Asymptotic behavior of the entropy of chains placed on cylinders

W. G. Dantas* and M. J. de Oliveira†

Universidade de São Paulo, Caixa Postal 66318 05315-970 São Paulo, São Paulo, Brazil

J. F. Stilck‡

Instituto de Física, Universidade Federal Fluminense, Av. Litorânea s/n, 24210-340, Niterói, RJ, Brazil

By using the transfer matrix approach, we investigate the asymptotic behavior of the entropy of flexible chains with M monomers each placed on strips with periodic boundary conditions (cylinders). In the limit of high density of monomers, we study the behavior of the entropy as a function of the density of monomers and the width of the strip, inspired by recent analytical studies of this problem for the particular case of dimers ($M=2$). We obtain the entropy in the asymptotic regime of high densities for chains with $M=2,\ldots,9$ monomers, as well as for the special case of polymers, where $M\to\infty$, and find that the results show a regular behavior similar to the one found analytically for dimers. We also verify that in the low-density limit the mean-field expression for the entropy is followed by the results from our transfer matrix calculations.

PACS number(s): 05.50.+q, 02.10.Ox, 02.70.−c

I. INTRODUCTION

In the 1930s, the dimer model was introduced to mimic the adsorption of diatomic molecules on a crystal surface [1]. Later, this model was applied in the study of many other physical systems such as ferroelectric and ferromagnetic materials [2–6]. The dimers can be modeled as chains with two basic units called monomers, occupying first neighbor sites of a lattice. A central question in the study of this model is to enumerate the number of ways to place p dimers on lattice with N sites, such that the density of monomers is given by $\rho=2p/N$. The special case of full occupancy, where $\rho=1$, was exactly solved for planar lattices using a technique based on pfaffians [7–9]. However, the more general case $\rho<1$, the so-called monomer-dimer problem, is still an open question. Recently, an analytic solution was obtained for the case where there is a single vacancy at a certain site on the boundary of a two-dimensional lattice [10,11].

On the other hand, in a previous work, two of us used the transfer matrix approach to calculate the entropy of flexible chains with M monomers, that we call M-mers, as a function of the density ρ of sites of the lattice occupied by monomers [12]. Since only the infinite energy related to the excluded volume interaction is considered, this is an athermal problem. The entropy was calculated through a numerically exact procedure for the model defined on strips of finite widths n and infinite length, with periodical boundary conditions in the transverse direction, which may be viewed as cylinders of perimeter n. The sequence of results for strips of finite widths was then extrapolated to the two-dimensional limit by means of finite-size scaling procedures.

By using computational methods and the asymptotic theory of Pemantle and Wilson [13], Kong [14–16] obtained, among other results, exact asymptotic expansions for the en-

tropy of the dimers placed on cylinders in the high density region. It may be appropriate to mention that the free energy $f(\rho)$ defined by Kong is actually the dimensionless entropy per lattice site $s(\rho)=S(\rho)/(Nk_B)$, which is related to the Helmholtz free energy of the system through

$$s(\rho) = -\frac{F(\rho)}{Nk_BT}, \tag{1}$$

where k_B is the Boltzmann constant and we have set the constant internal energy of the system equal to zero. He observed that the amplitude of the first term in this expansion depends on the parity of the cylinder perimeter n,

$$s_n(\rho) \sim s_n(1) - \varphi(1-\rho)\ln(1-\rho), \tag{2}$$

where

$$\varphi = \begin{cases} 1 & \text{if } n \text{ is odd,} \\ \dfrac{1}{2} & \text{if } n \text{ is even.} \end{cases}$$

The asymptotic behavior of the free energy in the low density limit $\rho\to0$ was also studied by Kong in the monomer-dimer problem [14].

