DIMERS ON SQUARE LATTICES: ORIENTATION DEPENDENT ACTIVITIES

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Past studies of a mixture of non-overlapping rigid polymers distributed on square lattices were limited to polymers having the same activity regardless of orientation. Here, we address the problem of a single species, dimers, possessing different activities depending on their orientation, in the absence of both dimer–dimer and dimer–lattice interaction energies. The lattices considered consist of two, three, four and five infinite strips of equally spaced lattice sites ($M=2, 3, 4,$ and $5$). We propose an improved approximation technique for the study of the statistics of this system of dimers distributed on the infinite two-dimensional lattice ($M=\infty$).

The idea of studying the statistics of dimers distributed on square lattices composed of a finite number, $M$, of infinite strips of equally spaced lattice sites is well known [1]. Various techniques have been developed to study the distribution of fully covered [2] (close packed) lattices, as well as partially covered lattices [3] (refs. [2] and [3] represent a partial list of works done on dimers). In these studies, it is widely assumed that dimers have the same activities irrespective of their orientation. It is in the presence of an external field that orientation plays an important role. A first step in investigating dimer–lattice interactions is to obtain the statistics of oriented, non-overlapping, dimers. In this article, we report the exact solution for dimers having distinct activities, $H$ and $V$, depending on the two possible orientations "horizontal" and "vertical". In our calculations, the horizontal direction is along the finite dimension, $M$, with $M=2, 3, 4,$ and $5$. For simplicity, we do not distinguish between "right" and "left", and, "up" and "down" orientations.

The general method and the notation used in this paper are those found in ref. [4]. There, we studied the statistics of non-overlapping rigid polymers of different lengths and different absolute activities, where no distinction was made as to orientation. The exact closed form solution for the one-dimensional problem (one strip, $M=1$) was shown to form the basis of approximate solutions for several strips ($M=2, 3,$ etc.) in terms of the molecular freedom per site at close packing. However, when orientation is considered, the one-dimensional solution cannot be used, since dimers, and polymers in general, are all “vertical”. We propose a new approximation method to deal with this problem. As we equate the two activities $H$ and $V$, this approximation gives better results than the one reported previously.

The general technique of obtaining exact solutions for problems involving polymers on square lattices has been summarized in ref. [4]. The partition function per site is given by the largest $z$-root of a polynomial $P_M(x; z)$ in the form

$$Z_M(x) = [R_M(x)]^{1/M},$$

where $M$ refers to the “horizontal” size of the lattice, $x$ stands for the activities of the various polymers, and $R_M(x)$ is the largest $z$-root of $P_M(x; z)$. Here, we consider only dimers, and the set of activities, $x$, stands for $V$ and $H$, the activities of “vertical” and “horizontal” dimers, respectively. The method of generating polynomial $P_M(x; z)$ can be found in ref [3]. As the size $M$ of the lattice increases, the order and the size of the polynomials increase rapidly; we list the results for $M=2, 3, $ and $4$:
\[ P_2(V, H; z) = z^3 - (1 + H + V) z^2 + V(H - V - 1) z + V^3. \]  

\[ P_3(V, H; z) = z^6 - (V + 2H + 1) z^5 - V(3V^2 + 5V + 2H^2 + 2H + 2) z^4 + (2V^2 - V - 1) V^2 z^3 \]
\[ + (3V^2 + 5V + 2H^2 - 2H + 2) V^4 z^2 - (V + 1 - 2H) V^6 z - V^9. \]  

\[ P_4(V, H; z) = z^9 - [V^2 + (H + 2) V + H^2 + 3H + 1] z^8 \]
\[- [4V^3 + (10 - H) V^2 + 3H^2 + 6H + 8] V - H^3 - 5H^2 + 5H + 2] V^7 z^7 \]
\[ + [6V^4 - (3H - 22) V^3 + (7H^2 + 5H + 29) V^2 - (3H^3 - 10H^2 - 6H - 16) V \]
\[ + 2H^4 + 3H^3 + 6H^2 + 2H + 3] V^5 z^5 \]
\[- [6V^4 + (3H + 22) V^3 + (7H^2 - 5H + 29) V^2 + (3H^3 + 10H^2 - 6H + 16) V \]
\[ + 2H^4 - 3H^3 + 6H^2 - 2H + 3] V^4 z^4 \]
\[- [4V^4 + (14 - 3H) V^3 + (5H^2 - 4H + 6) V^2 - (2H^3 - 9H^2 - H + 2) V + H^4 - H^2 + 2H - 1] V^3 z^3 \]
\[ + [4V^3 + (H + 10) V^2 + (3H^2 - 6H + 8) V + H^3 + 5H^2 - 5H + 2] V^2 z^2 \]
\[ + [V^2 - (H - 2) V + H^2 - 3H + 1] V z - V^2. \]

