Thermodynamics of dimers on a rectangular $L \times M \times N$ lattice

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The exact closed-form analytic solution of the problem of dimers on infinite two-dimensional and three-dimensional lattices is obtained. Entropy, isothermal compressibility, and constant pressure heat capacity of the system are given in terms of the normalized number density of dimers. The absolute activity of dimers is also given in terms of the normalized number density; it exhibits a behavior near close packing with a critical exponent exactly equal to 2, and with an amplitude $1/(4\phi)$, where $\phi$ is the molecular freedom per dimer at close packing.

I. INTRODUCTION

Two previous articles,\(^1\) referred to as papers I and II, were devoted to the study of dimers on two-dimensional lattices irrespective of their orientation. Paper I presented a new general mathematical technique for dealing with such problems. The technique was based on the work of McQuistan et al.\(^2\) Essentially, recurrence relations were developed which needed decoupling. The systematic decoupling of these linear relations involving constant coefficients was achieved by one of us.\(^3\) Paper I also made the connection between the partition function of dimers with absolute activity $x$ and the largest root of a polynomial $P(x,z)$. This polynomial depends on the size of the lattice $L \times M \times N$ where $L$ and $M$ are fixed and $N$ is allowed to become infinite. However, the calculations performed in paper I were limited to the value $x = 1$. Paper II is an extension of paper I; results were obtained for values of the activity in the range $0-10$ for the partition function, the grand potential, the number density, the entropy, the isothermal compressibility, and the constant pressure specific-heat capacity. An approximate expression was derived for the partition function in terms of the absolute activity for dimers on a square lattice, based on the assumption that the $x$ roots of the polynomial $P(x,z)$ increase exponentially with the number $M$ of compartments in any given row of the $1 \times M \times N$ lattice. No mathematical proof of this fact was supplied beyond the simple observation that this is true with a rather good approximation in the range $M = 1-4$. Results derived numerically by Gaunt\(^4\) for the locations of the maxima of entropy, isothermal compressibility, and constant pressure specific-heat capacity were recovered using the approximate expression.

This article has several objectives.

(1) We obtain the thermodynamic properties of aligned dimers on finite and infinite two- and three-dimensional lattices, explicitly in terms of the absolute activity and the normalized number density. For aligned dimers, the largest $x$ root of polynomials $P(x,z)$ is shown to exhibit the exponential behavior with the size $M$ of the lattice. Therefore, this paper gives the first rigorous mathematical justification for the calculations performed in papers I and II.

(2) Following an approach completely different from Kasteleyn's,\(^5\) we calculate the molecular freedom per dimer at close packing $\Phi$ for planar $L \times M \times N$ lattices $(N \to \infty)$, and we recover Kasteleyn's results for $M = 1, 2, 3, \text{and} 4$. However, Kasteleyn's formula is much more general since it allows one to obtain $\Phi$ for any value of $M$ and it predicts its exact value when both $M$ and $N$ are infinite. The advantage of our technique is that it can be extended to three-dimensional lattices $L \times M \times N \ (N \to \infty)$. As a special case, we calculate the exact value of $\Phi$ for the $2 \times 2 \times N$ lattice, a problem investigated by Hock and McQuistan.\(^6\)

(3) We show that it is possible to obtain an analytical fit to all the thermodynamical quantities for dimers on various square lattices we have calculated in paper II. This is achieved by using the exact analytic results for aligned dimers, where the molecular freedom per dimer at close packing $\Phi$ (which is 1 for aligned dimers) is replaced by the value calculated exactly by Kasteleyn,\(^5\) and a parameter $Q$ (which is 2 for aligned dimers) by 4. Agreement with the numerical values of paper II is astonishingly good.

(4) The success of analytical fit for various finite two-dimensional square lattices is extended to obtain exact analytical results for the infinite two- and three-dimensional lattices based on the knowledge of the molecular freedom per dimer at close packing. In support of the approximate analytical fit for finite three-dimensional lattices, we calculate the thermodynamical properties of dimers on a $2 \times 2 \times N$ lattice, a problem investigated recently by Hock and McQuistan.\(^6\)

The general outline of this article is as follows: Section II develops the solution of dimers of an $L \times M \times N$ lattice parallel to the $M$ axis; dimensions $L$ and $M$ are fixed while $N$ is allowed to become infinitely large. We think of the $(L,M)$ plane as "horizontal," and we refer to this case as the case of horizontal dimers. Here, there is perfect symmetry between dimers parallel to the $L$ axis and dimers parallel to the $M$ axis. The case of dimers parallel to the $N$ axis (or "vertical" dimers) is distinct from the case of horizontal dimers, since the dimers are parallel to the $N$ dimension which is allowed to become infinitely large. For this reason we discuss in a separate section, Sec. III, the case of vertical dimers, or dimers parallel to the $N$ axis. The purpose of Sec. III is to confirm the internal consistency of our method. Indeed, although the point of view is different, the results for vertical dimers should be the same as those for horizontal dimers, when both $N$ and $M$ are allowed to become infinite. In both cases, one discovers the exponential behavior of the largest root mentioned above. In Sec. IV, we derive the values of the thermodynamical quantities explicitly in terms of the normalized number density; we also give their graphical representations and make the comparison with those obtained in...
papers I and II for dimers irrespective of their orientation. Another achievement of this section is to obtain the closed-form analytic expression of the absolute activity in terms of the normalized number density, showing the behavior near close packing with a critical exponent exactly equal to two as conjectured by Gaunt. Section V develops a method for calculating the molecular freedom per dimer at close packing based on the knowledge of polynomial $P(x, z)$. The method is applied for dimers on lattices $1 \times 1 \times N, 1 \times 2 \times N, 1 \times 3 \times N, 1 \times 4 \times N$, and $2 \times 2 \times N$. Section VI discusses the analytical fit of the data available for dimers on a two-dimensional lattice and extends the analysis to the three-dimensional case. Finally, Sec. VII is the conclusion.

