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Packing flexible polymer chains on a lattice

Adolfo M. Nemirovsky and Maurício D. Coutinho-Filho
Departamento de Física, Universidade Federal de Pernambuco, Cidade Universitária, 50739 Recife, PE, Brazil

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We study the problem of arranging p self-avoiding flexible chains of molecular weight M on a hypercubic lattice of N sites with lattice coordination number z using a field-theoretic approach. The thermodynamic limit of pM becoming infinite, with the packing fraction $f=pM/N$ ranging from zero to 1, is considered. Hence the dimer, the Hamiltonian walk, and the single self-avoiding walk problems are included as particular cases. Mean-field theory is of the Flory type and it becomes exact at $z=\infty$. Systematic corrections in powers of z^{-1} can be evaluated. We calculate the weight- and volume-fraction-dependent connectivity constant and site entropy to second order in z^{-1} and compare it with known results in two and three dimensions. The site entropy, which vanishes at $f=0$, is a convex function of f (for any M) with a maximum at $f \gtrsim 0.6$ that moves towards higher f as either M or z increases. We also discuss the most efficient packing of M-mers at a given volume fraction and dimensionality.

I. INTRODUCTION

Combinatorial problems on regular lattices arise in a variety of physical problems. Long ago, Mayer[1] suggested that the entropy of mixing of liquids consisting of long polymer chains and small solvent molecules (or voids) can be calculated within a lattice approximation in which every site is either occupied by a solvent molecule (monomer) or by a chain segment. Similar lattice models were proposed to explain properties of the absorption of a gas of diatomic molecules (dimers), triatomic molecules (trimers), etc., on a regular surface.[2,3] When the energy of mixing vanishes, all thermodynamic properties of these models can be obtained from combinational factors, that is, by counting all possible arrangements of a given number of monomers and polymers on a regular lattice.

Lattice models have played a very important role in helping to explain many features of the melting transition of polymers,[4-6] liquid crystals,[7,8] polymer blends,[9] polymer incompatibility, and segregation,[10] and other thermodynamic properties of fluids containing macromolecules,[11] thus generating an extensive literature on these combinatorial problems. In one dimension, these models are, in general, easily solved. In contrast, for dimensionality $d=2$ only very few of them possess exact solutions such as the dimer problem on regular lattices[12,13] and Hamiltonian walks on two-dimensional Manhattan lattices.[14] For $d \geq 3$ none has been exactly solved and approximate methods are required. Approximations of the mean-field type (Flory, Huggins, and Bethe approximations[3,5,15-17]) are commonly used but also other approaches such as series expansion methods,[17,18] transfer matrix techniques,[19] and field theoretic methods[20] have been employed for some of these problems.

In this work we use an exact field-theoretic representation[21] for the problem of counting the number of configurations of p self-avoiding and flexible chains, occupying M contiguous lattice sites on a hypercubic lattice of N sites with periodic-boundary conditions. The volume fraction $f=(pM/N)$ is the fraction of the total lattice sites which are occupied by polymer segments. Figure 1 illustrates a typical configuration of a system of self-avoiding tetramers ($M=4$) on a square lattice. Recently, employing field-theoretic techniques we have considered the limit of a single infinite self-avoiding walk (SAW) from infinite dilution ($f=0$) to the compact limit of a Hamiltonian walk at $f=1$ ($N \to \infty$, $M \to \infty$, $p=1$, with $0 \leq f \leq 1$).[22] Bawendi, Freed, and Mohanty[23] and other authors[24-26] have studied the problem of M-mers on a lattice using similar methods, in the thermodynamic limit of infinite flexible chains of finite molecular weight at finite volume fractions ($N \to \infty$, $p \to \infty$, with $0 < f \leq 1$). Here we generalize both results studying a more general thermodynamic limit in which the product of pM is infinite with the fraction f ranging from 0 to 1 ($N \to \infty$, $pM \to \infty$, with $0 \leq f \leq 1$). Obviously, this last limit contains the other two as special cases. Hence, we provide a

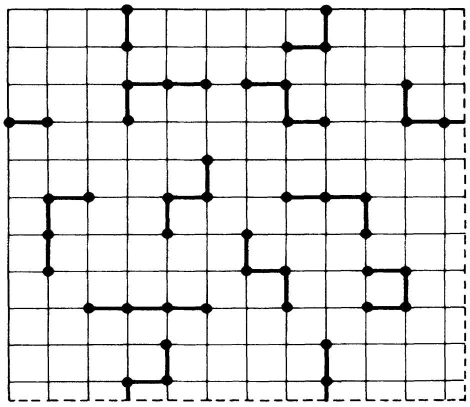

FIG. 1. Typical configuration of flexible and mutually avoiding tetramers ($M=4$) on a square lattice with periodic boundary conditions.

unified description of several combinational problems on regular lattices such as the Hamiltonian walk problem, the dimer problem, and the counting of configurations of a single SAW.

The derived mean-field (MF) approximation, which is similar to that of Flory-Huggins (FH), becomes exact in the limit of infinite lattice coordination number $z=\infty$. A systematic expansion that produces corrections to the MF approximation in powers of z^{-1} is obtained from the exact field-theoretic representation of the problem. We define a generalized volume fraction and molecular-weight-dependent connectivity constant which coincides with the usual connectivity constant in the limit of a single SAW at infinite dilution. The connectivity constant and entropy per site of M-mers on hypercubic lattices as a function of M and f are evaluated to $O(z^{-2})$.

In Sec. II, we discuss approximate methods required to study the problem of packing M-mers on regular lattices and the known exact results for a few special two-dimensional cases. Section III presents a field-theoretic representation of the packing problem from which our MF approximation and corrections to $O(z^{-2})$ for the connectivity constant and site entropy are derived in Sec. IV. Finally, in Sec. V our findings are analyzed in view of known results for these combinatorial problems.

II. THE PROBLEM OF PACKING *M*-MERS ON A LATTICE

In this section we review several results for the problem of counting configurations of M-mers on a regular lattice, and discuss some mean-field approaches to illustrate the interesting combinatorial aspects of this problem.

