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Universality class of interacting k-mers in a two-dimensional lattice system

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Monte Carlo 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 square lattice at half coverage. A $(2k\times 2)$ ordered phase, characterized by alternating files of k-mers separated by k adjacent empty sites, is separated from the disordered state by a order-disorder phase transition occurring at a finite critical temperature. Based on the strong axial anisotropy of the low-temperature phase for $k\geqslant 2$, an order parameter measuring the orientation of the particles has been introduced. Taking advantage of its definition, an accurate determination of the critical exponents has been obtained for three adsorbate sizes. Namely, $\nu=0.53(1)$, $\beta=0.02(1)$, $\gamma=1.14(3)$, and $\alpha=0.93(3)$ for $k=2$ (dimers); $\nu=0.54(1)$, $\beta=0.03(1)$, $\gamma=1.16(3)$, and $\alpha=0.89(3)$ for $k=3$ (trimers); and $\nu=0.53(2)$, $\beta=0.02(1)$, $\gamma=1.14(3)$, and $\alpha=0.89(4)$ for $k=4$ (tetramers). In the studied cases, the results reveal that the system does not belong to the universality class of the two-dimensional Ising model ($k=1$, monomers). We pointed out that the breaking of the orientational symmetry characterizing the low-temperature phase for particles occupying more than one site is the main source of this change in the universality class. Consequently, we suggested that the behavior observed for dimers, trimers, and tetramers could be generalized to include larger particle sizes ($k\geqslant 2$). Finally, hyperscaling relations have been validated, leading to independent controls and consistency checks of the values of all the critical exponents.

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I. INTRODUCTION

The two-dimensional lattice-gas model with nearest-neighbor interactions, has been extensively explored in the last decades. This is due in part to the fact that this system is known to provide a useful model for studies of phase transitions occurring in many adsorbed monolayer films.[1–9] Much more modest efforts have been devoted to the study of the simplest generalization of the model to structured gases. In fact, most of the studies are devoted to the adsorption of molecules with single occupancy; however, if some sort of correlation exists, like particles that occupy several k contiguous lattice sites (k-mers), the statistical problem becomes exceedingly difficult.[10–12] This difficulty is mainly associated to three factors which makes the k-mer statistics different from the usual single particle statistics: (i) there is no statistical equivalence between molecules and vacancies; (ii) the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied; and (iii) an isolated vacancy does not determine whether that site can become occupied or not. 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) (Ref. 13) and Au(111).[14,15]

The inherent complexity of the statistical thermodynamics of polyatomics still represents a major limitation to the development of approximate solutions for the thermodynamic functions, which certainly hampers their analysis. However, several attempts have been done in the past in order to understand the critical behavior of adsorbed monolayer films formed of k-mers. A seminal contribution to the theoretical study of phase transitions in monolayers of polyatomics has been made by Firpo *et al.*[16] Although this model was proposed to describe monolayers of long hydrocarbon chains spread at the gas-liquid interface, its theoretical foundation can be applied to describe gas-solid systems. In this approach, the configurational factor in the canonical partition function was obtained from the Di Marzio statistics for rigid rod molecules,[17] and the attractive interactions between the hydrocarbon chains were taken into account in the framework of a mean-field approximation. The theory predicts the existence of only one first-order phase transition corresponding to the two-dimensional gas-liquid condensation for small molecules.

More recently, by using Monte Carlo (MC) simulations, multiple-histogram reweighting[18,19] and finite-scaling techniques,[7,20] Rżysko and Borówko[21–24] have studied a wide variety of systems in presence of multisite occupancy. Among them, attracting dimers in the presence of energetic heterogeneity;[21] heteronuclear dimers consisting of different segments A and B adsorbed on square lattices;[22,23] and trimers with different structures adsorbed on square lattices.[24] In these leading papers, a rich variety of phase transitions was reported along with a detailed discussion about critical exponents and universality class. The authors found that the majority of systems belong to the two-dimensional Ising class of universality. However, in the case of heteronuclear dimers with repulsive A-A coupling and attractive interactions of B-B and A-B types the fluid exhibits a nonuniversal behavior.[23]