II. HORIZONTAL DIMERS

The method of McQuistan et al. as generalized in paper I calls for generating truncated lattices from the original one. Consider an $L \times M \times N$ lattice space. The horizontal dimers are assumed to be aligned and parallel to the $M$ axis. We view our lattice space as being made of $N$ arrays, each containing $L \times M$ cells. We now focus on the $N$ th array. Since all possible dimers occupying the lattice are parallel to the $M$ axis, dimers whose one end is in the $N$ th array will therefore have their other end within the same array. Using the notation of paper I, this means that one can only generate lattices of the A type (nontuncated).

The next step is to consider filling the $L \times M \times N$ lattice with $q$ dimers parallel to the $M$ axis, where $L$ and $M$ are fixed and $N$ is allowed to become infinitely large. Let $A(q - p; L, M, N - 1)$ be the total number of possible arrangements of $(q - p)$ dimers on the $L \times M \times (N - 1)$ lattice when the $N$ th array is occupied by $p$ dimers. Also, let $C(p; L, M)$ be the total number of possible arrangements of $p$ dimers on the $N$ th array containing $L \times M$ cells. It is obvious that the total number of distinct arrangements of $q$ dimers on the whole lattice when $p$ of these dimers are located in the $N$ th array is given by the product

$$C(p; L, M) \mid A(q - p; L, M, N - 1).$$

It is also obvious that the total number of arrangements of the $q$ dimers of the $L \times M \times N$ lattice is the sum of all possible arrangements when the $N$ th array is empty ($p = 0$), occupied by only one dimer ($p = 1$), by two dimers ($p = 2$), etc., until it is fully occupied ($p = p_{\text{max}}$). In other words, one has

$$A(q; L, M, N) = \sum_{p = 0}^{p_{\text{max}}} C(p; L, M) \mid A(q - p; L, M, N - 1).$$

(1)

Upon introducing the bivariate generating function

$$G(x, y) = \sum_{N = 0}^{\infty} \sum_{q = 0}^{\infty} x^q y^N A(q, L, M, N),$$

(2)

and using it in Eq. (1), one obtains

$$G(x, y) = 1 + \sum_{p = 0}^{p_{\text{max}}} x^p y C(p; L, M) G(x, y).$$

(3)

This, in turn, gives the closed-form expression of the bivariate function, as the inverse of a polynomial $D(x, y)$ which is of first order in the variable $y$. Following the method of paper I, one sets $y = 1/z$ and searches for the largest $z$ root of the polynomial

$$P(x, z) = D(x, 1/z),$$

(4)

which, in this case, has only one root, namely,

$$R_s(x; L, M) = \sum_{p = 0}^{p_{\text{max}}} x^p C(p; L, M).$$

(5)

One next step is to calculate the closed-form expression of the root $R_s(x; L, M)$. This we will achieve by recognizing that $C(p; L, M)$ is the total number of arrangements of fitting $p$ dimers parallel to the $M$ axis on the two-dimensional $L \times M$ lattice. The same approach is to be used over again. We think of this lattice as being made of $L$ rows, each row made up of $M$ cells. We single out the $L$ th row. Let $r$ be the number of aligned dimers filling the $L$ th row, thus allowing $(p - r)$ dimers to fill the remaining $(L - 1)$ rows. Then

$$C(p - r; L - 1, M)$$

is the total number of distinct arrangements of $(p - r)$ dimers parallel to the $M$ axis in the $(L - 1)$ rows of cells. Let $F(r; M)$ be the number of arrangements of $r$ dimers in the $L$ th row containing $M$ cells. As before, it then follows that

$$C(p; L, M) = \sum_{r = 0}^{r_{\text{max}}} F(r; M) C(p - r; L - 1, M).$$

(6)

Again, one introduces the bivariate generating function

$$G_r(x, y) = \sum_{L = 0}^{\infty} \sum_{r = 0}^{r_{\text{max}}} x^r y^L C(p; L, M).$$

(7)

Combining Eqs. (6) and (7), and using again the technique outlined in paper I, one is able to show that

$$\sum_{r = 0}^{r_{\text{max}}} x^r \left( \sum_{L = 0}^{L_{\text{max}}} F(r; M) \right) = \left( \sum_{r = 0}^{r_{\text{max}}} x^r F(r; M) \right)^L.$$

