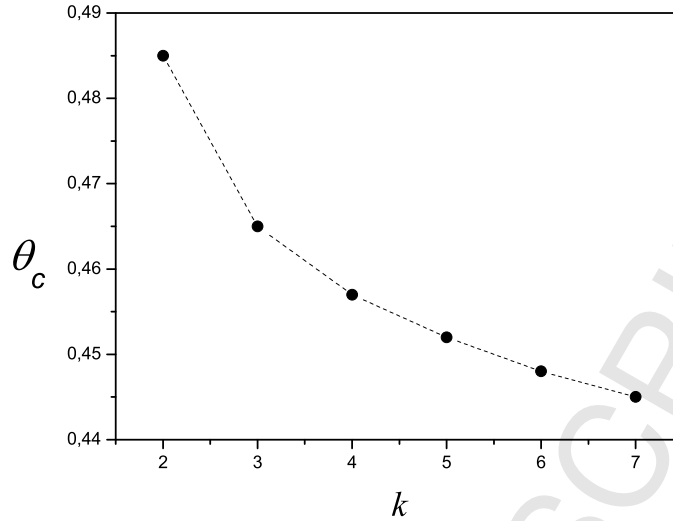


Fig. 6. Simulation results for the transition coverage  $\theta_c$  for different values of  $k$  ranging between 2 and 7.

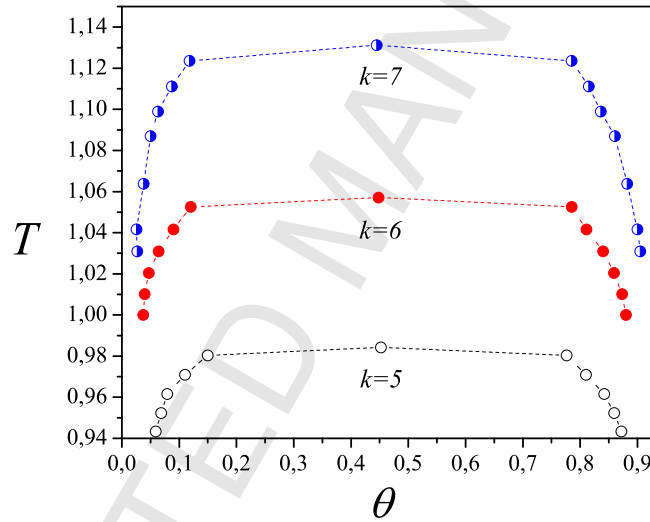


Fig. 7. MC phase diagrams obtained for  $k = 5, 6, 7$ . The symbology is indicated in the figure.

system and a 2D nematic system of adsorbed  $k$ -mers, both without interaction ( $w = 0$ ). In this case, the 2D nematic system can be thought of as a collection of several 1D systems; and consequently, the entropy per site ( $s = S/M$ ) must be equal in both systems  $s_{1D(w=0)} = s_{nem(w=0)}$  (Fig.8).

When the lateral interactions between  $k$ -mers are present, the previous equality is no longer valid. Nevertheless, it is still a good approximation to consider that  $s_{1D} = s_{nem}$  only for small interactions. This is the central assumption in the development of this analytical approximation:

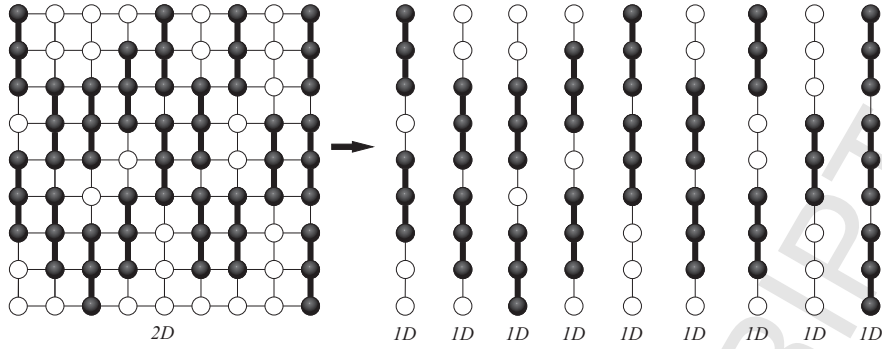


Fig. 8. Schematic representation of a 2D nematic system and a collection of several 1D system of adsorbed  $k$ -mers (trimers in the case of the figure,  $k=3$ ). In the absence of interactions between adsorbates, the 2D nematic system is equivalent to a collection of 1D system (in terms of entropy per site)

