

Entropy of chains placed on the square lattice

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We obtain the entropy of flexible linear chains composed of M monomers placed on the square lattice using a transfer matrix approach. An excluded volume interaction is included by considering the chains to be self-avoiding and mutually avoiding, and a fraction ρ of the sites is occupied by monomers. We solve the problem exactly on stripes of increasing width m and then extrapolate our results to the two-dimensional limit $m \rightarrow \infty$ using finite-size scaling. The extrapolated results for several finite values of M and in the polymer limit $M \rightarrow \infty$ for the cases where all lattice sites are occupied ($\rho = 1$) and for the partially filled case $\rho < 1$ are compared with earlier results. These results are exact for dimers ($M = 2$) and full occupation ($\rho = 1$) and derived from series expansions, mean-field-like approximations, and transfer matrix calculations for some other cases. For small values of M , as well as for the polymer limit $M \rightarrow \infty$, rather precise estimates of the entropy are obtained.

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I. INTRODUCTION

The term dimer was introduced in the 1930s [1] as an abbreviation for diatomic molecules in a model for their adsorption on crystal surfaces. Later dimer models were applied in the study of other physical systems such as ferroelectrics, and much is known about their thermodynamic properties [2]. One relevant question in these models is the entropy associated with the placing of the dimers on a regular lattice. For the particular case of full covering of the square lattice by dimers, this question was answered exactly some time ago, using a technique based on pfaffians [3–5]. However, even the generalization of this problem for the case of partial covering of the square lattice is still an open question today, no exact result being known.

In this paper we address a generalization of the problem of the entropy of dimers, considering entropy related to covering the square lattice with chains with M monomers each (we will call them M -mers) as a function of the fraction ρ of sites of the lattice occupied by monomers. The chains will be considered flexible, so that there is no energy associated to bend them. Since the only energy in the model is the infinite excluded volume interaction, which forbids the presence of more than one monomer on the same lattice site, the problem is athermal. It may be a simple model for the adsorption of monodisperse flexible chains on the surface of a crystal. Besides the exact solution of the problem for $M = 2$ and $\rho = 1$ mentioned above, other cases were already considered in the literature. Rather precise transfer matrix calculations were performed in the polymer limit $M \rightarrow \infty$ for Hamiltonian walks ($\rho = 1$) [6]. There are also mean-field approximations [7], Bethe-Husimi lattice calculations [8], and series expansions in q^{-1} , where q is the number of first neighbors of each site in the lattice [9], and in those calculations approximate values for the entropy are obtained for both the full ($\rho = 1$) and partial ($\rho < 1$) coverage cases.

In this paper we obtain estimates for the entropy of flexible M -mers placed on the square lattice, using transfer matrix techniques. This is done calculating numerically exact values for the entropy of the problem on strips with finite widths m and periodic boundary conditions, and then using finite-size scaling to extrapolate the results to the two-dimensional limit $m \rightarrow \infty$. We separate the problem in cases where M is finite or infinite (polymer limit). Also, the case of full coverage ($\rho = 1$) may be treated separately from the general case. In the general case, it is convenient to address the problem in an ensemble that is grand canonical with respect to the number of monomers placed on the lattice, whereas for full coverage it is easier to perform a microcanonical calculation.

The expressions we used to calculate the entropy are shown in Sec. II. The model is discussed in more detail and the transfer matrices are described in Sec. III. Our results for the entropies as well as the extrapolation procedure and their results, may be found in Sec. IV. The simple one-dimensional case is solved in Sec. V, and Sec. VI presents the final discussions and conclusions.

II. DETERMINATION OF THE ENTROPY

For the case of full coverage, it is convenient to obtain the entropy directly from Boltzmann's expression

$$s(\rho = 1) = \lim_{N \rightarrow \infty} \frac{S}{Nk_B} = \lim_{N \rightarrow \infty} \frac{1}{N} \ln \Omega, \quad (1)$$

where Ω are the number of ways to fill the lattice with N sites completely with M -mers. In the polymer limit $M \rightarrow \infty$, we consider a *single* Hamiltonian walk, that is, a self-avoiding walk (SAW) that visits all sites of the lattice.