The behavior of interacting dimers has also been analyzed by using graph theory.[25] In Ref. 25, a Sierpinski gasket with a fractal dimension of $\ln 3/\ln 2$ was used as substrate. However, the technique can be extend to other fractal graphs with low "ramification degree." With respect to repulsive couplings, the first papers dealing with phase transitions and ordering phenomena were published by Phares *et al.*[26] The authors calculated the entropy of dimers on semi-infinite square lattices by means of transfer matrix techniques. They concluded that there are a finite number of ordered structures for repulsive dimers in the critical regime. Based on these findings, in previous work we studied the phase diagram of dimers with repulsive nearest-neighbor interactions on square lattices[27] confirming the structural ordering predicted in Ref. 26. From these studies it is not possible to know completely the structure of the different low-temperature ordered phases occurring in the adlayer as the size k of the admolecules is increased. However, from the (4×2) phase appearing in dimers at 50% coverage, it was possible to predict the existence of a $(2k\times 2)$ structure for k-mers at half coverage, which was widely studied in Ref. 28. In this reference, a systematic analysis of critical exponents for each k-mer size was not carried out since it is not necessary to assume any particular universality class in order to calculate the critical temperatures from the order parameter cumulant's properties.[29]

In summary, despite over two decades of intensive work, there exists a lack of systematic studies of the critical exponents (and universality class) characterizing the critical behavior of repulsive linear k-mers (with $k\geqslant 2$) adsorbed on square lattices at half coverage. The objective of this paper is to provide a thorough study in this direction. For this purpose, extensive MC simulations in the canonical ensemble[29–31] supplemented by analysis using finite-size scaling theory (FSST) (Ref. 32) have been carried out. Our results allow to estimate the critical exponents and to test with high accuracy the validity of hyperscaling relations. The outline of the paper is as follows: In Sec. II we introduce the lattice-gas model and the order parameters characterizing the $(2k\times 2)$ structure. In addition, the simulation scheme is described. The MC results are presented in Sec. III. Finally, the general conclusions are given in Sec. IV.

II. BASIC DEFINITIONS AND MONTE CARLO SIMULATION SCHEME

A. The model

In this section, the lattice-gas model for the adsorption of linear rigid molecules is decribed. The surface is represented as a simple square lattice in two-dimensions consisting of $M=L\times L$ adsorptive sites, where L is the size of the system along each axis. The homonuclear linear molecule (or linear k-mer) is modelled 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 bond between segments of molecule cannot be broken and its length remains constant throughout the treatment. Thus, molecules adsorb or desorb as one unit, neglecting any possible dissociation.

In order to describe the 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 following values: $c_i=0$ if the corresponding site is empty and $c_i=1$ if the site is occupied. Under this consideration, the Hamiltonian of the system is given by

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

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_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.

B. Order parameters

In order to study the order-disorder phase transition occurring in the adsorbate, it is convenient to define a related order parameter. In this section, we will refer to two order parameters. The first one, $\varphi_1(k)$,[33] is obtained in terms of sublattice magnetizations and can be used for $k\geqslant 1$. In the particular case of $k=1$, $\varphi_1(k)$ corresponds to the well-known geometrical order parameter, $\varphi_{c(2\times 2)}$, used for describing the order-disorder phase transition occurring for repulsive monomers adsorbed on square lattices.[34,35]

The second quantity, $\varphi_2(k)$, is an order parameter measuring the orientation of the admolecules in the $(2k\times 2)$ ordered structure [Fig. 1 in Ref. 28 shows snapshots corresponding to two possible configurations of the $(2k\times 2)$ phase appearing for adsorbed dimers ($k=2$) in the critical regime]. The degeneracy of this phase is equal to $4k$. The figure suggests a simple way to build an order parameter. In fact, we see that the $(2k\times 2)$ ordered structure (being $k\geqslant 2$) adopts an orientation along one of the axes. Then, the $4k$ configurations can be grouped in two sets, according to the orientation of the phase. Taking advantage of this property, we define an order parameter, $\varphi_2(k)$, as

$$\varphi_2(k) = \left| \frac{N_v - N_h}{N} \right|, \tag{2}$$

where N_v (N_h) represents the number of k-mers aligned along the vertical (horizontal) axis and $N=N_v+N_h$. It is worthwhile to notice that, since the low-temperature phase is isotropic for monomers, $\varphi_2(k)$ can be used for $k\geqslant 2$.