$$s_{1D} \approx s_{nem} \quad \text{for small } w. \quad (5)$$

As is known, the 1D system of interacting  $k$ -mers (nearest-neighbour interactions) can be solved exactly [63] and the expression for the Helmholtz free energy per site is given by,

$$\begin{aligned} \beta f_{1D} = & \beta w \left( \frac{\theta}{k} - \alpha \right) - \frac{\theta}{k} \ln \left( \frac{\theta}{k} \right) - (1 - \theta) \ln(1 - \theta) + 2\alpha \ln(\alpha) \\ & + \left( \frac{\theta}{k} - \alpha \right) \ln \left( \frac{\theta}{k} - \alpha \right) + (1 - \theta - \alpha) \ln(1 - \theta - \alpha) + \beta \theta U_0, \end{aligned} \quad (6)$$

where,

$$\alpha = \frac{2\theta(1 - \theta)}{k \left[ 1 - \left( \frac{k-1}{k} \right) \theta + b \right]}, \quad (7)$$

and

$$b = \left\{ \left[ 1 - \left( \frac{k-1}{k} \right) \theta \right]^2 - \frac{4A}{k} (\theta - \theta^2) \right\}^{1/2}. \quad (8)$$

On the other hand, from the thermodynamic definition, the Helmholtz free energy per site for the 2D nematic phase is given by,

$$\beta f_{nem} = \beta u_{nem} - \frac{s_{nem}}{k_B}, \quad (9)$$

where  $u_{nem}$  and  $s_{nem}$  are the total energy per site and the entropy per site of the nematic phase in two dimensions respectively. Next, we apply the main assumption of this approximation given by Eq. (5), rewriting the previous equation for the nematic free energy as,

$$\beta f_{nem} \cong \beta u_{nem} - \frac{s_{1D}}{k_B}. \quad (10)$$

From the definition of the Helmholtz free energy per site for the 1D case ( $\beta f_{1D} = \beta u_{1D} - \frac{s_{1D}}{k_B}$ ) we can write  $f_{nem}$  in the following way,

$$\beta f_{nem} \cong \beta (u_{nem} - u_{1D}) + \beta f_{1D}. \quad (11)$$

As can be seen, we have reached an expression for the nematic free energy in 2D consisting in an energy term ( $u_{nem} - u_{1D}$ ) and an exact term  $f_{1D}$  ( $f_{1D}$  is given by Eq. (6)). This energetic term is the difference between the total energy per site of the 2D nematic phase and the total energy per site of the 1D system. In the 1D system, it is easy to identify the components of this energy: those are the energy between the surface (or the lattice) and the adsorbate, and the other component is the interaction energy between the end segments of neighbouring  $k$ -mers. The energy in the 2D nematic phase has also the contribution of the surface-adsorbate interaction and the one corresponding to the interaction between neighboring  $k$ -mers. The latter can be, in turn, subdivided into two different interactions: The one between the end segments of the  $k$ -mers (just like in 1D) and the lateral interaction between the central segments of these adsorbates. Following the previous reasoning and looking at Fig. 9, it is clear that the energy term of Eq. (11) ( $u_{nem} - u_{1D}$ ) represents only the lateral energy between the central segments of the adsorbed  $k$ -mers.