We start by introducing our mean-field result, derived in Sec. III, for the total number of configurations of a system of p polymer chains of molecular weight M on a lattice of N sites, given by the following p-chain partition function Z_p:

$$Z_p=\frac{N!}{2^p p!(N-pM)!}\left[\frac{z}{N}\right]^{p(M-1)} . \quad (1)$$

It can be understood as follows: the factorial term $[N!/(N-pM)!]$ gives the number of ways of choosing (pM) sites in a sequential order so the "first" chain occupies the sites numbered from 1 to M, the "second" one fills the sites with labels from $(M+1)$ to $2M$, etc. The $p!$ term is due to indistinguishability of the chains, while the 2^{-p} term results as the two ends of a given chain cannot be distinguished. Since only the first monomer of a given chain has about N choices, but all $(M-1)$ sequential polymer segments have (due to chain connectivity) only about z choices, each chain requires a correction factor of $(z/N)^{M-1}$. The older and widely used Flory-Huggins[15,16] approximation replaces z by $(z-1)$ to eliminate immediate self-reversal.

We now define a weight and volume fraction-dependent connectivity constant $\mu(M,f)$ from the asymptotic behavior of the partition function (of course, the connectivity constant also depends on the type of lattice and on lattice coordination number)

$$Z_p \sim \mu^{pM}/p! \quad (2)$$

in the thermodynamic limit of

$$N\rightarrow\infty,\ \ Mp\rightarrow\infty,\ \ 0\le f=pM/N\le 1 . \quad (3)$$

This limit contains as special cases the two limits recently studied by Refs. 22–26 using a field-theoretic representation of the problem. For infinite chains, the quantity μ reduces to the f-dependent connectivity constant which, for a square lattice, was recently evaluated by Duplantier and Saleur.[19] This, in turn, becomes the usual connectivity constant (also known as effective coordination number) in the $f=0$ limit.

For short chains in the infinite dilution limit, the exact values of μ can be easily obtained either by direct counting or by using the field-theoretic representation of the problem of Secs. III and IV which yields exact results in these cases. For example, the connectivity constant for the smallest M-mers on a hypercubic lattice of coordination number z is

$$\begin{aligned}&\mu(2,0)=(Nz/2)^{1/2} ,\\ &\mu(3,0)=[Nz(z-1)/2]^{1/3} ,\\ &\mu(4,0)=[Nz(z-1)^2/2]^{1/4} ,\\ &\mu(5,0)=\{Nz[(z-1)^3-(z-2)]/2\}^{1/5} .\end{aligned} \quad (4)$$

In this limit of $f=0$, the p partition function is that of an ideal gas of indistinguishable dimers, trimers, etc. As the molecular weight increases it becomes more difficult to obtain μ in closed form.

The connectivity constant for infinite self-avoiding walks on regular two- and three-dimensional lattices has been calculated by several authors using enumeration studies together with resummation techniques such as Padé approximants and the ratio method.[27] The quantity $\mu(\infty,0)$ has also been calculated for hypercubic lattices in four, five, and six dimensions.[28] Table I shows the best-known values of the connectivity constant for SAW's on hypercubic lattices with dimensionalities from 2 to 6.

In the dense limit of $f=1$, there are exact results for dimers $(M=2)$ on regular two-dimensional lattices.[12,13] This is the celebrated dimer problem, first solved on a square lattice by Kasteleyn and by Temperley and Fisher, independently.[12] Later, it was shown that regular two-dimensional-lattice zero-field Ising-model partition functions can be written as dimer problems on appropriate decorated lattices.[29] The dilute dimer system (monomer-dimer problem) in two dimensions, which is closely related to the Ising model in a field,[30] has not been exactly solved in two dimensions. Several workers have treated the monomer-dimer problem in two and three dimensions using Bethe and similar approximations.[3,17] Also, series expansion techniques were used to evaluate the grand partition function.[17,18] The exact and the best-known values of the full coverage dimer connectivity constants on square and simple cubic lattices are shown in Table I.

The Hamiltonian walk problem consists of counting the total number of configurations of a single SAW that fully covers the lattice and it has been exactly solved[14] on a two-dimensional Manhattan lattice and other special lattices.[31] For square lattices, this problem has been investigated by several authors. Gujrati and Goldstein[6] give the bounds

$$1.338\ldots \leq \mu(\infty,1) \leq 1.539\ldots$$

(the dots above indicate that these values are exactly known). Schmaltz, Hite, and Klein[32] using strip methods obtain $\mu(\infty,1)\sim 1.472$. Orland, Itzykson, and de Dominicis[20] employed field-theoretic methods to calculate the number of Hamiltonian circuits on regular lattices of any dimensionality and obtained a mean-field value of $\mu(\infty,1)=z/e$, which (at $z=4$) is in surprisingly good agreement with that of Schmaltz *et al.* They also showed that one-loop corrections to their mean-field value vanish. The quantity $\mu(\infty,f)$, $0\leq f\leq 1$, numerically evaluated by Duplantier and Saleur[19] using transfer matrix methods, is in excellent agreement with the best known results at $f=0$ and at $f=1$.

The mean-field connectivity constant $\mu(M,f)$ is easily calculated from (1) and (2)

$$\mu^{\mathrm{MF}}(M,f)=(z/e)(N/2z)^{1/M}(1-f)^{-(1-f)/f} . \tag{5}$$

The Flory-Huggins (FH) approximation replaces z by $z-1$. It is convenient to define the quantity $R(M,f)$ as the ratio

$$R(M,f)=\mu(M,f)/\mu(M,f=1) . \tag{6}$$

Our MF result and that of FH predict $R(M,f)$ to be the following universal function:

$$R^{\mathrm{MF}}(M,f)=(1-f)^{-(1-f)/f} , \tag{7}$$

which is independent of the molecular weight and of the type of lattice, and its value at $f=0$ is $R^{\mathrm{MF}}(M,0)=e$. To check this prediction, Table II shows either exact or best known values of $R(2,0)$ and $R(\infty,0)$ for regular two- and three-dimensional lattices. The mean-field prediction (7) for $f=0$ is much better for dimers than for SAW's, and it always improves (as compared with known values) as the lattice coordination number increases. As usual, mean field predicts a wider universality than observed, and of course, one expects that corrections to (7) should be weight and coordination number dependent. In fact, at equal z, they must also depend on the type of lattice. For example, a simple cubic (sc) lattice has $R(2,0)$ and $R(\infty,0)$ closer to MF values than a triangular lattice does, although both have $z=6$.