(8)

We have now reached the last step in our derivation, which is finding the expression of the right-hand side of the above equation. This is the problem of dimers in one-dimensional space, solved already by McQuistan et al. and derived differently in paper I. It is straightforward to show that

$$R_s(x; M) = \sum_{r = 0}^{r_{\text{max}}} x^r F(r; M)$$

$$= (z^M - 1 - z^M + 1)(z_1 - z_2).$$

(9)

In Eq. (9), $z_1$ and $z_2$ are the roots of the quadratic equation

$$z^2 = z = 0,$$

(10)

namely,

$$z_1 = \frac{1}{2} [1 + (1 + 4x)^{1/2}], \quad z_2 = \frac{1}{2} [1 - (1 + 4x)^{1/2}].$$

(11)

Finally, the root to be used for calculating all the thermodynamical quantities is

$$R_s(x; M) = \{R_s(x; M)^L \}^{L_{\text{max}}}$$

$$= (z_1^{M} - z_2^{M} + 1)(z_1 - z_2)^L.$$  

(12)

As anticipated in the Introduction, Eq. (12) exhibits an exact exponential behavior in $L$ and an almost exact exponential behavior in $M$, this behavior in $M$ becoming more and more accurate as $M$ becomes larger and larger. This follows from the fact that the positive root $z_1$ is, in absolute value, larger than the negative root $z_2$; thus, given the approximation for large values of $M$

$$R_s(x; L, M) = (z_1(x))^{L_{\text{max}}}.$$
We leave to Sec. IV the derivation of the thermodynamical quantities explicitly in terms of the normalized number density, including their graphical representations.

III. VERTICAL DIMERS

We now consider the case of dimers parallel to the $N$ axis. For simplicity, we will assume that $L = 1$. The analysis that follows can be easily extended to any value of $L$. However, since the purpose of this section is to exhibit the internal consistency of our method, there is very little to be gained by doing our discussion for any value of $L$. The case $M = 1$ is the one-dimensional problem whose solution is already known (e.g., paper I). We will study the cases $M = 2$ and 3, with the constraint that the dimers are parallel to the $N$ axis.

There is no point in repeating the lengthy proofs similar to those presented in paper I. The interested reader could get the computational details directly from the authors. We will simply state that the bivariant generating function associated with the number of distinct arrangements, $A(q; L = 1, M = 2, N)$, of $q$ dimers on the $1 \times 2 \times N$ lattice, is calculated to be

$$G(x, y) = (1 - xy)/D(x, y),$$  

where $D(x, y)$ is a polynomial in $x$ and $y$. Replacing $y$ by $1/z$, one looks for the $z$ root of

$$D(x, 1/z) = y^3[(1 + 1)z^2 - x(1 + 1)z + x^2].$$  

The $z$ roots of this cubic polynomial are easily found to be

$$(z_1)^3, \quad (z_2)^3, \quad \text{and} \quad -x,$$  

where $z_1$ and $z_2$ are the values listed in Eq. (11). The first root listed above is the largest root.

In the case $M = 3$, the bivariant generating function associated with the number of arrangements $A(q; L = 1, M = 3, N)$ of $q$ dimers parallel to the $N$ axis on a $1 \times 3 \times N$ lattice is

$$G(x, y) = (1 - x^3y^3)(1 - xy - x^3y^3)/D(x, y).$$  

Here $D(x, 1/z)$ is a sixth-order polynomial in $z$, namely,

$$D(x, 1/z) = y^6[x^3z^6 - (x + 1)z^2 - x(2 + 5x + 3x^2)z^4 - x^3(1 + x - 2x^2)z^4 + x^6(2 + 5x + 3x^2)z^4 - x^5(1 + 1)z - x^6].$$  

This polynomial has four real roots and two complex roots. The root of largest modulus is real and positive. We were able to obtain analytically the value of this root as well as another real root by making possible the following factorization:

$$D(x, 1/z) = y^3[z - x^3][z + x^3][z^4 - 2x^2z - x(2x - 1)z^2 - 2xz^2 + x^4].$$  

The largest root is $z_1$ raised to the third power. There is no need of repeating the calculations for higher values of $M$. The pattern is very clear, the largest $z$ root of the polynomial $D(x, 1/z)$ is $(z_1)$ raised to the $M$ th power. Thus, in the case of vertical dimers, the exponential behavior of the largest root is an exact behavior. Without denying the intrinsic value of the mathematical proof, it is worth recognizing that this exponential behavior for vertical dimers can be predicted on physical grounds. Indeed, consider the grand canonical partition function of dimers on a $1 \times M \times N$ square lattice with the restriction that all dimers are parallel to the $N$ axis. Think of this lattice as made of $M$ rows, each row containing $N$ cells. Fitting dimers in any of the $M$ rows should not affect the arrangements of the dimers on the other rows. In other words, we are dealing with independent probabilities. Therefore, the grand canonical partition function for large values of $N$ should be the partition function for one row made of an infinite number of cells multiplied by itself $M$ times, or,

$$\Delta_M(x) = (\Delta_1(x))^M.$$  

We have already shown in paper I that the partition function for dimers of absolute activity $x$ in one dimension is $z(x)$. The exponential behavior of the $z$ root follows. From this analysis, supported by the mathematical checking, it becomes clear that the thermodynamical properties of vertical dimers are the same as the thermodynamical properties of dimers in one dimension.

