

Critical behavior of repulsive linear k -mers on square lattices at half coverage: Theory and Monte Carlo simulations

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(Received 15 April 2003; published 6 November 2003)

Monte Carlo (MC) simulations have been used to study the critical behavior of repulsive linear k -mers on square lattices at 50% coverage. A $(2k \times 2)$ ordered phase, characterized by a repetition of alternating files of adsorbed k -mers separated by k adjacent empty sites, was found. This ordered phase is separated from the disordered state by a order-disorder phase transition occurring at a critical temperature T_c , which presents an intriguing dependence with the size k of the adsorbed molecules. In addition, two analytical techniques were combined with Monte Carlo simulations to predict the critical temperature of the order-disorder transformation. The first is based on a detailed mean-field approximation (DMFA), considering the exact interactions between the k -mers belonging to a region γ (the cluster) and a mean-field interaction with the rest outside γ . Different sizes for γ ($k \times 1, k \times 2, 2k \times 1, 2k \times 2$) were used in the calculations in order to discuss its influence in the determination of T_c . The second approach is based on a free energy minimization criterion (FEMCA). The dependence on k of the transition temperature $T_c(k)$ observed in MC is in remarkable qualitative agreement with DMFA and FEMCA. Both allow us to interpret the physical meaning of the mechanisms underlying the observed transitions.

DOI: 10.1103/PhysRevB.68.205407

PACS number(s): 05.70.Ce, 05.70.Np, 68.43.De

I. INTRODUCTION

The two-dimensional lattice-gas model¹ with repulsive interactions between the adparticles is of experimental interest because it provides the theoretical framework to study the order-disorder phase transition occurring in many physisorbed monolayer films. An example is the case of helium adsorbed on graphite, which has been widely studied.²⁻⁴ In this system, the size of the admolecule is somewhat larger than the lattice constant, so there is a repulsive interaction energy w between the adatoms. The presence of this kind of lateral interaction leads to a transition between ordered and disordered phases taking place when the thermal energy $k_B T$ is comparable in magnitude to w . Similarly, there exist many adsorption systems in which the size of the adsorbate does not correspond to the dimensions of the adsorption site. Typical systems, such as methane,⁵ ethane,⁶ propane-butane,⁷ etc., adsorbed in nanotubes of aluminophosphates, have been recently reported.

In spite of the obvious evidence of the character of polyatomic admolecules in many real situations, most developments in adsorption theory have mainly dealt with monoatomic adsorption.⁸⁻¹⁰ The inherent complexity of the multisite adsorption statistics still represents a major difficulty to the development of approximate solutions for the thermodynamic functions. This difficulty is mainly associated to three factors which makes the k -mers statistics different from the usual single particle statistics. Namely, (1) no statistical equivalence exists between particles and vacancies, (2) the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied, and (3) an isolated vacancy cannot serve to determining whether that site can ever become occupied or not.

However, several attempts were done in the past in order

to solve the k -mers problem. An early seminal contribution to dimer statistics was done by Fowler and Rushbrooke,¹¹ while an isomorphous system, namely, adsorption of binary liquid in two dimensions, was treated by Flory.^{12,13} More recently, leading contributions have been presented in Refs. 8, 14–18 treating with multisite adsorption on homogeneous and heterogeneous surfaces. In general, these studies were focused on (i) effect of the chemical structure of a noninteracting adsorbate on its mode of adsorption, (ii) influence of the surface heterogeneity on noninteracting k -mers adsorption, or (iii) description of the first-order phase transition occurring in the adsorbate for attractive nearest-neighbor interactions. On the other hand, there have been very few studies devoted to the order-disorder transition associated to multisite adsorption with repulsive lateral interactions. Among them, the structural ordering of interacting dimers has been analyzed by Phares *et al.*¹⁹ The authors calculated the entropy of dimer on semi-infinite $M \times N$ square lattice ($N \rightarrow \infty$) by means of transfer matrix techniques. They concluded that there are a finite number of ordered structures for dimers with repulsive nearest-neighbor interactions.

In previous work we have studied the phase diagram of dimers with repulsive nearest-neighbor interactions on square lattice²⁰ confirming the structural ordering predicted in Ref. 19. In addition, we have analyzed the influence of such structural ordering on interesting properties as adsorption isotherm and heat of adsorption,²¹ collective diffusion coefficient,²² and configurational entropy.²³ From these studies it is not possible to know completely the critical behavior in a lattice gas (structure of the different ordered phases occurring at low temperature and critical temperature characterizing each transition) as the size k of the admolecules is increased. However, from the (4×2) phase appearing in dimers at critical regime we can predict the existence of a

$(2k \times 2)$ structure for k -mers at half coverage.

Accordingly, the scope of the present work is to determine, via Monte Carlo (MC) simulation and two analytical approximations, the critical behavior of repulsive k -mers adsorbed at half coverage on a square lattice. For this purpose, the critical temperature $T_c(k)$ characterizing the transition from the disordered state to the $(2k \times 2)$ phase is obtained as a function of the size k of the adsorbed molecules. The outline of the paper is as follows. In Sec. II we describe the lattice-gas model, the simulation scheme, and we present the behavior of $T_c(k)$, obtained by using the MC method. In Sec. III we present the analytical approximations [detailed mean-field approximation (DMFA) and free energy minimization criterion (FEMCA)] and compare the MC results with the theoretical calculations. Finally, the general conclusions are given in Sec. IV.

