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Zipping transition in a model of two crosslinked polymers

Peter Leoni[1,3], **Carlo Vanderzande**[1,2] **and Luc Vandeurzen**[1]

[1] Departement WNI, Limburgs Universitair Centrum, 3590 Diepenbeek, Belgium
[2] Instituut Theoretische Fysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, 3001 Heverlee, Belgium

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Abstract
We study a model of two self-avoiding walks that are allowed to cross. An attractive energy is associated with each crossing. We present a number of exact results on the free energy of this model and show the existence of a zipping temperature, below which the number of crossings becomes macroscopic. We give heuristic arguments which show that in $d = 2$ and $d = 3$ this zipping transition occurs at infinite temperature. Exact enumeration and Monte Carlo simulations on the square lattice strongly support this conjecture and lead to a precise value for the crossover exponent.

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1. Introduction

Polymers in a good solvent are usually modelled as self-avoiding walks [1, 2]. There exists by now an extensive literature on the critical and topological properties of single self-avoiding walks, which should describe the situation of an extremely diluted polymer solution.

On the other hand, much less is known on the properties of a collection of several self-avoiding walks, which can either cross each other or can be mutually avoiding. Such situations occur naturally when studying networks of crosslinked polymers [3].

The first simple step in studying the implications of crosslinking on polymer properties consists of investigating the behaviour of two polymers that are close to each other in space and that can interact through attractive or repulsive interactions. This leads to models for pairs of self-avoiding walks with mutual interactions. Several models of this type have been investigated recently. In some of these, the two polymers are considered to be *mutually avoiding* and are thought to represent the two strands of DNA [4]. One is then, in particular, interested in the denaturation transition where the two strands decouple. Models of this kind have also been discussed in the context of diblock copolymers [5, 6].

[3] Aspirant Fonds voor Wetenschappelijk Onderzoek-Vlaanderen.

In this paper, we investigate in detail a model of two self-avoiding walks which are allowed to cross each other an arbitrary number of times. An attractive energy is associated with each crossing. One expects that below a certain transition temperature the two polymers share a macroscopic number of monomers, in which case we call the polymers *zipped*. In recent years, the zipping transition in this kind of model has been studied mainly on fractal lattices [7–9].

Here we investigate the Euclidean case. We present a number of rigorous results that hold in arbitrary dimension, together with a detailed numerical investigation of the model on the square lattice. Therefore, we performed both exact enumerations and Monte Carlo simulations using the pivot algorithm.

We would like to point out that besides the situations described above, the present model is also relevant for the behaviour of the self-avoiding walk (SAW) in a random environment [10–12]. Indeed, in their study of the *directed* polymer in a random environment (DPRM), Cook and Derrida [13] show how a model of two *random walks*, that gain an energy -1 at each mutual intersection point, can lead to an upper bound for the transition temperature T_c of the DPRM. Above that transition, randomness is irrelevant and the critical properties of the DPRM are just those of ordinary random walks. Moreover, the free energy of the DPRM equals its annealed average with probability one. Below the transition temperature, randomness is relevant, the quenched and annealed free energy become different and the properties of the DPRM are described by those of a zero temperature strong disorder fixed point. It is easy to check that exactly the same ideas apply to the SAW in a random medium. In that case as well, it is in principle possible to obtain information on the transition temperature below which disorder becomes relevant, from a study of the behaviour of two SAWs with an attractive energy associated to each crossing. We, therefore, hope that the results presented here could be a first step in further understanding of the problem of a SAW in a random medium.

This paper is organized as follows. In section 2 we define the model and its main properties of interest. In section 3 a number of exact results on the free energy and the order parameter are presented. In section 4, we give an heuristic argument on the location of the zipping temperature and a first estimate of the associated crossover exponent. We then present the results from our numerical investigation of the model. Finally, in section 5 some concluding remarks are given.

2. The model

Let $\mathcal{L}$ be some regular d-dimensional lattice. An N-step self-avoiding walk (N-SAW) ω on $\mathcal{L}$ is a sequence of distinct points $(\omega_0, \omega_1, \ldots, \omega_N)$ in $\mathcal{L}$ such that each point is a nearest neighbour of its predecessor. We assume that all the walks begin at the origin ($\omega_0 = 0$). Let Ω_N be the set of N-step walks starting at the origin. The cardinality of Ω_N is denoted as c_N. It is known that the number of different N-SAWs grows exponentially in N. One can show rigorously that [2]

$$\lim_{N\to\infty} \frac{1}{N} \ln c_N = \ln \mu \tag{1}$$

where μ is a lattice-dependent constant, called the *connective constant*. As an example, for the square lattice, μ is known to high accuracy $\mu = 2.638159 \pm 0.000002$ [14].

Another quantity of interest is any measure of the size of the N-SAWs. One can think in particular of the end-to-end distance or the radius of gyration. The average squared size of all N-SAWs, denoted as $\langle R_N^2 \rangle$, is generally believed to grow as a power of N,

$$\langle R_N^2 \rangle \sim N^{2\nu}. \tag{2}$$

The exponent ν is a universal quantity. Its value equals $\nu = 3/4$ in $d = 2$ [15].