IV. THERMODYNAMICAL QUANTITIES

This section gives the values of the thermodynamical quantities of horizontal dimers and vertical dimers in the limit as $N$ becomes infinitely large, while both $L$ and $M$ are fixed. We call $Z(x)$, $\Gamma(x)$, $\rho(x)$, and $\rho_0$ the partition function, the grand potential, the number density, and the close-packing density, respectively. If one site on the lattice is occupied by one end of a dimer, let $Q$ be the number of neighboring sites that the other end of the dimer can occupy. In the case of aligned dimers, the value of $Q$ would be 2. The general expressions of the thermodynamical quantities can all be calculated from the knowledge of the partition function (see, for example, Ref. 4); namely, one has

$$\Gamma(x) = (2/Q) \ln Z,$$  

$$\rho(x) = x\frac{d\Gamma}{dx}.$$  

In the limit of an infinitely large lattice, the number density at close packing is given in terms of $Q$ as

$$\rho_0 = (1/Q).$$  

The isothermal compressibility $K_T(x)$, the entropy per unit volume $S_T(x)$, and the constant-pressure specific-heat capacity per unit volume $C_v(x)$ will automatically follow:

$$K(x) = x\frac{d\rho}{dx} = k_B T \frac{d^2}{dx^2} K_T(x),$$  

$$S(x) = -\rho \ln(x) + \Gamma = S_T/k_B,$$  

$$C(x) = K(\Gamma/\rho)^2 = C_v/k_B.$$  

In the above equations, $k_B$ is Boltzmann's constant, and $T$ is the absolute temperature.

We now list the results for horizontal dimers on the $L \times M \times N$ lattice, where $N$ is infinitely large, $L$ can take on any positive value, and $M$ is restricted to be larger than 1 to allow dimers parallel to the $M$ axis to fit on the lattice. Following paper I, the partition function is the largest (and in this case the only) root computed is Sec. II raised to the power $(1/LM)$. This root is given by Eq. (12). It then follows that the partition function for horizontal dimers is given ex-
plicitly in terms of \( z_1(x) \) and \( z_2(x) \), Eq. (11), which are the roots of the quadratic equation, Eq. (10), namely,

\[
Z(x) = \left( \frac{z_1^{M+1} - z_2^{M+1}}{z_1 - z_2} \right)^{1/M}.
\]

There is nothing to be gained in writing down the expressions of the various thermodynamic quantities explicitly in terms of \( x \). However, we intend to discuss to some extent the close-packing situation. For this purpose we give the expression of the number density

\[
\rho_H(x) = \frac{(M + 1)x(z_1^M + z_2^M)}{M(1 + 4x)^{1/2}(z_1^M + z_2^M + 1)} - \frac{2x}{M(1 + 4x)}.
\]

(28)

Index \( H \) refers to the number density for horizontal dimers. However, the number density at close packing is not exactly \( 1/Q = 1 \); it really depends on whether \( M \) is even or odd. Indeed when \( M \) is even, any row with \( M \) cells and all of dimers contains exactly \( (M/2) \) dimers. But, if \( M \) is odd, any row reaching close packing would have one cell unoccupied; in this case the total number of dimers is \((M - 1)/2\); consequently,

\[
\rho_0 = \frac{1}{2}, \quad \text{for } M \text{ even},
\]

\[
\rho_0 = \frac{1}{2}(1 - 1/M), \quad \text{for } M \text{ odd}.
\]

(29)

For vertical dimers on an \( L \times M \times N \) lattice (dimers parallel to the \( N \) axis), we discovered that all the thermodynamical quantities are the same as those of dimers in one dimension. These quantities are calculated from \( z_1(x) \). The partition function \( Z(x) \) turns out to be precisely \( z_1(x) \) (see paper I). Using Eq. (11), we obtain the number density

\[
\rho(x) = \frac{2}{Q}(1 - 1/\sqrt{1 + 4x}).
\]

(30)

For the case of vertical dimers \( Q = (1/\rho_0) = 2 \). Let \( \theta \) be the normalized number density \( \rho/\rho_0 \). It is then possible to use Eq. (31) to express \( x \) explicitly in terms of \( \theta \), and one finds

\[
x = \theta(2 - \theta)/4(1 - \theta)^2.
\]

(31)

All thermodynamical quantities may now be calculated directly in terms of \( \theta \). The results are

\[
\Gamma(\theta) = \frac{2}{Q}\ln(2/\theta), \quad S(\theta) = -\theta \ln(2 - \theta)/(2 - 2\theta), \quad K(\theta) = \theta(2 - \theta)/(2 - 2\theta), \quad C(\theta) = \frac{2}{Q}\ln(2 - \theta)/(2 - 2\theta).
\]

