# Critical behavior of repulsive linear *k*-mers on triangular lattices

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Monte Carlo (MC) simulations and finite-size scaling analysis have been carried out to study the critical behavior in a submonolayer two-dimensional gas of repulsive linear *k*-mers on a triangular lattice at coverage $k/(2k+1)$. A low-temperature ordered phase, characterized by a repetition of alternating files of adsorbed *k*-mers separated by $k+1$ adjacent empty sites, is separated from the disordered state by an order-disorder phase transition occurring at a finite critical temperature, $T_c$. The MC technique was combined with the recently reported free-energy minimization criterion approach (FEMCA) [F. Romá *et al.*, Phys. Rev. B **68**, 205407 (2003)] to predict the dependence of the critical temperature of the order-disorder transformation. The dependence on *k* of the transition temperature, $T_c(k)$, observed in MC is in qualitative agreement with FEMCA. In addition, an accurate determination of the critical exponents has been obtained for adsorbate sizes ranging between $k=1$ and 3. For $k>1$, the results reveal that the system does not belong to the universality class of the two-dimensional Potts model with $q=3$ ($k=1$, monomers). Based on symmetry concepts, we suggested that the behavior observed for $k=1$, 2, and 3 could be generalized to include larger particle sizes ($k \geq 2$).

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## I. INTRODUCTION

Two previous articles,[1,2] referred to as papers I and II, respectively, were devoted to the study of repulsively interacting *k*-mers on square lattices at half coverage. In paper I, Monte Carlo (MC) simulations were used to deal with such a problem. 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 an order-disorder phase transition occurring at a critical temperature $T_c$. The $T_c$ dependence on the particle size showed an intriguing behavior, with a pronounced minimum at $k=2$. In addition, two theoretical approaches, the detailed mean-field approximation (DMFA) and the free-energy minimization criterion approach (FEMCA), were combined with Monte Carlo simulations to obtain the critical temperature of the order-disorder transformation. Predictions from FEMCA, based on a free-energy minimization criterion, showed a remarkable qualitative agreement with the simulation data and allowed us to interpret the physical meaning of the mechanisms underlying the observed transitions. Paper II was a step further, analyzing the universality class of the phase transition. For this purpose, an extensive work of MC simulations and finite-size scaling analysis was carried out. Based on the strong axial anisotropy of the low-temperature phase for $k \geq 2$, a new order parameter measuring the orientation of the admolecules was introduced. Taking advantage of its definition, an accurate determination of the critical exponents was obtained for adsorbate sizes ranging between $k=2$ and 4. The evaluation of the complete set of static critical exponents, $\alpha$, $\beta$, $\gamma$, and $\nu$ for different molecular sizes, has shown that, for linear *k*-mers with $k \geq 2$, this phase transition does not belong to the universality class of the two-dimensional Ising model ($k=1$). The main source for this behavior was associated with the breaking of the orientational symmetry occurring for $k \geq 2$, which does not occur for $k=1$. Moreover, the critical exponents reported in paper II do not correspond to a known universality class, according to the current classification of order-disorder transitions on surfaces given by Schick.[3] The aim of this paper is to study repulsive straight *k*-mers on triangular lattices using the same techniques developed in papers I and II.

The behavior of interacting dimers has also been analyzed by using graph theory.[4] In Ref. 4, a Sierpinski gasket with a fractal dimension of $\ln 3 / \ln 2$ was used as substrate. However, the technique can be extended to other fractal graphs with low "ramification degree." With respect to triangular lattices, leading contributions have been published by Hock and McQuistan[5] and Phares and Wunderlich.[6] The thermodynamics of noninteracting dimers was obtained from the knowledge of the occupational degeneracy of dimers partially covering the lattice. Later, Rżysko and Borówko[7] studied the interesting problem of heteronuclear dimers consisting of different segments *A* and *B* adsorbed on square and triangular lattices. The authors considered models with attractive *B-B* and *A-B* nearest-neighbor energies and variable *A-A* energy (attractive as well as repulsive). A rich variety of phase transitions was reported along with a detailed discussion about critical exponents and universality class. In the case of a triangular lattice, all systems belong to the class of universality of the two-dimensional Potts model with $q=3$.

In previous work, we have studied the adsorption thermodynamics of attractive and repulsive dimers on honeycomb and triangular lattices.[8] From the study of adsorption properties such as adsorption isotherm, heat of adsorption, and configurational entropy, two different ordered phases occurring in the adlayer were reported for repulsive couplings and low temperatures. Namely, (i) the low coverage ordered phase (LCOP), with 2/5 (5/9) of the sites occupied for a triangular
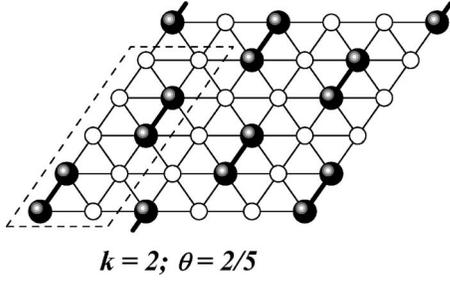
$k = 2; \; \theta = 2/5$

FIG. 1. Snapshot of the ordered phase for dimers at $\theta = 2/5$.