II. LATTICE-GAS MODEL AND MONTE CARLO SIMULATION SCHEME

A. The model

In this section we described the lattice-gas model for the adsorption of linear rigid molecules with multisite occupancy. In order to make the treatment as general as possible, we considered the adsorption of homonuclear linear k -mer molecules on hypercubic lattice modeled as k interaction centers at a fixed separation, which is equal to the lattice constant a . In the adsorption process, it is assumed that each monomer occupies a single adsorption site. The high-frequency stretching motion along the molecular bond has not been considered here. The k -mers bond length remains constant throughout the treatment. The surface is represented as an array of M adsorptive sites. In order to describe the system of Nk -mers adsorbed on M sites at a given temperature T , let us introduce the occupation variable c_i which can take the values $c_i=0$ if the corresponding site is empty and $c_i=1$ if the site is occupied. The energy involved in the adsorption of each k -mer unit is smaller than the bond energy between the k units. On the other hand, molecules adsorb or desorb as one unit, neglecting any possible dissociation. Under this consideration, the Hamiltonian of the system is given by

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

where w is the nearest-neighbor (NN) interaction constant which is assumed to be repulsive (positive), $\langle i,j \rangle$ represents pairs of NN sites, and ϵ_0 is the energy of adsorption of one given surface site. 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.

B. Monte Carlo method

We have used a standard importance sampling MC method in the canonical ensemble²⁴ and finite-size scaling techniques.²⁵ The lattices were generated fulfilling the following conditions.

(1) The sites were arranged in a square lattice of side $L (M=L \times L)$, with conventional periodic boundary conditions.

(2) Due that the surface was assumed to be homogeneous, the interaction energy between the adsorbed k -mer and the atoms of the substrate ϵ_0 was neglected for sake of simplicity.

(3) In order to maintain the lattice at half coverage $\theta = kN/M = 1/2$, the number of k -mers on the lattice was fixed as $N = M/2k$.

(4) Appropriate values of L/k were used in such way that the $(2k \times 2)$ adlayer structures are not perturbed.

A number Monte Carlo steps (MCS) per site between $10^5 - 10^6$ were discarded in each run to allow for equilibrium and the next $10^5 - 10^6$ MCS were used to compute averages. At temperatures far for the critical point fewer than 10^5 were found to be enough to obtain sufficient precision. In the vicinity of critical points up to 10^6 MCS had to be used because fluctuations are greatly enhanced.

In order to study the order-disorder phase transition occurring in the adsorbate, it is convenient to define a related order parameter. In particular, at $\theta=1/2$, a $(2k \times 2)$ ordered structure is formed in the adsorbate below the critical temperature. Figure 1 shows snapshots corresponding to two possible configurations of the (4×2) phase appearing for adsorbed dimers ($k=2$) at critical regime. Due to the periodic boundary conditions the degeneracy of this phase is equal to 8. These configurations allow us to decompose the original lattice into eight different sublattices (see Fig. 2).²⁶ The coverage on each sublattice is denoted as $\theta_i (i=1, \dots, 8)$. In this way, an order parameter φ can be defined for dimers as

$$\varphi = |\theta_1 - \theta_2| + |\theta_3 - \theta_4| + |\theta_5 - \theta_6| + |\theta_7 - \theta_8|, \quad (2)$$

where we sum the differences (in absolute value) between the coverage corresponding to two complementary sublattices. The term complementary refers to sublattices without superposition.

In general, the number of sublattices for k -mers will be $4k$, each one having a surface coverage $\theta_i (i=1, \dots, 4k)$. Thus, the generalized order parameter $\varphi(k)$ can be written as

$$\varphi(k) = A_k \sum_{i=0}^{2k-1} |\theta_{2i+1} - \theta_{2i+2}|, \quad (3)$$

where A_k is a normalization factor defined as

$$A_k = \begin{cases} \frac{2}{k} & \text{for even } k, \\ \frac{2k}{k^2+3} & \text{for odd } k. \end{cases} \quad (4)$$

When the system is disordered ($T > T_c$), all sublattices are equivalent and the order parameter is minimum. However, when a configuration of the $(2k \times 2)$ phase appears at low temperature ($T < T_c$), this is allocated on a sublattice (between a set of $4k$). Let us suppose that this configuration lies on the sublattice i . Then, the coverage θ_i is maximum

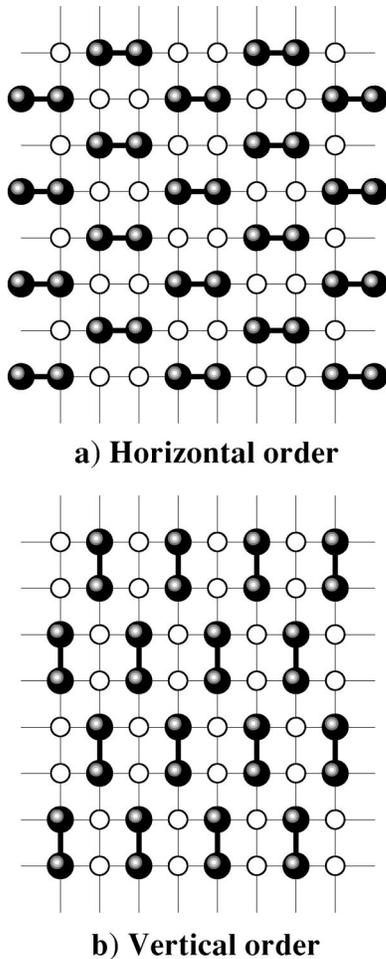


FIG. 1. Snapshot of the ordered phase for dimers at half coverage.