Taking this into account, we will calculate this term with the aid of the Mean Field approximation or BWA. Under the framework of this approximation the mean interaction energy can be calculated as  $\bar{N}_{11}w$  where  $\bar{N}_{11}$  represents the mean number of pairs of nearest-neighbour occupied sites on the lattice and  $w$  stands for the interaction energy between each neighbouring segment of different  $k$ -mers. The average number of pairs of occupied sites  $\bar{N}_{11}$  can be calculated as,

$$\bar{N}_{11} = \frac{1}{2}(\text{number of } k\text{-mers})(\text{number of neighbours})(\text{occupancy probability}). \quad (12)$$

As stated before, the energy term we are looking for ( $u_{nem} - u_{1D}$ ) represents the lateral energy between the central segments of the  $k$ -mers. Therefore, in

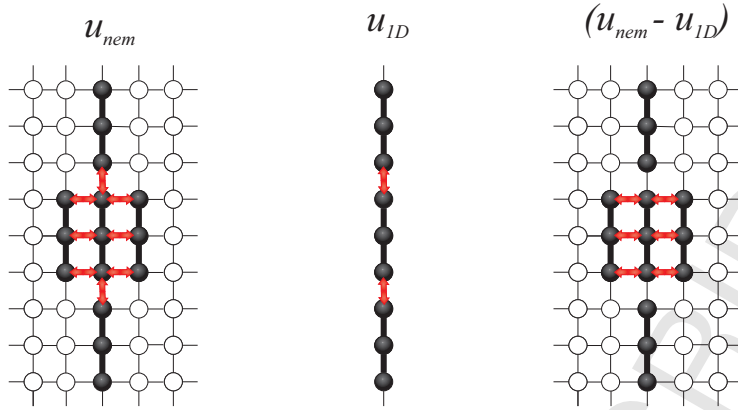


Fig. 9. Schematic representation of the first-neighbour interactions (red double-arrows) between adsorbed  $k$ -mers (trimers,  $k = 3$ , in this case) in the 2D nematic system and the 1D system. It is clear from the figure that the energy difference between these two systems ( $u_{nem} - u_{1D}$ ) represents only the lateral interaction energy.

the “number of neighbours” on Eq. (12), only the “lateral” neighbours must be taken into account. In this line, the number of neighbours  $\lambda$  is given by,

$$\lambda = k(c - 2), \quad (13)$$

where  $c$  is the lattice connectivity and for square lattices  $c = 4$ . The occupancy probability is directly related to the surface coverage  $\theta = \frac{kN}{M}$ , where  $N$  is the number of  $k$ -mers and  $M$  the number of lattice sites. Hence, we have,

$$\text{number of } k\text{-mers} = N, \quad (14)$$

$$\text{number of neighbours} = \lambda = k(c - 2) = 2k, \quad (15)$$

$$\text{occupancy probability} = \theta = \frac{kN}{M}. \quad (16)$$

By substituting these three equations on Eq. (12) the following expression can be obtained,

$$\overline{N}_{11} = \frac{k^2 N^2}{M}. \quad (17)$$

Therefore, the mean energy is  $U = \overline{N}_{11}w = w \frac{k^2 N^2}{M}$ , so the mean energy per site and, consequently, the energy term ( $u_{nem} - u_{1D}$ ) we are looking for is given by,

$$(u_{nem} - u_{1D}) = \frac{U}{M} = w \frac{k^2 N^2}{M^2} = w\theta^2. \quad (18)$$



Finally, by replacing the energy term in Eq. (11) we obtain the analytical expression for the Helmholtz free energy per site for the nematic phase in square lattices that we were looking for,

$$f_{nem} \cong w\theta^2 + f_{1D}. \quad (19)$$

As can be seen, we have obtained an expression for the 2D nematic free energy that depends on  $\theta$ ,  $w$  and  $k$  from which we can derive any other thermodynamic observable. For example, the adsorption isotherms (density or surface coverage dependence on the chemical potential) can be obtained from the known relationship [ $\mu = (\partial F/\partial N)$ ]. Since  $\theta = \frac{kN}{M}$  and  $\frac{F_{nem}}{M} = f_{nem}$ , the isotherms are obtained according to,

$$\mu(\theta) = k (\partial f_{nem}/\partial \theta), \quad (20)$$

where  $f_{nem}$  is given by Eq. (19).