(honeycomb) lattice, and (ii) the high coverage ordered phase (HCOP), with 2/3 of the sites filled for both lattices. In the particular case of triangular lattices, the LCOP resembles the $(4 \times 2)$ ordered structure of repulsive dimers on square lattices at half-coverage. As in the last case, from the LCOP appearing in dimers at $\theta = 2/5$, we can predict the existence of an ordered structure for repulsive straight $k$-mers on triangular lattices at coverage $k/(2k+1)$. A snapshot of this low-temperature phase, characterized by a repetition of alternating files of adsorbed $k$-mers separated by $k+1$ adjacent empty sites, is shown in Fig. 1 for $k=2$.

In this context, the scope of the present work is (i) to calculate, via MC simulations,[9–11] finite-size scaling analysis,[12] and FEMCA, the critical temperature as a function of the size of the adsorbed molecules for repulsive linear $k$-mers adsorbed on triangular lattices at $\theta = k/(2k+1)$; and (ii) to determine critical exponents and universality. The outline of the paper is as follows. In Sec. II, we describe the lattice-gas model and the simulation scheme. In Sec. III, we present the results. 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 describe the lattice-gas model for the adsorption of particles with multisite occupancy in the monolayer regime. We consider the adsorption of homonuclear $k$-mers on triangular lattices. The adsorbate molecules are assumed to be composed by $k$ identical units in a linear array with constant bond length equal to the lattice constant $a$. The $k$-mers can only adsorb flat on the surface occupying $k$ lattice sites. The surface is represented as a triangular array of $M = L \times L$ adsorptive sites, where $L$ is the linear size of the array. In order to describe a system of $N$ $k$-mers adsorbed on $M$ sites at a given temperature $T$, let us introduce the occupation variable $c_i$, which can take the values $c_i = 0$ or 1 if the site $i$ is empty or occupied by a $k$-mer unit, respectively. The $k$-mer retains its structure upon adsorption, desorption, and diffusion. The Hamiltonian of the system is given by

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

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 $\epsilon_o$ 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. Finally, $\epsilon_o$ is set equal to zero, without any loss of generality.

### B. Order parameter and Monte Carlo method

In order to study the order-disorder phase transition occurring in the adsorbate, it is convenient to define a related order parameter. For $k=1$, a standard geometrical order parameter can be built.[14] For this purpose, the lattice is separated into three intersecting sublattices, $\rho = 1, 2, 3$, and for each one of them the functions

$$f_\rho = \frac{3}{M} \sum_{i \in \rho} c_i \qquad (2)$$

are obtained. Then the order parameter $\varphi$ of the system is given by

$$\varphi = \frac{4}{\sqrt{6}} \left( \sum_\rho \varphi_\rho^2 \right)^{1/2}, \qquad (3)$$

where

$$\varphi_\rho = \frac{\delta_{\rho\tau\chi}}{2} \left[ f_\rho - \frac{(f_\tau + f_\chi)}{2} \right] \qquad (4)$$

and the $\delta$ takes the value 1 for a cyclic permutation of subindexes (1,2,3) and the value 0 otherwise.

As in paper II, an order parameter measuring the orientation of the admolecules in the ordered structure will be defined for $k>1$. Figure 1 shows a snapshot corresponding to one of the possible configurations of the low-temperature phase for dimers at $\theta = 2/5$. As it can be observed, the structure adopts an orientation along one of the lattice's axis. Taking advantage of this property, we define $\delta_k$ as

$$\delta_k = \frac{1}{2} \left( \left| \frac{N_1 - N_2}{N} \right| + \left| \frac{N_2 - N_3}{N} \right| + \left| \frac{N_3 - N_1}{N} \right| \right), \qquad (5)$$

where $N_x$ $(x=1,2,3)$ represents the number of $k$-mers aligned along one of the three axes of the lattice and $N = N_1 + N_2 + N_3$. It is worth noticing that, due to the fact that the low-temperature phase is isotropic for monomers, $\delta_k$ is restricted to $k \geq 2$.

When the system is disordered $(T > T_c)$, the three orientations are equivalents and $\delta_k$ is zero. As the temperature is decreased below $T_c$, the $k$-mers align along one direction and $\delta_k$ is different from zero $(\delta_k = 1$ at $T = 0)$. Then, $\delta_k$ appears as a good order parameter, evidencing the order-disorder phase transition.

As is well known for $k=1$, the system belongs to the universality class of the three-state Potts model[3,13–15] $(\nu = 5/6, \beta = 1/9, \gamma = 13/9$, and $\alpha = 1/3)$. In this case, the phase transition is accomplished by a breaking of the translational symmetry (the coverage of the sublattices is different for $T < T_c$). However, an additional breaking of the orientational symmetry occurs for $k \geq 2$. Consequently, a change in the

universality class is expected for linear molecules with $k$ $\geqslant 2$ with respect to the case of monomers.

In order to study the critical behavior of the system, we have used an efficient exchange MC method[16,17] and finite-size scaling analysis.[9,12,18,20] As in Ref. [16], we build a compound system that consists of $m$ noninteracting replicas of the system concerned. The $m$th replica is associated with the temperature $T_m$ [or $\beta_m = 1/(k_B T_m)$, $k_B$ being the Boltzmann constant]. In other words, each replica is in contact with its own heat bath having different temperature. Under these conditions, the algorithm to carry out the simulation process is the following.

(i) The compound system of $m$ replicas is generated. For this purpose, each replica is simulated simultaneously and independently as a canonical ensemble for $n_1$ MC steps by using a standard importance sampling MC method.[1,2,9,10,21] In order to determine the set of temperatures, $\{\beta_m\}$, we set the highest temperature, $T_{\max}(\beta_{\max})$, in the high-temperature phase where relaxation (correlation) time is expected to be very short and there exists only one minimum in the free-energy space. On the other hand, the lowest temperature, $T_{\min}(\beta_{\min})$, is somewhere in the low-temperature phase whose properties we are interested in. Finally, the difference between two consecutive temperatures is set as $(T_{\max} - T_{\min})/(m-1)$ (equally spaced temperatures).