($\theta_i=1$) and the coverage of the complementary sublattice is zero. In addition, the rest of the sum is zero or minimum. In conclusion, the definition (3) is computationally convenient and φ appears as a good order parameter evidencing the order-disorder phase transition. Finally, the reduced fourth-order cumulant U_L introduced by Binder,²⁷ can be calculated as

$$U_L(T) = 1 - \frac{\langle \varphi^4 \rangle_T}{3 \langle \varphi^2 \rangle_T^2}, \quad (5)$$

where the thermal average $\langle \dots \rangle_T$, in all the quantities, means the time average throughout the MC simulation.

C. Computational results

The standard theory of finite-size scaling^{24,25,27} allows for various efficient routes to estimate T_c from MC data. One of this method, which will be used in the next section, is from the temperature dependence of $U_L(T)$, which is independent of the system size for $T=T_c$. In other words, T_c is found from the intersection of the curve $U_L(T)$ for different values of L , since $U_L(T_c)=\text{const}$.

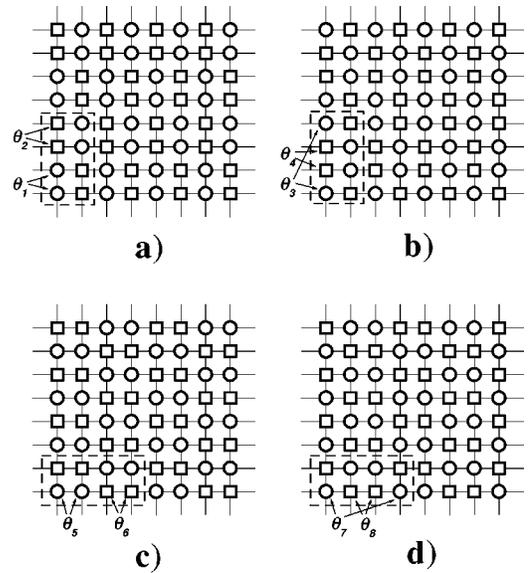


FIG. 2. Different sublattices defined for $k=2$.

The thermodynamic properties of the present model have been investigated by means of the computational scheme described in the previous section. The calculations were developed for linear k -mers with $k=2-5$ (as it is well known,²⁸ the value of T_c for $k=1$ is exact). The simulation lattice was a square lattice of size $L \times L$ with conventional periodic boundary conditions. Note, however, that the choice of appropriate linear dimensions L has to be done in such way that the ordered structures are not disturbed. In our case, for $(2k \times 2)$ ordered phase ($L=4k, 8k, 12k, 16k, 24k$) were used.

Hereafter we discuss the behavior of the critical temperature as a function of the size k , for adsorbed k -mers at monolayer. Figure 3 illustrates the reduced four-order cumulants $U_L(T)$ plotted versus $k_B T/w$ (where k_B is the Boltzmann constant) for several lattice sizes. From their intersections one gets the estimation of the critical temperature. As an example, the figure shows the results for two values of k [$k=2$, Fig. 3(a) and $k=3$, Fig. 3(b)]. The curves of the order parameter, which were used to obtain $U_L(T)$, are shown in the insets of the figure. The procedure was done for $k=2-5$ and the results are collected in Table I.

As can be observed, the critical temperature presents a nontrivial behavior as a function of the particle size k . An understanding of the intriguing dependence of $T_c(k)$ on k can be developed by following the subtle interdependence of energetic and entropic cost necessary to alter the ordered phase. This will be discussed in Sec. III C.

A systematic analysis of critical exponents for each k -mer size was not carried out since this was out of the scope of the present work. Although, they might be expected to belong to the two-dimensional Ising model's universality class, it is not clear that this would be true for k -mers in general. It is worth pointing out that we did not assume any particular universality class for the transitions analyzed here in order to calculate their critical temperatures, since the analysis relied on the order parameter cumulant's properties. However a preliminary finite-size scaling analysis of the size dependence of the specific heat's maximum reveals that critical exponents

