Entropy of rigid k-mers on a square lattice

Lucas R. Rodrigues [1,*] J. F. Stilck [2,†] and W. G. Dantas [3,‡]

[1]*Instituto de Física, Universidade Federal Fluminense, 24.210-346 Niterói, Rio de Janeiro, Brazil*

[2]*Instituto de Física and National Institute of Science and Technology for Complex Systems, Universidade Federal Fluminense, 24.210-346 Niterói, Rio de Janeiro, Brazil*

[3]*Departamento de Ciências Exatas, EEIMVR, Universidade Federal Fluminense, 27.255-125 Volta Redonda, Rio de Janeiro, Brazil*

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Using the transfer matrix technique, we estimate the entropy for a gas of rods of sizes equal to k (named k-mers), which cover completely a square lattice. Our calculations were made considering three different constructions, using periodical and helical boundary conditions. One of those constructions, which we call *profile method*, was based on the calculations performed by Dhar and Rajesh to obtain a lower limit to the entropy of very large chains placed on the square lattice. This method, so far as we know, was never used before to define the transfer matrix, but turned out to be very useful, since it produces matrices with smaller dimensions than those obtained using the usual approach. Our results were obtained for chain sizes ranging from $k = 2$ to $k = 10$ and they are compared with results already available in the literature. In the case of dimers ($k = 2$) our results are compatible with the exact result. For trimers ($k = 3$), recently investigated by Ghosh *et al.*, also our results were compatible, with the same happening for the simulational estimates obtained by Pasinetti *et al.* in the whole range of rod sizes. Our results are also consistent with the asymptotic expression for the behavior of the entropy as a function of the size k, proposed by Dhar and Rajesh for very large rods ($k \gg 1$).

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I. INTRODUCTION

We study a system of rigid rods formed by k consecutive monomers placed on the square lattice. This is a problem which has a long history in statistical mechanics. The particular case when $k = 2$ (dimers) in the full lattice limit, when the rods occupy all sites of the lattice, is one of the few exact solutions of interacting models which were obtained so far [1]. Another aspect of the thermodynamic behavior of long rodlike molecules was already anticipated by Onsager in the 1940s: he argued that at high densities they should show orientational (nematic) order [2], due to the excluded volume interactions. In a seminal paper, for the case of rods on the square lattice [3], Ghosh and Dhar found, using simulations, that for $k \geqslant 7$ at low density of rods an isotropic phase appears, but as the density is increased a continuous transition to a nematic phase happens. Evidence was found that close to the full lattice limit the orientational order disappears at a density $1 - \rho_c \sim k^{-2}$. The presence of the nematic phase at intermediate densities of rods was proven rigorously [4]. Because simulations at high densities of rods are difficult, an alternative simulational procedure allowed for more precise results for the transition from the nematic to the high density isotropic phase [5]. Recent results suggested this transition to be discontinuous [6].

Here we consider the estimation of the entropy of k-mers on the square lattice in the full lattice limit, for $k \geqslant 2$. This has been discussed before in the literature. Baumgärtner [7] generated exact enumerations of rods for $2 \leqslant k \leqslant 12$ on $L \times L$ square lattices, but did not attempt to extrapolate his results to the two-dimensional limit $L \to \infty$. His interest was actually more focused on the question if the system is isotropic or nematic in this limit. Bawendi and Freed [8] used cluster expansions in the inverse of the coordination number of the lattice to improve on mean field approximations. For dimers on the square lattice, their result is about 8% lower than the exact result [1], and there are indications that the differences are larger for increasing rod lengths k. A study of trimers ($k = 3$) on the square lattice using transfer matrix techniques similar to the ones we use here was undertaken by Ghosh, Dhar, and Jacobsen [9] and has led to a rather precise estimate for the entropy. Computer simulations have also been useful in this field, and estimates for the entropy of k-mers on the square lattice were obtained by Pasinetti *et al.* [10] for $2 \leqslant k \leqslant 10$, besides studying other statistical properties of the high density phase of the system. Another analytic approximation to this problem may be found in the paper by Rodrigues, Stilck, and Oliveira [11], where the solution of the problem of rods on the Bethe lattice for arbitrary density of rods [12] was performed for a generalization of this lattice called the Husimi lattice. These solutions on the central region of treelike lattices may be seen as improvements of mean field approximations to the problem. Again there are evidences that the quality of the estimates decreases for increasing values of k; while the difference of the estimate for dimers to the exact value is of only 0.03%, it already grows to 3% when compared to the estimate for trimers presented in [9].

The approach we employ here to study the problem is to formulate it in terms of a transfer matrix, as was done for trimers in [9]. It consists of defining the problem on

*lucasr@id.uff.br
†jstilck@id.uff.br
‡wgdantas@id.uff.br

strips of finite widths L with periodic and helical boundary conditions in the finite transverse direction. The leading eigenvalue of the transfer matrix determines the entropy of the system, as will be discussed below. The values of the entropies for growing widths are then extrapolated to the two-dimensional limit $L \to \infty$, generating estimates and confidence intervals for each case. For the case of periodic boundary conditions (pbc), besides using the conventional definition of the transfer matrix, in which L sites are added at each application of it, we used an alternative approach, inspired on the generating function formalism which was developed by Dhar and Rajesh in [13] to obtain a lower bound for the entropy of the system. This alternative procedure turned out to be more efficient for this problem than the conventional one, in the sense that the size of the transfer matrices were smaller, thus allowing us to solve the problem for larger widths L. For helical boundary conditions (hbc), only the conventional formulation of the transfer matrix was used.

Finally, we already mentioned that the possible orientational ordering of the rods in the full lattice limit was, for example, a point which motivated the exact enumerations in [7]. For dimers, it is known exactly that no orientational order exists [14], but on the square and hexagonal lattices, which are bipartite, orientational correlations decay with a power law [1], while there is no long range orientational order on the triangular lattice in the same limit [15]. This point is also investigated numerically for trimers in [9], with compelling evidence that the dense phase in the full lattice limit is not only critical but has conformal invariance. As already mentioned, so far all indications are that the high density phase of the system is isotropic on the square lattice, possibly with orientational correlations decaying with a power law.

This paper is organized as follows. The construction of the transfer matrices and determination of the leading eigenvalues and the entropies are described in Sec. II. The numerical results for the entropies of the rods on strips, the extrapolation procedure, and the estimates for the entropy of the rods on the square lattice may be found in Sec. III. Final discussions and the conclusion are found in Sec. IV.