When the system is disordered ($T>T_c$), the two orientations (vertical or horizontal) are equivalents and $\varphi_2(k)$ is zero. As the temperature is decreased below T_c, the k-mers align along one direction and $\varphi_2(k)$ is different from zero [being $\varphi_2(k)=1$ at $T=0$]. On the other hand, $\varphi_1(k)$ is a (minimum) maximum for ($T>T_c$) $T<T_c$.[33] In conclusion, $\varphi_1(k)$ and $\varphi_2(k)$ appear as good order parameters evincing the order-disorder phase transition, with $\varphi_2(k)$ more computationally convenient and better behaved in the limits $T\rightarrow 0$ and $T\rightarrow\infty$.

As the discussion above reveals, the phase transition is accomplished by a breaking of the translational symmetry. This fact is independent of the molecular size. However, an

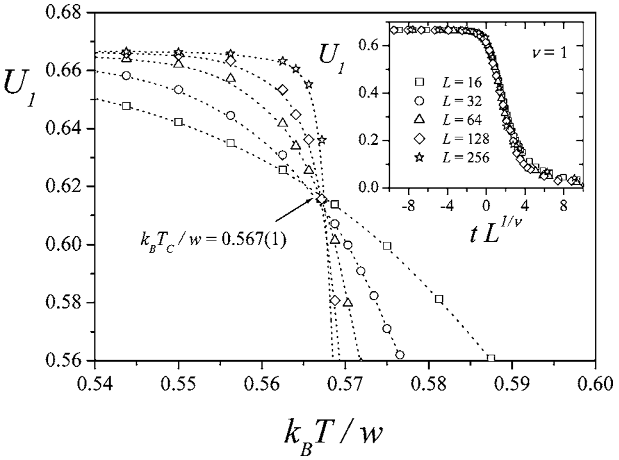

FIG. 1. Curves of $U_1(T)$ versus k_BT/w, for $k=1$ and different lattice sizes as indicated. From their intersections one obtained k_BT_c/w. Inset, data collapsing for the cumulants ($\nu=1$).

additional breaking of the orientational symmetry occurs for $k \geqslant 2$. Consequently, a change in the universality class is expected for linear molecules with $k \geqslant 2$, with respect to the well-known two-dimensional Ising class of universality corresponding to monomers.

C. Monte Carlo method

We have used a standard importance sampling MC method in the canonical ensemble.[29–31] The lattices were generated fulfilling the following conditions.

(1) The sites were arranged in a square lattice with conventional periodic boundary conditions.

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

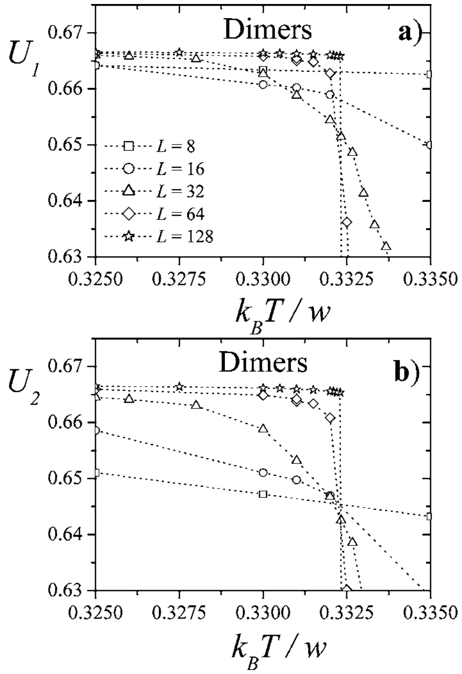

FIG. 2. $U_1(T)$ (a) and $U_2(T)$ (b) versus k_BT/w, for $k=2$ and different lattice sizes as indicated.

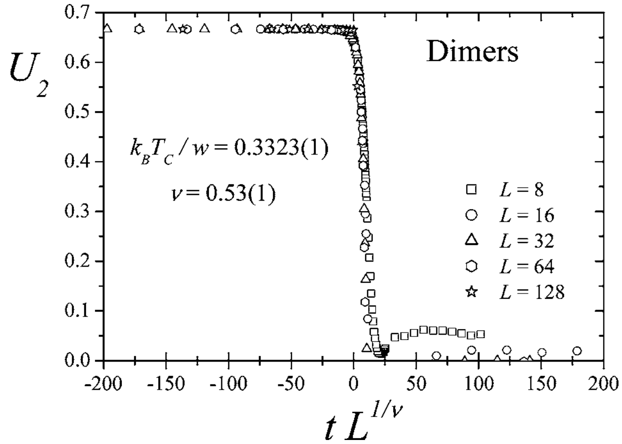

FIG. 3. Data collapsing for the cumulants in Fig. 2(b).