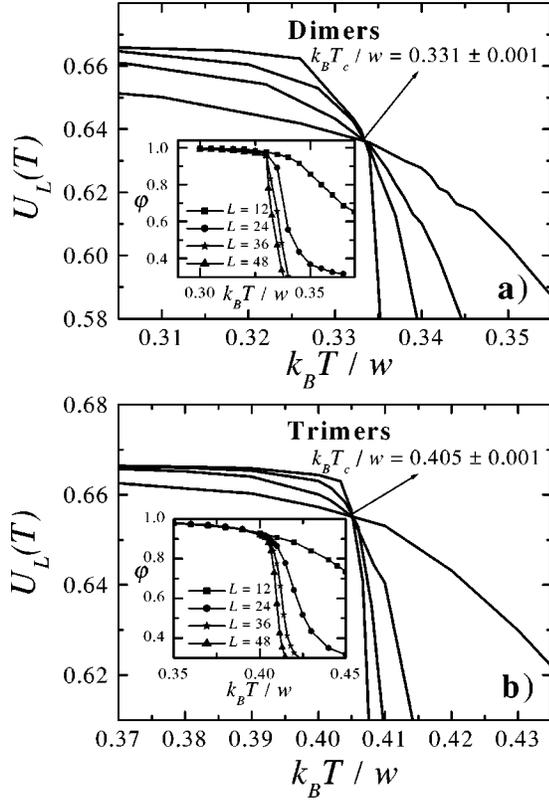


FIG. 3. $U_L(T)$ versus $k_B T/w$, for two sizes of the adsorbed molecule: $k=2$ (a) and $k=3$ (b). From their intersections one obtained $k_B T_c/w$. The order parameters corresponding to the curves of $U_L(T)$ are presented in the insets.

different from the two Ising ones have to be assumed in order for the critical temperatures from both ways to be consistent.

III. ANALYTICAL APPROXIMATIONS AND COMPARISON BETWEEN SIMULATED AND THEORETICAL RESULTS

A. Detailed mean-field approximation (DMFA)

In this section, we will extend the basic ideas of a cluster method, which has been applied successfully to describe the continuous transition occurring in repulsive monomers at critical regime.²⁹ The proposed system can be summarized in the following rules.

TABLE I. $T_c(k)$ for k ranging from 1 to 5. The value of $T_c(1)$ is exact (Ref. 28) while in the other cases, $k=2-5$, the data were obtained from the intersection of $U_L(T)$ versus $k_B T/w$.

k	$k_B T_c / w$	$\pm \Delta$
1	0.567	
2	0.331	0.001
3	0.405	0.001
4	0.482	0.002
5	0.546	0.006

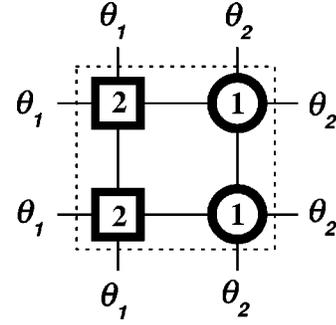


FIG. 4. Cluster of size 2×2 for dimers.

(i) The substrate consists of a set of neighbor sites grouped in a rectangular structure, the so-called cluster, which is embedded in an infinite lattice. Figure 4 shows a cluster of size 2×2 .

(ii) The k -mers adsorb into the cluster (i.e., each one of the k particles belonging to a k -mer must adsorb on a cluster site).

(iii) The interactions between the k -mers belonging to the cluster are explicitly accounted for. Additionally, a mean-field interaction with the rest of sites out the cluster boundaries is added.

(iv) Because the ordered phases may develop on different sublattices (as discussed in Sec. II), different sublattices are defined on the cluster. This is the main difference with the standard cluster method for monomers.²⁹

Hereafter, we calculate in the grand canonical ensemble, where the critical temperature is found from the condition $\theta=1/2$ and $\varphi \rightarrow 0$ ($T \rightarrow T_c^-$). An example for adsorbed dimers follows in order to make this point clear. Figure 4 shows a snapshot corresponding to a 2×2 cluster. This cluster is constituted by four sites, belonging to two different sublattices. Circles (squares) denote sites on the sublattice 1(2), where θ_1 and θ_2 are the mean coverages on each sublattice. The possible configurations for our example are shown in Fig. 5.

The grand partition function Ξ will be

$$\Xi = 1 + \lambda [e^{-4\theta_1\beta w} + e^{-4\theta_2\beta w} + 2e^{-2(\theta_1+\theta_2)\beta w}] + 2\lambda^2 e^{-(4\theta_1+4\theta_2+2)\beta w}, \quad (6)$$

where $\beta=1/k_B T$ and $\lambda=e^{\beta\mu}$ is the fugacity. From Eq. (6), it is possible to calculate the mean coverage on both sublattices

$$\theta_1 = \frac{1}{2\Xi} \{ \lambda [2e^{-4\theta_2\beta w} + 2e^{-2(\theta_1+\theta_2)\beta w}] + 4\lambda^2 e^{-(4\theta_1+4\theta_2+2)\beta w} \}, \quad (7)$$

$$\theta_2 = \frac{1}{2\Xi} \{ \lambda [2e^{-4\theta_1\beta w} + 2e^{-2(\theta_1+\theta_2)\beta w}] + 4\lambda^2 e^{-(4\theta_1+4\theta_2+2)\beta w} \}. \quad (8)$$

