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STATISTICAL

Semi-flexible Trimers on the Square Lattice in the Full Lattice Limit

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Abstract
Trimers are chains formed by two lattice edges, and therefore three monomers. We consider trimers placed on the square lattice, the edges belonging to the same trimer are either colinear, forming a straight rod with unitary statistical weight, or perpendicular, a statistical weight ω being associated to these angular trimers. The thermodynamic properties of this model are studied in the full lattice limit, where all lattice sites are occupied by monomers belonging to trimers. In particular, we use transfer matrix techniques to estimate the entropy of the system as a function of ω. The entropy $s(\omega)$ is a maximum at $\omega = 1$ and our results are compared to earlier studies in the literature for straight trimers ($\omega = 0$) and angular trimers ($\omega \rightarrow \infty$) and for mixtures of equiprobable straight and angular trimers ($\omega = 1$).

Keywords Trimers · Square lattice · Entropy · Polymers · Transfer matrix

1 Introduction and Definition of the Model

The study of rod-like molecules has a long history in statistical mechanics. Onsager [1] has argued that they should show oriententional (nematic) order at sufficiently high densities. Although his original argument was related to a continuum system, later rods placed on lattices were also considered, such as in the approximate study by Flory [2] somewhat later modified by Zwanzig [3].

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So far, these lattice models of rods, where each rod (k-mer) is composed by k consecutive sites aligned in one of the directions of the lattice, were much studied in the literature but the only case where an exact solution was found was for dimers ($k = 2$) on two-dimensional lattices and in the full lattice limit, when all lattice sites are occupied by rod monomers [4–7]. The full lattice dimer phase is isotropic. On the square lattice, it was found by Ghosh and Dhar [8] that nematic ordering appears for rods with $k \geq 7$ and at intermediate densities, at low and high densities the system is isotropic. The model has been studied extensively after the pioneering work by Ghosh and Dhar, mainly using computational simulations. With increasing rod densities, the first transition from the isotropic to the nematic phase is continuous and its universality class for two-dimensional lattices was determined [9–12]. The second transition, where the system leaves the nematic phase and enters the high-density isotropic phase, is more difficult to investigate through simulations: due to the high density of rods, the moves are very rare. An alternative simulational procedure allowed for more efficient simulations in the high-density region [13], and recently there were shown arguments in favor of the possibility of this high-density transition being discontinuous on the square lattice [14]. Finally, the entropy of these system of rods in the limit of the full lattice, a generalization of the classical problem of the entropy of dimers for general size k of the rods, was also the subject of contributions in the literature. It was estimated using transfer matrix techniques

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for trimers on the square lattice by Ghosh et al. [15], computational simulations were used to produce estimates, also on the square lattice for values of k between 2 and 10 [16] and transfer matrix techniques were applied also for $2 \leq k \leq 10$, leading to rather precise estimates for the full lattice entropies [17]. An analytic approximation to this problem is the exact solution of the problem on the Husimi lattice [18], a generalization of the solution of the problem on the Bethe lattice [19]. These solutions on the central region of treelike lattices may be seen as improved generalizations of simple mean field approximations.

In this paper, we address a generalization of the athermal problem of trimers on the square lattice mentioned above. If we allow the trimers to bend, they now may be in two configurations, and we may associate the energy 0 to the extended configuration and the energy ϵ to the angular one, so that now the model is thermal. The entropy per site of the system is now a function of the statistical weight of the bends $\omega = \exp[\epsilon/(k_B T)]$, where we still are considering the full lattice limit. Besides the case $\omega = 0$, which corresponds to straight trimers and was discussed above, two other particular cases of this problem were already studied before and discussed in the literature. In the limit $\omega \to \infty$, all trimers are in the angular configuration, and transfer matrix calculations on the square lattice were used by Froböse, Bonnemeier, and Jäckle to estimate the entropy [20]. When straight and angular k-mers are equiprobable ($\omega = 1$), similar techniques were used for k in the range between 2 and 7 for the full lattice limit [21].

In the two limiting situations of the model which were already studied and described above ($\omega = 0$ and $\omega \to \infty$), it is athermal, and here we consider the general case on the square lattice using transfer matrix techniques to study the thermodynamic properties in the full lattice limit. This is done defining the model on stripes of the square lattice of finite widths L in the horizontal x direction, extending in the vertical direction y. As discussed in more detail in [17], the initial condition at $y = 0$ is fixed and the transverse boundary condition is periodic, so that we are solving the model on cylinders with perimeters L. We then proceed defining a transfer matrix for the model, and in the thermodynamic limit, where the height of the lattice diverges and the properties of the model are determined by the leading eigenvalue of this matrix. Among them, we calculate particularly the entropy per site $s(\omega)$. Finally, we extrapolate the results for a finite sets of widths L to the two-dimensional limit $L \to \infty$ using finite size scaling techniques.