In the general case where a fraction ρ of lattice sites is occupied by monomers, we define the grand-canonical partition function

$$\Xi(z) = \sum_p z^{pM} \Gamma(M, N, p), \quad (2)$$

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where z is the activity of a monomer and $\Gamma(M,N,p)$ is the number of ways to place p chains with M monomers each on the lattice with N sites. For the polymer limit, again a single SAW is placed on the lattice, and the partition function is defined as

$$\Xi(z) = \sum_n z^n \Gamma(n,N), \quad (3)$$

where $\Gamma(n,N)$ is the number of ways to place a SAW with n monomers on the N -site lattice. The density of monomers may now be written as

$$\rho(z) = z \frac{d}{dz} \phi(z), \quad (4)$$

where the thermodynamic potential per lattice site is defined as

$$\phi(z) = \lim_{N \rightarrow \infty} \frac{1}{N} \ln \Xi(z). \quad (5)$$

In the thermodynamic limit, a Legendre transformation allows us to rewrite the potential as

$$\phi(z) \sim \max_{\rho} \{ \rho \ln z + s(\rho) \}, \quad (6)$$

and thus the entropy may be written as

$$s(\rho) = - \int_0^{\rho} \ln z(\rho') d\rho', \quad (7)$$

with $s(0) = 0$.

III. DEFINITION OF THE TRANSFER MATRIX

We proceed defining a strip of width m on the square lattice in the (x,y) plane, so that $1 \leq x \leq m$ and $-\infty \leq y \leq \infty$, with periodic boundary conditions in both directions. A transfer matrix may be built for this problem, inspired on the prescription due to Derrida [10] for infinite chains in strips. We thus consider the operation of including an additional step to the strip in the positive y direction, adding m new sites of the lattice. To properly take into account the statistical weight of the new step, we may define the state of the m vertical bonds of the lattice, which are incident to the new sites by specifying the following.

(1) The number of monomers already present in the chain that passes through the vertical bond (it is equal to 0 if no chain is present). These numbers may be put into a vector $|p\rangle$, with m components. It is necessary to keep track of this information so that we know when to end each chain.

(2) The pairs of bonds which are connected to each other through a path lying entirely below the reference line (see Fig. 1). These pairs may also be specified by a m -component vector $|v\rangle$, associating a different positive integer to each pair of connected bonds and 0 to the ones that are not connected to each other. This connectivity informa-

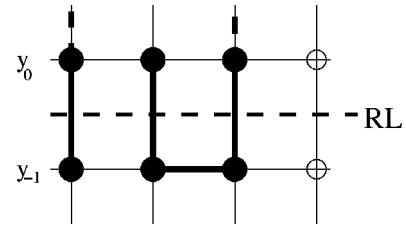


FIG. 1. Example of a state for $m=4$ vertical bonds. The reference line indicates the set of vertical bonds whose configuration is described.

tion prevents us from closing a ring at any level, since this configuration is not allowed in the model.

As an example of these definitions, we consider the case of pentamers ($M=5$) placed on a strip of width $m=4$. Among the possible configurations of a set of vertical bonds, the one depicted in Fig. 1 is described by the vectors $|v\rangle = (0,1,1,0)$ and $|p\rangle = (1,2,2,0)$. Elements of the line associated to this state of the transfer matrix \mathcal{T} are obtained considering the possible continuations of the state $\{|v\rangle, |p\rangle\}$ one step upwards, as shown in the two examples in Fig. 2. The resulting state in Fig. 2(a) is described by the vectors $|v\rangle = (0,0,0,0)$ and $|p\rangle = (2,0,4,0)$, while the final state in Fig. 2(b) corresponds to the vectors $|v\rangle = (0,0,0,0)$ and $|p\rangle = (2,0,0,0)$. Each monomer placed on a site between the two sets of vertical bonds contributes with an activity z to the partition function, so that the element of the transfer matrix, which corresponds to the first configuration, is equal to z^3 ; while the second configuration is associated to an element equal to z^4 in the transfer matrix. Only the second configuration contributes in the case of full occupancy.