(32-35)

By setting \( x = 1 \) in Eq. (31) one obtains the value of \( \theta \) that maximizes the entropy, namely,

\[
\theta_m = 1 - \frac{1}{\sqrt{5}} \quad \text{and} \quad S_{\text{max}} = \frac{2}{Q}\ln\left(\frac{1 + \sqrt{5}}{2}\right).
\]

(36)

The quantity \( K(\theta) \) related to the isothermal compressibility maximizes for \( \theta = 1 - 1/\sqrt{5} \) and its value is

\[
K_{\text{max}} = 1/3Q\sqrt{3}.
\]

(37)

Finally, the specific-heat capacity maximizes for the solution of the transcendental equation

\[
\ln\left[\frac{2 - \theta}{2(1 - \theta)}\right] = 2\theta/(2 - \theta),
\]

(38a)

which is found to be

\[
\theta = 0.844\ 518\ 622.
\]

(38b)

From the knowledge of the entropy, one can also calculate the molecular freedom per dimer at close packing.

\[
\phi = \exp(QS(\theta = 1)) = 1.
\]

(39)

In Fig. 1, we plotted entropy curves for a system of dimers on an \( L \times M \times N \) lattice parallel to the \( \theta \) axis, with \( N \) allowed to become infinitely large. These curves are labeled by the corresponding value of \( M \) and are, as predicted analytically, independent of the value of \( L \) (the number of \( M \times N \) layers). Figures 2 and 3 give \( K \) and \( C \) for the same system. These plots are in terms of the normalized number density \( \theta \).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1}
\caption{Plot of \( S \) vs \( \theta \) for horizontal dimers. Here \( S = (S_r/k_B) \), where \( S_r \) is the entropy per unit volume and \( k_B \) is Boltzmann's constant. \( \theta \) is the normalized number density. The limiting curve labeled \( M = \infty \) is the same for both vertical dimers on a finite lattice and horizontal dimers on the infinite lattice.}
\end{figure}
One finds that these curves can be divided into two sets of curves, corresponding to even and odd values of $M$, respectively. In the limit as $M$ becomes large, the limiting curve for "even" and "odd" series of curves is precisely the curve that one obtains for aligned dimers on the infinite lattice, which is also the curve calculated for the one-dimensional problem, as shown in Sec. III on vertical dimers. The limiting curve is represented by a continuous line.

We end this section with a discussion on close packing. We consider first the case of horizontal dimers. Near close-packing conditions we chose to look for the leading terms in the expression of the number density $\rho(x)$, given by Eq. (28). One finds that even and odd values of $M$ lead to slightly different results, namely,

$$x \sim A(M)/(1 - (\rho/\rho_0))^{\gamma},$$

where the critical exponent $\gamma$ is exactly 2 and the amplitude $A(M)$ depends on the parity of $M$

$$A(M) = (M+1)/2M,$$  \hspace{1cm} \text{for } M \text{ even},

$$A(M) = (M/2)(M-1),$$  \hspace{1cm} \text{for } M \text{ odd}.

These results are to be compared with Eq. (31) for vertical dimers. The critical exponent is again 2 and the amplitude agrees with the value for horizontal dimers only for large values of $M$, as one might expect. This critical behavior was anticipated a long time ago based on various numerical approximations (see, for example, Ref. 4). We now have an analytical expression predicting this behavior without rely-

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**FIG. 2.** Plot of $K$ vs $\theta$ for horizontal dimers. Here $K$ is $k_B T_0^2 K_T$, where $K_T$ is the isothermal compressibility per unit volume. $\theta$ is the normalized number density. The limiting curve labeled $M = \infty$ is the same for both vertical dimers on a finite lattice and for horizontal dimers on the infinite lattice.

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**FIG. 3.** Plot of $C = C_0/k_B$ vs $\theta$. Here $C_0$ is the constant pressure specific-heat capacity per unit volume. $\theta$ is the normalized number density of dimers. The limiting curve labeled $M = \infty$ is the same for both vertical dimers on a finite lattice and for horizontal dimers on the infinite lattice.
V. MOLECULAR FREEDOM PER DIMER AT CLOSE PACKING

In the previous section, the molecular freedom per aligned dimer at close packing was (not surprisingly) found to be 1. Here, we intend to show that the molecular freedom per dimer at close packing $\Phi$ can be calculated from the knowledge of polynomial $P(x,z)$. Let $z$ be the largest $r$ root of $P(x,z)$ for an $L \times M \times N$ lattice. The partition function in the large $N'$ limit is given by

$$Z(x) = (z(x))^{1/LM}.$$  \hspace{1cm} (42)