In Sect. 2, we describe the definition of the transfer matrix for the model and the method used to obtain the thermodynamic properties of the system from it. In Sect. 3, we present the results and compare them with previous ones where appropriate. Final comments and discussions are presented in Sect. 4.

2 Definition of the Transfer Matrix and Calculation of the Entropy

Consider a strip of transverse width L, with periodic boundary conditions in the transverse direction, such that every lattice site is occupied by a monomer which belongs to a linear or bend trimer. The statistical weight of a linear trimer is unitary and the Boltzmann factor associated to a bend trimer is equal to ω. A possible configuration of a section of a strip with width $L = 4$ is shown in Fig. 1.

The transfer matrix is defined in a similar way as in previous studies [15, 17, 20]. The states are defined by the configuration of the L vertical edges of the lattice crossed by horizontal reference lines R_i shown in the figure. Each time the transfer matrix is applied, L sites are added to the system, so that the line of the transfer matrix is defined by the configurations of the reference line R_i and its column by the configuration of the reference line R_{i+1}. The state may be represented by a vector with L components. If the vertical edge which corresponds to a component is not occupied by a trimer bond, the component is equal to zero; otherwise, it will be equal to the number of monomers already included in the trimer (1 or 2). For example, the state associated to the reference line R_1 is (0, 0, 0, 0), and the state corresponding to R_4 will be (0, 0, 1, 2). The combinatorial problem of building the transfer matrix is the following: given the state of reference line R_i, find all possible outputs for reference line R_{i+1}. To build the transfer matrix, we start with the state (0, 0, 0, ...0) and find all its possible outputs. Then, we proceed finding the second generation of output states. This iterative procedure ends when no new states are generated. In general, a larger matrix could be defined and the one we are considering is a particular block of this more general matrix, but as discussed in [17] there are evidences that the dominant eigenvalue is contained in the block we are considering.

For clearness, let us present in some detail the building of the transfer matrix for $L = 3$. We should notice that rotation and reflection symmetries are present in the system, so we may reduce the size of the matrix using them. In Fig. 2, we see that the possible outputs if we start with the state (0,0,0) are:

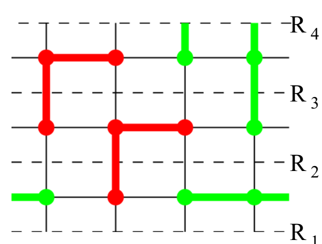

Fig. 1 Section of a lattice with $L = 4$

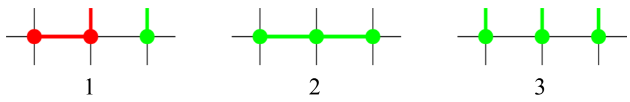

Fig. 2 Output states of the state (O, O, O) for $L = 3$

1. We may proceed by placing an angular trimer and starting a vertical trimer at the three sites above, generating a state such as (2, 1, 0), the statistical weight associated is ω, and there are six ways to do this;
2. A horizontal trimer may be placed on the three sites, and the statistical weight is unitary and the multiplicity is three. The output state is (0, 0, 0);
3. Three vertical trimers may be started at the sites, the statistical weight is unitary, the multiplicity is one, and the output state is (1, 1, 1);

The only output state of (1, 1, 1) is the state (2, 2, 2) and this new state has (0, 0, 0) as its only output state; the multiplicity and statistical weights are unitary. We therefore, using the order of the four states as they appear in the text above, have the following transfer matrix for the model on the $L = 3$ strip:

$$T_3 = \begin{pmatrix} 3 & 6\omega & 1 & 0 \\ \omega & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \tag{1}$$

For periodic boundary conditions in the longitudinal direction of the strip, we find that the canonical partition function on a lattice of width L and length M may be written as:

$$Z = \mathrm{Tr}\, T_L^M = \sum_i \lambda_{i,L}^M,$$

where the $\lambda_{i,L}$ are the eigenvalues of the transfer matrix T_L. Therefore, in the thermodynamic limit $M \to \infty$, the free energy of the model will be determined by the leading eigenvalue of the transfer matrix $\lambda_{1,L}$:

$$f_L(T) = -\frac{k_B T}{L} \ln \lambda_{1,L}(\omega) \tag{2}$$

and therefore the dimensionless entropy per site is given by

$$\begin{aligned} s_L(\omega) &= \frac{-1}{k_B}\frac{\partial f_L}{\partial T} \\ &= \frac{1}{L}\left(\ln \lambda_{1,L} + \omega \ln \omega \frac{1}{\lambda_{1,L}}\frac{\partial \lambda_{1,L}}{\partial \omega}\right). \end{aligned} \tag{3}$$

In general, the transfer matrices are quite sparse and this favors using numerical procedures related to the power method to determine their leading eigenvalue.