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

The thermodynamic equilibrium is reached by following Kawasaki's dynamics, generalized to deal with polyatomic molecules. The algorithm to carry out an elementary Monte Carlo step (MCS), is the following.

Given a square lattice of M equivalent adsorption sites,

(i) set the value of the temperature T;

(ii) set the value of the coverage, $\theta = kN/M = 1/2$, by adsorbing $N = M/2k$ linear molecules onto the lattice, each molecule occupying k adsorption sites;

(iii) a *k*-mer and a linear *k*-uple of empty sites 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,[36]

$$P = \min\{1, \exp(-\Delta H/k_BT)\}, \tag{3}$$

where $\Delta H = H_f - H_i$ is the difference between the Hamiltonians of the final and initial states and k_B is the Boltzmann constant;

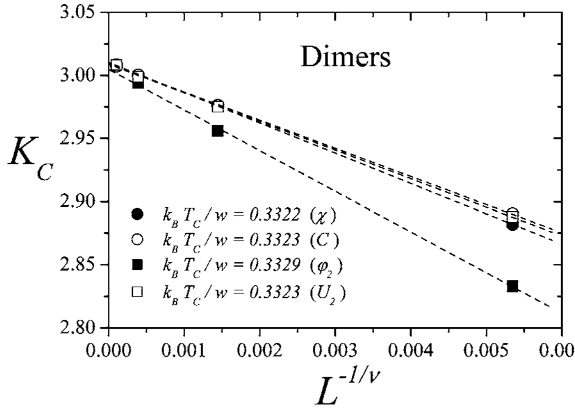

FIG. 4. Plot of $K_c(L)$ vs $L^{-1/\nu}$ for the maxima of the slopes of φ_2 and U_2, as well as of the maxima of C and χ. From extrapolation one gets the estimation of the critical temperature.

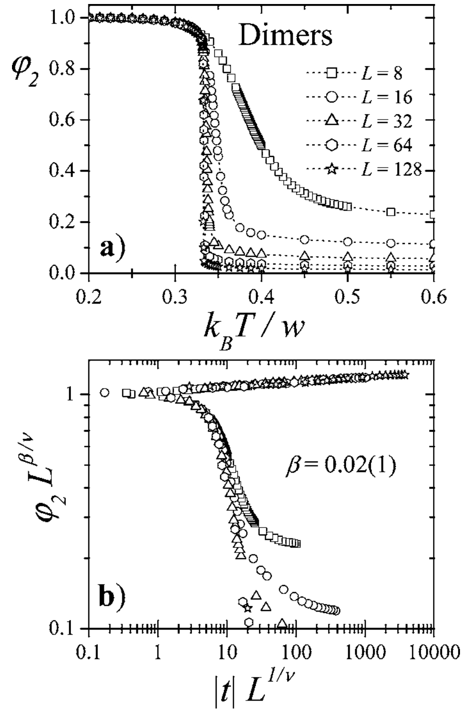

FIG. 5. (a) Size dependence of the order parameter, $\varphi_2(k=2)$, as a function of temperature. (b) Data collapsing ($\varphi_2 L^{\beta/\nu}$ vs $|t|L^{1/\nu}$) for the curves in (a).

(iv) 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; and

(v) repeat steps (iii) and (iv) M times.

The equilibrium state can be reached after discarding the first m' MCSs. Then, averages are taken over m successive MCSs. In each particular case, the values of m' and m were estimated by calculating the autocorrelation function of the order parameter. Details of this procedure will be presented in the next section.