Taking into account that

$$\theta = \frac{\theta_1 + \theta_2}{2} \quad (9)$$

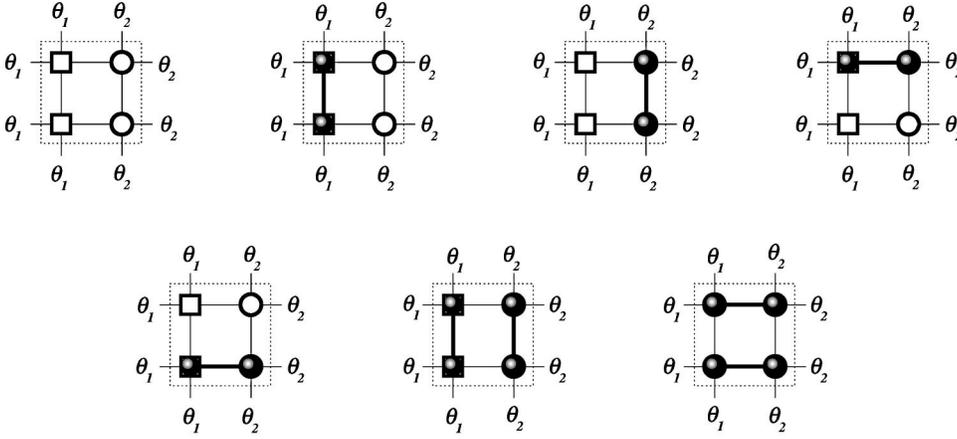


FIG. 5. Different configurations for dimers adsorbed on a cluster of size 2×2 .

and by defining the order parameter as

$$\varphi = \frac{\theta_1 - \theta_2}{2} \quad (10)$$

the critical temperature can be obtained from the condition $\theta = 1/2$ and $\varphi \rightarrow 0$ ($T \rightarrow T_c^-$). The procedure to solve this problem is as follows.

[(1)] Because $\theta = 1/2$, the fugacity can be determined from Eqs. (6)–(9);

$$\lambda = \frac{e^{3\beta w}}{\sqrt{2}}. \quad (11)$$

[(2)] From Eqs. (9) and (10)

$$\theta_1 = \theta + \varphi = \frac{1}{2} + \varphi, \quad (12)$$

$$\theta_2 = \theta - \varphi = \frac{1}{2} - \varphi. \quad (13)$$

[(3)] From Eqs. (11)–(13), the grand partition function is rewritten as

$$\Xi = 2 + \frac{e^{\beta w}}{\sqrt{2}} (e^{4\varphi\beta w} + e^{-4\varphi\beta w} + 2). \quad (14)$$

[(4)] From Eqs. (7), (8), and (10)–(13), we obtain

$$\varphi = \frac{e^{\beta w}}{\sqrt{8}\Xi} (e^{4\varphi\beta w} - e^{-4\varphi\beta w}). \quad (15)$$

[(5)] The right-hand side (RHS) of Eq. (15) is expanded in powers of φ around $\varphi = 0$ (which corresponds to $T = T_c$)

$$\varphi = \left(\frac{\sqrt{8}w\beta_c e^{w\beta_c}}{2 + \sqrt{8}e^{w\beta_c}} \right) \varphi + \dots, \quad (16)$$

where $\beta_c = 1/k_B T_c$. Then, by comparing the terms of order $O(1)$ of Eq. (16),

$$2 + \sqrt{8}e^{w\beta_c} = \sqrt{8}w\beta_c e^{w\beta_c}. \quad (17)$$

Finally, the numerical solution of Eq. (17) yields $k_B T_c / w = 0.826$.

By following the procedure detailed above, $k \times 1$, $k \times 2$, $2k \times 1$, and $2k \times 2$ clusters for $k = 2, \dots, 5$ were solved. The results of these calculations are shown in Sec. III C in comparison with the MC simulations.

We predict that the critical temperature as a function of the adsorbate size presents a local minimum for dimers. The critical temperature for dimers, trimers, 4-mers, and, roughly, for 5-mers is lower than the one for monomers (the Ising model). The overall behavior shown by the MC simulations is qualitatively well reproduced by the cluster approximation developed here, especially for the minimal critical temperature for dimers.

B. Free energy minimization criterion (FEMCA)

Hereafter, we present a thermodynamic analysis that sheds light on the underlying physics of the observed size dependence of T_c . Let us consider an ideal gas in a container of fixed volume. The total system is assumed to be isolated. By “isolated” it is meant that the system does not exchange energy with anything external to it. Then we split the sample into two parts (left and right) by means of a movable heat-conducting wall (a metallic piston in an isolated and closed cylinder containing gas at low pressure). As it is well known, the wall moves until the pressure and the temperature on both parts of the partition are the same. In this way, it is possible to determine the thermodynamical equilibrium.

This analysis, which is mainly based on the mechanical equilibrium between the different parts of the system, can be replaced by statistical arguments. In this framework, an isolated system will be in a state of thermodynamical equilibrium when the entropy S has reached a maximum^{30,31}

$$S = \text{maximum (isolated system)}. \quad (18)$$

The stability will be reached when the values of the free system’s parameters allow one to satisfy the condition (18). In our case, we can verify the condition (18) by arranging the piston in an adequate position. The position of the conducting wall is denoted by x . Then the entropy of the system will be

$$S(x) = S_l(x) + S_r(x), \quad (19)$$

where $S_l(x)$ [$S_r(x)$] represent the entropy on the left (right) for a given value of the position x of the barrier. The equilibrium is obtained by calculating the position $x = x_0$, which maximizes Eq. (19). Only $x = x_0$ corresponds to a state of equilibrium for the isolated system with a movable wall. If the position of the piston is fixed (x is not a free parameter), other states of equilibrium will be reached for different values of x . On the other hand, if the wall is allowed to move freely, these states will be out of the equilibrium and the entropy will not be defined.