As the width L grows, the number of states N_S increases and this sets an upper limit to the widths we were able to consider, due to the limitations of the computational resources at our disposal. Already considering the symmetries, these numbers are displayed in Table 1. We considered widths up to $L = 19$.

Table 1 Number of states (size of the transfer matrices) N_S for the widths L of the strips

L	N_S	L	N_S
3	4	12	7643
4	21	13	62,415
5	39	14	173,088
6	32	15	160,544
7	198	16	1,351,983
8	498	17	3,808,083
9	409	18	3,594,014
10	3210	19	30,615,354
11	8418		

3 Results

As described above, since we may calculate the largest eigenvalue of the transfer matrix as a function of ω, we can obtain the entropy per site $s(\omega)$ numerically using Eq. (3). As it happens for straight rods in the case $\omega = 0$ [17], the finite size behavior of those entropies can be separated in three sets of values $\{s_L\}$, depending on the value of the remainder $R = L/k$, where $k = 3$ is the number of monomers in the chain. This means that all entropy results should be grouped in three sets of values, with $R = 0$, 1, and 2. Each of those sets tends to a thermodynamic limit, s_∞, when $L \to \infty$, separately, following finite size scaling behaviors of the form

$$s_L^{(R)}(\omega) = s_\infty^{(R)}(\omega) + \frac{A(\omega)}{L^2} + o(L^{-2}), \tag{4}$$

also observed in the rigid chains limit and discussed in more detail in [17].

In the presentation of the results, it is convenient to define the parameter

$$\Omega = \frac{\omega}{1+\omega}, \tag{5}$$

whose range is between the values $\Omega = 0$ (straight chains) and $\Omega = 1$ (angular chains). We have used the BST method [22] to extrapolate the entropy values obtaining the estimates valid for the limit $L \to \infty$. The BST was applied considering the relation (4), which implies to set the value of the free parameter w of this method to 2. Doing so, we determine the curves shown in Fig. 3 considering the BST extrapolation in each set of values determined by the remainder R. In that figure, we show the entropy as a function of the parameter Ω. The values obtained in each of those sets are quite close. Actually, the differences among

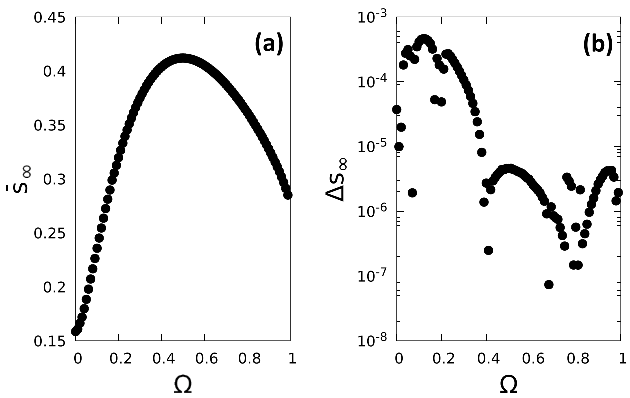

Fig. 3 Extrapolated entropy values (**a**) and their estimated errors (**b**) as functions of Ω, calculated using Eq. (6)

those values are within the uncertainty furnished by the BST extrapolation procedure.

The circles shown in plot (a) of Fig. 3 are the results of the final extrapolation, obtained considering each of the sets statistically independent and, for a given value of Ω, taking the values s_i and its error, σ_i, evaluated for each set, so that we get the final result for the extrapolation, $\bar{s}_\infty$ and its error, ΔS_∞ below:

$$\bar{s}_\infty = \frac{\sum_i s_i/\sigma_i^2}{\sum_i 1/\sigma_i^2}$$
$$\Delta s_\infty = \sqrt{\frac{1}{\sum_i 1/\sigma_i^2}}. \tag{6}$$

In plot (b) of Fig. 3, the errors associated to the estimates of the entropies are depicted, and we notice that, in general, they are smaller in the region of higher values of Ω, where angular trimers predominate.