TABLE I. Connectivity constants and site entropies of M-mers on hypercubic lattices.

Quantity	Dimension	Exact or best-known value	Second order (this paper)
$\mu(2,0)$	2	$(2N)^{1/2}$	$(2N)^{1/2}$
	3	$(3N)^{1/2}$	$(3N)^{1/2}$
$\mu(2,1)$	2	$0.5740\ldots N^{1/2}$ [a]	$0.56N^{1/2}$
	3	$0.671N^{1/2}$ [b]	$0.67N^{1/2}$
$\mu(\infty,0)$	2	2.6385[c]	2.84
	3	4.6838[c]	4.87
	4	6.7680[d]	6.89
	5	8.8313[d]	8.91
	6	10.8720[d]	10.93
$\mu(\infty,1)$	2	1.472[e]	1.48
$s(2,1)$	2	0.2915. . .[a]	0.27
	3	0.447[b]	0.44
$s(\infty,1)$	2	0.387[e]	0.39

[a] Reference 12.
[b] References 17 and 18.
[c] Reference 27.
[d] Reference 28.
[e] Reference 32.

TABLE II. Exact or best-known values of $R(M,0)$ for dimers and infinite walks on regular two- and three-dimensional lattices. The numbers in parentheses denote our results to $O(z^{-2})$ and the three dots indicate exact values. Mean field predicts $R^{\mathrm{MF}}(M,0)=e=2.7182\ldots$. The quantity $\mu(\infty,1)$ has only been calculated (numerically) for square lattices. For other lattices the values of $\mu(\infty,1)$, used to calculate $R(\infty,0)$, are the mean-field values.

Dimension	Type of lattice	Coordination number	$R(2,0)$	$R(\infty,0)$
2	Honeycomb	3	2.4296. . .[a]	1.67[c]
	Square	4	2.4635. . .[b](2.52)	1.79[c](1.91)
	Triangular	6	2.6308. . .[a]	1.88[c]
3	Diamond	4	2.53[d]	1.96[c]
	sc	6	2.58[d] (2.59)	2.12[c](2.20)
	bcc	8	2.61[d]	2.22[c]
	fcc	12	2.67[d]	2.27[c]
4	sc	8	(2.63)	2.30[e](2.34)
5	sc	10	(2.65)	2.40[e](2.42)
6	sc	12	(2.66)	2.46[e](2.47)

[a] Reference 13.
[b] Reference 12.
[c] References 27 and 32.
[d] References 17 and 18.
[e] Reference 28.

Bethe and related approximations for the problems of dimers[3,17] and that of infinite SAW's (Ref. 5) have been discussed at length in the literature. The Bethe approximation which is exact for Bethe lattices takes into account the effects of second-neighbor sites. For long, flexible, and mutually avoiding walks, the Bethe approximation, also known as the Huggins theory, gives[5]

$$\mu^{\mathrm{Bethe}}(\infty,f)=(z-1)[(z-2f)/z]^{-(z-2)/z}\times(1-f)^{-(1-f)/f}\;, \tag{8}$$

and for the monomer-dimer problem one has[17]

$$\mu^{\mathrm{Bethe}}(2,f)=\frac{(z-f)^{(z-f)/2f}}{z^{(z-2f)/2f}}(1-f)^{-(1-f)/f}(eN/2)^{1/2}\;. \tag{9}$$

In this approximation, the quantity $R(M,f)$ is not as universal as (7) predicts since it now depends on both M and z. For example, if $z=4$ one has $R^{\mathrm{Bethe}}(2,0)=2$ and $R^{\mathrm{Bethe}}(\infty,0)=2.54$, in closer agreement with the known results displayed in Table II. Still there is no dependence on the type of lattice, but only on the coordination number.

The entropy per site is defined by

$$s=N^{-1}\ln Z_p \tag{10}$$

in the thermodynamic limit of (3), and its mean-field value [from Eqs. (1) and (10)] is

$$s^{\mathrm{MF}}=f\ln(z/e)+(f/M)\ln(Me/2fz)-(1-f)\ln(1-f)\;. \tag{11}$$

For a given weight M, the MF site entropy vanishes at $f=0$, reaches a maximum at $f\gtrsim 0.6$ and then it decreases as f approaches unity. The maximum displaces towards $f=1$ as either the weight or the lattice coordination number increase. Tables III and IV show, respectively, predictions of various approximations together with known results for the site entropy and connectivity constant of dimers and infinite SAW's on square, cubic, and hypercubic lattices.

III. FIELD-THEORETIC REPRESENTATION OF *M*-MERS ON A LATTICE

We use the following field-theoretic representation of the grand partition function Z for a system of p nonoverlapping polymers of molecular weight M on a lattice of N sites:[21]

$$Z=\int D[\phi]D[\phi^\dagger]\prod_{i=1}^{N}[1+X_i(\phi,\phi^\dagger)]\times\exp[-H(\phi,\phi^\dagger)]\;, \tag{12}$$

$$X_i=\frac{h}{\sqrt{2}}\phi^\dagger_{i,1}+\sum_{\alpha=2}^{M-1}\phi^\dagger_{i,\alpha}\phi_{i,\alpha-1}+\frac{h^\dagger}{\sqrt{2}}\phi_{i,M-1}\;, \tag{13a}$$

$$H=\sum_{i,j}\phi^\dagger_{i,\alpha}V_{ij}\phi_{j,\alpha}\;, \tag{13b}$$

where the measure is

$$D[\phi]D[\phi^\dagger]=A\prod_{i=1}^{N}\prod_{\alpha=1}^{M-1}d\phi_{i,\alpha}d\phi^\dagger_{i,\alpha}$$