II. TRANSFER MATRIX, LEADING EIGENVALUES, AND ENTROPY

The transfer matrix will be determined by the approach used to describe the transverse configurations of the strips at different levels, which define the states of lines and columns of the matrix. The two approaches we used are described below. We consider a lattice in the (x, y) plane, with $1 \leqslant x \leqslant L$ and $0 \leqslant y \leqslant \infty$. Periodical or helical boundary conditions are used in the transverse direction, that is, horizontal bonds are placed between sites (L, y) and $(1, y)$ in the first case and (L, y) and $(1, y + 1)$ in the second case. Fixed boundary conditions are used in the longitudinal direction. For periodic boundary conditions, we use two approaches in order to obtain the transfer matrix, which we call *usual approach* and the *profile method*. Those two approaches, although defining the states of the matrix in different ways, will of course produce exactly the same results for the entropy per site of chains with length k placed on a lattice with width L. For helical boundary conditions, only the *usual approach* is used. In the following, we shall describe each of those approaches.

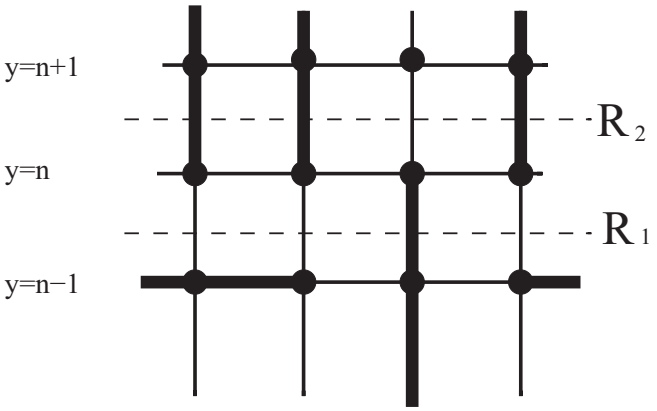

FIG. 1. Example of a possible continuation for a state defined by vertical bonds in a strip of width $L = 4$, identified by the reference line R_1, followed by a state connected to it defined by the reference line R_2.

A. Periodical boundary conditions

In the *usual approach*, at each application of the transfer matrix L new sites are incorporated into the lattice, while in the second approach a variable number of k-mers is added to the system at each step, so that the ensemble is grand canonical in this case.

1. Usual approach

This way of building the transfer matrix is the same used by Ghosh *et al.* [9] (named "Second Construction") to study the case of trimers ($k = 3$). It was also applied in previous works by two of the authors [16,17]. As mentioned in those papers, this method is inspired by the work of Derrida [18], which applied it to the problem of an infinite chain placed on a cylinder.

The states which define the transfer matrix in this formulation are determined by the possible configurations of the set of L vertical lattice edges cut by a horizontal reference line which is located between two rows of horizontal edges of the lattice, such as the dashed lines R_1 and R_2 in Fig. 1. These states may be represented by a vector, where each component corresponds to the number of monomers already connected to it, i.e., those located on sites below the reference line. Thus the components are restricted to the domain $[0, k - 1]$. So, from the information given by this vector, we can find all possible configurations of the vertical edges cut by the reference line situated one lattice spacing above, allowing us to define the transfer matrix of the problem. An illustration of possible configurations and their representative vectors for pbc can be observed in Fig. 1, where we have a state defined for the case $k = 3$ and $L = 4$. At the reference line R_1, separating the levels y_{n-1} and y_n, we have the vector $|v_1\rangle = (0, 0, 2, 0)$, while at R_2, linking the levels y_n and y_{n+1}, the configuration is represented by $|v_2\rangle = (1, 1, 0, 1)$. We proceed developing an algorithm to obtain the elements of the transfer matrix, for given values of k and L. However, we are limited by the

amount of computational memory and by the time necessary to compute those elements. For a given value of k, the number of states grows roughly exponentially with L. Even considering rotation symmetry, which makes states such $|v_1\rangle = (0, 1, 0)$ and $|v_2\rangle = (0, 0, 1)$ equivalent, and reflection symmetry, where $|v_1\rangle = (0, 1, 2, 3)$ and $|v_2\rangle = (3, 2, 1, 0)$ can be treated as the same state, this property imposes an upper limit to the widths that we are able to study for each rod size, k.

In principle, without considering the reduction of the size of the transfer matrix due to symmetries, one would suppose that this size would be equal to k^L, but the transfer matrix is actually block diagonal, each state being associated to one of the blocks. It happens that the leading eigenvalue always belongs to the block generated by the state $|v_0\rangle = (0, 0, \ldots, 0)$. So, instead of determining the entire transfer matrix, we proceed using the same strategy developed by Ghosh *et al.* [9] for trimers, generating the subset of states which starts with the state $|v_0\rangle$ and generating all other states connected to it.

Once we compute the transfer matrix, $\mathcal{T}$, to obtain the value of the entropy per site for the case of gas of monodisperse rigid chains with size k in a strip of size L, we may then compute the dimensionless entropy per lattice site

$$s_L = \lim_{N\to\infty} \frac{S}{Nk_B} = \lim_{N\to\infty} \ln \Omega, \tag{1}$$

where $N = L\ell$ is the number of the sites and Ω is the number of configurations of the rods of size k placed on the strip. So, that number is related with the transfer matrix as $\Omega = Tr(\mathcal{T}^\ell)$ and, if λ_1 is the largest eigenvalue of $\mathcal{T}$, we get, in the thermodynamic limit $\ell \to \infty$:

$$s_L = \frac{1}{L} \ln \lambda_1. \tag{2}$$

So, to obtain the entropy of a given width L, we should determine the largest eigenvalue for the transfer matrix. Fortunately, the typical transfer matrix is always very sparse, which allows us to use a method such as the power method, so that the determination of this eigenvalue becomes a possible task for quite large widths.

2. *Profile method*

This alternative method of defining the transfer matrix is inspired on the generation function approach used by Dhar and Rajesh to obtain lower bounds for the entropy of k-mers in the full lattice limit [13]. It is convenient in this case to consider the dual square lattice, whose center of elementary squares corresponds to sites in the lattice of the previous section, and represent the k-mers as $k \times 1$ rectangles on this lattice. Unlike the *usual approach*, where L sites are added at each multiplication of the transfer matrix, in this method a variable number of k-mers is added at each step. We consider the profile of the upper end of the strip at a particular point in filling it up with rods, such as the one shown in Fig. 2, as defining the states to build the transfer matrix. For a particular profile, we define the *baseline* as the horizontal line passing through the lowest points of the profile. We then consider the operation of adding rods to all points in the baseline, so that a new baseline is generated at a level at least one lattice parameter higher than the previous one. There may be more than one way to accomplish this, involving different numbers

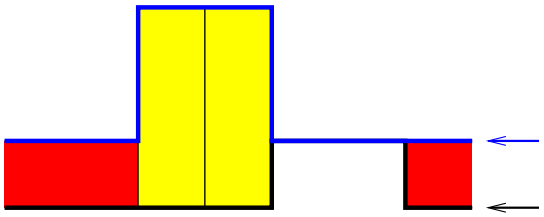

FIG. 2. Illustration of one step of the process of filling the strip of width $L = 7$ with trimers ($k = 3$). The initial profile is the thick black line and its baseline is at the level pointed by the black arrow. The height profile in this case will be (0,0,0,0,1,1,0); notice that there are two steps (5 and 6, from left to right) which are at the same height in both profiles. One possibility is to aggregate one horizontal rod (red on line) and two vertical rods (yellow on line). The new baseline is pointed at by the blue arrow and the new profile will be represented by (0,0,2,2,0,0,0). The contribution of this configuration is z^3.