For the polymer case $M \rightarrow \infty$, a single chain passes through the whole strip, so that it is enough to describe the connectivity at a particular set of m vertical bonds by indicating the bond that is connected to the initial monomer of the chain (in $y \rightarrow -\infty$) and the pairs of bonds connected to each other, exactly as was done in the original work of Derrida [10]. Thus, a single vector $|v\rangle$ is enough to describe the state in this limit.

Once the transfer matrix \mathcal{T} is obtained, the entropy of the model on the strip in the thermodynamic limit is related to the largest eigenvalue of the matrix. For the case of full occupancy ($\rho=1$), the number of configurations is given by

$$\Omega = \text{Tr}(\mathcal{T}^l), \quad (8)$$

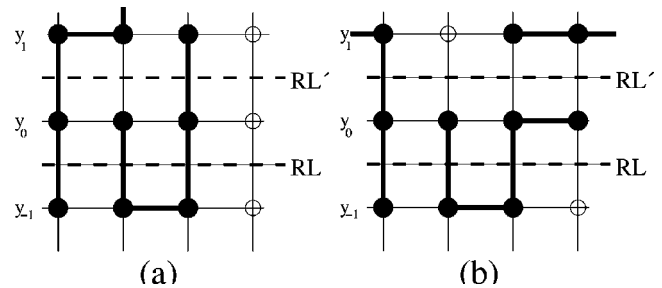


FIG. 2. Possible continuations (reference line RL') following the configuration depicted in 1 (reference line RL).

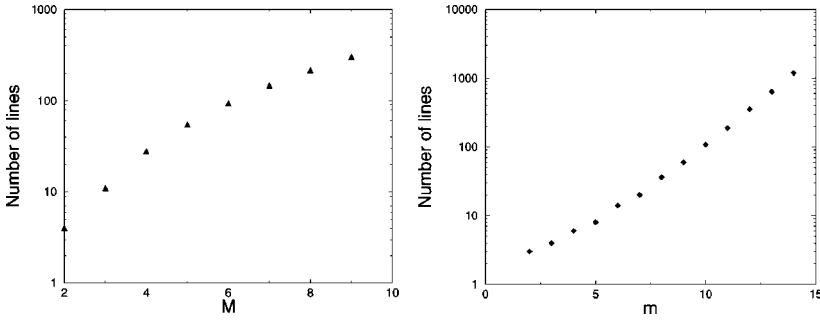


FIG. 3. Dimension of the transfer matrix as a function of the molecular weight ($m=2$) and width of the strip ($M=2$), respectively.

where $N=ml$ is the number of sites and the elements of the matrix \mathcal{T}' are defined by the limit

$$\mathcal{T}'_{i,j} = \lim_{z \rightarrow \infty} \frac{\mathcal{T}_{i,j}}{z^m}. \quad (9)$$

The entropy is then related to the largest eigenvalue λ' of this matrix, so that

$$s(\rho=1) = \frac{1}{m} \ln \lambda'. \quad (10)$$

For the general case, where a fraction ρ of lattice sites are occupied by monomers, the grand-canonical partition function is related to the transfer matrix through

$$\Xi(z) = \text{Tr}(\mathcal{T}^l), \quad (11)$$

and thus the density $\rho(z)$ will be

$$\rho(z) = \lim_{N \rightarrow \infty} \frac{z}{N} \frac{d}{dz} \ln \Xi(z) = \frac{z}{m} \frac{d}{dz} \ln \lambda, \quad (12)$$

where λ is the largest eigenvalue of the transfer matrix \mathcal{T} . This relation may be inverted to obtain the entropy as a function of the density using Eq. (7).