with A such that $Z=1$ when $X_i\equiv 0$, $\forall i$. The Latin and Greek subscripts denote lattice site and polymerization indices, respectively. The matrix V_{ij}^{-1} (propagator) equals unity if the sites i and j are nearest neighbors, vanishing otherwise and, in the Fourier representation, its inverse can be written as

$$V_{ij}=\sum_{\mathbf{q}}\exp[i\mathbf{q}(\mathbf{r}_i-\mathbf{r}_j)][Nf(\mathbf{q})]^{-1}\;, \tag{13c}$$

where the sum over $\mathbf{q}$ extends over the first Brillouin zone of the lattice, $\mathbf{r}_i$ is the position vector of lattice site i, and $f(\mathbf{q})$ is the nearest-neighbor lattice structure factor

$$f(\mathbf{q})=\sum_{i=1}^{z}\exp(-i\mathbf{q}\cdot\mathbf{a}_i)\;, \tag{13d}$$

where $\mathbf{a}_i$ are the vectors joining the site i with its z nearest neighbors. All lattice dependence is included in (13c). Here we specialize in hypercubic lattices but the approach can be easily applied to other lattice types.

The internal symmetry (polymerization) index serves to control the length of the chains. Also, to generate the desired monodispersive system of chains with molecular weight M, a complex field representation is required as discussed by Freed.[21] The expansion of the product $\prod_i(1+X_i)$ produces 2^N terms. A particular contribution has r factors of X associated with sites occupied by polymer segments and $(N-r)$ factors of unity representing unoccupied lattice sites, i.e., each site is either occupied by a single polymer segment or it is vacant. Every contribution can be viewed as a very large N-point correlation

TABLE III. Connectivity constants of SAW's at infinite dilution on hypercubic lattices: best-known results and various approximations.

Theory	Dimensionality 2	3	4	5	6
Flory-Huggins–Bethe	3	5	7	9	11
MF	4	6	8	10	12
Second order (this paper)	2.836	4.872	6.896	8.914	10.926
Best known	2.638[a]	4.683[a]	6.768[b]	8.831[b]	10.872[b]

[a] Reference 27.

[b] Reference 28.

TABLE IV. Site entropy at full coverage: exact or best-known results and various approximations.

Theory \ Quantity	$s(2,1)$ on sq lattices	$s(2,1)$ on sc lattices	$s(\infty,1)$ on sq lattices
Flory-Huggins	0.049	0.305	0.099
Bethe	0.261	0.440	0.405
MF	0.193	0.396	0.386
Second order	0.269	0.443	0.396
Exact or best known	0.261...[a]	0.448[b]	0.387[c]

[a] Reference 12.

[b] References 17 and 18.

[c] Reference 32.

function such that use of the Wick's expansion with the propagator of (13c) produces unity for every allowed configuration of p chains ($p=1,2,3,\ldots$), each of molecular weight M, and zero otherwise.

As usual, the magnetic-field-type source serves as a chemical potential and since each chain in (13a) is initiated by the field h and terminated by $h^{\dagger}$, every polymer has a factor $(hh^{\dagger})$ associated with it. Thus, the p-polymer partition function Z_p can be obtained as the following derivative of the grand partition function:

$$Z_p=\frac{1}{p!}\frac{\partial^p}{\partial(hh^{\dagger})^p}Z\bigg|_{h^{\dagger}=h=0} . \tag{14}$$

The field theory of Eqs. (12)–(14) is an exact representation of the problem of counting the total number of configurations of p-polymer chains of M monomers each on a hypercubic lattice with periodic-boundary conditions. One should mention that Orland *et al.*[20] introduced a similar representation to evaluate the number of Hamiltonian circuits. However, these authors do not introduce a polymerization index but rather fields that have an N-vector symmetry with $N=0$. Their elegant formulation, however, only works for single closed circuits ($M=\infty$) that fully cover the lattice ($f=1$).

IV. THE MEAN-FIELD APPROXIMATION AND CORRECTIONS TO MF

The mean-field approximation for the p-chain partition function Z_p of Eq. (14) is obtained[21,23] by just retaining the $\mathbf{q}=0$ modes of the fields, that is, by taking the field to have some constant value independent of the lattice site. The field integrals in (12) are just Gaussians and can be easily performed to yield Eq. (1).

In our approach, MF theory is exact in the limit of $z=\infty$. The $\mathbf{q}\neq 0$ modes of the fields can be systematically included to produce a perturbative expansion of Z_p in powers of z^{-1}. These corrections due to correlations among bonds are evaluated with the aid of diagrams consisting of one bond, two bonds, etc. The diagrammatic expansion of the partition function and rules to evaluate diagrams have been discussed at length in previous works. Here we summarize our findings and discuss the differences with previous calculations.

The p-chain partition function can be written symbolically as

$$\ln Z_p=\ln Z_p^{\mathrm{MF}}+pM(H^{(1)}z^{-1}+H^{(2)}z^{-2}+\cdots) , \tag{15}$$

where $H^{(r)}$ denotes the molecular weight and volume-fraction-dependent correction of order z^{-r} (more generally, it also depends on the lattice type). To calculate corrections to $O(z^{-r})$ one needs all clustered diagrams of up to $2r$ bonds. There is only one one-bond diagram [Fig. 2(a)], there are three two-bond diagrams since the bonds can either be sequential or nonsequential along the same chain [Figs. 2(b) and 2(c)] or belong to different chains [Fig. 2(d)]. Thus, for example, to calculate $H^{(1)}$ in (15) contributions from all these diagrams are required. For computational convenience it is better to group the diagrams in clusters, as in Fig. 3 where we show all clustered diagrams of up to four bonds required to perform a calculation to order z^{-2}.