of added rods. We will denote by z the fugacity of one rod, so that the contribution to the element of the transfer matrix corresponding to a particular choice of new rods added to the strip will be z^{n_r}, where n_r is the number of new rods added to the strip. Notice that no k-mer will be added which will not have at least one monomer located on the baseline. The profiles, which define the states of the transfer matrix, may be represented by a vector with L integer components, ranging between 0 (the intervals on the baseline) and $k - 1$. Thus, in general, there will be k^L possible states. However, as mentioned before, this general transfer matrix will be block diagonal, and as was done before for the case of trimers [9] we will restrict ourselves to the subset of states which include the horizontal profile $(0, 0, \ldots, 0)$, since in all cases where we were able to consider all profiles the leading eigenvalue of the transfer matrix was found in this block.

In the grand-canonical ensemble we are considering, let M be the number of times the transfer matrix is applied. In the thermodynamic limit $M \to \infty$ the partition function $Y_M(z)$ will be determined by the leading eigenvalue λ_1 of the transfer matrix $Y_M(z) \approx \lambda_1^M$, so that the thermodynamic potential will be

$$\Phi(T, V, \mu) = -k_B T \ \ln Y_M(z) = -k_B T M \ \ln \lambda_1(z), \tag{3}$$

where $z = e^{\beta\mu}$, with μ being the chemical potential of a rod. The entropy will be given by the state equation

$$\begin{aligned} S(z) &= -\left(\frac{\partial \Phi}{\partial T}\right)_{M,\mu} \\ &= k_B M \left[\ln \lambda_1(z) - z \ \ln z \frac{1}{\lambda_1(z)} \frac{\partial \lambda_1(z)}{\partial z}\right] \end{aligned} \tag{4}$$

and the total number of rods will be

$$\begin{aligned} N_r(z) &= -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,M} \\ &= M \frac{z}{\lambda_1} \left(\frac{\partial \lambda_1}{\partial z}\right). \end{aligned} \tag{5}$$

The dimensionless entropy per lattice site occupied by rods will then be

$$s(z) = \frac{S(z)}{k_B N_r(z) k} = \frac{\ln \lambda_1(z)}{\frac{kz}{\lambda_1}\left(\frac{\partial \lambda_1}{\partial z}\right)} - \frac{\ln z}{k}. \tag{6}$$

In the grand-canonical ensemble, the remaining extensive variable of the potential is usually the volume. The number of rods will be different in the configurations which contribute to the partition function, and by construction they occupy the lower part of the lattice in a compact way. For simplicity, let us consider widths L that are multiples of k. We then see that, for a given value of M, the height H of the region occupied by the rods will be in the range $[M, kM]$, so that the volume should be at least equal to $L \times kM$. Actually, it could be fixed at any value above this one without changing the results. This means that this condensed phase of k-mers actually coexists with the part of the lattice which is empty, and since the grand-canonical potential of the coexisting phases should be equal we conclude that $\Phi(T, V, \mu) = 0$, because this will be the potential of the phase which corresponds to the empty lattice. In other words, we recall that the grand-canonical potential is proportional to the pressure (force per unit length in the two-dimensional case), which should be the same in the coexisting phases. This condition of coexistence determines the activity of a rod

$$\lambda_1(z_c) = 1, \tag{7}$$

and substitution of this restriction into Eq. (6) leads to the final result for the entropy per site occupied by the rods in this formulation of the transfer matrix:

$$s_L = -\frac{\ln z_c}{k}. \tag{8}$$

In summary, in the formulation where the states are determined by the height profile of the k-mers in the strip, we solve numerically Eq. (7) for the activity z_c which corresponds to a vanishing pressure of the condensed phase of rods and then determine the entropy per site of this phase using Eq. (8).

It is then interesting to consider explicitly the simplest nontrivial case using the *profile method*, which is $L = k$. Starting with the horizontal profile, we notice that for $L = k$ there will be two possibilities to add a new set of rods and shift the baseline upwards: either a single horizontal rod or k vertical rods are added, and the new profile is again horizontal in both cases. Due to the periodic boundary conditions, in the first case there are $L = k$ different ways to place the horizontal rod. We thus conclude that there is a single profile state in this case and the size of the transfer matrix is 1×1 so that

$$\lambda_1 = kz + z^k. \tag{9}$$

We see then that z_c is defined by the equation $z_c^k + kz_c - 1 = 0$ and the entropy per site will be given by Eq. (8).

We proceeded using both methods described above to calculate the entropy for a set of rod sizes k and growing widths L. To reduce the size of the transfer matrices, we use rotational and reflection symmetries of the states. Since we want to obtain estimates for the entropies per site in the two-dimensional limit $L \to \infty$, it is important to reach the largest possible widths L for each rod size k. It should be noticed that in the *profile method* we have to solve numerically Eq. (7) for z_c, so that the leading eigenvalue λ_1 has to be calculated several times, while in the conventional method only one determination of the leading eigenvalue is needed. This seems to indicate that the *usual approach* should allow us to reach the largest widths. However, if we compare the numbers of states (size of the transfer matrices) in both methods, we obtain the results shown in Fig. 3. We notice that the transfer matrices are systematically larger for the *usual approach*, the difference increasing monotonically with the rod size. Therefore, at the end the *profile method* allowed us to reach the largest widths in all cases, which are determined by the limitations in time and memory of the computational resources available to us.

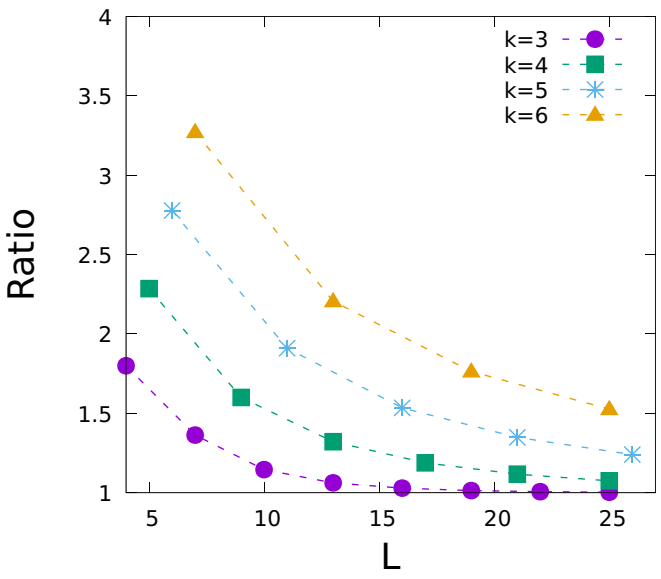

FIG. 3. Ratio between the number of states of the transfer matrix considering the *usual approach* and the *profile method*. The dashed lines are just a guide for the eye.