### 3.2 Comparison between simulation and theoretical results

Figure 10 shows the behaviour of the theoretical isotherms obtained from Eq. (20) for different values of  $k$  (different  $k$ -mer sizes) with a fixed value of the interaction energy ( $w = -0,6$ ). The characteristic loop that can be noted in the figure for  $k$ -mers of size  $k = 5, 6, 7$ , is due to the presence of the first order phase transition. Despite the fact that the loop in Fig. 10 can only be seen for the isotherms corresponding to  $k = 5, 6, 7$ , this transition is present for all the systems of this kind, regardless the  $k$ -mer size. It is clear from the presence of more pronounced loops that the interaction energy  $w_c$  shifts to less negative values (less attractive interactions) as  $k$  increases. Besides, the isotherms shift to lower values of the chemical potential (to the left) for increasing  $k$ , since larger molecules with attractive interactions will favour the adsorption.

In Fig. 11 theoretical isotherms with fixed  $k$  and different values of the interaction energy  $w$  are plotted along with the isotherms obtained from the MC simulations. This comparison between theoretical and simulation results is important because it shows that the theoretical approach adopted in the present study yields noticeably good qualitative results regarding the isotherms, despite the previously mentioned characteristic loop.

It can also be seen that the isotherms become steeper (MC) or the loop becomes more pronounced (NMF) for more attractive systems, since higher attractive interactions (lower temperatures) favours the condensation transition as expected.

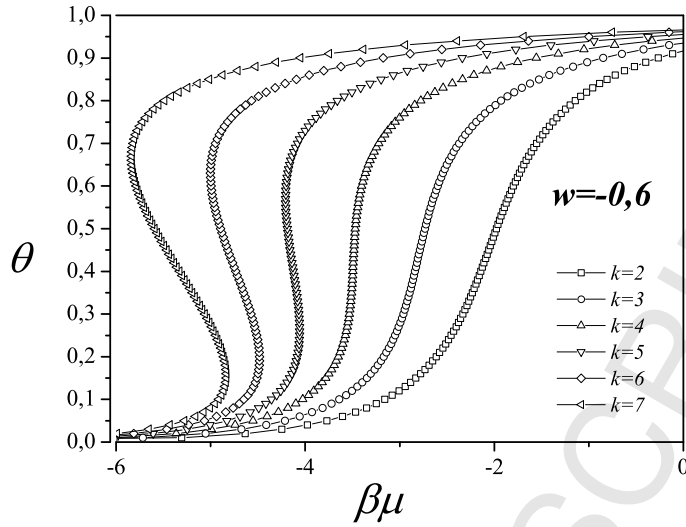


Fig. 10. Theoretical isotherms for fixed  $w$  ( $w = -0,6$ ) and different  $k$ -mer sizes ranging from 2 to 7.

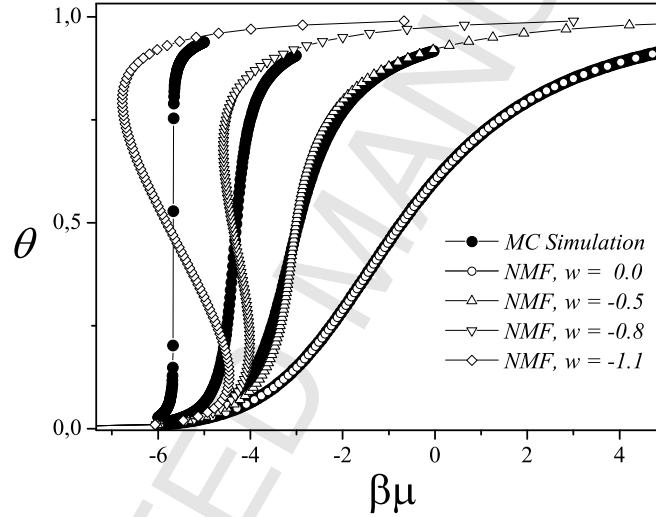


Fig. 11. Comparison between simulation and theoretical isotherms for tetramers ( $k = 4$ ) with different interaction energies adsorbed on square lattices.