(ii) Interchange vacancy-particle and diffusional relaxation.[22] The procedure is as follows: (a) One of the $m$ replicas is randomly selected. (b) A $k$-mer and a linear $k$-uple of empty sites, both belonging to the replica chosen in (a), are randomly selected and their positions are established. Then, an attempt is made to interchange its occupancy state with probability given by the METROPOLIS rule,[21]

$$P = \min\{1, \exp(-\beta_m \Delta H)\}, \tag{6}$$

where $\Delta H = H_f - H_i$ is the difference between the Hamiltonians of the final and initial states. (c) A $k$-mer is randomly selected. Then, a displacement to nearest-neighbor positions is attempted (following the METROPOLIS scheme), by either jumps along the $k$-mer axis or reptation by rotation around a unity of the $k$-mer. This procedure (diffusional relaxation) must be allowed in order to reach equilibrium in a reasonable time.

(iii) Exchange of two configurations $X_m$ and $X_{m'}$, corresponding to the $m$th and $m'$th replicas, respectively, is tried and accepted with the probability $W(X_m, \beta_m | X_{m'}, \beta_{m'})$. In general, the probability of exchanging configurations of the $m$th and $m'$th replicas is given by[16]

$$W(X_m, \beta_m | X_{m'}, \beta_{m'}) = \begin{cases} 1 & \text{for } \Delta < 0 \\ \exp(-\Delta) & \text{for } \Delta > 0, \end{cases} \tag{7}$$

where $\Delta = (\beta_m - \beta_{m'})[H(X_{m'}) - H(X_m)]$. As in Ref. [16], we restrict the replica-exchange to the case $m \leftrightarrow m+1$.

(iv) Repeat from step (ii) $m \times M$ times. This is the elementary step in the simulation process or Monte Carlo step (MCS).

The procedure (i)–(iv) is repeated for all lattice sizes. For each size, the equilibrium state can be well reproduced after discarding the first $n_2$ MCS. Then, averages are taken over

TABLE I. Parameters of the parallel tempering runs.

| $k$ | $L$ | $m$ | $n_1$ | $n_2$ | $n_{\mathrm{MCS}}$ | $T_{\min}$ | $T_{\max}$ |
|---|---|---|---|---|---|---|---|
| 1 | 30 | 40 | $10^5$ | $10^5$ | $5 \times 10^5$ | 0.279 | 0.392 |
|  | 60 | 40 | $10^5$ | $10^5$ | $5 \times 10^5$ | 0.311 | 0.360 |
|  | 90 | 40 | $10^5$ | $10^5$ | $5 \times 10^5$ | 0.290 | 0.381 |
|  | 120 | 40 | $10^5$ | $10^5$ | $5 \times 10^5$ | 0.325 | 0.346 |
| 2 | 10 | 41 | $5 \times 10^4$ | $5 \times 10^4$ | $10^5$ | 0.22 | 0.30 |
|  | 15 | 41 | $5 \times 10^4$ | $5 \times 10^4$ | $10^5$ | 0.22 | 0.27 |
|  | 20 | 61 | $5 \times 10^4$ | $5 \times 10^4$ | $10^5$ | 0.22 | 0.26 |
|  | 25 | 101 | $5 \times 10^4$ | $5 \times 10^4$ | $10^5$ | 0.23 | 0.25 |
|  | 30 | 131 | $2.5 \times 10^4$ | $2.5 \times 10^4$ | $5 \times 10^5$ | 0.23 | 0.25 |
| 3 | 14 | 101 | $1.5 \times 10^5$ | $1.5 \times 10^5$ | $3 \times 10^5$ | 0.300 | 0.400 |
|  | 21 | 61 | $2.5 \times 10^5$ | $2.5 \times 10^5$ | $5 \times 10^5$ | 0.320 | 0.380 |
|  | 28 | 51 | $2.5 \times 10^5$ | $2.5 \times 10^5$ | $5 \times 10^5$ | 0.335 | 0.360 |
|  | 35 | 51 | $10^6$ | $10^6$ | $2 \times 10^6$ | 0.337 | 0.347 |

$n_{\mathrm{MCS}}$ successive MCS. As was mentioned above, a set of equally spaced temperatures is chosen in order to accurately calculate the physical observables in the close vicinity of $T_c$.

The canonical expectation value of a physical quantity $A$ is obtained in the usual way as follows:

$$\langle A \rangle_{\beta_m} = \frac{1}{n_{\mathrm{MCS}}} \sum_{t=1}^{n_{\mathrm{MCS}}} A[X_m(t)]. \tag{8}$$

All calculations were carried out using the parallel cluster BACO of Universidad Nacional de San Luis, Argentina. This facility consists of 60 PCs each with a 3.0 MHz Pentium-4 processors. The values of the parameters used in the parallel tempering runs are shown in Table I.