B. Helical boundary conditions

An alternative way to define the boundary conditions of strips of width L is to make them helical. This was already used by Kramers and Wannier in their seminal paper about the Ising model [19]. To visualize these boundary conditions, if we consider the model on a cylinder with perimeter of size L, the transverse lattice edges are on a helix with pitch L as seen in Fig. 4. The states are defined, as in the *usual approach*, by the number of monomers already incorporated into the rods on the $L + 1$ edges cut by a line which divides the strip into two sectors. In the *usual approach*, this line, as may be seen in Fig. 1, is horizontal and cuts L edges, while for helical boundary conditions it is also parallel to the transverse edges for L steps, ending with a vertical step. This is illustrated by the dashed line in Fig. 4; at a given step the line starts at point A, cuts L vertical edges, and finally cuts an additional transverse edge. All sites below the curve are occupied by monomers. While for periodic boundary conditions L lattices sites are added to the system as the transfer matrix is applied (the sites between lines R_1 and R_2 in Fig. 1), a single site is added for helical boundary conditions, the line which defines the new state starts at point B, and the last two steps of the previous line are replaced by the dotted steps. For the particular case

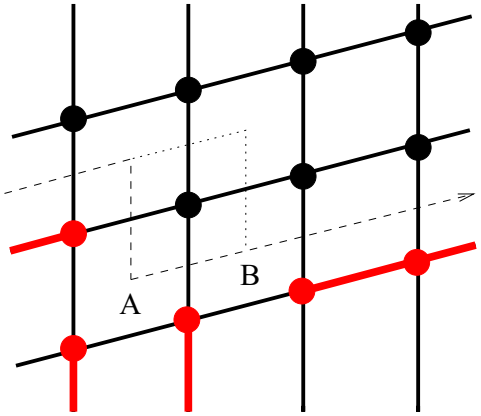

FIG. 4. Strip of width $L = 4$ with helical boundary conditions in the transverse direction. The $L + 1$ lattice edges crossed by the dashed line, starting at point A and in the direction indicated by the arrow, define the vector which represents the state at this point. An additional site is incorporated when the transfer matrix is applied, so that the new starting point of the line is B. Trimers are represented by thick lines (red on line).

in the figure, the state associated to the line starting at A is (0,0,0,0,0), while there are two possibilities for the state B, (0,0,0,0,1) or (0,0,0,1,0), since a new trimer has to start at the edge incorporated in this step and it may be horizontal or vertical.

Thus an important aspect of this boundary condition, as compared to the periodic one, is that only one or two elements of each line of the transfer matrix are equal to 1; all others vanish, so in general they lead to sparser transfer matrices, which of course is desirable if we use the power method to calculate the leading eigenvalue. The drawback is that the reflection and rotation symmetries are not present in this case.

III. NUMERICAL RESULTS

In this section, we discuss the numerical results obtained using the three approaches to determine the transfer matrix for the case of a monodisperse gas of rigid chains with size k, filling a strip of width L with periodical and helical boundary conditions.

Besides presenting the values of the entropy for each case, we also discuss the question of the transfer matrix dimension, which turns out to be the major obstacle in obtaining the entropy for a given (k, L) pair. Also, after collecting some figures for the entropies we should deal with the task of how to extrapolate them to obtain an estimate for $s_\infty(k)$, from a set $\{s_L(k)\}$, to the two-dimensional limit, i.e., when $L \to \infty$. For that, we are aware that, for critical two-dimensional isotropic statistical systems, presenting only short-range interactions, conformal invariance predicts that in a cylinder of width L, the entropy per site must follow the asymptotic behavior [20],

$$s_L(k) = s_\infty(k) + \frac{A}{L^2} + o(L^{-2}), \tag{10}$$

where A is related to the central charge.

Using the methods previously described to build the transfer matrix, we could determine the entropy of a given size of rods k for different values of L, limited by the amount of computer memory required in each case and/or by the processing time. Once we have obtained the elements of the matrix, the calculation of its dominant eigenvalue was carried out using the power method to diagonalize the matrix,

$$\mathcal{T}' = \mathcal{T} + p\mathcal{I}, \tag{11}$$

where p is a positive real number and $\mathcal{I}$ is the unitary matrix. Such procedure was necessary because the original matrix, $\mathcal{T}$, usually has a set of dominant eigenvalues, which, despite always presenting at least one of those eigenvalues at the real axis, has others with the same modulus in the complex plane. Such a feature turns out to make it difficult for the power method to work properly. However, using that translation we can shift all the eigenvalues along the real axis, making the positive real one the only dominant eigenvalue, λ' for the matrix $\mathcal{T}'$. Then, to recover the value which we are looking for, λ, we have $\lambda = \lambda' - p$.

The choice of the parameter p may be a sensitive issue in order to get the right results for the dominant eigenvalues in an efficient way. We adopted the strategy to fix this parameter maximizing the ratio between the real positive eigenvalue and the one with the second largest modulus. However, in the cases we verified here, even spanning the values of p over a large interval, such as [1 : 100], only minor differences among the results ($\approx 10^{-14}$) appear. In fact, the only noticeable effect caused by changing the size of this translation is observed in the number of steps needed for the power method to converge with a given precision (in our case this precision is about 10^{-13}). For growing values of p the number of steps increases, roughly, in a linear fashion.

Just as it happens for trimers [9], each other k-mer has its entropy values following the relation Eq. (10) in separate sets depending on the remainder, R, of the division L/k. Hence, if for trimers we have three sets (values with remainders 0, 1, and 2), in other cases there will be k sets of values for the entropy obeying the asymptotic behavior, as we can see in Fig. 5(a) for the case $k = 4$. Such behavior obviously poses an additional difficulty in order to get from each set a good extrapolation for the entropy in the two-dimensional limit, when $L \to \infty$.

Now we start to discuss the results obtained from each of the approaches presented in the previous section, considering its peculiarities and the limitations of each of them concerning widths which could be reached.

A. Periodic boundary conditions

For these boundary conditions, we applied the *usual approach* and the *profile method*. As already mentioned before, the *profile method* turns out to be more effective for larger values of k and L. We will thus restrict ourselves to presenting the results furnished by that method, after remarking that we have verified that for trimers the number of states we have obtained using the *usual approach* are equal to the ones in Ref. [9] obtained from the second construction. Of course, as already mentioned before, both approaches lead to the same values for the entropies.

