Estimation of connective constants for two-dimensional lattices from self-avoiding walks in the two-dimensional continuum

Gustavo A. Arteca* and Shuangxi Zhang
Département de Chimie et Biochimie, Laurentian University, Ramsey Lake Road, Sudbury, Ontario, Canada P3E 2C6
(Received 8 June 1998)

The attrition rate of random walks with excluded volume, $\langle P_{W\to W'}\rangle$, represents the mean number of ''failed'' (or ''rejected'') chains between any two successfully embedded *independent* configurations W and W'. In this work, we study $\langle P_{W\to W'}\rangle$ as a function of the number of monomers and the excluded volume interaction for chains in the two-dimensional continuum. Our result can also be applied to lattice models, provided that an ''effective'' radius of excluded volume is introduced. The relation between the $\langle P_{W\to W'}\rangle$ values in the continuum and in lattice models leads to a simple analytical approximation for the connective constants of all common two-dimensional lattices.
[S1063-651X(98)02211-9]

PACS number(s): 05.50.+q, 87.15.By, 02.70.Lq

Polymers in solution behave as flexible molecules, whose instantaneous spatial configurations can be approximated by random walks on a lattice or the continuum [1]. In this work, we are interested in some properties of two-dimensional (2D) polymers. These models are a convenient tool to study adsorption and critical phenomena on surfaces [2]. When modeling polymer behavior in a good solvent [3], two approaches are commonly followed: random walks with excluded volume interaction in the 2D continuum, or self-avoiding walks (SAW's) embedded in a particular 2D lattice. Here, we discuss some relations between these two models.

In our case, we deal with the simplest SAW model, one where chains have n identical monomers (i.e., the ''nodes'' or ''vertices'' of the walk). Many properties of this model have been well characterized [4]. A great deal of work has been devoted to study the mean shape properties of SAW's, in particular their leading scaling behavior [5]. The nature of the corrections to scaling in a number of properties still remains controversial, particularly in two dimensions [6].

A key property of a *lattice* model in dimension d is the number of allowed SAW configurations with n nodes (or ''entropy'' of the walks), denoted by c_n. Although no mathematical proof yet exists, numerical evidence shows that c_n obeys asymptotic power-law scaling [4]:

$$c_n \approx \alpha \mu^n n^{\gamma-1}, \quad n \gg 1, \tag{1}$$

where μ is the lattice-dependent *connective* (or ''connectivity'') *constant*. This quantity measures the effective coordination of the nodes in a long SAW. (It also corresponds to the reciprocal of the critical point singularity in the susceptibility.) The *critical* (or ''susceptibility'') *exponent* γ is believed to be universal, i.e., it only depends on the dimensionality of the lattice. In the case of $d=2$, a nonrigorous argument provides what is believed to be the *exact* values for these parameters in the *honeycomb lattice* [7]: $\mu=(2+2^{1/2})^{1/2}=1.8477...$ and $\gamma=43/32$ (where γ should be the same for all 2D lattices). The exact values of μ for other 2D lattices are not known, although numerical estimations and some rigorous bounds are available [8]. The best current estimates appear in the last column of Table I [9–11]. (The four 2D lattices discussed here are indicated in Fig. 1. We shall use the shorthand notation HC lattice, *K* lattice, *S* lattice, and *T* lattice when referring to the honeycomb, Kagomé, square, and triangular lattices, respectively.)

Connective constants are important parameters in the modeling of lattice polymers, since they can be used for computing some configurationally averaged physical properties. In this work, our goal is to estimate the different connective constants by using *a single unified approach*. To this end, we will establish a relationship between walks with excluded volume in the 2D continuum and SAW's in particular 2D lattices. Since all the lattices are particular cases of the continuum, the latter can provide insights on underlying common properties not available from single-lattice studies. Testing this conjecture is one of the objectives of the present work.

Our basic idea is as follows. Consider random walks with n nodes and constant bond length b, generated in the con-

TABLE I. Estimated connective constants for the 2D lattices in Fig. 1. [The parameter r_-, computed from the density of nodes δ in a lattice, underestimates the effective excluded-volume radius. The connective constants $\mu(r_{ex})$ are computed by using Eq. (7) with various approximations for r_{ex} in terms of r_-. ''Exact'' results correspond to numerical estimates in the *K*, *S*, and *T* lattices. The result for the HC lattice is an analytical conjecture based on 2D spin models.]