Now consider pairs of N-SAWs $\left(\omega^{(1)}, \omega^{(2)}\right)$ with the same starting point and let the number of vertices they have in common be denoted as $I\left(\omega^{(1)}, \omega^{(2)}\right)+1$. We define $g_N(I)$ as the number of pairs of SAWs that have $I+1$ vertices in common. With each crossing (apart from the starting point) we associate an energy -1. The equilibrium statistical mechanics of this model is then determined by the following (canonical) partition function (for fixed size N):

$$T_N(\beta) = \sum_{I=0}^{N} g_N(I)\, \exp(\beta I) \tag{3}$$

where β is the inverse of the temperature T. $\beta = 0$ corresponds to the case that the polymers are independent (i.e. infinite temperature), $\beta < 0$ to a repulsive interaction between the two walks and $\beta > 0$ to attractive interactions. We expect that there exists a critical temperature β_z such that for $\beta > \beta_z$, and for large N, the two SAWs share a macroscopic number of vertices. In that case we call the two SAWs *zipped*. In this paper we investigate the transition from the zipped to the unzipped phase, mostly for the square lattice.

The free energy of the zipping model (in the thermodynamic limit) is given by

$$t(\beta) = \lim_{N\to\infty} \frac{1}{N} \ln T_N(\beta). \tag{4}$$

Unfortunately, it is not possible to prove rigorously that the limit in (4) exists for all values of β, but we establish partial proofs in the next section.

The expected number of intersections between two N-SAWs is given by

$$\langle I_N \rangle (\beta) = \frac{1}{T_N(\beta)} \sum_{I=0}^{N} I g_N(I)\, \exp(\beta I) = \frac{\mathrm{d}}{\mathrm{d}\beta} \ln T_N(\beta)$$

so that the expected fraction of crossings is given by

$$\langle m_N \rangle (\beta) = \frac{\langle I_N \rangle (\beta)}{N}. \tag{5}$$

This quantity is closely related to the order parameter

$$m(\beta) := \frac{\mathrm{d}}{\mathrm{d}\beta} \lim_{N\to\infty} \frac{1}{N} \ln T_N(\beta) = \frac{\mathrm{d}}{\mathrm{d}\beta} t(\beta). \tag{6}$$

3. Some exact results about the zipping problem

In this section we prove that the free energy function $t(\beta)$ exists for $\beta \leqslant 0$ and has to be non-analytic at some point and hence there must exist an (inverse) critical temperature β_z, which we call the *zipping temperature*. In the second part of this section, we reduce our configuration space $\Omega_N \times \Omega_N$ to a smaller one for which we can prove rigorously that the free energy exists. If we assume the existence of the free energy, we will be able to derive a number of mathematical properties for $t(\beta)$ and $m(\beta)$.

3.1. Existence of a phase transition

For $\beta \leqslant 0$, we can bound the partition sum $T_N(\beta)$ as follows:

$$T_N(-\infty) \leqslant T_N(\beta) \leqslant T_N(0). \tag{7}$$

However, $T_N(0)$ is just the partition function of two non-interacting SAWs and is therefore given by c_N^2. Moreover, at $\beta = -\infty$, the only remaining term in (3) is the term with $I = 0$.

This means that the only contribution in the partition sum comes from the pairs of SAWs with only one crossing, i.e. the origin. Any such pair (ω_1, ω_2) can be seen as a SAW of length $2N$ in two distinct ways, depending on the chosen starting point. However, the pair (ω_2, ω_1) gives rise to the same two SAWs of length $2N$. Hence, we see that the number of such pairs $g_N(0)$ is the same as the number of $2N$-step walks c_{2N}. After taking the appropriate limits in (7) we obtain for $\beta \leqslant 0$

$$2 \ln \mu \leqslant t(\beta) \leqslant 2 \ln \mu.$$

These inequalities prove the existence of the free energy for negative β-values and moreover they show that

$$t(\beta) = 2 \ln \mu \qquad \beta \leqslant 0. \tag{8}$$

Next, we obtain from (3) the lower bound for the partition function for $\beta \geqslant 0$

$$T_N(\beta) \geqslant g_N(N) \exp(\beta N) \geqslant c_N \exp(\beta N) \tag{9}$$

where the last term in (3) represents the term for which the two SAWs coincide. If we also assume the existence of the free energy for positive β-values, we have

$$t(\beta) \geqslant \ln \mu + \beta. \tag{10}$$

Together (8) and (10) show that $t(\beta)$ is non-analytic and that there must exist a zipping temperature

$$0 \leqslant \beta_z \leqslant \ln \mu \tag{11}$$

such that $t(\beta) = 2 \ln \mu$, for $\beta \leqslant \beta_z$ and $t(\beta) > 2 \ln \mu$ for $\beta > \beta_z$.

Finally, it is also possible to find an upper bound for $t(\beta)$ for positive β-values. In that case, we have for $\beta \geqslant 0$

$$T_N(\beta) \leqslant c_N^2 \exp(\beta N) \tag{12}$$

and thus

$$t(\beta) \leqslant 2 \ln \mu + \beta. \tag{13}$$

Both bounds tell us that for $\beta \geqslant 0$

$$\ln \mu + \beta \leqslant t(\beta) \leqslant 2 \ln \mu + \beta. \tag{14}$$

3.2. Convergence of the free energy for a subclass

In the previous subsection we have seen that it is not possible to prove the existence of the free energy for $\beta > 0$. Following tradition in the field [2, 16] we, therefore, turn to the subclass of unfolded walks for which existence of the free energy can usually be more easily proved. In some cases, such as that of a SAW near a surface or interface [16], existence of the free energy for a subclass can be used as a lemma in proving the existence of the free energy for the class of all SAWs. For the present case, we were not able to perform a similar final step. Nevertheless, we think that existence of the free energy for the unfolded walks is interesting in itself and we, therefore, present a proof below.