The main difference with previous related approaches[22–26] is that our clusters contain extra diagrams absent in the works of Refs. 22–26. This is because we study the problem in the thermodynamic limit (3) thus generalizing the two limits studied before. For example, for the two-bond cluster of Fig. 3(b) we have contributions from three diagrams, instead Refs. 23–26 (Ref. 22) have nonvanishing contributions only from the first (second) and the third diagrams. The diagrams of Fig. 3 are evaluated to yield

$$H^{(1)}(M,f)=-[(M-2)/M]+[(M-1)^2/M^2]f, \quad M\geq 2 ; \tag{16a}$$

$$H^{(2)}(2,f)=(f^2/12)+(f^3/8) , \tag{16b}$$

$$H^{(2)}(3,f)=-(\tfrac{1}{6})+(f/9)-(32f^2/81)+(32f^3/81) , \tag{16c}$$

$$H^{(2)}(4,f)=-(\tfrac{1}{4})+(5f/8)-(27f^2/32)+(81f^3/128) , \tag{16d}$$

$$\begin{aligned}H^{(2)}(M,f)=&-[(3M-10)/2M]\\&+[(3M^2-12M+10)/M^2]f\\&-[(M-1)^2(10M-22)/3M^3]f^2\\&+[2(M-1)^4/M^4]f^3, \quad M\geq 5 .\end{aligned} \tag{16e}$$

Chains with less than five monomers have fewer than four bonds; hence not all diagrams of Fig. 3 give contri-

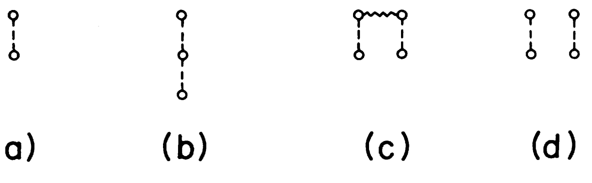

FIG. 2. One- and two-bond diagrams required to calculate first order in z^{-1} corrections to the p-chain partition function. There are three two-bond diagrams since the bonds can either be sequential (b) or nonsequential along the same chain (c) or belong to different chains (d).

butions to their partition functions. For example, only Figs. 3(b), 3(e), and 3(i) are required for the dimer problem.

Using Eqs. (2), (5), (10), (11), (15), and (16) we obtain both the connectivity constant and the site entropy to $O(z^{-2})$

$$\mu^{(2)}=\mu^{\mathrm{MF}}\exp(H^{(1)}z^{-1}+H^{(2)}z^{-2}+\cdots)\ , \tag{17}$$

$$s^{(2)}=s^{\mathrm{MF}}+f(H^{(1)}z^{-1}+H^{(2)}z^{-2}+\cdots)\ . \tag{18}$$

V. DISCUSSION

Equations (17) and (18), together with (16), (5), and (11), give, to $O(z^{-2})$, the molecular weight M and volume fraction f-dependent connectivity constant and entropy per site of M-mers on hypercubic lattices of coordination number z. The mean-field approximations (5) and (11) are exact in the $z\rightarrow\infty$ limit and they agree with the leading contribution of the Flory-Huggins and Bethe approximations [Eq. (1) with z $(z-1)$, and Eqs. (8) and (9)]. In addition, our z^{-1} corrections to these quantities for infinite walks and dimers [Eqs. (16a), (17), and (18)] are in accordance with the z^{-1} corrections predicted by the Bethe approximation since both include all correlations of up to two bonds. Second-order predictions, however, already differ as the Bethe approximation is treelike with no closed circuits, i.e., correlations among three and four bonds are *only partially* included in the Bethe approximation but *fully* incorporated in our approach.

Figures 4 and 5 display, respectively, the quantity $R(M,f)$ defined in (6) as a function of the volume fraction for dimers and infinite walks on square lattices. The

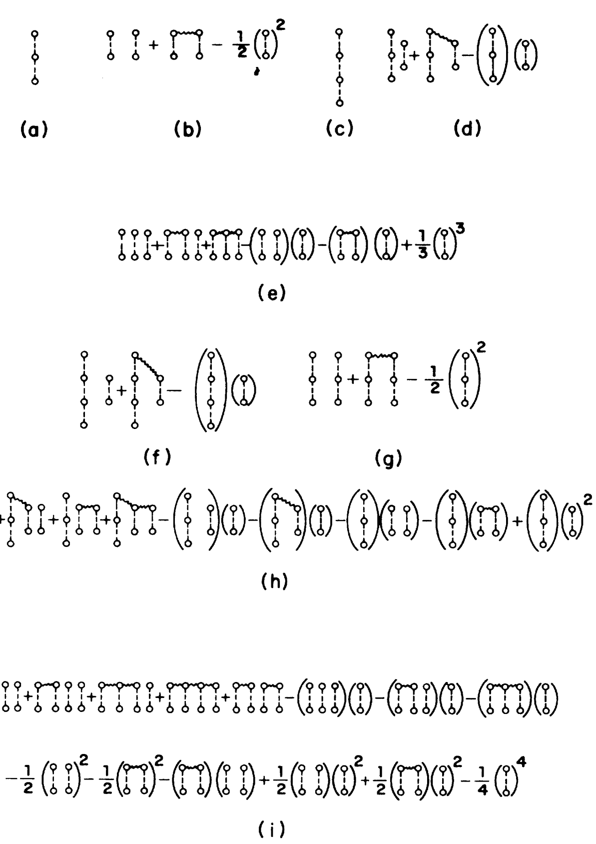

FIG. 3. All clustered diagrams of up to four bonds that give nonvanishing contributions in the limit (3). These diagrams must be evaluated to obtain the corrections to the p-chain partition function to $O(z^{-2})$. In general, z^{-r} corrections require up to $2r$-bond diagrams.