The internal energy per lattice site, $u$, is obtained as simple averages,

$$u = \frac{1}{L^2} \langle H \rangle_T. \tag{9}$$

The specific heat $C$ is sampled from energy fluctuations,

$$C = \frac{1}{L^2 k_B T^2} [\langle H^2 \rangle_T - \langle H \rangle_T^2]. \tag{10}$$

The quantities related with the order parameter, such as the susceptibility $\chi$ and the reduced fourth-order cumulant $U_L$ introduced by Binder,[9] can be calculated as

$$\chi = \frac{L^2}{k_B T} [\langle z^2 \rangle_T - \langle z \rangle_T^2], \tag{11}$$

$$U_L(T) = 1 - \frac{\langle z^4 \rangle_T}{3 \langle z^2 \rangle_T^2}, \tag{12}$$

where $z(\equiv \varphi$ or $\delta_k)$ represents the order parameter and the thermal average $\langle \cdots \rangle_T$, in all the quantities, means the time average throughout the MC simulation.
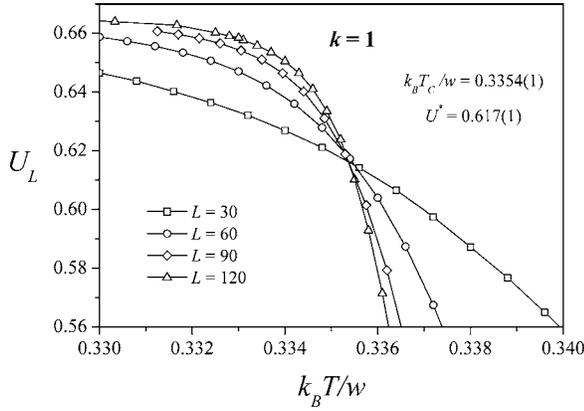
FIG. 2. Curves of $U_L(T)$ vs $k_B T/w$ for $k=1$ and different lattice sizes as indicated. From their intersections one obtains $k_B T_c/w$.

## III. RESULTS

The calculations were developed for linear $k$-mers, with $k$ ranging between 1 and 3, on a triangular $L \times L$ lattice at coverage $k/(2k+1)$. In addition, conventional periodic boundary conditions were considered. Note, however, that the choice of appropriate linear dimensions $L$ has to be done in such a way that the ordered structures are not disturbed. Thus, for $k=1$, the effect of finite size was investigated by examining lattices varying from $L=30$ to 120. In the case of $k=2$ and 3, $L=10,15,20,25,30$ and $L=14,21,28,35$ were used, respectively, with an effort reaching almost the limits of our computational capabilities.

The critical temperatures have been estimated from the plots of the reduced four-order cumulants $U_L(T)$ plotted versus $k_B T/w$ for several lattice sizes. In the vicinity of the critical point, cumulants show a strong dependence on the system size. However, at the critical point the cumulants adopt a nontrivial value $U^*$, irrespective of system sizes in the scaling limit. Thus, plotting $U_L(T)$ for different linear dimensions yields an intersection point $U^*$, which gives an accurate estimation of the critical temperature in the infinite system.

Hereafter we discuss the behavior of the critical temperature as a function of the size $k$, for monolayer adsorption of $k$-mers. Figure 2 illustrates the reduced four-order cumulants
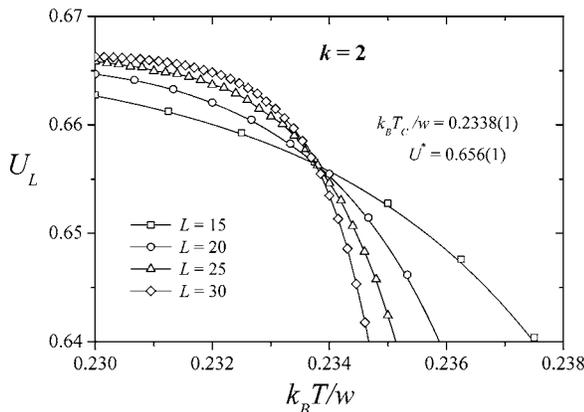

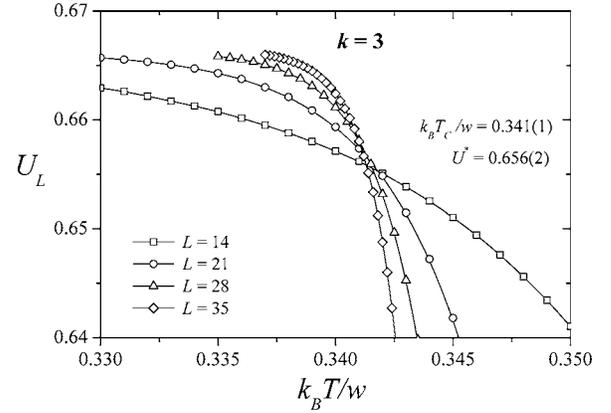
FIG. 3. Same as Fig. 2 for dimers ($k=2$).

$U_L(T)$ plotted versus $k_B T/w$ for several lattice sizes and $k$ =1. From their intersections one gets the estimation of the critical temperature. The value obtained for the critical temperature was $k_B T_c/w=0.3354(1)$, with $U^*=0.617(1)$. Our calculation of the critical temperature is in good agreement with the transfer-matrix result of Kinzel and Schick.[23] With respect to Monte Carlo calculations, Metcalf[24] in the 1970s and Chin and Landau[25] in the 1980s obtained similar values of the critical temperature. Namely, $k_B T_c/w \approx 0.35$. Due to the lattice sizes and the number of MCS used in this contribution, our estimate of $T_c$ is expected to be more accurate than those reported previously.