The dimension of the transfer matrix, for a given value of k, grows nearly exponentially as a function of L—as we can see in Fig. 1(b)—considering the behavior for each set of

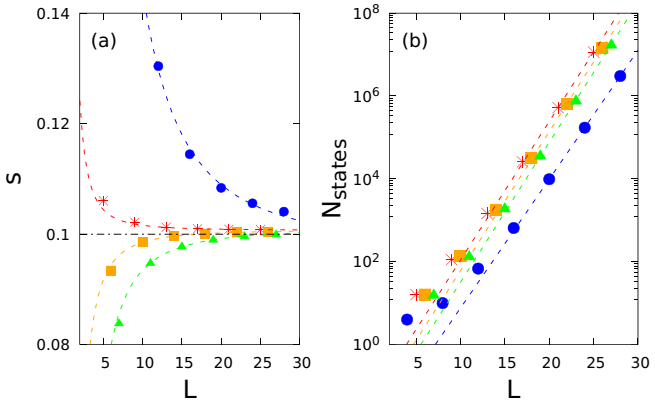

FIG. 5. Panel (a): behavior of the entropy for tetramers ($k = 4$) as a function of L separated by sets, where dots, stars, squares, and triangles are related to the remainders $R = 0, 1, 2$, and 3, respectively. The dashed lines are fittings of each set according to the relation given by Eq. (10). Panel (b) shows how the number of states of the transfer matrix grows as a function of L for each of the sets. The dashed lines here are used just as a guide for the eyes, indicating the exponential behavior of that number when L is large enough.

values of a given remainder R. Then, for a high value of k the number of elements for the set $\{s_L\}$ cannot be as large as it is when we consider smaller chains. The dimension reached in our calculations using the *profile method* for each set of remainder R is discriminated in Table I.

Using the entropy values in each set, we can obtain an extrapolated result for $s_\infty(k)$. This was done using the approach known as the BST extrapolation method [21]. Since this method can be functional even in situations where the number of entries to extrapolate is not that big, it appears to be convenient to use it in our problem. As is described in Ref. [21], the BST method has a parameter ω, which in our case should be set as $\omega = 2$, due to the relation Eq. (10). Also, because the desired limit, s_∞, is obtained from a table of extrapolants, $T_m^{(i)}$, where m is related to the extrapolant generation, then the uncertainty of the estimate will be defined as

$$\sigma = 2\left|T_m^{(1)} - T_m^{(0)}\right|, \tag{12}$$

TABLE I. Number of elements for the set $\{s_L\}$ for different sizes of the chains. Each set R_i is related to the remainder, $i = 0, 1, 2, \ldots$, for the division L/k.

k	R_0	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
2	16	15								
3	11	10	10							
4	8	7	7	7						
5	7	6	6	6	6					
6	7	6	6	6	6	6				
7	6	5	5	5	5	5	5			
8	6	5	5	5	5	5	5	5		
9	5	4	4	4	4	4	4	4	4	
10	4	4	4	4	4	4	4	4	4	3

TABLE II. Extrapolated entropy values for each set of a given chain size k. Results for periodic boundary conditions. For each value of k, the extrapolated entropies and uncertainties for remainders $R = 0, 1, \ldots, k-1$ are presented. Those values and their uncertainties were obtained using the BST method with $\omega = 2$ and with the uncertainty determined by Eq. (12).

k	$s_i(\sigma_i)$	k	$s_i(\sigma_i)$	k	$s_i(\sigma_i)$
2	0.2915609067(66)	3	0.1584937(64)	4	0.100669(73)
	0.29156090403(14)		0.15850495(19)		0.1007572(55)
			0.158510(25)		0.1007747(48)
					0.100780(87)
5	0.0700(33)	6	0.054(29)	7	0(2)
	0.0703370(82)		0.05210(76)		0.04030(68)
	0.070350(44)		0.0522275(66)		0.040475(85)
	0.07038344(58)		0.052244(84)		0.0404471(96)
	0.070303(71)		0.05228(15)		0.040530(11)
			0.052193(66)		0.040548(16)
					0.040561(44)
8	0.0164(23)	9	0.016(14)	10	0.015(14)
	0.03243(22)		0.02664(25)		0.02223(23)
	0.03243(16)		0.02567(24)		0.02226(27)
	0.03243(11)		0.02660(43)		0.02229(31)
	0.0324476(43)		0.026633(29)		0.022316(57)
	0.032466(11)		0.026704(73)		0.022337(12)
	0.032483(22)		0.0267322(91)		0.022355(55)
	0.032499(38)		0.026752(67)		0.02237(11)
			0.02677(14)		0.02238(16)
					0.22400(21)

when $m \to \infty$. In practical terms, this limit is applied considering the difference between the two approximants before the last generation. As an example, if we get N entries, then the extrapolated value is obtained from the $(N-1)$th generation, while the uncertainty is calculated from the two approximants of the $(N-2)$th generation.

So, using the BST extrapolation method we were able to obtain the values shown in Table II for each set associated with the remainder of the ratio L/k. To finally get a value $\bar{s}_\infty(k)$, representing the extrapolation for all sets considered, we calculate an average and a total uncertainty weighted by the uncertainties of each value of s_i, obtained for some remainder R. Once we consider the values $s_i(k)$ statistically independent of each other, the average and its deviance have to obey the following relations:

$$\bar{s}_\infty = \frac{\sum_i s_i/\sigma_i^2}{\sum_i 1/\sigma_i^2},$$
$$\Delta s_\infty = \sqrt{\frac{1}{\sum_i 1/\sigma_i^2}}, \tag{13}$$

where s_i is the extrapolated value of the entropy for some set of ratios R, while σ_i is the uncertainty related to it, which is obtained from Eq. (12). The results of the final values of the entropies of each size k are shown in Table V, which also shows, for comparison, the corresponding values obtained from Monte Carlo numerical simulations developed by Pasinetti *et al.* [10].

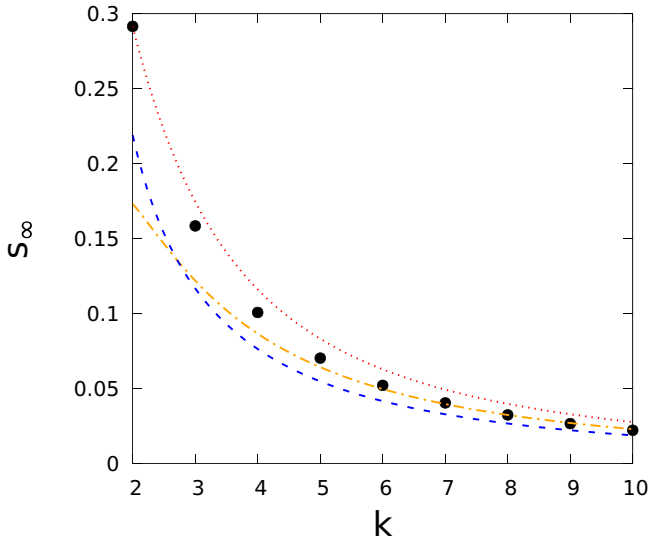

FIG. 6. Extrapolated entropies of rods filling a square lattice as a function of the size of chains, k. The blue dashed and the red dotted lines correspond, respectively, to the lower and upper bounds, obtained in [13] and [22] [Eqs. (14) and (15), respectively]. The dashed-dotted line follows the behavior predicted by Dhar and Rajesh [13] when $k \to \infty$, i.e., $s = \ln k/k^2$.