Thermodynamic quantities, such as the internal energy per lattice site, E, is obtained as simple averages,

$$E=\frac{1}{L^2}\langle H\rangle_T. \tag{4}$$

The specific heat C is sampled from energy fluctuations,

$$C=\frac{1}{L^2 k_B T^2}(\langle H^2\rangle_T-\langle H\rangle_T^2). \tag{5}$$

The quantities related with the order parameter, such as the susceptibility χ, and the reduced fourth-order cumulant U introduced by Binder,[29] can be calculated as

$$\chi=\frac{L^2}{k_B T}(\langle\varphi^2\rangle_T-\langle\varphi\rangle_T^2), \tag{6}$$

$$U(T)=1-\frac{\langle\varphi^4\rangle_T}{3\langle\varphi^2\rangle_T^2}, \tag{7}$$

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

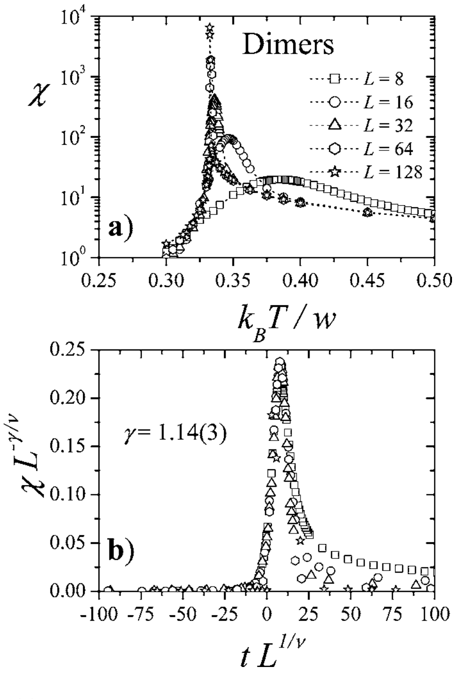

FIG. 6. (a) Size dependence of the susceptibility, χ (with $k=2$), as a function of temperature. (b) Data collapsing ($\chi L^{-\gamma/\nu}$ vs $tL^{1/\nu}$) for the curves in (a).

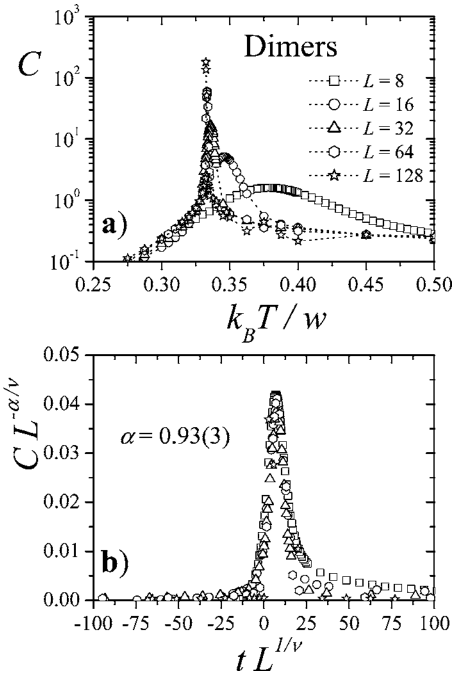

FIG. 7. (a) Size dependence of the specific heat, C (with $k=2$), as a function of temperature. (b) Data collapsing ($CL^{-\alpha/\nu}$ vs $tL^{1/\nu}$) for the curves in (a).

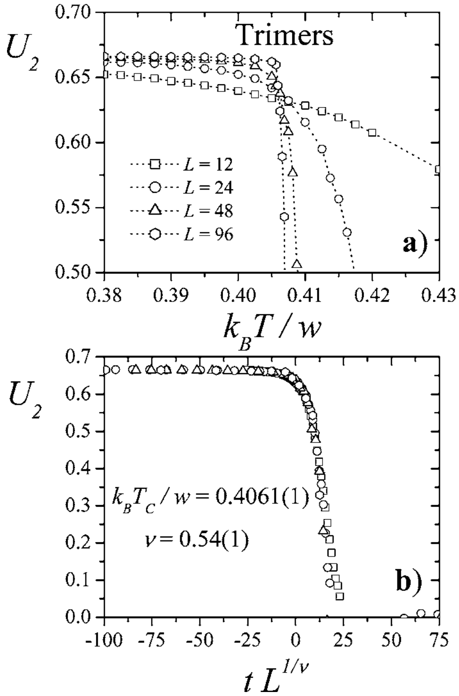

FIG. 8. (a) $U_2(T)$ versus k_BT/w, for $k=3$ and different lattice sizes as indicated. (b) Data collapsing for the curves in (a).