Figures 3 and 4 show the results of $U_L(T)$ for $k=2$ and 3, respectively. In the case $k=2$, the value estimated for $k_B T_c/w$ [=0.2338(1)] agrees very well with previous determinations reported in the literature.[8] In Ref. 8, a value $k_B T_c/w \approx 0.23$ was obtained from the inflection on the function $s(T)$, $s(T)$ being the configurational entropy of the adlayer as a function of the temperature. With respect to $k=3$, the value obtained for $k_B T_c/w$ [=0.341(1)] is reported.

The values of the critical temperature, which are collected in Table II for $k=1-3$, present a nontrivial behavior as a function of the particle size $k$. To understand the dependence of $T_c(k)$ on $k$, it is convenient to appeal to the recently reported FEMCA.[1] In this theoretical framework, $T_c$ depends on the ratio of the energy per lattice site and entropy per lattice site differences, $u_\infty - u_0$ and $s_\infty - s_0$, respectively, between a fully disordered state ($T \to \infty$) and the ground state ($T \to 0$),



FIG. 4. Same as Fig. 2 for trimers ($k=3$).

TABLE II. Values of $T_c$, $\alpha$, $\beta$, $\gamma$, $\nu$, and $U^*$ (as indicated in the text) for $k$ ranging from 1 to 3. In the case $k=1$, the critical exponents correspond to the well-known two-dimensional Potts model with $q=3$.

| $k$ | $k_B T_c/w$ | $\alpha$ | $\beta$ | $\gamma$ | $\nu$ | $U^*$ |
|---|---|---|---|---|---|---|
| 1 | 0.3354(1) | 1/3 | 1/9 | 13/9 | 5/6 | 0.617(1) |
| 2 | 0.2338(1) | 0.95(3) | $\approx 0.0005$ | 1.17(3) | 0.50(1) | 0.656(1) |
| 3 | 0.341(1) | 1.00(4) | $\approx 0.0000$ | 1.20(4) | 0.50(1) | 0.656(2) |

$$T_c \approx \frac{\Delta u}{\Delta s} = \frac{u_\infty - u_0}{s_\infty - s_0}. \qquad (13)$$

In this case, the mean energy and the entropy for the ordered state are $u_0 = s_0 = 0$. Then, the critical temperature depends on the mean energy and the entropy of the disordered state. $u_\infty$ can be calculated from the quasichemical approximation,[26]

$$\frac{u_\infty}{w} = \left(\frac{\lambda\theta}{2k} - \alpha\right) \overset{c=6, T\to\infty;}{\underset{\theta=k/(2k+1)}{=}} \frac{2k+1}{5k+4}, \qquad (14)$$

$c$ being the lattice connectivity. In addition,

$$\lambda = (c-2)k + 2, \qquad (15)$$

$$\alpha = \frac{\lambda c}{2k} \frac{\theta(1-\theta)}{\left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta + b\right]}, \qquad (16)$$

and

$$b = \left\{\left[\frac{c}{2} - \left(\frac{k-1}{k}\right)\theta\right]^2 - \frac{\lambda c}{k}[1 - \exp(-w/k_B T)]\theta(1-\theta)\right\}^{1/2}. \qquad (17)$$

With respect to the entropy,

$$s_\infty/k_B = \ln 3 - (2/3)\ln 2 \quad \text{for } k = 1, \qquad (18)$$

and

$$\begin{aligned}\frac{s_\infty}{k_B} &= \frac{\theta}{k}\ln\frac{c}{2} - (1-\theta)\ln(1-\theta) - \frac{\theta}{k}\ln\frac{\theta}{k} \\ &\quad + \left[1 - \frac{(k-1)}{k}\theta\right]\ln\left[1 - \frac{(k-1)}{k}\theta\right] \\ &\overset{c=6;}{\underset{\theta=k/(2k+1)}{=}} \frac{\ln 3}{2k+1} - \frac{k+1}{2k+1}\ln\left(\frac{k+1}{2k+1}\right) - \frac{1}{2k+1} \\ &\quad \times \ln\left(\frac{1}{2k+1}\right) + \frac{k+2}{2k+1}\ln\left(\frac{k+2}{2k+1}\right) \quad \text{for } k \geq 2.\end{aligned} \qquad (19)$$

In the last equation, the entropy was obtained from the extension to higher dimensions of the exact configurational factor of linear chains adsorbed on one-dimensional lattices.[19] Under these considerations, the critical temperature results,

$$\frac{k_B T_c(k)}{w} \approx \frac{u_\infty/w}{s_\infty/k_B} = \begin{cases} 1/(3\ln 3 - 2\ln 2) = 0.5237 & \text{for } k = 1 \\ \dfrac{(2k+1)^2}{\left\{(5k+4)\left[\ln 3 - (k+1)\ln\left(\dfrac{k+1}{2k+1}\right) - \ln\left(\dfrac{1}{2k+1}\right) + (k+2)\ln\left(\dfrac{k+2}{2k+1}\right)\right]\right\}} & \text{for } k \geq 2. \end{cases} \qquad (20)$$

Figure 5 presents the theoretical predictions obtained from FEMCA [Eq. (20)] for the critical temperature as a function of the size $k$. For high values of $k$, $k_B T_c(k)/w$ increases 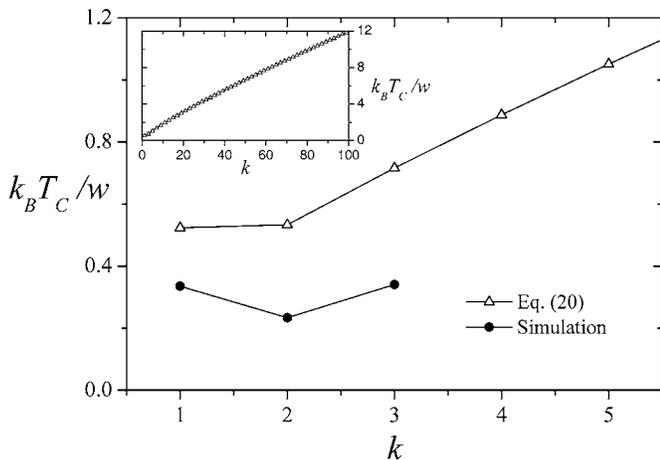monotonically as $k$ is increased (see inset). In the other extreme, the theoretical curve shows a marked break at $k=2$, which is in good qualitative agreement with the minimum obtained from Monte Carlo simulations.

