# First-Order Theory of Self-Avoiding Walks Based on Loop Exclusion

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Self-avoiding walks may be constructed through a progressive exclusion of walks with loops. A study of the process leads to critical exponents $\nu \simeq (4+D)/4D$ and $\gamma \simeq 8/(4+D)$ for dimension $4 \geq D \geq \frac{4}{3}$. The equations agree with the $\epsilon$ expansion to first order, fit the (known) values for $D = 3, 2$, and also those (suggested) for $D < 2$. The probability of an exclusion due to a loop of length $j$ appears to be asymptotically equal to $(\gamma-1)j^{-2}$, for $4 > D > \frac{4}{3}$ ("strong universality").

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Self-avoiding walks (SAW's) of length $N >> 1$ are described with the help of critical exponents $\nu$ and $\gamma$,

$$R_N^2 = AN^{2\nu}, \tag{1}$$

and

$$W_N = A'\mu^N N^{\gamma-1}, \tag{2}$$

where $R_N^2$ and $W_N$ are the mean square end-to-end distance and the number of SAW's, respectively; $A$, $A'$, and $\mu$ are lattice dependent, but $\nu$ and $\gamma$ depend on the dimension $D$ alone. For $D \geq D_c = 4$ we have the ideal values $\nu = \frac{1}{2}$ and $\gamma = 1$; at $D = 1$ SAW's constitute rigid rods, $\nu = 1$ and $\gamma = 1$. The theory of critical phenomena gives very accurate (or exact) $\nu$ and $\gamma$ for $D = 4-\epsilon$, 3, and 2.[1-3] However, the dependence on a continuous variable $1 < D < 4$ is also of great interest, e.g., in connection with attempts to relate random fractals, like percolating clusters and branched polymers, to SAW's at an equivalent (noninteger) dimension.[4,5] For that purpose one may utilize an equation $\nu = 3/(D+2)$, derived by Flory[6] with the help of a mean-field approximation. This equation disagrees with the (exact) $\epsilon$ expansion already to the first order. Still, it gives a quite accurate value for $D = 3$ and the exact values for $D = 2$ and 1, but the physical reason for its remarkably good performance is puzzling.[7] Furthermore, its validity in the region $1 < D < 2$ is uncertain in view of recent Monte Carlo experiments.[8] Finally, no similar equation has been derived for $\gamma$.

SAW's may be derived from random walks with the help of a progressive exclusion of walks with loops. A construction of SAW's through "dimerization"[8,9] offers one possible way to carry out this progressive exclusion. (Alternative constructions linked to exclusion are the conventional stepwise growth, $N \rightarrow N+1$, requiring exclusion of loops formed by the newly added step, or the progressive increase of the excluded loop length in restricted walks of constant $N$.[10]) This Letter studies in detail the loop exclusion in the course of a dimerization. On this basis it derives approximate analytical equations, correct to $O(\epsilon)$, for $\nu(D)$ and $\gamma(D)$.

Pairs of "monomer" SAW's of length $N >> 1$ are linked together to produce "dimer" walks of length $2N$. Dimers in which one half intersects the other, forming a loop, are excluded. (We need not worry about internal intersections since each monomer is a SAW.) Upon completion of the exclusion, the remaining dimers constitute an ensemble of SAW's of length $2N$. Clearly $W_{2N} = (W_N)^2 f_{\rm suc}$, where $f_{\rm suc}$ is the fraction of the ("successful") dimers in which one half does not intersect the other. In view of Eq. (2), $W_{2N} = (A'\mu^N N^{\gamma-1})^2 f_{\rm suc} = A'\mu^{2N}(2N)^{\gamma-1}$, giving

$$f_{\rm suc} \sim N^{-(\gamma-1)}. \tag{3}$$

The exclusion of dimers in which an $m$th and an $n$th segment, belonging to the first and to the second monomer, respectively, form a loop of length $j = m + n$ [see Fig. 1(a)] is carried out in a succession of steps. $n$ is varied from 1 to $N$ and, for each $n$, $m$ is varied from 1 to $N$. $\phi_{m,n,N}$ is the loop's probability at the $(mn,)$th step. More precisely, $\phi_{m,n,N}$ is the fraction of dimers in which the $m$th and the $n$th segments form the loop $j = m + n$ in an ensemble of dimers in which, on the second monomer, (i) segments 1 to $n-1$ are already completely self-avoiding with respect to the first monomer, (ii) the $n$th segment is self-avoiding for loops of length up to $j-1$ only, and (iii) segments $n+1$ to $N$ are not yet self-avoiding with respect to the first monomer. We have [using $x = \exp(\ln x)$ and expanding $\ln x$]

$$f_{\rm suc} = \prod_{n=1}^{N}\prod_{m=1}^{N}(1-\phi_{m,n,N}) = \exp\int_1^N\int_1^N(-\phi_{m,n,N}+\ldots)\,dm\,dn. \tag{4}$$