III. COMPUTATIONAL RESULTS

The critical behavior of the present model has been investigated by means of the computational scheme described in the proceeding section and FSST.[29–31] The FSST implies the following behavior of C, φ, χ, and U at criticality,

$$C = L^{\alpha/\nu}\tilde{C}(L^{1/\nu}t), \tag{8}$$

$$\varphi = L^{-\beta/\nu}\tilde{\varphi}(L^{1/\nu}t), \tag{9}$$

$$\chi = L^{\gamma/\nu}\tilde{\chi}(L^{1/\nu}t), \tag{10}$$

$$U(T) = \tilde{U}(L^{1/\nu}t) \tag{11}$$

for $L\rightarrow\infty$, $t\rightarrow 0$ such that $L^{1/\nu}t$=finite, where $t\equiv T/T_c-1$. Here α, β, γ, and ν are the standard critical exponents of the specific heat ($C\propto|t|^{-\alpha}$ for $t\rightarrow 0$, $L\rightarrow\infty$), order parameter ($\varphi\propto t^{\beta}$ for $t\rightarrow 0^+$, $L\rightarrow\infty$), susceptibility ($\chi\propto|t|^{\gamma}$ for $t\rightarrow 0$, $L\rightarrow\infty$), and correlation length ξ ($\xi\propto|t|^{-\nu}$ for $t\rightarrow 0, L\rightarrow\infty$), respectively. $\tilde{C}, \tilde{\varphi}, \tilde{\chi}$, and $\tilde{U}$ are scaling functions for the respective quantities.

In our simulations, the approach towards equilibrium has been monitored by calculating the autocorrelation function of the order parameter. A crude estimate of this quantity allowed us to establish a criterion for determining m'. The procedure was the following: In all the studied cases ($k=1,\cdots,4$) and for the largest lattice size ($L\approx 120$), the relaxation time associated to the autocorrelation function of the order parameter was measured. Then, m' was taken as 10 times this characteristic time. The resulting values for m' ranged between 10^5 for monomers and 10^6 for dimers, trimers, and tetramers. In addition, $m=m'$ configurations were used to compute averages. Finally, findings from this preliminary study suggest that the dynamical exponent z depends on k, varying from $z\approx 2.2$ for monomers (in good agreement with other results reported in the literature[37]) to $z\approx 3$ for dimers, trimers, and tetramers. An accurate determination of z, which is out of the scope of the present paper, would require more detailed simulations.

In order to understand the basic phenomenology, we first consider the well-known lattice gas of repulsive monomers. Figure 1 illustrates the reduced four-order cumulants $U_1(T)$ plotted versus k_BT/w for several lattice sizes. From their intersections one gets the estimation of the critical temperature. The value obtained for the critical temperature was $k_BT_c/w=0.567(1)$, which is in excellent agreement with exact value calculated by Onsager.[38] In addition, the fixed value of the cumulants, $U_1^*=0.615(3)$, corresponds to the value of the two-dimensional Ising model. Once we know T_c, the critical exponent ν can be calculated from the full data collapsing of U_1. The results are shown in the inset of the figure, where an excellent fit was obtained for $\nu=1$. On the other hand, the data of C, φ_1, and χ (data do not shown here) scaled extremelly well using $\alpha=0$, $\beta=0.125$, $\gamma=1.75$.

We now analyze the case corresponding to $k=2$. Figures 2(a) and 2(b) show Binder cumulants plotted versus k_BT/w, being $U_1(T)$ and $U_2(T)$ obtained from φ_1 and φ_2, respectively. As it can be noticed, the curves from φ_1 show large finite-size effects and the intersection point seems to converge to a fixed point for large values of L. On the other hand, the cumulants obtained from φ_2 are well behaved and allow a more accurate estimation of (T_c, U^*). For these reasons, throughout this paper we will work with φ_2.