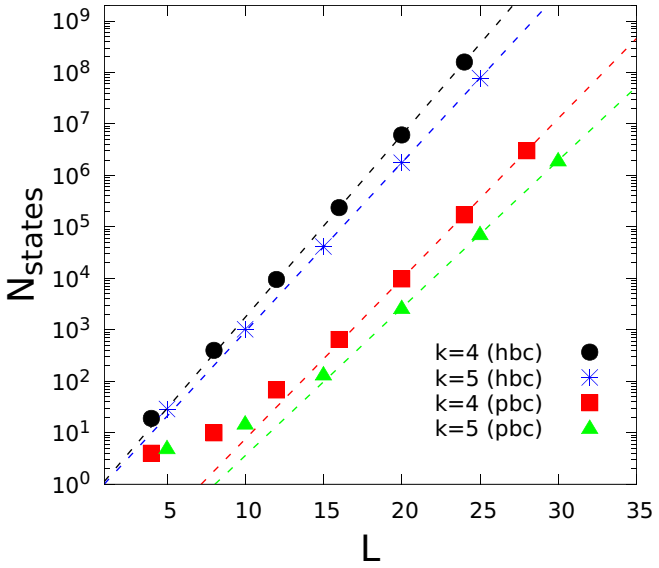

FIG. 7. Dimension for the transfer matrix as a function of the width L, considering results coming from the periodical (pbc) and helical (hbc) boundary conditions obtained for $k = 4$ and $k = 5$.

Notice from Table II that, as the size k of the rods grows, the precision for the values s_i is smaller, since the number of entries for each set $\{s(k)\}$ diminishes. It is also perceivable that the sets associated with the remainder $R = 0$ lead to the worst results for the extrapolation. This happens because such cases have a slower approach to the limit $\bar{s}_\infty(k)$. Therefore, that set, although related to the smaller transfer matrix dimensions, needs a larger number of entries to produce a better result. On the other hand, our final results are in excellent agreement with the exact value obtained for the dimer case ($k = 2$) [1], with $s_\infty(2) = G/\pi$, where $G \approx 0.9159655941772\ldots$ is Catalan's constant. From Table V we see that our estimate coincides with this exact result up to the 11th decimal place. Also, for the case $k = 3$, we can compare our result with that obtained by Ghosh *et al.* [9], i.e., $\bar{s}_\infty(3) = 0.158520(15)$, which is also in accordance with the one shown in Table V. For the rest of the cases, we have also a good agreement with the results obtained by Pasinetti *et al.* [10] through numerical simulations, although our extrapolations exceed their values, in precision, at least in one order of magnitude.

In Fig. 6 we can see how the entropy globally behaves as a function of the chain size k. First of all, such values are constrained between two limits. A lower bound,

$$s(k) \geqslant s_{2k\times\infty} \geqslant \frac{\ln k}{k^2}\left(1 - \frac{\ln\ln k}{2\ln k} + \cdots\right), \tag{14}$$

obtained by Dhar and Rajesh [13], considering a lattice with dimensions $2k \times \infty$ and $k \gg 1$. The upper bound was calculated by Gagunashvili and Priezzhev [22], being expressed by the equation

$$s(k) \leqslant \frac{\ln(\gamma k)}{k^2}, \tag{15}$$

where $\gamma = \exp(4G/\pi)/2$, with G being the already mentioned Catalan's constant. Notice that this upper limit coincides with the exact value of the dimer entropy on the square lattice when $k = 2$.

We can also observe that, as k grows, the behavior for $s(k)$ has a tendency to approach that one predicted by Dhar and Rajesh [13], $s = \frac{\ln k}{k^2}$, for the case of very large chains. Actually, beyond $k = 5$ the difference between our values and the asymptotic prediction differs less than 3%.

B. Helical boundary conditions

The transfer matrices obtained through this approach display a larger number of states than those obtained considering periodical boundary conditions. A comparison between those numbers can be seen in Fig. 7, where besides noting the exponential dependence between the number of states and the width L, for a given value of k, already seen in the pbc case, we also can perceive that these numbers can be almost 1000 times bigger when the matrix is calculated considering helical boundary conditions. In part this drawback is compensated by the fact that for helical boundary conditions the transfer matrix is much sparser when compared to the case of periodic boundary conditions, as already mentioned, but this also has the effect that the number of iterations needed in the power method to reach a selected convergence will be larger for helical boundary conditions.

Evidently, because of that, the largest value of L attained for each size of the chains is smaller than those reached for the pbc calculations. Then, once the eigenvalues, as it also happens for the periodical case, are arranged in sets of sizes sharing the same remainder for the division L/k, the number of elements for each set is smaller when compared with those shown in Table I. For this boundary condition those numbers are presented in Table III.

TABLE III. Dimension of each set related to the remainder R, as it shown in Table I, but obtained for helical boundary condition.

k	R_0	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
2	14	14								
3	8	8	7							
4	6	6	5	5						
5	5	5	5	5	4					
6	4	4	4	4	4	4				
7	4	3	3	3	3	3	3			
8	4	4	4	3	3	3	3	3		
9	4	3	3	3	3	3	3	3	3	
10	3	3	3	3	3	3	3			

Another similarity found in those two approaches is the disposition for the leading eigenvalues of the transfer matrix. Just as it happens for the periodical boundary conditions, the largest eigenvalue is degenerate on the complex plane, at least one of them being located at the real axis. Again, because in this case the transfer matrix is even sparser than those obtained for the periodical boundary conditions, we have used the power method in order to get this leading eigenvalue. As already mentioned in the previous discussion for the pbc case, to circumvent this degeneracy, which puts the power method in jeopardy, we diagonalize a transformed matrix $\mathcal{T}'$, translating all the diagonal elements from the original matrix, $\mathcal{T}$, by a real number p—as it is illustrated by Fig. 8. Doing so, we produce another leading eigenvalue free from any degeneracy and we can recover the value we are looking for only subtracting p from the largest eigenvalue of $\mathcal{T}'$.

However, unlike the pbc case, the choice of p in this situation can be a sensitive issue. Also, we noticed that the estimates for the leading eigenvalue as the iterations are done show a pattern which has oscillations of a period of about $2kL$ with slowly decreasing amplitude. This behavior is distinct to what happens for pbc, where the convergence, after a short transient, is usually monotonical. Therefore, great care has to be used in establishing the condition for numerical convergence.