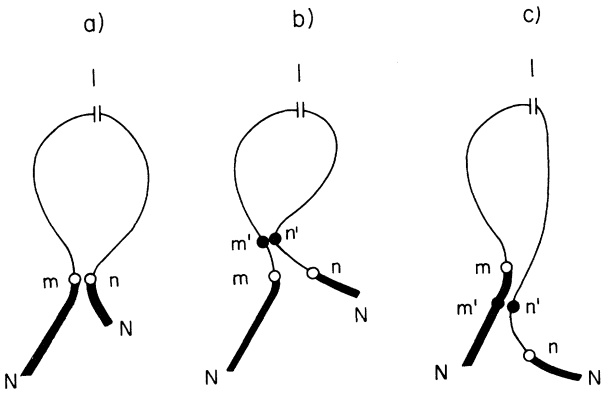


FIG. 1. Geometrical effects of the exclusion of dimers with loops: (a) Segments $m$ and $n$, on the first and second monomer, respectively, form a loop $j=m+n$; the effective dimer's length is shortened from $2N$ to $(N-m)+(N-n)=2N-j$. (b) Segments $m'<m$ and $n'<n$ form an "enclosed" loop $j'=m'+n'$, shortening the effective length between $m$ and $n$ from $j$ to $j-j'$. (c) Segments $m'>m$ and $n'<n$ form a "crossed" loop $j'=m'+n'$, shortening the effective length between $m$ and $n$ from $j$ to $m'-n'=j'-2n'$ (for $m=n=j/2$).

If we *assume*

$$\phi_{m,n,N}\rightarrow\phi_j=(\gamma-1)j^{-2},\quad \text{for } j>>1, \tag{5}$$

then Eq. (4) at once reproduces Eq. (3) to within leading order of $N$. True, other expressions, not depending on $j$ alone, might achieve as much. Yet $\phi_{m,n,N}$ should be independent of $N$, as well as of $m$ and $n$ separately, with the exception of the crossover regions $j\rightarrow N$ and ($m$ or $n$) $\rightarrow j$. Ruling out that these crossover regions provide the dominant contribution to the double integral justifies Eq. (5). Equation (5) predicts a *strong universality*, a power law independent of $D<D_c$. The coefficient equals $\gamma-1=O(\epsilon)$. Consequently, correlations between multiple loops are presumed to contribute terms of order higher than first in $\epsilon$. The present estimates are limited to the first order alone.

We now consider the increase of $R_N^2$ upon dimerization. Prior to the exclusions, the *random linking* of pairs of monomers of (average) $R_N^2$ produces dimers of $R_{2N}^{2*}=2R_N^2=2AN^{2\nu}$, with the asterisk denoting the stage preceding exclusions. Upon completion of the sequence of exclusions, we are left with true SAW's, having $R_{2N}^2=A(2N)^{2\nu}$. The corresponding swelling is

$$\Delta=R_{2N}^2/R_{2N}^{2*}=2^{2\nu-1}. \tag{6}$$

$\Delta$ is decomposed into stepwise variation

$$\Delta=\prod_{n=1}^{N}\prod_{m=1}^{N}\delta_{n,m},$$

where $\delta_{n,m}$ is the ratio of $R^2$'s, after and before the exclusion at an $(m,n)$th step. Prior to this exclusion the dimers consist of two fractions, $\phi_j$ and $1-\phi_j$, respectively, in which the $n$th and $m$th segments do, or do not, form the loop $j=m+n$. The $\phi_j$ fraction has its *effective* length shortened from $2N$ to $2N-j$ [see Fig. 1(a)]; the $1-\phi_j$ fraction is unaffected. $\delta_{n,m}$ is the ratio of (the average) $R^2$ after and prior to the exclusion of the $\phi_j$ fraction. Thus, to a first approximation,

$$\delta_{n,m}\simeq(2N)^{2\nu}/[\phi_j(2N-j)^{2\nu}+(1-\phi_j)(2N)^{2\nu}].$$

Introducing Eq. (5) and expanding $(2N-j)^{2\nu}$ in a series leads to

$$\delta_{n,m}\simeq 1+\nu(\gamma-1)/Nj. \tag{7}$$

Higher-order terms of the expansion are proportional to $(2\nu-1)(\gamma-1)=O(\epsilon^2)$ and are therefore neglected. The same applies to the neglected progressive variation of $R_x^2$ ($x=2N$ or $2N-j$) by a factor $\simeq 2^{2\nu-1}$, as $n$ varies from 1 to $N$ [cf. Eq. (6)]. Furthermore, $R^2$ of the length $2N-j$ is affected by the presence of extra "dangling" lengths $m$ and $n$. However, in view of the remark following Eq. (5), this should contribute terms that are of order higher than first in $\epsilon$. Transforming $\prod\prod\delta_{n,m}$ into $\exp[\int\int(\delta_{n,m}-1)-\dots]$ [similarly to Eq. (4)] gives $\Delta\simeq 2^{2\nu(\gamma-1)}$. Together with Eq. (6) this leads to