From these arguments, it can be concluded that the procedure to calculate the state of equilibrium for an isolated system requires two steps: (i) to obtain the entropy of the system by fixing the parameters of interest in accessible values and (ii) to choose the set of these parameters so that the entropy reach the maximum. In the following, a closed system in contact with a large thermal reservoir at temperature T is studied. With these assumptions, the equilibrium condition for the system is that the total free energy $F = U - TS$ must be a minimum^{30,31} in comparison with any other state to which the system might go without violating fundamental conservation laws. Then,

$$F = U - TS = \text{minimum (closed system)}, \quad (20)$$

where U represents the mean energy.

To obtain the equilibrium state, we must calculate the entropy of the system as a function of the energy $S(U)$. This process implies that we should isolate the system for different energies and to calculate the entropy corresponding to each energy. Then, the equilibrium state at temperature T (characterized by S and U) is determined from the condition (20).

An example of this type of analysis is the following derivation for an ideal gas. The procedure requires the following.

(i) To obtain the relationship $S(U)$. For the ideal gas is well-known that^{32,33}

$$S = Nk_B \ln \left[\left(\frac{V}{N} \right) \left(\frac{CU}{N} \right)^{3/2} \right], \quad (21)$$

where N is the number of particles, V is the volume, and C is a constant.

(ii) To build the function F , this is

$$F = U - TNk_B \ln \left[\left(\frac{V}{N} \right) \left(\frac{CU}{N} \right)^{3/2} \right]. \quad (22)$$

(iii) To minimize F with U as the free parameter

$$\frac{\partial F}{\partial U} = 1 - TNk_B \frac{\left[\left(\frac{V}{N} \right) \left(\frac{C}{N} \right)^{3/2} \right]}{\left[\left(\frac{V}{N} \right) \left(\frac{CU}{N} \right)^{3/2} \right]} \frac{3}{2} U^{1/2} = 0, \quad (23)$$

$$U = \frac{3}{2} Nk_B T. \quad (24)$$

In this way we have obtained the mean energy at temperature T . This quantity corresponds to a equilibrium state of the system.

It is straightforward that between two possible states, an isolated (closed) system prefers the state having the maximum entropy (minimum free energy F). Based on these concepts we will develop an approximation to determine T_c in the canonical ensemble and we will apply the methodology to our system.

In a closed system of adsorbed particles with repulsive interactions, the phase transition occurring in the adsorbate is a continuous (second-order) phase transition. In other words, the entropy varies continuously from a completely ordered state (when $T \rightarrow 0$) to a disordered state (when $T \rightarrow \infty$). Around T_c , S changes abruptly (but continuously).²³ Then, it is possible to analyze the phase transition taking into account the function F in the two extreme states (maximum order and maximum disorder). Accordingly,

$$F_\infty = \lim_{T \rightarrow \infty} F \quad \text{and} \quad F_0 = \lim_{T \rightarrow 0} F \quad (25)$$

then

$$F_\infty \ll F_0 \Rightarrow T > T_c, \quad (26)$$

$$F_\infty \gg F_0 \Rightarrow T < T_c, \quad (27)$$

$$F_\infty = F_0 \Rightarrow T \approx T_c. \quad (28)$$

The last equation allows us to determine T_c . This calculation is not exact due to the fact that the system does not pass from a extreme order to an extreme disorder. There exist intermediate states between the two extreme states. However, as we will show in the following analysis, Eq. (28) provides a very good approximation for T_c .

Let us consider a well-known system, the ferromagnetic Ising model without external field. The Hamiltonian of this system is

$$H = -J \sum_{(i,j)} \sigma_i \sigma_j, \quad (29)$$

where J is the exchange interaction, σ_i is the spin variable associated to the site i ($\sigma_i = \pm 1$), and (i,j) represents pairs of NN sites. For a lattice of N spins and connectivity z , the mean energy and the entropy can be calculated in two extreme states

$$U_0 = -\frac{1}{2} zJN \quad \text{and} \quad S_0 = k_B \ln 2 \quad (\text{order}), \quad (30)$$

$$U_\infty = 0 \quad \text{and} \quad S_\infty = k_B N \ln 2 \quad (\text{disorder}). \quad (31)$$

In the thermodynamical limit, the free energy per spin f will be

$$f_0 = \lim_{N \rightarrow \infty} \frac{F_0}{N} = -\frac{1}{2} zJ \quad (\text{order}), \quad (32)$$

$$f_\infty = \lim_{N \rightarrow \infty} \frac{F_\infty}{N} = -k_B T \ln 2 \quad (\text{disorder}). \quad (33)$$

Evidently, the system prefers the ordered (disordered) state as $T \rightarrow 0(\infty)$. However, a temperature exists in which both free energies are equal. This temperature will be used as a criterion of the estimation of the critical temperature T_c . Taking into account Eq. (28),

$$f_0 = f_\infty \Rightarrow T \approx T_c \Rightarrow k_B T_c / J \approx z / \ln 4. \quad (34)$$

For $z=4$ we have $k_B T_c / J \approx 2.88$, which is a rough estimation to the real value of 2.269.