The theoretical critical point is obtained from the fact that the critical isotherm shows an inflexion point with infinite slope, precisely at the transition coverage. In this way, the theoretical critical point (transition temperature  $T_c$  and transition coverage  $\theta_c$ ) can be obtained through the following relations,

$$\left(\frac{\partial\mu}{\partial\theta}\right)_{w=w_c;\theta=\theta_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2\mu}{\partial\theta^2}\right)_{w=w_c;\theta=\theta_c} = 0, \quad (21)$$

with  $\mu(\theta)$  from Eq. (20).

Figure 12 shows a comparison between the results of the critical interaction

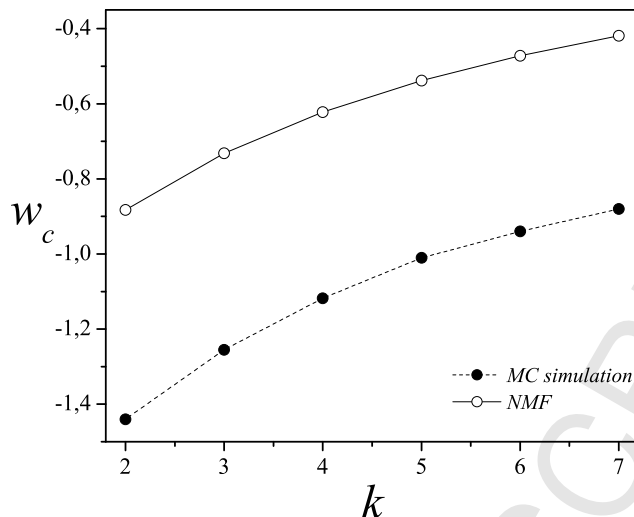


Fig. 12. Comparison between theoretical (NMF) and MC simulation results for the interaction energy  $w_c$  for different  $k$ -mer sizes ( $k$ ).

energy for each  $k$ -mer size ( $k$ ), obtained by means of MC simulations and the MCM, and that obtained from the NMF approximation using the previous relations.

Although it is clear that the approximation fails to accurately reproduce the precise numerical values of the critical interaction energy for each  $k$ , it does manage to represent its behaviour acceptably as a function of the  $k$ -mer size.

A similar analysis can also be made on the behaviour of the transition temperature and the transition coverage, shown in Fig. 13 and 14 respectively. Again, a good qualitative agreement is noticeable even though the numerical values are not well reproduced. In addition, it can be seen that the difference between the MC and the NMF results enlarges as  $k$  increases. This behaviour can be explained observing that as the adsorbate becomes larger, the difference between the 1D and the 2D nematic entropy per site ( $s_{1D}$  and  $s_{nem}$ ) is more pronounced. Given that the main assumption of the analytical approximation is that  $s_{1D} \approx s_{nem}$  (Eq. (5)) for small interactions, it is reasonable that the results behave in the indicated manner above. Nevertheless, the comparison with the theoretical approximation supports and gives confidence to the simulation results presented in section 2.3.

#### 4 Conclusions

In this paper, the phase behavior of aligned linear  $k$ -mers with attractive interactions adsorbed on square lattices has been studied. The results were obtained by means of Monte Carlo simulations complemented by Histogram

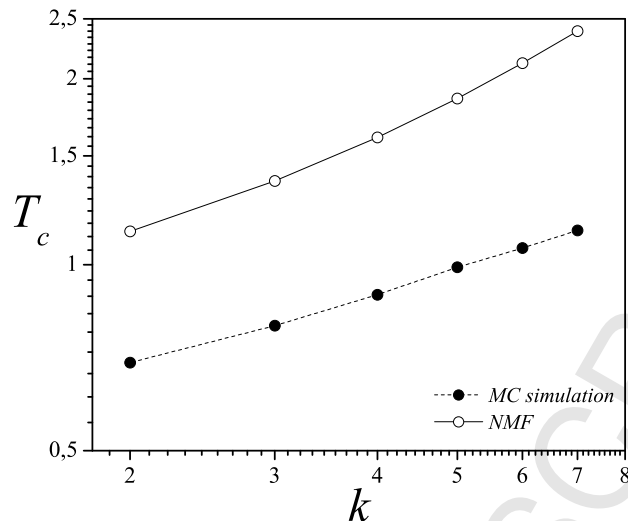


Fig. 13. Theoretical and MC simulation results for the transition temperature  $T_c$  (in logarithmic units) for different  $k$ -mer sizes ( $k$ ).

