

From Dilute to Dense Self-Avoiding Walks on Hypercubic Lattices

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A field-theoretic representation is presented to count the number of configurations of a single self-avoiding walk on a hypercubic lattice in d dimensions with periodic boundary conditions. We evaluate the connectivity constant as a function of the fraction f of sites occupied by the polymer chain. The meanfield approximation is exact in the limit of infinite dimensions, and corrections to it in powers of d^{-1} can be systematically evaluated. The connectivity constant and the site entropy calculated throughout second order compare well with known results in two and three dimensions. We also find that the entropy per site develops a maximum at $f \gtrsim 1 - (2d)^{-1}$. For $d=2$ ($d=3$), this maximum occurs at $f \sim 0.80$ ($f \sim 0.86$) and its value is about 50% (30%) higher than the entropy per site of a Hamiltonian walk ($f=1$).

KEY WORDS: Self-avoiding walks; field theory; connectivity constant; entropy; d^{-1} expansion; polymer melt.

1. INTRODUCTION

Long polymer chains in solution, melt, or solid state are usually modeled by self-avoiding walks on regular lattices or in the continuum.^(1,2) The properties of self-avoiding walks have played an important role in our understanding of the statistical mechanical theories of, for example, polymer crystallization, polymer liquid crystals, segregation problems involving different types of polymers,^(1,2) and the large-scale universal static and dynamical properties of dilute and semidilute solutions of polymers.⁽²⁾

One of the most studied quantities in the extensive literature on self-

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avoiding walks (SAW) on regular lattices is the connectivity constant defined by⁽²⁾

$$\ln \mu = M^{-1} \ln Z_1 \quad (1)$$

in the thermodynamic limit of $N \rightarrow \infty$ and $M \rightarrow \infty$. The quantity Z_1 is the one-chain partition function, that is, the total number of configurations of a single self-avoiding polymer of molecular weight M (number of lattice sites occupied by the chain) confined into a volume N (total number of sites of the regular lattice). Figure 1 shows a self-avoiding polymer chain on a square lattice.

A dilute SAW (polymers in dilute solutions) corresponds to the limit of vanishingly small monomer volume fraction f [$f = (M/N) \rightarrow 0$ as $M, N \rightarrow \infty$]. In the opposite limit of finite concentrations, such that $0 < f \leq 1$, we have a dense SAW which describes properties of melts or of the solid state of macromolecules. At $f = 1$, the walk covers all lattice sites (a Hamiltonian walk).

In the dilute limit of $f = 0$, the connectivity constant $\mu(0)$ [$\mu(0)$ denotes the connectivity constant at $f = 0$] for regular lattices in two and three dimensions was calculated using enumeration studies in conjunction with Padé approximants or the ratio method.⁽³⁾ Also, $\mu(0)$ for hypercubic lattices in four, five and six dimensions was evaluated employing the

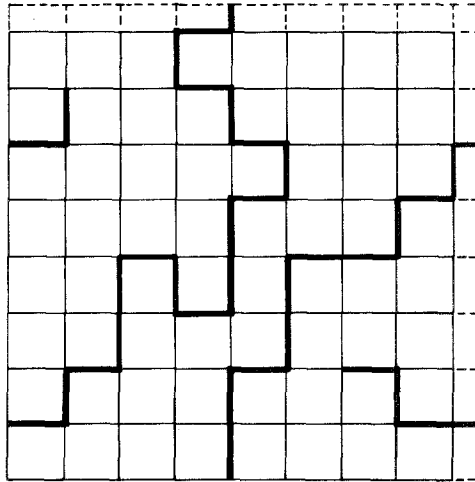


Fig. 1. A typical configuration of a self-avoiding polymer chain of molecular weight M on a square lattice of N sites. Periodic boundary conditions along all directions are taken. In the thermodynamic limit of $N, M \rightarrow \infty$, the volume fraction $f = M/N$ varies from 0 to 1 as the model describes denser paths ranging from a dilute SAW to a Hamiltonian walk.

same methods.⁽³⁾ The best values for square and simple cubic lattices are $\mu(0) = 2.6385 \pm 0.0003$ and $\mu(0) = 4.6835 \pm 0.0010$, respectively. The quantity $\mu(0)$ is very important in computer simulation of dilute polymer chains.² For example, the survival probability of (computer-generated) chains of M sites on a regular lattice with coordination number z is proportional to $[\mu(0)/(z-1)]^M$ (all other walks are self-intersecting).