In order to better evaluate this behavior, Table 2 shows some of the final extrapolated entropy values and their errors. Also, we highlight three special cases for this problem. The case $\Omega = 0$, previously mentioned as the limit where we have only rigid trimers, was already studied by Gosh et al. [15] and Rodrigues et al. [17]. In these works, that case was studied using transfer matrices calculated for strips of widths up to $L = 27$ and $L = 36$, respectively. Rodrigues et al. accomplish to reach such large widths using a different method to determine the transfer matrix, called *Profile Method*, which renders, in general, matrices with smaller dimensions. Still, our result, obtained from the extrapolation of data considering widths up to $L = 19$, agrees with the more precise estimate reference [17]. Another particular case mentioned before can be seen for the case $\Omega = 1/2$, which means $\omega = 1$. This situation represents system of straight and angular trimers with equal statistical weight

Table 2 Some values for the final extrapolated entropy as determined by Eq. (6). Smaller errors are found for larger values of Ω, where the errors coming from the BST methods are minimum. The third column highlights the values for the entropy calculated in previous studies considering special cases, straight chains, $\Omega = 0$, mixed trimers gas, $\Omega = 1/2$, and angular trimers, $\Omega = 1$

Ω	Extrapolated values	Other results
0.0	0.158539(37)	0.15850494(19) [17]
0.1	0.23572(41)	
0.2	0.319592(49)	
0.3	0.37486(11)	
0.4	0.4036371(27)	
0.5	0.4119467(46)	0.412010(20) [21]
0.6	0.4052574(28)	
0.7	0.38767859(85)	
0.8	0.36172496(57)	
0.9	0.3278335(26)	
1.0		0.276931500(50) [20]

in the full lattice limit. A previous result obtained in [21] was calculated from transfer matrix approach considering widths up to $L = 12$ and is also consistent with the present value exhibited in Table 2 for $\Omega = 1/2$. Finally, our results do not include the case $\Omega = 1$, since the numerical calculation for the entropy from the general case studied here displays strong fluctuations as long as we consider $\Omega \to 1$. This case should be considered separately, as it was by Forböse et al. [20], whose result is shown in Table 2.

It is also interesting to find out how the curve shown in Fig. 3 behaves close to those three special points, $\Omega = 0, 1/2$ and $\Omega = 1$. This is illustrated in Fig. 4. We have found three power-law kind of behaviors, each one with a particular exponent. In the vicinity of $\Omega = 0$, which means to consider a system with only chains in the straight configuration, we may see that entropy can be approximated as a function of Ω as

$$s_1 \approx s_{\Omega=0} + A\Omega^{3/2}, \tag{7}$$

where $s_{\Omega=0}$ is the value of the entropy for the rigid trimers case and A is a coefficient numerically estimated as $A \approx 2.67$. On the other hand, close to the point $\Omega = 1$ (angular trimers only), we found that the entropy behavior tends to be like,

$$s_2 = s_{\Omega=1} + B(1 - \Omega)^{4/5}, \tag{8}$$

where $s_{\Omega=1}$ is the numerical value for the entropy when $\Omega = 1$ and $B \approx 0.32$. Finally, when we look at the function $s(\Omega)$ in the neighborhood of $\Omega = 1/2$, where we have straight and angular trimers with equal weight, we get a quadratic relation for the entropy