In general, for a system of k -mers at temperature T

$$f_0 = u_0 - T s_0 \quad \text{and} \quad f_\infty = u_\infty - T s_\infty, \quad (35)$$

where u and s represent the mean energy per site and the entropy per site in the thermodynamical limit, respectively,

$$u = \lim_{M \rightarrow \infty} \frac{U}{M} \quad \text{and} \quad s = \lim_{M \rightarrow \infty} \frac{S}{M}. \quad (36)$$

If $f_0 = f_\infty$, this is

$$u_0 - T s_0 = u_\infty - T s_\infty \quad (37)$$

then $T \approx T_c$ and

$$T_c \approx \frac{\Delta u}{\Delta s} = \frac{u_\infty - u_0}{s_\infty - s_0}. \quad (38)$$

From Eq. (38), it is possible to calculate the critical temperature and to interpret the dependence of T_c with k , for a system of repulsive linear k -mers on a square lattice at half coverage. In this case, the mean energy, the entropy, and the free energy for the ordered state ($T=0$) are $u_0 = s_0 = f_0 = 0$. Then, the critical temperature depends on the mean en-

ergy and the entropy of the disordered state. In first term, u_∞ will be calculated from the mean-field approximation

$$\frac{u_\infty}{w} \approx \frac{N\theta}{2M} [6 + 2(k-2)] = \frac{k+1}{4k}, \quad (39)$$

where $\theta = 1/2$. Equation (39) is exact for monomers ($k=1$), due to the fact that in this case all sites in the border are equivalents. In order to calculate the entropy of the disordered state, the configurational factor of monomers for $k=1$ is employed:

$$\Omega = \frac{M!}{N!(M-N)!} \quad (40)$$

and the configurational factor of Guggenheim³⁴ for $k \geq 2$ is

$$\Omega \approx \zeta^N \frac{M!}{N!(M-kN)!} \left[\frac{(bN+M-kN)!}{M!} \right]^{z/2}, \quad (41)$$

where $\zeta = z/2$ and $b = [(z-2)k+2]/z$. Thus,

$$s_\infty = \lim_{M \rightarrow \infty} \frac{k_B \ln \Omega}{M}. \quad (42)$$

In the particular case of $z=4$ and $\theta=1/2$, the entropy per site of the disordered state results in

$$\frac{s_\infty}{k_B} = \ln 2 \quad \text{for } k=1 \quad (43)$$

and

$$\frac{s_\infty}{k_B} \approx \frac{1}{2k} \ln 4k + \frac{1}{2} \ln 2 + \left(\frac{1}{2k} + \frac{3}{2} \right) \ln \left(\frac{1}{4k} + \frac{3}{4} \right) \quad \text{for } k \geq 2. \quad (44)$$

Finally, from Eqs. (38), (39), (43), and (44), we obtain $T_c(k)$:

$$\frac{k_B T_c(k)}{w} \approx \frac{u_\infty/w}{s_\infty/k_B} = \begin{cases} 1/\ln 4 = 0.721 & \text{for } k=1, \\ (k+1) \left[2 \ln 4k + 2k \ln 2 + (6k+2) \ln \left(\frac{1}{4k} + \frac{3}{4} \right) \right] & \text{for } k \geq 2. \end{cases} \quad (45)$$

C. Comparison between theoretical and simulated results

Figure 6 shows the comparison between the simulated results previously presented in Table I and the theoretical predictions obtained from DMFA and FEMCA for the critical temperature as a function of the size k . The MC simulations reveal two main characteristics for the behavior of the critical temperature versus the size k of linear rigid k -mers: (i) the curve presents a minimum for $k=2$ and (ii) for $k>2$, the critical temperature is monotonically increasing on k . Both characteristics are well reproduced by FEMCA and DMFA for clusters of sizes $(k \times 2)$ and $(2k \times 2)$. On the other hand, the curves corresponding to DMFA and clusters of sizes $(k \times 1)$ and $(2k \times 1)$ do not reproduce the minimum in $k=2$. This behavior can be understood as follows.

Equation (38) shows that $k_B T_c(k)/w$ depends on the mean energy and the entropy of the disordered state. The behavior of these quantities as a function of k allows us to understand the arguments presented in the previous paragraph. In first term, we will analyze the entropy. In the one-dimensional case, s_∞ diminishes as k is increased. The explanation is simple: at $\theta=1/2$, the number of entities per lattice site n_e (and for this reason, the number of accessible states) diminishes as k increases [$n_e(k) \propto 1/2k$]. From Ref. 35, $s_\infty(k=1)=0.693$, $s_\infty(k=2)=0.477$, and $s_\infty(k=3)=0.375$, for monomers, dimers, and trimers adsorbed in 1D, respectively. In 2D, the situation changes slightly: (i) the entropy is similar for monomers and dimers and (ii) for $k>2$, s_∞ diminishes as k is increased. From Ref. 23, $s_\infty(k=1)$

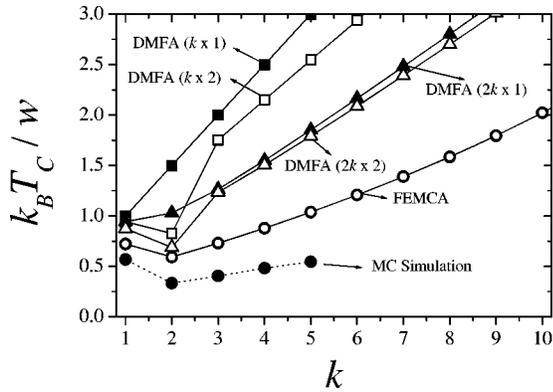


FIG. 6. Comparison between simulated and theoretical results for $k_B T_c / w$ vs k . The symbology is indicated in the figure.