Hamiltonian walks (HW) produce the most compact packing of a single SAW, as all lattice sites are now occupied by monomers.³ For a two-dimensional square (SQ) lattice, Gujrati and Goldstein⁽⁸⁾ give the bounds

$$\mu^M(1) \leq \mu^{\text{SQ}}(1) \leq \mu^{\text{iCE}}(1) \quad (2)$$

where $\mu^M(1) = G/\pi \approx 1.338$ is the exact value of the connectivity constant of an HW on a Manhattan lattice calculated by Kasteleyn⁽⁹⁾ (G is the Catalan constant), and $\mu^{\text{iCE}}(1) = (4/3)^{3/2} \approx 1.5396$ is the analog for the six-vertex model solved by Lieb.⁽¹⁰⁾ Schmaltz *et al.*,⁽¹¹⁾ using strip methods, calculated $\mu^{\text{SQ}}(1) \sim 1.472$ in accordance with the bounds of ref. 8. To our knowledge, no data are available for Hamiltonian walks in three (or more) dimensions.

Orland *et al.*⁽¹²⁾ presented a field-theoretic representation of the problem of counting the total number of closed Hamiltonian paths on regular lattices of any dimensionality with periodic boundary conditions. They predicted the mean field value of $\mu(1) = z/e$ and showed that one-loop corrections vanish. In two dimensions and for a square lattice ($z=4$), their mean field value is surprisingly close to that of Schmaltz *et al.*⁽¹¹⁾ Unfortunately, it is not clear how to extend their elegant formulation of the Hamiltonian walk problem to the case that the walk does not visit all sites, that is, for $0 \leq f < 1$. Recently, Duplantier and co-workers have obtained interesting results for two-dimensional dense self-avoiding walks.^(6,7,13) In particular, Duplantier and Saleur⁽¹³⁾ evaluated numerically the connectivity constant $\mu^{\text{DS}}(f)$ as a function of the fraction of sites f occupied by the walk on a square lattice using transfer matrix methods, obtaining a $\mu^{\text{DS}}(f)$ which agrees nicely with the best results at $f=0$ (ref. 3) and $f=1$ (ref. 11).

In this paper we use a field-theoretic representation of self-avoiding walks on regular lattices, first proposed by Freed,⁽¹⁴⁾ to study the problem of calculating the total number of configurations of a single self-avoiding chain on a hypercubic lattice in d dimensions as it crosses over from the dilute case of $f=0$ to the Hamiltonian walk limit as f approaches one. This

² For a recent review on Monte Carlo simulation of lattice models of polymers, see Baumgartner.⁽⁴⁾ See also Kremer and Binder.⁽⁵⁾

³ For a nice description of the properties of Hamiltonian walks and a complete list of references, see Duplantier and David.⁽⁶⁾ See also Duplantier.⁽⁷⁾

field representation of the SAW problem has been used to treat the problem of packing flexible,⁽¹⁵⁾ semiflexible,⁽¹⁶⁾ and rod polymers⁽¹⁷⁾ on lattices. Also, interaction energies in polymer-solvent or blend systems and models of polymers with monomers occupying several lattice sites have been considered.^(18,19) Mean field theories are of the Flory type, but now corrections to it in powers of z^{-1} ($z = 2d$ for hypercubic lattices) can be systematically calculated, leading to good agreement between theoretical estimates and available experimental and numerical data. Previous studies⁽¹⁴⁻¹⁹⁾ have considered the many-chain limit of

$$p \rightarrow \infty, \quad N \rightarrow \infty \quad \text{with} \quad 0 < pM/N \leq 1 \quad (3a)$$

where p is the number of walks of molecular weight M , and only the dense walk case of $f \neq 0$ has been considered. Instead, here we study the thermodynamic limit of

$$M \rightarrow \infty, \quad N \rightarrow \infty \quad \text{with} \quad 0 \leq f = M/N \leq 1 \quad (3b)$$

To illustrate the theory, the connectivity constant as a function of f is evaluated. The mean field approximation is in accord with that of Orland *et al.*⁽¹²⁾ in the $f = 1$ limit. Leading corrections to second order in z^{-1} are obtained and the agreement between the calculated connectivity and available data in two and three dimensions is good. These comparisons show that mean field becomes better, and corrections to it due to bond correlations are smaller with increasing monomer volume fraction or space dimensionality. This is expected since we generate a d^{-1} expansion of the full theory and mean field is exact at $d = \infty$.