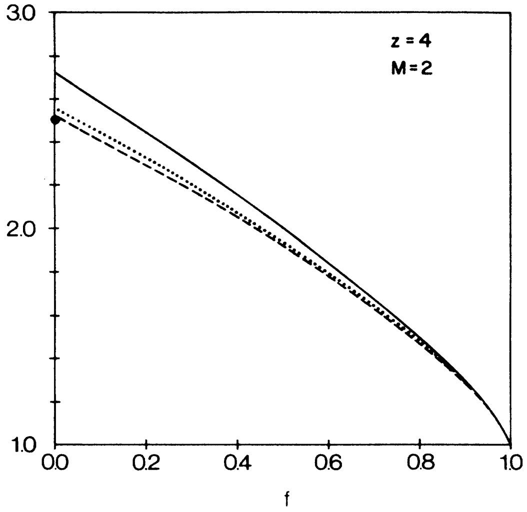

FIG. 4. Quantity $R(M,f)$ defined by Eq. (6) vs volume fraction for dimers ($M=2$) on a square lattice ($z=4$). Mean-field (MF) prediction (solid line) is lattice and molecular weight independent. The figure also shows $R(M,f)$ corrected through first order (dotted line) and second order (dashed line) in z^{-1}. The exact value of $R(2,0)$ is indicated by a black dot.

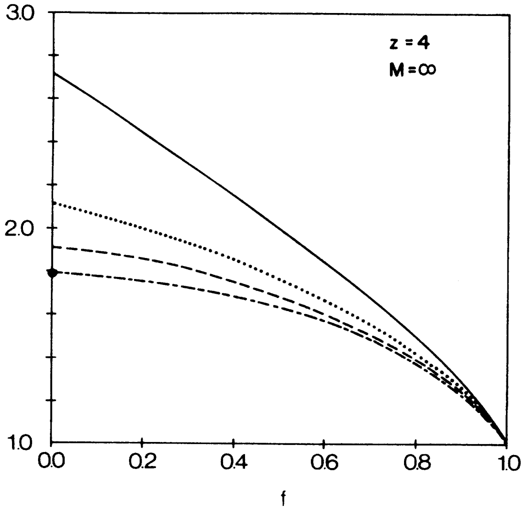

FIG. 5. $R(M,f)$ vs f for infinite walks ($M=\infty$) on a square lattice ($z=4$). The mean-field, first-, and second-order results are indicated by solid, dotted, and dashed lines, respectively. The dot-dashed line is the result of Duplantier and Saleur (Ref. 19). The best-known value of R at $f=0$ is indicated by a black dot.

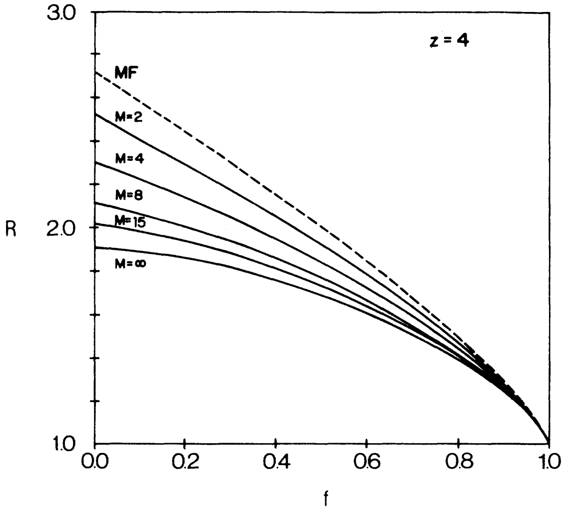

FIG. 6. Molecular weight dependence of $R(M,f)$ to $O(z^{-2})$ vs f. The MF prediction (dashed line) is also shown for comparison. Dimers are the closest to MF, and as the molecular weight increases, corrections grow larger.

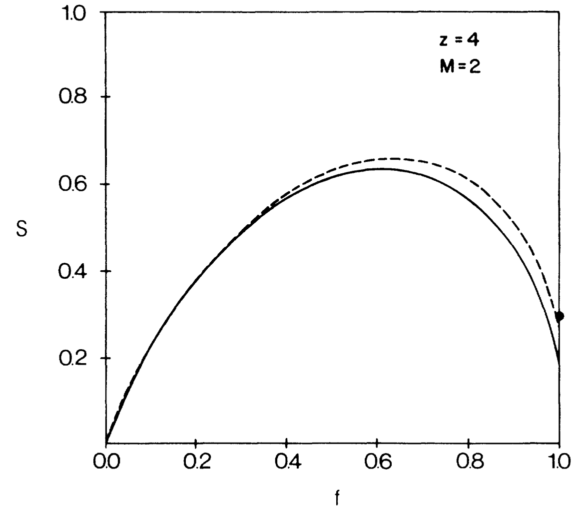

FIG. 8. Site entropy of dimers on a square lattice. Mean field is the solid line while $s(2,f)$ to $O(z^{-2})$ is indicated by a dashed line. A black dot shows the exact value of $s(2,1)$.

mean-field function R, Eq. (7), which always overestimates $R(M,f)$ is also shown for comparison. We find that $R(2,f)$ is much closer to the mean-field prediction than $R(\infty,0)$. The exact value of $R(2,0)$ and the best-known value of $R(\infty,0)$ are indicated in the figures and displayed in Table II. This table also shows the best-known values of these quantities for other regular two- and three-dimensional lattices, and of $R(\infty,0)$ for hypercubic lattices in four, five, and six dimensions. The recently calculated[19] $R(\infty,f)$ is also shown in Fig. 5.

The M dependence of $R(M,f)$ to $O(z^{-2})$ versus f for square lattices is illustrated in Fig. 6. It is evident that the mean-field prediction becomes more accurate, i.e., corrections in z^{-1} are smaller, as the molecular weight decreases. On the other hand, Fig. 7 shows the dependence of $R(\infty,f)$ to $O(z^{-2})$ versus f on the dimensionality of the hypercubic lattice. Of course, MF improves as z increases, since it is exact at $z=\infty$.