$$(2\nu-1)/2\nu\simeq\gamma-1. \tag{8}$$

The above estimate of the effect of exclusions on $R_{2N}^2$ may be reexpressed more formally as

$$R_{2N}^2=D^*(N_{\text{eff}})=2AN_{\text{eff}}^{2\nu}. \tag{9}$$

The notation requires explanation: The "effective" length $N_{\text{eff}}=N\times[\Delta(N^{2\nu})]^{1/2\nu}$, where $\Delta(N^{2\nu})$ denotes the swelling $\Delta=2^{2\nu(\gamma-1)}$ estimated in Eqs. (7) and (8). The present notation stresses that $\Delta$ has been computed with respect to $N$ raised to the power $2\nu$, which is the quantity associated with $R_{2N}^2$; in the expression for $N_{\text{eff}}$ the $1/2\nu$ root of $\Delta(N^{2\nu})$ is taken to express it as a length. Finally, $D^*$ denotes an operator corresponding to a *random* linking of *effective* lengths, saying "Take $N_{\text{eff}}$, raise it to power $2\nu$, multiply by $A$ [cf. Eq. (1)], and double the result, to obtain $R_{2N}^2$ of the dimer SAW's." [One easily verifies that the recipe reproduces Eq. (8).]

Equation (9) helps us to estimate a second effect of exclusions, notably upon the dependence of $\phi_j$ on $j$. We consider again the pair of segments $m$ and $n$ on the two monomers. Prior to the exclusions,

the monomers are mutually uncorrelated. Hence the probability that $m$ and $n$ intersect one another, forming the loop $j=m+n$, scales as the segments' density in a hypersphere in $D$ space, viz., $\phi_j^* \sim R_j^{-D} \sim j^{-\nu D}$. (Here we take for the sake of simplicity $m \simeq n \simeq j/2$.) This initial dependence applies to dimers in which other segment pairs, $n'$ and $m'$, may form loops $j'=m'+n'$. If $1 \leq n' < n$ (while $1 \leq m' \leq N$), such dimers are excluded in the sequence preceding the $(m,n)$th step. This causes the drop from the initial $\phi_j^*$ to $\phi_j \sim j^{-2}$ [cf. Eq. (5)], by the time the process attains the $n$th step. In analogy with Eq. (9), this drop is estimated by *assuming*

$$\phi_j \sim \phi^*(j_{\text{eff}}) \sim (j_{\text{eff}})^{-\nu D}. \tag{10}$$

Here, however, $j_{\text{eff}}=j\times[\Delta(j^{-2})]^{-1/2}$. Or, the effect of exclusions is estimated with respect to the *reciprocal square length*, $j^{-2}$, since this quantity is associated with $\phi_j$. Except for that difference, the estimation of $\Delta(j^{-2})$ parallels entirely that of $\Delta(N^{2\nu})$ before. At an $(m',n')$th step the dimers consist of two fractions, $\phi_{j'}$ and $1-\phi_{j'}$, respectively, with or without the loop $j'=m'+n'$. We first consider the case $m' < m$ [illustrated in Fig. 1(b)], where an "enclosed" loop $j'$ shortens the effective length between $m$ and $n$ from $j$ to $j-j'$. Similarly to $\delta_{n,m}$ the ratio of the reciprocal square lengths, after and prior to the exclusion of the $\phi_{j'}$ fraction, is estimated as $\delta(j^{-2})_{n',m'<m} \simeq j^{-2}/[\phi_{j'}(j-j')^{-2}+(1-\phi_{j'})j^{-2}]$. For a "crossed" loop, $m' > m$ (see Fig. 1(c)], the length is shortened from $j$ to $j'-2n'$, for $j' < j+2n'$ (for longer $j'$ there is no effect). $\delta(j^{-2})_{n',m'>m}$ is therefore estimated correspondingly, with $(j'-2n')^{-2}$ replacing $(j-j')^{-2}$. The total variation, $\Delta(j^{-2})$, is obtained by taking products of $\delta(j^{-2})_{n',m'}$ over $m'$ and $n'$. Passing to integrals [again, as in Eq. (4)] gives