It is of interest to consider how the asymptotic results found by Kong are generalized if chains with more than two monomers are considered. In this work, using the transfer matrix approach to calculate the entropy for finite cylinders with perimeter n, we obtain estimates for the amplitude φ not only for the dimer case, but also for larger chains $M=3,4,\ldots,9$. We find that in general expression (2) describes well the behavior of $s(\rho)$ in the high density limit, but the number of different values of the amplitude, as well as their numerical values, change as chains with different molecular weights M are considered. Also, we study the low density limit for the same values of M mentioned before.

*wgd@gibbs.if.usp.br
†oliveira@if.usp.br
‡jstilck@if.uff.br

This paper is organized as follows. In Sec. II we present the expressions used to estimate the amplitudes φ and we discuss how the transfer matrix for the problem is defined and obtained. The numerical results may be found in Sec. III and the conclusions are presented in Sec. IV.

II. USEFUL EXPRESSIONS, DEFINITION OF THE TRANSFER MATRIX, AND ITS CONSTRUCTION

Although it is rather natural to study the system in the canonical ensemble, where the number of monomers on the lattice is fixed, to apply the transfer matrix technique it is convenient to allow this number to fluctuate. We thus define the grand-canonical partition function as

$$\Xi(z) = \sum_p z^{pM} \Gamma(M, N, p), \qquad (3)$$

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. The density of monomers may be written as

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

where $\phi(z)$ is the thermodynamic potential per lattice site, defined as

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

In the thermodynamic limit we may use a Legendre transformation to rewrite the potential as

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

which implies that

$$\frac{ds}{d\rho} = -\ln z,$$

and therefore the entropy will be given by

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

with $s(0) = 0$.

Now, we may attempt to generalize the high density expansion for dimers and suppose that the behavior of the entropy in this region is given by the expression

$$\frac{s_n(\rho) - s_n(1)}{(1-\rho)} = A_n - \varphi_n \ln(1-\rho), \qquad (8)$$

thus, using Eq. (7) we obtain

$$\int_\rho^1 \ln z_n(\rho') d\rho' = A_n(1-\rho) - \varphi_n(1-\rho)\ln(1-\rho). \qquad (9)$$

Differentiating this last equation with respect to ρ, we have

$$\ln z_n = C_n - \varphi_n \ln(1-\rho), \qquad (10)$$

where $C_n = A_n - \varphi_n$. This expression was useful to obtain evidence that for all cases we studied the asymptotic behavior

supposed in Eq. (8) is valid, allowing us to estimate the amplitudes φ_n.

Transfer matrix

To build the transfer matrix for this problem we define a strip of width n on the square lattice in the plane (x, y), so that $1 \le x \le n$ and $-\infty \le y \le \infty$. The position of a site may be defined by (x, y), where $1 \le x \le n$ and y are integer numbers. Periodic boundary conditions are assumed in both directions. Generalizing the prescription due to Derrida [17] for the transfer matrix of an infinite chain placed on cylinders, we define the state of a set of n vertical bonds of the lattice connecting the sites at $y_0 - 1$ to the sites at y_0 specifying the number of monomers already connected to this bond located on sites with $y < y_0$ (in the range $[0, M-1]$) and the pairs of bonds which are connected to each other by a chain whose monomers are all located at sites with $y < y_0$. This last information is essential to prevent the presence of rings in the allowed configurations. With the information above about the configuration of the vertical bonds located between $y_0 - 1$ and y_0, we may find all possible configurations of the vertical bonds between y_0 and $y_0 + 1$, thus defining a transfer matrix. Actually, it is not difficult to develop an algorithm for the steps involved in this procedure, which allows us to obtain the elements of the transfer matrix exactly. Restrictions in memory and computer time set an upper limit to the values of n and M we are able to handle, since the size of the transfer matrix grows very fast as they increase. More details about this procedure may be found in the previous paper [12].