IV. NUMERICAL RESULTS

The size of the transfer matrix increases very fast with both the molecular weight M and the width m of the strip grow. This sets an upper limit to the widths that we were able to consider for each chain of a given molecular weight. One may observe in Fig. 3 that the growth of the size of the transfer matrix is roughly exponential.

Furthermore, as was already observed in similar calculations for polymers [11], the values of the entropy for each class of M -mers are split into subsets with different finite-size scaling behaviors in each subset according to the width of the strips, so that extrapolations must be done within each subset. These splittings seem to be related to frustration effects in the limit of the fully occupied lattice, and the subsets are indicated in Table I, where all the widths we considered are given.

The data of each subset were extrapolated to the two-dimensional limit $m \rightarrow \infty$ using the Shanks transformation [12], since we expect finite-size corrections to be exponential. Since at least three values for the entropy are needed in

a subset to obtain an estimate for the two-dimensional entropy and its confidence interval, not all subsets may be extrapolated, so that, for example, no estimate could be found for hexamers ($M=6$), where we calculated entropies for widths up to $m=7$. The final estimate was chosen to be the highest possible extrapolant, and the error associated to it was obtained from the previous generation of extrapolants, through

$$\epsilon = \lim_{l' \rightarrow \infty} 2|s_{l'-1} - s_{l'+1}|. \quad (13)$$

The extrapolated values of the entropies for $\rho=1$ and their uncertainties are displayed in Table II, together with values obtained with other techniques and best values found in the literature.

Our results may be compared with other values in the literature. One may notice that the mean-field estimates are systematically smaller than the values obtained here, but no such general trend is apparent for the Bethe-Husimi lattice results. The estimate for dimers agrees with the exact value

TABLE I. Entropies calculated for each M -mer, divided in subsets with the same finite-size scaling behavior.

Molecular weight	Entropies of each subset
$M=2$	$\{s'_1\} = \{s_2, s_4, s_6, \dots, s_{14}\}$
$M=3$	$\{s'_2\} = \{s_3, s_5, s_7, \dots, s_{13}\}$
$M=4$	$\{s'_1\} = \{s_3, s_6, s_9, s_{12}\}$
$M=5$	$\{s'_2\} = \{s_2, s_4, s_5, s_7, s_8, s_{10}, s_{11}\}$
$M=6$	$\{s'_1\} = \{s_4, s_8\}$
$M=7$	$\{s'_2\} = \{s_2, s_6, s_{10}\}$
$M=8$	$\{s'_3\} = \{s_3, s_5, s_7, s_9\}$
$M=9$	$\{s'_1\} = \{s_5\}$
$M=10$	$\{s'_2\} = \{s_2, s_3, s_4, s_6, s_7, s_8\}$
$M=11$	$\{s'_1\} = \{s_6\}$
$M=12$	$\{s'_2\} = \{s_3\}$
$M=13$	$\{s'_3\} = \{s_2, s_4\}$
$M=14$	$\{s'_4\} = \{s_5, s_7\}$
$M=15$	$\{s'_1\} = \{s_2, s_3, s_4, s_5, s_6\}$
$M=16$	$\{s'_1\} = \{s_4\}$
$M=17$	$\{s'_2\} = \{s_2\}$
$M=18$	$\{s'_3\} = \{s_3, s_5\}$
$M=19$	$\{s'_1\} = \{s_3\}$
$M=20$	$\{s'_2\} = \{s_2, s_4\}$
$M \rightarrow \infty$	$\{s'_1\} = \{s_2, s_4, s_6, \dots, s_{12}\}$
	$\{s'_2\} = \{s_3, s_5, s_7, \dots, s_{13}\}$

TABLE II. Entropy of M -mers on the square lattice for full coverage ($\rho=1$) obtained through different techniques. The series results listed are truncations at second order in q^{-1} .