The largest \( z \)-root can be obtained analytically in closed form for the case \( M = 2 \). In all other cases, the roots are computed numerically. The partition function follows from eq. (1), which, in turn, gives the exact solution to the problem for the corresponding value of the lattice size, \( M \).

The case of physical interest is the infinite two-dimensional problem, or \( M = \infty \). A measure of the difference between the statistics of the infinite two-dimensional case and the statistics for \( M = 2, 3, 4, \) and \( 5 \), is obtained by comparing the close packing situations for infinite and finite \( M \)-values. The appropriate thermodynamic variable which makes this comparison possible is the entropy per site divided by Boltzmann's constant

\[ S_M = \ln(Z_M) - \frac{1}{2} \theta_H \ln(H) - \frac{1}{2} \theta_V \ln(V). \]

In this equation, \( \theta_H \) and \( \theta_V \) are the fractions of lattice sites occupied by horizontal and vertical dimers. The molecular freedom per site at close packing is defined as

\[ \Phi_M = \lim_{V, H \to \infty} \exp(s_M). \]

In computing this quantity it is convenient to hold the ratio, \( \alpha = V/H \), constant. We have shown in earlier work [3,4] how this could be done from the knowledge of the polynomial \( P_M \). However, for the case of dimers distributed on square lattices, Kasteleyn [2] has derived a closed form equation for the molecular freedom at close packing for any size \( M \). From his calculations, if one sets \( V = \alpha H \), it is easy to show that the fraction of lattice sites occupied by vertical dimers at close packing, \( \theta_V \), is

\[ \{\theta_V\}_{CP} = 2\delta + \left( 1/M \right) \left( M - 2[M/2] \right), \]

where \( [M/2] \) means the integer part of \( M/2 \) and \( \delta \) is given by

\[ \delta = \frac{1}{M} \sum_{i=1}^{\lfloor M/2 \rfloor} \left( 1 - \frac{\cos\left( \pi i/M + 1 \right)}{\left[ \alpha^2 + \cos^2\left( \pi i/M + 1 \right) \right]^{1/2}} \right). \]

It then follows that the molecular freedom at close packing for the lattice of finite size, \( M \), is given in terms of \( \alpha \) as

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\[ \Phi_M(\alpha) = \alpha^{-\delta} \prod_{l=0}^{\lfloor M/2 \rfloor} \left\{ \left[ \alpha^2 + \cos^2 \left( \ln M + l \right) \right]^{1/2} + \cos \left( \ln M + l \right) \right\}^{1/M}. \]  

(9)

Since at close packing the lattice is fully covered with dimers, the fraction of lattice sites occupied by horizontal dimers is \( \theta_H^{\text{CP}} = 1 - \theta_V^{\text{CP}}. \) In the limit as \( M \) becomes infinite, one has

\[ \Phi_\infty(\alpha) = \alpha^{-\left(1/\pi\right) \text{arctan}(\alpha)} \exp \left( \frac{1}{\pi} \int_0^{\alpha} \frac{\text{arctan}(y)}{y} \, dy \right). \]  

(10)

A measure of how accurate the results would be, if the thermodynamics of the system of dimers on the infinite two-dimensional lattice is approximated by that of dimers distributed on the lattice of finite size \( M \), can be achieved by comparing the results obtained from eqs. (9) and (10). We have actually carried out exact calculations up to and including lattices of size \( M = 5 \), but reported the polynomials necessary to do these calculations up to \( M = 4 \), due to space considerations.