One combines this equation and Eqs. (21) and (25) to obtain

$$S(x) = -\rho \ln(x) + (2/Q) \ln(z(x))^{1/LM}.  \hspace{1cm} (43)$$

One multiplies Eq. (43) by $Q$, replaces $(Q\rho)$ by $\theta$, the normalized number density, and exponentiates both sides of the resulting equation:

$$\exp(QS(x)) = (z(x))^{1/LM}/x^\theta.  \hspace{1cm} (44)$$

In the close-packing limit, the absolute activity $x$ becomes increasingly large, while the normalized number density $\theta$ approaches unity. In this limit, the left-hand side of Eq. (44) is identified as the molecular freedom per dimer at close packing, namely,

$$\Phi = \lim_{x \to \infty} [(z(x))^{1/LM}/x]^{1/2}.  \hspace{1cm} (45)$$

In other words, the largest $r$ root $z(x)$ of polynomial $P(x,z)$ should behave at large values of $x$ like

$$z(x) = \sim (\Phi x)^{1/LM}.  \hspace{1cm} (46)$$

This observation allows one to calculate $\Phi$ in the following manner.

1. Set $z = \lambda x^{1/LM}$ in the expression of the polynomial $P(x,z)$.

2. Factor out $x^a$, where $a$ is the highest exponent of $x$ in the expression of $P(x,z)$, and obtain $V(\lambda, x)$ as

$$V(\lambda, x) = P(x, \lambda x^{1/LM}/x^a).  \hspace{1cm} (47)$$

(3) Take the limit of $V(\lambda, x)$ as $x$ approaches infinity, namely,

$$\lambda = \lim_{x \to \infty} V(\lambda, x).  \hspace{1cm} (48)$$

(4) Find the roots of $V(\lambda)$, i.e., solve

$$V(\lambda) = 0.  \hspace{1cm} (49)$$

(5) The largest root of $V(\lambda)$, say $\lambda_1$, gives the molecular freedom at close packing, namely,

$$\Phi = \lambda_1^{1/LM}.  \hspace{1cm} (50)$$

We use this procedure to calculate $\Phi$ for the lattices mentioned in the Introduction: $1 \times 1 \times N$, $1 \times 2 \times N$, $1 \times 3 \times N$, $1 \times 4 \times N$, and $2 \times 2 \times N$. The polynomials $P(x,z)$ for two-dimensional lattices are found in paper II (Table I). The polynomial $P(x,z)$ for the three-dimensional lattice $2 \times 2 \times N$ was derived in Refs. 2 and 3. Listed in Table I are the expressions for $V(\lambda)$ for various lattices and their associated roots. As expected, we recover the results of Kasteleyn,5 namely,

<table>
<thead>
<tr>
<th>Lattice</th>
<th>$1 \times 1 \times N$</th>
<th>$1 \times 2 \times N$</th>
<th>$1 \times 3 \times N$</th>
<th>$1 \times 4 \times N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi$</td>
<td>$1$</td>
<td>$\frac{1}{2}(1 + \sqrt{5})$</td>
<td>$2 + \frac{\sqrt{3}}{2}$</td>
<td>$1 + \sqrt{2}$</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>$1$</td>
<td>$1 + \sqrt{5}$</td>
<td>$1$</td>
<td>$1 - \sqrt{2}$</td>
</tr>
</tbody>
</table>

We also obtain a result not predicted by Kasteleyn's formula, the molecular freedom per dimer at close packing for the three-dimensional lattice $2 \times 2 \times N$.

$$\Phi = (2 + \sqrt{3})^{1/2} (2 \times 2 \times N).$$  \hspace{1cm} (51)

(See Table I.)

VI. GENERALIZATION

This section is concerned with the generalization of the results obtained for aligned dimers to the case of dimers on two- and three-dimensional lattices irrespective of their orientation. In performing this generalization, we are guided by the following facts.

1. The partition function is given by Eq. (42).

2. For increasing values of $L$ and $M$, the root $z(x)$ has an almost exact exponential behavior in $L$ and $M$. This behavior becomes more accurate with increasing values of $L$ or $M$, as shown in the case of horizontal dimers.

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TABLE II. Thermodynamical properties of dimers on a $2 \times 2 \times N$. The values of $\theta, S, K,$ and $C$ are calculated for selected values of the absolute activity $x$ using Eqs. (31) and (33)–(35).