Once the transfer matrix $\mathcal{T}$ is obtained, we may find the entropy in the thermodynamic limit using the largest eigenvalue of this matrix λ. The grand-canonical partition function is related to the transfer matrix by the expression

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

where ℓ is the length of the strip and we adopt periodical boundary conditions in the longitudinal direction as well. The density of monomers in the thermodynamic limit $\ell \to \infty$, $\rho(z)$, will then be given by

$$\rho(z) = \lim_{N \to \infty} \frac{z}{N} \frac{d}{dz} \ln \Xi(z) = \frac{z}{n} \frac{d}{dz} \ln \lambda, \qquad (12)$$

where λ is the largest eigenvalue of the transfer matrix $\mathcal{T}$ and $N = n\ell$. Thus using expressions (10) and (12) and supposing that the behavior in the high density limit of the entropy for chains with M monomers is given by the relation (8), we may estimate the amplitudes φ for the set the molecular weights M, and perimeters of the cylinders n we were able to handle.

III. NUMERICAL RESULTS

A roughly exponential growth of the size of the transfer matrix with both the molecular weight M and the width of the strip n prevents us from obtaining results for larger chains or cylinders. In this paper we show results for chains
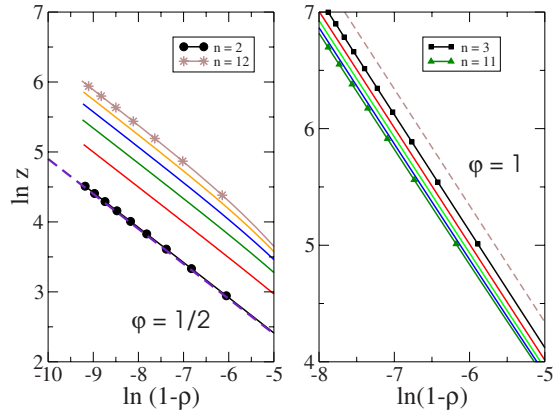
FIG. 1. (Color online) Results for the amplitude φ for dimers ($M=2$). At the left panel the widths of the strips are even values ranging between $n=2$ and 12, while at the right panel results for odd values of the widths between $n=3$ and 11 are displayed. The dashed lines indicate slopes equal to the known value of φ in each case.

with molecular weight ranging between 2 and 9 and widths of the strips ranging between 2 and 12 (dimers case) and 2 ($M=9$ case). First, we analyze the high density limit behavior of the entropy for the molecular weights and widths of the strips mentioned. Later, we will turn our attention to the low density limit for the same cases. For each pair of values for n and M, we obtain the elements of the transfer matrix using the algorithm mentioned above in a numerically exact fashion. Then, we take advantage of the $\mathbb{C}_n$ symmetry of the states and use the power method to find the largest eigenvalue of the matrix λ and its derivative with respect to z.

A. High density limit

We start with our results for dimers, which are in agreement with the values obtained by Kong [15,16], with $\varphi=1$, if n is odd and $\varphi=1/2$, if n is even, as is shown in Fig. 1.

For chains with $M=3$ (trimers), our results also lead to two values of the amplitude: $\varphi=1/3$ for widths that are multiples of 3 and $\varphi=1$ otherwise. Our results for $M=4$ (tetramers) show three values for the amplitude φ,

$$\varphi = \begin{cases} 1 & \text{if } n \text{ is odd,} \\ \dfrac{1}{2} & \text{if } n \text{ is a multiple of 2, but not of 4,} \\ \dfrac{1}{4} & \text{otherwise.} \end{cases}$$

Finally, in the case $M=5$ (pentamers), we found $\varphi=1/5$ if n is a multiple of 5 and $\varphi=1$ in all other cases. Unfortunately, in this case we only were able to consider widths up to $n=5$ due to computational limitations caused by the fast growth of the transfer matrix with n. All these results are summarized in Fig. 2.