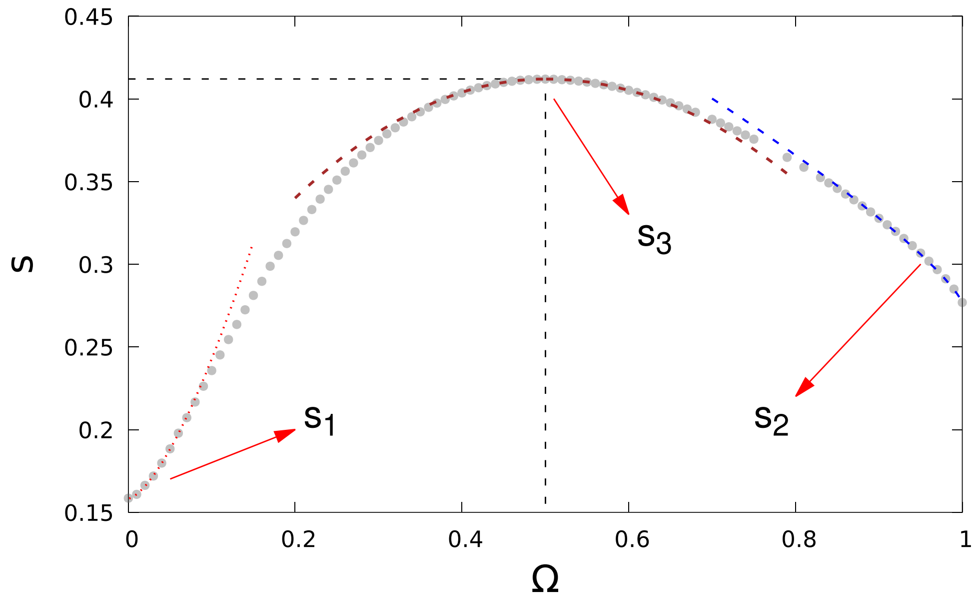

Fig. 4 Same curve found in Fig. 3, but emphasizing three asymptotic regimes for the entropy behavior as a function of Ω. The curves s_1, s_2 and s_3, explicited in Eqs. (7), (8), and (9). Each one of those regimes is related to the special cases mentioned in Table 2

$$s_3 = s_{\Omega=1/2} - C(1/2 - \Omega)^2, \tag{9}$$

with $C \approx 0.7$.

The fact that the maximum of the entropy is located exactly at $\Omega = 1/2$, which means $\omega = 1$, is not really surprising, once this case favors no particular arrangement (straight or angular), therefore corresponding to the situation where the number of configurations is maximum. Obviously, when we get away from this point, we are favoring one of the configurations. Since the case of rigid trimers is the one with the least number of different configurations for trimers occupying all sites of the lattice, this explains the asymmetry of the curve around the point $\Omega = 1/2$.

4 Final Discussion and Conclusion

The entropy of trimers fully occupying the square lattice was already estimated before in three particular cases: when they are straight, composed by three monomers on colinear sites [15–17]; when they are angular, so that the two edges which join the monomers are perpendicular [20]; and for a mixture of equiprobable straight and angular chains [21]. Here we generalize the problem studying a canonical ensemble of trimers in straight and angular configurations, associating an unitary statistical weight to the first configuration and a weight ω to the second one. We thus, using transfer matrix methods, obtain estimates for the entropy $s(\omega)$ for ω in the range $[0, \infty]$, which are consistent with the earlier results in the literature.

The estimates are obtained from numerical diagonalization of the transfer matrices of the model on strips of the square lattice with finite widths L and periodic boundary conditions in the transverse direction. The precision of the estimates is essentially determined by the largest width of the strips we are able to manage, since we use finite size scaling techniques to extrapolate the results on strips of finite widths to the two-dimensional limit $L \to \infty$. As usual, the size of the transfer matrices grows exponentially with L (see Table 1) and this leads to an upper limit $L = 19$ we have reached in this study. The computational part is divided in two stages: first the transfer matrix has to be built, and this is a combinatorial problem which involves logical and integer variables only, and in the second stage the leading eigenvalue of the transfer matrix, for a given value of the statistical weight ω, has to be determined. As the transfer matrix is very sparse, the determinations of the dominant eigenvalue are done using a variant of the power method.

The extrapolation of the entropies of strips of finite widths L to the two-dimensional limit $L \to \infty$ was done using the BST method [22], supposing that the asymptotic finite size scaling behavior of the results is of the form given by Eq. (4). This is discussed in some detail for straight trimers in [15]. Although in many cases the data are consistent with this behavior, as was already found for straight k-mers for other values of k [17], it would still be very interesting to have results for larger widths, in order to confirm this asymptotic behavior. In particular, the amplitude A in Eq. (4), as discussed in [15], is related to the central charge of the phase, and the present results do not allow precise estimates for it.

Finally, we used an alternative procedure of extrapolation of the results for finite strips, adapted from the one employed by Froböse et al. [20] in their study of angular trimers. It relies on the observation mentioned above that the results for strips of widths L should be divided in three groups, according to the value of the rest R of the division of L by 3. We notice, in general, that the results for the entropies of the group $R = 0$ approach the asymptotic value from above, while the one for $R = 1, 2$ approach it from below. We therefore consider the largest 3 or 6 widths L and define the extrapolated entropy to be the mean value of the entropies for these widths. The error will be given by the standard deviation of this set of entropies. For brevity, we will not present these results here, but they were consistent with the ones obtained using the BST method.

As is clear from the discussion above, it would be interesting to have results for larger strips. One possibility we are considering is to apply an alternative way to define the transfer matrix to this problem, which was already used in [17] for straight k-mers with considerable success, in the sense that it has lead, in that athermal problem, to smaller matrices, and therefore made it possible to solve that problem for larger widths than the ones accessible with the conventional procedure. In this grand canonical transfer matrix procedure, at each application of the transfer matrix, a variable number of trimers is added to the system. We are presently working on this problem.

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Declarations

Conflict of Interest The authors declare no competing interests.

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