The theoretical approach allows us to interpret the physical meaning of the main features of the critical temperature. In fact, Eq. (13) shows that $k_B T_c/w$ depends on the mean energy and the entropy of the disordered state. In the first term, we will analyze the entropy. When one passes from $(k=1, \theta=1/3)$ to $(k=2, \theta=2/5)$, the number of entities per lattice site, $n_e$, and for this reason, the number of accessible states, diminishes [in general, $n_e(k) \propto 1/(2k+1)$]. On the other hand, 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. Thus, $s_\infty(k=1, \theta=1/3) = 0.6365$ [see Eq. (18)] and $s_\infty(k=2, \theta=2/5) \approx 0.6339$ (Ref. 8) for monomers and dimers adsorbed in triangular lattices, respectively. 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
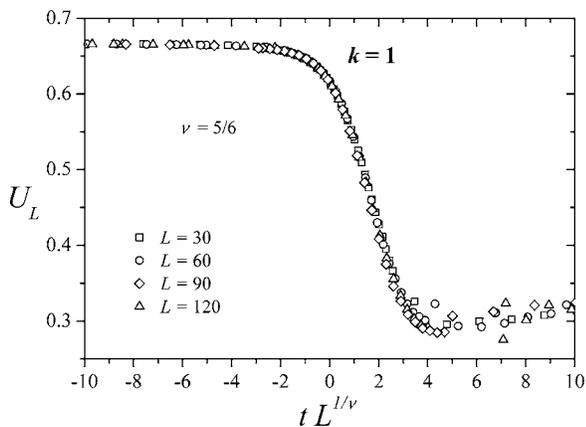


FIG. 5. Comparison between simulated and theoretical results for $k_B T_c/w$ vs $k$. The symbology is indicated in the figure.

FIG. 6. Data collapsing for the cumulants in Fig. 2.

diminution in the number of entities) and $s_\infty$ diminishes as $k$ is increased for $k > 2$.

With respect to the mean energy, the approximated solution given in Eq. (14) shows that $u_\infty(k)$ increases until an asymptotic value for higher $k$'s: $u_\infty(1) = 0.333$, $u_\infty(2) = 0.357$, $u_\infty(3) = 0.368$, $u_\infty(4) = 0.375, \ldots, u_\infty(\infty) = 0.40$.

Now we can interpret the two different regimes observed in the curve of Fig. 5. While $u_\infty(k)$ changes slightly in all range of $k$, $s_\infty(k)$ presents an abrupt change at $k = 2$. Physically, this change in the entropy, which is responsible for the marked break appearing in the curve of $k_B T_c(k)/w$ versus $k$, is associated with the possibility of orientation of the adsorbed molecules for $k \geq 2$.

As was shown in Figs. 3 and 4, the intersections of the cumulants for $k = 2$ and 3 suggest that the system suffers a
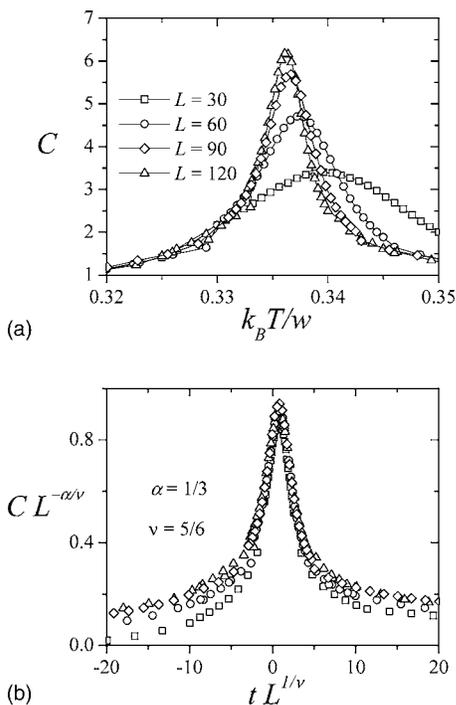


FIG. 7. (a) Size dependence of the specific heat, $C$ (with $k = 1$), as a function of temperature. (b) Data collapsing ($CL^{-\alpha/\nu}$ vs $tL^{1/\nu}$) for the curves in (a).
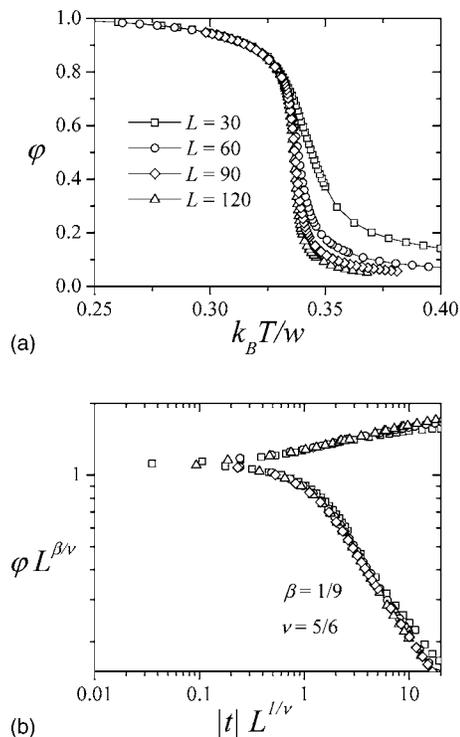