2. THE MODEL

The partition function Z_p of a monodisperse system of p self-avoiding walks of $M - 1$ steps each on a hypercubic lattice of N sites and with periodic boundary conditions admits the following exact field-theoretic representation⁽¹⁴⁾:

$$Z_p = \frac{1}{p!} \left. \frac{\partial^p Z[h, h^+]}{\partial (hh^+)^p} \right|_{h=h^+=0} \quad (4)$$

where Z is the grand partition function

$$Z[h, h^+] = \int D[\phi] D[\phi^+] [1 + X_i(\phi, \phi^+)] \exp[-H(\phi, \phi^+)] \quad (5)$$

The complex sources h and h^+ are coupled to the fields ϕ and ϕ^+ , X_i and H are functionals of these fields given by

$$X_i = \frac{h}{\sqrt{2}} \phi_{i,1}^+ + \sum_{\alpha=2}^{M-1} \phi_{i,\alpha}^+ \phi_{i,\alpha-1} + \frac{h^+}{\sqrt{2}} \phi_{i,M-1} \tag{5a}$$

$$H = \sum_{i,j} \sum_{\alpha=1}^{M-1} \phi_{i,\alpha}^+ V_{ij} \phi_{j,\alpha} \tag{5b}$$

and the measure is

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

with A such that $Z=1$ when $X_i \equiv 0, \forall i$. The subscripts i and α denote the lattice site i at the spatial position \mathbf{r}_i and the polymerization index, respectively. A complex field representation is required, as a real one would not generate the desired monodisperse system of molecular weight M .⁽¹⁴⁾ The matrix V_{ij}^{-1} (propagator) equals unity if i and j are nearest neighbors and vanishes otherwise. It is convenient to use the Fourier representation

$$V_{ij} = \sum_{\mathbf{q}} \exp[i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)] [\mathcal{N}f(\mathbf{q})]^{-1} \tag{5c}$$

where the sum over \mathbf{q} extends throughout the first Brillouin zone of the lattice, and $f(\mathbf{q})$ is the nearest neighbor structure factor

$$f(\mathbf{q}) = \sum_{i=1}^z \exp(-i\mathbf{q} \cdot \mathbf{a}_i) \tag{5d}$$

with $\{\mathbf{a}_i\}$ the vectors joining the site i at \mathbf{r}_i with its z nearest neighbors.

The partition function Z_p of Eq. (4) can be viewed as a “very large” Mp -point correlation function such that the use of Wick’s theorem⁽²⁰⁾ with the propagator of Eq. (5c) produces all possible configurations of p mutually and self-avoiding walks of $M-1$ steps each. This field representation is not restricted to hypercubic lattices, but applies to any regular lattice in d dimensions provided that the appropriate structure factor $f(\mathbf{q})$ is used in (5c). In this work we specialize to the single-chain problem ($p=1$) on a hypercubic lattice and in the thermodynamic limit of Eq. (3b).

The representation used by Orland *et al.*⁽¹²⁾ to evaluate the number of Hamiltonian circuits is similar to that of Eqs. (4) and (5). However, these authors do not introduce a polymerization index and instead fields are n -vectors in the $n \rightarrow 0$ limit. Their formulation is somewhat simpler than ours, but it only works for $f=1$.

3. THE MEAN FIELD APPROXIMATION

The mean field approximation to Eqs. (4) and (5) is obtained⁽¹⁴⁻¹⁹⁾ by just retaining the $\mathbf{q}=0$ components of the fields. Then, the one-chain partition function Z_1^{MF} can be derived from (4) and (5) after some algebra as

$$Z_1^{\text{MF}} = \frac{N!}{2(N-M)!} \left(\frac{z}{N}\right)^{M-1} \quad (6)$$

This can be understood as follows: the combinatorial factors give the number of ways of choosing M sites out of N available ones. The $(z/N)^{M-1}$ factor corrects for the fact that the chain is a connected object, so each site (but the first one) does not have about N choices, but only about z ones. This procedure counts twice each configuration, since a polymer chain does not have a direction associated to it. A Flory-Huggins type of mean field theory would replace z by $z-1$, correcting for immediate self-reversals. We will find that this is a reasonable approximation in the dilute limit, but it becomes worse as f approaches one. At $f=1$, the mean field of (6) becomes much better than the Flory-Huggins approximation. In our approach, MF theory gives the leading contribution in z^{-1} , while fluctuations induce corrections that we can systematically evaluate. In contrast, the replacement of z by $z-1$ in (6) would account for *only some* of the full corrections in powers of z^{-1} .