A self-avoiding walk $\omega \in \Omega_N$ can be written as $(\omega_0, \ldots, \omega_N)$ where each ω_i is a site of a regular lattice. Consider next the particular case of a d-dimensional hyper cubic lattice and denote the last coordinate of ω_i as y_i. Then, we define the subset of the *unfolded* walks $\mathcal{C}_N \subset \Omega_N$ as the set of all N-SAWs satisfying

$$0 = y_0 \leqslant y_i < y_N \qquad \forall i = 1, \ldots, N-1. \tag{15}$$

Now, consider the set $\mathcal{L}_N$ containing all pairs of N-step walks from $\mathcal{C}_N$ with the same ending point, i.e.

$$\mathcal{L}_N := \left\{ \left(\omega^{(1)}, \omega^{(2)}\right) \in \mathcal{C}_N \times \mathcal{C}_N : \omega_N^{(1)} = \omega_N^{(2)} \right\}. \tag{16}$$

The cardinality of $\mathcal{L}_N$ is written as p_N and the number of such pairs with $I+1$ sites in common is denoted as $p_N(I)$. The set of these latter pairs is written as $\mathcal{L}_{NI}$. As in the more general problem, we associate an energy -1 to every site the walks in the pair have in common (apart from the origin). This leads to the introduction of the partition sum

$$L_N(\beta) = \sum_{I=0}^{N} p_N(I)\ \exp(\beta I). \tag{17}$$

We shall prove that the free energy for this class exists, i.e.

$$l(\beta) := \lim_{N\to\infty} \frac{1}{N} \ln L_N(\beta) \tag{18}$$

converges for every β.

Therefore, fix $N,\ N'$ and $I,\ I'$ arbitrary in $\mathbb{N}$. Let $\left(\omega^{(1)},\ \omega^{(2)}\right) \in \mathcal{L}_{NI}$ and $\left(\Gamma^{(1)},\ \Gamma^{(2)}\right) \in \mathcal{L}_{N'I'}$. We then construct $\left(\Upsilon^{(1)},\ \Upsilon^{(2)}\right) \in \mathcal{L}_{N+N',I+I'}$ by concatenating $\Gamma^{(i)}$ with $\omega^{(i)}$ (for each $i = 1, 2$). This concatenation is performed in a standard way [2], i.e. by putting the starting point of $\left(\Gamma^{(1)},\ \Gamma^{(2)}\right)$ on the end point of $\left(\omega^{(1)},\ \omega^{(2)}\right)$. Thanks to (15) the results $\Upsilon^{(i)}$ are indeed self-avoiding for each i. It follows that

$$p_N(I) \cdot p_{N'}(I') \leqslant p_{N+N'}(I + I'). \tag{19}$$

Let us next fix β and consider the product of the partition functions $L_N(\beta)$ and $L_{N'}(\beta)$:

$$\begin{aligned} L_N(\beta) \cdot L_{N'}(\beta) &= \sum_{I=0}^{N} \sum_{I'=0}^{N'} p_N(I) p_{N'}(I)\ \exp[\beta(I + I')] \\ &\leqslant \sum_{I=0}^{N} \sum_{I'=0}^{N'} p_{N+N'}(I + I')\ \exp[\beta(I + I')] \\ &\leqslant (N + N' + 1) L_{N+N'}(\beta). \end{aligned}$$

So we see that $\ln L_N(\beta)$ satisfies the generalized subaddivity with respect to the array $\ln(N+1)$ and since

$$\sum_{N=0}^{\infty} \frac{\ln(N+1)}{N(N+1)} < \infty$$

we know [17] that for each β

$$\lim_{N\to\infty} \frac{\ln L_N(\beta)}{N}$$

exists in $]-\infty, +\infty]$. However, for each β the partition function is bounded,

$$\begin{aligned} L_N(\beta) &= \sum_{I=0}^{N} p_N(I)\ \exp(\beta I) \leqslant (2d)^N \sum_{I=0}^{N} \exp(|\beta|\, I) \\ &\leqslant (2d)^N (N+1)\ \exp(|\beta|\, N) \leqslant (4d)^N\ \exp(|\beta|\, N) \end{aligned}$$

where d denotes the dimension. When we take the logarithm and divide by N we see that for each $\beta,\ 1/N \ln L_N(\beta)$ is bounded by $\ln(4d) + |\beta|$ so that the free energy $l(\beta)$ exists and is finite for all β.

3.3. General properties of the free energy

If we *assume* the existence of the free energy $t(\beta)$, then we can prove a number of mathematical properties. More precisely, we prove the following assertions:

(i) The free energy is non-decreasing with β.
(ii) The free energy is a convex function, i.e. $\forall\ \beta_1,\ \beta_2$ and $\forall 0 < p < 1$:

$$t(p\beta_1 + (1-p)\beta_2) \leqslant p\,t(\beta_1) + (1-p)\,t(\beta_2).$$

(iii) The free energy is bounded in every interval in β.
(iv) The free energy is a continuous function that possesses left-hand and right-hand derivatives.
(v) The right-hand derivative is not less than the left-hand derivative and both derivatives increase with β.
(vi) The derivative $t'(\beta)$ exists, except perhaps for an enumerable set of values.
(vii) The convergence of the row

$$\left(\frac{1}{N}\ln T_N(\beta)\right)_{N=1}^{\infty}$$

is in fact uniform over any bounded interval in β.