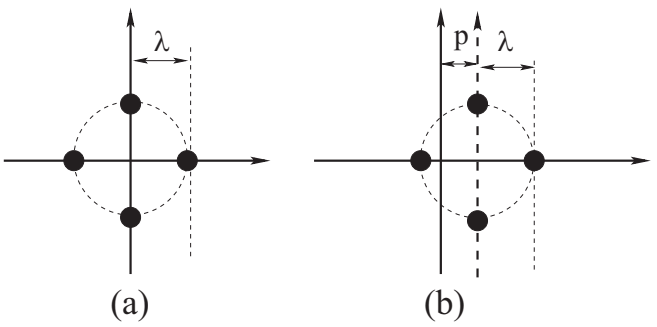

FIG. 8. Illustration on how the largest eigenvalues for a transfer matrix $\mathcal{T}$ are distributed with the same modulus on the complex plane (a) and how the translation produced by the parameter p turns the eigenvalue located at the real axis into the only dominant eigenvalue for a transformed matrix $\mathcal{T}'$. This example corresponds to the situation we get for $k = 4$ with hbc, where the largest eigenvalue is fourfold degenerate.

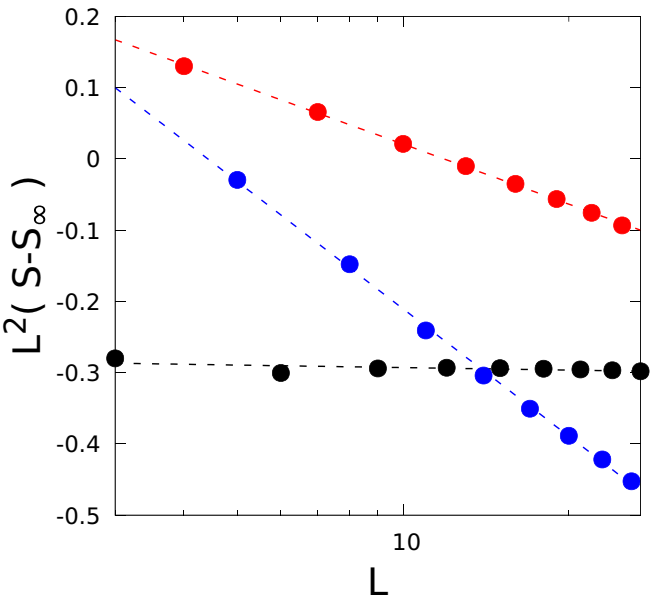

FIG. 9. Behavior of the trimer entropies, separating the behavior of remainders $R = 0$, 1 and $R = 2$ (black, blue, and red dots, respectively) as a function of $\ln L$. The linear behavior for $R = 1$ and $R = 2$ shows that $s(L)$ follows the behavior predicted by Eq. (16), while the logarithmic term is absent for $R = 0$, which follows the same dependence observed for the pbc case. The estimates of s_∞ were obtained via BST extrapolation as discussed below.

The asymptotic behavior for the entropy, as a function of L, in this case, is not the same as the one found in the pbc case [Eq. (10)] [23]. In fact, we have found that aside from the dimer case, where the behavior is the same as predicted by Eq. (10), the entropies exhibit a logarithmic correction in the form

$$s(L) = s_\infty + \frac{1}{L^2}(A \ln L + B). \tag{16}$$

Figure 9 shows this kind of behavior obtained for $k = 3$, where we can see clearly an evidence of such logarithmic correction, which is not present for the pbc calculations. This additional term shows rather clearly in our data for small values of k larger than 2, but, as expected due to the fact that as k grows there are more sets to extrapolate for each k with less points in each of them, evidence is not so clear for larger rods.

Despite that, we still are able to perform the extrapolations and determine the asymptotic value for the entropy, s_∞, using the same BST approach. Unlike what is discussed in the Appendix of [21], where a function with a logarithmic correction is analyzed showing a poor performance of the method, our calculations, despite displaying some fluctuations for the average value and its uncertainty, were less affected by the presence of the logarithm term. However, while for pbc we have applied the extrapolation considering a fixed value for the parameter ω, which was set at $\omega = 2$, in the hbc case, we estimate the value of s_∞ considering two cases: for the sets of remainder $R = 0$ we have kept $\omega = 2$, just as we have done for the ccp case. This was motivated by the fact that, at least for rather small values of k, we found evidences that $A = 0$

TABLE IV. Same results shown in Table II for the hbc case.

k	$s_i(\sigma_i)$	k	$s_i(\sigma_i)$	k	$s_i(\sigma_i)$
2	0.2915609040290(83)	3	0.1585113(35)	4	0.1007852(60)
	0.2915609040300(11)		0.15852375(20)		0.10078178(76)
			0.15856889(35)		0.100737621(73)
					0.10066(80)
5	0.07035(16)	6	0.05224(14)	7	0.04045(50)
	0.0704471(21)		0.05209(24)		0.04037(17)
	0.07028(40)		0.05247(51)		0.04128(39)
	0.07026(93)		0.05297(62)		0.09952(50)
	0.0709(81)		0.05321(41)		0.06014(52)
			0.0646(79)		0.03978(49)
					0.04075(55)
8	0.03240(44)	9	0.02660(40)	10	0.02229(36)
	0.03233(13)		0.02645(11)		0.022150(68)
	0.03207(15)		0.02634(64)		0.022063(12)
	0.03199(14)		0.02627(34)		0.0219984(15)
	0.03193(18)		0.026223(45)		0.0219569(27)
	0.03188(24)		0.026186(82)		0.0219318(15)
	0.03183(30)		0.02615(13)		0.021913(16)
	0.03204(34)		0.02612(17)		0.021893(55)
			0.02646(20)		0.021873(90)
					0.021998(61)

TABLE V. Results for the entropy of k-mers in the full lattice limit. The first column contains averages calculated from the entropies shown in Table II using the relations shown in Eq. (13), for periodic boundary conditions. The second column shows averages calculated from the entropies shown in Table IV, for helical boundary conditions. The third column displays the results obtained by Pasinetti *et al.* through computer simulations [10].

k	TM (pbc)	TM (hbc)	MC [10]
2	0.29156090404(14)	0.2915609040293(66)	0.2930(20)
3	0.15850494(19)	0.15853458(17)	0.1590(20)
4	0.1007670(36)	0.100738034(73)	0.1010(20)
5	0.07038320(58)	0.0704470(21)	0.0700(30)
6	0.0522274(65)	0.05232(11)	0.0520(30)
7	0.0404963(64)	0.04048(14)	0.0400(30)
8	0.0324516(39)	0.032088(67)	0.0320(30)
9	0.0267234(85)	0.026266(23)	0.0270(30)
10	0.022337(12)	0.0219643(10)	0.0210(30)

in this case. However, for sets associated with nonvanishing remainders, we have determined the entropy as a function of ω over a domain $\omega \in [1, 2]$, adopting the value of s_∞, which minimizes the uncertainty defined by Eq. (12).