Using Eqs. (1) and (6) together with Stirling's formula, we obtain the mean field connectivity constant

$$\mu^{\text{MF}}(f) = (z/e)(1-f)^{-(1-f)/f} \quad (7)$$

which at $f=1$ is in agreement with that of Orland *et al.*⁽¹²⁾ The limit $f=0$ produces $\mu^{\text{MF}}(0)=z$, in disagreement with the Flory-Huggins value of $\mu^{\text{FH}}(0)=z-1$. The entropy per site is defined as

$$s = N^{-1} \ln Z_1 \quad (8)$$

in the limit (3b), and its mean field value

$$s^{\text{MF}} = f \ln(z/e) - (1-f) \ln(1-f) \quad (9)$$

vanishes at $f=0$ and reaches a maximum at $f=1-z^{-1}$. The Flory-Huggins mean field connectivity $\mu^{\text{FH}}(f)$ and site entropy $s^{\text{FH}}(f)$ are obtained from (7) and (9) just by the replacement of z by $z-1$.

4. CORRECTIONS TO MEAN FIELD

Correlations among bonds due to the chain connectivity can be fully taken into account in a systematic fashion, thus producing corrections to mean field theory in powers of z^{-1} . This is done by incorporating the $\mathbf{q} \neq 0$ modes of the fields ϕ and ϕ^+ , not included in the lowest approximation, Eq. (6). These corrections can be cast in a diagrammatic form suited to calculation. Then, the full value of the total entropy of the system, $\ln Z_1$, may be formally written as^(15,16,19)

$$\ln Z_1 = \ln Z_1^{\text{MF}} + \text{clustered diagrams} \tag{10}$$

Diagrams can be classified according to the number of bonds they contain. For example, the first correction to mean field consists of a single bond diagram as shown in Fig. 2a. The next correction contains two two-bond diagrams, as the bonds can either be sequential or nonsequential along the chain. This is illustrated in Figs. 2b and 2c. There are three three-bond diagrams shown in Figs. 2d–2f. [The many-chain problem produces one (two) additional two (three)-bond diagram(s), since bonds can now also be on different chains.] Clustered diagrams are grouped according to their topology as shown in Fig. 3.

Rules to evaluate these diagrams are obtained from Eqs. (4) and (5) by systematically including the $\mathbf{q} \neq 0$ modes of the fields. The diagrammatic rules have been derived by Bawendi *et al.*,^(15,16) and they are formulated in

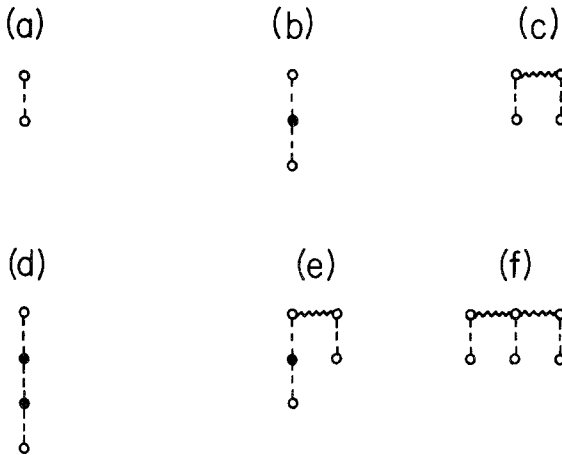


Fig. 2. Corrections to the mean-field approximation are conveniently written in terms of diagrams of m -bonds. This figure shows all possible one-, two-, and three-bond diagrams. Nonsequential bond are joined by a wiggly line.

a somewhat different but equivalent and more general form by Nemirovsky *et al.*,⁽¹⁹⁾ so they are not repeated here. We apply these rules in the form discussed in ref. 19 to evaluate the diagrams of Fig. 3. The rules remain the same as in previous work,⁽¹⁹⁾ but the weight of individual diagrams is modified, as we consider the limit of (3b) in contrast to that of (3a) studied before.⁽¹⁴⁻¹⁹⁾ Figure 3 presents all diagrams, up to $O(z^{-2})$, giving non-vanishing contributions to $\ln Z_1$ in the limit (3b). Thus, only diagrams of up to four bonds are required (in general, calculations to order z^{-m} require the evaluation of diagrams up to $2m$ bonds). The values associated with the