We now prove these statements.

(i) This is trivial.
(ii) To establish the convexity of $t(\beta)$, we first prove that $\ln T_N$ is a convex function. Because this latter function is bounded from above in each interval in β, it is sufficient to prove [18] that for all β_1 and β_2

$$\ln T_N\left(\frac{1}{2}\beta_1 + \frac{1}{2}\beta_2\right) \leqslant \frac{1}{2}\left(\ln T_N(\beta_1) + \ln T_N(\beta_2)\right).$$

This is essentially a simple application of the Cauchy–Schwarz inequality:

$$\begin{aligned} T_N(\beta_1)\cdot T_N(\beta_2) &= \sum_{I=0}^{N}\left(\sqrt{g_N(I)}\,\mathrm{e}^{\beta_1 I/2}\right)^2 \sum_{I'=0}^{N}\left(\sqrt{g_N(I')}\,\mathrm{e}^{\beta_2 I'/2}\right)^2 \\ &\geqslant \left(\sum_{I=0}^{N} g_N(I)\,\mathrm{e}^{(\beta_1+\beta_2)I/2}\right)^2 \\ &= T_N^2\left(\frac{\beta_1+\beta_2}{2}\right). \end{aligned}$$

Taking the logarithm yields the desired result. However, the limit (point-wise) of convex functions is again convex. This can easily be seen. Take $\beta_1, \beta_2 \in \mathbb{R}$ and $p \in]0, 1[$:

$$\begin{aligned} t\,(p\beta_1 + (1-p)\beta_2) &= \lim_{N\to\infty}\frac{1}{n}\ln T_N\,(p\beta_1 + (1-p)\beta_2) \\ &\leqslant \lim_{N\to\infty}\frac{1}{n}\left[p\ln T_N(\beta_1) + (1-p)\ln T_N(\beta_2)\right] \\ &= pt(\beta_1) + (1-p)t(\beta_2) \end{aligned}$$

where we used extensively the assumption that the free energy (as a limit) exists.
(iii) The fact that the free energy is bounded in every interval in β is a direct consequence of the bounds (14).
(iv) A convex function that is bounded in every interval can be proved to be continuous and to possess left-hand and right-hand derivatives everywhere.

(v) Moreover, in the theory of convex functions one can also show that the right-hand derivative is not less than the left-hand derivative and that both derivatives increase with β.

(vi) Under the same conditions one can also prove that the derivative exists except perhaps for an enumerable set of values.

(vii) Since $T_N(\beta)$ is given by

$$T_N(\beta) := \sum_{I=0}^{N} g_N(I)\ \exp(\beta I)$$

we see that $1/N \ln T_N(\beta)$ is a analytic function of β. We can bound this set of functions uniformly (i.e. independent of n) as follows (for $\beta > 0$):

$$\beta \leqslant \frac{\ln c_N}{N} + \beta \leqslant \frac{\ln T_N(\beta)}{N} \leqslant 2\frac{\ln c_N}{N} + \beta \leqslant 2\ln(2d) + \beta$$

where d is the dimension. For any compact interval in β, the set of analytic functions $1/N \ln T_N$ is bounded uniformly and therefore this set has to be equicontinuous [19]. For every equicontinuous set of functions that converge pointwise to a function $t(\beta)$, it can be shown that the convergence is uniform [19]. So we conclude that we have a uniform convergence on any compact interval in β.

3.4. The order parameter

We now show that the order parameter is zero in the high-temperature phase ($\beta \leqslant \beta_z$) and becomes one in the limit of zero temperature ($\beta \to \infty$). Remember that

$$m(\beta) = \frac{\mathrm{d}}{\mathrm{d}\beta} \lim_{N\to\infty} \frac{1}{N} \ln T_N(\beta) = \frac{\mathrm{d}}{\mathrm{d}\beta} t(\beta). \tag{20}$$

Since for $\beta \leqslant \beta_z$ the free energy is constant, we immediately see that $m(\beta) = 0$ for $\beta \leqslant \beta_z$. On the other hand, we now show that $m(\beta) \to 1$ for $\beta \to \infty$. Observe that $m(\beta)$ is the derivative of the convex function $t(\beta)$ (we proved the existence of this derivative except for perhaps an enumerable set of points). Property (v) ensures us that $m(\beta)$ is non-decreasing. We now show that this function is bounded by 1. For this purpose, suppose that there exists β_0 such that $m(\beta_0) > 1$. We then know that the tangent through $t(\beta_0)$ cuts the upper bound (14) of $t(\beta)$ in $\beta = (2\ln\mu + \beta_0 m(\beta_0) - t(\beta_0))/(m(\beta_0) - 1)$. Since the function $t(\beta)$ is convex, we know that it lies above the tangent and hence it has to cut the upper bound as well. This leads to a contradiction and we conclude that

$$m(\beta) \leqslant 1 \qquad \forall\beta.$$

Because any non-decreasing, bounded function has to converge, we know that $\lim_{\beta\to\infty} m(\beta)$ exists.