FIG. 8. (a) Size dependence of the order parameter, $\varphi$ (with $k = 1$), as a function of temperature. (b) Data collapsing ($\varphi L^{\beta/\nu}$ vs $|t|L^{1/\nu}$) for the curves in (a).

phase transition at coverage $k/(2k+1)$. In order to corroborate this finding, the critical exponents will be calculated in the following.

In the first term, we study exhaustively the well-known lattice gas of repulsive monomers. Once we know $T_c$ (see Fig. 2), the critical exponent $\nu$ can be calculated from the full data collapsing of $U_L$. The results are shown in Fig. 6 ($t \equiv T/T_c - 1$), where an excellent fit was obtained for $\nu = 5/6$. Given $k_B T_c/w = 0.3354(1)$ and $\nu = 5/6$, $\alpha$, $\beta$, and $\gamma$ were obtained from the collapse of the curves of $C$, $\varphi$, and $\chi$, as is shown in Figs. 7–9, respectively. The data scaled extremely well using $\alpha = 1/3$, $\beta = 1/9$, and $\gamma = 13/9$, which corroborates that the case of $k = 1$ corresponds to the universality class of the two-dimensional Potts model with $q = 3$. The values of the critical exponents along with the intersection point of the cumulants are collected in Table II.

The finite-size scaling study was carried out for $k = 2$ (Figs. 10–13) and $k = 3$ (data not shown here). The resulting values of the critical exponents, which are listed in Table II, point out clearly the existence of a different universality class from that of the three-state Potts model.

As can be demonstrated, the set of critical exponents for dimers and trimers fulfills the well-known inequalities of Rushbrooke,[27] $\alpha + 2\beta + \gamma \geq 2$, and Josephson,[28] $d\nu + \alpha \geq 2$ ($d$ being the dimension of the space), leading to independent controls and consistency checks of the values of all the critical exponents.

The identical results (within numerical errors) obtained for the critical exponents corresponding to dimers and trimers corroborate our hypothesis that the breaking of the orientational symmetry occurring for $k \geq 2$ (i) affects the nature of
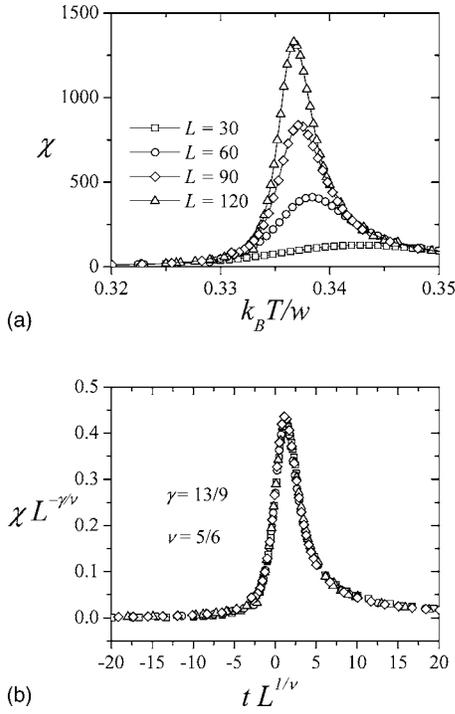
FIG. 9. (a) Size dependence of the susceptibility, $\chi$ (with $k=1$), as a function of temperature. (b) Data collapsing ($\chi L^{-\gamma/\nu}$ vs $tL^{1/\nu}$) for the curves in (a).

the phase transition and (ii) is the main source of the change in the universality class, with respect to the well-known two-dimensional three-state Potts class of universality corresponding to monomers.

Surprisingly, the exponents obtained for repulsive $k$-mers ($k>1$) on a triangular lattice at $\theta=k/(2k+1)$ are very similar to those characterizing the critical behavior of $k$-mers ($k>1$) on square lattices at $\theta=1/2$.[2] However, we think that these two phase transitions belong to different universality classes. Some evidences support our arguments: (i) the value obtained for the fixed-point cumulant $U^*$ varies from square to triangular lattices,[29] and (ii) the low-temperature phase has two and three possible orientations for square and triangular lattices, respectively. Then, the order parameters characterizing both phase transitions have different symmetries.
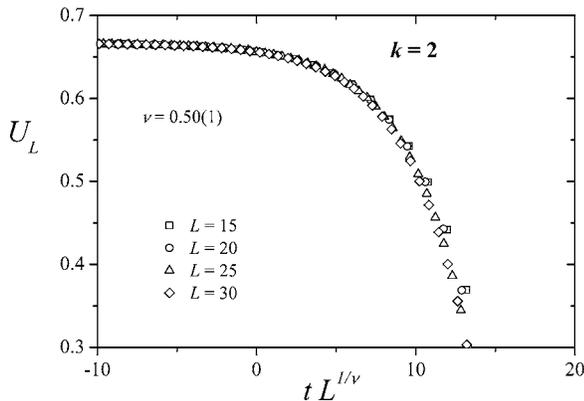