M	Mean Field [8]	Bethe [8]	Series [9]	Husimi [8]	Transfer matrix	Best value
2	0.19315	0.26162	0.26867	0.26740	0.29120 ± 0.00071	0.29156 [4]
3	0.39268	0.42284	0.41699	0.41295	0.41201 ± 0.00002	
4	0.46301	0.48166	0.48889	0.48951	0.51486 ± 0.0045	
5	0.49229	0.50669	0.51008	0.50888	0.49917 ± 0.00091	
7	0.51008	0.52217	0.52170	0.52284	0.54770 ± 0.15301	
$M \rightarrow \infty$	0.3863	0.4055	0.3967	0.40670	0.3870 ± 0.0009	0.3866 [11]

obtained by Fisher and co-workers [3–5], and the entropy for Hamiltonian walks ($M \rightarrow \infty$) is consistent with both transfer matrix calculations [6] and the result of series expansions up to third order in q^{-1} [13], which is $s_\infty \approx 0.38629$. In this series, the first-order term is absent, while in the square lattice case ($q=4$), the second- and third-order terms cancel each other; and thus the third order entropy has the mean-field value as shown in Table II.

Another relevant question is the value of the molecular weight which maximizes the entropy at full occupancy (Fig. 4). Mean-field and Bethe lattice results show maximum entropy at $M=8$ for a lattice with coordination number $q=4$ Refs. [7,8], while series up to second order in q^{-1} on the square lattice as well as Husimi lattice calculations for $q=4$ result in a maximum entropy at $M=7$. Our results suggest that this maximum actually occurs at $M=4$ on the square lattice, if we suppose that that only one maximum exists in the curve $s(\rho=1) \times M$, and also disregard the value obtained for $M=7$ due to the large uncertainty associated to it.

For partial occupancy of the lattice, the results are similar to the ones shown in Fig. 5 for the entropy of dimers as a function of the fraction of occupied lattice sites, ρ . For all the cases, we considered that the entropy displays a single maximum. The density at which this maximum occurs increases with M , getting closer to $\rho \approx 0.79$, the value found in the polymer limit. The densities and maximum entropies are

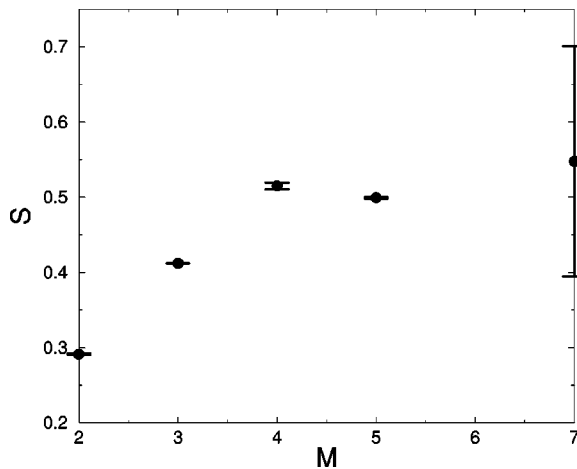


FIG. 4. Entropy at full occupancy of the lattice as a function of the molecular weight M .

listed in Table III, and it may be noticed that the largest value for the maximum entropy occurs for tetramers, as was also found for $\rho=1$.

In the polymer limit $M \rightarrow \infty$, the model of a polymer placed on a strip in the grand-canonical ensemble displays a first-order phase transition at a critical activity z_c , with the coexistence of a nonpolymerized phase ($\rho=0$) and a polymerized phase ($\rho=\rho_c > 0$) [14]. As the width m of the strip is increased, the discontinuity in the density at the transition becomes smaller and in the two-dimensional limit $m \rightarrow \infty$, a continuous transition is found at $z_c \approx 0.3790522$ [15]. The entropy of a polymer on a strip of finite width is therefore not defined for $\rho < \rho_c$, as may be seen in Fig. 6, where the extrapolated value of the entropy as a function of the density for polymers is depicted. As larger widths are considered, the step in the entropy decreases; and in the two-dimensional limit, we have $s(\rho=0)=0$.