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\theta$</th>
<th>$S$</th>
<th>$K$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.037 41</td>
<td>0.035 16</td>
<td>0.005 84</td>
<td>0.006 24</td>
</tr>
<tr>
<td>0.02</td>
<td>0.070 37</td>
<td>0.058 37</td>
<td>0.010 35</td>
<td>0.011 74</td>
</tr>
<tr>
<td>0.03</td>
<td>0.099 75</td>
<td>0.076 48</td>
<td>0.013 90</td>
<td>0.016 64</td>
</tr>
<tr>
<td>0.05</td>
<td>0.150 12</td>
<td>0.103 67</td>
<td>0.019 04</td>
<td>0.023 09</td>
</tr>
<tr>
<td>0.07</td>
<td>0.192 06</td>
<td>0.123 40</td>
<td>0.022 48</td>
<td>0.032 15</td>
</tr>
<tr>
<td>0.09</td>
<td>0.227 78</td>
<td>0.138 47</td>
<td>0.024 85</td>
<td>0.038 19</td>
</tr>
<tr>
<td>0.12</td>
<td>0.272 76</td>
<td>0.155 43</td>
<td>0.027 17</td>
<td>0.045 84</td>
</tr>
<tr>
<td>0.16</td>
<td>0.321 26</td>
<td>0.171 39</td>
<td>0.028 91</td>
<td>0.054 14</td>
</tr>
<tr>
<td>0.20</td>
<td>0.360 60</td>
<td>0.182 67</td>
<td>0.029 79</td>
<td>0.060 92</td>
</tr>
<tr>
<td>0.30</td>
<td>0.433 98</td>
<td>0.199 87</td>
<td>0.030 30</td>
<td>0.073 67</td>
</tr>
<tr>
<td>0.50</td>
<td>0.525 53</td>
<td>0.214 37</td>
<td>0.029 14</td>
<td>0.089 69</td>
</tr>
<tr>
<td>0.70</td>
<td>0.582 80</td>
<td>0.219 40</td>
<td>0.027 55</td>
<td>0.099 67</td>
</tr>
<tr>
<td>0.90</td>
<td>0.623 31</td>
<td>0.224 96</td>
<td>0.026 08</td>
<td>0.106 60</td>
</tr>
<tr>
<td>2.00</td>
<td>0.735 60</td>
<td>0.215 75</td>
<td>0.020 69</td>
<td>0.124 53</td>
</tr>
<tr>
<td>5.00</td>
<td>0.832 60</td>
<td>0.197 56</td>
<td>0.014 75</td>
<td>0.135 73</td>
</tr>
<tr>
<td>7.00</td>
<td>0.860 40</td>
<td>0.189 32</td>
<td>0.012 86</td>
<td>0.137 20</td>
</tr>
<tr>
<td>10.0</td>
<td>0.886 00</td>
<td>0.180 29</td>
<td>0.011 05</td>
<td>0.137 21</td>
</tr>
<tr>
<td>13.0</td>
<td>0.902 43</td>
<td>0.173 64</td>
<td>0.009 84</td>
<td>0.136 17</td>
</tr>
<tr>
<td>19.0</td>
<td>0.923 01</td>
<td>0.164 21</td>
<td>0.008 26</td>
<td>0.132 97</td>
</tr>
</tbody>
</table>

(3) The behavior at large values of $x$ of the root $z(x)$, for a given lattice size, is given by Eq. (46), or, more precisely, by

$$z(x) = (\phi L M x)^{1/2},$$

where the molecular freedom per dimer at close packing, referred to as $\phi L M$, depends on the lattice size. For two-dimensional lattices, Kasteleyn’s formula gives

$$\Phi(1, M) = \left(\prod_{i=1}^{M} \left(\cos \frac{\pi r}{M + 1} + \log \left(1 + \cos^2 \frac{\pi r}{M + 1}\right)\right)^{1/2}\right),$$

and for the infinite two-dimensional lattice,

$$\Phi(1, \infty) = \exp \left[\frac{2G}{\pi} \right] = 1.791 622 812 ..., \quad \text{(53)}$$

where $G$ is Catalan’s constant. Several people computed the molecular freedom per dimer at close packing on the infinite three-dimensional lattice. Nagle’s $^5$ value is

$$\Phi(1, \infty) = 2.4423.$$

As reported in the previous section, we computed exactly $\Phi(2, 2)$ as

$$\Phi(2, 2) = (2 + \sqrt{3})^{1/2}.$$

Based on all these facts, it is safe to assume that the root $z(x)$ for an $L \times M \times N$ lattice is approximately given by

$$z(x) = (x(xM)^LM = \left[1 + \sqrt{1 + 4x}\right]L^M,$$

where $x(x)$ is the root for the one-dimensional lattice, namely, the one listed in Eq. (11). Unfortunately, Eq. (57) leads to a molecular freedom per dimer at close packing equal to 1. Clearly, this approximation is extremely bad for large values of $x$. One is able to improve on this by requiring Eq. (52) to be satisfied also. This is possible if one replaces Eq. (57) by

$$z(x) = \left[1 + \sqrt{1 + 4\Phi L M x}\right]L^M.$$

The above approximation becomes more accurate with increasing values of $L$ or $M$. With this in mind, we compute all the thermodynamic quantities for dimers on an $L \times M \times N$ lattice ($N \rightarrow \infty$)

$$Z(x) = \frac{1}{2} \left[1 + \sqrt{1 + 4\Phi L M x}\right], \quad \Gamma(x) = (2/\Omega) \ln Z(x),$$

$$\rho(x) = (2/\Omega) \left[1 - 1/\sqrt{1 + 4\Phi L M x}\right],$$

$$\frac{x(\theta)}{\theta} = \frac{4\Phi L M x (1 - \theta)^2}{Q},$$

$$S(\theta) = -\frac{1}{Q} \ln \left(\frac{\Phi L M (1 - \theta)}{Q\theta}\right) + 2 \ln \frac{2 - \theta}{2 - 2\theta},$$