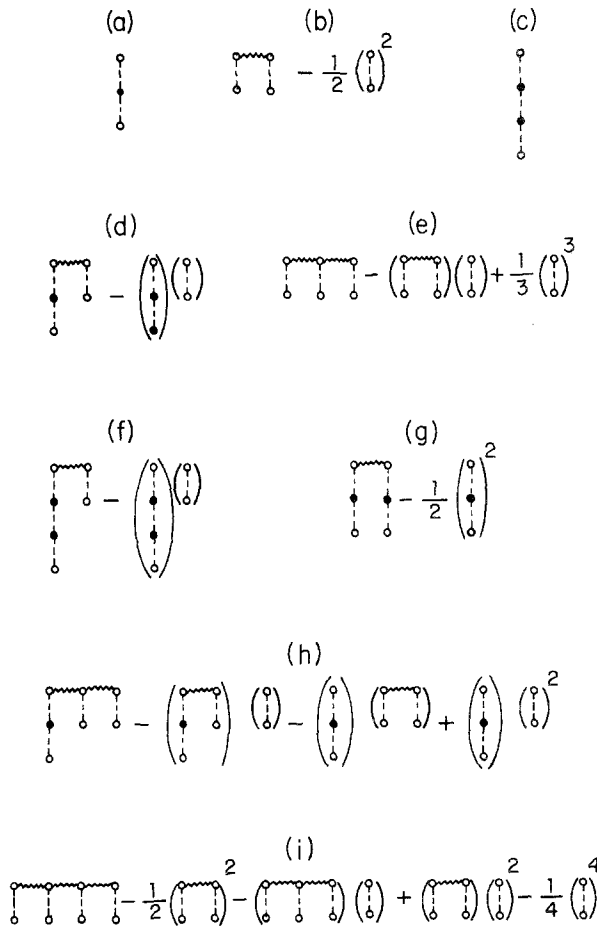


Fig. 3. All clustered diagrams to $O(z^{-2})$ contributing to the entropy of a single SAW on a hypercubic lattice and in the thermodynamic limit (3b).

diagrams of Fig. 3 are listed in Table I. Using Eqs. (1) and (10) and Table I, we obtain, to first order in z^{-1} ,

$$\ln \mu^{(1)} = \ln \mu^{\text{MF}} - (1-f)/z + O(z^{-2}) \quad (11a)$$

$$s^{(1)} = f \ln \mu^{(1)} \quad (11b)$$

and to second order

$$\ln \mu^{(2)} = \ln \mu^{(1)} + [1 - 14(1-f) + 16(1-f)^2 - 12(1-f)^3]/6z^2 + O(z^{-3}) \quad (12a)$$

$$s^{(2)} = f \ln \mu^{(2)} \quad (12b)$$

Figures 4 and 5 show the connectivity constant μ and site entropy s , respectively, as a function of the monomer volume fraction f for a self-avoiding walk on a square lattice. For comparison, we display the two MF quantities μ^{MF} and μ^{FH} (s^{MF} and s^{FH}), the second-order result $\mu^{(2)}$ ($s^{(2)}$) and the connectivity constant μ^{DS} (and site entropy s^{DS}) predicted by Duplantier and Saleur.⁽¹³⁾ The best values of $\mu(0)$ and $\mu(1)$ mentioned in the Introduction are also indicated. In either figure, all curves have the same qualitative shape. A Flory-Huggins type of mean field theory is closer to the best results than the alternative MF in the dilute limit, but it becomes much worse for a denser walk case. In fact, as remarked by Orland *et al.*,⁽¹²⁾ Eq. (7) for $f=1$ gives $\mu^{\text{MF}}(1)=4/e$, in surprisingly good agreement with the value predicted by Schmalz *et al.*⁽¹¹⁾ This is consistent

Table I. Evaluation of Diagrams to $O(z^{-2})^a$

Diagram from Fig. 3	Value of the diagram
a	$-M/z$
b	Mf/z
c	M/z^2
d	$-4Mf/z^2$
e	$8Mf/3z^2$
f	$-2Mf/z^2$
g	$(-5M + 2Mf)/2z^2$
h	$8Mf/z^2$
i	$(-6Mf + 2Mf)/z^2$

^a Values of the diagrams contributing throughout $O(z^{-2})$ to the total entropy of a single SAW of molecular weight M on a hypercubic lattice of N sites and of lattice coordination number $z=2d$; $f=M/N$ is the fraction of sites occupied by the polymer chain and the thermodynamic limit of (3b) is taken.