In our calculations, numerical errors set an upper limit to the densities we may consider. As we approach the full oc-
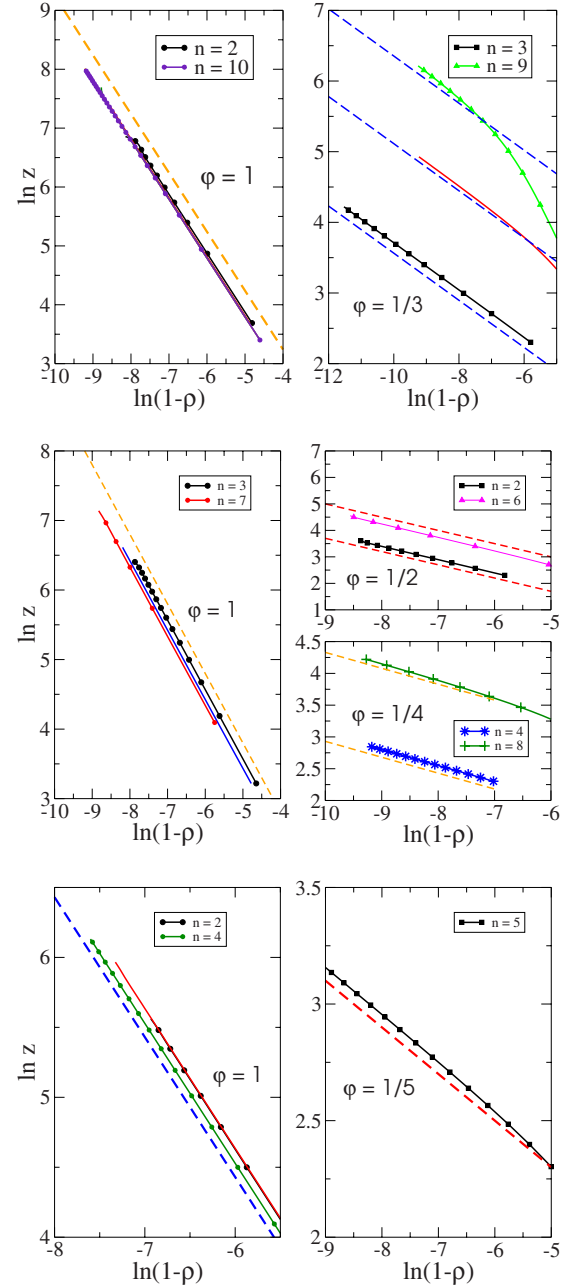

FIG. 2. (Color online) Plots which lead to the estimated values of the amplitude φ for $M=3,4$ and $M=5$. Top: Results for trimers ($M=3$), with widths ranging between $n=2$ and 10. In this case for widths that are multiples of three we find $\varphi=1/3$ for all other widths the results lead to $\varphi=1$. Only the extreme widths n in each case are labeled. Middle: Case $M=4$, for widths in the range $n=2–8$. In this case three values of the amplitude are found. For widths which are even but not multiples of 4, $\varphi=1/2$. If n is odd $\varphi=1$ and $\varphi=1/4$ in all other cases. Bottom: Data for $M=5$, with $n=2–5$. Again, two values for φ are found. If n is a multiple of five, then $\varphi=1/5$ and $\varphi=1$ for the other cases. The dashed lines are drawn with the conjectured slope φ for each case.

cupancy limit $\rho \rightarrow 1$, the values of the activity z become very large and this makes the numerical errors in the calculations grow. Finally, we extend our analysis to the polymer case
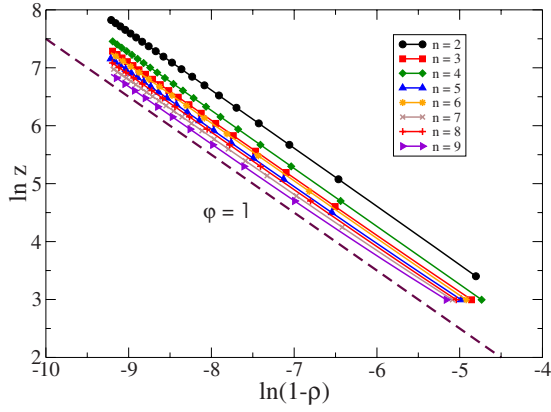
FIG. 3. (Color online) Polymer case ($M \to \infty$) in which only one amplitude $\varphi = 1$ was found for all widths studied ($n = 2, 3, \ldots, 9$).