Lattice	r_-/b	$\mu(r_-)$	$\mu(2r_-)$	$\mu(3r_-/2)$	μ (''exact'')
HC	0.643	2.023	1.525	1.796	1.84775906...[a]
K	0.606	2.730	2.123	2.451	2.555[b]
S	0.564	2.766	2.220	2.512	2.6381585[c]
T	0.525	4.198	3.459	3.851	4.150781[d]

[a]Reference [7].
[b]Reference [9].
[c]Reference [10].
[d]Reference [11].

*Author to whom correspondence should be addressed.

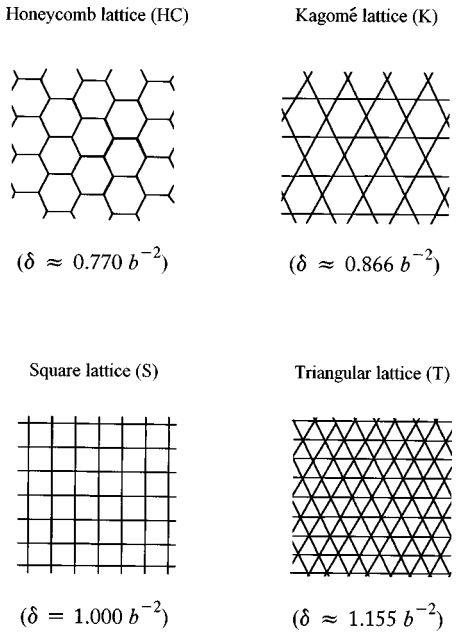

FIG. 1. Four 2D lattices studied in this work. The density of nodes δ is given below each lattice. (The density δ is defined as the number of effective nodes per unit cell divided by the area of the cell, measured in units of the lattice spacing b.)

tinuum using a *naive* Monte Carlo simulation. In this approach, chains are ''grown'' step by step subject to two criteria: (i) there are no bond-bond intersections (i.e., self-avoidance); (ii) *nonconnected* nodes are never closer to each other than a distance r_{ex} (i.e., excluded volume interaction). Chains that fail either criterion during ''growth'' *are rejected and not continued*. The result is an ensemble of strictly independent (uncorrelated) chain configurations W_i. These chains are a subset of all the possible chains in the continuum (or a lattice), and they span a fraction $V(\{W_i\})$ of configurational space volume. This fraction can be estimated with the *configurational transition probability* w_t. (The value w_t is defined as the probability that two chain conformers W and W', generated *consecutively* by a naive Monte Carlo algorithm, are in the set of ''accepted'' configurations $\{W_i\}$.) In a lattice, w_t can be expressed as the ratio between the number of SAW's and the total number of all possible n-node walks in the lattice, that is,

$$w_t = c_n / k^n, \quad n \gg 1, \tag{2}$$

where k is the number of nearest neighbors in the lattice (i.e., those at a distance b). In a d-dimensional hypercubic lattice, $k=2d$. For the lattices in Fig. 1, the values are $k_{HC}=3$, $k_K=4$, $k_S=4$, and $k_T=6$. The probability w_t is also related to the *mean attrition rate*, $\langle P_{W\to W'}\rangle$, representing the mean number of rejected chains between two accepted (*independent*) conformers W and W':

$$w_t = \langle P_{W\to W'}\rangle^{-1}. \tag{3}$$

The mean attrition rate of the walks describes the well-known phenomenon of ''critical slowing down'' of naive Monte Carlo searches, where the production of acceptable conformers becomes more and more difficult as n or r_{ex} increase. This phenomenon is particularly severe in two dimensions, since long chains on a plane have a larger chance to violate self-avoidance than chains in 3-space. A number of improved Monte Carlo searches have been designed to remedy the configurational attrition [4]. In our case, we will actually profit from the critical slowing down to produce estimations of connective constants.

In the 2D continuum, $\langle P_{W\to W'}\rangle$ depends only on n and $y=r_{ex}/2b$, the dimensionless excluded volume radius, where $y\in(0,1)$. Our first goal is to construct an expression for $\langle P_{W\to W'}\rangle$ as a function of n and y. Second, by using Eqs. (1) and (2), we will derive conclusions for the connective constants in 2D lattices.