$=0.693$, $s_\infty(k=2)=0.635$, and $s_\infty(k=3)=0.462$, for monomers, dimers, and trimers adsorbed in 2D, respectively. The reason for this is the following. In two dimensions a new degree of freedom appears for the adsorbed particles whose size is $k \geq 2$: dimers, trimers, etc., can rotate on the lattice. The new accessible states for dimers due to possible rotations compensate the diminution in the number of entities with respect to monomers. Consequently, the variation in the entropy between monomers and dimers is small. However, due to the fact that the new degree of freedom appears for $k \geq 2$, the diminution in the entropy is reestablished (associated to the diminution in the number of entities).

With respect to the mean energy, the approximated solution given in Eq. (39), shows that $u_\infty(k)$ diminishes until an asymptotic value for higher k 's: $u_\infty(1)=0.5$, $u_\infty(2)=0.375$, $u_\infty(3)=0.333$, $u_\infty(4)=0.312$, \dots , $u_\infty(\infty)=0.25$. Note that $u_\infty(k)$ diminishes abruptly (slightly) in the range $k=1-2$ ($k=2-\infty$).

Now we can interpret the two main characteristics in the numerical curve $k_B T_c(k)/w$ versus k presented in Fig. 6. (1) From $k=1$ to $k=2$, the mean energy value diminishes appreciably. On the other hand, the entropy remains practically constant. Thus, in agreement with FEMCA [Eqs. (38) and (45)], $k_B T_c(k)/w$ decreases between $k=1$ and $k=2$. (2) For $k \geq 2$, the entropy diminishes monotonically and the mean energy stabilize its value. Thus, $k_B T_c(k)/w$ increases monotonically as k is increased, such as is predicted by FEMCA.

In addition, as we discuss above, the possibility of orientation of the adsorbed molecules originates the minimum appearing in the curve of $k_B T_c(k)/w$ versus k . Based on these arguments it is possible to understand the results obtained from DMFA. For linear clusters [($k \times 1$) and ($2k \times 1$)] the curves increase monotonically and do not reproduce the minimum in $k=2$. When a new degree of freedom is included in the clusters, allowing the rotation of the dimers, the

results from DMFA are in good qualitative agreement with MC simulations [see the curves for ($k \times 2$) and ($2k \times 2$) in Fig. 6].

IV. CONCLUSIONS

In the present work, we have addressed the critical properties of repulsive linear k -mers on two-dimensional square lattice at half coverage, and shown the dependence of the critical temperature on the size k . The results were obtained by using MC simulations and two analytical approaches DMFA and FEMCA, which were introduced in this contribution.

Several conclusions can be drawn from the present work. On one hand, the critical temperature dependence on the particle size of an ordered phase ($\theta=1/2$) of repulsive straight particles have been reported and we found that dimers present the minimum value. An analysis of the delicate balance between the size dependence of entropy and energy per site allowed to interpret this minimum and the overall behavior of T_c versus k .

On the other hand, the comparison between DMFA and MC simulations allowed us to test the validity of this analytical approximation in the present problem. In this sense, we can conclude that for linear clusters [($k \times 1$), ($2k \times 1$), etc.] the theoretical results disagree with the computational simulations. Contrarily, for rectangular clusters [($k \times 2$), ($2k \times 2$), etc.] DMFA is in good qualitative agreement with the simulations.

Moreover, FEMCA appears as a meaningful theoretical argument to account for the main features of the critical temperature since (i) provides results in very good qualitative agreement with MC simulations and (ii) constitutes a theoretical framework in order to interpret the behavior of T_c vs k . According to Eq. (38), T_c depends on the ratio of the energy and entropy differences between a fully disordered state ($T \rightarrow \infty$) and the ground state ($T \rightarrow 0$). In other words, an increase in $\Delta u(\Delta s)$ with respect to $\Delta s(\Delta u)$ implies an increase (decrease) in T_c . This important result can be generalized beyond the specific system studied in the present contribution. In the particular case of repulsive linear k -mers, the k dependence of T_c is as follows: the mean energy diminishes appreciably from $k=1$ to $k=2$ while the entropy remains practically constant. Consequently, T_c for dimers lowers with respect to the one for monomers. For $k > 2$, the entropy diminishes monotonically and the mean energy stabilize its value. Thus, T_c increases monotonically as k is increased.

The two models presented in this paper represent very important tools in order to study the phase behavior of different interacting lattice gases. In particular, future efforts will be directed to obtain T_c versus k for other existing ordered phases in the whole range of coverage.

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