The value obtained for k_BT_c/w [=0.3323(1)] agrees very well with previous determinations reported in the literature,[27,28] while $U_2^*=0.643(3)$ suggests that the system

TABLE I. Values of α, β, γ, ν, T_c and U^* (as indicated in the text) for k ranging from 1 to 4. In the case $k=1$, the value of T_c is exact (Ref. 38) and the critical exponents correspond to the well-known two-dimensional Ising universality class.

k	α	β	γ	ν	k_BT_c/w	U^*
1	0(log)	0.125	1.75	1	0.567296	0.615(3)
2	0.93(3)	0.02(1)	1.14(3)	0.53(1)	0.3323(1)	0.643(3)
3	0.89(3)	0.03(1)	1.16(3)	0.54(1)	0.4061(1)	0.638(4)
4	0.89(4)	0.02(1)	1.14(3)	0.53(2)	0.4853(2)	0.649(4)

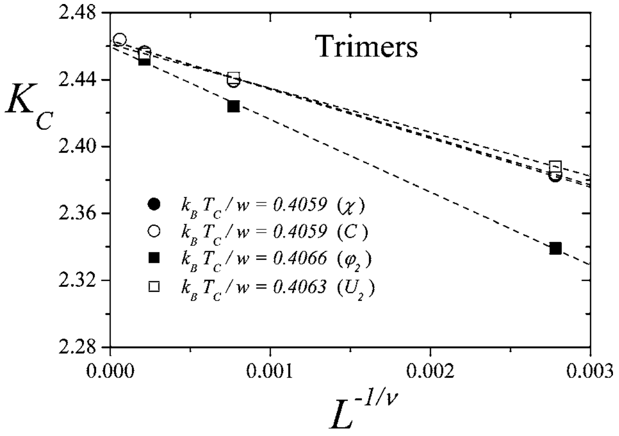

FIG. 9. Same as Fig. 4 for trimers ($k=3$).

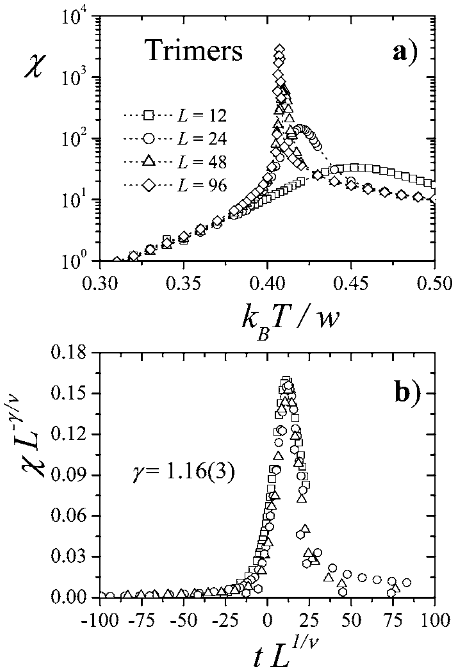

FIG. 11. Same as Fig. 6 for trimers ($k=3$).

does not belong to the universality class of the two-dimensional Ising model. In order to corroborate this finding, the critical exponents are calculated in Figs. 3–7.

In Fig. 3, we plot U_2 vs $tL^{1/\nu}$. According to the theoretical prediction of Eq. (11), the critical exponent ν is determined in such a way all curves (for different sizes) collapse into a universal curve. In this case, $\nu=0.53(1)$. Once ν is known, Eqs. (8)–(11) allow for a efficient route to estimate T_c from the extrapolation of the positions $K_c(L) \equiv w/k_B T_c(L)$ of the maxima of the slopes of φ and U, as well as of the maxima of C and χ. For all these quantities one expects that[29,31,32]

$$K_c(L) = K_c(\infty) + \text{const}\, L^{-1/\nu}, \quad L \to \infty, \tag{12}$$

where the constant depends on the quantity considered. Figure 4 shows the extrapolation towards the thermodynamic limit of $K_c(L)$ according to Eq. (12). The results obtained give an additional proof of the numerical values of T_c and ν calculated in Figs. 2 and 3, respectively.

Given $k_B T_c/w=0.3323(1)$ and $\nu=0.53(1)$, β, γ, and α were obtained from the collapse of the curves of φ_2, χ, and C, as it is shown in Figs. 5–7, respectively. The resulting values of the critical exponents, $\alpha=0.93(3)$, $\beta=0.02(1)$, $\gamma=1.14(3)$, point out clearly the existence of a different universality class from that of two-dimensional Ising model. The values of the critical exponents along with the critical temperature and the intersection point of the cumulants are collected in Table I.