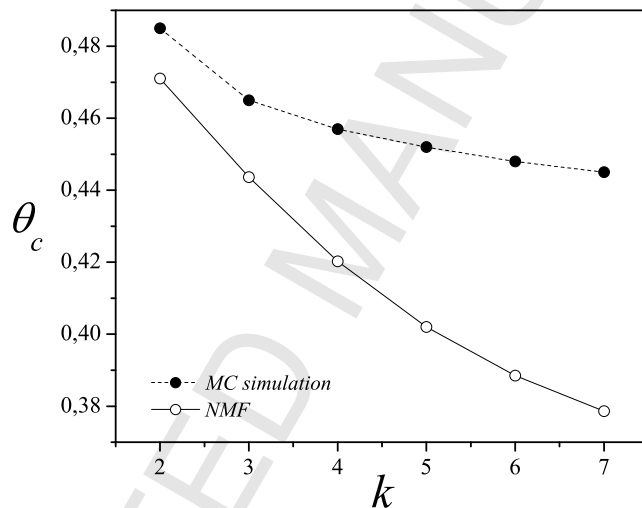


Fig. 14. Theoretical and MC simulation results for the transition coverage  $\theta_c$  for different  $k$ -mer sizes ( $k$ ).

Reweighting Techniques and the “Maximum Cumulant Method”. In addition, an analytical approach was introduced in order to validate the simulation method. The theoretical scheme was built by combining the exact analytical expression for the partition function of interacting  $k$ -mers adsorbed in one dimension, and a generalization of the classical Bragg-Williams approximation in which the adsorbate can occupy more than one adsorption site.

It was found that, for temperatures below a certain transition temperature, the system undergoes a condensation phase transition which is observed as a clear discontinuity in the adsorption isotherms. The theoretical-computational framework was then applied to obtain the dependence of the transition tem-

perature and the transition coverage on the adsorbate size  $k$ , as well as to calculate the corresponding temperature-density phase diagrams. The calculations were developed for  $k$ -mers of length  $k$  ranging between 2 and 7. The main properties characterizing the phase behavior of the system are briefly summarized here as follows.

(1) The transition temperature is a monotonically increasing function of  $k$ , being  $T_c \sim k^{0.4}$ . A similar behavior was reported in the case of isotropic  $k$ -mers [62]. This tendency can be explained in terms of the interaction energy between neighbouring  $k$ -mers: in the “condensed phase” the  $k$ -mers adsorb in compact islands, so the energy needed to take out one  $k$ -mer from this configuration will be equal to  $[2(c-1) + (k-2)(c-2)]w$ . For square lattices ( $c=4$ ), this energy results  $(2k+2)w$ , showing that as  $k$  increases the “condensed phase” becomes more stable and correspondingly the transition temperature is shifted to higher values.

(2) The results obtained regarding the transition coverage showed that  $\theta_c$  diminishes as the size of the  $k$ -mers increases. Unlike the case of monomers, the statistical equivalence between empty and occupied sites is missing for polyatomic species, and the transition coverage is expected to shift from 0.5 as  $k$  increases.

The comparison between theory (Nematic Mean Field approximation) and MC simulations showed a good qualitative agreement. This finding allowed us to validate the computational results and test the accuracy of the analytical approach.

Considering the complexity in the study of these nonspherical adsorbates, it is important to note the usefulness of the “Maximum Cumulant Method” as a tool to predict the phase behavior of the system. Thus, the application of MCM, combined with a correct theoretical interpretation of the results, seems to be a promising way toward an accurate description of adsorption systems in the presence of phase transitions.

## 5 ACKNOWLEDGMENTS

This work was supported in part by CONICET (Argentina) under project number PIP 112-201101-00615; Universidad Nacional de San Luis (Argentina) under project 03-0816; and the National Agency of Scientific and Technological Promotion (Argentina) under project PICT-2013-1678. The numerical work were done using the BACO parallel cluster (composed by 70 PCs each with an Intel i7-3370 / 2600 processor) located at Instituto de Física Aplicada, Universidad Nacional de San Luis - CONICET, San Luis, Argentina.