Doing so, we obtain the results shown in Table IV, where we notice that, in some cases, the uncertainties have the same order of magnitude as those found from pbc calculations, although they were obtained from smaller sets of values of the entropy (see Table III). This is possible because even with less elements to use in the extrapolations, the values for the entropies, in the hbc case, are closer to the asymptotic limit when compared to those obtained with pbc. While for the periodical boundary conditions, as we can see from Fig. 5(a), this relaxation can be quite slow, particularly for the values in the set with remainder $R = 0$, the same does not occur for helical boundary conditions. Then, if this boundary condition is somehow handicapped by smaller values of L attained, the extrapolation is not much affected, since the values for finite widths are closer to their asymptotic limit.

Given the results shown in Table IV we proceed to the final values for the entropy per site, considering rigid chains of size k placed at the sites of a square lattice, using Eq. (13). The final results for such entropies are shown in Table V. We do not have a complete agreement between the results obtained from the pbc and hbc extrapolations. We notice that for six values of k (3, 4, 5, 8, 9, and 10) the confidence intervals for the entropy per site obtained for periodic and helical boundary conditions have no intersection, while for dimers ($k = 2$) both intervals contain the exact result and for trimers they are also consistent, although more precise, with the previous result by Ghosh, Dhar, and Jacobsen [9]. We suspect that the inconsistencies are due to a possible underestimation of the uncertainties by the BST method due to the logarithmic term in the asymptotic behavior of the approach to the two-dimensional limit of the entropy per site for helical boundary conditions when the remainder is nonvanishing, together with the fact that as k grows the number of points to extrapolate in each case becomes smaller. The relative discrepancies increase with k, which may be an indication of the effect of the reduction of the number of cases to extrapolate on the quality of the results. We thus believe that in general the estimates provided by the results from strips with periodic boundary conditions are more reliable. In general, it is apparent that the estimates obtained here are essentially consistent with the ones obtained through computer simulations [10], but are more accurate.

Considering the essential divergence between the estimates obtained for both boundary conditions using the BST method (the gap between the confidence intervals for $L = 10$ is of the order of 30 times the uncertainty), we have also produced estimates for helical boundary conditions using a simple alternative method: for each size k of the rods, we find the values of s_∞ A and B of the asymptotic behavior Eq. (16), which reproduce the three entropies for the largest widths L for each remainder $R = 0, 1, 2, \ldots, k-1$. This procedure thus produces k estimates for s_∞, besides estimates for the amplitudes A and B. The mean value of the estimates for s_∞ and its dispersion for each rod length k are displayed in Table VI. Of course this procedure is rather crude, since to estimate the entropies of the strips with three different widths, we use the same weight for different values of L, but we notice that the results are compatible with the exact value and the extrapolated estimates for dimers, with the estimate in [9] and the estimate for periodic boundary conditions for trimers. For $k = 4$, 5, 6, and 7 we also have an agreement with the estimates coming from the results with pbc, but for the rest the confidence intervals for the new estimates are below the ones obtained with pbc. So we see that, although larger uncertainties are obtained in the alternative extrapolation procedure for hbc, there are still some cases where the results are not compatible with the ones provided by the calculations with pbc, although the relative discrepancies are much lower than the ones found comparing results for both boundary conditions using the BST extrapolation procedure and these cases

TABLE VI. Results for the entropy of k-mers in the full lattice limit. Estimates obtained using an alternative procedure to extrapolate the results for helical boundary conditions, described in the text.

k	TM (hbc)
2	0.29156104(25)
3	0.158511(14)
4	0.100822(86)
5	0.070381(70)
6	0.052213(58)
7	0.04029(21)
8	0.03210(15)
9	0.02632(13)
10	0.02202(11)

are restricted to the larger values of k, where it is clear that the method in all approaches leads to less precise results.

IV. FINAL DISCUSSION AND CONCLUSION

In the present work, we have dealt with the problem of determining the configurational entropy for collinear chains of size k, named k-mers, fully covering a square lattice. To do so, we have employed transfer matrix calculations using three different constructions. Two of them were employed for periodical boundary conditions, the so-called *usual approach*, already used by Ghosh *et al.* [9] to obtain the entropy for trimers ($k = 3$), and the *profile method*, based on the calculation developed by Dhar and Rajesh [13] in order to estimate a lower boundary for the value of the entropy as a function of the chain size, k, considering $k \gg 1$. To our knowledge, this second approach was never used in the transfer matrix method and it has been useful to deal with this problem. Since we seek to determine the entropy for full coverage in the thermodynamic limit from the results obtained for the entropy of the k-mers placed on strips with finite widths equal to L, our results tend to be better when we reach large values of L. The *profile method*, in the majority of cases, produces transfer matrices with smaller dimensions than those obtained via the *usual approach*, allowing us to obtain better numerical results for the entropies. We notice that in the *usual approach* the entropy is directly related to the leading eigenvalue of the transfer matrix, while in the *profile method*, which is grand canonical, it is necessary to find the value of the activity of a k-mer which corresponds to a leading eigenvalue with a unitary modulus. So, while in the first approach we need to find the leading eigenvalue only once, in the second approach it is necessary to repeat this operation several times to reach the required numerical precision. Nevertheless, the *profile method* allowed us to reach larger widths. Another construction we have applied for these calculations was the *usual approach* considering helical boundary conditions. However, even being less effective to reach large values of L, this approach has a tendency to generate values closer to the asymptotic limits associated with the thermodynamic limit, although displaying greater uncertainties.

Although we have not presented results on details about the convergence of the results of the entropies on strips of finite widths to the two-dimensional values, as was, for instance, done for trimers in [9] it was clear that the scaling form Eq. (10) is followed by our results, for periodic boundary conditions. This is an indication that the phase in the full lattice limit is critical and conformal invariant for periodic boundary conditions. We plan to come back to this point in the future.

Our results show values that are in accordance with some previous results in the available literature, such as the case for dimers ($k = 2$), the only case which was exactly solved and for which our result agrees up to the 11th decimal place, and also for the trimer case, where the entropy obtained here agrees with the one estimated by Ghosh *et al.* in [9]. Another source for comparison are the simulational results obtained by Pasinetti *et al.* [10], which also are in complete agreement with our values, although they are less precise. We may also compare our results with recent estimates for the entropies for the same problem provided by a sequence of Husimi lattice closed form approximations [11], which are numerically exact solutions on treelike lattices that may be considered *beyond mean field* approximations. These results, for k in the range {2–6}, in a similar way to ours, become less precise for growing values of k. While the relative differences between the present and the former estimates are of the order of 3% for $k = 2, 3$, they reach about 40% for the higher values of k. It is also noteworthy that the behavior displayed by the entropies s and the sizes k seemingly obey the relation predicted by Dhar and Rajesh [13], $s \approx \ln k/k^2$, when $k \to \infty$. As it has been mentioned previously, from $k = 5$ up to $k = 10$ our results differ from that expression by less than 3%.

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