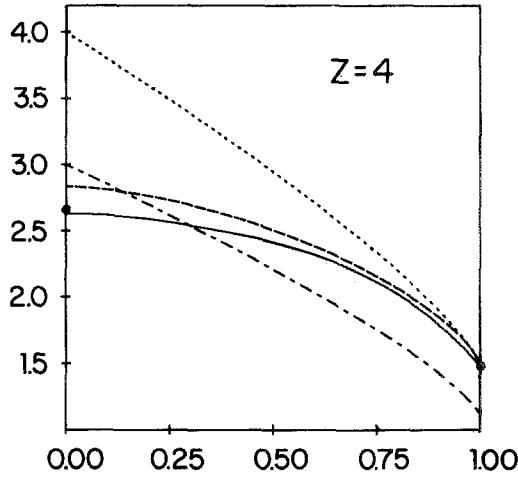


Fig. 4. Plot of the connectivity constant μ versus the volume fraction f for a single SAW on a square lattice: the dotted line is the mean field prediction [Eq. (7)], Flory-Huggins theory produces the dot-dashed line, the dashed line is the connectivity constant $\mu^{(2)}$ to $O(z^{-2})$ [Eq. (12a)], and the curve μ^{DS} (solid line) is the result of Duplantier and Saleur.⁽¹³⁾ The best values of the connectivities at $f=0$ (ref. 3) and $f=1$ (ref. 11) are indicated by black dots.

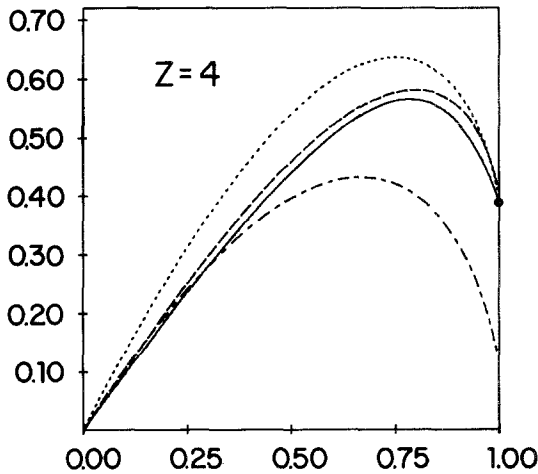


Fig. 5. Site entropy versus the volume fraction for a single SAW on a square lattice. The mean field [Eq. (9)] and the Flory-Huggins result are indicated by dotted and dot-dashed lines, respectively. The curves $s^{(2)}$ (dashed line) and s^{DS} (solid line) are our result to $O(z^{-2})$ [Eq. (12b)] and that of Duplantier and Saleur.⁽¹³⁾

with the fact that corrections to our MF theory are much more important at smaller values of the volume fraction than at larger ones. At $f=1$ first-order corrections to $\ln \mu$ vanish [see Eq. (11a)], also in accordance with the results of Orland *et al.*, in which one-loop (z^{-1}) corrections are zero for Hamiltonian circuits. Here we have also evaluated second-order corrections to $\ln \mu(1)$, which are found to be very small [Eq. (12a) for $f=1$].

When $f=0$, first-order (z^{-1}) corrections are quite important. In fact, they make $\mu^{(1)}(0)$ coincide (to this order) with the Flory–Huggins result. That is, first order at $f=0$ accounts for immediate self-reversals, changing the connectivity from z to $z-1$. However, second-order corrections, which are negative, give $\mu < z-1$, as expected. Notice that the connectivity $\mu^{\text{DS}}(f)$ is the closest to the two best results at $f=0$ and $f=1$ and that our curves become closer to that of Duplantier and Saleur as higher corrections are incorporated ($\mu^{\text{MF}}(f)$ is about 50% higher than μ^{DS} at $f=0$, but $\mu^{(2)}(0)$ is only about 7% off). First-order $\mu^{(1)}(f)$, not shown in Fig. 4, falls between mean field and $\mu^{(2)}(f)$. It is clear from Figs. 4 and 5 that our mean field overestimates the values of the connectivity and site entropy. As correlations among bonds are incorporated, the theory predicts lower values for μ and s .