The entropy per site versus the volume fraction for dimers and infinite walks on square lattices are shown in Figs. 8 and 9, respectively. The quantity $s(\infty,f)$ of Ref. 19 together with the exact and best-known values of $s(2,0)$ and $s(\infty,0)$ are also displayed. In two dimen-

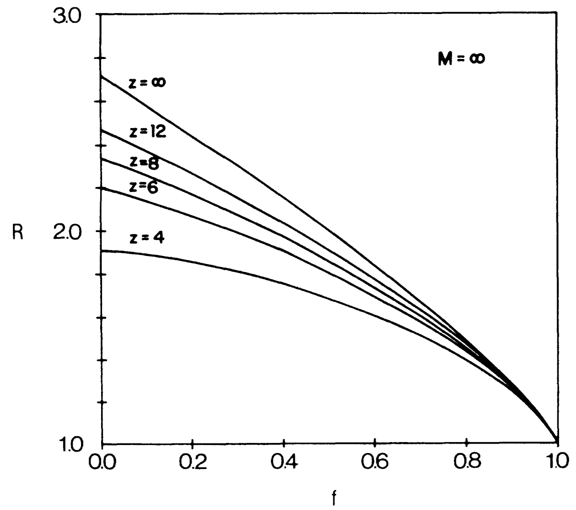

FIG. 7. Dependence of R on the dimensionality of hypercubic lattices. We show $R(\infty,f)$ to $O(z^{-2})$ vs f for $d=(z/2)=2$, 3, 4, 6, and ∞ (MF). As the coordination number grows larger, corrections to MF become smaller.

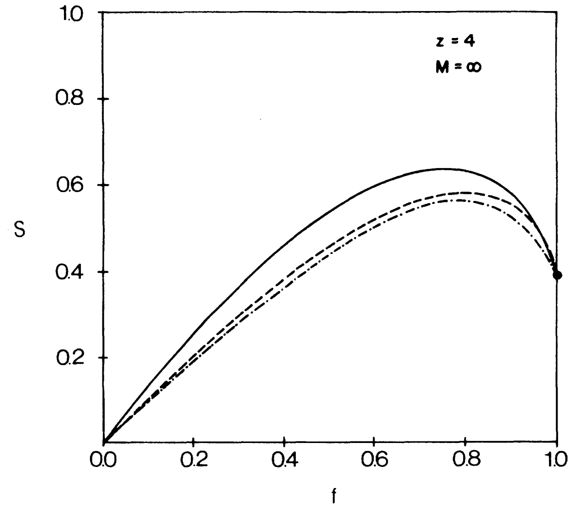

FIG. 9. Same as Fig. 8 but for infinite SAW's instead of dimers. Also shown by a dot-dashed line is the prediction of Ref. 19 for $s(\infty,f)$. The black dot at $f=1$ indicates the best-known value of s for Hamiltonian walks.

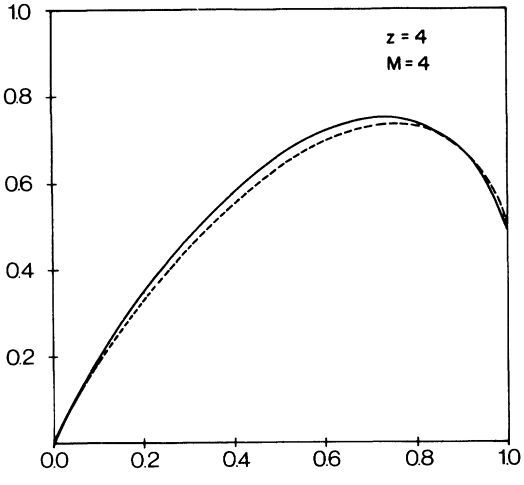

FIG. 10. Same as Fig. 8 but for tetramers.

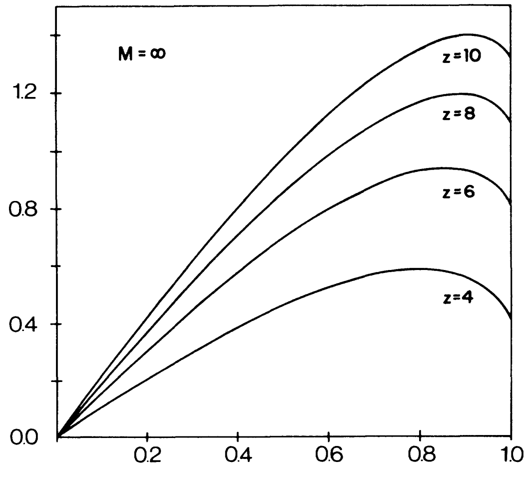

FIG. 12. Same as Fig. 11 but for infinite SAW's.

sions, the mean-field approximation is very good for dimers at low fraction ($f \lesssim 0.3$) and for infinite walks near $f=1$. Equations (16a), (16b), (16e), and (18) indicate that corrections to the site entropy of dimers are $\propto f^2$ to $O(z^{-1})$ and $\propto f^3$ to $O(z^{-2})$, while corrections for s of infinite walks are $\propto (1-f)$ to $O(z^{-1})$ and, if $f \approx 1$ they are very small in second order. For Hamiltonian walks, the mean-field value and the z^{-1} correction (which vanishes) are in agreement with the findings of Orland *et al.* Furthermore, we find that for M-mers at full coverage, first-order contributions are $\propto (M^2 z)^{-1}$ so, in two dimensions and, say, for $M=6$, corrections to $O(z^{-1})$ are already less than 1% of the MF value and smaller than second-order corrections $\propto z^{-2}$.

Curves $s(2,f)$ and $s(\infty,f)$ of Figs. 8 and 9 have the same qualitative shape. Mean-field theory always underestimates (over estimates) the site entropy of dimers (infinite walks) and corrections to MF are always positive (negative). The $M=2$ [$M=\infty$] chain on square lattice has a mean-field site entropy maximum of $s(2,f=0.61)=0.64$ [$s(\infty,f=\frac{3}{4})=0.64$] while to $O(z^{-2})$ the maximum is $s(2,f=0.64)=0.66$ [$s(\infty,f=0.80)=0.71$].