Next, we show that it has to converge to 1. Suppose that

$$\lim_{\beta\to\infty} m(\beta) = 1 - \lambda$$

for some $\lambda > 0$. This means that

$$(\forall\varepsilon > 0)\,(\exists M > 0)\,(\forall\beta \geqslant M)\,(|m(\beta) - (1-\lambda)| < \varepsilon)\,.$$

In particular we can choose $\varepsilon = \lambda/2$. Then there is an $M > 0$ such that for all $\beta \geqslant M$

$$m(\beta) \leqslant 1 - \lambda/2.$$

If we apply the mean value theorem of Lagrange to $t(\beta)$, we derive the existence of $c \in]\beta_z,\ \beta[$ such that

$$m(c) = \frac{t(\beta) - t(\beta_z)}{\beta - \beta_z} = \frac{t(\beta) - 2\ln\mu}{\beta - \beta_z}.$$

We now show that m is non-decreasing, so that $m(c) \leqslant m(\beta)$, together with the lower bound (14) on $t(\beta)$

$$(\ln\mu + \beta) - 2\ln\mu \leqslant t(\beta) - 2\ln\mu = m(c)(\beta - \beta_z) \leqslant m(\beta)\beta \leqslant (1 - \lambda/2)\beta.$$

And hence for all $\beta \geqslant M$

$$\frac{\lambda}{2}\beta \leqslant \ln\mu$$

which clearly leads to a contradiction. We can conclude that

$$\lim_{\beta\to\infty} m(\beta) = 1. \tag{21}$$

We can also show that for any finite β, the order parameter is the limit of the fraction of shared sites, i.e.

$$m(\beta) = \lim_{N\to\infty} \langle m_N \rangle(\beta). \tag{22}$$

This follows immediately from property (*vii*) that says the row

$$\left(\frac{1}{N}\ln T_N(\beta)\right)_{N=1}^{\infty}$$

converges uniformly over any bounded interval in β, since we can interchange derivatives and limits for uniformly convergent series of functions.

4. Numerical results

Having established the existence of a zipping temperature, we now want to obtain more information on the location of β_z and if possible about the critical exponents associated with this transition. Unfortunately, we have not been able to put a more rigorous bound on β_z than that given above, i.e. $0 \leqslant \beta_z \leqslant \ln\mu$. However, we can give several arguments that show $\beta_z = 0$ exactly in two dimensions and probably also in three dimensions. The first one is an intuitive, geometrical, argument that is known under the name of codimension additivity and which goes back to Mandelbrot [20]. The second and third argument use numerical techniques such as exact enumerations and dynamic Monte Carlo methods.

4.1. Codimension additivity

From (22) and the fact that $m(\beta) > 0$ in the zipped phase, we have

$$\langle I_N \rangle(\beta) \sim N \qquad \beta > \beta_z. \tag{23}$$

In the unzipped phase, we expect

$$\langle I_N \rangle(\beta) \approx c \qquad \beta < \beta_z \quad N \gg 1 \tag{24}$$

where c is some constant (in N). Finally, at the zipping temperature, one can expect from the analogy with such problems as the adsorption of a SAW onto a hyperplane [21] and from general scaling arguments that

$$\langle I_N \rangle(\beta_z) \sim N^{\varphi} \tag{25}$$

where $\varphi < 1$ is the *crossover exponent*. Hence, only at the zipping transition should the number of contacts grow as a power (strictly less then 1) of N.

The *codimension additivity* argument says that the codimension of the intersection points of two D-dimensional (fractal) objects is given by the sum of their codimensions, i.e. by $2\,(d - D)$, where d is the dimension of the embedding space. Hence, if D_I is the fractal dimension of the set of intersection points, one obtains

$$D_I = 2D - d. \tag{26}$$

This intuitive argument implies, e.g. in $d = 3$, that two generic lines do not intersect, whereas two arbitrary planes have a line as intersection. The argument can be established as a theorem for two transversal manifolds [22]. For statistical fractals such as SAWs, it probably holds only approximately, but it is still of interest to see what we learn from the set of intersections of two SAWs [4].

The fractal dimension of a SAW is $D = 1/\nu$. Hence (26) predicts that the dimension of the intersection points of two SAWs in $d = 2$ equals $D_I = 2/3$. Therefore, we expect the number of intersection points N_I to grow as

$$N_I \sim (R_N)^{D_I} \sim N^{\nu D_I} \sim N^{1/2} \qquad (d = 2). \tag{27}$$

In three dimensions the ν-exponent of a SAW is not known exactly but the Flory-value $\nu = 3/5$ gives a very good estimate. Hence we find to a good approximation

$$N_I \sim N^{1/5} \qquad (d = 3) \tag{28}$$

Finally, for $d \geqslant 4$ (where ν takes on the random walk value $1/2$) we get

$$N_I \sim N^{(4-d)/2} \qquad (d \geqslant 4) \tag{29}$$

In these considerations we did not take into account any interaction between the SAWs hence they could be of relevance at $\beta = 0$ in the zipping problem. Comparing (27) and (28) with (25) we are led to the conclusion that in $d = 2$ and $d = 3$, the non-interacting SAWs are precisely at the zipping point and that in $d = 2$, $\varphi = 1/2$, while in $d = 3$, $\varphi \approx 1/5$. In $d \geqslant 4$, from (29), we predict that $\beta_z > 0$.

This argument by itself is too rough to believe but further evidence for its correctness can be given. For example, exact renormalization group calculations of the zipping problem on Sierpinski gasket type fractals were performed by Kumar and Singh [7]. For the case of a simple Sierpinski gasket with $d = \ln 3/\ln 2$ it was shown that indeed $\beta_z = 0$ exactly. Moreover, the crossover exponent was also determined exactly with the result $\varphi = 0.7491$. On the other hand, using the exactly known fractal dimension of the SAW on a Sierpinski gasket $D = 1/\nu = \log(2.3819)/\log(2)$, the codimension additivity argument leads to the (approximate) prediction $\varphi_a = 0.7342$, which is indeed very close to the exact value.