Figure 6 displays the connectivity constant for a cubic lattice as a function of the volume fraction. In three dimensions, the only accurate result we are aware of is $\mu(0) \sim 4.68$, as discussed in the Introduction. Again we find the same pattern as for $d=2$. Higher-order corrections

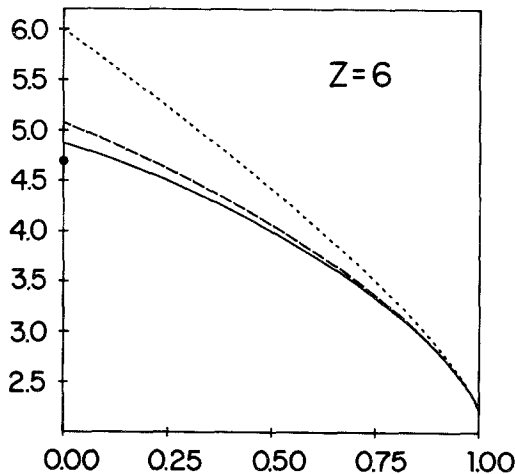


Fig. 6. The volume fraction dependence of the connectivity constant for a cubic lattice ($z=6$) with increasing order in z^{-1} : curves shown are the mean field result (dotted line) and the first-order (dashed line) and second-order (solid line) results.

predict lower values for $\mu(f)$. As walks become denser, one would expect that mean field theory improves as corrections to $O(z^{-2})$ became very small. Thus, it is likely that the predicted mean-field value at $f=1$, $\mu(1)=6/e$, is a very good approximation to the exact value. As f approaches zero, "errors" grow larger and $\mu^{MF}(0)$ and $\mu^{(2)}(0)$ are, respectively, somewhat less than 30% and about 4% higher than the best value. Again, $\mu^{(1)}$ falls between μ^{MF} and $\mu^{(2)}$. The trends found in Figs. 4, 6, and 8, which show $\mu^{MF}(f)$ and $\mu^{(2)}(f)$ in two, three, and four dimensions, respectively, confirm the expectation that corrections to MF due to bond correlations are smaller with increasing dimensionality since MF is exact at $d = \infty$. (At $d=4$ our $\mu^{(2)}(0)$ is less than 2% higher than its best known value given by Fisher and Gaunt.⁽³⁾)

Figures 5, 7, and 9 display the site entropy $s(f)$ as a function of the volume fraction f for a SAW on a hypercubic lattice in two, three, and four dimensions, respectively. Figure 5 shows that while our mean field s^{MF} always overestimates the value of the site entropy, the Flory–Huggins value s is higher than s^{DS} at very low volume fraction, but it becomes much smaller for higher values of f . The entropy per site develops a maximum at $f \gtrsim 1 - z^{-1}$. The maximum of s^{MF} at $f = 1 - z^{-1}$ moves to the right (to higher volume fraction) and becomes smaller, so approaching the Duplantier–Saleur entropy s^{DS} , as fluctuations are taken into account. The maximum of s^{FH} at $f = 1 - (z - 1)$ is further away from that of s^{DS} , and its

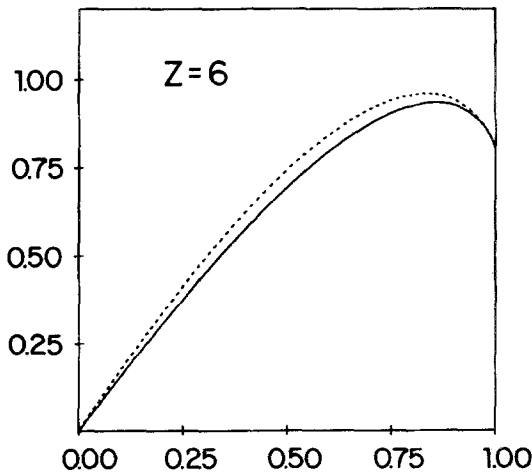


Fig. 7. Plot of the site entropy versus fraction for a single SAW on a cubic lattice ($z = 6$). The curves are the mean field entropy per site (dotted line), and the site entropies $s^{(1)}$ to $O(z^{-1})$ (dashed) and $s^{(2)}$ to $O(z^{-2})$ (solid line).