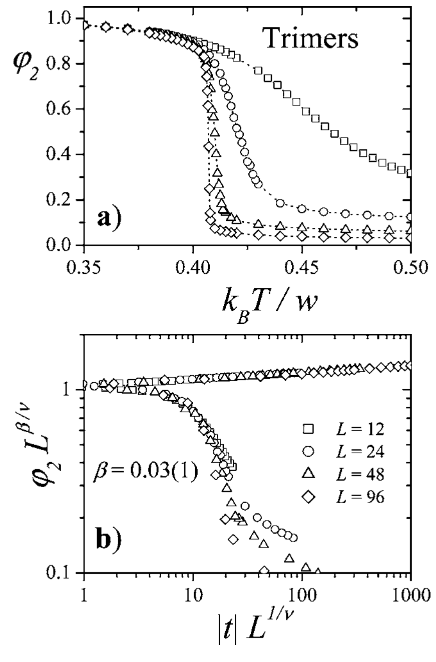

FIG. 10. Same as Fig. 5 for trimers ($k=3$).

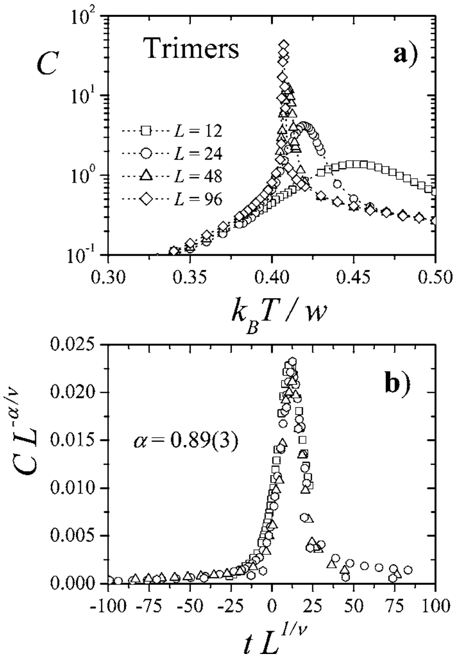

FIG. 12. Same as Fig. 7 for trimers ($k=3$).

Finally, the finite-size scaling study was carried out for $k=3$ and $k=4$, with an effort reaching almost the limits of our computational capabilities. For $k=3$, the collapsing data are shown in Figs. 8–12. In the case $k=4$, the curves are not shown here. In both cases, a very well correlation was obtained for the values of T_c, α, β, γ, and ν listed in Table I. As can be demonstrated, the set of critical exponents for dimers, trimers and tetramers fulfills the well-known inequalities of Rushbrooke,[39] $\alpha+2\beta+\gamma \geqslant 2$, and Josephson,[40] $d\nu+\alpha \geqslant 2$ (being d 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, trimers, and tetramers corroborate our hypothesis that the breaking of the orientational symmetry occurring for $k \geqslant 2$: (i) affects the nature of the phase transition and (ii) is the main source of the change in the universality class, with respect to the well-known two-dimensional Ising class of universality corresponding to monomers.

IV. CONCLUSIONS

In the present work, we have addressed the critical properties of repulsive linear *k*-mers adsorbed on two-dimensional square lattices at one-half coverage, and discussed the dependence of the universality class on the size *k*. The results were obtained by using Monte Carlo simulations and finite-size scaling theory.

Several conclusions can be drawn from the present work. On the one hand, we have introduced an order parameter, φ_2, which is particularly useful for describing systems with multisite occupancy. This parameter is well behaved, computationally convenient, and performs better than previous order parameters obtained in terms of sublattice magnetizations. The physical basis of φ_2 relays in the breaking of the orientational symmetry occurring for linear *k*-mers with $k \geqslant 2$ at the critical regime.

On the other hand, the evaluation of the complete set of static critical exponents, α, β, γ, and ν for different molecular sizes, shows that for linear *k*-mers with $k \geqslant 2$, this phase transition does not belong to the universality class of the two-dimensional Ising model ($k=1$). The main source for this behavior is the breaking of the orientational symmetry occurring for $k \geqslant 2$, which does not occur for $k=1$. Moreover, the critical exponents reported in the present paper for $k \geqslant 2$ do not correspond to a known universality class, according to the current classification of order-disorder transitions on surfaces given by Schick.[41]

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

The order parameter, φ_2, seems to be a promising parameter for describing the critical behavior of repulsive dimers on square lattices at $\theta=2/3$.[27] Work in this sense is in progress.

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