($M \to \infty$). As was shown in [12], the entropy for this case displays different finite size scaling corrections for even and odd widths. Nevertheless, the data show a single amplitude $\varphi = 1$ in this limit, as may be seen in Fig. 3.

We may conclude that the results shown above suggest that the dependence of the entropy with the width of the strip close to the full occupancy limit obtained by Kong for the dimer model may be extended for larger chains, including more possibilities for the amplitude φ. Apparently, the values of the amplitude are related to the split of the leading eigenvalues of the transfer matrix into subsets with different finite size scaling behaviors found in [12]. These splits seem to be related to frustration effects in the limit of full occupancy. An empirical rule that we found to label these subsets is the determination of the integer α which satisfies the relation

$$\alpha n = kM, \tag{13}$$

where k is the smallest integer for which a solution is found. The widths associated to the same value of α share the same estimate of the amplitude, as may be seen in Table I. Another way to look at relation (13) is to rewrite it as $\alpha/k = M/n$, so that α is the numerator of the fraction M/n after it is simplified. We notice that α may be interpreted as the length of the smallest rectangle of width n which may be totally filled by chains with M monomers each. The number of chains we can place in this rectangle is k. We notice that if M is prime, we find $\alpha = M$ for all widths n which are not multiples of M, while $\alpha = 1$ if n is a multiple of M. In general, the number of different values for α is equal to the number of divisors of M, including 1 and M itself.

Our results suggest that the amplitude φ is related to the integer α by the simple relation

$$\varphi = \frac{\alpha}{M}, \tag{14}$$

which is obeyed by all numerical results presented here. However, we have no physical or mathematical argument to justify this hypothesis. Nevertheless, the numerical evidence supports this relation. If we suppose that the polymer limit $M \to \infty$ is approached by a sequence of prime values of M, then we would conclude that $\alpha = M$ in this limit, which is

TABLE I. Values for the integer α, which satisfies the relation (13) for some widths and molecular weights.

M	n	α	k	M	n	α	k	M	n	α	k	M	n	α	k
2	2	1	1	3	2	3	2	4	2	2	1	5	2	5	2
	3	2	3		3	1	1		3	4	3		3	5	3
	4	1	2		4	3	4		4	1	1		4	5	4
	5	2	5		5	3	5		5	4	5		5	1	1
	6	1	3		6	1	2		6	2	3		6	5	6
	7	2	7		7	3	7		7	4	7		7	5	7
	8	1	4		8	3	8		8	1	2		8	5	8
	9	2	9		9	1	3		9	4	9		9	5	9
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
6	2	3	1	7	2	7	2	8	2	4	1	9	2	9	2
	3	2	1		3	7	3		3	8	3		3	3	1
	4	3	2		4	7	4		4	2	1		4	9	4
	5	6	5		5	7	5		5	8	5		5	9	5
	6	1	1		6	7	6		6	4	3		6	3	2
	7	6	7		7	1	1		7	8	7		7	9	7
	8	3	4		8	7	8		8	1	1		8	9	8
	9	2	3		9	7	9		9	8	7		9	1	1
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮

consistent with the observed amplitude $\varphi = 1$.