In later work, the same authors studied generalized Sierpinski gaskets with a rescaling factor b [8]. In table 1 we compare for a few b-values the exactly determined φ-value with those coming from the codimension argument.

As can be seen, one obtains from the codimension argument estimates for the crossover exponent that are correct up to a few percent. A similar trend holds for larger b values where approximate values for ν and φ were obtained from a Monte Carlo renormalization study [9].

Below we present numerical results that show, on the square lattice also, $\beta_z = 0$. Moreover, the value of the crossover exponent turns out to be very close to $1/2$.

[4] Equation (26) was also obtained in [8] on the basis of finite-size scaling.

Table 1. Estimates φ_a of the crossover exponent as determined from the codimension additivity argument, compared with the exact value [8]. The second column and third column give respectively the fractal dimension of the gasket and the ν-exponent of the SAW.

Sierpinski parameter b	d_f	ν	φ_a	Exact value of φ
2	1.5849	0.7986	0.7342	0.7491
3	1.6309	0.7936	0.7056	0.7246
4	1.6609	0.7884	0.6905	0.7117
5	1.6826	0.7840	0.6808	0.7042

4.2. Exact enumerations

The method of exact enumerations as applied to the zipping problem consists of generating all pairs of SAWs on a computer and counting how many intersections they have. Due to the exponential growth of this number, one is limited to rather small systems. Using a standard backtracking technique, we were able to generate the coefficients $g_N(I)$ for pairs of SAWs on the square lattice for N up to 14 (see table 2, and define $g_0(I) = \delta_{I,0}$). From these data we can calculate several thermodynamic quantities for finite systems, which in turn lead to estimates of β_z and φ.

Firstly, we investigate the behaviour of the fraction of shared sites $\langle m_N \rangle(\beta)$,

$$\langle m_N \rangle(\beta) = \frac{\mathrm{d}}{\mathrm{d}\beta}\frac{1}{N}\ln T_N(\beta) = \frac{1}{T_N(\beta)}\sum_{I=0}^{N} I g_N(I)\,\exp(\beta I). \tag{30}$$

Plots of this quantity for different N-values are shown in figure 1. From the intersection points of the curves for different N, finite size estimates of β_z can be obtained. Unfortunately, these do not allow us to accurately estimate the location of the zipping temperature in the thermodynamic limit. In the inset of figure 1 we show the average number of crossings between the two SAWs at infinite temperature. If this point corresponds to the zipping temperature these data should follow the power law (25). We see that there is a reasonable fit with this assumption and moreover we obtain as a first estimate $\varphi = .68 \pm .02$ (from a log–log plot of the data with $N \geqslant 9$).

The second derivative of the free energy

$$\begin{aligned} C_N(\beta) &= \frac{\mathrm{d}^2}{\mathrm{d}\beta^2}\frac{\ln T_N(\beta)}{N} \\ &= \frac{1}{N}\left[\frac{1}{T_N(\beta)}\sum_{I=0}^{N} I^2 g_N(I)\mathrm{e}^{\beta I} - \left(\frac{1}{T_N(\beta)}\sum_{I=0}^{N} I g_N(I)\mathrm{e}^{\beta I}\right)^2\right] \\ &= \frac{1}{N}\left[\left\langle I_N^2\right\rangle(\beta) - (\langle I_N\rangle(\beta))^2\right] \end{aligned}$$

gives a specific heat-like quantity $C_N(\beta)$. In figure 2 we show this quantity for different values of N. As could be expected when a second order phase transition is present, there is a peak in the specific heat that grows with N. The location of this peak $\beta_m(N)$ shifts to higher temperatures when N is increased. From the theory of finite-size scaling it follows that $\beta_m(N)$ approaches its $(N \to \infty)$-limit with a power law. We verified that our data are consistent with this type of convergence and the assumption $\beta_z = 0$.

In the inset of figure 2 we show the maximum value of the specific heat $C_N(\beta)$ versus N. This quantity grows as

$$C_N(\beta_m) \sim N^{2\varphi-1}. \tag{31}$$

Table 2. The coefficients $gN(I)$ obtained by exact enumerations on the square lattice for lengths up to $N = 14$.

I	$N=1$	$N=2$	$N=3$	$N=4$	$N=5$	$N=6$	$N=7$
0	12	100	780	5 916	44 100	324 932	2374 444
1	4	32	336	2 040	17 112	116 216	912 648
2		12	136	1 464	11 200	90 208	683 496
3			44	464	6 288	48 096	428 656
4				116	1 584	22 872	212 520
5					372	5 096	86 168
6						980	16 664
7							2 988

I	$N=8$	$N=9$	$N=10$	$N=11$
0	17 245 332	124 658 732	897 697 164	6444 560 484
1	6 348 344	47 895 656	336 679 592	2483 937 608
2	5 171 728	38 432 984	283 878 552	2080 000 160
3	3 157 816	25 471 816	185 802 176	1429 252 984
4	1 901 224	15 542 240	124 257 456	966 255 528
5	821 608	8 183 416	67 700 584	578 121 080
6	294 376	3 251 600	33 058 016	299 229 808
7	50 576	1 027 496	11 833 840	132 418 384
8	8 052	160 504	3 360 776	43 510 872
9		23 380	478 112	11 231 232
10			63 732	1466 064
11				181 060