$$\Delta(j^{-2}) \sim j^{-2(\gamma-1)}, \tag{11}$$

where the decrease is shared equally by the enclosed and crossed loops. [It is important to note that $\Delta(j^{-2})$ diverges with $j$, whereas $\Delta(N^{2\nu})$ is merely equal to a factor; this difference seems to be related to the additional divergence of small intersegmental distances.[11]] From Eq. (11) it follows that $j_{\text{eff}}=j\times[\Delta(j^{-2})]^{-1/2} \sim j^{\gamma}$. Introducing this into Eq. (10) and comparing with Eq. (5) leads to

$$\phi_j \sim j^{-\gamma\nu D} \sim j^{-2}. \tag{12}$$

Therefore $\gamma\nu D=2$. Combining this result with Eq. (8) gives

$$\nu=(4+D)/4D, \tag{13a}$$

and

$$\gamma=8/(4+D). \tag{13b}$$

Expansion at $D=4-\epsilon$ gives $\nu=\frac{1}{2}(1+\epsilon/8+\epsilon^2/32)$ and $\gamma=1+\epsilon/8+\epsilon^2/64$ which agrees with the correct expansion[1] to first order, but gives a much too small second-order term. At $D=3$, present results are $\nu=0.583$ and $\gamma=1.142$ to be compared with the accurate estimate[2] $\nu=0.588$ and $\gamma=1.162$. At $D=2$ the result reproduces the presumably exact value[3] $\nu=\frac{3}{4}$ and gives $\gamma=\frac{4}{3}$, believed until recently to be exact, but slightly smaller than the very recent[3] $\gamma=1.344$. Throughout $2 \leq D \leq 3$, Eq. (13a) and the Flory equation differ very slightly. For $D<2$, however, Eq. (13a) predicts a much steeper increase, comparable to that of Ref. 8. Thus Ref. 8, Eq. (13a), and the Flory equation give, respectively, $\nu(1.5)=0.94$, 0.92, and 0.86; $\nu(\frac{4}{3})=1$, 1, and 0.90. Below $D=\frac{4}{3}$, Eq. (13a) gives a nonphysical $\nu>1$. This is interpreted as a transition to rigid rods, $\nu=1$, already at $D=\frac{4}{3}$; at that point $\gamma$ reaches $\frac{3}{2}$.

The strong universality of progressively excluded loops, $\phi_j \sim j^{-2}$ for $D<D_c$ (above $D_c$ one has the ideal $\phi^0 \sim j^{-D/2}$), plays a major role here. A similar power law has been proposed[12,13] for somewhat differently defined "tadpole" loops; see, however,, Ref. 14. (The present loops are relevant to a construction of SAW's through dimerization, $N \rightarrow 2N$; the tadpole loops are relevant to the stepwise construction $N \rightarrow N+1$.) Finally, one should note that the basic assumptions of the present and the Flory theory are entirely different. In the Flory theory, the (mean-field) binary repulsions are balanced by the (ideal) entropy of stretching, both terms greatly overestimated.[7] Here $\nu$ (of swelling) and $\gamma$ (of exclusion) become interrelated; first, because exclusion causes swelling, and second, because swelling decreases exclusion, keeping it at the marginal level $\phi_j \sim j^{-2}$. A more negative power would make the exclusion negligibly small; a less negative power would lead to a tearing exponential increase of $R_N^2$ with $N$ [as can be verified by following Eqs. (7) and (8)].

[1]P. G. de Gennes, Phys. Lett. **38A**, 399 (1973).

[2]C. Le Guillou and Z. Zinn-Justin, Phys. Rev. B **21**, 3876 (1980).

[3]B. Nienhuis, Phys. Rev. Lett. **49**, 1062 (1982).

[4]Z. Alexandrowicz, "Conjecture Relating Percolation, Branched Polymers and Linear Walks" (to be published).

[5]R. Rammal, G. Toulouse, and J. Vannimenus, J. Phys. (Paris) **45**, 389 (1984).

[6]P. J. Flory, J. Chem. Phys. **17**, 303 (1949).

[7]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979), pp. 43–46.

[8]Z. Alexandrowicz, Phys. Rev. Lett. **50**, 736 (1983).

[9]Z. Alexandrowicz, J. Chem. Phys. **51**, 561 (1969).

[10]Z. Alexandrowicz, Phys. Rev. Lett. **43**, 366 (1979).

[11]J. des Cloizeaux, J. Phys. (Paris) **41**, 223 (1980).

[12]C. Domb and F. T. Hioe, J. Phys. C **3**, 223 (1970).

[13]Z. Alexandrowicz, Phys. Lett. **78A**, 98 (1980).

[14]The author of Ref. 11 calculates a power law differing in $O(\epsilon^2)$ from the reciprocal square dependence; still he considers the case of tadpole loops of $j \ll N$ while those relevant to the stepwise construction are in the range $j \rightarrow N$.