In order to test the conjecture above for the amplitude of the high density limit asymptotic form of the entropy, we extended the transfer matrix calculations to higher values of the molecular weight M, although with increasing values of M we are restricted to decreasing maximum widths n. As may be seen in Fig. 4, all results for chains with molecular weights $M = 6-9$ are consistent with the conjecture for the amplitudes φ. There are cases, like $M = 6$, $n = 3$, where numerical errors prevented us from obtaining results at densities high enough to observe the asymptotic behavior. An example where the asymptotic regime also was reached only at very high densities may be seen in results for $M = 3$, $n = 9$ in Fig. 2. As a consequence of these limitations, only some of the possible values for the amplitude φ are observed in the results for chains with larger molecular weight presented in Fig. 4.

B. Low density limit

In the low density limit $\rho \to 0$, Kong [14] obtained from an asymptotic expansion the following behavior for the entropy of dimers placed in a strip with width n,

$$s_n(\rho) \sim -\frac{\rho}{2} \ln \rho + \mathcal{O}(\rho). \tag{15}$$

The expression above resembles the one predicted by the mean-field approximation [18,19], which is

$$s(\rho) = -(1-\rho)\ln(1-\rho) - \frac{\rho}{M} \ln\left(\frac{2\rho}{M}\right) + \left(1 - \frac{1}{M}\right)(\ln q - 1), \tag{16}$$
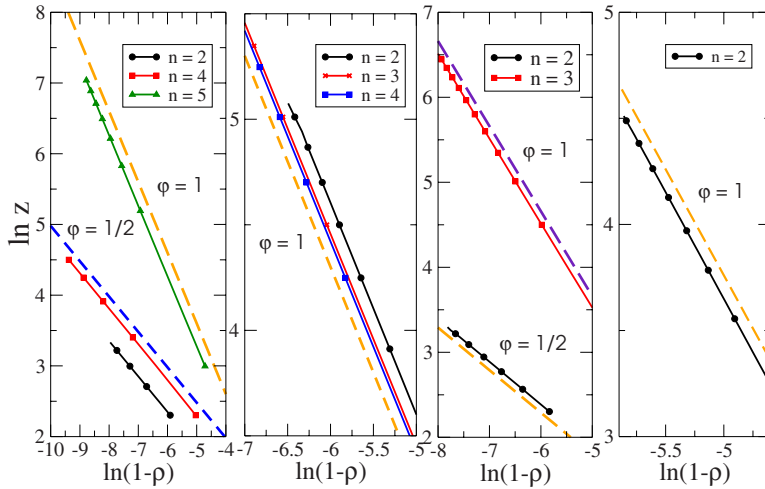
FIG. 4. (Color online) Results for the entropy in the high density limit for chains with molecular weight M between 6 and 9, in increasing values from left to right. The observed values of the amplitudes are consistent with the conjecture made in the text.

where q is the coordination number. For small values of the density ρ, the leading contribution comes from the second term, which for dimers is identical to the one obtained by Kong.

It is then rather natural to conjecture that for other values of M the leading contribution to the entropy is the one predicted by the mean-field approximation, since for small densities the interchain interactions may be neglected. Thus we conjecture that for all values of the molecular weights in the low density limit we have the asymptotic behavior

$$s(\rho) \sim -\frac{\rho}{M}\ln\left(\frac{2\rho}{M}\right). \tag{17}$$

In order to test expression (17) in the low density limit, we built curves for different molecular weights and widths of strips. Our results, as shown in Fig. 5, are consistent with the conjecture for all the chains analyzed here, since curves of $Ms(\rho)/\rho$ as a function of $\ln(2\rho/M)$ are linear with a slope equal to 1 in all cases.
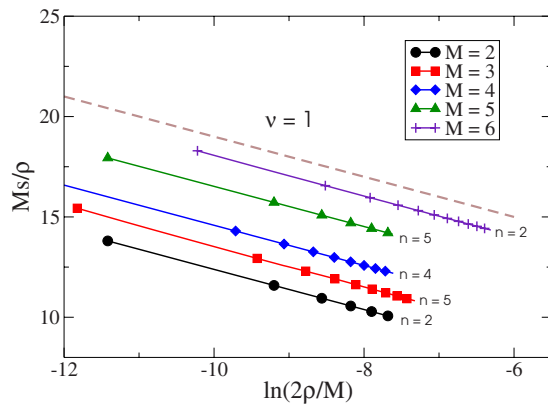

FIG. 5. (Color online) Results for the low density limit with M varying between $M=2$ and 6. In all cases, independently of the width analyzed, we observe linear relations with slope $\nu=1$ (indicated by the dashed line), satisfying the mean-field prediction.