**References**

- [1] L. Onsager, *Ann. N.Y. Acad. Sci.* 51 (1949) 627.
- [2] B. H. Zimm, *J. Chem. Phys.* 14 (1946) 164.
- [3] A. Isihara, *J. Chem. Phys.* 18 (1950) 1446; *J. Chem. Phys.* 19 (1951) 1142.
- [4] P. J. Flory, *J. Chem. Phys.* 10 (1942) 51; *Principles of Polymers Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- [5] M. L. Huggins, *J. Phys. Chem.* 46 (1942) 151; *Ann. N.Y. Acad. Sci.* 41 (1942) 1; *J. Am. Chem. Soc.* 64, (1942) 1712.
- [6] E. A. Guggenheim, *Proc. R. Soc. London A*183, (1944) 203.
- [7] E. A. DiMarzio, *J. Chem. Phys.* 35 (1961) 658.
- [8] R. Zwanzig, *J. Chem. Phys.* 39 (1963) 1714.
- [9] F. Romá, J. L. Riccardo, A. J. Ramirez-Pastor, *Langmuir* 22 (2005) 3192.
- [10] D. A. Matoz-Fernandez, D. H. Linares, A. J. Ramirez-Pastor, *Langmuir* 27 (2011) 2456.
- [11] R. L. C. Vink, *Phys. Rev. Lett.* 98 (2007) 217801.
- [12] A. Ghosh, D. Dhar, *Eur. Phys. Lett.* 78 (2007) 20003.
- [13] D. Dhar, R. Rajesh, J. F. Stilck, *Phys. Rev. E* 84 (2011) 011140.
- [14] J. Kundu, R. Rajesh, D. Dhar, J. F. Stilck, *Phys. Rev. E* 87 (2013) 032103.
- [15] J. Kundu, R. Rajesh, *Phys. Rev. E* 89 (2014) 052124.
- [16] J. Kundu, R. Rajesh, *Phys. Rev. E* 91 (2015) 012105.
- [17] K. F. Freed, *Renormalization Group Theory of Macromolecules*, Wiley Interscience, New York, 1987.
- [18] S.-D. Lee, *J. Chem. Phys.* 89 (1988) 7036.
- [19] A. Samborski, G. T. Evans, C. P. Mason, M. P. Allen, *Mol. Phys.* 81 (1994) 263.
- [20] B. Tjijpto-Margo, G. T. Evans, *J. Chem. Phys.* 93 (1990) 4254.
- [21] J. W. Evans, *Rev. Mod. Phys.* 65 (1993) 1281.
- [22] J. Talbot, G. Tarjus, P. R. Van Tassel, P. Viot, *Colloids Surf. A* 165 (2000) 287.
- [23] G. Kondrat, *J. Chem. Phys.* 124 (2006) 054713.
- [24] N. I. Lebovka, N. N. Karmazina, Y. Y. Tarasevich, V. V. Laptev, *Phys. Rev. E* 84 (2011) 061603.