V. ONE-DIMENSIONAL CASE

A particular case where results may easily be obtained analytically is the one-dimensional problem ($m=1$). In this case, the dimension of the transfer matrix \mathcal{T} is equal to M , and we have

$$\mathcal{T}_{i,j} = \delta_{i,1} \delta_{j,1} + z(\delta_{i+1,j} + \delta_{i,M} \delta_{j,1}), \tag{14}$$

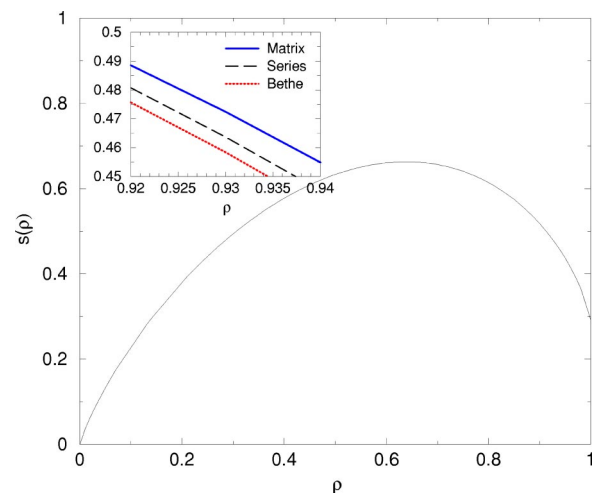


FIG. 5. Entropy for dimers as a function of the density. In the inset, results of values obtained in this work are compared with results from series expansion [9] and Bethe lattice [8] calculations.

TABLE III. Maximum values of the entropy as a function of the density.

M	Density of maximum entropy	Maximum entropy
2	0.64	0.66
3	0.71	0.70
4	0.76	0.74
5	0.76	0.73
7	0.78	0.72
$M \rightarrow \infty$	0.79	0.56

where $1 \leq i, j \leq M$. One may easily obtain the secular equation of this matrix, which is

$$\lambda^M - \lambda^{M-1} - z^M = 0. \quad (15)$$

The density may then be found as a function of the largest eigenvalue λ by using the secular equation above and also expression (12). One obtains

$$\lambda = \frac{1 - \alpha\rho}{1 - \rho}, \quad (16)$$

where $\alpha = (M-1)/M$. Then the entropy may be found by performing the integration in Eq. (7), changing the integration variable from ρ to λ . The result is

$$s = (1 - \alpha\rho)\ln(1 - \alpha\rho) - (1 - \rho)\ln(1 - \rho) - \rho(1 - \alpha)\ln[\rho(1 - \alpha)]. \quad (17)$$

This result is equal to the expression that is obtained if the coordination number of the Bethe lattice result [expression (22) in Ref. [8]] is taken equal to 2. The entropy in the one-dimensional case vanishes, as expected, for $\rho=1$, and the maximum is located at a value of the density which is equal to $1/2$ for monomers ($\alpha=0$) increasing monotonically with α and approaching 1 in the polymer limit $\alpha \rightarrow 1$ (Fig.