$$K(\theta) = \frac{2(1 - \theta) \ln \left(\frac{2 - \theta}{2 - 2\theta}\right)}{Q\theta},$$

$$C(\theta) = \frac{2(1 - \theta)(2 - \theta) \ln \left(\frac{2 - \theta}{2 - 2\theta}\right)}{Q\theta} \quad \text{for } Q = 2, 4, 6 \text{ for one-}, \text{two-}, \text{or three-dimensional lattices},$$

$$\theta_m = 1 - 1/\sqrt{1 + 4\Phi L M},$$

a relation whose accuracy increases with increasing values of $L$ and $M$ and which becomes exact for $(L = 1, M = \infty$ and $L = \infty, M = \infty$, i.e., for the infinite square lattice and the infinite simple cubic lattice, respectively. The case $L = 1$ and $M = 1$ is the infinite one-dimensional problem.

As a check of these mathematical expressions and their accuracy, we find them to agree with the exact numerical results derived in paper II for $(L = 1, M = 2, 3, 4)$ within $1.7\%$ for the partition function $Z$. The partition function for $(L = 1, M = 2)$ computed from the approximate relation (59) agrees within $1.5\%$ with the exact values we compute numerically using the method of papers I and II.

We plotted in Figs. 4–6, $S(\theta), K(\theta), C(\theta)$ for infinite one-, two-, and three-dimensional lattices (referred to as the 1D, 2D, and 3D curves, respectively). These curves are obtained from Eqs. (62)–(64). For comparison, we also plotted the points obtained by extrapolation in paper II for dimers on the infinite two-dimension lattice. In Fig. 4, the points obtained by extrapolation for $S(\theta)$ are astonishingly close to the exact analytical fit. This is consistent with the fact that (in paper II) two different methods of extrapolation lead to results agreeing within a $3\%$ deviation. However, the extrapolation of paper II is not as good for $K(\theta)$ and $C(\theta)$ as made explicit in Figs. 5 and 6, respectively. The reason for this comes from the cumulative effect of errors in the numerical computation of $K$ and $C$.

VII. SUMMARY CONCLUSION

Guided by the study of aligned dimers and the results previously obtained in papers I and II, we were able to obtain an analytical fit of the thermodynamical quantities of dimers on a rectangular $L \times M \times N$ lattice, where $N$ is allowed to become infinite and $L$ and $M$ are fixed. The closed-form analytical expressions, Eqs. (59)–(64), are good to better than $1.7\%$ error for low values of $L$ and $M$, but are exact for the infinite one-, two-, and three-dimensional lattices. In addition, other major results are the following.
(1) As exhibited by Eq. (61), the behavior of the absolute activity near close packing has a critical exponent
\[ \gamma = 2, \]
with the associated amplitude
\[ A = \frac{\theta(2 - \theta)}{4\Phi(L,M)} \rightarrow \frac{1}{4\Phi(L,M)}. \] (66)

(2) Surprisingly enough, \( K(\theta) \) and \( C(\theta) \) are independent of the molecular freedom of dimers at close packing. The value of the occupation density \( \theta \) for which \( K \) is maximum is \( \theta = 1 - 1/\sqrt{3} \), and \( K_{\text{max}} = 1/12\sqrt{3} \) for the infinite square lattice and \( 1/18\sqrt{3} \) for the infinite cubic lattice. The value of \( \theta \) for which \( C \) is maximum is \( \theta = 0.844 \ 518 \ 622 \). Finally, the value of \( C \) at the maximum is \( 0.183 \ 259 \ 44 \) for the infinite square lattice and \( 0.122 \ 172 \ 96 \) for the infinite cubic lattice.

(3) The entropy per unit volume divided by Boltzmann's constant \( S(\theta) \) maximizes at \( \theta = 1 - 1/\sqrt{5} = 0.552 \ 786 \ 404 \) for the infinite one-dimensional lattice, at \( \theta = 0.650 \ 069 \ 136 \).

FIG. 5. Plot of \( K \) vs \( \theta \) for dimers irrespective of their orientations. Curve 1D corresponds to the infinite one-dimensional case. Curve 2D corresponds to the infinite two-dimensional case, and the data points nearby are those obtained by extrapolation in paper II. Curve 3D corresponds to the infinite three-dimensional case. Curve \( 2 \times 2 \times N \) is the approximate analytical fit of the data points nearby for dimers on a \( 2 \times 2 \times N \) lattice. These points are obtained exactly using the techniques of papers I and II.
for the infinite square lattice, and at $\theta = 0.69527$ for the infinite cubic lattice. The corresponding values of $S$ are 0.481 211 826, 0.328 462 937, 0.253 73, respectively. These results are to be compared with previous numerical approximations.$^{1,4}$

(4) We developed a new method for calculating molecular freedom of dimers on three-dimensional lattices. However, at this stage, it does not give a closed-form expression similar to Kasteleyn's formula on two-dimensional lattices.

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$^{5}$P. W. Kasteleyn, Physica 27, 1209 (1961).