- [25] Y. Yu. Tarasevich, V. V. Laptev, N. V. Vygornitskii, N. I. Lebovka, *Phys. Rev. E* 91 (2015) 012109.
- [26] Y. Yu. Tarasevich, A. S. Burmistrov, T. S. Shinyaeva, V. V. Laptev, N. V. Vygornitskii, N. I. Lebovka, *Phys. Rev. E* 92 (2015) 062142.
- [27] K. Binder, *Applications of the Monte Carlo Method in Statistical Physics: Topics in Current Physics*, Vol. 36, Springer, Berlin, 1984.
- [28] K. Binder, D. P. Landau, *Phys. Rev. B* 21 (1980) 1941.
- [29] D. P. Landau, *Phys. Rev. B* 27 (1983) 5604.
- [30] K. Binder, D. P. Landau, *Phys. Rev. B* 30 (1984) 1477.
- [31] D. P. Landau, K. Binder, *Phys. Rev. B* 31 (1985) 5946.
- [32] D. P. Landau, K. Binder, *Phys. Rev. B* 41 (1990) 4633.
- [33] M. Borówko, W. Rżysko, *J. Colloid Interface Sci.* 244 (2001) 1.
- [34] W. Rżysko, M. Borówko, *J. Chem. Phys.* 117 (2002) 4526.
- [35] W. Rżysko, M. Borówko, *Surf. Sci.* 520 (2002) 151.
- [36] W. Rżysko, M. Borówko, *Surf. Sci.* 600 (2006) 890.
- [37] W. Rżysko, M. Borówko, *Phys. Rev. B* 67 (2003) 045403.
- [38] A. J. Ramirez-Pastor, J. L. Riccardo, V. D. Pereyra, *Surf. Sci.* 411 (1998) 294.
- [39] F. Romá, A. J. Ramirez-Pastor, J. L. Riccardo, *Phys. Rev. B* 68 (2003) 205407.
- [40] F. Romá, A. J. Ramirez-Pastor, J. L. Riccardo, *Phys. Rev. B* 72 (2005) 035444.
- [41] P. M. Pasinetti, F. Romá, J. L. Riccardo, A. J. Ramirez-Pastor, *Phys. Rev. B* 74 (2006) 155418.
- [42] F. Romá, J. L. Riccardo, A. J. Ramirez-Pastor, *Phys. Rev. B* 77 (2008) 195401.
- [43] A. J. Ramirez-Pastor, J. L. Riccardo, V. D. Pereyra, *Langmuir* 16 (2000) 10167.
- [44] J. E. González, A. J. Ramirez-Pastor, V. D. Pereyra, *Langmuir* 17 (2001) 6974.
- [45] A. Patrykiewicz, S. Sokolowski, K. Binder, *Surf. Sci. Rep.* 37 (2000) 207.
- [46] M. S. Nazzarro, A. J. Ramirez-Pastor, J. L. Riccardo, V. D. Pereyra, *Surf. Sci.* 391 (1997) 267.
- [47] T. L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960.
- [48] A. Z. Panagiotopoulos, *J. Phys.: Condens. Matter* 12 (2000) R25.
- [49] A. M. Ferrenberg, R. H. Swendsen, *Phys. Rev. Lett.* 61 (1988) 2635.
- [50] A. M. Ferrenberg, R. H. Swendsen, *Phys. Rev. Lett.* 63 (1989) 1195.

- [51] H. Müller-Krumbhaar, K. Binder, Monte Carlo methods in statistical physics  
Top. Curr. Phys. 7 (1979).
- [52] G. J. dos Santos, D. H. Linares, A. J. Ramirez-Pastor, J. Stat. Mech. 7 (2017)  
073211.
- [53] M. J. Hostetler, W. L. Manner, R. G. Nuzzo, G. S. Girolami, J. Phys. Chem.  
99 (1995) 15269.
- [54] J. J. Potoff, J. I. Siepmann, Phys. Rev. Lett. 85 (2000) 3460.
- [55] J. J. Potoff, J. I. Siepmann, Langmuir 18 (2002) 6088.
- [56] R. H. Swendsen, J-S. Wang, Phys. Rev. Lett. 57 (1986) 2607.
- [57] D. J. Earl, M. W. Deem, Phys. Chem. Chem. Phys. 7 (2005) 3910.
- [58] K. Hukushima, K. Nemoto, J. Phys. Soc. Japan 65 (1996) 1604.
- [59] T. L. Hill, Thermodynamics of Small Systems, Dover, New York, 1962.
- [60] A. Clark, The Theory of Adsorption and Catalysis, Academic Press, New York  
and London, 1970.
- [61] A. J. Phares, P. M. Pasinetti, D. W. Grumbine Jr., F. J. Wunderlich, Physica  
B 406 (2011) 1096.
- [62] P. Longone, M. Dávila, J. L. Riccardo, A. J. Ramirez-Pastor, Adsorption. 19(2-  
4) (2013) 509-519 .
- [63] A. J. Ramirez-Pastor, A. Aligia, F. Romá, J. L. Riccardo, Langmuir 16 (2000)  
5100.