I	$N=12$	$N=13$	$N=14$
0	46 146 397 316	329 712 786 220	2351 378 582 244
1	17 522 509 064	127 590 211 512	900 808 708 088
2	15 157 903 344	109 989 170 344	794 657 453 648
3	10 354 082 824	77 587 671 112	558 960 250 616
4	7 378 438 288	55 776 597 560	415 728 001 944
5	4 518 295 216	36 086 342 064	273 590 657 880
6	2 580 260 304	21 393 298 248	171 731 368 512
7	1 229 281 704	11 296 447 376	95 094 944 616
8	501 685 656	5049 942 624	47 285 608 752
9	151 539 024	1898 840 144	19 691 049 952
10	35 599 448	531 605 584	6874 344 608
11	4 319 832	114 982 960	1784 949 432
12	492 604	12 969 968	356 997 976
13		1384 284	37 628 712
14			3 762 156

When, as predicted above, $\varphi = 1/2$, this divergence should be replaced by a logarithmic one. From a simple log–log fit of these data, we get the rough estimate $\varphi = .69$. We have also tried some more sophisticated analysis methods on our enumeration results, but these failed to give better insight in the problem, mainly due to the shortness of the series.

In conclusion, the exact enumeration data are consistent with the prediction $\beta_z = 0$. The value of the crossover exponent seems to be considerably higher then the prediction coming from the codimension additivity argument. However, from the study of such problems as the theta point of SAWs [23, 24] or branched polymers [25, 26], it is known that in general

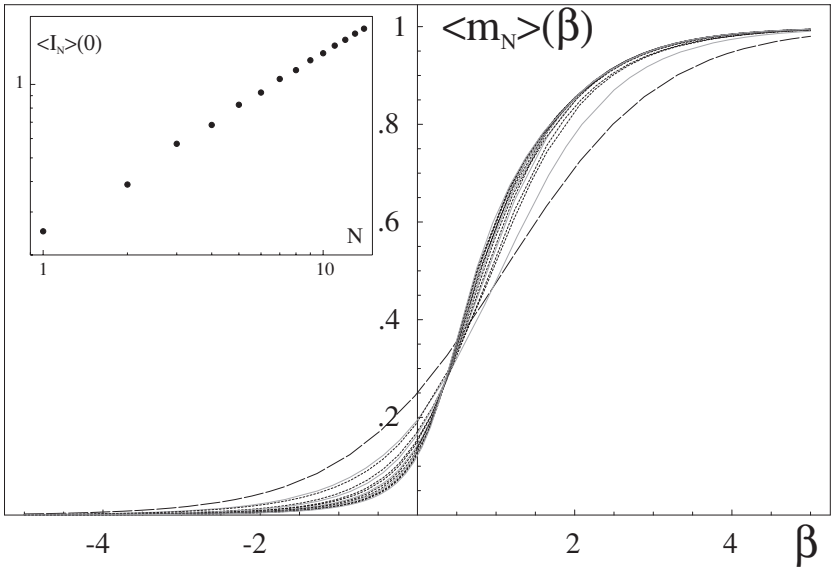

Figure 1. The average fraction of crossings $\langle m_N \rangle(\beta)$ for different N-values as obtained from the exact enumerations. The inset shows (on a log–log plot) the average number of crossings at $\beta = 0$ as a function of N.

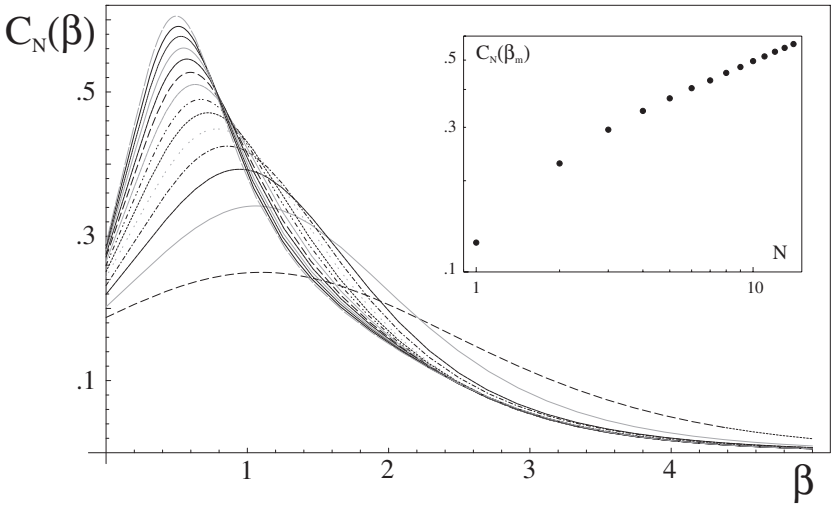

Figure 2. The specific heat $C_N(\beta)$ for $N = 1, \ldots, 14$ as obtained from the exact enumerations. The inset shows (on a log–log plot) the maximum value of the specific heat as a function of N.

a precise determination of the crossover exponent from exact enumeration data can be quite difficult. For that reason, we also studied the zipping problem using a Monte Carlo technique.