Two important properties must be noted. In the limit $y\to 0^+$, nodes can be close, but the walks are still self-avoiding, since there are no bond-bond intersections. In the limit $y\to 1^-$, there is *only one* possible polymer configuration: the linear rod. In this case, the attrition rate must *diverge* for all $n>2$. Thus, qualitatively, $\langle P_{W\to W'}\rangle$ would be expected (i) to increase (possibly exponentially) with n for a fixed y value and (ii) to have a singularity [possibly $(1-y)^{-\sigma}$, $\sigma>0$] for all $n>2$. We have tested these conjectures by computing $\langle P_{W\to W'}\rangle$ in random walks with variable n and y. The 2D chains were generated by the naive Monte Carlo approach discussed before, using steps of constant length b. (When comparing with 2D lattices, the parameter b will be the lattice spacing.) For every pair of values (n,y), we monitored the number of rejected conformers, $P_{W_i\to W_{i+1}}$, between two consecutive ''accepted'' configurations W_i and W_{i+1}. The mean attrition rate is then computed by averaging $P_{W_i\to W_{i+1}}$ over 1000 pairs of consecutive ''accepted'' conformers. (We have verified the reliability of our sampling by checking the scaling behavior of the mean radius of gyration of the ''accepted'' chains, $\langle R_G^2\rangle^{1/2}\sim n^{\nu}$. With the same configurations used to calculate $\langle P_{W\to W'}\rangle$, we obtain $\nu\approx 0.75\pm 0.02$ in good agreement with the exact result, $\nu=3/4$ [7].)

The evaluation of $\langle P_{W\to W'}\rangle$ is computationally intensive for chains with $n>100$ (for all y values) and for short chains with $y>0.5$. (For example, at $y=\frac{2}{3}$, the mean number of rejected conformers increases rapidly from $\langle P_{W\to W'}\rangle \approx 7082$ to $\langle P_{W\to W'}\rangle \approx 2.76\times 10^8$ when the chain length is doubled from $n=15$ to $n=30$.) For this work, we have computed $\langle P_{W\to W'}\rangle$ for seven y values spanning a wide range of excluded volumes ($y=1/3000$, 1/6, 1/3, 1/2, 2/3, 5/6, and 11/12). For each y value, we have evaluated $\langle P_{W\to W'}\rangle$ in chains with variable length. For low excluded volume ($y=1/3000$), we carried out simulations with $n=10,15,20,...,80$. For the highest excluded volume ($y=11/12$), we produced results only for chains with $n=5,6,7,...,15$. For intermediate values of y, we have computed $\langle P_{W\to W'}\rangle$ in at least eight different chain lengths (see Fig. 2). In all cases, the simulations employ a powerful random number generator with period $\sim 2\times 10^{18}$ [12].

Our numerical results (Fig. 2) confirm the exponential growth of the mean attrition rate with n for all y values. All linear regressions of the type $\ln\langle P_{W\to W'}\rangle$ versus n have correlation coefficients $\mathcal{C}\geqslant 0.9999$. Thus, we propose the following general form for the mean attrition rate:

$$\langle P_{W\to W'}\rangle = a(y)\zeta(y)^n. \tag{4}$$

From the slopes in Fig. 2, it is clear that the function $\zeta(y)$

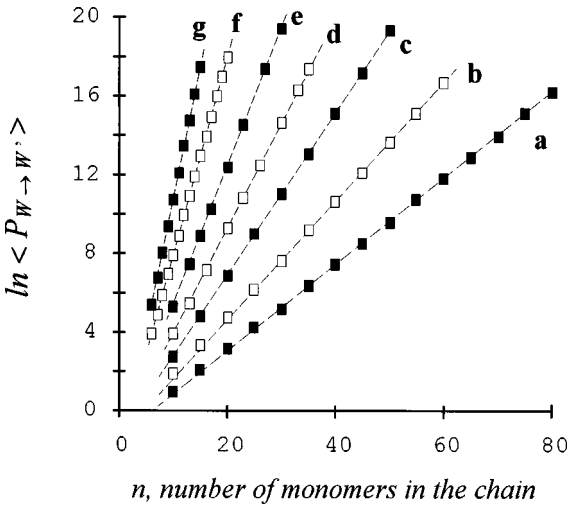

FIG. 2. Dependence of the rate of attrition in the 2D continuum as a function of the number of monomers and the excluded volume. [The letters indicate different values of the excluded volume variable $y=r_{ex}/2b$, where $y=1/3000$ (a), 1/6 (b), 1/3 (c), 1/2 (d), 2/3 (e), 5/6 (f), and 11/12 (g).]

diverges at $y\to 1^-$. Our results for $\zeta(y)$ as a function of $(1-y)$ show a singularity, characterized with good precision as

$$\zeta(y)=B(1-y)^{-s}, \quad B=1.25\pm 0.02, \quad s=0.44\pm 0.01, \tag{5}$$

with $\mathcal{C}=0.9997$ and 95% confidence intervals. Equation (5) is the main result needed for our present discussion. Nevertheless, we have also analyzed the preexponential $a(y)$ in Eq. (4). After examining several fitting schemes, its most accurate two-parameter representation appears to be

$$a(y)=\frac{A(1-y)}{(2-y)^p},$$

$$\text{where } A=0.98\pm 0.02, \quad p=1.9\pm 0.1, \tag{6}$$

with $\mathcal{C}=0.9966$ and 95% confidence intervals. [Note that the numerator in Eq. (6) still ensures the divergence of $\langle P_{W\to W'}\rangle$ at $y\to 1^-$, since $1-ns<0$ for all $n\geqslant 3$.]