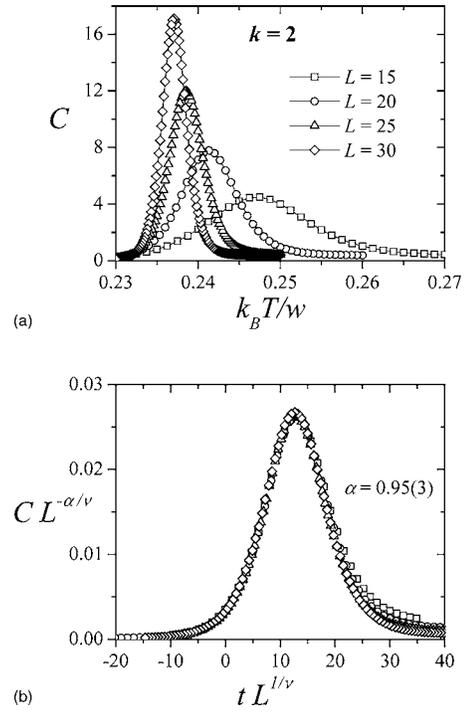FIG. 10. Data collapsing for the cumulants in Fig. 3.



FIG. 11. Same as Fig. 7 for dimers ($k=2$).

## IV. CONCLUSIONS

In the present work, we have addressed the critical properties of repulsive linear $k$-mers on two-dimensional triangular lattices at coverage $k/(2k+1)$, and we showed the dependence of the critical temperature on the size $k$. The results were obtained by using MC simulations and theoretical calculations from FEMCA.
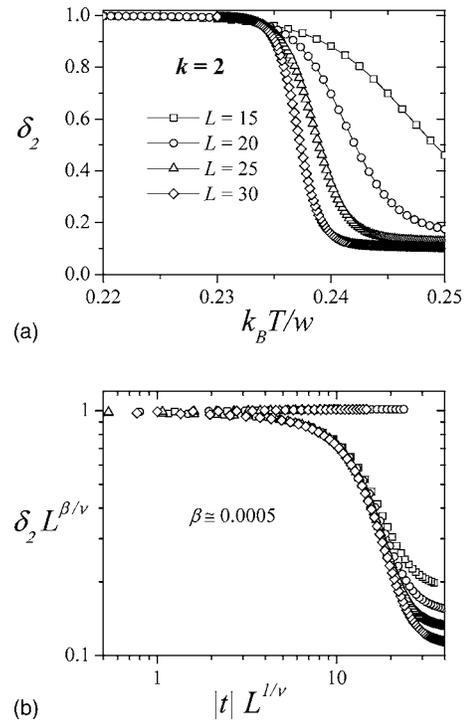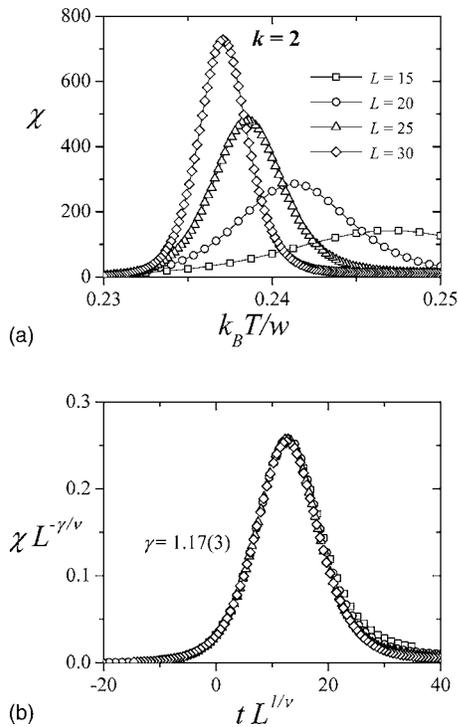


FIG. 12. Same as Fig. 8 for dimers ($k=2$).

(a)

(b)

FIG. 13. Same as Fig. 9 for dimers ($k=2$).

The critical temperature dependence on the particle size of the low-coverage ordered phase $[\theta=k/(2k+1)]$ of repulsive straight particles has been reported, and it was found that dimers present the minimum value. FEMCA showed that an analysis of the delicate balance between the size dependence of entropy and energy per site allows us to interpret qualitatively the behavior of $T_c$ versus $k$.

On the other hand, the evaluation of the complete set of static critical exponents, $\alpha$, $\beta$, $\gamma$, and $\nu$ for different molecular sizes, shows that for linear $k$-mers with $k \geq 2$, this phase transition does not belong to the universality class of the two-dimensional Potts model with $q=3$. The main source for this behavior is the breaking of the orientational symmetry occurring for $k \geq 2$, which does not occur for $k=1$. Moreover, the critical exponents reported in the present paper for $k \geq 2$ do not correspond to a known universality class, according to the current classification of order-disorder transitions on surfaces given by Schick.[3]

A detailed scaling analysis shows that usual hyperscaling relations (inequalities of Rushbrooke and Josephson) are fulfilled and lead to independent controls of the values of all the critical exponents.

Future efforts will be directed to obtain the critical behavior for other existing ordered phases in the whole range of coverage.

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[29] Even though this criterion has been widely used in the literature in order to identify the universality class of a given transition (see, for example, Ref. 7), it is not easy to establish a theoretical framework of general applicability. In fact, recent studies (on models with the same universality class) have found a nonuniversal behavior of $U^*$.[30]

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