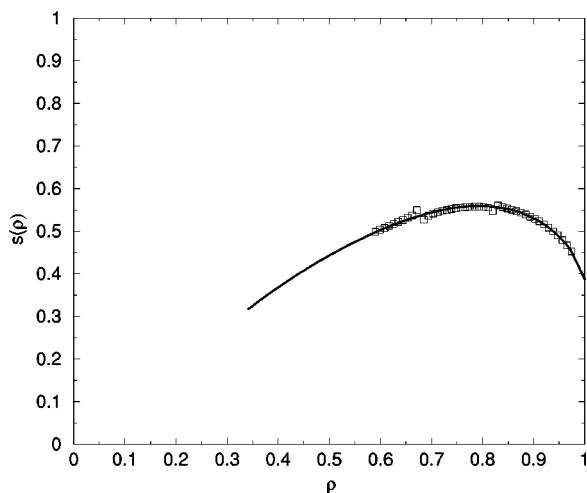


FIG. 6. Entropy of polymers as a function of the density. The squares correspond to extrapolations of the values on strips of finite widths and the full line is the result for a strip of width $m=7$.

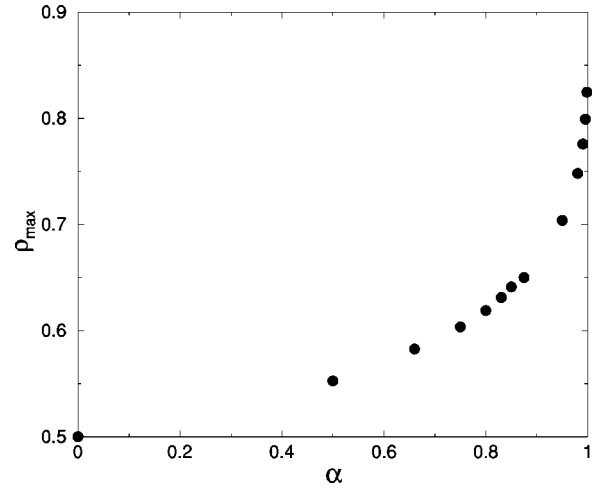


FIG. 7. Density of maximum entropy as a function of $\alpha = 1 - 1/M$.

7), where the entropy vanishes for all values of ρ . The value of the maximum entropy is a decreasing function of α .

For a given value of M , the density that maximizes the entropy is obtained through the equation

$$(1 - \alpha\rho)^{-\alpha}(1 - \rho)[\rho(1 - \alpha)]^{-(1-\alpha)} = 1. \quad (18)$$

VI. CONCLUSION

In this paper we estimate the entropy of chains with M monomers, each placed on the square lattice as a function of the fraction ρ of lattice sites occupied by monomers. The estimates were obtained by extrapolating numerically exact values for the entropy on strips of finite widths m , calculated using a transfer matrix approach, to the two-dimensional limit $m \rightarrow \infty$.

On the square lattice, our calculations indicate that the absolute maximum of the entropy $s_M(\rho)$ occurs for tetramers ($M=4$). In the one-dimensional case, the maximum entropy of $s_M(\rho)$ is a monotonically decreasing function of M , the absolute maximum $s_1(1/2) = \ln(2)$ being obtained for monomers and approaching 0 as $M \rightarrow \infty$.

The problem of the thermodynamic properties of the athermal model of chains formed by M monomers placed on a regular lattice has been the subject of several simulational studies [16–19]. While some of these investigations estimate the insertion probability $p(p, M, N)$ (the probability that an additional M -mer placed on the lattice with p chains on the N -sites lattice does not overlap with any of the p chains that are already present on the lattice), and then proceed calculating the osmotic pressure through integration [16,17], the pressure may also be estimated directly, the so-called repulsive wall method [18]. Extensive scanning method simulations were also performed [19], and this method leads directly to an estimate of the entropy, which may be compared with our results. Since the smallest value of M in the simulations is $M=10$, no direct comparison is possible with our results. Nevertheless, at all densities considered in the simulations ($\rho=0.27, 0.40, 0.53$, and 0.63) the results of the simulations for the entropy, properly renormalized, interpo-

late our estimates for $M=7$ and for polymers ($M\rightarrow\infty$).

Finally, the problem of M -mers confined inside strips of finite width with closed boundary conditions, is an extension of earlier work done on the thermodynamic properties of chains inside strips in the polymer limit [20].

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