IV. CONCLUSIONS

In this work, we study the asymptotic behavior of the entropy for chains placed on strips using the transfer matrix approach. Generalizing the results by Kong [14–16] for the case of dimers in the high density limit, we conjecture similar asymptotic forms for the entropy of chains with larger molecular weights. We propose an empirical rule to determine the number of different amplitudes of the asymptotic behavior close to the full occupancy limit, as well as to find the values of these amplitudes. Unfortunately, computational limitations prevent us from studying larger chains and larger widths. However, it seems reasonable to expect that our results apply also to other cases. An analytic approach similar to the one made by Kong [15,16], using the Pemantle-Wilson asymptotic theory [13] would be very useful to support our conclusions. However, it may not be easy to carry out this task for chains with molecular weight larger than $M=2$.

Another interesting result is that in the low density limit the free energy is well-fitted by the mean-field approximation [18,19] for any width n for all the values of M we were able to consider. Again, it would be interesting to obtain an exact result in this limit in order to verify this conclusion.

The asymptotic behaviors found by Kong for dimers and conjectured here for larger chains, besides their intrinsic importance, may be helpful to guide studies using other techniques, such as numerical simulations. It may be remarked that, particularly in the high density region, simulations may be difficult due to high relaxation times, as may be seen, for example, in a recent study of rigid chains by Ghosh and Dhar [20].

ACKNOWLEDGMENTS

[1] R. H. Fowler and G. S. Rushbrooke, Trans. Faraday Soc. **33**, 1272 (1937).

[2] P. W. Kasteleyn, J. Math. Phys. **4**, 287 (1963).

[3] M. E. Fisher, J. Math. Phys. **7**, 1776 (1966).

[4] C. Fan and F. Wu, Phys. Rev. B **2**, 723 (1970).

[5] S. R. Salinas and J. F. Nagle, Phys. Rev. B **9**, 4920 (1974).

[6] J. F. Nagle, C. S. O. Yokoi, and S. M. Battacharjee, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz (Academic Press, New York, 1989), Vol. 13.

[7] M. E. Fisher, Phys. Rev. **124**, 1664 (1961).

[8] P. W. Kasteleyn, Physica (Amsterdam) **27**, 1209 (1961).

[9] H. N. V. Temperley and M. E. Fisher, Philos. Mag. **6**, 1061 (1961).

[10] W. J. Tzeng and F. Y. Wu, J. Stat. Phys. **110**, 671 (2003).

[11] F. Y. Wu, Phys. Rev. E **74**, 020104(R) (2006); **74**, 039907(E) (2006).

[12] W. G. Dantas and J. F. Stilck, Phys. Rev. E **67**, 031803 (2003).

[13] R. Pemantle and M. C. Wilson, J. Comb. Theory, Ser. A **97**, 129 (2002).

[14] Y. Kong, Phys. Rev. E **75**, 051123 (2007).

[15] Y. Kong, Phys. Rev. E **74**, 011102 (2006).

[16] Y. Kong, Phys. Rev. E **74**, 061102 (2006).

[17] B. Derrida, J. Phys. A **14**, L5 (1981).

[18] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).

[19] J. F. Stilck and M. J. de Oliveira, Phys. Rev. A **42**, 5955 (1990).

[20] A. Ghosh and D. Dhar, Europhys. Lett. **78**, 20003 (2007).