4.3. Monte Carlo simulations

The idea of dynamic Monte Carlo methods (applied to the zipping model) is to invent a (discrete-time) Markov chain with state space $\Omega_N \times \Omega_N$, and having $\pi(\omega_1, \omega_2) =$

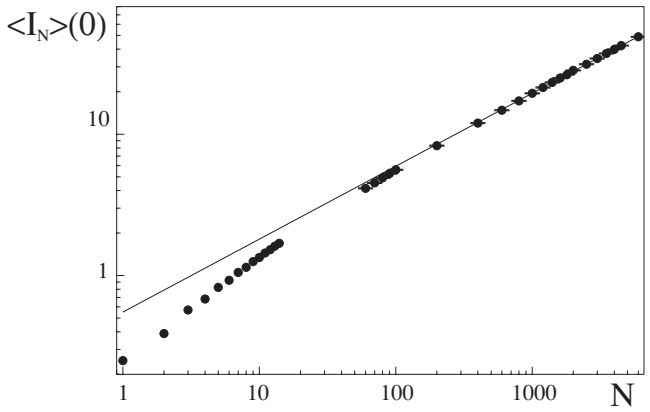

Figure 3. Log–log plot of the average number of crossings for the zipping problem in $d = 2$ at $\beta = 0$ as obtained from the exact enumerations (full circles) and the pivot algorithm (full circles with error bars corresponding to a 95% confidence level). Also shown is a straight-line fit through the data for the largest N values.

$\exp(\beta I(\omega_1, \omega_2))/T_N(\beta)$ as its unique equilibrium distribution. Starting from an arbitrary initial configuration, once the system has reached equilibrium, we measure time-averages, which converge (as the run-time tends to infinity) to π-averages. To ensure that there exists only one equilibrium distribution, the underlying Markov chain has to be irreducible or ergodic. In practice, this means that every state can be reached from every other state in a finite number of steps.

A very efficient algorithm of this type for studying SAWs of length N, is the well known *pivot algorithm* [27]. This technique can be used for the zipping model at $\beta = 0$ in a trivial way (since the two walks are independent). We have therefore performed extensive simulations, again on the square lattice, for N up to 6000. For each N-value, we determined 50 000 independent SAW-pairs. For these we calculated the number of crossings I. In figure 3 we show our results for $\langle I_N \rangle(0)$. We include both the results of the exact enumerations (full circles) and of the pivot algorithm (full circles with error bars indicated). As can be seen on this log–log plot, there is a crossover from the behaviour for small N to the asymptotic power law growth which only sets in at $N \approx 100$. From a fit of the data for large N (see inset) we obtain a more precise estimate of the exponent φ which is $.516 \pm .005$.

The fact that $0 < \varphi < 1$, together with the arguments given at the beginning of this section (see (23)–(25)) provides convincing evidence that indeed $\beta_z = 0$. As in the case of the Sierpinski gasket, the numerically determined value of the crossover exponent seems to be a few percent higher then that derived from the codimension additivity argument. However, our data cannot rule out that $\varphi = 1/2$ exactly.

5. Conclusions

In this paper we studied a simple model for the zipping of two polymers. We established a number of rigorous results. As an example, we showed the existence of a phase transition in the model. These results were quite general and most of them hold on arbitrary lattices. Using an heuristic argument we were led to conclude that in $d = 2$ and $d = 3$ the polymers are zipped as soon as the interaction energy becomes attractive. This result was supported in $d = 2$ by exact enumeration and Monte Carlo simulations. From these latter calculations an

accurate estimate of the crossover exponent was obtained: $\varphi = .516 \pm .005$, a value which is close to the prediction of the codimension additivity argument that gives $\varphi = 1/2$.

Models similar to ours have been studied recently in the literature. As a first example, we mention the diblock copolymer model introduced by Orlandini *et al* [5, 6]. That model differs from ours in the fact that the two SAWs are also mutually self-avoiding. In that case, numerical evidence shows convincingly that $\beta_z > 0$ for all lattices studied. Moreover, it could be shown exactly that in $d = 2$ the crossover exponent equals $9/16 = .5625$. Another model that is rather similar in spirit to the present one is the lattice version of the Poland and Sheraga model [28] of DNA, studied in [29]. In that model the two SAWs can only intersect at homologous sites, i.e. $\omega_i^{(1)} \neq \omega_j^{(2)}$, $i \neq j$. When $\omega_i^{(1)} = \omega_i^{(2)}$ an energy -1 is gained. This model is now known to have a first order zipping transition at a $\beta_z > 0$ [4, 30]. Finally, we mention that a model of two interacting *directed* polymers was solved exactly by Iglói [31]. Also in that model, the two polymers only zip at a finite temperature.

There is an interesting analogy between models of pairs of polymers such as those discussed above, and the behaviour of a SAW near a flat hyperplane. In that situation, one investigates a SAW that gains an energy -1 for each monomer that lies in the hyperplane. In the case that the SAW can cross the hyperplane, it is believed that for any finite temperature, the polymer is adsorbed to the hyperplane, meaning that a macroscopic number of monomers lies there [16]. On the other hand, if the SAW has to stay on one side of the hyperplane, adsorption only occurs below a strictly finite adsorption temperature. We can interpret our model as one for the adsorption of one polymer into another, and our results also suggest that in this case, where crossing is allowed, there is always adsorption of the two polymers into one another. On the other hand, in the model introduced in [5] the two SAWs cannot cross, and as discussed above, they only zip below a finite temperature.

Finally, we think it would be of interest to investigate the present model in higher dimensions. Also the implications of the current work for the problem of a SAW in a random environment (see introduction) deserve further examination.

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