For shorter chains ($2<M \lesssim 10$) it is found that corrections to MF are always negative, unless for a small region close to $f=1$, where corrections are very small but positive. This is illustrated in Fig. 10 for tetramers ($M=4$). The entropy per site to $O(z^{-2})$ versus f for dimers (infinite walks) on hypercubic lattices of various dimen-

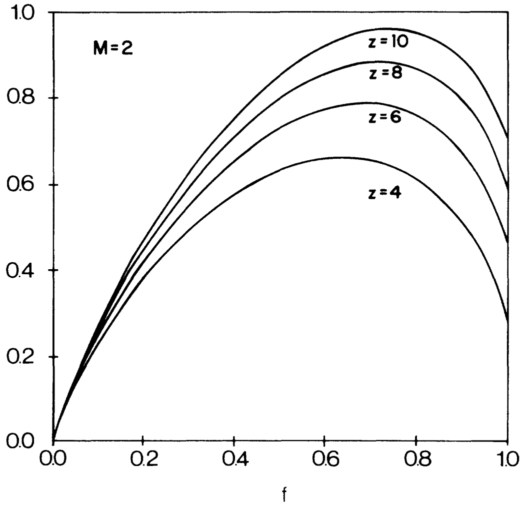

FIG. 11. Site entropy to $O(z^{-2})$ of dimers on hypercubic lattices vs packing fraction for various values of z. As expected, as z increases the entropy per site grows and the maximum displaces to higher packing fractions.

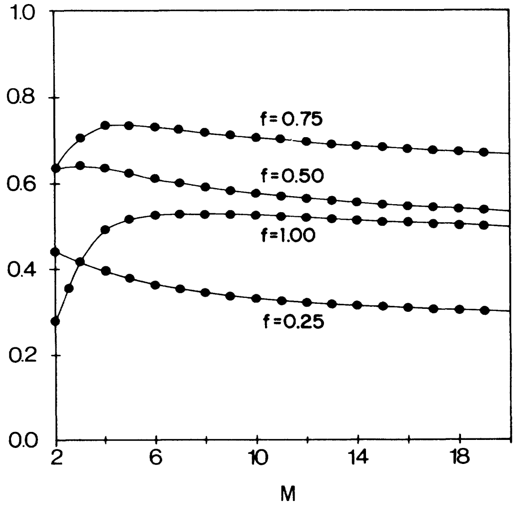

FIG. 13. Plot of the entropy per site to $O(z^{-2})$ as a function of the polymer weight (integer numbers) for various values of the volume fraction (the solid lines are a guide).

TABLE V. Maximum values of the site entropy of M-mers on cubic lattices.

	Mean-field theory			Second order		
Dimension	$s_{\max}$	M	f	$s_{\max}$	M	f
2	0.761	6	$\frac{3}{4}$	0.734	5	0.77
3	1.042	10	$\frac{5}{6}$	1.023	10	0.85
4	1.267	14	$\frac{7}{8}$	1.255	14	0.89
5	1.453	18	$\frac{9}{10}$	1.444	18	0.91
6	1.610	22	$\frac{11}{12}$	1.604	22	0.92

sionalities is shown in Figs. 11 and 12. Qualitative shapes of the curves are similar; as dimensionality increases the site entropy grows and its maximum is displaced towards $f=1$.

It is of interest to determine the most efficient packing (to obtain maximum entropy) of M-mers on a hypercubic lattice at a given volume fraction. In Fig. 13 we plot the entropy per site $s(M,f)$ to $O(z^{-2})$ at fixed values of f ($f=0.25$, 0.50, 0.75, and 1) versus the molecular weight. We find that at low volume fraction ($f \lesssim 0.25$) dimers have the highest site entropy, but as f increases s develops a maximum at a higher M ($M \lesssim 8f$ for $f>0.25$), while at full coverage dimers have the least entropy per site and the maximum is $s=0.52$ at $M=7$. For higher weight, the entropy slowly approaches to that of a Hamiltonian walk (for $M \approx 20$ the site entropy is still about 25% higher than that of $M=\infty$).

Finally, Table V displays the absolute maxima of the entropy per site for hypercubic lattices from two to six dimensions as both the weight and the fraction f are allowed to vary independently. On a square lattice, the maximum of $s=0.734$ is at $M=5$ and $f=0.77$. This can be contrasted against the exact $s(2,1)=0.291\ldots$ and the best-known $s(\infty,1)=0.387$. Also, as dimensionality increases, the maximum of s becomes higher and displaced towards denser packing.

VI. CONCLUSIONS

We have used a field-theoretic representation for the problem of packing M-mers on a hypercubic lattice and considered a more general thermodynamic limit than previous related studies.[22-26] Our approach can fully describe the crossover from dimers to infinite walks, and from the limit of infinite dilution to unit packing fraction. Hence, we have presented a unified description of several combinatorial problems such as the dimer problem, and the counting of configurations of single self-avoiding walks at infinite dilution and at the most compact packing (the Hamiltonian walk problem).

The molecular weight and volume-fraction-dependent connectivity constant is easily (exactly) evaluated for short chains at infinite dilution (ideal gas of M-mers); instead as $M \to \infty$ (with any f) and when $f \neq 0$ (for any M) our approach provides a solution through a systematic z^{-1} expansion. The ratio $R=[\mu(M,f)/\mu(M,1)]$ is predicted by MF to be a decreasing function of f alone, hence *independent* of lattice type and polymer weight. This is checked against known data. Deviations are much larger for SAW than for dimers but second order (z^{-2}) corrections to R improve MF results substantially. As expected, when dimensionality increases MF predictions become more accurate.

The entropy per site, which vanishes at $f=0$, is a convex function of f (for any M) with a maximum at $f \gtrsim 0.6$ and is more asymmetric as M grows. Its maximum displaces towards higher concentrations as z or M increases. At low f, dimers provide the most efficient packing (i.e., maximum site entropy at a given f) but as f approaches unity dimers have the lowest entropy per site, which is maximized when $M \approx 2z-1$. As a concluding remark one should mention that although we have only treated hypercubic lattices, other types of lattices can be easily considered using the appropriate structure factor. First-order (z^{-1}) corrections are lattice independent but second-order corrections already carry information on the lattice structure.

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