We have checked the robustness of the fitting in Eq. (5) by performing correlations of the following form: $\ln\{(2-y)^2\langle P_{W\to W'}\rangle/(1-y)\}$ versus $\ln(1-y)$, at *constant n values*. When pooling our data for all y and $10\leqslant n\leqslant 30$, we obtain (i) a slope accurately represented as $(-0.44\pm 0.03)n$ and (ii) an intercept that increases linearly as $\sim(0.225\pm 0.025)n$, with correlation coefficients $\mathcal{C}\geqslant 0.9991$. These results agree well with the numerical values in Eq. (5). [Note that $\exp(0.225\pm 0.025)=1.252\pm 0.031$.] In summary, within the accuracy of our simulations, Eqs. (4)–(6) provide a detailed representation of the dependence of the mean attrition rate with chain length and excluded volume.

If we now substitute our expression for $\langle P_{W\to W'}\rangle$ into the transition probability w_t [Eqs. (2) and (3)], we deduce a relation between the SAW's and the excluded volume effects in the continuum, i.e., $\zeta^{-n}=a\alpha n^{\gamma-1}(\mu/k)^n$. After retaining the dominant terms for $n\to\infty$, it becomes $\zeta^{-1}=\mu/k$. This identity establishes a link between the effect of an excluded volume interaction (contained in ζ) and the connective constant μ. In other words, we can now define a formal excluded-volume-dependent ''connective constant'' for walks in the 2D continuum, $\mu=\mu(r_{ex})$. Conversely, this result also allows one to associate an ''effective'' (or mean) excluded volume to the connective constant μ for a given lattice. Using Eq. (5), we obtain our main result:

$$\mu(r_{ex})=kB^{-1}(1-r_{ex}/2b)^s. \tag{7}$$

Equation (7) is a heuristic representation of the connective constant of *any* 2D lattice. It describes μ in terms of *the size of a region, centered at a lattice node, where other nodes are effectively excluded as monomers of a SAW*. The radius of such a region can be estimated from the compactness of the lattice. Here, we will use the *node density in a 2D lattice* as a measure of compactness.

Let δ be the number of nodes per unit area in a 2D lattice, with b the lattice spacing. The parameter δ is easily computed from the number of nodes belonging to a unit cell. For example, the T lattice has a triangular unit cell [with $\mathcal{A}=b^2\sin(\pi/3)/2$, where $\mathcal{A}$ denotes area], each of whose vertices belong to six neighboring cells. As a result, each cell contains effectively $\frac{1}{2}$ node, and thus we get $\delta_T=1/(2\mathcal{A})=2b^{-2}/3^{1/2}$. Similarly, each cell in the S lattice contains one effective node and $\delta_S=b^{-2}$. A similar analysis for the HC and K lattices gives $\delta_{HC}=4b^{-2}/3^{3/2}$ and $\delta_K=3^{1/2}b^{-2}/2$, respectively. (Note that the unit cell in the K lattice has *eight* vertices, two of which are shared by two cells each, and six of which belong to three cells simultaneously. Thus, each unit cell contains effectively three vertices.) Finally, if we associate a disklike area δ^{-1} with each vertex, we obtain a low estimate for a radius of excluded volume as the radius of this disk, i.e., $r_-=(\pi\delta)^{-1/2}$. The choice $r_{ex}=r_-$ should overestimate the μ value, since it is equivalent to considering only compact chains (i.e., chains whose nodes have high coordination). In contrast, a reasonable high estimate for the radius of excluded volume would be $2r_-$, considering the distance between nodes placed at the centers of their respective disks. Thus, we conjecture that a good first approximation to an effective excluded volume could be the average between these two values, i.e., $r_{ex}=3r_-/2$.