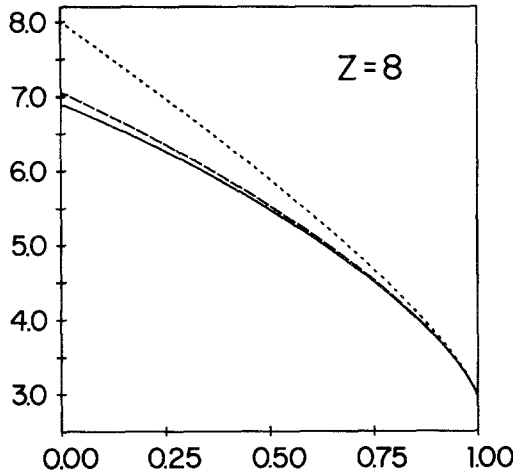


Fig. 8. Same as Fig. 6, but with $z = 8$ (hypercubic lattice in four dimensions). The lines have the same designation as in Fig. 6. Notice that the differences among the connectivity constants are somewhat smaller than those for $d = 2$ (Fig. 4) and $d = 3$ (Fig. 6).

value at $f = 1$ is much worse [compared to $s^{DS}(1)$] than those associated with $s^{MF}(f)$. Figures 7 and 9 suggest that the MF approximation for the entropy is rather good already at $d = 3$ and $d = 4$ as corrections to it grow smaller. Again, the maximum of s^{MF} , located at $f = 1 - z^{-1}$, becomes smaller moving toward higher f as corrections are incorporated.

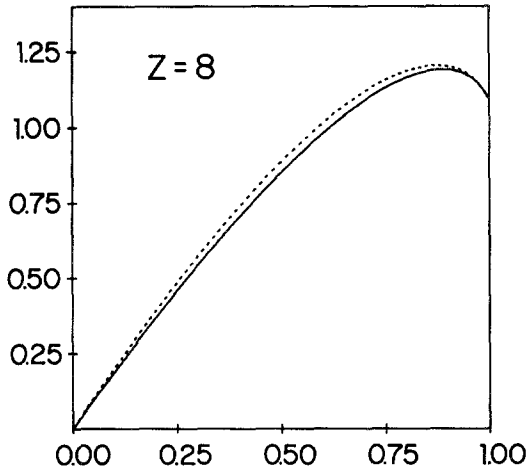


Fig. 9. Same as Fig. 7, but with $z = 8$. The lines have the same designation as in Fig. 7. As space dimensionality increases, mean field improves, and thus corrections to it become less significant.

It is now easy to understand the shape of the curve $s(f)$. At small volume fraction the entropy is low, since there are few monomers available to contribute. The maximum does not occur at $f=1$, because the presence of unoccupied sites provides more configurations to the system. As $d \rightarrow \infty$, the “orientational” entropy always overcomes the “translational” entropy. The maximum of the entropy per site is almost 50% (somewhat less than 20%) higher than the site entropy of a Hamiltonian walk for $d=2$ ($d=3$), and it occurs at $f \approx 0.80$ ($f \approx 0.86$).

5. CONCLUSIONS

Using a field-theoretic representation of a self-avoiding walk of molecular weight M on a hypercubic lattice of N sites and with lattice coordination number $z=2d$, we study the thermodynamic limit of $N, M \rightarrow \infty$ such that the monomer volume fraction $f=M/N$ remains finite with $0 \leq f \leq 1$.

The volume-fraction-dependent connectivity constant μ^{MF} and site entropy are evaluated in the mean-field approximation and contrasted against predictions of a Flory–Huggins type of mean field theory. Moreover, our approach takes fully into account correlations among bonds due to the chain connectivity, which are neglected in the lowest approximation. This produces corrections to the MF approximation in the form of powers of z^{-1} . In this work we specialize to hypercubic lattices, so $z=2d$, but the formalism can be easily applied to any regular d -dimensional lattice.

The connectivity constant and the site entropy to $O(z^{-2})$ in two dimensions are compared with accurate values at $f=0$,⁽³⁾ and at $f=1$,⁽¹¹⁾ and also against the recently numerical estimates $\mu^{\text{DS}}(f)$ of Duplantier and Saleur.⁽¹³⁾ The agreement is quite good. At higher dimensions, Figs. 6–9 suggest that our second-order results become even better, since corrections to mean field are smaller. Mean field theory also improves at higher volume fraction. At $f=1$, $\mu(1)$ coincides with the mean field connectivity predicted by Orland *et al.*⁽¹²⁾ for a Hamiltonian path and first-order (z^{-1}) corrections vanish, also in accordance with ref. 12. In addition, we have evaluated corrections to $O(z^{-2})$.

The site entropy as a function of the volume fraction is found to develop a maximum at $f \gtrsim 1-z^{-1}$. In two dimensions this maximum occurs at $f \sim 0.80$ and it is about 50% higher than the entropy per site of a Hamiltonian walk. As dimensionality increases, the maximum moves toward higher f , thus approaching $f=1$, and the difference between the maximum value of the site entropy and that of a Hamiltonian walk becomes less significant.

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