The behavior of the root \( R_M \) was shown to increase exponentially with the size, \( M \), of the lattice only when all the polymers are aligned [3,4]. In other cases, slight deviations from the exact exponential behavior have been observed. Based on these observations, it is possible to obtain a good approximation for the partition function, \( Z_M \), of a system of dimers distributed on the lattice of size \( M \), if the partition function, \( Z_N \), of dimers distributed on the lattice of size \( N < M \) is known. Let us consider the quantity

\[ A_{M,N}^{(H,\alpha)} = Z_N \left[ \left( \Phi_M/\Phi_N \right)^2 H, \alpha \right], \quad N < M, \]  

(11)

where it is understood that in the expression of the known partition function, \( Z_N \), which depends on activities \( V \) and \( H \), \( V \) has been replaced first by \( \alpha H \), then, in the resulting expression which now depends on \( H \) and \( \alpha \), \( H \) is replaced by \( \left( \Phi_M/\Phi_N \right)^2 H \). Let us treat the quantity \( A_{M,N}^{(H,\alpha)} \) as if it were a partition function. An entropy function, \( S_{M,N}^{(H)} \), can then be computed having the form:

\[ S_{M,N}^{(H)} = s_N + \theta \ln \left[ \Phi_M(\alpha)/\Phi_N(\alpha) \right], \quad N < M. \]  

(12)

Here \( s_N \) is the exact entropy function of the system of dimers distributed on the lattice of size \( N \), and \( \theta = \theta_H + \theta_V \) is the fraction of lattice sites occupied by both horizontal and vertical dimers as computed from the "pseudo" partition function \( A_{M,N}^{(H,\alpha)} \). Let us exponentiate both sides of eq. (12), and take the limit of close packing (i.e., \( \theta = 1 \)) using eq. (6). It follows

\[ \lim_{\theta \to 1} \ln S_{M,N}^{(H)} = \Phi_M(\alpha). \]  

(13)

Clearly, the "pseudo" partition function given by eq. (11) produces the exact molecular freedom per site at close packing for the lattice of size \( M \). On the other hand, as \( \theta \) approaches zero (loose packing), the "pseudo" entropy function approaches zero. Therefore, one would expect that the "pseudo" partition function is a good approximation of the exact partition function of the system of dimers distributed on the lattice of size \( M \), under the conditions of loose packing and near close packing. In ref. [3], we considered dimers having all the same activity, \( \alpha = x \) (i.e., \( \alpha = 1 \)). We observed that \( A_{M,1}^{(H)}(x, 1) \) gave a very good fit for the thermodynamic quantities with \( M = 2, 3 \) and 4 over the entire range of lattice site occupation. \( A_{M,1}^{(H)}(x, 1) \) is explicitly given by

\[ A_{M,1}^{(H)}(x, 1) = \frac{1}{4} \left[ 1 + \sqrt{1 + 4\Phi_M(1)^2 x} \right]. \]  

(14)

This approximation improved as the size \( M \) of the lattice increased from 2 to 4. This led us to incorrectly conjecture that it became exact at \( M = \infty \). Wheeler [5] showed that the series expansion for the entropy ob-

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*Polynomials are available from the authors upon request.*

*In eq. (14) \( \Phi_M \) refers to the molecular freedom per site not per dimer.*
tained by using eq. (14) at $M=\infty$ does not agree with the exact expansion obtained by virial and lattice counting methods. A close inspection of eq. (11) where $M$ is set to be infinite clearly indicates that $A_{\infty}^{(N)}$ is $N$-dependent, which precludes that $A_{\infty}^{(1)}$ is exact. It would be appropriate to refer to $A_{\infty}^{(1)}$ as a “first approximation” and to $A_{\infty}^{(N)}$ as the “$N$th approximation” of the partition function of a system of dimers distributed on the infinite two-dimensional lattice. The same could be said about $S_{\infty}^{(N)}$ and its relationship to the entropy per site. Expression (14) is valid for $V=H=x$, or $\alpha=1$. We propose to extend its domain to include other values of $\alpha$. We accomplish this by introducing an effective activity per dimer when the vertical activity is $V$, and the horizontal activity is $H$, corresponding to lattice site occupations $\theta_H$ and $\theta_V$, respectively. We call such an activity $x$ and write it as

$$x = V^{\theta_V} H^{\theta_H} = \alpha^{\theta_V} H .$$

The exact partition function for dimers on the one-dimensional lattice was found to be [3]:

$$Z_1 = \frac{1}{2} (1 + \sqrt{1 + 4x}) .$$

One way of extending the domain of $Z_1$ would be to replace $x$ in eq. (16) by the right hand side of eq. (15). This, of course, is purely artificial in that the one-dimensional lattice cannot have horizontal dimers. In the resulting expression, one chooses to replace $\theta_H/\theta_V$ by $(2/\pi) \arctan(\alpha)$ which is the value of $\theta_H$ on the infinite two-dimensional lattice. As done in eq. (11), we then replace $H$ by $(\Phi_x/\Phi_y)^2 H$ where the molecular freedom on the one-dimensional lattice $\Phi_y$ is unity. This final expression is what we call the “first approximation” to the partition function for dimers distributed on the infinite two-dimensional lattice. Using eq. (10), it follows that:

$$A_{\infty}^{(1)}(H, \alpha) = \frac{1}{2} \left\{ 1 + 1 + 4H \exp \left( \frac{2}{\pi} \int_{0}^{\alpha} \frac{\arctan(y)}{y} dy \right) \right\}^{1/2} .$$

For convenience, let $X(H, \alpha)$ be the coefficient of 4 appearing under the square root sign in eq. (17). The first approximation for the lattice site occupations by horizontal and vertical dimers for a given set of values $H$ and $\alpha$ are

$$\theta_H = \{ 1 + 4X(H, \alpha) \}^{-1/2} \{ 1 - (2/\pi) \arctan(\alpha) \} ,$$

$$\theta_V = \{ 1 + 4X(H, \alpha) \}^{-1/2} (2/\pi) \arctan(\alpha) .$$

By adding the above two expressions one obtains the total lattice site occupation $\theta$. Similar, closed form analytic expressions are easily derived for the second approximation using the corresponding polynomial given by eq. (2). However, no closed form expressions could be calculated for the higher approximations, since it is not possible to obtain closed form expressions for the roots of the higher order polynomials involved, and solutions have to be calculated numerically. We give a selection of numerical results in table 1. Three sets of data are presented corresponding to the values of $\alpha=0.1$, 0.5, and 2.5, respectively. The two expressions computed are the total lattice site occupation, $\theta$, and the entropy per site, $S_{\infty}^{(N)}$, up to and including the fifth approximation ($N=1, 2, 3, 4,$ and 5). The values of $H$ listed are 0.2, 1, 4, and $\infty$. At $H=\infty$, all approximations give the same results and match the exact values, as shown in eq. (13). As noticed in earlier works, oscillations do occur with the order $N$ of the approximation, which is the size of the lattice used to develop the approximation. The data falls into two categories: the even and odd approximations. If one extrapolates the data to higher approximations on a graph where the numerical results, for a given set of values of $H$ and $\alpha$, are plotted against the reciprocal of the order of the approximation, $1/N$, one finds an estimate of what the exact values should be. This estimate is within 10% of what the first approximation gives. It is for this reason that we presented the closed form expressions (17), (18) and (19).

An illustration of the extrapolation mentioned above is the graph of $S_{\infty}^{(N)}$ versus $1/N$ for $H=1$ and $\alpha=1$. For this set of values of the vertical and horizontal activities, the entropy is maximum. This graph is given in
Table 1
The fraction of lattice sites occupied by dimers, $\theta$, and the corresponding approximate entropy per site (divided by Boltzmann’s constant) are presented using approximations $N=1$ to 5, for a given set of values of $\alpha$ and $H$: $\alpha=0.1, 0.5, $ and $2.5; H=0.2, 1, 4$ and $\infty$. These data are representative of the accuracy of the approximations as the horizontal and vertical activities are varied.

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<th>$H$</th>
<th>$\theta$ (%)</th>
<th>$S_{\infty}^{(N)}$</th>
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<tbody>
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<td>$N=1$</td>
<td>$N=2$</td>
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<td>$\alpha=0.1$</td>
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Fig. 1. Graph of the $N$th approximation of the entropy per site, $S_{\infty}^{(N)}$, plotted against the reciprocal $1/N$ of the order of the approximation, when both horizontal and vertical activities of dimers are equal.
fig. 1. The data is shown to fall on two separate curves we refer to as “odd series” and “even series”. The value of the maximum entropy per site as estimated from the extrapolation of these two curves is below the estimates obtained by both Gaunt (point G on fig. 1) and Phares, Shaw and Wunderlich (point PSW on fig. 1) [3]. The point corresponding to \( N = 6 \) was obtained by solving exactly the problem of dimers having all the same activity and distributed on a lattice with 6 infinite strips, since the 6th approximation requires the knowledge of the exact solution for the associated lattice.

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