We have tested these ideas using Eq. (7) for the connective constants, where r_{ex} is given its various approximations in terms of δ. Our results appear in Table I for the lattices in Fig. 1. As indicated by Table I, our $\mu(r_{ex})$ values represent good approximations to the actual numerical estimates for μ [7,9–11]. As expected, $\mu(r_-)$ overestimates μ (''exact''), whereas $\mu(2r_-)$ is an underestimation. The values computed with the average effective excluded volume, $\mu(3r_-/2)$, have (at worst) only a 7% deviation from the ''exact'' results. [Empirically, the ''exact'' results for μ could be fitted by using $r_{ex}=\varepsilon r_-$, where ε is a lattice-dependent constant. The numerical values for ε decrease from 1.394 in the HC lattice to 1.071 in the T lattice, following an approximately linear dependence with the lattice density δ. This result indicates that a better representation of the effective radius of excluded volume could include a correction factor in terms of δ with respect to the expression $r_{ex}\sim r_-=(\pi\delta)^{-1/2}$. A rough estimation suggests $r_{ex}=2(\pi\delta)^{-1/2}-\mathcal{O}(\delta^m)$, with $m\sim 0.5$.]

In conclusion, Eq. (7) appears to provide a simple analytical (and semiquantitative) expression for the connective constant of any 2D lattice. The present computation of μ requires only two pieces of information: the number of first neighbors in the lattice (k), and a measure of excluded volume in terms of the node density (δ). Without any major changes, the present approach could thus be extended to study the attrition rate of walks in the 3D continuum, as a tool to estimate the connective constants of common 3D lattices.

In principle, our μ estimates could be improved by refining the fitting of $\langle P_{W\rightarrow W'}\rangle$ with longer chains, and by devising better measures of effective excluded volume. Nevertheless, our main result lies in the evidence presented that the properties of the continuum *can be used* to relate different lattices. Note that the continuum contains the 2D lattices as particular examples, and therefore it provides the framework for a unified description valid for all lattices.

In closing, we note that our main results are based on numerical (nonrigorous) evidence for the mean attrition rate. We believe that this work should stimulate research on the analytical (rigorous) behavior of $\langle P_{W\rightarrow W'}\rangle$ as a function of chain length and excluded volume.

This work was supported by FRUL (Laurentian) and by grants from NSERC (Canada).

[1] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience Publishers, New York, 1969); S. G. Whittington, Adv. Chem. Phys. **51**, 1 (1982); M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1988).

[2] R. Vilanove and F. Rondelez, Phys. Rev. Lett. **45**, 1502 (1980); M. T. Batchelor and C. M. Yung, *ibid.* **74**, 2026 (1995).

[3] P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979); J. des Cloizeaux and G. Jannick, *Polymers in Solution: Their Modelling and Structure* (Oxford University Press, New York, 1990).

[4] N. Madras and G. Slade, *The Self-Avoiding Walk* (Birkhäuser, Boston, 1996); A. D. Sokal, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford University Press, New York, 1995).

[5] A. J. Guttmann, J. Phys. A **17**, 455 (1984); **22**, 2807 (1989); B. Li, N. Madras, and A. D. Sokal, J. Stat. Phys. **80**, 661 (1995); J. Douglas, C. M. Guttman, A. Mah, and T. Ishinabe, Phys. Rev. E **55**, 738 (1997); S. Caracciolo, M. S. Causo, and A. Pelissetto, *ibid.* **57**, R1215 (1998).

[6] Z. Djordjevic, I. Majid, H. E. Stanley, and R. J. Santos, J. Phys. A **16**, L519 (1983); D. C. Rapaport, *ibid.* **18**, L39 (1985); J. W. Lyklema and K. Kremer, Phys. Rev. B **31**, 3182 (1985); D. L. Hunter, N. Jan, and B. MacDonald, J. Phys. A **19**, L543 (1986); J. Dayantis and J. F. Palierne, Macromol. Theory Simul. **5**, 1143 (1996); S. R. Shannon, T. C. Choy, and R. J. Fleming, J. Chem. Phys. **105**, 8951 (1996).

[7] B. Nienhuis, Phys. Rev. Lett. **49**, 1062 (1982); J. Stat. Phys. **34**, 731 (1984).

[8] T. Hara, G. Slade, and A. D. Sokal, J. Stat. Phys. **72**, 479 (1993).

[9] M. E. Fisher and M. F. Sykes, Phys. Rev. **114**, 45 (1959).

[10] A. J. Guttmann and I. G. Enting, J. Phys. A **21**, L165 (1988).

[11] A. J. Guttmann and J. Wang, J. Phys. A **24**, 3095 (1991).

[12] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran* (Cambridge University Press, Cambridge, 1992), pp. 271–273.